COMBINED APPLICATIONS OF CATIONIC FLOURS AND ENZYMATICALLY MODIFIED SUGAR BEET PULP IN PAPERMAKING

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The influence of cationic wheat flours on the properties of suspensions and laboratory handsheets prepared from a mixture of SAQ semichemical pulp and recovered fibres, with and without addition of enzymatically modified sugar beet pulp (EMSBP), was investigated. The main effects of cationic flour and EMSBP are related to the improvement of handsheet strength properties (tensile and burst index, internal bond strength, CMT_{30} and bending resistance), which are higher in the case of simultaneous addition of cationic starches and enzymatically modified sugar beet pulp than in the case of separate addition. It was also observed that cationic flours partially compensate the negative influence of the enzymatically modified sugar beet pulp on drainage time and filtrate loading (COD, BOD_5), as well as on the bending resistance and air permeability of handsheets.

Keywords: cationic flours, sugar beet pulp, enzymatic hydrolysis, semichemical pulp, recovered fibres, COD, BOD_5

INTRODUCTION

At present, paper industry suffers a considerable environmental pressure, requiring an increase in pulp yield, lower pollution, less addition of chemicals and the increase of fibre recycling. The combination of all these factors is not simple at all. To achieve these objectives, new processes and additives are constantly being developed.

Paper industry uses a large number of starch derivatives in different stages of the manufacturing process, for various purposes. The most common starch used for paper manufacture is prepared from maize, potato and cassava. In 2004, out of the about 5 million tons of starch used, grain starch represented[1] up to 67%. Starch utilisation in papermaking depends on the paper grade, required paper properties, the fibrous raw materials employed and the technology applied. Starch is used as a wet end additive, to increase paper strength, in size press, to improve the finish, appearance, strength and printing properties, and in coating operations, as an adhesive.

The cost of starch represents an important part of the global paper production costs. Therefore, cheaper and more environment friendly substitutes are searched for. The efforts to replace starch by cheaper food industry products with high starch content were partially achieved[2] by the utilization of starch containing approximately 30% flour. Potato starch and conventionally produced starch-rich wheat flours are obtained through a series of wet processes, resulting in high water consumption and high discharge of pollutants. Wheat is milled and chemically modified in dry processes, eliminating the large water consumption and the discharge of pollutants resulting from the starch-rich wheat flour production.[3] Consequently, the total energy and water consumption in the production of chemically modified flour is significantly reduced, compared to the conventional production of chemically modified wheat starch. The chemically modified wheat flour is less pure than the conventional starch products, containing 2-10% protein – as compared to only 0.2-0.5% in conventionally refined starch products. The chemically modified wheat flours are suitable for papermaking application as both powder and cold solution, by spraying technologies and size press application on the paper surface.

Paper manufacture with the addition of dry micronised sugar beet pulp is well-known.[4] In the Cartiera Favina mill of Italy, paper is prepared from recovered fibres, with the addition of micronised sugar beet pulp.[5] The influence of dry and wet pre-treated sugar beet pulp on recovered fibre suspension and on the paper properties, as well as the possible sugar beet pulp exploitation in core board manufacture was investigated at a laboratory scale.[6] Wet beaten sugar beet pulp is suitable for increasing the specific bond strength, as well as for partially substituting the recovered fibres and semichemical pulp in fluting and test liners.[7]

The present work compares the influence of cationic wheat flours, as possible starch substitutes, on the properties of suspensions, handsheets and pollution of filtrates from a mixture composed of SAQ semichemical pulp, recovered fibres, without and with addition of enzymatically modified sugar beet pulp.

EXPERIMENTAL

Materials

Soda-AQ (SAQ) semichemical pulp, prepared from mixed hardwoods (40% poplar, 35% birch, 25% hornbeam), was beaten in a laboratory Valley hollander to 28 °SR, according to the ISO 5264-1 standard.

Recovered fibres (34 °SR) were prepared according to EN 643, from the following waste paper classes: 3% mixed papers and boards (sorted), 16% corrugated paper and board from department stores, 65% old corrugated boxes (sorted) and 16% new cuttings from corrugated board manufacture. The recovered fibres were fiberised for 10 min in a laboratory Escher Wyss pulper (Germany).

Enzymatically modified sugar beet pulp (EMSBP) was prepared by enzymatic hydrolysis of sugar beet pulp with the commercial cellulase Rohament® CL and pectinase Gamapect Plus with arabinose activity, purchased from AB Enzymes (Germany). Enzymatic hydrolysis was performed for 8 hours at 50 °C; hydrolysis degree = 32%, fibre yield = 68%. The hydrolysis degree is specified as the quantity of matter dissolved during the enzymatic hydrolysis. The yield of L-arabinose, determined by HPLC, was of 4.5% on sugar beet pulp and cleanness was of 98.5%. The enzymatically modified sugar beet pulp was fiberised for 6 min in a laboratory mixer, at 4000 RPM, to 0.01-1.5 mm particles.

Commercial cationic starch PerlBond 930 (specific cationic charge 366 μeq/g) was supplied by Lyckeby (Sweden).

Chemically modified cationic wheat flours (A, B, C) were supplied by Ceresan (Germany). The specific cationic charge of flour A was 208 μeq/g, of flour B – 246 μeq/g and of flour C – 303 μeq/g.

Paper stock preparation

A fibre mixture used in the manufacture of fluting and test liners under mill conditions was prepared from 55% SAQ semichemical pulp and 45% recovered fibres. The fiberised enzymatically modified sugar beet pulp was added to the fibre mixture up to a final content of 10%.

3% crystalline aluminium sulphate (pH 4.6) was added to the fibre mixtures, to eliminate the disturbing soluble and colloidal materials. Subsequently, 1.2% cationic starch or cationic flours A, B and C were added after 20 min of gelation, at 95 °C. The properties of the fibre suspensions and those of the laboratory handsheets were investigated according to standard methods.

Figures 1 to 7 illustrate two reference fibre mixtures: the basic fibre mixture is composed only of SAQ semichemical pulp and recovered fibres (SAQ+RF), while the second reference fibre mixture contains, besides SAQ semichemical pulp and recovered fibres, 10% enzymatically modified sugar beet pulp (SAQ+RF+EMSBP). The influence of cationic flours and cationic starch addition to both reference fibre mixtures is also presented.

Methods

Paper stocks were characterized by *water retention value* (WRV) – according to the TAPPI UM 256 method; *drainage time*, determined as the time required to drain 700 mL water from 1000 mL 0.2% suspension in a Schopper-Riegler apparatus.

Handsheets (127 g/m^2) of each paper stock, prepared according to ISO 5269-2, were tested for *tensile index* – ISO 1924-2; *burst index* – ISO 2758; *internal bond strength*, measured as Scott Bond Energy according to the TAPPI method 506 wd-83; *bending resistance*, measured by a two-point method, at a 15° bending angle, 25 mm of clamp and blade distance, according to the TAPPI 556 pm-95 method; *air permeability* – Gurley – according to ISO 5636-5; *flat crush resistance* (CMT_{30}) – according to ISO 3035.

Filtrate loading was evaluated by the *Chemical Oxygen Demand* (COD) and *Biochemical Oxygen Demand* (BOD_5), according to ISO 6060 and EN 1899-1 methods.

RESULTS AND DISCUSSION

The influence of cationic flours and cationic starch on the internal bond strength of the handsheets made from the basic fibre mixture, without (SAQ+RF) and with 10% enzymatically modified sugar beet pulp (SAQ+RF+EMSBP), is plotted in Figure 1. The internal bond strength of the handsheets from the SAQ+RF mixture increased by 43-45%, when applying cationic flours, and by 57%, when applying cationic starch.

Enzymatically modified sugar beet pulp significantly increased the strength properties of the investigated fibre mixture. The internal bond strength of the handsheets from the SAQ+RF+EMSBP fibre mixture was 40% higher than that of the handsheets without addition of EMSBP. Cationic flours further increased the internal bond strength of the handsheets by 18-23%, whereas cationic starch – by as much as 35%.

The combined application of enzymatically modified sugar beet pulp and starch-based cationic agents increased the internal bond strength of the SAQ+RF handsheets by 66-90%. The influence of the starch-based cationic agents on internal bond strength was more significant in the handsheets made from a mixture of SAQ+RF than in a mixture containing enzymatically modified sugar beet pulp (SAQ+RF+ EMSBP). The highest increase in the internal bond strength of the handsheets from both mixtures was achieved by the application of cationic starch. The increase of internal bond strength is a consequence of the more numerous hydrogen bonds between fibres. Cationic flours and cationic starch are attached to the negative charge of wood fibres and EMSBP. This hydrophilic complex covers cellulose fibres and binds water, thus creating hydrogen bridges among the fibres under drying, converted into hydrogen bonds.

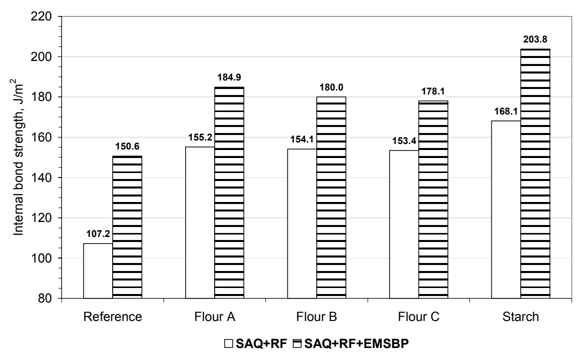

Figure 1: Influence of cationic flours and cationic starch on the internal bond strength of handsheets from a fibre mixture without (SAQ+RF) and with 10% enzymatically modified sugar beet pulp (SAQ+RF+EMSBP)

A higher internal bond strength has a positive effect on paper strength properties. The application of cationic flours and cationic starch, especially, in combination with EMSBP increases the tensile index, burst index and CMT_{30} of the handsheets from the fibre mixture without (SAQ+RF) and with 10% enzymatically modified sugar beet pulp (SAQ+RF+EMSBP), as shown in Table 1. The increase in strength properties was significantly higher if cationic flours or cationic starch were applied in combination with EMSBP. The increase of the burst index and CMT_{30} was higher than that of the tensile index.

Table 1
Increase of strength properties (in %) by application of EMSBP, cationic flours and cationic starch

Fibre mixture	SAQ+RF			SAQ+RF+EMSBP	
Addition	EMSBP	Cationic flours	Cationic starch	Cationic flours	Cationic starch
Tensile index, N·m/g	23	22-24	22	39-41	36
Burst index, kPa·m^2/g	38	35-41	43	63-71	66
CMT_{30}, N	32	45-50	36	45-48	51

The influence of cationic flours and cationic starch on the bending resistance of the handsheets prepared from the basic fibre mixture without (SAQ+RF) and with 10% enzymatically modified sugar beet pulp is presented in Figure 2. The application of cationic flours increased the bending resistance of the SAQ+RF handsheets by 11-21%, whereas cationic starch application – by only 7%.

The addition of enzymatically modified sugar beet pulp to the SAQ+RF fibre mixture reduced bending resistance by 6%. However, the application of cationic flours increased the bending resistance of the SAQ+RF+EMSBP handsheets by 12-14%, while the application of cationic starch – by 9%.

Starch-based cationic agents increased the bending resistance of the handsheets made from both mixtures. The bending resistance of the handsheets from the SAQ+RF mixture increased by 2-7%, when adding enzymatically modified sugar beet pulp and starch-based cationic agents. The application of starch-based cationic agents eliminates, to some extent, the negative influence of the enzymatically modified sugar beet pulp addition on the bending resistance of the handsheets made from the SAQ+RF fibre mixture.

The air permeation resistance of the handsheets prepared from the basic fibre mixture (SAQ+RF) decreased by the application of cationic flours by 6-13%, whereas the application of cationic starch led to as much as 31% (Fig. 3).

A 10% addition of enzymatically modified sugar beet pulp to the SAQ+RF fibre mixture increased air permeation resistance by 287%, which is obviously a result of a more dense paper structure, as EMSBP addition created more bonds among fibres. Cationic starch-based agents eliminated to some extent the negative influence of the enzymatically modified sugar beet pulp on air permeation resistance.

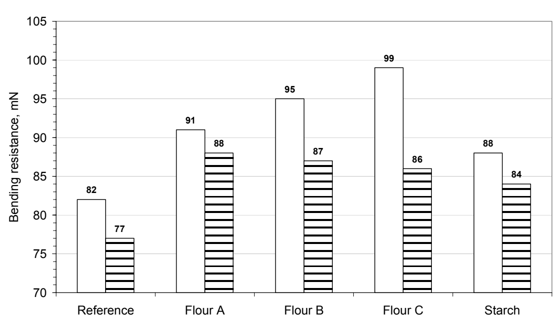

Figure 2: Influence of cationic flours and cationic starch on the bending resistance of handsheets from a fibre mixture without (SAQ+RF) and with 10% enzymatically modified sugar beet pulp (SAQ+RF+EMSBP)

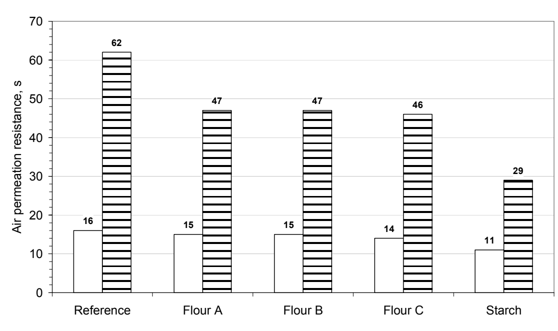

Figure 3: Influence of cationic flours and cationic starch on the air permeation resistance of handsheets from a fibre mixture without (SAQ+RF) and with 10% enzymatically modified sugar beet pulp (SAQ+RF+EMSBP)

Cationic flours reduced the air permeation resistance of the SAQ+RF+EMSBP handsheets by 24-26%, whereas cationic starch – by as much as 53%. The reduction of air permeation resistance is important in fluting and test liner manufacture, as these paper grades should have a low air permeation resistance for assuring a high absorption of adhesives.

Figure 4 illustrates the influence of cationic flours with increased specific cationic charge on the drainage time of the basic fibre mixture without and with a 10% EMSBP content. For the sake of comparison, the influence of a commercial cationic starch is presented. Cationic starch-based agents improve drainage by binding the fines on the fibre surface. In the absence of enzymatically modified sugar beet pulp, the drainage time was reduced to the largest extent by cationic starch (by 12%), whereas cationic flours reduced drainage time only from 0 to 9%. An increased influence of cationic flours was noticed when increasing their charge. The addition of enzymatically modified sugar beet pulp to the basic fibre mixture (SAQ+RF) increased drainage time by 211%, as EMSBP is hydrophilic and retains water (Fig. 4). However, the application of starch-based cationic agents significantly reduced the drainage time of this mixture, more than that of a fibre mixture containing only SAQ semichemical pulp and recovered fibres. Cationic flours reduced drainage time by 37-47%, whereas cationic starch – by 69%.

The influence of cationic flours and cationic starch on the water retention value (WRV) of the paper stocks studied is illustrated in Figure 5. Cationic flours increased the WRV of the simple fibre mixture (SAQ+RF) only marginally (by 0-2.8%), whereas cationic starch had no influence on it. EMSBP addition increased the WRV of the SAQ+RF fibre mixture by 18%, because of the high hydrophilicity of the enzymatically modified sugar beet pulp. Cationic flours and cationic starch reduced only marginally the WRV of the SAQ+RF fibre mixture, but significantly that of the EMSBP-containing fibre mixture. With increasing the specific charge of cationic flours, the WRV of the mixture containing EMSBP decreased. The highest effect was achieved by the addition of cationic starch to the SAQ+RF+EMSBP mixture, which reduced the WRV practically to the level of the SAQ+RF mixture.

Generally, a higher water retention value (WRV) inhibits water removal from the paper web in the press part, thus reducing the paper machine output and increasing steam consumption in the drying section. In the case of the mixtures containing enzymatically modified sugar beet pulp, the application of starch-based cationic agents partially eliminates the adverse effect of EMSBP.

The influence of EMSBP, cationic flours and cationic starch on the COD and BOD_5 of paper stock filtrates is presented in Table 2 and Figures 6 and 7. Cationic starch-based agents bind the anionic trash present especially in recovered fibres and also in SAQ semichemical pulp, which significantly reduces the COD and BOD_5 load of the filtrates from the SAQ+RF mixture. The efficiency of cationic flours depends on the specific anionic charge. Flour C, with the highest cationic charge, has even a higher efficiency in the COD and BOD_5 load reduction than cationic starch. EMSBP addition significantly increases the COD and BOD_5 load, as a large portion of EMSBP remains in the filtrate. The application of either cationic flours or cationic starch reduces the negative impact of EMSBP to an acceptable level, which is lower than the load of the SAQ+RF filtrate (Figs. 6 and 7).

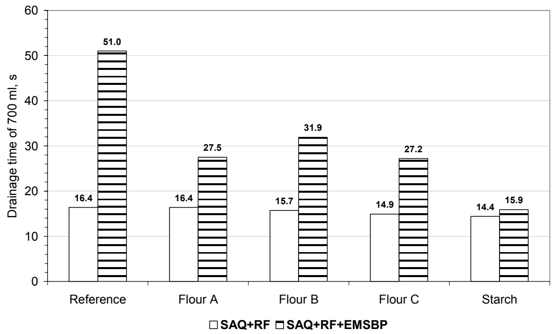

Figure 4: Influence of cationic flours and cationic starch on the drainage time of a fibre mixture without (SAQ+RF) and with 10% enzymatically modified sugar beet pulp (SAQ+RF+EMSBP)

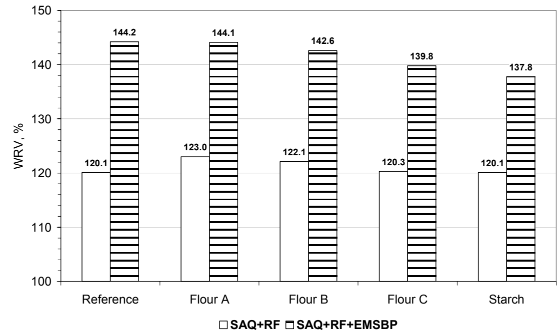

Figure 5: Influence of cationic flours and cationic starch on the WRV of a fibre mixture without (SAQ+RF) and with 10% enzymatically modified sugar beet pulp (SAQ+RF+EMSBP)

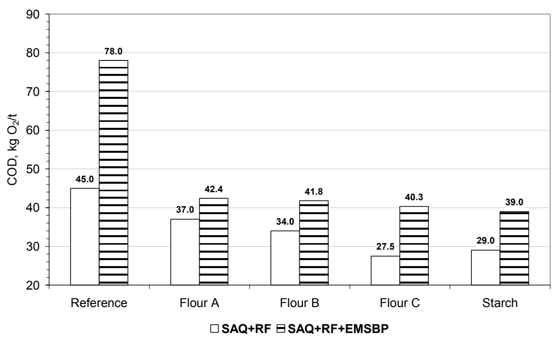

Figure 6: Influence of cationic flours and cationic starch on the COD of filtrates from a fibre mixture without (SAQ+RF) and with 10% enzymatically modified sugar beet pulp (SAQ+RF+EMSBP)

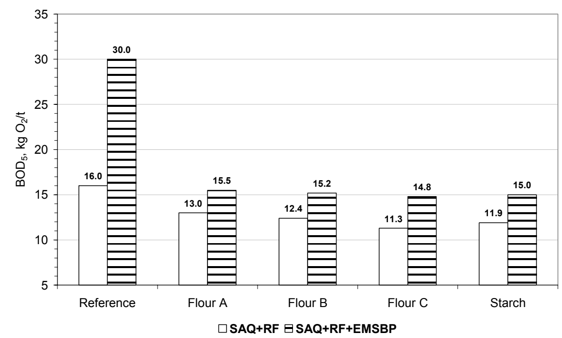

Figure 7: Influence of cationic flours and cationic starch on the BOD_5 of filtrates from a fibre mixture without (SAQ+RF) and with 10% enzymatically modified sugar beet pulp (SAQ+RF+EMSBP)

Table 2
Change in the COD and BOD_5 of filtrates (in %) by the application of EMSBP, cationic flours and cationic starch

Fibre mixture	SAQ+RF			SAQ+RF+EMSBP	
Addition	Cationic flours	Cationic starch	10% EMSBP	Cationic flours	Cationic starch
COD kg O_2/t	-18 to -39	-36	+73	-46 to -48	-50
BOD_5 kg O_2/t	-19 to -29	-26	+88	-48 to -51	-50

CONCLUSIONS

Modified wheat flours can partially or fully replace commercial cationic starch for the application to paper stock in the production of various paper grades, as a function of the required properties of suspension and paper. The advantage of cationic wheat flours is their lower price and the more environment friendly production, comparatively with cationic starch. Cationic flours and cationic starch improved internal bond strength and significantly increased tensile and burst index, as well as the CMT_{30} of the handsheets from a simple mixture of SAQ semichemical pulp and recovered fibres; the influence of cationic flours is similar to that of the cationic starch of similar specific cationic charge. The cationic starch-based agents reduced the COD and BOD_5 load of the filtrates, also improving, to some extent, bending resistance, air permeation resistance and drainage time, while slightly reducing the WRV of the simple fibre mixture.

The enzymatically modified sugar beet pulp (EMSBP), a fibrous residue of L-arabinose isolation by enzymatic hydrolysis, is an environment friendly alternative to increase the strength properties of paper and to partially replace wood fibres. EMSBP enhances the positive effect of cationic starch-based agents on internal bond strength, tensile and burst index and CMT_{30}. However, the application of EMSBP has a negative impact on both bending resistance and air permeation resistance. The COD and BOD_5 loads of the filtrates significantly increased on the application of EMSBP.

The negative effects of EMSBP can be at least partially eliminated by the combined application of EMSBP and cationic flours or cationic starch. Air permeation resistance is reduced, by the application of cationic flours and cationic starch, to an acceptable level for fluting manufacture. Drainage time reduced cationic starch nearly to the level of the simple SAQ+RF fibre mixture, while the reduction caused by cationic flours was lower. The negative effect of EMSBP on the COD and BOD_5 loads of the filtrates is almost wholly eliminated by the application of cationic flours or cationic starch.

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