PROPERTIES AND FLOCCULATION EFFICIENCY OF CATIONIZED BIOPOLYMERS AND THEIR APPLICABILITY IN PAPERMAKING AND IN CONDITIONING OF PULP AND PAPER SLUDGE

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Safe biodegradable "green" alternatives with minimal environmental and health risks have received widespread research interest. Thirty different kinds of bio-based flocculants (modified starches, modified celluloses, native chitosan, and lignin-based flocculant) were pre-tested using a simple jar test for the examination of the applicability of new organic flocculants in papermaking and in conditioning of waste activated sludge from the pulp and paper industry. Three starch-based and two cellulose-based polymers were chosen for further flocculation and filtrations tests. Key optimization parameters for the polymer were identified as the increasing of molecular weight and nitrogen content. The starch-based polymer had the best performance in both applications, but in neither of the cases did it function as well as the commercial polyacrylamide-based polymers. The importance of the molecular weight came up in the experiments. The developed starch-based polymer was cationic and had the charge density used in industry. On the other hand, although cationic flocculants are the most used in sludge conditioning, also anionic and non-ionic polymers are needed, depending on the characteristics of the sludge to be flocculated. Overall action of the tailored polymers was also studied in order to predict their potential as papermaking retention and dewatering aids.

Keywords: Biodegradable flocculants; Starch; Cellulose; Papermaking retention; Dewatering

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INTRODUCTION

Large amounts of wet sludge are produced annually in municipal and industrial wastewater treatment. Already the pulp and paper industry produces more than ten million tons of primary sludge, waste activated sludge (WAS), and de-inking sludge. Due to legislation and increased taxes, landfills are quickly being eliminated as a final destination for wastes in Europe (Monte et al. 2009), and other disposal methods, such as incineration and fertilizer use, are becoming more important. For proper disposal, mechanical dewatering plays a key role in the treatment chain of sludge. WAS is a difficult type of sludge to dewater. The dry solids content after traditional dewatering process can still be less than 15%. Flocculation is an important stage of mechanical dewatering, especially when using cationic flocculants, but also anionic and non-ionic flocculants are needed, depending on the sludge to be flocculated. Proverbial synthetic

flocculants are highly efficient, but they have poor biodegradability with respect to fertilizer use, and the environmental aspects are more and more the focus of critical discussions. In Germany sludges treated with polyacrylamides will be excluded from application on areas under cultivation by the end of 2013. Safe biodegradable "green" alternatives with minimal environmental and health risks, based on biopolymers such as starch or cellulose, have thus a strong research interest.

Flocculating agent systems are extensively used to improve the retention of fibre fines and fillers in papermaking. The flocculating agents are often polyelectrolytes whose mechanisms of operation depend on the molecular weight and charge density. The efficiency of the flocculating agents in papermaking is generally evaluated by measuring the state of flocculation or retention efficiency under the desired flow/process conditions.

The cationizing agent most commonly used today is 2,3-epoxypropyltrimethyl-ammonium chloride or, alternatively, a corresponding cationizing agent with a chloro-hydrin functional nature. These compounds have the characteristic that they can establish an ether bond with the OH groups of starch. Thus, they react with starch so as to form a compound that is stable over a very wide pH range. They are particularly stable over the basic pH range. This characteristic is advantageous during long-term storage, since high pH gives an increased resistance to microbiological attack.

The flocculation efficiency of the various cationic starches depends on (a) the amino group type and follows the order: quaternary > tertiary > secondary > primary, and (b) the chemical structure of the flocculants, i.e. the flocculants prepared by grafting have higher flocculation efficiency than those prepared via etherification. Structural aspects of starch have been found that with a decrease of molar mass and radius of gyration, and hence the flocculation efficiency decreases (Shirzad-Semsar et al. 2007).

Bio-based flocculants can be produced from starch (amylose and amylopectin based) (Pavlovic and Brandao 2003; Khalil and Abdel-Halin 2001), cellulose (Ott et al.1989), chitosan (Ashmore and Hearn 2000; Roussy et al. 2004), phosphate-modified glucomannan (Xie et al. 2007), or by grafting acrylamide onto natural polysaccharides such as guar gum (Nayak and Singh 2001), and carboxymethyl cellulose (Biswal and Singh 2004). Starch derivatives have potential to replace petroleum-based flocculants and chelating agents (Oelmeyer et al. 2002; Bratskaya et al. 2005) for applications where the sludges are used on cultivated areas by reason of tighter environmental laws. A high degree of substitution (DS) in cationization of up to 1.1 in a one-step synthesis of the samples can be controlled by adjusting the molar ratio of cationization agent to anhydroglucose unit. A two-step reaction yields products of a DS of up to 1.5 (Heinze et al. 2004). Adsorption of polysaccharides onto mineral surfaces has been investigated and explained in many papers (Weissenborn et al. 1995; Liu et al. 2000). The recent patents (Karppi et al. 2007; Likitalo and Käki 2005) have been shown, that the molecular weight of the flocculant, at least for sludge applications, should get much higher concerning applications of papermaking retention and dewatering.

The flocculation performance of 30 different kinds of the bio-based polymers was first examined using a simple jar test, where a suspension of 0.05 % kaolin and 0.1 % thermo-mechanical pulp (TMP) fines was used for the flocculation studies. The best modified ones were further tested using more realistic filtration tests and compared with some commercial polyacrylamide-based flocculants.

EXPERIMENTAL

Materials

Various starch-based materials, such as enzymatically hydrolysed potato starch (N%: 0.4-2.8%), hydroxypropylated starches or acetylated potato starch (DS = 0.9-2.5), maize starch (amylose rich, N% = 1.3-1.57%), or enzymatically hydrolysed barley starch (N% = 0.66%)) have been chemically or enzymatically modified before the cationization. The starting material for the cationized modification of carboxymethyl cellulose, lignin, and chitosan were commercial samples. The acetylated samples were prepared using VTT´s own technology. The flocculants had not been optimized for further studies with respect to molecular weight, molecular weight distribution, chemical structure of the polymers, or the nature or ratio of functional groups on the polymeric backbone.

For the flocculation and filtration tests, the starting material was hydroxypropyl starch (MS=0.4, M_w=2.3 MDaltons) made in a pilot plant (Peltonen et al. 1998). As a hydroxyethyl cellulose sample, Aqualon's Natrosal 250 MBR (M_w=220000) was used. To increase the molar mass of selected samples, epiclorohydrin (Fluka) was used as a crosslinking agent. The mostly used cationization reagent, Raisacat 151 (2,3-epoxy-propyl-trimethylammonium chloride, industrial grade, Ciba Speciality Chemicals OY, Mietoinen, Finland) was used. All of the above-mentioned chemicals were used as received without further purification. If not otherwise mentioned, all other chemicals were of industrial grade.

The used furnish in the papermaking drainage and in flocculation measurements was a thermomechanical pulp (TMP)-based news-type recipe with a filler content of 30%. The fines content of the furnish was 25%. The flocculants in sludge application were tested using waste activated sludge (WAS) from a pulp mill. The samples were fresh and taken daily when needed. The total solids content of the WAS was 0.9±0.2%, the average particle size was 70±5 µm, the capillary suction time (CST) was 16±2 s, and the pH was 7.9±0.3.

Methods

Acetylation

The potato starch used in acetylating was provided by Periva Oy (Kokemäki, Finland). The used starch acetate was manufactured according to VTT´s patents (FI 107386). Reaction was carried out in the mixture of acetic acid anhydride and acetic acid in the presence of sodium hydroxide at reflux temperature, typically for 6 hours. Crude product was typically washed with an excess of water and dried.

Cationization of starch

Starch granules were suspended in water (e.g. 20% w/v), typically at 30°C, and were adjusted to pH 11.0 with NaOH. A commercial etherifying agent containing 2,3-epoxypropyltrimethylammonium chloride (RAISACAT, Raisio Chemicals Oy) was added to the slurry. The reaction temperature was raised to 80°C, and the reaction was stopped after 7-20 hr by adjusting to pH 6.5 with HCl (34% v/v). The slurry was filtered and washed with water and then with ethanol. The sample was freeze-dried.

Crosslinking

The crosslinking of the hydroxypropyl starch sample was carried out typically as follows: an aqueous suspension of 70 g hydroxypropyl starch and 0.5 mL epiclorohydrin in 1000 mL of water (pH over 11) was stirred at low speed at room temperature and then stirred for 1 hour at 60°C. On the next day, 35 g 50% NaOH (catalyst for the cationic reaction) and 85 g Raisacat 151 were added to the solution at room temperature and stirred for 10 hours at 80°C. The pH of suspension was adjusted to 7, and the product was purified with ultrafiltration (Microza UF Module, PALL Corporation) and freeze dried.

Analysis

The quantitative determinations of nitrogen in chemical substances were done by the Kjeldahl method. Gel permeation chromatography (GPC) was used to analyze molar mass distributions and mass average molar masses. A refractive index detector was used to determine the absolute molar masses in 1 M NaOH. The molar masses of the cross-linked samples were also evaluated by the viscosity measurement with a Brookfield DV-II+Pro viscometer at 25 °C.

A simple jar test was conducted as a pre-test for the examination of the applicability of new organic flocculants. 4 beakers of suspension of 0.05 % kaolin or 0.1 % TMP fines were used for flocculation studies at pH 4 and pH 7. Immediately after the addition of flocculants, all the suspensions were stirred at a constant speed of 100 rpm for 10 min, followed by slow agitation at 40 rpm for 10 min. The suspensions were then allowed to settle for 15 min. The turbidity of the suspension was measured with a Hach Model 2100P Portable Turbidimeter. The dose of flocculants was varied within the range of 0 to 4 ppm.

Flocculants

Starch- and cellulose-based polymers with different charge densities and molecular weights were screened in pre-tests, and the best ones were chosen for flocculation and filtration tests (Table 1, A-E). The pre-tested flocculants were further modified and compared to commercial polyacrylamide-based flocculants (C-PAM) used in industry (Table 1, F-I). The molar masses of the crosslinked samples A, C, and D measured by the viscocity measurements indicated increasing molar masses respectively.

The aim was to examine the applicability of new organic flocculants in conditioning of WAS from a paper mill. The sludge was coagulated with ferric sulphate and/or flocculated using flocculants having different charge densities and molecular weights (Table 1). The success of flocculation was determined by using a visual estimation of floc appearance and the dewatering methods discussed below.

Also the capillary suction time (CST) measurements using a Triton Electronics CST meter were conducted, indicating the ability of the liquid phase to propagate in the filter paper. Particle size measurements were carried out using a Malvern 2600c analyser. However, the CST values were too low to obtain reliable differences between different flocculants. The particle size measurement proved to be unsuitable for floc size determination.

Table 1. Flocculants Used in Flocculation and Filtration Tests and the Information for Modified Polymers. *

Polymer	Charge density [meqv/g]	M_w (g/mol)	M_n (g/mol)	PDI	Material	Special information
A=	+0.78	2.3 M	330000	7	HPS	
B=	+0.95	0.22 M	67000	3.3	HEC	
C=	+1.1	2.22 M	300000	7.5	HPS	Crosslinking product of A
D=	+3.74	2.08 M	430000	4.9	HPS	Crosslinking product of A
E=	+0.33	0.17	32000	5.2	HEC	
F=	~+1	~5-7 M	-	-	C-PAM	Comm. flocculant
G=	~+1	~1.5 M	-	-	C-PAM	Comm. flocculant
H=	~+1.2	~9.5 M	-	-	C-PAM	Comm. flocculant
I=	~+1.2	~4.5 M	-	-	C-PAM	Comm. flocculant

HPS = Hydroxypropyl Starch, HEC = Hydroxyethyl Cellulose and C-PAM= Commercial Cationic Polyacrylamide

Sludge Treatments

Two different types of laboratory-scale dewatering methods were tested for WAS, a batch type gravity filtration procedure and continuous belt filter pressing (Fig. 1). Gravity filtration tests were carried out using a filter cloth (Tamfelt DP313, permeability 2500 m^3/m^2h) in a funnel, when the sludge was coagulated and/or flocculated in a separate mug and decanted to the funnel in an identical manner. Success of the filtration was determined by measuring the amount of filtrate, the DS-content of the gathered cake and the filtrate, and the turbidity of the filtrate.

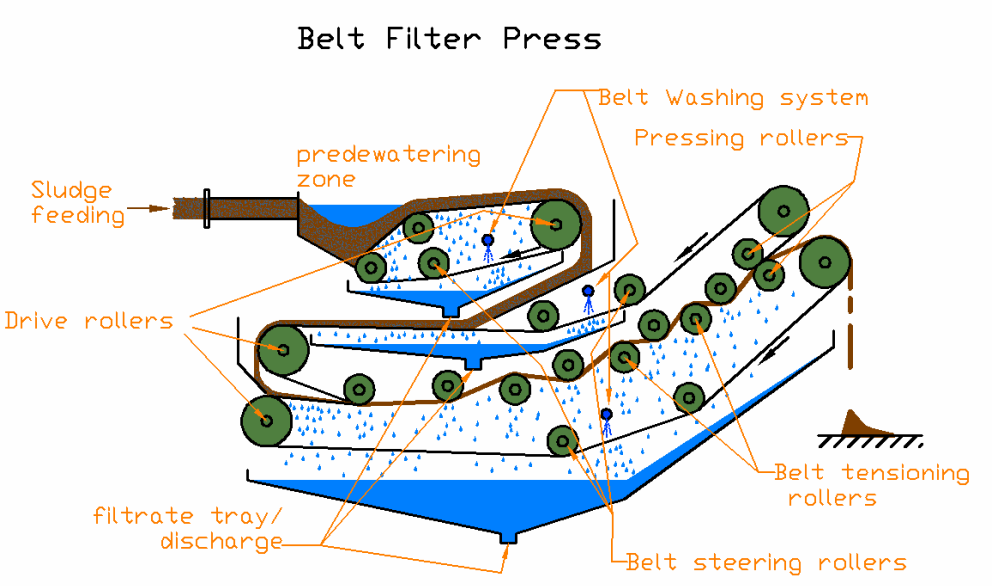


Fig. 1. Schematic illustration of the belt filter press

Laboratory-Scale Drainage and Flocculation Measurement Equipment

Drainage and retention efficiency of each polymer were studied with a laboratory-scale drainage device, as shown in Fig. 2. The device consists of a sample chamber, a filtrate flask, a scale, a vacuum pump, and a manometer. The wire in the bottom of the sample chamber was a 200 mesh metallic screen. The cumulative filtrate mass was measured with a scale and recorded by a computer. The experiments were carried out with a typical news furnish containing 30% of filler with an initial total consistency of 8 g/L. Each sample was prepared by mixing the polymer manually in the sample chamber for 30 seconds at a temperature of 50°C. The pressure in the filtrate flask was initially set to -10 kPa. After the measurement, the filtrate in the flask was collected and analysed for turbidity. The efficiency of the polymers was evaluated as the change in the dewatering rate and the change in turbidity of the filtrate.

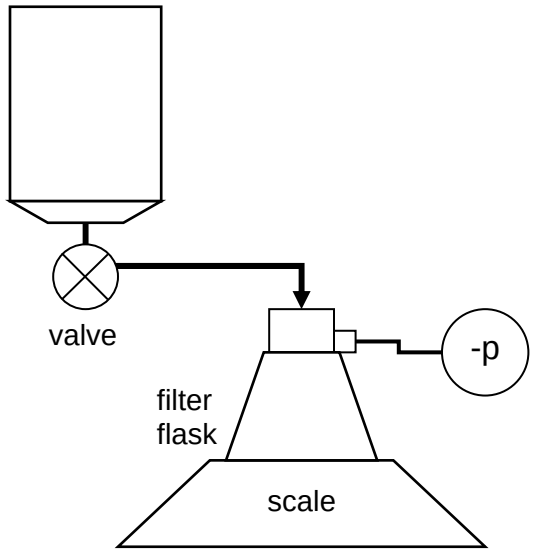


Fig. 2. Schematic illustration of the laboratory drainage device

The state of flocculation in the furnish following the addition of the polymers was studied in a laboratory flow loop system with a contraction channel simulating the conditions in a headbox of paper machine. The flow geometry and measurement set-up are presented in Fig. 3.

The flocculation and retention capabilities of the polymers were evaluated using an image analysis technique. The average size of flocs was determined downstream after the abrupt contraction in the slit channel using a pulsed light emitting diode (LED) light source and a fast CCD camera. After correcting the images for uneven illumination, the floc size was determined in the flow direction and the transverse direction as a run-length average of the median thresholded image (Kellomäki and Karema 1999; Karema and Salmela 2001; Salmela and Kataja 2005). The retention efficiency was evaluated by calculating the mean intensity and deviation of the intensity of the light transmitted through the channel. The light scattering efficiency of pulp decreases as the filler particles attach onto fibres. As a result, the mean intensity and deviation of intensity are increased when more light is able to pass the pulp layer flowing in the channel.

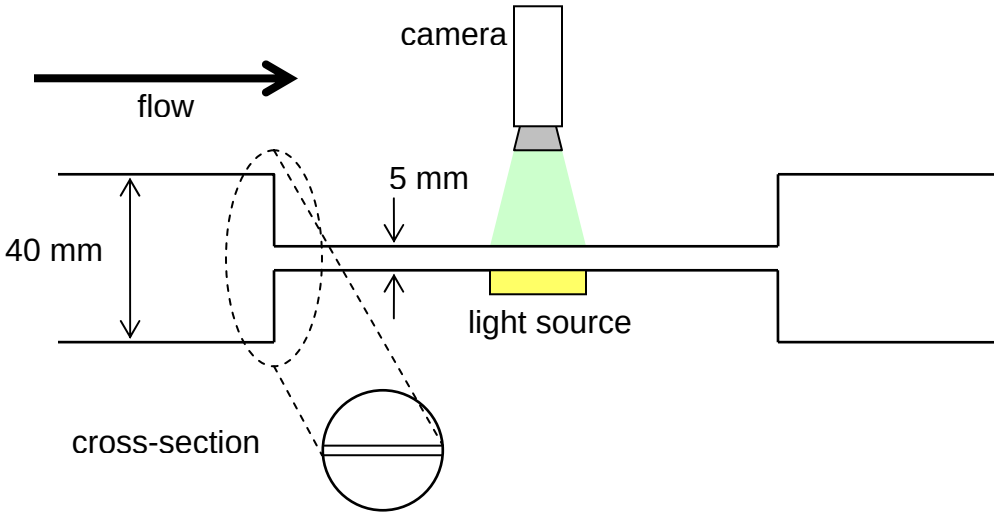


Fig. 3. Schematic illustration of the flow loop system with circular tube of 40 mm in diameter and a rectangular slit channel with height of 5 mm

RESULTS AND DISCUSSION

Pre-Test Result and the Further Developed Polymers

Thirty flocculants for the jar test were selected randomly from other projects. As source material either hydrolysed potato (N%: 0.4-2.8 %) or acetylated potato starch (DS = 0.9-2.9), maize starch (amylose rich, N% = 1.3-1.57 %), or enzymatically hydrolysed barley starch (N% = 0.66%) were used.

Table 2. Turbidity Results of Jar Test Study

	TMP fines		Kaolin	
	1 ppm	2 ppm	1 ppm	2 ppm
5 x cationized potato starch	**++**	**++**	**++**	**+**
2 x cationized maize starch	**++**	**+++**	**+**	**- -**
2 x enzymatic + cationized barley	**+**	**-**	**++**	**- -**
9 x cationized + modified starch	**-**	**-**	**++**	**++**
3 x cationized CMC	**--**	**-**	**- -**	**- -**
3 x acetylated starch	**+**	**+++**	**+**	**- -**
cationized starch acetate	**-**	**++**	**+**	**-**
cationized chitosan	**+**	**+++**	**-**	**- - -**
commercial cationic starch	**++**	**+++**	**+**	**- -**
3 x commercial cationized PAM	**+++**	**+++**	**+**	**+**
2 x cationized hydroxyethyl cellulose	**++**	**++**	**+**	**- - -**
cationized lignin	**-**	**-**	**-**	**- - -**

Symbol values : +++ = under 5, ++ = 6 to 20, + = 20 to 49, - = 50 to 100, - - = 101 to 199 and - - - = over 200 NTU. NTU = nephelometric turbidity units.

Also one sample was made of chitosan and cationized lignin. Total nitrogen content of the flocculants was typically very low, below 1%, i.e. medium cationization DS values of 0.14. As a general observation from the studies (Table 2) it can be said that products that had been subjected to anionic modifications, such as crosslinked and cationized CMC-flocculants, acted as dispersing agents, whereas an increasing degree of acetylation or increased nitrogen content improved the efficiency of the flocculant. Also, lowering of the pH in the suspension improved the efficiency of the flocculants.

Figure 4 presents the influence of the side chain of modified starch (HPS) on the effectiveness of TMP fines flocculation. The bigger the side chain was, from methyl to stearyl, the more ineffective was the flocculation. The comparison of the best flocculants to commercial flocculants revealed that at small dosage the commercial flocculants were more effective than the modified starches.

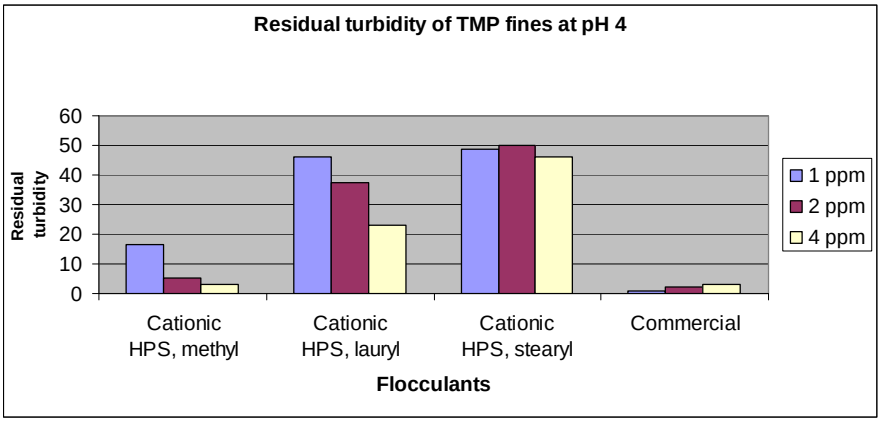


Fig. 4. Effect of side chain of the modified starch to the flocculation of TMP fines at pH 4

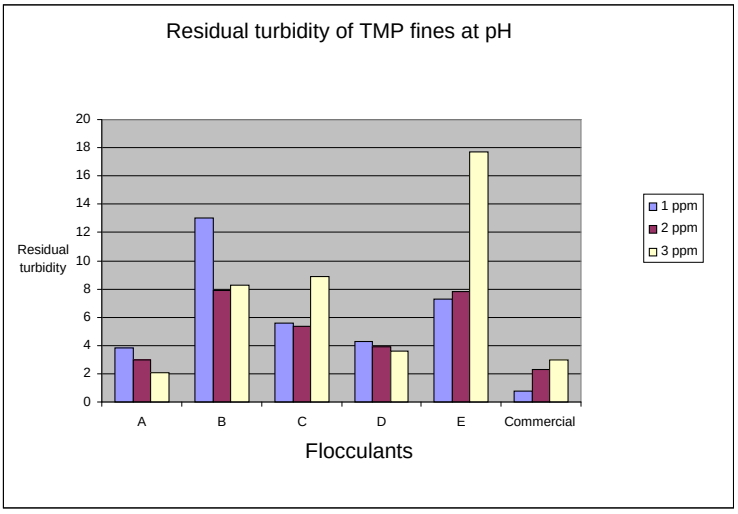


Fig. 5. Comparison of modified flocculants compared to a commercial flocculant in relation to the flocculation efficiency

Based on the jar test results it was concluded that the molecular weight or nitrogen content of bio-based polymer should increase. The best candidates for the application studies were further developed to optimize the flocculation properties. The optimization parameters for the polymer were chosen as increasing the molecular weight and the nitrogen content. Table 1 lists information pertaining to the modified polymers considered during the project. The jar test data of the modified polymers revealed that the best flocculants achieved almost at same efficiency level than the commercial products (Fig 5.).

Sludge Treatment

In an ideal situation, a flocculating polymer intended for sludge dewatering produces flocs that are large and stable enough for filtration, gives a clear filtrate (turbidity and dry solids are low), yields a high dry solids content of the cake, and the amount of clear filtrate is also high.

The cellulose-based polymers did not produce flocs in sludge application, based on estimating floc appearance visually. The starch-based polymers functioned clearly better. The tested polymer D, which was a cross-linked starch based polymer, functioned the best of all the developed polymers in this application (Table 3). It also had the highest molecular weight of the developed polymers. However, the best flocs were obtained using commercial flocculants with smaller dosages. The most satisfactory flocs for further dewatering tests were obtained using the commercial flocculant H with the molecular weight of 9.5 MMW. The use of ferric sulphate produced better flocs only with flocculants C and I.

Table 3. Visual Estimation of Floc Appearance. *

No flocs	Slightly flocky	Good flocs	Excellent flocs
Reference (0)	C (15) + Ferric	I (4) + Ferric	H (8)
Reference (0) + ferric	D (8)	I (8) + Ferric	H (8)
A (4)	D (15)	I (15) + Ferric	
A (8)	D (15) + Ferric	H (4) + Ferric	
A (15)	I (4)	H (4) + Ferric	
C (4) + Ferric	I (8)		
C (4)	I (15)		
C (15)			
D (4)			
D (4) + Ferric			
D (8) + Ferric			

* Polymer dose (kg/t DS) in parenthesis

The filtration tests gave similar results to the visual estimation of floc appearance. There was no cake on the filter when filtering sludge flocculated using cellulose-based polymers. Correspondingly, the filtrates had similar total solids content (TS) to the reference with no flocculant addition. Starch-based polymers produced better filtration results. When the sludge was flocculated using the polymer D (polymer dose 15 g/t TS), the DS of the cake obtained was fairly good, 4.3%. However, the filtrate was turbid and

the TS of the filtrate was high (>0.6%). The TS values of the cakes when using either of the commercial polymers were >5.0%. The filtrates were clearer (TS < 0.4%) than when using the starch-based polymers. The commercial polymer I produced more turbid filtrate (380 FTU) than the polymer H (260 FTU). Also the filtration rate with the polymer H was higher and the polymer needed for flocculation lower than with the polymer I.

The continuous belt filtering was carried out with the starch-based polymer D and the commercial polymer H. The TS 10 % obtained using the polymer D was fairly good. The TS with the polymer H was, however, a bit higher (12 %), and the filtrate was clearer. The polymer needed for flocculation was 1.5-fold higher for the polymer D than for the polymer H.

Drainage and Flocculation Efficiency in Papermaking

The effect of polymer additions on free water removal rate from the furnish was analysed by measuring cumulative mass of the filtrate as a function of time during the dewatering process (Fig. 6). The total filtration times when the maximum amount of filtrate was achieved are presented in Table 4. All flocculants increased the dewatering rate of the furnish. This is not surprising, since all the polymers evaluated were cationic and therefore flocculation is expected at least due to electrostatic attraction. A decrease in specific surface area of the pulp through flocculation of fines and fillers onto fibres leads to an increase in porosity of the consolidating pulp layer during the dewatering process.

Despite the similar charge density and molecular weight of polymers C and G, the commercial CPAM-based polymer G outperformed the starch-based polymer C in dewatering efficiency. Furthermore, the starch-based polymers C and D achieved almost identical dewatering behaviour, albeit the noticeable difference in both charge density and molecular weight. The highest dewatering rate was achieved with C-PAM having relatively low charge density but very high molecular weight. The performance of the cellulose-based polymer as a flocculating agent proved very weak.

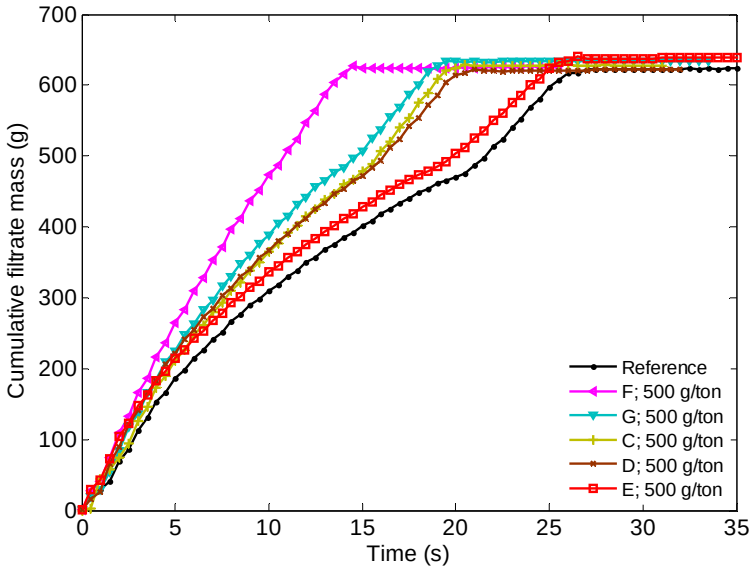


Fig. 6. Cumulative filtrate mass as a function of time for polymer dosage of 0.5 kg/ton

Table 4. Total Filtration Times of the Pulp Samples *

	500 g/ton	1000 g/ton
Reference	26.5 s	26.5 s
F (CPAM)	15 s	14 s
G (CPAM)	20 s	16.5 s
C (Starch)	20.5 s	20 s
D (Starch)	21 s	20.5 s
E (Cellulose)	27 s	28.5 s

* (time when maximum filtrate amount is achieved)

The effect of different polymers on retention was characterized in terms of turbidity. Filtrate turbidity values are presented relative to the value of reference pulp in Fig. 7. The commercial CPAMs F and G were able to reduce the turbidity to 20% of the reference. The tailored starch-based polymers C and D decreased turbidity to 30% of the reference, whereas the cellulose-based polymer E only yielded turbidity that was approximately 65% of the reference. The reason for the poorer performance of the cellulose-based polymer in dewatering and retention might be the significantly lower charge density and somewhat lower molecular weight.

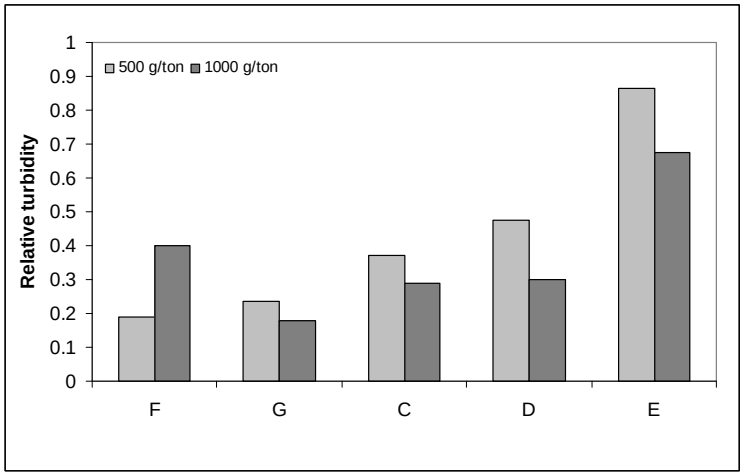


Fig. 7. Filtrate turbidities relative to the reference pulp filtrate

The starch-based flocculant C and the commercial flocculant F were selected for studies in a laboratory flow loop system. The cross-sectional area of the flocs produced by the different polymers relative to the reference without additives is shown in Fig. 8. Similarly, the relative mean intensity and deviation of intensity are presented in Fig. 9. As seen from the results, the commercial polymer F produced 1.9 to 2.3 times larger flocs, depending on the flow conditions and polymer dosage, when compared to the reference. The increase in intensity and deviation of intensity indicate that filler particles were attached onto fibres.

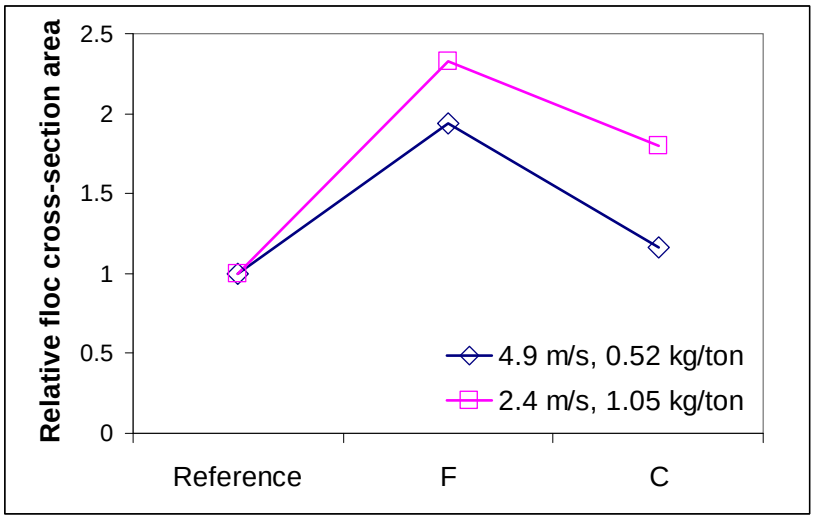


Fig. 8. Cross-sectional area of the flocs relative to the reference pulp. Similar flow conditions and polymer dosage are connected with a line.

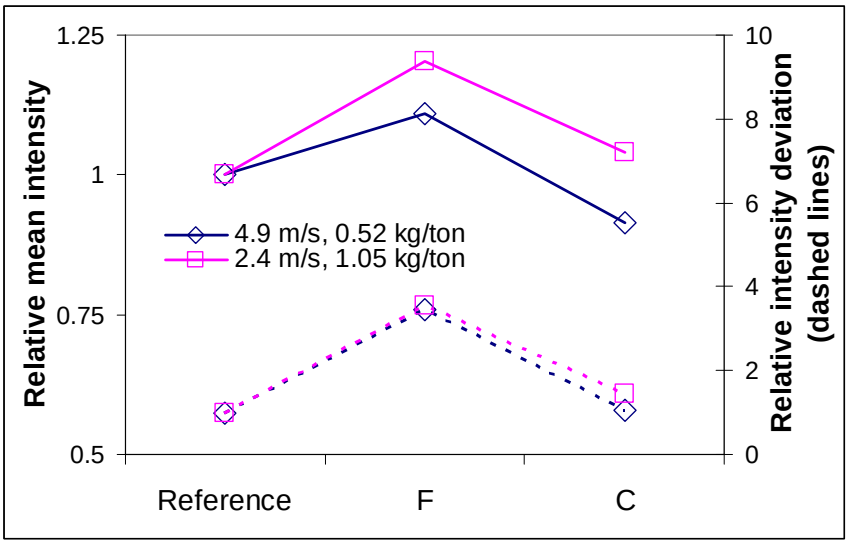
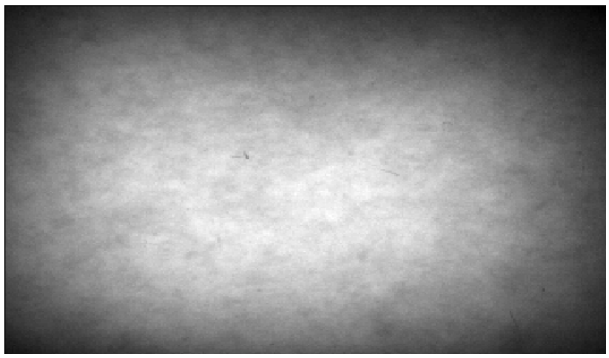


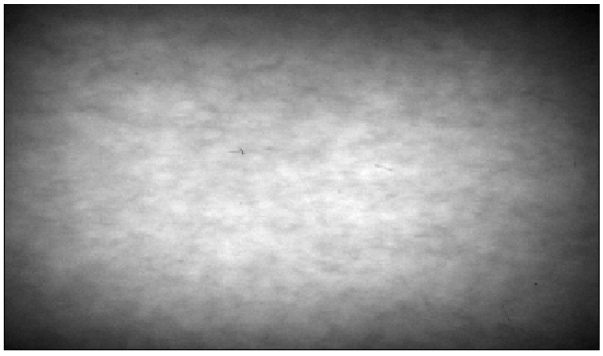
Fig. 9. Mean intensity (solid lines) and deviation of intensity (dashed lines) relative to the reference pulp. Similar flow conditions and polymer dosage are connected with a line.

The polymer C was able to increase the flocculation level with high dosage and slow flow velocity, but as the velocity was doubled and the dosage halved the floc size remained almost unchanged. Furthermore, the intensity quantities indicate that a major part of the fillers remained in the water phase.

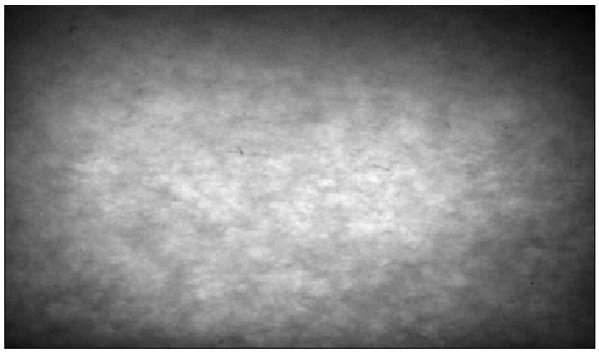
Figure 10 shows an example of the acquired images for each studied case. Clear flocculation into localized mass concentrations (variations in gray levels) was observed for pulp treated with polymer F, whereas the flocculation pattern produced by polymer C was quite close to that of the reference pulp without additives.



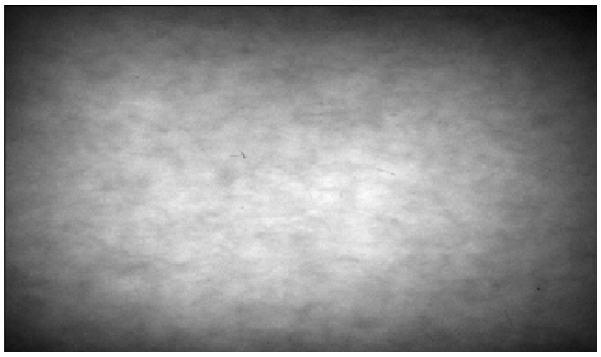
reference, 2.4 m/s



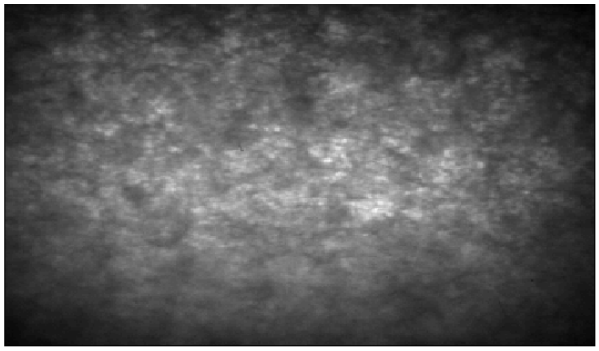
reference, 4.9 m/s



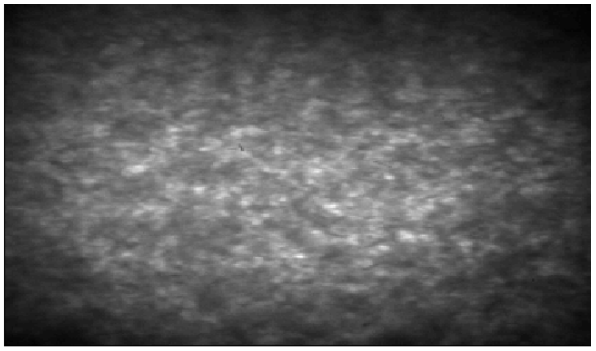
polymer C, 2.4 m/s, 1.05 kg/ton



polymer C, 4.9 m/s, 0.52 kg/ton



polymer F, 2.4 m/s, 1.05 kg/ton



polymer F, 4.9 m/s, 0.52 kg/ton

Fig. 10. Examples of transilluminated pictures of the flow in the channel with different flow conditions and polymer dosages. These images were corrected for uneven illumination for further analysis.

CONCLUSIONS

1. Promising modified bio-based flocculants from jar tests were evaluated further. A starch-based polymer functioned best in both sets of experiments, but in neither of the cases did it function as well as the commercial polyacrylamide-based polymers. The importance of the molecular weight was highlighted by the experimental results.

2. The flocculation and retention efficiency of the starch-based polymers were generally lower than those of commercial C-PAM. In shearless dewatering conditions with auxiliary filtrating fibre network, the retention and dewatering properties were quite good compared to the studied C-PAMs. However, the flow studies at higher shear conditions showed that the starch-based polymers could not produce a significant flocculation level as would be needed to maintain sufficient retention properties with studied dosages. The performance of the cellulose-based polymer as flocculating agent was very weak.
3. The molecular weight of the prepared flocculant should be much higher in order to perform well in applications of papermaking retention and dewatering. Also, the effective dosage of the flocculant should be lower, which might be feasible when the molecular weight is higher. The different charge densities, the molecular structure, and rigidity should also be tested more closely in further studies.

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