ELSEVIER

Chemical Engineering Journal 80 (2000) 51–63

Chemical Engineering Journal

www.elsevier.com/locate/cej

New equipment for detection of polymer induced flocculation of cellulosic fibres by using image analysis — application to microparticle systems

Lars Wågberg*, Jonny Eriksson[1]

SCA Research AB, Box 3054, 85003, Sundsvall, Sweden

Abstract

The present investigation has shown that the use of image analysis can be a very efficient way to study the state of flocculation of cellulosic fibres. By an FFT analysis of the grey-values of the collected images, of the flowing fibres, it was possible to evaluate both a degree of flocculation of the fibres and an average diameter of the formed flocs. Calibration with model flocs correlated very well with earlier published data.Investigations regarding flocculation of unbleached cellulosic fibres caused by a microparticle based retention aid, i.e. a combined addition of a high molecular mass cationic polyacrylamide (C-PAM) and a bentonite clay, and a site blocking polymer (SBP) (a dimethylamine epichlorohydrine condensate) were also conducted. The results from these measurements show that a preadsorption of the SBP to a surface coverage of 50% of the fibres (i.e. of its saturation adsorption) resulted in a higher degree of flocculation upon addition of the C-PAM of the microparticle based flocculant. This is probably due to a more extended conformation of the C-PAM out from the surface of the cellulosic fibres. These results were also in accordance with earlier published theories. A simultaneous addition of SBP and C-PAM in the microparticle system was not as efficient, regarding flocculation, as a pre-adsorption of the SBP. This can be explained by the fact that the way that both the SBP and the C-PAM are adsorbed is affected by the way the polymers are added. In accordance with earlier publishd data the results indicate that the adsorption of SBP is strongly affected by the presence of the C-PAM.The results nevertheless show that an addition of a SBP has a positive effect on microparticle based retention aids.Finally the present results clearly demonstrate that the polymer addition levels in flocculation studies (which are relevant for practical use) are comparably low compared with saturation adsorption on the fibres and the difference in flocculating ability of differently charged C-PAM is small compared with their corresponding saturation adsorption. Further investigations in this area are strongly recommended.

Keywords: Acrylamide; Adsorption; Bentonite; Kinetics; Cationic compounds; Cellulose fibres; Equipment; Flocculation; Image analysis; Polyelectrolytes; Synthetic polymers

---

1. Background

Synthetic polymers and polyelectrolytes have been used for a long time to improve retention and dewatering in modern papermaking. The working mechanism behind these polymers is very dependent on the type of polymer and the combination of the polymer and other components. Thorough reviews on the topic have been given by [1,2] and will not be further discussed here. One crucial step in understanding the action of these polymers is to find suitable methods to study the very rapid effect following the addition of the polymers. In this respect two different routes have been chosen:

1. Detection of the ability of the polyelectrolyte to retain fines from the cellulosic fibres used in papermaking or mineral fillers added to improve the quality of the paper. These measurements are often designed to simulate the dewatering in the wet end of the paper machine and commonly the equipment is composed of some kind of jar with a wire in the bottom (see for example [3]). The change in the amount of material retained in the jar following the addition of the polymers is taken as a measure of the efficiency of the additive.
2. Detection of the flocculation of fibres or fines following the addition of the polymers. Reviews on this have been given by [4,5]. In this respect it is possible to carefully detect the kinetics of the flocculation and how this is affected by different parameters. Naturally a study of the polymer-induced flocculation of the cellulosic fibres is a study of an unwanted phenomenon being diagnostic of the overall action of the additive. However, with this

---

* Corresponding author. Tel.: +46-60-193041; fax: +46-60-193801.
E-mail address: lars.wagberg@kep.mh.se (L. Wågberg).

[1] Present address: Institute for Surface Chemistry (YKI), Stockholm, Sweden.

1383-5866/00/$ – see front matter © 2000 Elsevier Science B.V. All rights reserved.
PII: S1383-5866(00)00077-0

technique it is possible to get a measure of how the additive will affect the formation, i.e. the standard deviation of the basis weight of the paper, of the formed paper which is a very important quality parameter.

The best way of evaluating the efficiency of the different additives would be to measure both the state of flocculation of the furnish and the retention effect of the additive. To the knowledge of the authors this has only been conducted by [6] and the methods used in their investigation only showed the potential of the approach and did not treat the topic in any depth.

Needless to mention it is vital to get more efficient tools to evaluate the state of flocculation of papermaking furnishes in order to optimise the more and more common use of retention aids in the production of all kinds of papers. The development of the computer capacity allowing for the use of image analysis to study polymer induced fibre flocculation has opened new and fast ways of directly studying the fibre flocs and their size distribution instead of utilising indirect light scattering techniques [7–9]. In [7] no attempt was made to characterise the state of flocculation in any quantitative way and in [8] image analysis was applied to high-speed photos and not on directly collected images. No attempt was made to directly collect the images and to evaluate a size distribution of flocs formed.

During the last 10 years there has been a rapid change from single component retention aid systems to systems containing both a high molecular mass cationic polyelectrolyte and an anionic microparticle [10,11]. In the application of these systems the cationic polyelectrolyte is added first followed by the anionic microparticle. In order to achieve full efficiency of the system it is very important to shear the initially formed flocs completely before the anionic component is added. In this way the large-scale flocs are destroyed and smaller scale flocs are formed, according to the original idea of the system. The main advantages of the microparticle-based systems can be summarised as:

1. Increased efficiency over a larger range of polymer additions
2. A more pronounced reflocculation after the flocs have been disrupted
3. Increased dewatering together with flocculation
4. Increased porosity of the produced paper (can also be a disadvantage depending on paper quality demands).

This list can be made more extensive but today the microparticle based systems are becoming more and more dominating and in Sweden these systems today have about 70% of the retention aid market [12].

The increasingly common use of these kinds of systems has stimulated a lot of research during the last years [13,14] and today there are at least a semiquantitative model for describing the action of the different components in the system. In [13,14] it was also discussed that the addition of a site blocking polymer (SBP) could be very beneficial for the efficiency of the system. The addition of the SBP could be very interesting for systems with a lot of dissolved and colloidal material or for systems with highly charged cellulose fibres since the consumption of the cationic polyelectrolyte, in the microparticle system, would be very high in these systems. The way of adding the SBP in the most convenient way is however not established.

The purpose of the present work was first to evaluate a new way of measuring flocculation with a system based on image analysis and secondly to evaluate how this system could be used for optimisation of the SBP addition in microparticle based retention aid systems.

2. Experimental

2.1. New equipment

In order to have a good control of the fibre suspension, polymer addition and image collection, an equipment according to Fig. 1 was constructed. The furnish is kept in a storage chest, with a maximum volume of 80 dm^3. The system is then constructed around a transparent flow channel with the dimensions 390 × 170 × 3 mm (where the thickness of the channel is 3 mm and the width is 170 mm). The inlet pipe, with an inner diameter of 30 mm, to the flow channel is transformed into a flat channel by using a widening section with an angle, in the direction of the flow, of 60°.

The flow channel was constructed from hardened glass, and below the flow channel a 150 W fibre optic light source with rheostat for variable light intensity was positioned. The light source, Fostec 8375 delivered by Parameter AB, Sweden, was giving a diffuse light proved to be stable enough

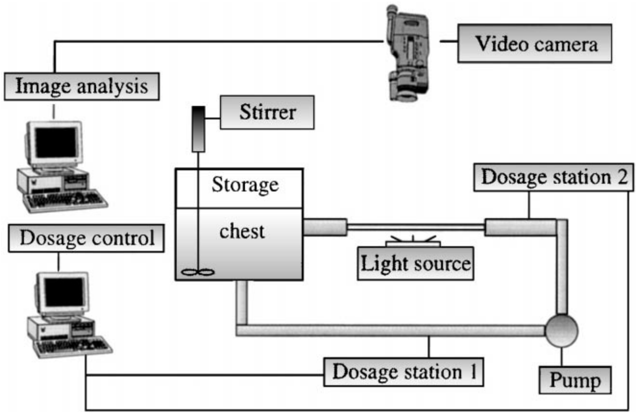

Fig. 1. A schematic representation of the new equipment for detection of fibre flocculation. The system is built around a flow channel with the dimensions 390 × 170 × 3 mm (where the thickness of the channel is 3 mm and the width is 170 mm). A light source is placed below the flow channel and the image of the fibre flocculation is collected by a video-camera positioned above the flow channel and stored in a connected computer. Polymer can be added through a specially constructed computer controlled pump-system at two different positions. The fibre suspension is pumped through the system with a frequency controlled centrifugal pump. When polymer is added the fibre suspension is pumped to the sewer whereas the suspension is recirculated when no polymer is added.

for the camera settings used. Above the flow channel a video-camera, Panasonic F15 HS with a shutter speed of 1/2000 providing images with the size of 480×640 pixels (when analysed, image area 65×65 mm), was positioned. The collected images were transferred to a computer and analysed by an image analysis program written in Matlab, from Comsol. With this program it was possible to get an average grey-value of the image, which in turn was a measure of the fibre concentration in the channel (see further the discussion below on the data analysis), and the standard deviation of the grey-value. Since the video-camera was equipped with an electronic shutter it was possible to collect images at a frequency of 2 kHz which in turn made it possible to resolve flocs of 1 mm at a velocity of 1 m s^{-1} in the measuring zone. The fibre suspension was pumped through the system with a frequency controlled centrifugal pump from Johnson Pump, Sweden, and when polymer is added the fibre suspension is pumped to the sewer whereas the suspension is recirculated when no polymer is added. Two polymer dosage stations controlled by a computer gave the possibility to add polymer before and after the pump. The delay times between polymer addition and flocculation was 0.5 and 3 s for polymer addition in dosage station 2 and dosage station 1, respectively, at a flow rate of 1 m s^{-1} in the flocculation detection zone.

2.2. Material

2.2.1. Fibres

Three different types of fibres were used during the trials:

1. An unbleached TMP (Thermomechanical pulp) from SCA Graphic Sundsvall, Ortviken, Sweden. After reslushing in a disintegrator the pulp was dewatered and washed with distilled water and pH was adjusted to 5.
2. An ECF (elementary chlorine free) bleached chemical softwood pulp from SCA Graphic Sundsvall, Östrand Mill, Sundsvall, Sweden. The pulp, delivered in dry lap form, was beaten in an Escher Wyss refiner, R 1L, according to an internal SCA standard at an edgeload of 0.5 Ws m^{-1} until a desired beating result (i.e. 25 SR) was reached. This pulp was then dewatered by filtration and washed carefully to remove both dissolved material and to convert the carboxyl groups of the fibres to their sodium form. This was done by diluting the dewatered pulp to 3% concentration and by addition of 10^{-3} M $NaHCO_3^-$ and NaOH to a pH of 9. After 15 min the fibres were dewatered again and washed at pH 2 after addition of HCl. After 30 min the pulp was dewatered and washed with deionised water to a conductivity of less than 2 μS cm^{-1} and a pH of 5. The pulps were then dewatered and stored in refrigerator until use. Before use in the experiments the pH of the pulps was adjusted to 8 and stored long enough to avoid drift in pH.
3. Unbleached chemical softwood fibres from the SCA Munksund Mill, Piteå, Sweden. The fibres were collected in the mill after the refiners in the pulp mill, dewatered to a conceantration of around 15% dry solids and delivered to SCA Research in wet lap form. Before use the fibres were washed according to the following procedure. From the initial concentration the fibres were diluted with deionised water to a concentration of 35 g l^{-1}, stirred during 20 min and then dewatered. This was repeated four times. In the fourth washing step the pulp was diluted as in the earlier steps and $NaHCO_3$ was added to a concentration of 1 mM and the pH value was adjusted to pH 8 with NaOH in order to converted the carboxyl groups on the fibres to their sodium form. After 20 min stirring the pulp was dewatered and the once again washed with deionised water in order to remove excess sodium. Conductivity measurements on the last filtrate showed a value of 20 μS cm^{-1}.

The total charge of the pulp was determined by conductometric titration [15] and the surface charge was determined by polyelectrolyte adsorption [16] and the following results were achieved

Total charge 200 μeq. g^{-1}
Surface charge 15 μeq. g^{-1}

The amount of fine material from the cellulosic fibres, smaller than 75 μm, was found to be 7.1% of the total material.

2.2.2. Synthetic flocs

Synthetic flocs [17] with a specific flocsize of 1.23 mm ± 0.11 prepared from bleached beechwood pulp, according to [4], were used for calibration.

2.2.3. Chemicals

A cationic copolymer APTAC:ACM, kindly supplied by Allied Colloids Ltd., England, consisting of acrylamide and aminopropyltrimethylammoniumchloride was used in the flocculation and adsorption experiments. The chemical structure of the polymer is shown in Fig. 2.

Polymers with different degrees of substitution of cationic APTAC groups were prepared and this naturally resulted in polyelectrolytes with different charge densities. The SBP used was a dimethylamine epichlorohydrine condensate from Allied Colloids, Bradford, UK. The measured charges of the polymers, from polyelectrolyte titration [18], and

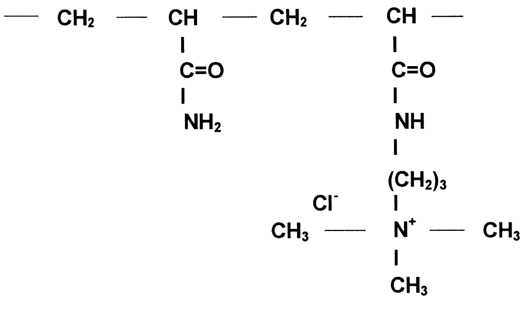

Fig. 2. Chemical structure of the ACM:APTAC copolymer used.

Table 1
Summary of composition, charge and molecular mass of the used polymers

Polymer type	Charge density (meq. g^{-1})	Molecular mass × 10^6
SBP	5.64	0.002/0.04
10/90 (APTAC/ACM)	0.39	2
20/80 (APTAC/ACM)	0.80	3
40/60 (APTAC/ACM)	1.51	1

their molecular mass, determined by size exclusion chromatography (SEC) according to [19], are summarised in Table 1. The polymer charges were determined at pH 8 which also was the pH at which all measurements in this report were conducted.

There is a fairly large discrepancy between the charge that can be calculated from the expected composition of the polymers and the measured values. One explanation to this might be that these specially prepared polymers are carefully cleaned through a precipitation. In this procedure acetone is added to the water phase which causes a precipitation of the polymers leaving the unreacted monomer in solution. Obviously this causes a preferential precipitation of the low charge fraction, and probably also high molecular mass fraction, of the polymer in question. The experimentally determined charge of the polymer was used when trying to interpret the data from the adsorption measurements.

As indicated in the table the SBP had a bimodal molecular mass distribution and about 80% could be found in the low molecular mass fraction.

The copolymers were delivered as powders, and were used without further purification. They were dissolved in distilled water, stirred overnight and kept at a concentration of 4 g l^{-1} solution until shortly before application. The SBP was delivered as a concentrated solution and was diluted with deionised water to a desired concentration 2–3 h before use.

In the polyelectrolyte titration, which was used to determine the concentration of polyelectrolyte in solution, an anionic polyelectrolyte, potassium polyvinyl sulphate (KPVS), was used and this polyelectrolyte was delivered by Wako Pure Chemicals, Japan. It was delivered as a dry powder and was used without further purification. Orthotoluidine Blue (OTB), a cationic indicator from Kebo AB, Sweden, was used as indicator in the polyelectrolyte titrations.

In order to determine the surface charge of the fibres an poly-diallyldimethylammonium chloride (DADMAC) from Allied Colloids, Bradford, England was used. In order to remove the low molecular mass fraction of this polymer it was subjected to ultrafiltration according to a procedure outlined in [16] and the ultrafiltration cell was fitted with a filter with a molecular mass cut-off of 300 000. The molecular mass of the polymer was determined to 1.2×10^6 by size exclusion chromatography according to [19].

In the experiments with the microparticle systems montmorillonite clay was used as one part of the retention aid system. The clay was delivered by Allied Colloids, Bradford, England, as a dry powder and was allowed to swell over night in deionised water. Only the fraction that did not settle was collected and used in the experiments.

All other chemicals, NaOH, HCl, etc. were of analytical grade.

2.3. Methods

2.3.1. Experimental conditions

2.3.1.1. Relation between light absorption, from image analysis, and fibre concentration. In order to clarify if there was a relationship between light absorption and fibre concentration, images from batches of different fibre concentrations and different flow rates were analysed. The concentration was varied between 0.5 and 8 g l^{-1}, and the flow rate was varied between 0.4–1.2 m s^{-1}. In order to be able to predict the flocculation correctly, according to the definitions given by [5] (see also the definitions given later in this paper) it is necessary to have a fixed relationship between light absorption and fibre concentration. It is also vital that this relationship is not affected by the state of flocculation of the fibres and therefor it was decided to measure the light absorption at different flow rates since the flow rate definitely will affect the state of flocculation of the fibres.

2.3.1.2. Calibration with model fibre flocs. A calibration measurement was performed by adding specially prepared (synthetic) fibre flocs to a dispersion of bleached chemical fibres and by measuring the change in the signal from the equipment. The fibre suspension was always diluted with distilled water to a concentration of 1 g l^{-1} and the amount of synthetic flocs added was kept constant at 10% of the total fibre concentration. These results from the new equipment were then compared with the results achieved in [4] where, however, a different concentration of model flocs was used.

2.3.1.3. Flocculation following addition of cationic polyacrylamides. A dispersion of unbleached chemical fibres, washed according to the procedure described earlier, was diluted to 5 g l^{-1} with distilled water in the storage tank of the flocculation equipment described in Fig. 1 and the pH was adjusted to 8 with NaOH. When the SBP was preadsorbed to the fibres it was added to the storage tank and allowed to adsorb for 10 min before the experiments started. When the SBP was mixed together with the C-PAM it was added at dosage station where the C-PAM was always added in the flocculation experiments. Bentonite was always added at dosage station 2. The delay time between dosage station 1 and dosage station 2 was around 2.5 s and the delay time between dosage station 2 and the detection cell was 0.5 s.

2.3.1.4. Adsorption measurements and charge determination. In order to determine the adsorption of the different polyelectrolytes on the unbleached chemical fibres a number of adsorption experiments were conducted. In these experiments 0.5 g dry fibres were diluted with distilled water, pH was adjusted to 8 and different amount of polymer solution was added to a total volume of 100 ml. After 10 min the suspensions were filtered and the concentration of unadsorbed polymer was determined by using the polyelectrolyte titration according to a method described in [20] with the aid of an equipment first described by [18].

Charge determination of the different polymers was conducted by using the polyelectrolyte titration method [21]. With a polymer concentration of 0.1 g l^{-1}, pH adjusted to 8, different amount of the polymer was titrated using KPVS. Knowing the charge of the KPVS the charge of the polymer can be calculated assuming a 1:1 stoichiometry between the charges on the two polymers.

Polyelectrolyte adsorption was used to determine the surface charge of the fibres according to [16]. In this method it is assumed that a high molecular mass poly-DADMAC is adsorbed to the charges on the external surface of the fibres through an ion-exchange process. These measurements were all conducted at pH 8 and with an adsorption time of 30 min. The total charge of the fibres was determined with the aid of conductometric titration [15].

2.3.2. Analysis of data

2.3.2.1. Light transmittance. According to the Lambert–Beer law there is a relation between the absorbance and the concentration of the absorbing species. Light scattering from the cellulosic fibres will however affect the grey-level value of the collected images and it is therefor essential to determine if there is a direct correlation between fibre concentration and light absorption. The camera measures the transmitted light and in the design of the equipment it has been assumed that the average grey-level in the pictures collected by the camera should be a good estimate of the average concentration of the fibre dispersion. In the same way the variation in grey value should be an estimate of the variation in fibre concentration. However, in order to test this assumption different fibre suspensions were tested and the light transmittance data from the digital camera were then recalculated to light absorption data in order to see if there is a Lambert–Beer type of correlation between light absorption and concentration.

2.3.2.2. Degree of flocculation. In order to quantify the data from the collected images the data were treated in the same way as described by [5]. By using this methodology the change in the state of flocculation following polyelectrolyte addition is calculated as a degree of flocculation and as an average diameter of the formed fibre flocs. Assuming that the average grey-level in the pictures is a measure of the fibre concentration and that the variation in grey value is a measure of the variation of the fibre concentration the degree of flocculation of the fibre dispersion, following polymer addition, is defined as [5]:

$$ff = \sqrt{V_2^2 - V_1^2}/V_1 \qquad (1)$$

where $V_1 = \sigma(e_1)/\bar{e}_1$; $V_2 = \sigma(e_2)/\bar{e}_1$; $\sigma(e_1)$, standard deviation of grey-value of the images collected without polymer addition; $\sigma(e_2)$ standard deviation of grey-value of the images collected with polymer addition; $\bar{e}_1$, average grey-value of transmitted light without polymer addition.

By normalising the data to the average grey-value of a certain fibre concentration and a certain fibre type only the changes upon polymer addition is detected and in this way different types of fibres can be compared even if they have different correlation coefficients in the Lambert–Beer evaluation mentioned earlier.

With the available software it is possible to take the image analysis a step further. By making a Fast Fourier Transform (FFT)-analysis of the image, it is possible to get the variation in local grey scale (and hence local concentration), in different wavelength (i.e. size) ranges. This gives an opportunity to detect what is happening with flocculation in different wavelength ranges when chemicals are added to the furnish. The results from the FFT evaluation is a standard deviation in grey value in a certain size range. By comparing the standard deviation in grey value in different size ranges with and without polyelectrolyte addition it is possible to determine how the flocculation is distributed on different floc sizes. In a formal way this is done by computing a cumulative function *S*, according to equation Eq. (2). The position where this function has reached 50% of its final value is defined as an average diameter of the formed flocs. Examples of this treatment will be given later in the paper

$$S = 1/\bar{e}_1\left(\sum_i \left(\sigma\,(e_2)_i^2 - \sigma\,(e_1)_i^2\right)^{1/2}\right) \qquad (2)$$

where $\sigma(e_2)_i$, standard deviation of grey value in size range i with polymer addition $\sigma(e_1)_i$, standard deviation of grey value in size range i without polymer addition. The rest of the symbols have the same meaning as in Eq. (1).

By using these two definitions it is possible to condense the data from the flocculation measurements into to entities and this enables a good evaluation of the otherwise fairly complex images from the digital camera.

3. Results and discussions

3.1. Relations between light absorption from image analysis and concentration

In order to test the assumption that there is a Lambert–Beer type of relationship between light absorption from the image analysis measurements and fibre concentration, two different pulps were tested. The results from these experiments are shown in Fig. 3 and as can be seen there is a linear relationship for both the chemical pulp and for the TMP but the slopes are different for the two pulps. There might be several reasons to this difference. First of all one of the pulps, the TMP, contains more fines material, and if

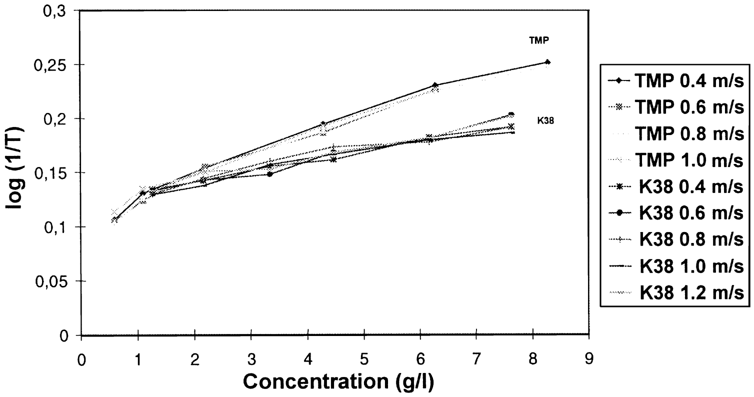

Fig. 3. Light absorption measurements, calculated from the collected images of the flowing fibre dispersions, at different flow rates (m s^{-1}) for the two different pulps. The interval between 1 and 6.5 g l^{-1} shows a linear correlation between log 1/*T* and concentration, independent of the flow rate, i.e. the state of flocculation of the fibres.

light scattering contributes to the detected signal it would be natural that the TMP would give a higher apparent light absorption. On the other hand it is also natural that the TMP would give a higher light absorption since this pulp contains more lignin and hence has an inherently higher light absorption than the bleached chemical pulp. Since both these relationships are exponential they would both give linear correlations in Fig. 3. In order to sort out which of these factors that are most dominating the light scattering coefficients and the light absorption coefficients (used as extinction coefficients in the Lambert–Beer equation) of the pulps can be used. Typical light scattering coefficients (measured in air) for a TMP is 54 m^2 kg^{-1} and for a chemical pulp the corresponding value is around 25 m^2 kg^{-1}. Corresponding values for the light absorption coefficients (also measured in air) are, typically, 2.7 and 0.4 m^2 kg^{-1} for the TMP and the sulphate pulp, respectively. Since the ratio of the slopes for the two pulps in the figure is 2.2, it is tempting to postulate that the light scattering is dominating the measurement since the ratio between the light scattering for the two pulps is also 2.2 (measured in air). It should though be remembered that the correlation between the transmittance and light scattering is not simple, it should be stressed that further measurements are needed to determine which of the two factors that are dominating the measured signal. It is also suggested that the bleached chemical pulp should be covered with lignin to a *k*-value similar to that of the TMP in order to be able to compare the pulps correctly. Nevertheless, the linear relationships in Fig. 3 indicates that a modified Lambert–Beer type of relationship for the present set-up can be suggested according to the following equation

$$A = (\varepsilon_1 + \varepsilon_2) \cdot b \cdot c \tag{3}$$

where ε_1, apparent extinction coefficient from light absorption; ε_2, apparent extinction coefficient from light scattering; *b*, distance between the walls of the measuring chamber (3 mm); *c*, concentration of the fibres.

Needless to say the validity of this equation has to be further tested but the results in Fig. 3 definitely show that relation (3) can be used to study simple systems consisting of for example one single pulp. Therefor the evaluation method, where a flocculating index is calculated from the collected images together with the size of the formed flocs, should be safe at least for the applications used in the present investigation.

The results in Fig. 3 also show that the linearity of the curves is good in the concentration interval 1–6.5 g l^{-1} and also that it is independent of the flow rate, i.e. the state of flocculation of the fibres and fines. This further supports the statement earlier that Eq. (3) can be used for the systems studied in the present work. Concentrations outside this interval give a deviation from linearity and therefor these concentration ranges should be avoided. Furthermore the reasons to the deviation from linearity should be determined.

3.2. Calibration with model flocs

As was mentioned in the experimental section a calibration measurement was performed using model flocs. According too earlier publications [4] these flocs have an average floc diameter of 1.23 ± 0.11 mm. By using the same type of flocs in the present investigation it was possible to compare the results to the results found earlier [4] and the results are presented in Table 2. A slightly higher floc size of these flocs would be expected because of the fact that the bleached chemical softwood fibres are adhered to the synthetic flocs.

Table 2
Comparison of the floc size measurements of model flocs from the present investigation and [4]

	Present investigation	Wågberg, 1985
Total fibre concentration (g l^{-1})	1	2
Floc diameter (mm)	1.7	1.5

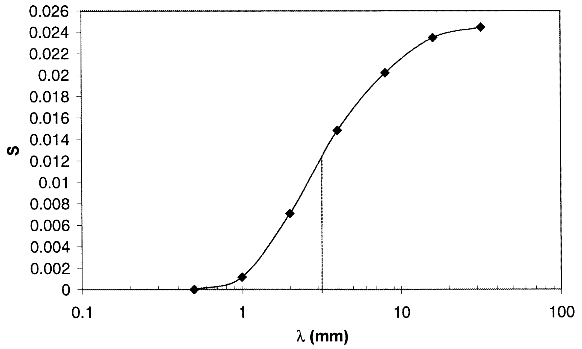

Fig. 4. Determination of the average floc diameter by applying Eq. (2) for the measurements with model flocs. The difference in variance between a reference system and the system with addition of synthetic fibre flocs is plotted as a cumulative function. The wavelength at which the *S*-function reaches 50% of its final value is used to evaluate the average floc diameter. This value then has to be divided by 2 to get the correct floc diameter due to the principles of the FFT evaluation.

As can be seen in the table there is a good agreement in floc size as determined with the different equipment. One reason for the small difference could be the difference in the fibre concentration used. In [4] it was found that increasing the fibre concentration diminished the influence of fibres adhering to the flocs.

The floc size was determined by the methodology outlined in Eq. (2) and according to this equation a cumulative curve can be constructed showing how the difference in variance between the two measurements are distributed on different floc sizes. For the evaluation of these model flocs the reference state was chosen as the fibre dispersion without addition of fibre flocs but with the same total fibre concentration. The results from this calculation is shown in Fig. 4 and it should be stressed that the size determined at the 50% level has to be divided by two to get the correct floc size since the FFT analysis presents the results as full sine curves.

The floc size was calculated within a certain wavelength range where the upper limit was chosen to $\lambda = 32$ mm. Above this wavelength there are poor statistics since the detected area becomes a significant part of the measuring area. The lower limit was set by the limitation in the size of the pixels, with the chosen measuring area, and in relation to floc sizes it was not meaningful to measure flocs smaller than 0.25 mm ($\lambda = 0.5$mm).

3.3. Polymer adsorption of different polymers

In order to evaluate how the different polyelectrolytes adsorb to the fibres a number of adsorption experiments were conducted. The results from these experiments are shown in Fig. 5.

As can be seen in the figure there is a large difference between the different polyelectrolytes. This difference can naturally be caused by a difference in molecular mass, and hence a different possibility for the polyelectrolytes to penetrate the porous fibre wall, or a difference in charge of the polymers or both. In order to check which of these factors that were most important the data in Fig. 5 were replotted to show the amount of adsorbed charges for the different polymers.

From the results in Fig. 6 it is clear that the charge of the polymer is very important for the adsorption and despite the rather large difference in charge for the different C-PAM they show approximately the same amount of adsorbed charges. Furthermore the amount of adsorbed charges for the C-PAM is very close to the surface charge as determined with the polyDADMAC, i.e. 15 μeq. g^{-1}. For the SBP the situation is a bit different and in Fig. 6 it can be seen that the SBP can reach reach around 30 meq. g^{-1}. This indicates that the SBP penetrates the porous fibre wall a bit more than the C-PAM but since the adsorption still is far from the total charge of the fibres the polymer is still adsorbed to the external surface of the fibres to a large extent. This information will be very

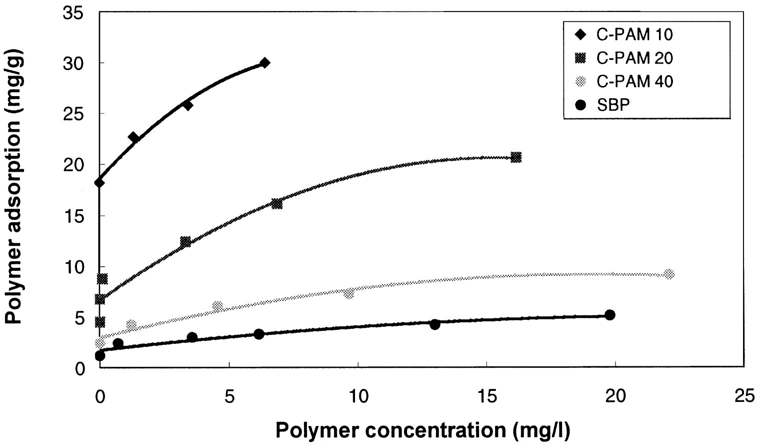

Fig. 5. Adsorption in mg g^{-1}, of the different polyelecrolytes used in the investigation. The fibre concentration during the experiments was kept constant at 5 g l^{-1} and the pH was 8 for all the experiments. Time for adsorption was 10 min. SBP is an abbreviation of site blocking polymer and this is a dimethylamine epichlorohydrine condensate. The properties of all these polyelectrolytes can be found in Table 1.

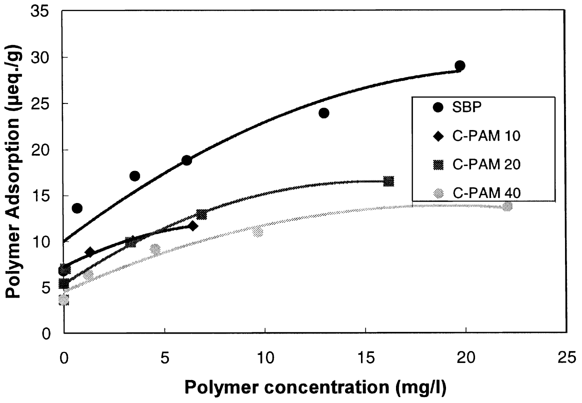

Fig. 6. Adsorption, in µeq. g^{-1}, of the different polyelecrolytes used in the investigation. The fibre concentration during the experiments was kept constant at 5 g l^{-1} and the pH was 8 for all the experiments. Time for adsorption was 10 min. SBP is an abbreviation of site blocking polymer and this is a dimethylamine epichlorohydrine condensate. The properties of all these polyelectrolytes can be found in Table 1.

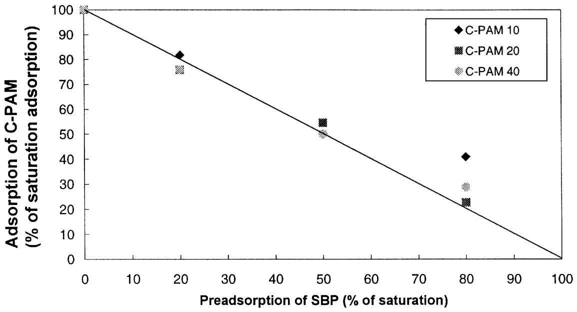

Fig. 7. Adsorption of C-PAM, in % of saturation adsorption as evaluated from Fig. 5, as a function of degree of surface saturation of the SBP polyelectrolyte. The fibre concentration during the experiments was kept constant at 5 g l^{-1} and the pH was 8 for all the experiments. Time for adsorption was 10 min for both the presaturation and for the C-PAM adsorption. SBP is an abbreviation of site blocking polymer and this is a dimethylamine epichlorohydrine condensate. The properties of all these polyelectrolytes can be found in Table 1.

important for the interpretation of the flocculation results achieved with different polymer additions.

In Fig. 6 it is also shown that the adsorption of SBP shows no clear levelling off in comparison to the different C-PAM polymers. This can most probably be linked to the fact that the polyelectrolyte will decrease its dimension when the concentration is increased and this will increase its penetration into the fibre wall. The larger sensitivity of the SBP to increased polymer concentration, compared with the C-PAM polymers, is probably due to the fairly low molecular mass of this polymer. Obviously the size of the SBP, specially its low molecular mass fraction, is close to the dimensions of the pores in the fibre wall and therefor only small changes in the extension of the polymer can result in considerable changes in the adsorbed amount.

As was mentioned in the introduction it is interesting to replace the more expensive C-PAM with the more highly charged and cheaper SBP. However, in order to make sure that they adsorb to at least approximately the same groups on the fibres it was necessary to first saturate the fibres to different degrees with the SBP and then to adsorb C-PAM to these presaturated fibres. In these experiments the SBP polymer was allowed to adsorb for 10 min and then the excess was removed by filtration. After a mild wash the fibres were again reslushed and the adsorption of C-PAM to these fibres was measured after another 10 min adsorption time. The saturation adsorption of the SBP was determined from Fig. 5. The results from these measurements are shown in Fig. 7 where the adsorption of C-PAM, in % of saturation adsorption, is shown as a function of degree of surface saturation of the SBP.

The results in Fig. 7 show that the different polymers adsorb to the same sites on the fibres since a preadsorption of the SBP to a certain level blocks the adsorption of the C-PAM to approximately the same extent. This is true up to a preadsorption of approximately 80% where there is a large deviation especially for C-PAM 10. The reason to this deviation can either be a changed conformation of the adsorbed polyelectrolyte (C-PAM 10) or a desorption of the SBP. Earlier work [22] has, however, shown that a higher charged polyelectrolyte is more efficient in displacing another similarly charged polyelectrolyte. It therefor seems likely, from the results in Fig. 7, that the increased adsorption at higher degrees of surface coverage of SBP is most probably due to a changed conformation, i.e. more extended out from the surface, of the adsorbing C-PAM. This possible change in polymer conformation would also render the C-PAM 10 more efficient as a flocculating polymer in the microparticle system if the theories proposed by [13] are valid.

3.4. Flocculation of cellulosic fibres by microparticle based systems

3.4.1. Influence of SBP addition and the mode of SBP addition

As was mentioned in the introduction, earlier work by [14,13] has indicated that the addition of a site-blocking polymer can significantly improve the efficiency of the microparticle systems. In these investigations the SBP was added before the C-PAM but a very interesting practical way of adding the SBP would be to mix it with the C-PAM before it was added to the fibre/water mixture. This idea was tested with the C-PAM 20 polymer and the results from these investigations are shown in Fig. 8.

In accordance with earlier results [13] the pre-addition of the SBP significantly improved the efficiency of the C-PAM. The results in Fig. 8 also show that a simultaneous addition of the SBP and the C-PAM resulted in floccuation results somewhat in between the pure micro-particle based system and the system with pre-adsorbed SBP. The reason behind this can most probably be found in the results presented by [23] where it was shown that the C-PAM was able to adsorb together with the SBP in addition ranges similar to

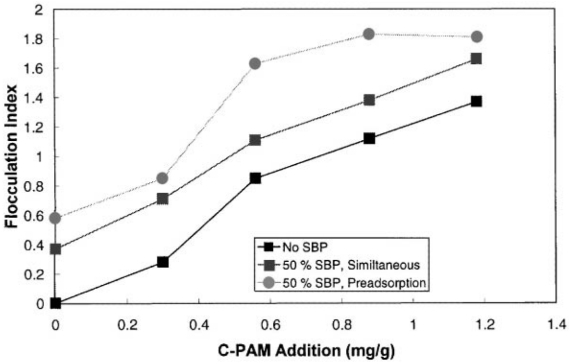

Fig. 8. Flocculation index as a function of added C-PAM 20. Different modes of SBP addition were tested. Both simultaneous and separate addition was tested. In the simultaneous addition the SBP was pre-mixed with the C-PAM and with separate addition the SBP was added 10 minutes before addition of C-PAM. The level of surface coverage of the SBP was 50% as determined from the adsorption isotherms in Fig. 5. pH was kept constant at 8 during the measurements.

Table 3
An estimation of the collision frequency between the polymer molecules and the fibres[a]

Type of polymer	N_{12} ($\mathrm{m^{-3}\cdot s^{-1}}$)	Time for coll. (s)
SBP−1	5.3×10^{21}	9×10^{-13}
SBP−2	6.5×10^{19}	8×10^{-11}
C-PAM 1	6.2×10^{17}	2×10^{-9}
C-PAM 2	1.9×10^{18}	5×10^{-10}

[a] The last column is calculated simply by dividing the frequency with the number concentration of fibres. The values used to calculate the data are collected from the results earlier in the report and these data are also summarised above the table.

the experiments reported in this paper. This means that the SBP will not adsorb *before* the C-PAM and it will hence not be as efficient in promoting the flocculation, when added together with the C-PAM, compared with the case when it was pre-adsorbed to the fibres. Another difference between the two modes of addition is that in the separate mode the SBP has a long time to adsorb and to find its equilibrium conformation. In the simultaneous addition mode there is a very dynamic situation where the SBP and C-PAM adsorbs at the same time. This means that the C-PAM will adopt a different conformation on the surface, compared with the separate addition mode, despite the fact that there is an adsorption of both SBP and C-PAM. This means that the way the surface coverage of the fibres by the polymers has been achieved is important for the efficiency of retention aid. In the theory proposed by [13] this is taken care of by the chain expansion term which describes the extension of the polymer out from the fibre surface. However, this theory does not take into consideration how the layer has been formed and therefor the present results shows that a development of the theory is necessary. Another reason behind the difference might be that the time for adsorption for the polymers in the simultaneous addition mode is that the polymers simply not have time enough to reach the same equilibrium conformation as in the separate addition mode.

When looking at the results it might seem obvious that the SBP should not be adsorbed preferentially over the C-PAM. However, considering the much higher number concentration of the SBP it could be assumed that this molecule would show a much more rapid initial adsorption. In order to quantify the initial adsorption rate of the polyelectrolytes it is necessary to calculate the collision frequency between the fibres and the polymers. In order to do this the following equation was used [24]

$$N_{12} = 1.294(a_1 + a_2)^3\, G \cdot n_1 \cdot n_2 \qquad (4)$$

where N_{12}, collision frequency ($\mathrm{m^{-3}\ s^{-1}}$); a_1, a_2, radius of the polymers and the fibres respectively (m); n_1, n_2, number concentration of the fibres and the polymers ($\mathrm{m^{-3}}$); G, average shear field in the dispersion ($\mathrm{s^{-1}}$).

To make some rough calculations Eq. (4) together with the appropriate data for the different polymers were used and the results from these calculations are given in Table 3. The values used to reach these data were

Fibre concentration	5×10^{9} ($\mathrm{m^{-3}}$) (according to [25] and the fibre concentration used in the present investigation)
SBP-1 concentration	1.7×10^{21} ($\mathrm{m^{-3}}$) (low molecular mass fraction from a concentration of 5.6 g $\mathrm{m^{-3}}$)
SBP-2 concentration	2.1×10^{19} ($\mathrm{m^{-3}}$) (high molecular mass fraction from a concentration of 1.4 g $\mathrm{m^{-3}}$)
C-PAM 1	2.0×10^{17} ($\mathrm{m^{-3}}$) (from a concentration of 1 g $\mathrm{m^{-3}}$)
C-PAM 2	6.0×10^{17} ($\mathrm{m^{-3}}$) (from a concentration of 3 g $\mathrm{m^{-3}}$)
Fibre diameter	1×10^{-4} (m) according to [26][2]
G	483 ($\mathrm{s^{-1}}$) from a similar set-up in [5]

As can be seen from this table the times for collision are extremely short and it can be concluded that the C-PAM and the SBP will collide with the fibres very fast. These values in combination with the molecular mass data in Table 1 can furthermore be used to estimate how much polymer that will adsorb in 1 s provided all colliding polymers will adsorb. This is done with the following, simple equation.

$$\Gamma = \frac{N_{12} \cdot M_\mathrm{w}}{n_\mathrm{f} \cdot N_\mathrm{A} \cdot w_\mathrm{f}} \qquad (5)$$

where Γ, polymer adsorption in g polymer/g fibre; M_w, molecular mass of the polymer; w_f, weight of one fibre (i.e. 1/number of fibres per g); N_A=Avogadros number.

---

[2] Naturally fibres are not spherical but for simplicity in the calculations the volume of one fibre has been recalculated to a sphere with the same volume and the diameter used in the calculation is the diameter of this sphere.

Table 4
Estimated adsorption of the different polymers from data in Table 1 and Table 3, after 1 s[a]

Type of polymer	Adsorption after 1 s (mg g^{-1})
SBP 1	3.5
SBP 2	0.86
C-PAM1	0.62
C-PAM2	1.9

[a] For this calculation it has been assumed that all collisions lead to adsorption and the numerical values used are those used for calculating the collision frequencies. Note that the adsorption has been calculated for each single molecular species and not for mixtures.

If the adsorption of the different polymers in Table 2 is estimated with this equation the following result is achieved, see Table 4.

From this table it is clear that the C-PAM can start to compete for the sites on the fibres when the added amount is increased.

It might also be mentioned that since the collision frequency is so high it is very likely that other factors, such as collision efficiency factors will be more important than the frequency as such. These factors are not known for the present system but are definitely worth more attention in future research.

Brownian diffusion might also be important for the present adsorption discussion. When calculating this contribution it is a bit difficult to calculate a collective diffusion cofficient for the fibres and the polymers since the fibres will naturally have a very limited Brownian motion. So when estimating the influence of diffusion it was assumed that

1. The polymer molecules in the volume that is occupied by the fibres will immediately be adsorbed by the fibres.
2. The diffusion of the polymer molecules in 1 s will lead to a depleated layer around the fibres with a thickness corresponding to the diffusion distance in this stime interval.

For SBP 1 the molecular size (i.e. radius of gyration) was estimated from data by [27] for poly-diallyldimetahylammonium chloride (DADMAC) since there are no publlished data available for the SBP in question. The radius of gyration was estimated to 55 Å and by using Eq. (6), the diffusion coefficient for the polymer could be estimated.

$$D = \frac{kT}{6\pi\eta r} \tag{6}$$

where D, diffusion coefficient; k, Boltzmannis constant (1.38×10^{-23}); T, absolute temparature (293 K used); η, dynamic viscosity of water (1×10^{-3} Ns m^{-2}); r, radius of the polymer.

The diffusion constant was calculated to be 3.9×10^{-11} (m^2 s^{-1}). In 1 s the diffusion distance will be 8.8×10^{-6} m. By adding this to the radius of a spherical cellulose fibre the total radius will be 58.8×10^{-6} m for the volume depleated with polymer, i.e. the polymer contained in this volume will be adsorbed to the fibre. From the concentration of polymer (i.e. 1.7×10^{21} (m^{-3})) the polymer contained in this volume will be 85×10^{-7} g polymer/g fibre which is far from the adsorption induced by turbulence. It may hence be concluded that the influence from Brownian diffusion is negligable for the present system. However, since there are so many assumptions behind these calculations they should only be taken as an estimate of the order of magnitude of the influence of the different processes. Nevertheless they demonstrate

1. the importance of the turbulence for the adsorption
2. that C-PAM might compete with the SBP for the surface sites on the fibres which was the origin for the present part of the discussion.

In order to check the hypothesis, of the competition of surface sites between C-PAM and SBP, further the influence of the level of SBP addition was investigated and the results from these measurements are shown in Figs. 9 and 10. Fig. 9 represents measurements with separate addition of SBP and C-PAM whereas Fig. 10 represents measurements with simultaneous addition.

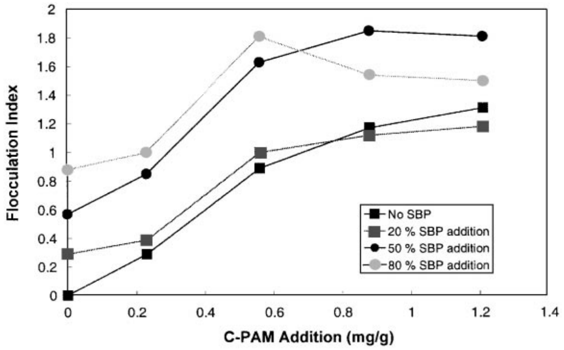

Fig. 9. Flocculation index as a function of added C-PAM 20. Different levels of SBP addition were tested and these results represent experiments with separate addition of SBP and C-PAM 20. The SBP was added 10 min before addition of C-PAM and the level of surface coverage of the SBP was 20, 50 or 80% as determined from the adsorption isotherms in Fig. 5. pH was kept constant at 8 during the measurements.

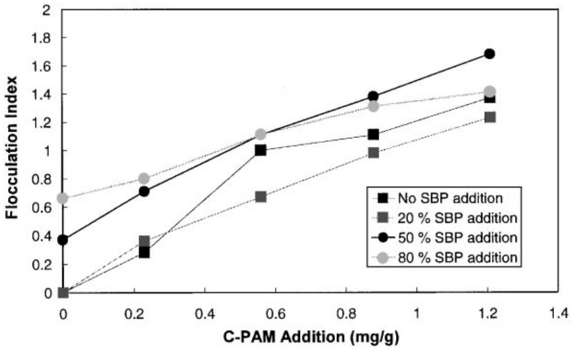

Fig. 10. Flocculation index as a function of added C-PAM 20. Different levels of SBP addition were tested and these results represent experiments with simultaneous addition of SBP and C-PAM 20. The SBP was added 10 min before addition of C-PAM and the level of surface coverage of the SBP was 20, 50 or 80% as determined from the adsorption isotherms in Fig. 5. pH was kept constant at 8 during the measurements.

By comparing Fig. 9 and Fig. 10 it is obvious that a preaddition of the SBP is much more efficient than a simultaneous addition of the two polyelectrolytes. Furthermore the results in Fig. 9 closely follow the theoretical predictions from [13] regarding the addition of SBP in microparticle based retention aid systems. The results in Fig. 10 supports the earlier discussion regarding simultaneous adsorption of SBP and C-PAM and at higher additions of SBP the adsorption of C-PAM seems to be too much hindered to allow for an efficient use of the SBP. This is also in full accordance with earlier published results ([23]). At higher addition of C-PAM it is on the contrary clear that there is almost no positive effect of the site blocker. This is most probably due to the fact that the C-PAM is only adsorbed to a minor extent and most probably in a mixed layer together with SBP.

3.4.2. Influence of the charge of the C-PAM

Since the adsorption of the C-PAM was significantly different, at saturation adsorption (see Fig. 5), it was considered important to investigate how a change of the charge of the polymer will affect the degree of flocculation both in the pure microparticle based system and in a system with addition of a SBP. In Fig. 11 it is shown that there is only a minor effect of the charge density of the polymer on the flocculating ability of the pure microparticle based system, i.e. without SBP addition. This might at first seem hard to explain but considering that the collision frequency for the different polymers with the fibres are similar and that the addition levels investigated in Fig. 11 are far from the saturation adsorption it is maybe not that surprising. In [13] it was discussed whether the interaction between the bentonite and the C-PAM was driven by a charge interaction or by non-ionic interaction between the C-PAM and the bentonite. The present results suggest that the interaction is not dominated by charge interactions, since there is no difference between the different polymers, but more careful experiments are needed where the flocculation and adsorption are measured simultaneously. This type of investigations are presently conducted in our laboratory.

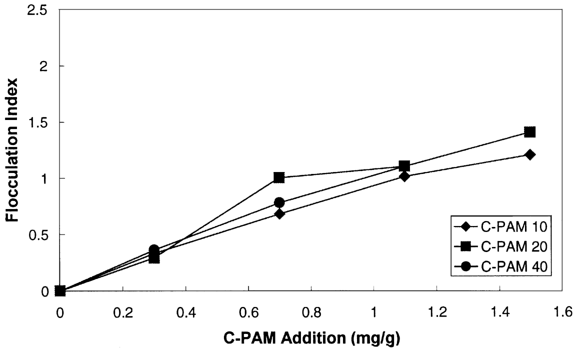

Fig. 11. Flocculation index as a function of addition of different C-PAM. pH was kept constant at 8 during the measurements and the fibre concentration was 5 g l^{-1}. The addition of bentonite was 2.5 mg g^{-1} in all measurements.

Similar types of experiments but with SBP addition were also conducted and results from those measurements are given in Figs. 12 and 13. For the experiments summarised in Fig. 12 the SBP has been preadsorbed to 50% of its saturation adsorption (i.e. 1.4 mg g^{-1} from Fig. 5) and for the experiments in Fig. 13 the C-PAM and the SBP are simultaneously added. The SBP addition for the mode of simultaneous addition was kept on the same level as for the pre-adsorption mode.

As for the results in Fig. 11 there are no overall large differences between the different C-PAM's. In Fig. 12 it can be noted that the most highly charged C-PAM (C-PAM 40) starts to show a decrease in flocculation at addition levels higher than 1 mg g^{-1} which indicates that the optimum for this bentonite addition has been passed for this particular bentonite addition. This is also in accordance with the theory for microparticle based retention aids [13]. However, since the differences between the different

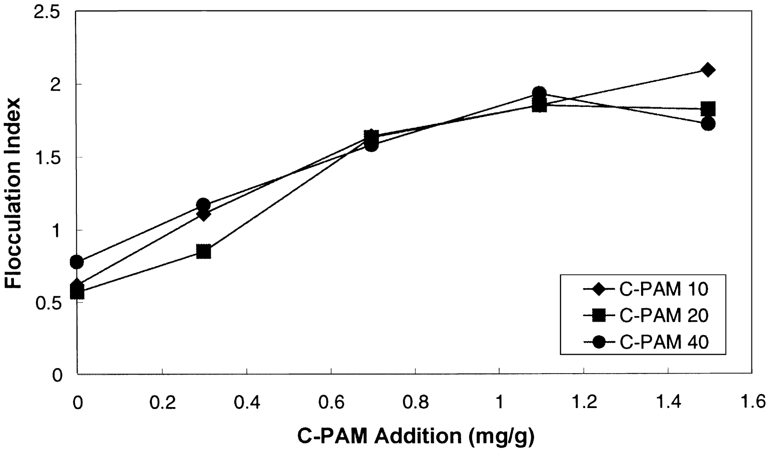

Fig. 12. Flocculation index as a function of C-PAM addition. Different types of C-PAM were tested and these results represent experiments with pre-adsorption of the SBP. The SBP was added 10 min before addition of C-PAM and the level of surface coverage of the SBP was 50% as determined from the adsorption isotherms in Fig. 5. pH was kept constant at 8 during the measurements and the addition of bentonite was kept constant at 2.5 mg g^{-1}.

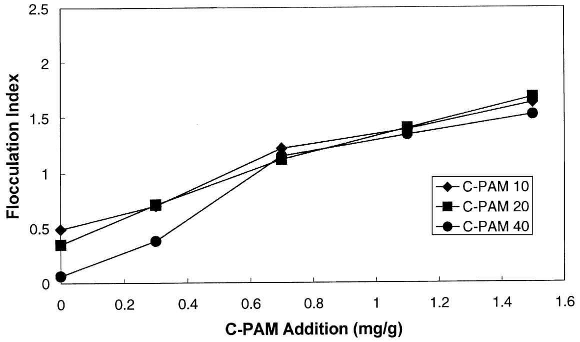

Fig. 13. Flocculation index as a function of C-PAM addition. Different types of C-PAM were tested and these results represent experiments with simultaneous addition of SBP and C-PAM. The SBP addition corresponded to a surface coverage of the fibres of 50% as determined from the adsorption isotherms in Fig. 5. pH was kept constant at 8 during the measurements and the addition of bentonite was kept constant at 2.5 mg g^{-1}.

polymers in Fig. 12 is so small it is obvious that other factors are important for the understanding of and subsequent optimisation of the microparticle based retention aids. Probably the factors controlling the extension of the polyelectrolyte out from the surface of the fibres and the factors determining the adsorption of the polyelectrolyte on the bentonite particles are more important parameters to study. This is definitely recommended for further studies.

It is also obvious that the charge of the C-PAM is no factor that can improve the efficiency of the simultaneous addition mode of the SBP compared with the pre-adsorption of the C-PAM. On the contrary the results in Figs. 12 and 13 all show that a preadsorption of the SBP is much more efficient than a simultaneous addition of the two polyelectrolytes.

There is another feature in Figs. 12 and 13 that needs some discussion and that is the difference in flocculation at zero C-PAM addition. First of all there is an overall difference between Figs. 12 and 13 and that is the average level of flocculation and the degree of flocculation is higher for the pre-adsorption of the SBP. The reason to this is probably that the SBP has not had time enough to adsorb to the fibres when it is added only 3 s before the detection of flocculation. This once again stresses the importance to determine the adsorption at short contact times. Another difference is the difference in flocculation index at zero addition of C-PAM in Fig. 13. There is no obvious explanation for this difference but most probably the difference can be explained by improper mixing of the chemicals at these short contact times. At present there is no information available on the influence of mixing at these short contact times but this issue is also studied in present investigations in our laboratory.

4. Conclusions

It is possible to determine the state of flocculation of cellulosic fibres with the equipment described in the present work. Measurement of floc size of synthetic fibre flocs shows very good agreement with earlier published data. Since different fibres give different correlations between light absorption and fibre concentration it is difficult to compare the state of flocculation of different pulps without chemical additives. It is possible though to compare the chemical induced flocculation of different types of fibres where the state of flocculation, caused by the additives, is compared with the state of flocculation without additives. Adsorption of C-PAM and a site blocking polymer (SBP) (a dimethylamine epichlorohydrine condensate) on cellulosic fibres show that these polyelectrolytes adsorb to the same type of sites since a preadsorption of the SBP results in an equivalent decrease of the C-PAM (in % of saturation adsorption). Preadsorption of the SBP to a surface coverage of 50% (of its saturation adsorption) resulted in a higher degree of flocculation upon addition of the C-PAM of the microparticle based flocculant. This is probably due to a more extended conformation of the C-PAM out from the surface of the cellulosic fibres. These results were also in accordance with earlier published theories. A simultaneous addition of SBP and C-PAM in the microparticle system was not as efficient, regarding flocculation, as a pre-adsorption of the SBP. This can be explained by the fact that the way that both the SBP and the C-PAM are adsorbed is affected by the way the polymers are added. In accordance with earlier publishd data the results indicate that the adsorption of SBP is strongly affected by the presence of the C-PAM. Addition of SBP has, after all, a positive effect on microparticle based retention aids. Addition levels in flocculation studies (which are relevant for practical use) are comparably low compared with saturation adsorption and the difference in flocculating ability of differently charged C-PAM is small compared with the saturation adsorption. More work should be focused on understanding the relationship between polyelectrolyte adsorption and flocculation at short contact times. This work is also underway in our laboratory.

Acknowledgements

Dr John Kettle is thanked for linguistic revisions of the manuscript and SCA Research AB is thanked for allowing the publication of the data in this investigation.

References

[1] T. Lindström, in: C.F. Baker, V.W. Punton (Eds.), Fundamentals of Papermaking, Transactions Ninth Fundamental Research Symposium, Mechanical Eng. Publ, London, 1989, p. 311.
[2] A. Swerin, L. Ödberg, in: C.F. Baker (Ed.), Fundamentals of Papermaking, Transactions of the 11th Research Symposium held at Cambridge, Pira International, Leatherhead, UK, 1997, pp. 265.
[3] K. Britt, Tappi 56 (3) (1973) 83.
[4] L. Wågberg, Svensk Papperstidn. 6 (1985) R48–R56.
[5] L. Wågberg, T. Lindström, Coll. Surf. 27 (1987) 29.
[6] J. Tichy, A. Karnis, Transactions Tech. Sect. CPPA TR 19 (1978).

[7] F. Onabe, K. Sakurai, Fundamentals of papermaking, in: C.F. Baker, V.W. Punton (Eds.), Transactions Ninth Fundamental Res. Symposium, Mechanical Eng. Publ, London, 1989, p. 219.
[8] L. Beghello, D. Eklund, Nordic Pulp Paper Res. J. 12 (2) (1997) 119.
[9] L. Beghello, T. Lindström, Nordic Pulp Paper Res. J. 13 (4) (1997) 269.
[10] K. Andersson, A. Sandström, K. Ström, Nordic Pulp Paper Res. J. 1 (2) (1986) 26.
[11] J.G. Langley, E. Litchfield, TAPPI 1986 Papermakers Conference Proceedings, TAPPI PRESS, Atlanta, 1986, p. 89.
[12] B. Wernås, AB CDM, Gothenburg, Sweden (1999) (private communication).
[13] A. Swerin, L. Ödberg, L. Wågberg, Coll. Surf. A: Phys. Eng. Aspects 113 (1996) 25.
[14] L. Wågberg, M. Björklund, I. Åsell, et al., Tappi J. 79 (6) (1996) 157.
[15] S. Katz, R.P. Beatson, A.M. Scallan, Svensk Papperstidning 6 (1984) R48–R53.
[16] L. Wågberg, L. Ödberg, G. Glad-Nordmark, Nordic Pulp Paper Res. J. 4 (1989) 71.
[17] G. Jacquelin, British Pat. No. 1109895 (1968).
[18] D. Horn, Prog. Coll. Polym. Sci. 65 (1978) 251.
[19] A. Swerin, L. Wågberg, Nordic Pulp Paper Res. J. 9 (1) (1994) 18.
[20] L. Wågberg, L. Winter, T. Lindström, Papermaking raw materials, in: V. Punton (Ed.), Transactions of the Eight Fundamental Research Symposium held at Oxford, Mech. Eng. Publ., London, UK, 1985, pp. 917.
[21] H. Terayama, J. Polym. Sci. 8 (1952) 243.
[22] S.A. Sukhishivili, S. Granick, J. Chem. Phys. 109 (6) (1998) 6869.
[23] A. Swerin, G. Glad-Nordmark, L. Ödberg, J. Pulp Paper Sci. 23 (8) (1997) J389.
[24] P.G. Saffman, J.S. Turner, J. Fluid Mech. 1 (1956) 16.
[25] S.G. Mason, Pulp Paper Mag. Can. 51 (1950) 93.
[26] M. Falk, L. Ödberg, L. Wågberg, et al., Coll. Surf. 40 (1989) 115.
[27] C.W. Burkhardt, K.J. McCarthy, D.P. Parazak, J. Polym. Sci.: Part C: Polym. Lett. 25 (1987) 209.