Deflocculation of Cellulosic Suspensions with Anionic High Molecular Weight Polyelectrolytes

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Pulp fibers have a strong tendency to form flocs in water suspensions, which may cause their undesirable distribution in the paper sheets. This flocculation can be controlled by adding, *e.g.,* an anionic high molecular weight polyelectrolyte in the fiber suspension. The objective of this study was to investigate the effect of anionic polyelectrolytes on deflocculation kinetics, dewatering, and rheology of cellulosic suspensions. The results showed that both microfibrillated cellulose (MFC) and macroscopic pulp fibers can be dispersed using anionic polyacrylamides (APAM). The higher the molecular weight of APAM, the higher is its effect. Adsorption experiments illustrate that anionic polyelectrolytes do not strongly attach to cellulose surfaces but they can be partly entrapped or can disperse nanocellulose fibrils (increase the swelling). Based on rheological experiments, the MFC network became weaker with APAM addition. Similar to the flocculation mechanism of cellulosic materials with polymers, deflocculation is also time dependent. Deflocculation occurs very rapidly, and the maximum deflocculation level is achieved within a few seconds. When mixing is continued, the floc size starts to increase again. Also dewatering was found to be strongly dependent on the contact time with the APAMs. These results indicate that the positive effects of anionic deflocculants are quickly diminished due to shear forces, and therefore, the best deflocculating effect is achieved using as short a contact time as possible.

Keywords: Deflocculation; Dewatering; Anionic polyacrylamide; Pulp fibers; Nanofibrillated cellulose; Microfibrillated cellulose; Rheology

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INTRODUCTION

The formation of a paper sheet has a great influence on many of the sheet properties such as paper strength and printability (Norman 2008). It is defined as the local basis weight variation determined by the fiber distribution in the plane of the sheet. Pulp fibers have a tendency to aggregate in water suspensions and form flocs that, if not broken, persist in the formed sheet of paper, resulting in an undesirable nonuniform fiber distribution. For long fibers, aggregation and network formation are caused primarily by mechanical entanglement (Wasser 1978; Kerekes 2006; Yan and Norman 2006a; Yan *et al.* 2006b). One way to estimate flocculation based on the properties of the fiber suspension is the crowding factor (N_C), defined as $N_C = 2/3 C_v (l/d)^2$, where C_v is volume fraction of fibers, l is fiber length, and d is fiber diameter (Kerekes 2006). As the value of the crowding factor increases, the frequency of collisions of fibers increases from occasional to frequent. It has been found that when the crowding factor is over 60, persistent flocs will appear in the stirred suspensions (Kerekes 2006). Usually, at papermachine headbox consistencies, values are between 20 and 60, indicating that fibers collide frequently with each other, but are below the flocculating threshold (Kerekes 2006).

However, the crowding factor does not include the surface properties of the fiber and the properties of the suspension. It has been shown that the surface properties of the fiber, such as charge and friction forces between surfaces, affect the flocculation tendency of the suspension (Beghello 1998b; Klingenberg 2001; Zauscher and Klingenberg 2001; Martinez *et al.* 2003; Silveira *et al.* 2002, Yan and Norman. 2006a; Yan *et al.* 2006b). The viscosity of the water phase near the surface is also assumed to have a strong influence on flocculation tendency (Lee and Lindström 1989; Zhao and Kerekes 1993; Yan *et al.* 2006c). The chemical environment, especially the electrolyte content, will also affect the fiber flocculation tendency (Beghello and Eklund 1999; Zauscher and Klingenberg 2001).

One of the most important factors affecting flocculation is the addition of retention chemicals. Retention chemicals such as cationic polyacrylamides are usually high molecular weight polyelectrolytes and they are used to flocculate small particles such fiber fines and fillers and bind them to the paper sheet (Roberts 1996). Several different multicomponent retention systems such as PEO/cofactor (van de Ven *et al.* 2005; Qasaimeh 2011; Qasaimeh *et al.* 2011) can also be used to increase retention of small particles. In addition to retention chemicals binding small particles to fibres, they simultaneously improve dewatering, because small particles can prevent the water flow through the fiber mat by blocking the flow channels (Hubbe and Heitmann 2007; Hubbe *et al.* 2009). However, these retention chemicals may also cause undesired high flocculation of fibers. Usually this flocculation can be controlled in papermachines by choosing the addition points in a way that the flocs are broken as they are subjected to high shear for a long enough period (Sikora and Stratton 1981; Hubbe 1986, 2007).

By controlling fiber length, consistency, agitation, addition point of chemicals, and chemical environment, flocculation can be controlled to a certain point (Beghello 1998b; Beghello and Eklund 1999; Yan and Norman 2006a; Yan *et al.* 2006b; 2006c). However, especially in high consistency formers (Nomura *et al.* 1989; Cichoracki *et al.* 2001), these means are not enough, and therefore certain additives are needed to control flocculation (Kerekes 2006).

Several mechanisms have been suggested to describe deflocculation by polymers. One suggested mechanism is that adsorbed polymer layers alter the fiber surface properties such as friction and charge (electrosteric repulsion). Early publications have shown that by adsorbing polymers such as guar gum (De Roos 1958) on fibers, friction between fibers is altered and formation can be improved. They suggested that adsorbed layers were in the form of a hydrated mantle, which helped lubricated fibers to slide relative to each other. More recently, it has been shown that carboxymethylation of fibers or addition of carboxymethyl cellulose can also decrease the friction between fibers (Beghello 1998b; Yan *et al.* 2006c; Olszewska *et al.* 2013). These studies also suggested that the surface charge of the fiber has a significant effect on flocculation. With increasing charge of the fiber, flocculation has been found to decrease. Similarly, xyloglucan has also been found to decrease flocculation by decreasing friction between fibers (Christiernin *et al.* 2003; Yan *et al.* 2006c). Dissolved, non-adsorbing polymers between fibers can also prevent flocculation. Lee and Lindström (1989) noticed an improved formation of the paper when using water soluble polyelectrolytes, anionic polyacrylamides (APAMs). These kinds of dispersants are usually high molecular weight polyelectrolytes, which increase the viscosity of the suspending medium, and hence decrease the flocculation of fibers. They also act as drag reducing additives in turbulent flow as they dampen the turbulence in flowing fiber suspensions. The drag reduction has been seen to correlate very well with improved formation (Svedberg 2012). Another possible explanation for the working mechanism of dispersants is that they prevent close contact between fibers due to their large physical size (Wasser 1978).

The properties of non-adsorbing dispersants have been noticed to have a significant effect on deflocculation efficiency (Wasser 1978; Palonen and Jokinen 1986; Lee and Lindström 1989; Svedberg 2012). Usually the higher the molecular weight; the higher the deflocculation effect (Wasser 1978; Svedberg 2012). However, with the increasing molecular weight, these types of deflocculants usually have a detrimental effect on dewatering (Lee and Lindström 1989). In contrast, the charge density of deflocculants has only a small effect on deflocculation (Svedberg 2012). The physical structure of the deflocculant is also important (Svedberg 2012). The most efficient structure is linear, but partially branched polymers can be used as deflocculants if high enough dosages are used. With highly branched anionic polyelectrolytes the deflocculating effect was found to be negligible (Svedberg 2012).

The purpose of this study was to investigate how the properties of anionic high molecular weight deflocculants, APAMs, affect the flocculation level and the dewatering of the fiber suspension. The effect of pulp consistency on the efficacy of the dispersants was also studied. Studies have shown that the dosing point is important for deflocculants. The lower the contact time; the higher the deflocculation effect (Palonen and Jokinen 1986). However, the effect of time on deflocculation has not been extensively studied; therefore, one of the main goals of this investigation was to study the effect of contact time on deflocculation and dewatering of the pulp in the presence of a deflocculant. This was done by monitoring the particle size of the suspension in-situ (Lasentec) during the experiment. Adsorption experiments with the quartz crystal microbalance with dissipation (QCM-D) were made to estimate the affinity between different deflocculants and cellulose. To simulate the strength of the fiber network with different deflocculants, the rheology of the suspensions was studied using microfibrillar cellulose as a model material for macroscopic pulp fibers.

EXPERIMENTAL

Polymers and cellulosic materials

Four different APAMs used in experiments were provided by Kemira Ltd., Finland. These PAMs were classified based on molecular weight (MW) and charge density (CD). The molecular weights were low (LMW), medium (MMW), and high (HMW), and the charge densities were high (HCD) and low (LCD). The properties of the APAMs are shown in Table 1. The molecular weights were given by the producer. Charge densities were determined by polyelectrolyte titration (Koljonen *et al.* 2004).

The pulp used in the experiments was a fully bleached kraft pulp, delivered dried from a Finnish pulp mill. It was disintegrated to SR^{o}22 (ISO 5263-1) and washed to the sodium form (Swerin *et al.* 1990).

Table 1. Properties of APAMs Used in the Experiments

APAM	Molecular weight (M_w) (10^6 g/mol)	Charge density (CD) (meq/g)
LMW-LCD	7	-1.1
LMW-HCD	7	-3.5
MMW-LCD	12	-1.0
HMW-HCD	15-17	-3.2

Microfibrillar cellulose (MFC) and nanofibrillar cellulose (NFC) were prepared from bleached kraft pulp, which was washed to its sodium-form (Swerin *et al.* 1990). The MFC was ground with a Masuko Supermasscolloider (Japan) three times and the NFC with a high-pressure fluidizer (Microfluidizer M-110EH, Microfluidics Corp, Newton USA) for 30 passes, according to the procedure described by Eronen *et al.* (2011). The charge of the pulp used as a starting material was determined by conductometric titration (Katz *et al.* 1984) to be about 65 μeq/g.

Adsorption Experiments

The adsorption experiments were made to get information about the adsorption properties of APAMs. They were made by using a quartz crystal microbalance with dissipation, QCM-D, instrument from Q-sense, Sweden (Rodahl *et al.* 1995). This instrument measures the resonance frequency (f) of a piezoelectric crystal at its fundamental resonance frequency (5 MHz) and several overtones. The lowering of the resonance (Δf) frequency occurs as material is adsorbed on the crystal surface. These crystals can be modified by deposition of other materials such as cellulose (Ahola *et al.* 2008). Roughly, Δf is proportional to the adsorbed mass per unit surface (Eq. 1),

$$\Delta m = -\frac{C\Delta f}{n} \tag{1}$$

where C is device sensitivity constant (17.7 ng Hz^{-1} cm^{-2} for a 5 MHz quartz crystal) and n is overtone number.

QCM-D also measures the dissipation energy into the adsorbed layer as it is sheared. Changes in this rate as more material is adsorbed (ΔD) gives information on the viscoelastic properties of the layer. A rigid adsorbed layer gives no change in the dissipation energy but for loose viscoelastic layers there is an increase in dissipated energy as a function of adsorption.

However, Δf depends on the total oscillating mass, including water, coupled to the oscillation. By measuring several frequencies and related dissipation, it becomes possible to determine whether the adsorbed layer is rigid or water-rich, which is not possible by looking only at the frequency response.

The adsorption of anionic deflocculants was studied on the NFC surface. For film preparation the nanofibril gel was diluted to a consistency of 0.2%, stirred with ultrasonic microtip, and centrifuged at 10400 rpm (10000G) in order to the remove remaining fibril aggregates. Films were prepared on silica QCM-D crystals (Q-Sense AB, Sweden). Polyethyleneimine (PEI) (M_w 50000 g/mol) was used as an anchoring substance to improve the coverage of the fibrils on the surface. The model films were prepared by spin coating according to the procedure presented by Ahola *et al.* (2008).

Because NFC surfaces have high hygroscopicity and swelling ability (Spence *et al.* 2010), they were stabilized by pumping a buffer solution of 10 mmol/L of NaCl (pH 8) through the QCM-D measurement cell before the adsorption experiments. In the adsorption measurements concentrations of APAMs were 0.025 g/L. The pH was adjusted to 8 with NaOH and salt concentration to10 mmol/L of NaCl. A peristaltic pump was used to make the samples flow through the measurements cell at a rate of 0.1 mL/min.

Rheological Measurements

To simulate the effect of APAM on fibre-fibre interactions, the rheology and deflocculation of a MFC suspension with APAMs was studied using a dynamic rotational rheometer (ARG2, TA Instruments). APAMs were dissolved in distilled water and then combined with diluted MFC suspension and mixed with an ultrasonicator (Branson digital sonifier 450, USA) for 2 min at 25% amplitude.

Rheological measurements were performed with the concentric cylinders geometry (radii 14.00 and 15.19 mm) having an anodized aluminium surface (Al_2O_3). Fiber suspensions are prone to wall depletion (Buscall 2010), since the fibres tend to drift away from the solid-liquid boundary, that is, the walls of the enclosure. This has to be taken into account in planning experiments and analysing the results. The anodized (Al_2O_3) surface carries a small positive surface charge in water at the given pH (~6) (Ntalikwa 2007) creating a better adhesion between the cylinder walls and the bulk of the suspension. Before the oscillatory experiments, an intensive pre-shear period (at 500 s^{-1} for 20 min) was implemented to break down the flocculated MFC network structure. Then the sample was left to rest for 20 min with the application of a small oscillation at 6.25 rad/s and 0.5% strain, which is within the linear viscoelastic region. When the flow of the suspension is stopped after the pre-shear period, the MFC network relaxes, pushing it in better contact to the walls of cylinders, thus decreasing the likelihood for depletion. Then, the amplitude sweep was measured from 0.01% to 1000% strain at a frequency of 6.283 rad/s. In the amplitude sweep, the storage modulus (G') represents the part of the applied energy that is stored in the system and the loss modulus (G'') implies the viscous losses during the oscillation (Ferry 1980). The gel strength of the suspensions was determined from the storage modulus level in the linear viscoelastic region at the strain of 0.05%.

The floc structure of the suspensions was studied in the rheometer by using a transparent polymethylmethacrylate (PMMA) cup, radius 14.87 mm, with the same inner cylinder as in the rheological characterization, and the suspension was photographed after controlled shearing. This geometry was chosen since it is suitable for photography purposes: the narrow gap concentric cylinders provided the necessary contrast for photographing, thus allowing the linking the changes in the structure to changes in the rheological response. The imaging method is described in detail in Karppinen *et al.* (2012). Suspensions were sheared at four constant shear rates (500, 30, 5, and 0.5 s^{-1}) for 10 min. After each shear rate period, a 10 min oscillatory time sweep was measured at 0.5% strain and 1 Hz frequency. The photographs were taken with a Nikon D90 camera (Nikon Corporation, Japan) with a macro objective controlled by NKRemote software (Breeze Systems Limited, UK) after shearing the suspension at shear rate 5 s^{-1} for 10 min.

Deflocculation Experiments

A focused beam reflectance measurement device (Lasentec D600-L, Mettler-Toledo AutoChem Inc., USA) was used for the deflocculation experiments. The details of the measurement principles are presented elsewhere (Taipale *et al.* 2010). A mixing vessel and an impeller with a design similar to the Dynamic Drainage Jar (DDJ) experiments were used (Britt and Unbehend 1976). The stirring speed was 1000 rpm. The total sample volume was 600 mL, and sample consistencies were 0.5 % and 1.5 %. The suspension was stirred for 25 s prior to deflocculant (APAM) addition, and the total measuring time was 300 s with 2 s sampling intervals. The concentrations of APAM solutions were 0.025 g/L in the deflocculation experiments. The APAM dosages were: 0.025, 0.05, 0.1, 0.2, and 0.5 % of dry pulp. The experiments were performed in ambient temperature at pH 8 with NaOH, and the salt concentration was 10 mmol/L NaCl. Retention aids were not used in the experiments.

With the focused beam reflectance measurement, the number of particles can be measured in a several different particle size ranges. In order to evaluate the change in the amount of particles in a certain particle size range, a relative count index (N_r) was calculated by using Eq. 2,

$$N_r = \frac{N_1}{N_0} \tag{2}$$

where N_0 is the number of particles (counts) at a certain particle size range before deflocculant addition, and N_1 is the number of particles (counts) at a certain particle size range after deflocculant addition.

Dewatering Measurement

Dewatering indicates the ease of removing water from the paper web. In this work, the dewatering time was measured by using a dynamic drainage analyzer (DDA, AB Akribi Kemikonsulter, Sweden). The mixing vessel and impeller were similar in design to those in the flocculation tests. The pulp was mixed after a deflocculant (APAM) addition with a stirrer speed of 1000 rpm before dewatering. Four different mixing times were used (30, 60, 90, and 300 seconds) in order to study the effect of polymer mixing time on dewatering. The pressure was kept at 0.1 kPa, and the wire was 200 mesh. In the dewatering experiments, the stock consistency was 0.5 % and the volume was 600 mL. The concentrations of APAM solutions were 0.025 g/L in the dewatering experiments. The APAM dosages were: 0.025, 0.05, 0.1, 0.2, and 0.5 % of dry pulp. The experiments were performed in ambient temperature and pH 8; the ionic strength was kept constant by adding 10 mmol/L of NaCl to the pulp.

RESULTS AND DISCUSSION

Adsorption Experiments

The adsorption of deflocculants was studied using QCM-D. The experiments were made with NFC model surfaces to mimic polymer/fiber surface interactions. As presented in the materials and methods section, the QCM-D instrument measures resonance frequency (*f*) of a piezoelectric crystal. It decreases as material adsorbs on the crystal surface, where Δ*f* is proportional to the adsorbed mass per unit surface. Figure 1 presents adsorption of two different deflocculants as a function of time on the NFC surface. After a period of 500 seconds, the APAMs (concentration 0.025 g/L) are injected into the system (at a rate of 0.1 mL/min). Surprisingly, it was found that both APAMs adsorbed onto cellulose to some extent. This is surprising because both the cellulose surface and APAMs possess anionic charge and therefore should repel each other. However, the NFC model surface is porous (Kontturi *et al.* 2013), indicating that some polymer can be entrapped or can disperse nanocellulose fibrils (increase the swelling), an effect that contributes to Δ*f*. In any case, the APAMs were seemingly poorly attached to the surface. Evidence of this can be seen as a noticeable increase in the frequency after water rinsing started, indicating the detachment of APAM from the surface. The QCM-D instrument also measures the dissipation energy of the adsorbed layer. Changes in dissipation (Δ*D*) give information of the viscoelastic properties of the layer. The higher the Δ*D*, the looser the layer. APAMs seem to have increased the Δ*D* somewhat, indicating either that some loose polymer tails were attached to the cellulose surface or some dispersion and swelling of NFC with entrapped APAM had occurred. The effects were larger with low M_w APAM than those with high M_w, supporting the idea of dispersion of the nanofibrils. Hence, one could assume that a high M_w polymer will tend to form a looser adsorption layer, contributing more to Δ*D* than that of a low M_w polymer (Saarinen *et al.* 2009). Water rinsing decreased Δ*D* significantly, indicating that most of the APAM was washed away from the surface. The effect seems to be more pronounced with low molecular weight APAM.

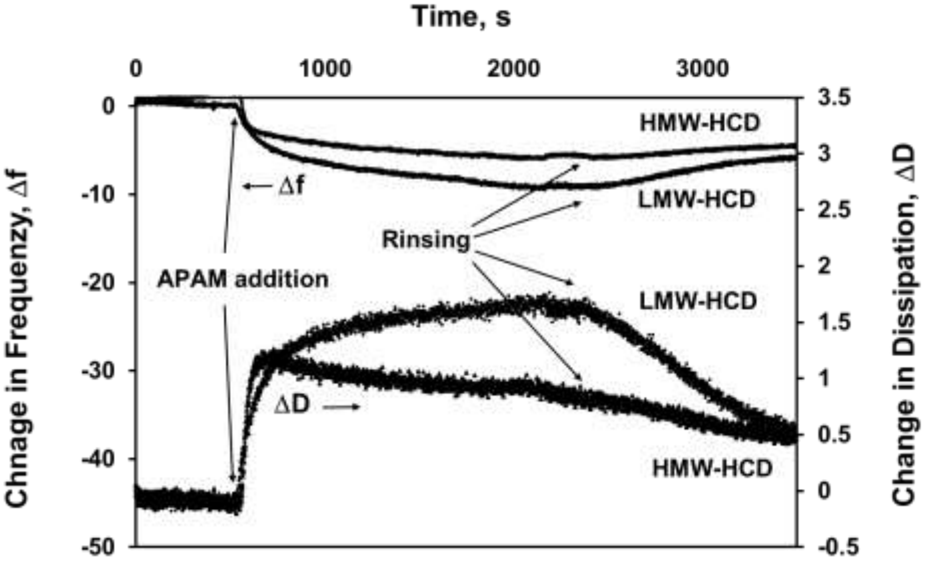

Fig. 1. Adsorption of APAMs (Δ*f*, left) and the dissipation (Δ*D*, right) on nanocellulose surface as a function of time. The concentrations of APAMs were 0.025 g/L, and they were injected to cells at a rate of 0.1 mL/min by using a peristaltic pump.

Rheology

The effect of APAM on cellulosic fiber interactions was studied with a rheometer, using microfibrillar cellulose (MFC) suspensions as a model for the pulp suspensions. Three different APAMs were added at five different concentrations, (w-% of MFC mass):

0.5, 1, 5, 10, and 25. The gel strength in the linear viscoelastic region was measured by an amplitude sweep.

Figure 2 shows the storage modulus *G*' of the MFC suspensions with different polymers as a function of polymer concentration. All APAMs except LMW-LCD decreased the gel strength of the suspensions even at the lowest concentration, 0.5 w-% of the MFC mass. At 1% concentration, all APAMs decreased the gel strength, and the effect was somewhat greater with high charge density APAMs. The gel strength is dependent on the strength of the average fiber-fiber contact point and the number of contact points in a certain volume (Giri *et al.* 2000). According to the adsorption tests, APAMs interact to some extend with the MFC surface, which suggests that APAMs may slightly lower the strength of the fiber-fiber interaction and reduce the number of contacts between the fibrils. In similar manner, the APAM chains may get trapped between the approaching fibrils and reduce collisions and thus reduce flocculation. APAMs also increase the viscosity of the suspending medium, which decreases the turbulence in the flow and results in weaker flocs (Zhao and Kerekes 1993).

The low molecular weight APAMs, LMW-HCD and LMW-LCD, first decreased the gel strength of the MFC suspension. Then there was a constant gel strength at the polymer concentrations of 1 to 10% for the low molecular weight, high charge APAM (LMW-HCD) and slightly decreasing gel strength for low molecular weight, low charge APAM (LMW-LCD). The initial decrease was caused by the dispersive effect of the polymers, which decreases the contacts between the fibers and thus weakens the gel. With high charge density APAM, the minimum of the gel strength was achieved at lower concentration than with the low charge density APAM. This indicates that the amount of negative charges in the system is essential to the network strength. With the highest amount of the polymer, 25% (w/w (MFC)), the gel strength started to increase again, especially with the high charge, low molecular weight APAM. The highly charged polymer chains are extended and rigid and they start to behave gel-like at higher concentrations. This increases the stiffness of the whole suspension. The higher charge density of LMW-HCD, compared to LMW-LCD, results in a higher storage modulus of the suspending medium, which is also reflected in the higher gel strength of the whole suspension.

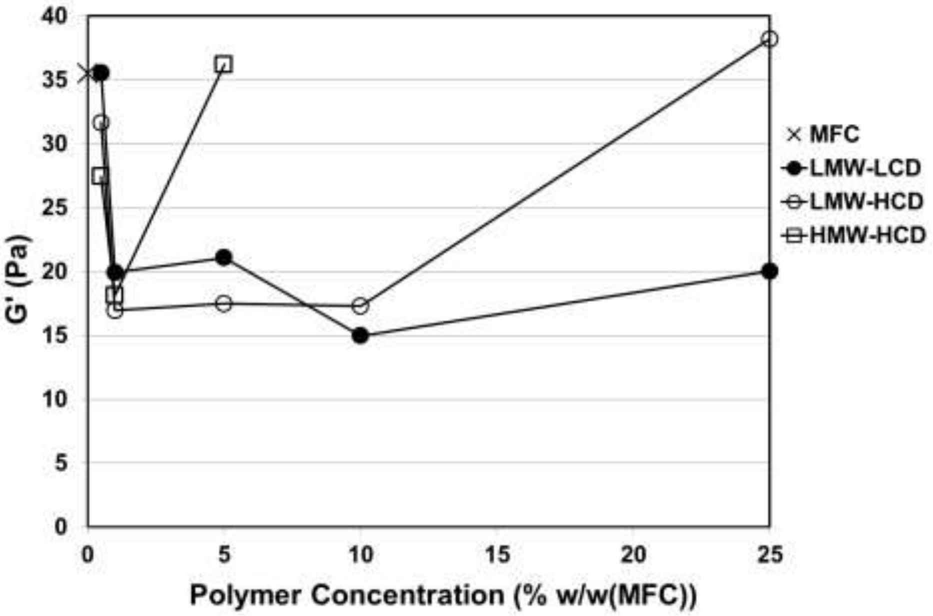

Fig. 2. Storage modulus for 0.5% MFC suspensions with three different APAMs, measured at 0.05% strain and 1 Hz frequency

The high molecular weight and high charge APAM (HMW-HCD) decreased the gel strength the most at the two lowest concentrations (0.5% and 1% w/w (MFC)). This indicates that a high molecular weight anionic polymer weakens the gel strength of the MFC suspension most efficiently at low polymer additions. For the high molecular weight APAM, the gel strength started to increase already at 5% w/w (MFC) HMW-HCD. This can be explained by the very high M_w and hence a high viscosity of the polymer solution which starts to dominate the MFC/APAM gel strength. At higher concentrations of HMW-HCD, no reliable results could be obtained due to the high viscosity of the polymer solution.

Figure 3 shows the floc structure for the neat MFC suspension and the MFC suspension with APAM (LMW-HCD) at the concentration of 1% (w/w (MFC). The images were taken through the transparent sample cup of the rheometer after shearing the suspensions at the apparent shear rate of 5 s^{-1} for 10 min. At this low shear rate, a heterogeneous floc structure can be created in the MFC suspension (3a). The extended APAM chains between the slightly negative MFC fibrils reduced the collisions and entanglements between the fibrils. This suppressed flocculation, which is apparent as a more uniform structure of the APAM containing suspensions (a representative image with APAM (LMW-HCD) is shown in 3b). In addition to steric hindrance, also the higher viscosity of the suspending medium decreases the movement of the fibrils relative to each other, preventing floc formation. When the shearing was continued at a lower shear rate (0.5 s^{-1}), the difference between the neat MFC suspension and the suspensions containing APAM diminished, and all suspensions had visually equally heterogeneously flocculated structures.

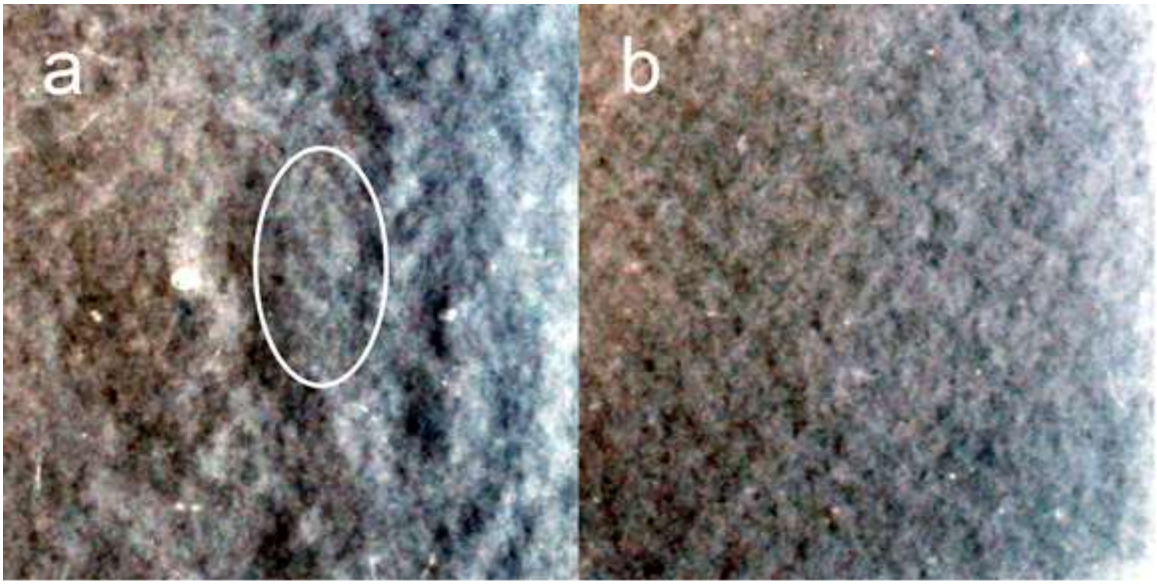

Fig. 3. Images of the MFC suspension structure after shearing at 5 s^{-1} for 10 min in the rheometer. The suspension is photographed through the outer cylinder of the concentric cylinders geometry, and the gap between the cylinders is 1 mm. a) MFC 0.5 w-% (a floc highlighted), b) MFC 0.5 w-% with 1 % (w/w (MFC)) APAM (LMW-HCD). The area of the photographs is 10 mm x 10 mm.

Deflocculation

The deflocculation of pulp fibers by addition of different APAMs was studied as a function of time. Figure 4 presents a typical size distribution curve of particles before and after 60 seconds of APAM (HMW-HCD) addition (0.2% of dry pulp). After deflocculant addition, one can clearly see that the number of particles increased, especially in the size range of 1 to 50 μm, and it decreased to some extent in the size range 80 to 200 μm. This indicates that the biggest fiber flocs dispersed into smaller flocs when the APAM (HMW-HCD) was added to pulp. Even though the focused beam reflectance measurement might not be optimal for measuring particle size (due to the fact that fibers are very long but narrow particles), the differences between different samples were reproducible. In addition, the method has been successfully used for fiber suspension flocculation studies earlier (Blanco *et al.* 2002; Ordóñez *et al.* 2009; Taipale *et al.* 2010). Therefore, the method is expected to be applicable to compare different deflocculants and dosage levels, and explain how different parameters affect the deflocculation of the pulp. Because the changes in the measured particle sizes and in the particle counts were biggest in the 1 to 50 μm particle size range, it was decided to concentrate in this study on the 1 to 10 μm and 10 to 50 μm size ranges. The relative count indices (changes in the number of particles) at these ranges were monitored as a function of time.

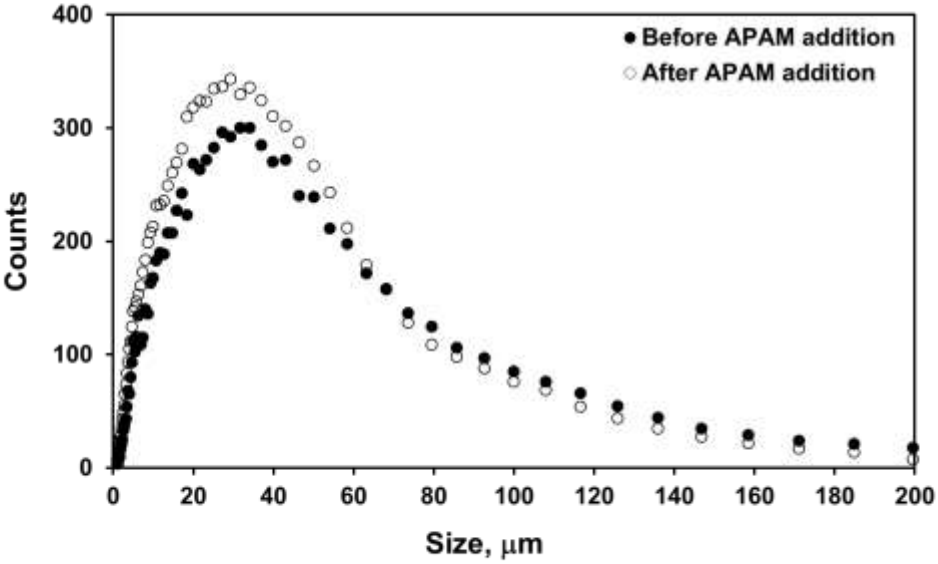

Fig. 4. The particle size distribution of the pulp suspension (0.5% consistency) before and after 60 seconds of APAM (HMW-HCD) addition (0.2% of pulp). The mixing speed was 1000 rpm.

Figures 5 and 6 present relative particle count indices as a function of time with four different APAM (HMW-HCD) dosages in the particle size range of 1 to 10 μm. The pulp consistency was 0.5% and 1.5% in Figs. 5 and 6, respectively (mixing speed 1000 rpm). Shortly after APAM (HMW-HCD) addition, there was a steep increase in the relative count index in the particle size range of 1 to 10 μm, indicating a rapid dispersion of fiber flocs to smaller fragments. This is reported to be due to the change in the viscosity when high molecular weight deflocculants are added (Zhao and Kerekes 1993). For flocs to form, fibers must crowd together and stay crowded. When the viscosity increases, the fibers flow more evenly and their relative motion decreases. As contacts between fibers decrease, the crowding is also decreased, which leads to diminished flocculation (Wasser 1978; Lee and Lindström 1989; Zhao and Kerekes 1993). This can be seen in both 0.5% and 1.5% consistencies. As was also seen in the gel strength measurements, dosing seems to have had a significant effect on deflocculation, especially at the higher pulp consistency. At the pulp consistency of 0.5%, the highest relative count index was achieved at 0.2% APAM (HMW-HCD) concentration, whereas at the pulp consistency of 1.5% the deflocculation effect was highest at 0.5% APAM (HMW-HCD) dosage. The deflocculation was quite low when lower dosage levels of APAM (HMW-HCD) were used at the pulp consistency of 1.5 % (Fig. 6).

One of the most interesting observations is the effect of time on deflocculation. In polymer flocculation studies, the effect of time has been found to be a very important parameter (Sikora and Stratton 1981; Hubbe 1986). It has been observed that after an addition of a cationic polyelectrolyte, fiber flocculation increases rapidly, and the maximum floc size is achieved in a few seconds (Hubbe 2007). If the mixing is continued, the floc size decreases to a certain level, depending on the dosage and the properties of the flocculant, and on the prevailing mixing conditions. High shear forces tend to break down formed flocs due to a disruption of the attachment points on a particle surface and the breakage of the covalent bonds within the bridging polymer chains (Sikora and Stratton 1981).

In deflocculation (Figs. 5 and 6), there is a rapid increase in the number of small particles (1 to 10 μm range) after the addition of APAM (HMW-HCD), indicating the dispersion of larger flocs to smaller ones. Similar to flocculants, maximum deflocculation is achieved quite rapidly, after which the amount of small particles starts to gradually decrease (some reflocculation occurs). The pulp consistency also seems to have had a significant effect on reformation of flocs. At the higher pulp consistency (1.5%), the reflocculation effect of fibers seems to have been significantly stronger than that at the 0.5% pulp consistency. This is probably due to fact that the collision frequency is higher at higher pulp consistency, hence increasing the probability of reflocculation.

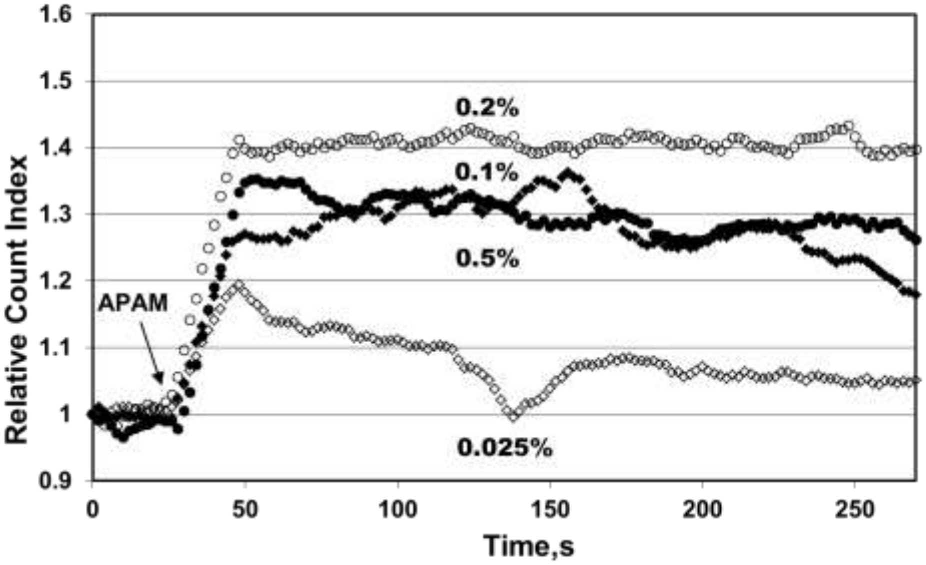

Fig. 5. Relative particle count index at 1-10 μm size range as a function of time when adding APAM (HMW-HCD) (% of pulp) (at 25 s). Pulp consistency 0.5% and mixing speed 1000 rpm.

Palonen and Jokinen (1986) concluded that the best deflocculating effect can be achieved using as short a contact time as possible. The present results support this conclusion. It seems that after the addition of a deflocculant, pulp fibers disperse very quickly but the effect is partly reversible.

Another similarity in deflocculants compared to flocculants is that there is a certain optimal dosing level. There is typically an optimum dosing level of flocculants, after which flocculation starts to deteriorate quite rapidly (Blanco *et al.* 2002; Hubbe 2007). In our deflocculation experiments at 0.5% pulp consistency (Fig. 5), the highest deflocculation was achieved with 0.2% APAM (HMW-HCD) addition, whereas with 0.5% addition, the deflocculation effect was notably lower. Similar optimum dosing effects were also seen in gel strength experiments, Fig 2.

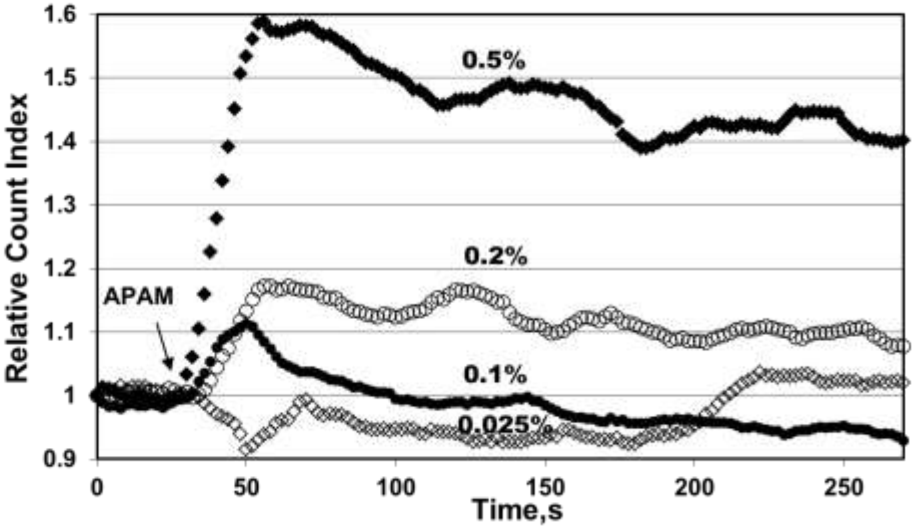

Fig. 6. Relative particle count index at 1-10 μm size range as a function of time when adding APAM (HMW-HCD) (% of pulp) (at 25s). Pulp consistency 1.5% and mixing speed 1000 rpm.

Similar to observations made in the 1 to 10 μm particle size range, the deflocculation effect was also seen in the 10 to 50 μm particle size range (Fig. 7). There was a steep increase in the relative particle count index shortly after APAM (HMW-HCD) addition, indicating rapid dispersion of fiber flocs to smaller fragments. As for the 1 to 10 μm particle size range, the highest relative count index values are achieved at 0.5 % APAM addition. There was also a slight decrease in the relative count index as mixing continues. However, the changes were clearly lower than in the 1 to 10 μm particle size range.

Molecular weight has a significant effect on the deflocculation efficiency. Previous experiments (Wasser 1978; Lee and Lindström 1989; Yan *et al.* 2006c) have shown that paper formation is significantly better when the molecular weight of the deflocculant is higher. They assumed that the improvement in paper formation was due to increased deflocculation, and hence, a more evenly dispersed fiber suspension. Wasser (1978) observed that from molecular weights of 2 to 3 million g/mol, the efficiency of a deflocculant rapidly increased, and it was 10 times higher with a 15 million g/mol deflocculant. The present results are consistent with these results. A higher molecular weight of the deflocculant led to a higher deflocculating effect (Fig. 8).

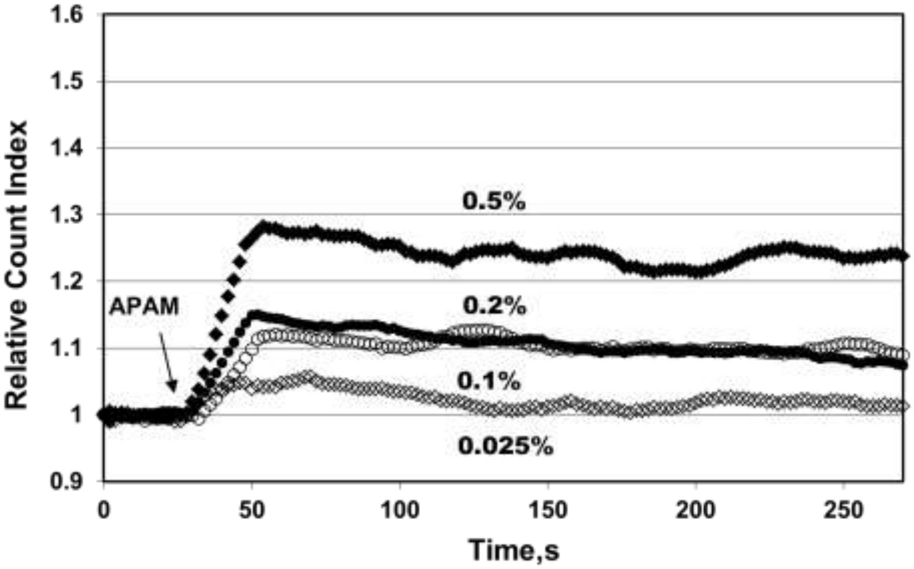

Fig. 7. Relative particle count index at 10-50 μm size range as a function of time when adding APAM (HMW-HCD) (% of pulp) (at 25 s). Pulp consistency 1.5% and mixing speed 1000 rpm.

As mentioned above, the dosage of deflocculants affects the deflocculation level. Previously, it has been noticed that an increase in the dosage of a deflocculant also increases the deflocculation level (Wasser 1978; Lee and Lindström 1989; Yan *et al.* 2006c). Although not yet observed, Wasser (1978) speculated that there should be a maximum, after which deflocculation would not increase. The present results support this assumption. As can be seen in Fig. 8, deflocculation reached a maximum at a certain dosage, depending on the deflocculant. The higher the molecular weight, the lower the amount needed to achieve maximum deflocculation. With APAM (LMW-HCD), the maximum deflocculation effect was found to be somewhere between 0.2 and 0.5%. With APAM (HMW-HCD) the maximum was achieved at around 0.2%, after which the deflocculating effect started to diminish. This is probably because the viscosity of the suspension is increased significantly when high amounts or high molecular weight deflocculants are used, leading to a poor mixing of the polymer and pulp fibres. As a result, deflocculation is diminished.

If one compares the deflocculation results of the pulp suspension in Fig. 8 with the gel strengths of the MFC/APAM suspensions in Fig. 2, similar trends are evident. For both materials an optimum dosage was found; that is, there was a polymer concentration that deflocculated the suspensions most. In addition, the molecular weight of the APAMs was important for both their deflocculation efficiency of pulp and for the gel strength of the MFC suspension at low polymer concentration. Based on the rheological measurements, which show that the gel strength of the fiber network decreased with the low polymer additions, it can be assumed that there were less contacts between the fibers. This can be caused by the high viscosity of the polymer solutions, which has been reported to reduce fiber contacts. On the other hand, the negatively charged polymer chains between the MFC fibers may repel the slightly negative fibers and thus reduce the collisions between them.

There were also differences between the pulp and MFC suspensions. The two types of suspended materials were chemically similar, but the particle size was totally different. MFC fibers have diameters even down to nanoscale with larger aggregates and length of several microns (Vartiainen *et al.* 2011; Spence *et al.* 2011; Wang *et al.* 2012), whereas pulp fibers have diameters between 30 and 40 µm and are several millimeters long. Hence, when comparing with MFC and pulp fibers, the relative size of the APAM polymers is larger with relation to the former. This affects the results in two ways. First, MFC fibers require a higher concentration of the polymers to achieve the lowest gel strength. This can be explained by the higher amount of small fibrils and the higher specific surface area of the MFC than that of pulp fibres. Second, the main property affecting the deflocculation of the pulp was the molecular weight of the polymer, whereas for MFC fibers, the charge density was also important, especially at higher polymer concentrations. This indicates that the stabilization and dispersing mechanisms of MFC could be more sensitive to charge effects than pulp fibers. Indeed, it has been shown that NFC/MFC suspensions can be stabilized by negative charge (Saito *et al.* 2006).

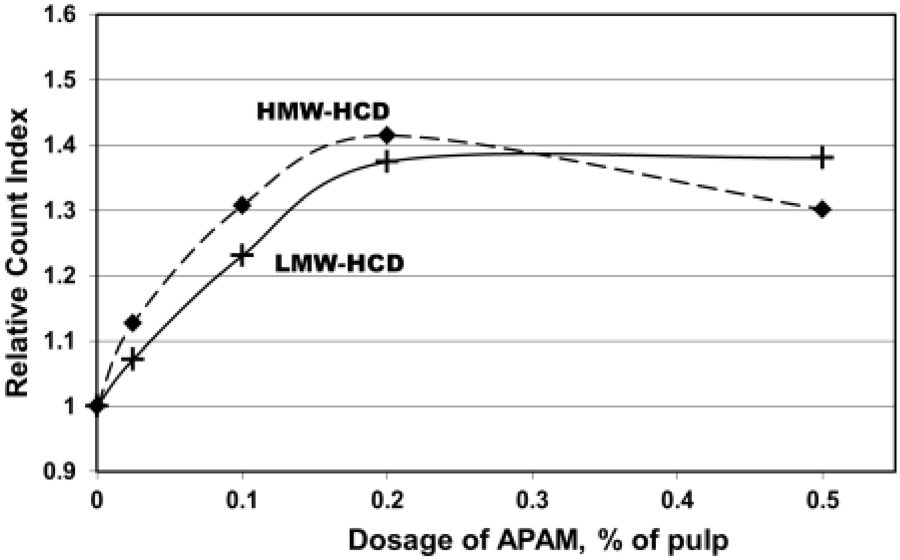

Fig. 8. Deflocculation of pulp suspension (size range 1-10 µm) with two different deflocculants after 60 seconds of deflocculant addition (% of pulp). Pulp consistency 0.5% and mixing speed 1000 rpm.

Dewatering Results

Dewatering refers to the ease of removing water from the paper web in the forming section of paper machine. It has great importance, *e.g.*, to the energy consumption and runnability of the paper machine (Hubbe and Heitmann 2007). In previous studies, it has been shown that high molecular weight anionic deflocculants have a detrimental effect on dewatering. Palonen and Jokinen (1986) observed a decreasing dewatering effect of deflocculants especially at high dosages. Also Wasser (1978) and Lee and Lindström (1989) observed decreased dewatering when anionic deflocculants were used. Similarly in the present experiments, these high molecular weight deflocculants deteriorate dewatering significantly (Fig. 9). There are two explanations for this. One hypothesis is the choke effect caused by the pulp fines (Hubbe and Heitmann 2007; Hubbe *et al.* 2009). The fines block the channels through which water is able to flow out. This explanation seems reasonable because it was observed in the particle size measurements that the number of small particles increases as the deflocculant is added to pulp suspension. Thus there are more small particles to block water flow channels, which will lead to decreased dewatering. However, because the high molecular weight deflocculant was more effective in dispersing particles (Fig. 8) at low dosages, the choke effect does not seem to be the only explanation for decreased dewatering. Figure 9 shows that the higher molecular weight, the higher the dewatering time. Similar observations were also seen by Wasser (1978) and Lee and Lindström (1989). Because the dosing of the deflocculants also decreases dewatering, it seems obvious that the change in the viscosity of the suspending medium also affects dewatering of the pulp (Lee and Lindström 1989; Zhao and Kerekes 1993). As the viscosity of the suspending medium increases more when higher molecular weight deflocculant is added, it will increase the flow resistance of the water through wire, which can be seen as an increased dewatering time.

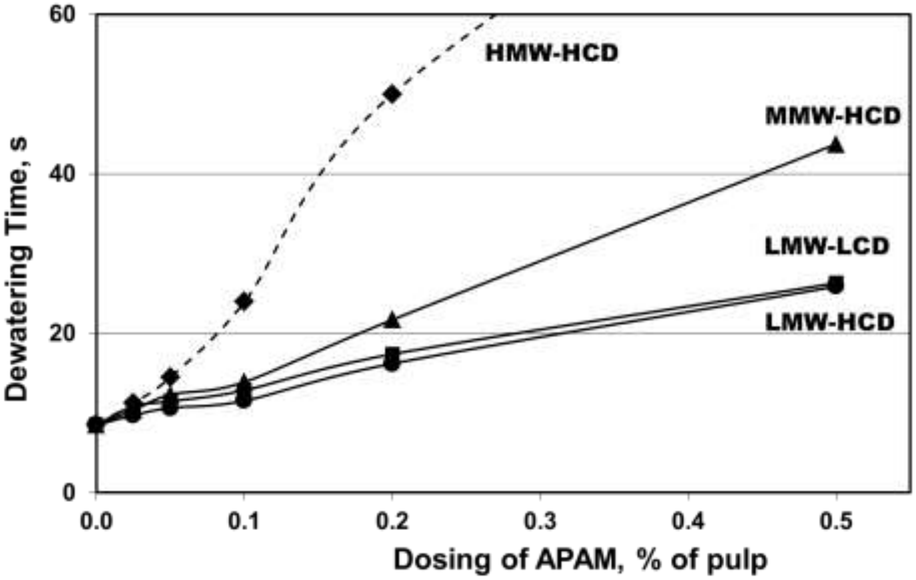

Fig. 9. The effect of four different APAMs on dewatering time of pulp suspension as a function of APAM dosage (% of pulp). Pulp consistency was 0.5% and mixing speed 1000 rpm (contact time 30 s).

To our knowledge, there are few studies on the effect of time on the deflocculation and dewatering. As mentioned above, Palonen and Jokinen (1986) concluded that a short contact time is desirable to achieve the highest deflocculating effect of pulp. As was seen in the deflocculation experiments, the mixing time had a significant effect on deflocculation level and floc re-formation. Therefore, the effect of the mixing time (contact time between APAM and fibres prior dewatering) on dewatering time was also tested. Figure 10 presents dewatering time of pulp suspension as a function of contact time between APAM and fibres prior to dewatering (0.1% dosage of APAMs (LMW-HCD) and (HMW-HCD)). As can be seen, the dewatering time without any deflocculant was approximately 8 seconds. When APAMs were added, the dewatering time increased. The contact time between APAM and fibres had a significant effect on the dewatering time. After 10 seconds contact time (mixing), the dewatering time was significant for LMW-HCD and very high for HMW-HCD. When APAMs and fibres were mixed for 30 seconds prior to dewatering, the dewatering time was already lower, while after 300 seconds the dewatering time was almost the same as without any additives. This clearly indicates that something happens in the pulp suspension in the presence of the deflocculant as mixing continues. As was seen in the particle size measurements, the flocs start to reform when mixing continues, which would probably help drainage of the water by opening flow channels. However, the magnitude of change in the dewatering experiments was very high, considering there was much more diminutive changes in the relative particle count index over the same time period. It seems that the contact time of deflocculant in pulp suspension is a very important parameter, which is well-known in flocculation phenomena. In addition to reflocculation, another explanation for improved dewatering as a function of mixing time is deformation of polymer chains (Tanaka *et al.* 1993). The deformation of polymer chains decreases the viscosity of the pulp, which will lead to improved dewatering.

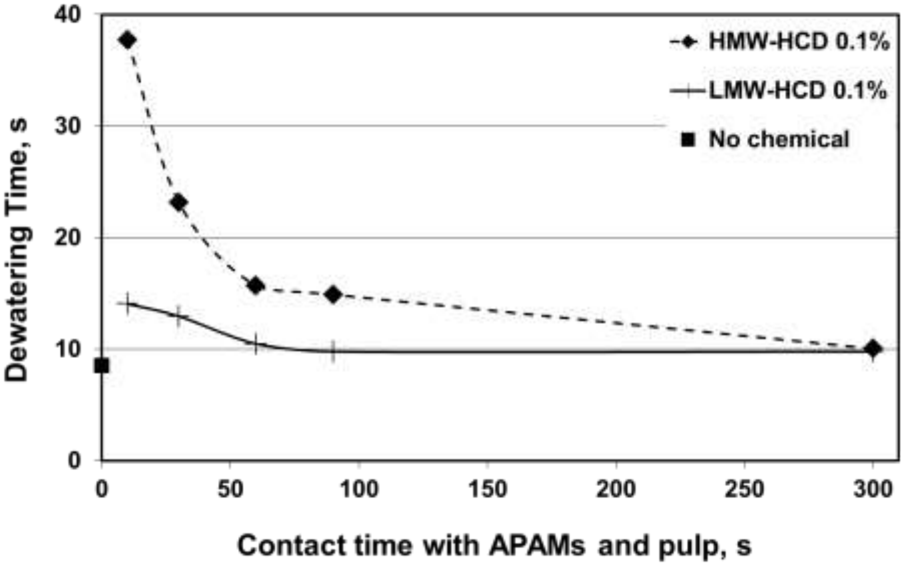

Fig. 10. The effect of contact time between APAM and fibres on dewatering time. Pulp consistency was 0.5% and mixing speed 1000 rpm. Addition levels of APAMs were 0.1% of dry pulp.

CONCLUSIONS

1. There is an optimum dosage level for different APAMs to achieve deflocculation of cellulosic suspensions (fibers or microfibrils). Generally, the deflocculation level increases with increasing polymer dosing, until the maximum deflocculation effect is achieved, after which it starts to gradually decrease.
2. The higher the M_w of deflocculant, the more it promotes deflocculation, weakens the strength of flocs, and inhibits the dewatering of cellulosic suspensions.
3. Deflocculants have a significant deteriorating effect on dewatering (especially high M_w APAM). Dewatering time is also highly dependent on the contact time with the deflocculant.

4. The positive effects of anionic deflocculants are quickly diminished due to shear forces, and therefore, the best deflocculating effect is achieved using as short a contact time as possible. On the other hand, a longer contact time is beneficial for efficient dewatering.

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