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SOME ASPECTS OF RETENTION AIDS

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ABSTRACT

Fundamental aspects on polymer adsorption and flocculation phenomena are reviewed. Special emphasis is placed on recent developments. Examples are the mode of action of microparticle retention aid systems and of retention systems based on polyethylene oxide/phenolic resin.

Fibre flocculation and the strength of fibrous networks are affected by retention aids and this is discussed in connection with investigations on retention and formation in the laboratory and on pilot-scale paper machines.

INTRODUCTION

This review article deals primarily with retention aids. Other papers presented at this symposium are devoted to other paper chemicals such as sizing agents and strength aids. Some of the discussion in this paper, e.g. on the adsorption of polyelectrolytes, is of course of relevance for some of these other areas as well. There are already extensive reviews available concerning retention aids and retention mechanisms (1, 2) and this review is therefore concentrated on more recent developments especially those not covered in the earlier reviews. We do not, however, claim to have covered all developments. There is, of course, some emphasis on the work done at STFI, primarily since this work is very familiar to us.

To understand what happens in a papermaking furnish containing fibres, fillers and paper chemicals, it is very instructive to consider the collision frequencies between the various components. In the first section of this paper a condensed discussion on collision frequencies is given. Since practically all retention aid systems contain polymers, some aspects, primarily kinetic, on polymer adsorption are treated in the next section. Retention mechanisms are then discussed, and in this section we concentrate on newer developments such as microparticle retention aid systems and on areas where significant new knowledge has emerged, e.g. with regard to the polyethylene oxide-phenol formaldehyde resin system. A short discussion on the influence of disturbing substances on the effectiveness of retention aids is included.

The strength of fibre flocs (fibre networks) and the attachment of fillers to fibres are discussed in the following section since these quantities are very important for retention/formation. In order to compare the laboratory experiments with the real situation on a paper machine, results from experiments on pilot machines are discussed. Most of the reports are from experiments on the FEX paper machine at STFI. This machine operates at hydrodynamic conditions very close to those on a real machine and there are many dosage positions for chemicals. This review does not include any discussion on the properties of the paper produced except with regard to the formation.

COLLISION FREQUENCIES

In this section only the most basic formulae are given together with some data for a typical furnish. Collisions between particles can be induced either by diffusion or by shear. If collisions are induced by shear, the collision frequency K_{shear} is

$$K_{shear} = \frac{4}{3}\alpha G(a_1 + a_2)^3 \qquad [1]$$

where a_1 and a_2 are the radii of the colliding particles and G is the shear level. If the flow is turbulent, G can be estimated from

$$G_{turb} = (\varepsilon / \nu)^{1/2} \qquad [2]$$

where ε is the energy dissipation per unit mass and ν the kinematic viscosity. α is a collision efficiency factor which takes into account the hydrodynamic interactions between the particles during collision. Particles tend to follow the streamlines during collisions. α also includes the dispersive and electrostatic interactions between the colliding particles. For a discussion of the collision efficiency factor, the reader is referred elsewhere (3-5). This factor should, however, been taken into consideration, especially when a small particle collides with a large particle (fibre). In this case, α can lower the collision frequency by one or two orders of magnitude.

The collision frequency for diffusion K_{diff} is given by

$$K_{diff} = \frac{2kT}{3\eta}\frac{(a_1 + a_2)^2}{a_1 a_2} \qquad [3]$$

where η is the viscosity of the medium, k the Boltzmann constant and T the absolute temperature. In this case, the collision efficiency factor α need not be considered since it is sufficiently close to unity for our estimates.

From these formulae it is easy to calculate the half time, $t_{1/2}$, for various processes. The half time for polymer adsorption is the time it takes for half the number of polymers to collide and be adsorbed onto the cellulosic fibres. In most of the calculations given in this paper, we consider a standard fine paper furnish with 5 kg/m^3 fibres ($5 \cdot 10^{10}$ fibres/m^3, equivalent radius 60 µm), 1 kg/m^3 filler particles ($1 \cdot 10^{14}$ filler particles/m^3, radius 1 µm) and 1 g/m^3 of a high molecular weight polymer (MW=$6 \cdot 10^6$; 10^{17} molecules/m^3, radius 0.1 µm). Polymer adsorption and flocculation are here discussed in relation to collision frequencies (half times) in this standard furnish. Similar discussions have been presented, e.g. by Gregory (6). Discussions in the papermaking field have been presented by van de Ven (7, 8) and Alince (9).

POLYMER ADSORPTION

Kinetics of adsorption

Almost all retention aid systems contain a high molecular weight polymer as one component. The adsorption of this polymer on the components in the furnish is essential for the mode of action of these retention aid systems as discussed in the next section. There are several reviews on the adsorption of polymers on solid surfaces including cellulosic fibres (10-13). The reader is referred to these articles for more complete reviews on polymer adsorption. Here we treat some aspects, mostly kinetic, of special interest to the papermaker.

The first step in polymer adsorption is the transport of the polymer to the surface of fibres and fillers. If there is no barrier to adsorption, the kinetics of adsorption can be approximately described by the collision frequency between polymers and fibres or fillers. There should be no chemical barrier to adsorption at least for the adsorption of a positively charged polymer on a negatively charged particle. The hydrodynamic interactions, which can greatly reduce the collision efficiency between solid particles, do not seem to be very significant for polymers adsorbing on solid surfaces.

If the formulae for collision frequencies and the standard furnish conditions are used, the half time for polymer adsorption on fibres is for the shear case $48/G$. On a paper machine, the shear level varies but for points at which polymers are added it is typically in the range 100-1000 s^{-1} (14). It can thus be understood that polymers can be adsorbed onto cellulosic fibres in a fraction of a second. From Eq. [1] it is also clear that the size of the polymer does not influence the half time.

A physical picture is that the large fibres are transported by the shear field through the solution and collide with all the polymer molecules in the volume swept out independent of the size of the polymer. If instead the half time due to adsorption by diffusion is calculated, a value of 8000 s is obtained for the standard conditions. In a 0.5 % fibre suspension, it takes such a long time before half the polymer molecules have reached a fibre surface. It is obvious that adsorption due to shear is in all practical situations the dominant process.

There is indeed experimental evidence for this fast adsorption in a sheared solution. Falk et al. (15) measured directly the adsorption of cationic polyelectrolytes on cellulosic fibres during very short contact times in turbulent pipe flow. In these experiments, G was 400 s^{-1}. They found that polymer adsorption occurred on the cellulosic fibres during the shortest contact times, 0.5 s, which they could achieve. Fig. 1 shows results from experiments of flocculation of cellulosic fibres in a flow loop (16). The flocculation index is a measure of the flocculation induced by added flocculant. There is substantial flocculation already after 0.2 s. For this flocculant, this means that the adsorption of polymer must have taken place in this short time.

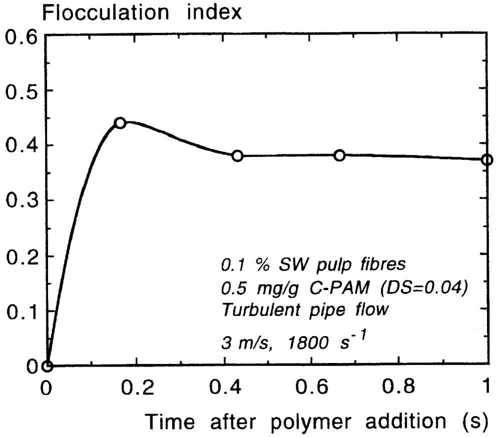

Fig. 1 Flocculation index as a function of time after the addition of cationic polyacrylamide (C-PAM; degree of substitution, DS=0.04) at an average flow velocity of 3.0 m/s, corresponding to a shear rate of 1800 s^{-1}. The added amount of C-PAM was 0.5 mg/g. Softwood pulp fibre suspension at 0.1 % concentration. From (16).

Lang and Stratton (17) studied the adsorption of polyelectrolytes on fairly large latex particles in a stopped flow device. Although these experiments are on the borderline where diffusion effects start to be of importance, the authors concluded that, in furnishes with a high shear level, polymer adsorption on such large objects as fibres is very rapid.

Two comments may be made. From Eqs. [1] and [3] it is clear that collisions induced by shear are important for large particles whereas diffusion is more important for small particles and macromolecules. As a rule of thumb it is often stated that shear is important for particles larger than 1 μm and diffusion for particles smaller than 1 μm. The exact dividing line depends on shear level and collision efficiencies. However, this rule of thumb applies for collisions between particles of the same size. For collisions between particles of different sizes, as in the example above, the relevant equations must be used to estimate the kinetic characteristics of the process.

The other comment is that Eq. [1] gives the collision frequency for the idealized case when the suspension is fully dispersed. In a suspension of cellulosic fibres, the fibres flocculate on the same time-scale as that in which the polymer is adsorbed ($t_{1/2} = 9/G$ for the standard furnish assuming $\alpha = 1$). If the flocs of cellulosic fibres are not immediately disrupted, this means that pockets of solution containing unadsorbed polymers can exist within the flocs. The size of such pockets can be of the order of 50 µm. For a polymer with radius 0.1 µm it takes approximately 10 min to diffuse a distance of 50 µm. If polymer has been added on a paper machine, unadsorbed polymer may occur within flocs even if there was good mixing at the point of addition. These unadsorbed polymers can be released at some later stage when the flocs are disrupted. The released polymers can contribute to the reflocculation of the furnish. It should therefore again be stressed that formulae such as Eq. [1] refer to a very idealized situation. In practice it is of course also difficult rapidly to mix a polymer solution homogeneously into a suspension of cellulosic fibres and it is very likely that, at least at the beginning, the polymer molecules are not evenly distributed over the stock components. Gregory (18) has very clearly demonstrated how flocculation can be influenced by the mode of polymer addition.

The polymer are not adsorbed only onto the fibres. They can of course also adsorb onto filler particles in the furnish. If the half time for polymer adsorption on the fillers is calculated for the model furnish, a time of $t_{1/2} = 3900/G$ is obtained. The adsorption on cellulosic fibres is thus clearly favoured over the adsorption on fillers. For adsorption on filler particles, diffusion is again too slow a process to be of practical importance giving a half time for adsorption of approximately 200 s.

Simultaneous adsorption of polymers

What will happen if more than one polymer is added simultaneously to the furnish e.g. one high molecular weight and one low molecular weight cationic polymer? Since the collision frequency with fibres in the shear case is not governed by the size of the polymer molecule, one would theoretically expect that, at least at short times, the relative amounts of the two polymers adsorbed on the fibres would be the same as the relative amounts in solution.

Experiments to investigate this have been carried out by Tanaka et al. (19) using one low molecular weight fluorescently labelled and one high molecular weight unlabelled cationic polyacrylamide. The adsorption of these two polymers on large polystyrene latex particles (diameter 3.1 µm) in a stirred suspension is shown in Fig. 2a.

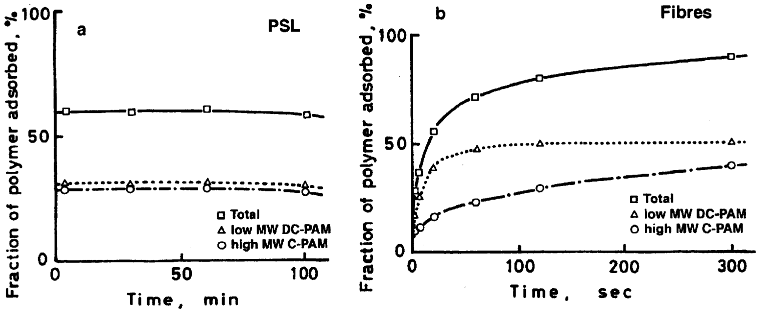

Fig. 2 Competitive adsorption of mixed polymers (high MW C-PAM and low MW DC-PAM) onto (a) polystyrene latex particles (PSL) and (b) cellulosic fibres from a bleached kraft pulp. PSL 5.0 g/l, fibres 5.0 g/l, polymer 0.025 g/l (C-PAM 0.0125 g/l, DC-PAM 0.0125 g/l; 0.5 % on PSL, 0.5 % on fibres), 500 rpm. □ = from polyelectrolyte titration; △= from fluorescence intensity; ○ = □ –△. Note: Fig 2a, time in min; Fig. 2b, time in sec. From (19).

Equal amounts of the two polymers were added and equal amounts are adsorbed in agreement with theory. The experiments also show that there is no exchange of low molecular weight polymers for high molecular weight polymers during the time of the experiment. Both polymers were, however, of such a high molecular weight that the driving force for exchange should be quite low. Fig. 2b shows the results of corresponding studies of the adsorption on cellulosic fibres. In this case, the situation is more complicated since only the low molecular weight molecules have access to the pores in the cell wall. However, during very short times where the diffusion into the pores is not significant, the adsorption is approximately the same for the high and low MW polymer. The physical picture to facilitate interpretation of these results is that the large particles (fibres) sweep the solution. The volume swept by the fibre will contain both low MW and high MW polymers in proportion to the added amounts.

The situation in the case of diffusion will be different. If the two polymers are adsorbing on large objects like fibres, the half time for adsorption will be directly proportional to the size of the polymer. However, for typical furnishes these times will still be so long that adsorption due to diffusion processes can be neglected.

Redistribution of polymers

In practice it is very difficult to mix polymers into a fibre suspension in such a way that the polymers are evenly distributed. One question that naturally arises is whether a polymer that has been adsorbed on one particle will migrate to another particle with no adsorbed polymer. Such a redistribution is clearly most likely to take place in connection with flocculation and the breakage of flocs. The adsorption isotherms for cationic polyelectrolytes are generally of such a high affinity character that, for the amounts used in practice, there will be insignificant amounts of dissolved polymer in solution. The mechanism where an adsorbed polyelectrolyte desorbs and diffuses into the solution to be adsorbed on another particle will therefore be very slow. The dominant mechanism for transfer will be that a fibre or a filler particle deposits on a fibre surface with adsorbed polymer. When this particle is detached from the fibre surface e.g. by shear, it may take the polymer molecule with it.

That transfer does indeed occur can be shown by a rather simple experiment (20). A cationic polymer is adsorbed on cellulosic fibres in a suspension and a suspension of negatively charged filler particles is then added to the suspension. If the z-potential for the filler particles in solution is monitored as a function of time, it is found that the z-potential becomes more positive due to the transfer of cationic polymers from the fibres to the filler particles.

The z-potential experiment does give only a qualitative measure of the amount of polymer transferred. A number of transfer experiments have been performed where fluorescently labelled polyacrylamides and nitrogen analyses have been used to follow the transfer of polymers from fibres to fillers. Fig. 3 shows the fraction of a cationic polyacrylamide transferred from cellulosic fibres to 1.2 μm $CaCO_3$ particles (20). The experiments were done in a Britt Jar (21) at 1000 rpm. The transferred amounts are given as a function of time and as a function of the time (pre-adsorption time) during which the polymers were adsorbed on the cellulosic fibres before the filler was added and the shear established.

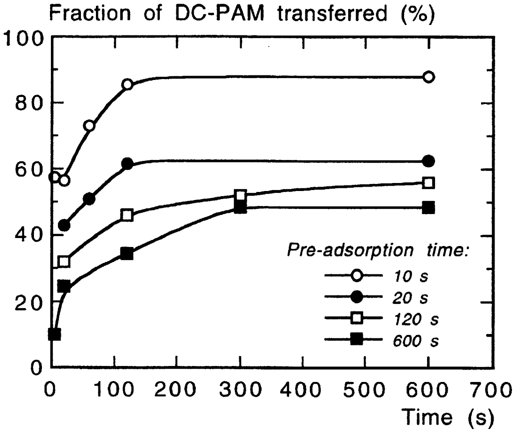

Fig. 3 Effect of pre-adsorption time on the transfer of DC-PAM from cellulosic fibres to calcium carbonate particles (diameter 1.2 μm). Fibres: 1.0 %, DC-PAM: 1 mg/g fibre, $CaCO_3$ particles: 0.5 %, stirring speed: 1000 rpm. From (20).

It can be seen that with only short pre-adsorption times a very substantial part of the polymer is transferred to the filler particles and the transfer occurs rather rapidly. With longer pre-adsorption times, the amount transferred to the filler particles is smaller and the transfer is slower. These results were interpreted as indicating that during short pre-adsorption times the adsorbed polymers do not have time to penetrate to any significant extent into the pores of the cellulosic fibres. They will be rather loosely attached to the fibre and will easily transfer to filler particles. The final distribution of cationic polyacrylamide between fibre and filler is roughly governed by the outer surface areas of the particles. This was verified by experiments with fillers of different particle sizes. The affinity of the polymer to the two surfaces should not differ greatly since the fibre and filler surfaces have approximately the same z-potential. It should be observed that, even though the experiments last a long time, the polyacrylamide will have a reduced possibility to penetrate into the cellulosic fibres since the adsorbed polymers will interact with colliding filler particles and other fibres. The collision frequency is very high at these shear levels. The half time for collisions between fillers and fibres is $48/G$ if the influence of the collision efficiency factor α is neglected, but even with α taken into account the collision frequency is still high.

During longer pre-adsorption times the polymer has the chance to penetrate and interact with more charges on the fibres. In this case the final distribution is approximately given by the plateau levels of the adsorption isotherms. The polymer molecules are preferentially distributed to the particle with the higher plateau level of the adsorption isotherm. In other studies (22) where well characterized latex particles were used as model particles for fillers it was similarly found that the final distribution was governed by the charges available on the respective particles. On the latex particles all the charges are available for interaction with the cationic polymer but on the fibres only the charges on the outer surfaces are available. From adsorption studies (23) it has been found that on a bleached kraft pulp of the order of 3-4 % of the total charges are available to interact with a high molecular weight ($\geq 10^6$) polymer.

The fact that a redistribution of polymer molecules occurs does not immediately imply that intact polymer molecules are being transferred. On the contrary, without going into detail, experiments performed by Tanaka et al. (24, 25) show that there is a significant reduction in molecular weight for the polymers transferred from cellulosic fibres to polystyrene latex particles (model substance for fillers). This is illustrated in Fig. 4.

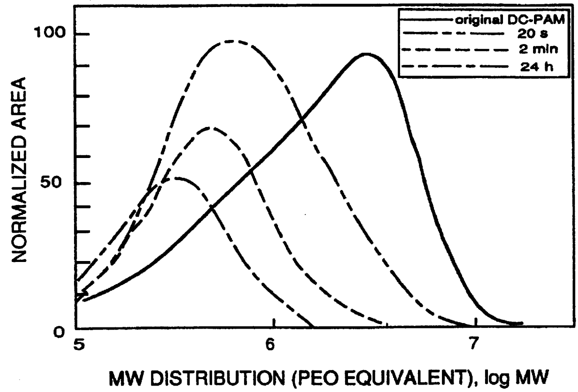

Fig. 4 The molecular weight distributions (MWDs) for cationic polyacrylamides transferred to latex particles (model for filler particles, diameter 0.65 µm). Britt Jar experiments at 1000 rpm. Different pre-adsorption times of 0.1 % C-PAM on pulp fibres. MWDs were determined by size-exclusion chromatography. From (25).

Polymeric retention chemicals are by no means the only chemicals that can be redistributed in a papermaking stock. It has been shown that alum flocs (26) and AKD-size particles (25) can also be rather efficiently redistributed. The latter effect is of course of great interest for the dosage position of sizing agents.

According to these laboratory experiments, redistribution occurs with such a high frequency that redistribution is certainly important in papermaking. For polymers, the effect of redistribution may be somewhat complicated due to the cleavage of the polymers. If only a fragment of a polymer is transferred to another fibre this fragment may be of too low a molecular weight and may also reconform (see below) too quickly to be a very efficient flocculant. Experiments on the FEX paper machine at STFI are presently under way to investigate transfer under realistic papermaking conditions.

Polymer conformation

Another factor which is of great importance for the flocculating efficiency of the adsorbed polymers is their conformation on the surface. The equilibrium conformation of an adsorbed polymer on a surface is different from the conformation of the same polymer in solution (11). Especially highly charged polymers adsorbing on an oppositely changed surface have an equilibrium conformation with an extension into the solution that is rather small compared to the radius of gyration of the polymer in solution (27, 28). The equilibrium conformation will, however, not be reached immediately after adsorption on the surface. From a papermaking point of view, it is interesting to know the half time of the reconformation process, since the polymer conformation immediately after adsorption may give efficient flocculation while the fully relaxed conformation may be less efficient. From measurements of the kinetics for the release of counterions, Wågberg et al. (29) concluded that the reconformation half time was of the order of 30 s for a high molecular weight cationic polyacrylamide. For a low molecular weight ($MW=8\cdot10^3$) highly charged polyelectrolyte (polybrene) the reconformation was faster than 10 s which was the shortest time that could be investigated. Pelssers et al. (30) studied the flocculation of polystyrene latex with polyethylene oxide (PEO) polymer. To interpret their flocculation results they introduced a characteristic time for the reconformation of the adsorbed PEO layer, and they found this time to be approximately 3 s. The molecular weight of the polymer was in this case $4\cdot10^6$. Cohen Stuart and Tamai (31) also obtained values of the order of a few seconds when they investigated the relaxation of adsorbed layers of PEO by a streaming potential technique. Ödberg et al. (28) used the fact that the thickness of an adsorbed polyelectrolyte layer changes when the electrolyte concentration changes. By rapidly changing the electrolyte concentration in the ellipsometer cell and following the change in the measured thickness of the adsorbed layer by ellipsometry a relaxation time of approximately 20 s was found for a high molecular weight ($4\cdot10^6$) cationic polyacrylamide. This is illustrated in Fig. 5.

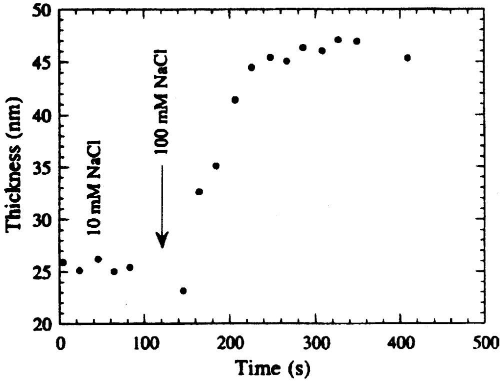

Fig. 5 Polymer reconformation kinetics as indicated by ellipsometric measurements of the adsorbed C-PAM layer thickness on a silicon surface as a function of time. At the time shown by the arrow, the electrolyte concentration in the cell was changed from 10 mM NaCl to 100 mM NaCl. 1 mM $NaHCO_3$ was present as buffer throughout. From (28).

All these experiments have been done for different polymers. It seems, however, that the reconformation time for a high molecular weight polymer ($\geq 10^6$) of the type used as a retention aid is of the order of 10 s. The somewhat longer times obtained by Wågberg et al. (29) may depend on the fact that this experiment also to some extent involved the penetration of the polymer into larger pores close to the surface of the cellulosic fibres. For a lower molecular weight polymer, MW$\leq 10^5$, the reconformation time should be quite short.

What are the practical consequences of these reconformation times? As has already been pointed out, the collision frequencies are so high in a typical papermaking furnish that there is a very high probability that an adsorbed polymer will interact with a filler particle or with another fibre. This will interrupt the reconformation process and keep the adsorbed polymers in a more extended conformation. However, fibres may become locked in flocs. Polymers being adsorbed onto fibres or filler in a floc may continue to reconform to a flat conformation and become inefficient as a retention aid. It is a well known fact that if a retention aid is added far ahead of the headbox, the efficiency is significantly reduced (32).

Branched polymers

The results discussed so far were obtained for linear polymers such as cationic polyacrylamides and non-ionic polyethylene oxide. In papermaking, however, branched and crosslinked polymers are also being used. One example is the commonly used polyethylenimines.

A study of the adsorption onto cellulosic fibres of cationic polyethylenimines of different molecular weights was recently made by Petlicki and van de Ven (33). They found that the adsorption (see Fig. 6) depended rather strongly on the amount added. Their interpretation was that these branched polymer molecules adsorbed onto the surfaces of the fibres in the conformation that they had in solution and they did not reconform to any large extent after having adsorbed onto the surface. At higher concentrations, the polymer molecules in solution have a lower radius of gyration due to interactions between the molecules. A larger number of these molecules can then pack onto the surfaces of the fibres.

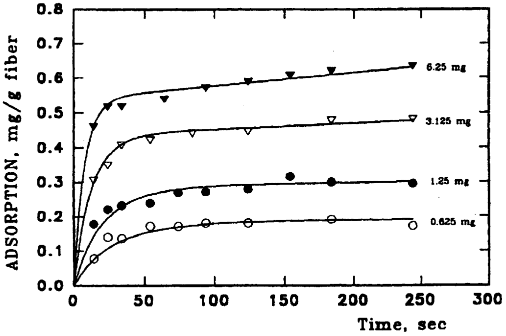

Fig. 6 Adsorption of polyethylenimine (Polymin P) onto pulp fibres at a consistency of 0.2 % at various initial polymer additions (mg/g fibre) indicated in the figure at a stirring speed of 80 rpm. Electrolyte concentration $2.5 \cdot 10^{-4}$ M KCl and pH 6. From (33).

There thus seems to be some difference in behaviour between linear and branched (crosslinked) polymers. This difference has not, however, been systematically investigated. Different research groups have concentrated either on linear or on branched polymers. There has to our knowledge been no attempt to investigate in detail the reconformation of branched polymers on surfaces. Branched polymers could be expected to have a reduced tendency to reconform to a flat conformation, which could be an advantage. Is there a significant reconformation of starch molecules? Horn et al. (34, 35) investigated adsorbed polyethylenimine (Polymin P) by scanning force microscopy and found that the area covered corresponded to the radius of the polymer in solution. The thickness was, however, reduced by a factor of approximately five for the high molecular weight (10^6) polyethylenimine. It should, however, also be pointed out that at very short adsorption times, of the order of a few seconds, linear polymers should also have approximately the same conformation on the surface as in solution. It was found (15) that the amount of a cationic polyacrylamide adsorbed onto cellulosic fibres at short times was close to the amount of polymer molecules with the solution conformation that could be packed onto the surfaces of the fibres.

RETENTION MECHANISMS

Some kinetic aspects

The main purpose of a retention aid is to attach the filler particles or size droplets to the long fibres so that they can be retained in the sheet being formed. Almost all retention aids contain a polymer as one component. It is therefore of interest to consider the kinetics of polymer adsorption on fibres and fillers and to compare it to the collision frequencies between these particles. As already mentioned, the half time for polymer adsorption on cellulosic fibres for our standard furnish is $48/G$. If the corresponding calculation is done for the adsorption of polymers onto the filler particles, a value of $3900/G$ us obtained. The adsorption on fibres is thus favoured over the adsorption on fillers at least for the idealized conditions of Eqs. [1-3]. The adsorption of polymers on the filler particles by a diffusion mechanism is in practice not an important process, having a half time of approximately 200 s under our standard conditions. The time it takes for half the fillers to have collided with a fibre is given by $48/G$ if the collision efficiency factor α is neglected, but α should be significantly less than unity for collisions between fibres and fillers. The adsorbed polymer can, however, to some extent bridge the distance between fibres and fillers created by the hydrodynamic interactions and this increases α. Under shearing conditions polymer adsorption and filler/fibre collisions are thus parallel processes. If the total amount of polymer added corresponds approximately to the amount that is needed to cover the outer surface of the fibres, which is often the case, at least the filler particles that first collide with the fibres will collide with a surface that is not fully covered by adsorbed polymer molecules. This will probably mean that the filler particles will not be so firmly attached to the fibres. Polymers that have just adsorbed will, on the other hand, have a more extended conformation and this will make them efficient as bridging flocculants.

There is of course also the possibility that the filler particles collide among themselves forming filler flocs that can be mechanically retained in the paper being formed. The half time for filler flocculation, i.e. the time it takes the number of filler particles to be reduced to half by flocculation, is $415/G$, and this time is longer than the time for deposition of the filler particles on the cellulosic fibres. The collision efficiency factor α should be larger for filler collisions. It can thus be concluded that, for the standard furnish, there are good possibilities for the deposition of single filler particles on the fibre surfaces. However, polymer adsorption on filler and filler collisions, i.e. filler flocculation, are also rapid processes for realistic values of G (100-10000 s^{-1}). It is therefore clear that, especially if the fibres get locked in flocs, filler flocculation will be possible in a real system.

Fibre flocculation and fibre floc strength are of course also influenced by adsorbed retention polymers. This is discussed later in this review.

Model experiments

In order to examine whether retention can be interpreted as being a deposition of particles on fibres where the particles are retained on the particles by chemical flocculants, model experiments have been made by Middleton and Scallan (36) and by van de Ven and co-workers (37-39). In some of these experiments, polymers have been added either to fibres or to fillers to such a level that the particles become recharged and there is no flocculation. Fibres and fillers were then mixed in a stirred suspension and the amount of filler particles in the suspension monitored. This was done by continuously withdrawing a fibre-free sample from the suspension and measuring the filler concentration turbidimetrically. The results were interpretated using a modified Langmuir equation (36, 37). The modification takes into account the fact that the filler particles added may not necessarily cover all the available area on the fibres. As in the Langmuir equation for the adsorption of gases on a solid surface, there is a rate constant k_1 for the deposition of filler particles on the fibre surface and a rate constant k_2 for the detachment of filler particles from the fibre surface.

The experiments were made at a moderate shearing rate (10-100 s^{-1}) and at a low fibre concentration (0.5 g/l). This means that the kinetics of deposition were so slow that the process was easy to follow. Under these conditions, the deposition of filler particles was found to follow the Langmuir kinetic model. An example of the deposition of calcium carbonate particles on fibres is given in Fig. 7. In this case, there is also a deposition of particles on the fibres without the addition of any retention aid since the fillers are positively charged. The deposition rate k_1 was well described by the collision frequency between filler and fibres when the hydrodynamic interactions were taken into account (37). The deposition rate was found to be the same whether or not the polymer (PEI) had been adsorbed onto the $CaCO_3$ particles. One might perhaps expect that the additional electrostatic attraction caused by the adsorbed PEI should give a faster deposition rate. However, the attractive electrostatic forces have a range of only 1-10 nm and this distance is insignificant compared to the total distance a particle moves during a collision.

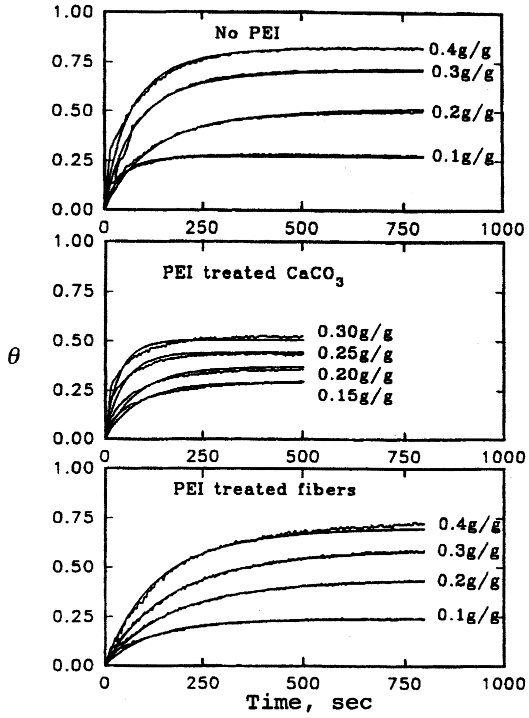

Fig. 7 Fractional coverage θ of pulp fibres by $CaCO_3$ particles versus time. The numbers on the right indicate the initial concentration of $CaCO_3$ per gram of fibre. The wavy lines are the experimental observations and the solid lines are the best fit to a derived equation describing Langmuir adsorption kinetics. From (37).

The detachment rate given by k_2 can be used to characterize the bond strength between the fibre and the filler. k_2 should be given by an expression such as

$$k_2 = k_2^0(G)e^{-E/kT} \qquad [4]$$

where E is the bond strength and $k_2^0(G)$ depends on the shear level G. In the experiments with PEI and $CaCO_3$ particles, it was found that PEI did not significantly increase the bond strength between fibre and fillers. It should be interesting to extend this type of study both to more realistic shear levels and to bridging-type retention chemicals, where the rate of detachment should be significantly reduced.

Experiments were also carried out in which the polyelectrolyte was added to the mixture of fibres and fillers and also in such large quantities that the suspension contained non-adsorbed polymers when the second component was added. In this case, the filler deposition was reduced since there was a high possibility that both particles were recharged before collision occurred. It was also found that the steady-state deposited amount tended to decrease with time when the added amounts were large, see Fig. 8.

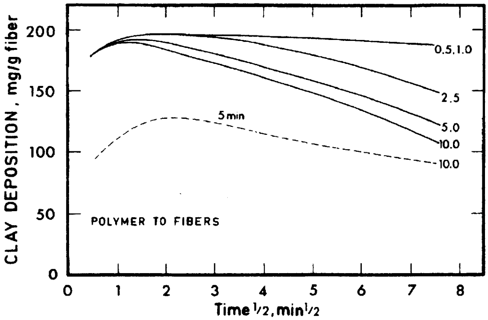

Fig. 8 Deposition of clay (0.2 g) introduced into a suspension of fibres (1 g) treated with dosages of polyethylenimine (PEI) in the range 0.5-10 mg. Broken curve, 5 min delay between the polymer and clay addition. From (39).

The latter observation was interpreted as meaning that increasing polymer adsorption occurred on both fibres and the deposited fillers and that this gradually weakened the bond between the fibre and the filler. An alternative explanation is that when filler particles are detached from the fibre surface they adsorb more polymers as do the fibres, and that this reduces the tendency to redeposition. It was also found in these experiments that, when the conditions were such that the clay could aggregate before deposition, the deposition process was faster. This is not expected from the simple theory according to which the deposition rate on fibres does not depend upon the size of the depositing object. However, the collision efficiency factor α becomes larger when the sizes of the colliding objects become more equal and this explains the higher deposition efficiency for the larger particles.

Microparticle retention aid systems

A particular kind of two-component flocculant system is the microparticle-containing retention aid. The microparticulate retention aid systems have, since the introduction of the first two commercial systems based on cationic starch together with anionic colloidal silica (40) and on cationic polyacrylamide together with anionic montmorillonite (41), increased in use. There are also systems containing cationic polyacrylamide and colloidal silica (42). In recent years several new systems have been developed, which will be briefly discussed later. The literature on the flocculation mechanism of microparticle systems will be reviewed.

The scientific literature on small particle technology in general is rapidly growing (43). In the field of papermaking there have been only a few publications on the mechanisms of microparticle systems. There is, however, a vast industrial experience among papermakers and chemical suppliers using these flocculant systems, and a multitude of case histories describing mill applications of microparticle systems.

Lindström (44) characterised the microparticle systems as reversible or at least partially reversible retention/dewatering systems. He also pointed out the difference between these systems and conventional two-component systems consisting of two polymeric flocculants. The microparticle systems often have a positive effect on both retention and drainage in the wire section and on the dewatering in the press section of the paper machine. The microparticle retention/dewatering aid combinations have some common features which, it has been claimed, distinguish them from a polymeric two-component retention aid system (44):

- Significant reflocculation takes place after dispersion of a suspension flocculated by a microparticle retention aid system. The systems may be classified as reversible or at least partially reversible flocculants.
- A more rapid dewatering is often observed both in the wire section and in the press section.
- The dried sheet often exhibits a higher porosity when a microparticle retention/dewatering system is used.

Fundamental work on flocculation using these flocculants is scarce (45-48). However, investigations on the interactions between the cationic polyacrylamides and anionic particle sols, by adsorption (49, 50) and flocculation measurements (50, 51) have been made. A recent article by Lafuma (52) reviews the work by the French group. Wall et al. (53) and Walldal et al. (54) studied the kinetics of flocculation of cationic amylopectin by colloidal silica using stopped-flow techniques and turbidimetric detection, and they concluded that electrostatic interactions were dominant.

Flocculation mechanism in microparticle systems

There are several mechanisms according to which flocculation can be classified, of which the mechanism of interparticle bridging is one. When negatively charged particles are flocculated with positively charged polymers, both bridging and charge reduction play important roles as discussed by Vincent (55). For a detailed discussion of this aspect, and other aspects of polymer-induced flocculation, the reader is referred to overview articles and textbooks on the subject (1, 44, 56, 57).

The bridging mechanism means that the polymer is adsorbed onto the particles and that physical bridges are formed between particles when they collide. This flocculation mechanism, first suggested by Ruehrwein and Ward (58) and by Michaels (59), was investigated by La Mer and Healy (60, 61). The bridging mechanism explains experimental results in several systems relevant to papermaking, e.g. flocculation of lignin sols (62) or cellulosic fibres (63).

Several experimental investigations of microparticle flocculants suggest that flocculation is governed by both electrostatic interactions and interparticle bridging in flocculation by the cationic flocculant alone as well as in the additional flocculation induced by added microparticles. Fig. 9 shows results from fibre flocculation experiments where a microparticle system containing cationic polyacrylamide, C-PAM (MW=6·10^6, charge density=0.55 meq/g), and anionic colloidal silica, Coll. Si, was used.

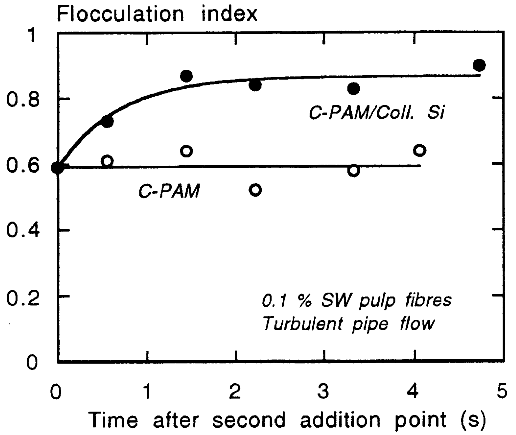

Fig. 9 Flocculation index as a function of time after the second addition point of the second component for C-PAM alone (○) and for a microparticle system, C-PAM/colloidal silica (●). Softwood pulp fibre suspensions in deionized water. Turbulent pipe flow at 0.9 m/s (360 s^{-1}). Added amounts were 1 mg/g for both C-PAM and colloidal silica. The time between addition of the first and second component was 9.5 s, i.e. for C-PAM alone the first measuring point is 9.5 s after C-PAM addition. From (64, 65).

The flocculation effect of adding colloidal silica is quite substantial. Estimates of the amounts of added charges from C-PAM and from microparticles (16, 65, 66) indicate that a maximum in the flocculation occurs when the polymer charges on particle surfaces have been neutralized to a significant degree by adsorbed microparticles. Wall et al. (53) showed in kinetic studies of the flocculation between cationic amylopectin and colloidal silica, see Fig. 10, that the amount of colloidal silica required to reach the flocculation maximum depended on the charge density of the colloidal silica – the higher the charge density (lower particle size), the higher the amount of amylopectin to reach a flocculation maximum.

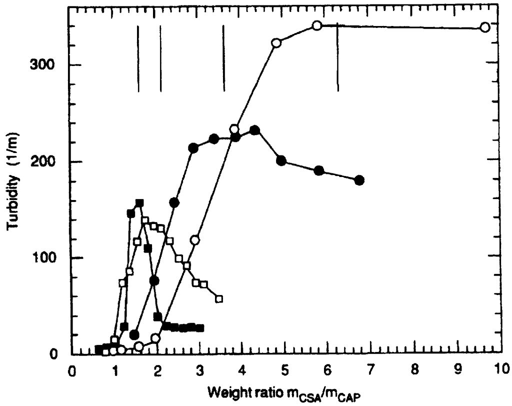

Fig. 10 The flocculation amplitude in stopped-flow turbidimetric measurements as a function of the weight ratio of colloidal silica to cationic amylopectin, m_{CSA}/m_{CAP}, at different particle diameters of colloidal silica (nm): ■ 5.5, □ 7.5, ● 12 and ○ 21. From (53).

These investigations suggest that the flocculation mechanism in microparticle systems involves charge interactions and interparticle bridging. A schematic illustration, see Fig. 11, of the mechanism has been given by Hoffmann (67).

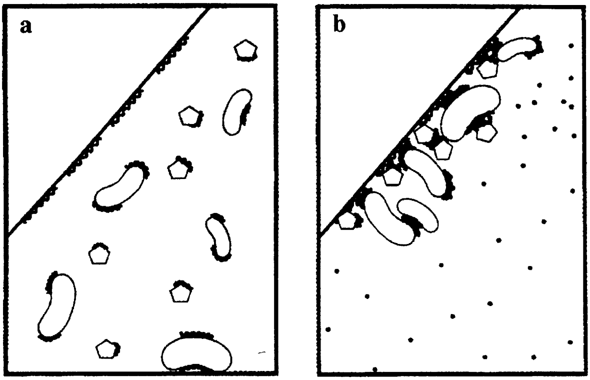

Fig. 11 Schematic illustration of (a) a fibre surface with cationic polymer adsorbed onto the fibre surface, cellulosic fines and filler particles, (b) interparticle bridging by microparticles during reflocculation. From (67).

It should be possible to extend existing flocculation models to account for these effects. The advantage of such work would, of course, be that the flocculation efficiency could be predicted as a function of the amount of added flocculant.

Swerin et al. (68) extended the bridging mechanism to include the effect of microparticles. Fig. 12 illustrates the interactions involved.

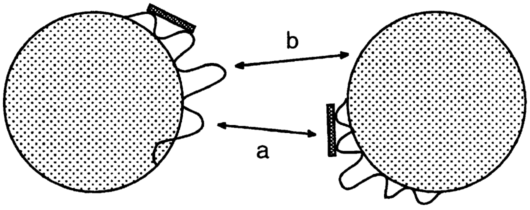

Fig. 12 Schematic illustration of bridging flocculation between two particles with adsorbed cationic polymers and anionic particles adsorbed onto extended polymer segments. The arrows show two types of interactions which induce flocculation: a) between anionic particle and polymer segments, b) between polymer segments and surface sites free from adsorbed polymer. The figure is not drawn to scale. From (68).

A mathematical expression for the flocculation efficiency in microparticle systems was derived based on the original bridging model (60, 69). The standard expression for the flocculation efficiency factor E for bridging (E_{bridge}) is given by

$$E_{bridge} = 2\theta(1-\theta) \qquad [5]$$

where θ is the degree of surface coverage of particle surfaces by adsorbed cationic polymer. The expression for the flocculation efficiency by microparticles $E_{\mu part}$ is

$$E_{\mu part} = 2\theta^2\tau(1-\tau) \qquad [6]$$

where τ is the degree of surface coverage of microparticles onto sites on the particle surfaces which carry adsorbed bridging polymer (68). If the added amount of microparticle is high, sites with cationic polymer will be saturated and hence the flocculation efficiency decreases. The other type of interaction, i.e.

conventional bridging (arrow b in Fig. 12), will decrease with increasing τ because sites will be blocked. As a first approximation, a linear function to describe this decrease was assumed. Eq. [5] then becomes

$$E_{bridge} = 2\theta(1-\tau)(1-\theta) \qquad [7]$$

The model can be used to explain a large flocculation efficiency at high fractional coverages of cationic polymer in a microparticle system (68, 70). Experiments were conducted on the FEX experimental paper machine (68) to show the practical use of the flocculation model. Fig. 13 shows the filler retention and formation number (coefficient of variation of grammage, 0.3-30 mm wavelength interval) as a function of added amount of microparticles (montmorillonite).

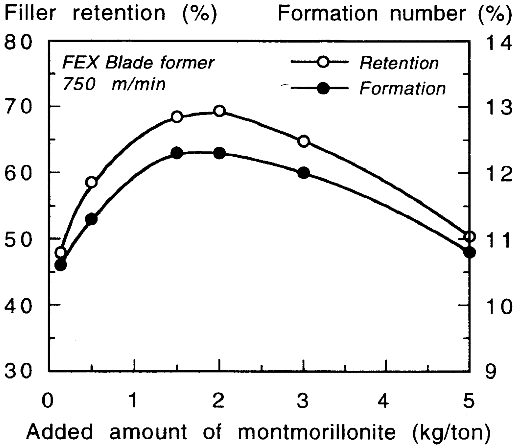

Fig. 13 Filler retention and formation number as a function of added amount of montmorillonite for a fine paper stock in pilot paper machine experiments. The level of added C-PAM was 500 g/ton. From (68).

Both the filler retention and the formation number showed a maximum in the range 1.5 to 2 kg/ton of added microparticles. The effect of added microparticles is typical of a bridging action – when particle surfaces become fully covered by adsorbed microparticle, flocculation decreases.

Laboratory experiments on the adsorption of montmorillonite onto cellulosic fibres with pre-adsorbed C-PAM by Wågberg et al. (70) supported this picture. Fig. 14 shows the adsorbed amount as function of added C-PAM.

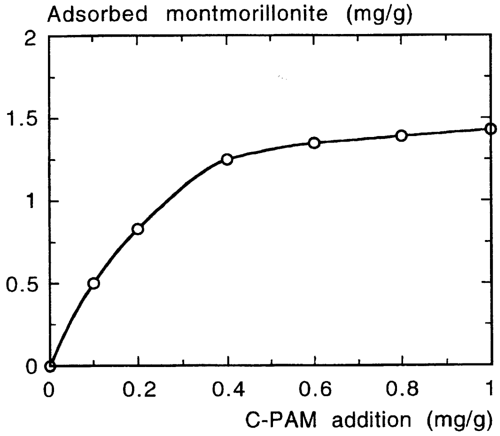

Fig. 14 Adsorption of montmorillonite on cellulosic fibres with pre-adsorbed C-PAM as a function of added amount of C-PAM. From (70). In the original publication there was an error in the units for the C-PAM addition. The correct version of the figure is given here.

At a C-PAM addition of about 500 g/ton (i.e. 0.5 mg/g) the montmorillonite adsorption was in the range of 1.5 kg/ton. At higher amounts, the montmorillonite adsorption levelled off.

Optimisation of microparticle retention/drainage aid systems have been performed (71, 72). Flocculation, zeta-potential and drainage were monitored on-line.

Some aspects on reversibility of flocculation

The most common description of the mode of action of a microparticle flocculant in a mill situation is that the cationic polymer is added to form initial flocs. These flocs are broken and a high degree of flocculation in the stock occurs when microparticles are added close to the headbox. When the degree of reflocculation in microparticle systems is discussed, it is important to define what is actually meant by reversibility in a flocculant system. The flocculation induced by microparticle addition is sometimes called reflocculation. In the present context, a reversible flocculant is capable of promoting reflocculation after high-shear deflocculation in the same way as was discussed by Lindström (44).

To compare reflocculation between different flocculants, the type of shear and the shear level as well as the amount added and the contact time have to be specified. Almost all types of flocculant systems, including single-component systems, exhibit reversibility in the flocculation.

An example of the reversible behaviour with single-component flocculants is given by experiments in which the reflocculation after high-shear deflocculation was investigated in laboratory experiments by altering the propeller speed in a flocculation jar (Britt jar) and by subsequent floc size measurements (45, 66). Fig. 15 shows the floc diameter as a function of time after flocculant addition in experiments with suspensions of microcrystalline cellulose flocculated by cationic polyacrylamide of different degrees of substitution.

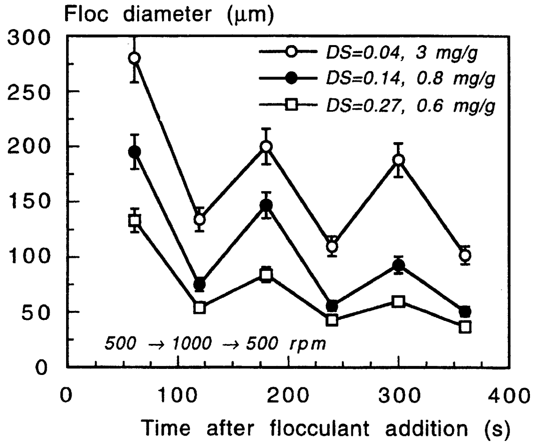

Fig. 15 Floc diameter as a function of time after flocculant addition for suspensions of microcrystalline cellulose, MCC. The shear level was changed by changing the propeller speed between 500 and 1000 rpm every 60 s. C-PAMs of different degrees of substitution (DS) were used as flocculants. The levels of addition correspond to twice the amount needed to reach zero electrophoretic mobility. The diameter of the original MCC particles was 22 µm. From (45, 66).

As alternating low and high shear levels were applied, the average floc diameter was alternatingly large and small, showing a decaying trend with time. The initial degree of flocculation was high, and the degree of reflocculation after a period of high shear was substantial, as seen in the second and third measurements at low shear. The degree of reflocculation, given as the floc size at the second measurement at low shear divided by the floc size at the first at low shear, was about 0.7 for the two C-PAMs of lowest degree of substitution and about 0.6 for the C-PAM of DS=0.27. Eriksson and Alm (73) investigated reflocculation in suspensions of latex particles by monitoring the flocculation before and after a high-shear zone. They found that a C-PAM of higher DS gave a higher reflocculation. A similar experimental set-up to investigate reflocculation as that reported in (73) has been used by Krogerus (74) to study reflocculation in single-component and microparticle flocculants.

The largest flocs (see Fig. 15) were obtained with C-PAMs of low DS, for which the bridging action of the polymers is most pronounced. At a higher charge density, there is a tendency for the polymer chains to adopt a flatter conformation on the particle surface because of a greater charge interaction. A high charge density also tends to give more compact flocs by reaction-limited aggregation (high fractal character) as suggested by model experiments on the flocculation of latex particles (73, 75).

Several processes can account for a decrease in reflocculation after the high-shear deflocculation as shown here for cationic polyacrylamides. These processes can be summarized as reconformation towards a flatter configuration (29); floc breakage giving the possibility for further reconformation (76, 77) and polymer chain cleavage (24, 78-80) with a less efficient bridging as a result. It is also possible that floc breakage can induce polymer desorption, but no experimental studies seem to be available to verify this effect. In a model for the loss of flocculation ability, Pelton (81) assumed that small particles that are detached from a fibre surface leave a deactivated area on the fibre surface. This gives a certain degree of irreversibility in the flocculation.

The degree of reflocculation in the microparticle systems can be compared with that in the single-component systems (45, 66). At low levels of added cationic flocculants, microparticles reduce the reflocculation. This is expected, because there will be only a few cationic groups available for interaction with anionic particles, and the microparticles rapidly saturate these groups and act as a dispersant. The degree of reflocculation passes through a maximum as a function of the added amount. It was also found that the amount of microparticles needed to reach the maximum reflocculation was displaced towards higher levels with increasing amount of added polymer. These effects were more pronounced for cationic flocculants with a higher degree of substitution. These results clearly suggest that the flocculating effect of microparticles is governed mainly by charge interactions with adsorbed cationic polymers.

Fig. 16 shows the effect of a late addition of a microparticle. When the microparticle was added, the decaying trend in floc size was broken. Large flocs were formed and the degree of reflocculation was high.

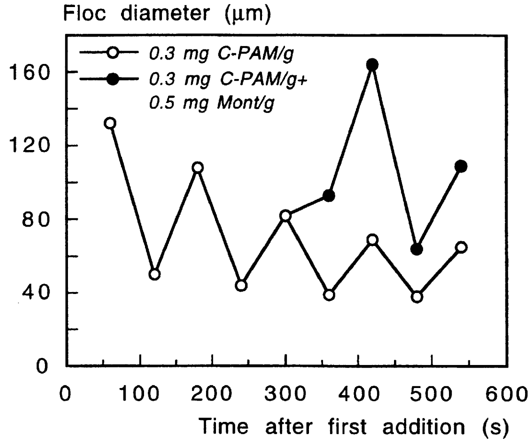

Fig. 16 Floc diameter as a function of time after addition of C-PAM to suspensions of microcrystalline cellulose. C-PAM (DS=0.27) was used as flocculant, alone or together with a late addition of anionic montmorillonite, Mont. Other experimental details, see Fig. 15. From (45, 66).

The large degree of flocculation occurring as a result of a late microparticle addition suggests that processes such as the breakage of initially formed flocs and the reconformation of adsorbed cationic polymers towards a flat configuration do not eliminate the flocculation induced by microparticle addition. Apparently, even after long shearing, sites for interaction with montmorillonite remain on the surfaces of floc fragments.

Fibre flocculation experiments (16) suggest that the sites available for interaction can even increase as a result of floc breakage. Fig. 17 shows the flocculation index as a function of time after addition of (a) C-PAM alone and of (b) a C-PAM/montmorillonite system.

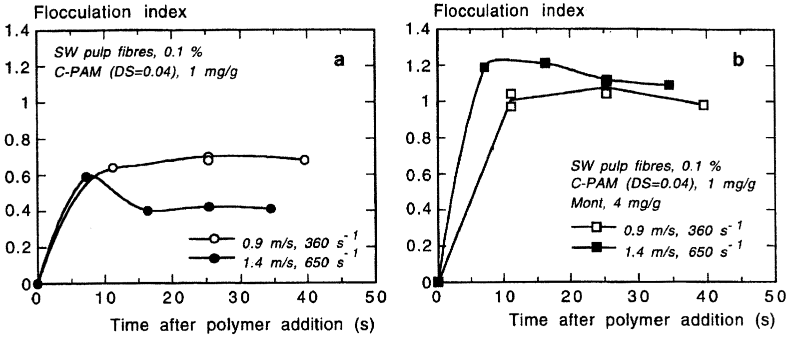

Fig. 17 Flocculation index as a function of time after the addition of C-PAM in (a) C-PAM and (b) C-PAM/Mont systems. Softwood pulp fibre suspensions. The flow velocities, 0.9 and 1.4 m/s, correspond to shear rates of 360 and 650 s^{-1} respectively. The added amount of C-PAM was 1 mg/g and of Mont 4 mg/g. Mont was added 2.2 or 1.4 s before measurement, depending upon the flow velocity. From (16).

For the single-component, C-PAM, system, an increase in the shear level in the flowing suspension gives irreversible floc breakage and the flocculation index decreases. With the microparticle system, C-PAM/montmorillonite, an increase in the shear level gives, on the contrary, an increased flocculation. It is suggested that the floc breakage at the higher shear level creates a larger number of sites available for interaction with the microparticles. The proposed increased availability of cationic polymer molecules is supported by model experiments on aggregates of latex spheres flocculated by bridging polymer in an investigation by Sikora and Stratton (80). When the flocs were disrupted by shear, the number of available adsorbed polymer molecules increased as probed by the adsorption of a cationic surfactant.

The adsorbed polymers may during the initial flocculation become locked in an extended conformation. When the flocs are broken up, the polymers are available for interaction with the microparticles. One can even speculate that polymers which are not adsorbed may be entrapped in liquid pockets inside flocs. These polymers could adsorb and contribute to flocculation after floc breakage.

In experiments on reflocculation using a two-component flocculant system containing PEI and A-PAM (45, 66), the reflocculation increased after every high-shear deflocculation. This suggests that polymers, both PEI and A-PAM, not adsorbed during initial flocculation can be adsorbed once the initial flocs are broken up, creating strong reflocculation. This mechanism could also occur in the case of microparticle flocculants.

Hedborg and Lindström (82) defined a reversibility index based on results from retention experiments at two different stirring speeds, first at 1000 rpm (Ret_{1000}), and after 60 s at 500 rpm ($\mathrm{Ret}_{1000/500}$). A second experiment was carried out at 500 rpm (Ret_{500}) as a reference. An index of reversibility was defined as

$$\text{Reversibility index} = (\mathrm{Ret}_{1000/500} - \mathrm{Ret}_{1000}) / (\mathrm{Ret}_{500} - \mathrm{Ret}_{1000})$$

Table 1 shows the reversibility index (as defined above) and drainage measured as the drained volume using a Schopper-Riegler equipment (82).

Flocculant system	Added amount of anionic component (%)	Reversibility index	Drainage (ml)
Cat. Starch/A-PAM	0	0.47	619
	0.02	0.29	630
	0.05	0.23	661
	0.08	0.7	668
Cat. Starch/Coll. silica	0	0.47	619
	0.15	0.74	713
	0.3	1.36	761
	0.45	0.87	761

Table 1 Results from experiments on the reversibility in flocculation and drainage capacity for different two-component flocculant systems, cationic starch/anionic polyacrylamide and cationic starch/anionic colloidal silica. The added amount of cationic starch was 2 % in all cases. Fine paper stock containing 60/40 hardwood/softwood pulp and 17 % $CaCO_3$ filler. Data from (82).

The microparticle system exhibited a much higher reversibility index and increased drainage. However, the comparison (82) was made between microparticle systems and a two-component system consisting of cationic starch and anionic polyacrylamide. A better reference might have been a system containing a low MW cationic coagulant and a high MW A-PAM.

To account for the increase in drainage experienced when microparticle systems are used, it is claimed that the stock reflocculates to smaller and denser flocs when the anionic microparticle is added. Experimental results reported by Wall et al. (53) support this explanation. However, these results are limited to model systems containing only the two flocculants, cationic potato starch and colloidal silica. Some evidence of smaller flocs has also been obtained using flow visualization techniques (47). Reflocculation after high-shear deflocculation was investigated in fibre suspensions by installing a static in-line mixer in the pipe in experiments with a flowing suspension (65). The floc diameter was monitored as a function of added amount of montmorillonite with and without the mixer installed for the same C-PAM/montmorillonite system and at the same flow velocity. Flocs formed after deflocculation were smaller. With high amounts of montmorillonite, where the two cases differed significantly in floc size, the flocculation indices were almost the same. This suggests that flocs were more compact after reflocculation.

It was claimed by Lindström (44) that paper produced using microparticle flocculants would show a higher porosity than when a conventional two-component flocculant was used. However, there are very few results published to support this suggestion. Smith (42) concluded from a laboratory study that an increase in retention due to flocculation gave an increased porosity regardless of whether or not a microparticle flocculant was used. No comparisons from paper machine trials seem to be available.

New microparticle systems

There are several newer developments in the use of microparticle flocculants. These include new types of microparticles, e.g. organic polyacrylate gel particles which are used in combination with cationic polyacrylamides (83), on-site production of microparticles such as silica sols (84, 85), modified silica sols (86, 87) or aluminium hydroxide sols (88). Other developments include modifications of existing systems, e.g. micro-aggregated silica sols in combination with cationic polyacrylamide (89, 90) or polymeric aluminium species (46, 91, 92).

However, the scientific literature contains little information about these systems. The system consisting of a micro-aggregated silica sol and cationic polyacrylamide has been investigated in some detail (90). Fig. 18 shows the retention effect for a series of silica sols with the same charge density but with different degrees of micro-aggregation.

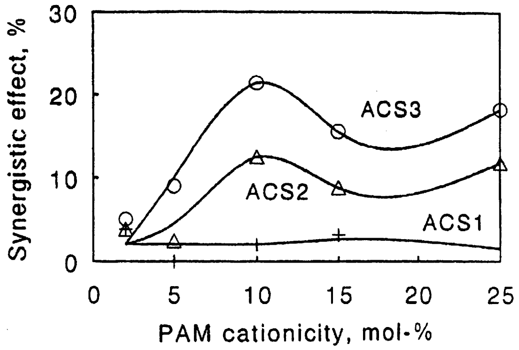

Fig. 18 Increase in fines retention on addition of anionic colloidal silica compared to the case with cationic flocculant alone (synergistic effect) as a function of cationicity (mole-%) of cationic polyacrylamide in Britt Jar retention experiments. A synergistic effect of zero means that no additional retention effect was obtained by adding the colloidal silica. The series ACS1-3 denotes an increasing degree of micro-aggregation of the colloidal silica. From (90).

The best retention effect together with a cationic polyacrylamide was obtained with a highly micro-aggregated silica sol. Transmission electron micrographs confirmed that the micro-aggregated colloidal silica with the best retention effect consisted of elongated particles, a pearl-necklace structure. Andersson and Lindgren (90) suggest that the C-PAM/colloidal silica system needs some extension of the colloidal silica in order to create bridges between adsorbed cationic polymers and thus induce flocculation. The size of the primary particles in the micro-aggregated sol should be kept low since the high specific surface area and the high charge density of the silica sol will otherwise be partly lost.

Experience from pilot paper machine studies by Albinsson (93) using a micro-aggregated colloidal silica confirm the laboratory investigations, as is evident in Table 2.

Retention aid system	Added cationic polymer (kg/ton)	Added micro-particle (kg/ton)	Filler retention (%)
C-PAM (DS=30 mole-%)	0.3	–	12
	0.8	–	48
	1.3	–	80
Cationic starch/coll. Si	3	2	13
	7	2	31
	13	2	35
C-PAM/micro-aggregated colloidal silica	0.3	0.3	19
	0.8	0.3	68
	1.3	0.3	92

Table 2 Filler retention for different amounts of retention aids. From (93).

In the C-PAM/micro-aggregated colloidal silica system the retention is considerably higher than for the cationic starch/colloidal silica system. Most of the retention increase, however, stems from the C-PAM alone.

The polyethylene oxide-phenol formaldehyde resin retention system

The polyethylene oxide (PEO)-phenol formaldehyde resin (PFR) flocculating system goes back to patents (94, 95) in the water purification field. In the late seventies and early eighties, PEO started to be used as a retention aid in newsprint furnishes. The reason for trying PEO as a flocculant in these systems was that they contain such high levels of anionic disturbing substances that it is often not cost efficient to use cationic polyelectrolytes as flocculants. It was soon found that the efficiency of PEO varied quite substantially among mills (96). The hypothesis was soon formulated that an interaction with a co-factor was necessary for PEO to work properly and that the level of this co-factor varied among mills. If a phenolic resin or a kraft lignin was added to the furnish, much less variation in the performance was found. Phenolic resin and kraft lignin both contain acidic phenolic OH-groups that can interact with the ether oxygen in PEO via hydrogen bonds. Substances similar to kraft lignin and phenolic resin can be expected to be present in the white waters of paper machines running mechanical grades, which explained why the PEO system worked in certain mills.

The mechanism of PEO-phenolic resin systems was not immediately clear. In a mechanical furnish, for instance, PEO does not adsorb onto fibres. The first attempt to explain the mechanism was made by Lindström and co-workers (97, 98). They took as their starting point the interaction between the phenolic resin and the PEO-molecules. The hypothesis formulated by Lindström was that PEO and phenolic resin form a network which is swept through the solution by the cellulosic fibres. During this sweeping action, small particles such as fillers and fines are trapped in the network. The network eventually collapses onto fibres and in this way the small particles are retained in the sheet. This mechanism can explain many observations made. Firstly it explains why adsorption of PEO onto the fibres is not necessary. It also explained why the concentration of small particles to be flocculated and retained did not influence the flocculation efficiency significantly. In model experiments, Lindström et al. (97) flocculated latex particles with PEO/phenolic resin and found the relative reduction in turbidity to be the same for a wide range of latex concentrations. There was also a very clear dependence of the flocculation efficiency on the size of the latex particles, the larger particles being much more efficiently flocculated. Experiments were also carried out in which latices of different sizes were fractionated by flocculation. These observations could be easily explained by the network hypothesis. The mesh size of the network was simply such as to retain large particles while small would pass through the mesh. This fractionation effect would be more difficult to explain if flocculation took place by some kind of bridging mechanism. A further observation made in the model experiments was that the flocculation of latex was lost if the fibres were added more than 30 s after the addition of the PEO phenolic resin. This was ascribed to the network having a transient nature and collapsing after some time. The concentration of polymer used in these experiments is low and a network with the proper mesh size does not fill all the space. In the network model, one must therefore assume that fragments of network are formed in the suspension. These network fragments are then taken up by the fibres and flocculate the small particles. If the suspension is not stirred, the network fragments would flocculate among themselves and eventually collapse without giving much flocculation.

During recent years there has been a renewed interest in flocculation by the PEO systems, especially in Canada and Australia. This is most probably because of the large production of newsprint in these countries for which, as already mentioned, PEO is used as a retention aid.

In Canada, groups led by van de Ven in Montreal and Pelton in Hamilton, have been active in PEO flocculation research. Van de Ven and Alince (99) state that there are problems with the network hypothesis. Their most serious objection to the mechanism is perhaps that they find that PEO functions together with co-factors, e.g. kraft lignin, that do not form a network with PEO. The authors also found conditions for the PEO/kraft lignin system when a clay was efficiently flocculated, while larger $CaCO_3$ particles were not flocculated. An argument put forward against the network flocculation model both by van de Ven and Alince (99) and by Pelton et al. (100) is that the network can far from fill the entire volume. This is, however, not necessary since it is only necessary that fragments of network are formed and that these fragments are transported through the solution by the fibres. That a network at least in many cases is formed in the PEO/co-factor system is quite clear. A pronounced increase in viscosity is e.g. observed when phenolic resin is added to a suspension containing PEO (100).

The mechanism suggested by van de Ven and Alince is that the flocculation by PEO/co-factor is a bridging type flocculation (99). When a polymer adsorbs onto a surface, the polymer lowers its entropy since the number of possible conformations is reduced. Furthermore the polymer loses its translational entropy. This reduction in entropy must be compensated for by a gain in energy. The loss of conformational entropy is, however, dependent upon the stiffness of the polymer molecule. A stiff molecule loses less entropy than a flexible molecule. The hypothesis for the bridging mechanism is that the co-factor, e.g. kraft lignin, associates itself with PEO and makes the PEO polymer more stiff. In the case of kraft lignin, the stiffness could be due to electrostatic repulsions between the associated kraft lignin molecules. When the stiffness exceeds a certain value, the adsorption energy is enough for adsorption. This is illustrated in Fig. 19.

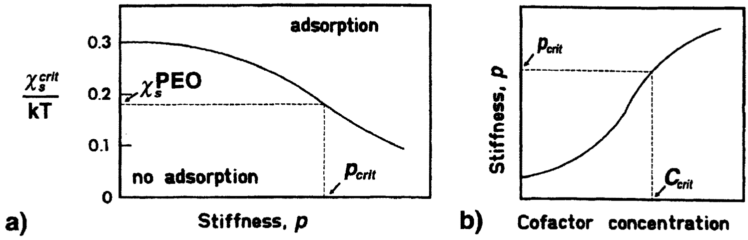

Fig. 19 Adsorption phase diagram. (a) When the adsorption energy of a polymer segment χ_s of a chain of stiffness p is less than the critical value χ_s^{crit} no adsorption occurs. Stiffening of a PEO chain above the critical value p_{crit} results in adsorption. The stiffness can be increased by association with a co-factor. (b) The stiffness is larger than p_{crit} when the concentration of the co-factor is larger than a critical concentration c_{crit}. From (99).

A further advantage of the stiffening of the polymer molecule could be that the molecule takes on a more extended conformation at the surface. The reconformation at the surface is perhaps also of less importance. Experiments on the deposition of precipitated calcium carbonate particles (PCC) on bleached hardwood pulp fibres were used to verify the bridging hypothesis (99). Kraft lignin was added to PCC. Since the PCC was positively charged, the kraft lignin adsorbed onto the PCC. PEO did not adsorb onto PCC with adsorbed kraft lignin. When, however, PEO was added to a pulp/PCC suspension with excess kraft lignin, a typical bridging type behaviour was observed, with a maximum in flocculation efficiency with increasing PEO addition. This was taken as evidence that stiffened PEO molecules could adsorb and induce flocculation.

The authors also studied the deposition of clay on fibres (99, 101). In this case, an interesting observation was made. PEO adsorbs onto clay but not onto fibres. Nevertheless a deposition of clay particles onto fibres was observed. This deposition decreased however with time. These observations were interpreted in the following way. When PEO adsorbs onto clay, it loses so much conformational entropy that the interaction energy with the pulp fibres is enough to give adsorption and bridging. That the bridges formed are not permanent is due to a reconformation of the polymer on the clay surface. When the polymer layer on the clay becomes too thin, the clay detaches from the fibres due to electrostatic repulsion between the negatively charged clay and fibre surfaces. The importance of reconformation was shown by treating the clay with PEO and waiting for various periods of time before the addition of fibres. When long waiting times were used, there was no deposition on the fibres. This flocculation mechanism was called "asymmetric polymer bridging" by the authors. The deposition experiments with clay were also performed in the presence of kraft lignin. In this case, the deposition was permanent. This was interpreted as a stiffening and as a reduced tendency to reconformation due to the interaction of adsorbed PEO molecules with kraft lignin. These points are illustrated in Fig. 20.

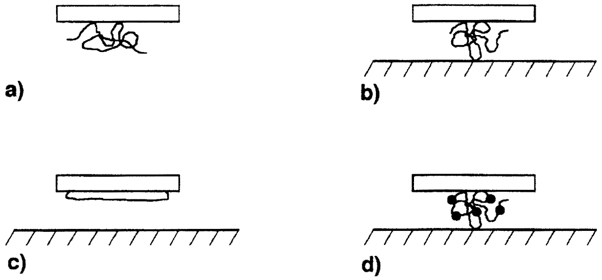

Fig. 20 Schematics of filler-induced transient polymer bridging and association-induced permanent polymer bridging. (a) PEO adsorbs on clay. (b) PEO-coated clay deposits on fibres. (c) Flattening of PEO chains causes a smaller gap resulting in increased electrostatic repulsion and detachment. (d) Flattening is absent for the PEO/co-factor polymer bridge. Configuration (d) can also be reached by association-induced PEO adsorption on fibres, followed by clay deposition. From (99).

The flocculation in a PEO/phenolic resin (PFR) system has also been extensively studied by Pelton and co-workers (100). Most of the experiments verified the original observations made by Lindström (97, 98). One difference was that Lindström found that, if fibres were added more than 30 s after PEO to a latex suspension, there was no flocculation, due to the collapse of the network. Pelton et al. (100) found that much longer waiting times are possible. Fig. 21 illustrates the possible events that can occur in the PEO/PFR system.

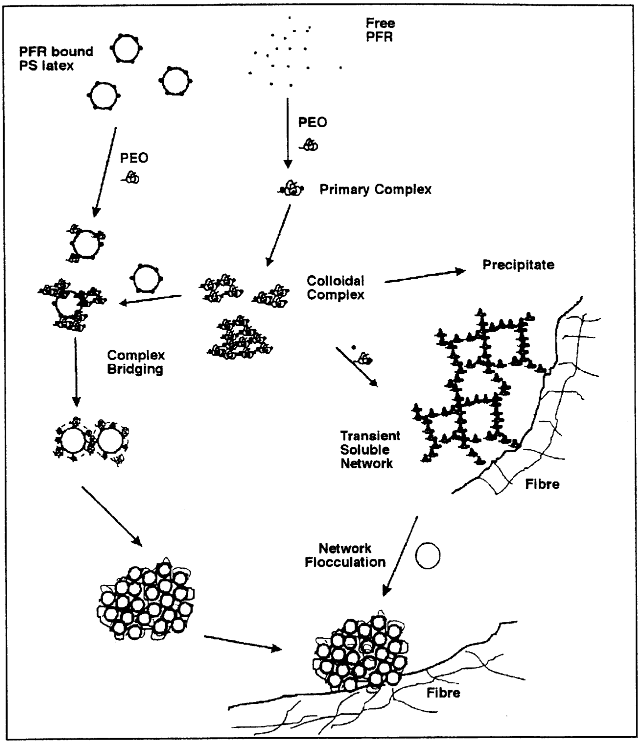

Fig. 21 A schematic illustration of the formation of primary and complex aggregates and flocculation processes in PEO/co-factor flocculant systems. From (100).

Based mostly on kinetic arguments, they suggested that PEO and PFR rapidly formed primary complexes that then formed larger colloidal PEO/PFR complexes. These complexes then adsorbed onto the latex particles causing aggregation of latex particles partly by interaction between the adsorbed complexes. Finally the latex flocs deposit on the fibres. This mechanism has similarities with the mechanism proposed by van de Ven and Alince (99), e.g. it is only after interaction between PEO and FPR that there is a significant adsorption and flocculation. The authors call their mechanism complex bridging. Pelton et al. argues against the network mechanism mostly on kinetic grounds. The argument is that the formation of the large network should be slow. However, in the viscosity experiments the network effect seems to appear quite rapidly.

A very interesting development by the group in Hamilton is to use polyacrylamide molecules on which short pendant PEO chains are attached (102). PEO is sensitive to degradation, especially in the presence of certain metal ions, but the polyacrylamide backbone is much less sensitive. The polyacrylamide with pendant PEO groups worked as well as PEO together with PFR as flocculant provided that this comb polymer contained at least 2 mole % PEO groups and that the PEO pendant chains contained at least 10 monomer units.

A mechanism for flocculation in the PEO/co-factor system that has not so far been discussed is the suggestion that the co-factor adsorbs onto the fibre and provides anchoring points for the PEO molecules. Stack et al. (103) showed that phenolic resin did indeed adsorb onto microcristalline cellulose above a certain ionic strength. The adsorption of PFR also coincided with the precipitation of the phenolic resin. The view of these authors was, however, that the flocculation was a network mechanism without much involvement of the adsorbed PFR. Another interesting observation made by Stack et al. was that the presence of certain surfactants used in deinking plants can significantly reduce the efficiency of the PEO/PFR system (104). It was shown that e.g. alkoxylated fatty acids interacted quite strongly with PFR and that this prevented PFR from interacting with PEO and inducing flocculation. The authors suggested that the PFR was solubilized in surfactant micelles. However, ethylene oxide groups in the surfactant could just compete with PEO for interaction with the PFR.

To summarize, it can be concluded that the mechanism for the PEO/co-factor system is not quite established. There are a few difficulties with the network theory. The alternative explanations e.g. the polymer stiffening theory can not, however, be regarded as fully verified. Can the stiffening in fact lead to such a strong adsorption that efficient flocculation is achieved? PEO/PFR is known to be quite a strong flocculant. Since PEO is mostly used on machines using mechanical pulp grades one should like to see well defined experiments for these furnish components rather than model experiments with bleached fibres and latex. There is of course also the possibility that the different co-factors give flocculation by different mechanisms.

DISTURBING SUBSTANCES

It is a well known fact that the efficiency of cationic polymers as flocculants is low in systems containing high amounts of dissolved anionic polymers. The anionic polymers can be dissolved wood polymers such as hemicelluloses, and also carboxymethylcelluloses from recycled coated broke. The reduced efficiency is attributed to the formation of polyelectrolyte complexes between cationic retention aids and the anionic polymers. That these types of complexes do form has been verified in many studies (105-107). In this section, some kinetic aspects of polyelectrolyte complex formation are briefly discussed using the equations already presented. The kinetics of polyelectrolyte complex formation are compared to the kinetics of flocculation. Strategies for reducing the effects of disturbing substances will not, however, be discussed.

Consider the standard furnish to which 1 g/m^3 of a high molecular weight polymer has been added. The concentration of a disturbing anionic polymer can be rather high e.g. 50-500 g/m^3. Let us assume that this polymer has a molecular weight of 10^5 and a radius of 0.02 μm. The reaction rate between the polymers will be governed by the collision frequency between the cationic polymer and the anionic wood polymer. It is assumed that there is no barrier to this reaction. For polymer molecules, collisions are due to diffusion and Eq. [3] should therefore be used. If the anionic wood polymers have approximately the same charge density as the added high MW molecules, 1 % of the anionic wood polymers must react with the cationic polymer in order to neutralize the charge of this molecule. The time for this reaction to take place can be calculated from Eq. [3] by regarding the reaction as a deposition of the low molecular weight polymer on the high molecular weight cationic polymer. If this is done for the deposition of 1 % anionic polymer, a time of 5 ms is obtained. If instead 10 % of the anionic wood polymers present need to react to neutralize the cationic retention aid, the neutralization time is 50 ms. These times are, of course, only estimates and depend on exact concentrations and radii of the polymers.

The reaction times of 5-50 ms should be compared to the flocculation times, the half times for deposition of fillers and polymers on fibres. These times were in the simplified case the same and given by $48/G$. If G is 1000 s^{-1}, half times of approximately 5 ms are obtained. In the case of filler deposition on fibres, the half time can be substantially, longer due to a low value of the collision efficiency factor α.

From these estimates, it is clear, as observed in practice, that reactions between cationic retention aids and anionic polymers can seriously interfere with the flocculation of filler to fibres since both processes take place on approximately the same time-scale. After a cationic polymer has adsorbed onto a fibre surface, it can continue to react with (adsorb) anionic wood polymers and become deactivated as a flocculant. This deactivation also takes place after fibre/fibre or fibre/filler deflocculation. This will reduce the reflocculation tendency. Since the deactivation of the cationic polymer takes place on the same time-scale as flocculation, there can in favourable cases be a significant flocculation effect e.g. if the polymer is added close to the headbox or at a position with high consistency.

There have been rather few experiments on the kinetics of polyelectrolyte formation. Ahrabi et al. (108) studied the reaction between retention aids and anionic wood polymers by a stopped flow technique and found that the complexes did indeed form on a millisecond time-scale. Their results were consistent with a diffusion controlled reaction. Similar results were also obtained by Okubo et al. (109).

FIBRE FLOCCULATION AND NETWORK STRENGTH

The understanding of both fibre flocculation and fibre network strength is of key importance in papermaking. Whenever retention aids are used, both the fibre flocculation and the fibre network strength are affected.

In the network, the fibres are not fully dispersed. Even in a random network there are regions that have a higher fibre concentration than the average fibre concentration. These regions in the network are regarded as flocs. If a chemical flocculant is added, the fraction of fibres in flocs increases. The effect of flocculants on the network strength is discussed below.

The primary fibre flocculation mechanisms have been summarized by Kerekes (110) as being due to colloidal attraction between fibre surfaces due mainly to the addition of coagulants or flocculants; mechanical surface linkage causing fibres to hook; elastic fibre bending and surface tension if air is present in the fibre suspension. The different mechanisms contribute to an overall fibre flocculation effect depending on e.g. the fibre concentration and the hydrodynamic situation. Colloidal attraction due to chemical flocculants can be the dominating fibre flocculation mechanism at low fibre concentrations, below the threshold concentration for network formation, whereas they play a successively smaller part with increasing fibre concentration.

Flocculation in papermaking suspensions by the addition of retention aids has been studied in various flow loop equipments. Wågberg (111) used a laser-optical technique to measure the variations in local fibre concentration and investigated a number of different retention aid systems (63, 112, 113). Björklund and Wågberg (114) investigated the influence of electrolyte concentration on the fibre flocculation by cationic starches. Beghello et al. (115) presented a new design with combined laser-optical detection and high-speed video photography to evaluate the flocculation. This equipment also enables flocs in the flow direction and in the cross-flow direction to be analysed. However, no results on the effect of chemical flocculants are reported. The use of NMR imaging techniques to image flowing fibre suspensions (116-118) have also involved the effect of chemical additives. Li and Ödberg (119) used NMR imaging combined with pressure drop measurements to estimate the shear stress at the surface of fibre plugs in a flocculated fibre suspension.

Chatterjee (120) investigated the polymer-induced fibre flocculation where the fibre concentration (0.1-0.2 %), the flow velocity in turbulent pipe flow (1-2 m/s) and the C-PAM polymer dosage (0-0.8 mg/g) were changed. An attempt was made to rationalize the results in terms of the fibre crowding factor introduced by Kerekes and Schell (121). The expression

$$FI = A_f(1 - e^{-\kappa N}) \qquad [8]$$

was used to describe the results. FI is the flocculation index, A_f and κ fitting parameters to experimental data and N is the normalised cumulative number of collisions based on the number of collisions between fibres and polymer and the crowding factor. Every collision between fibres was assumed to induce fibre flocculation. Fig. 22 shows the experimental flocculation index as a function of the normalised cumulative number of collisions.

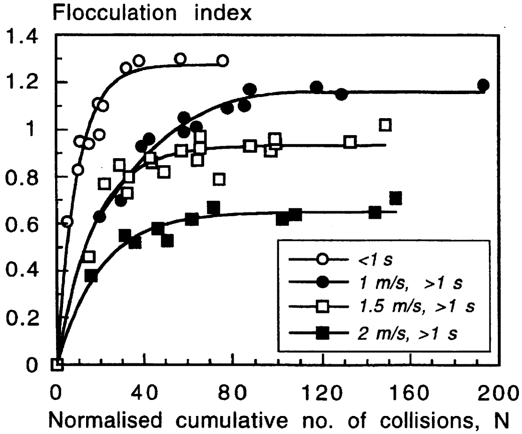

Fig. 22 Flocculation index as a function of the normalised cumulative number of collisions. Data replotted from (120).

The normalised data fall on the common line for different fibre concentrations and different polymer dosages. However, the different curves for different flow velocities indicate that the fraction of successful collisions is a function of the flow velocity and this factor was not incorporated in the model.

Breaking length of fibre plugs

In early work on fibre network strength by Forgacs et al. (122), measurements were made on plugs of suspended fibres. A fibre plug was extruded from an inner pipe into a surrounding pipe containing water. The length at which the plug fractures is a measure of the network strength. One problem with breaking length measurements of this type is that the type of shear applied is not well defined.

The influence of chemical flocculants on the fibre network strength has been the subject of only a few studies. The possible influence of chemical flocculants was pointed out by Wahren (123). Breaking length measurements of fibre plugs (124-126) showed an increase in the fibre network strength when alum and other electrolytes were added as well as when a medium molecular weight cationic polyelectrolyte was added.

Rheological measurements

Rheological techniques have been adapted to the study of pulp fibre suspensions, viz. steady shear (127, 128), oscillatory shear, steady shear and relaxation measurements (123). Rheometers with specially designed cell geometries must be used, e.g. Couette cells with wide gaps (123) or plate-reservoir cells with a large gap (129, 130).

In absence of chemical flocculants, the mechanical model of Meyer and Wahren (131) predicts that three contacts per fibre are needed to obtain an elastic fibre interlocking, which was suggested to be the dominant fibre flocculation mechanism. The number of contact points corresponds to a threshold fibre concentration for three-dimensional fibre networks. Experimental results (132) verified the existence of this threshold. Soszynski and Kerekes (133) confirmed that elastic fibre interlocking is the governing mechanism. Soszynski (134) also showed that the number of contact points is three to four per fibre in experiments on flocs of nylon fibres.

The effect on the fibre network strength of the addition of a high molecular weight cationic polyelectrolyte was only recently documented (45, 48, 135). A measurable shear strength in the fibre suspension was found at a lower fibre concentration when a chemical flocculant was added. Fig. 23 shows the threshold fibre concentration, c^*, at which there is a measureable shear strength as a function of added amount of cationic polyacrylamides of different degrees of substitution.

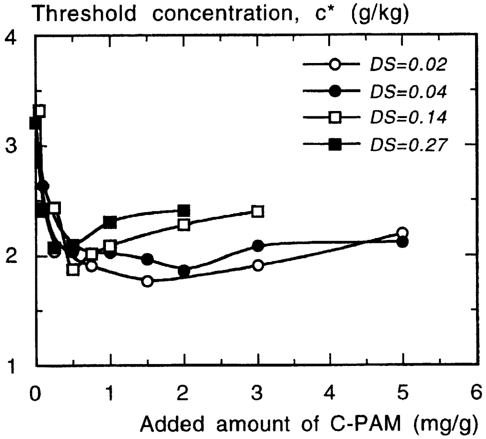

Fig. 23 The threshold concentration (c^*) for measurable shear strength as a function of added amount of C-PAM of different degrees of substitution (DS) for softwood pulp fibre suspensions. From (45, 136).

The effect of chemical flocculants on the fibre network strength was attributed to a combination of an increase in the number of active fibres constituting the network, i.e. an increase in the average number of contact points per fibre, and an increase in the bonding strength in the fibre-fibre contact points. When a chemical flocculant was added, there was a measurable shear strength at a lower fibre concentration than in the absence of the flocculant. In each experiment, the threshold concentration showed a minimum at approximately the point of maximum elastic shear modulus, G', measured at higher fibre concentrations. A scaling relation for the network strength in relation to the fibre concentration minus the sediment fibre concentration, $c\text{-}c_{sed}$, was suggested by Wahren (123) to account for different fibre lengths. It was suggested by Ritala and Huiku (137) that the critical concentration for network formation should be used instead of c_{sed}. When chemical flocculants are added, the critical fibre concentration is altered and the following scaling law can be suggested (45, 136)

$$G'=a(c-c^*)^b \quad [9]$$

where *a* and *b* are constants.

Under normal papermaking conditions, the fibre flocculation induced by chemical flocculants combines with the fibre flocculation from elastic fibre bending, as illustrated in Fig. 24. According to the mechanism for elastic fibre bending, there is a mechanical interlocking of fibres into fibre flocs.

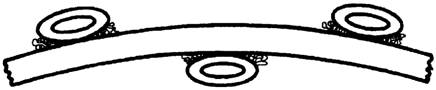

Fig. 24 A diagram illustrating the contribution of chemical flocculants adsorbed onto fibre surfaces in the region of the contact point to the fibre flocculation due to elastic fibre bending.

The polymer adsorbed at contact points between fibres gives a significant contribution to the strength of fibre flocs and one result is an increased fibre-to-fibre friction. Recent investigations on fibre flocculation (138, 139) give estimates of the strength of fibre flocs in relation to basic parameters such as the frictional coefficient in fibre contact points (134, 140). This approach could be useful for a better understanding of how chemical flocculants contribute to the strength of fibre flocs by increasing the binding strength in the contact points.

Contribution of fibre flocs to the fibre network strength

In a flocculated fibre suspension with a concentration above the threshold for network formation, flocs are an inherent part of the network and contribute to the network strength. It is quite logical that the network shows a yielding behaviour determined by the weakest parts in the network, i.e. the regions between the flocs. This is also supported by experiments (130, 141). In order to understand more completely the rheology of fibre suspensions, investigations of both floc strength and network strength are needed, with and without chemical additives. It was concluded from measurements of the tensile strength of individual fibre flocs in the wet state (142) that floc fracture shows multiple yield points. The flocs have concentrated regions separated by weaker interfaces where the number of contact points per fibre is low.

A model experiment was carried out to highlight the importance of dispersion of flocs for the network strength. A suspension was prepared from dried Jacquelin flocs (143) and the rheology was measured for this sample using a plate-reservoir cell. After measurement of the elastic shear modulus in oscillatory shear, the sample was transferred to a beaker and magnetic stirring was used to disperse the fibres. The elastic shear modulus was measured again after stirring for 1 h and overnight. The weight concentration of fibres was the same in all measurements. Fig. 25 shows the results.

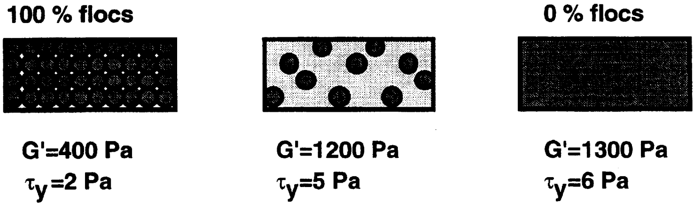

Fig. 25 Model experiment using "synthetic" fibre flocs (Jacquelin flocs). A 5 % by weight suspension of fibre flocs was formed from bleached beechwood pulp. The average diameter of the flocs was 1.2 mm. Strain sweep measurements was made to monitor the elastic shear modulus, G', (left, 100 % flocs). The yield strength, τ_y, was estimated from $\tau_y = G'\gamma_c$, where γ_c is the critical strain. The sample was taken out from the cell and magnetic stirring was used to disperse fibre flocs. The suspension was measured after 1 h stirring (middle, less than 50 % of fibres in flocs) and stirring overnight (right, 100 % free fibres). (Swerin, unpublished results 1995).

The results indicate the importance of the distribution of the number of contact points per fibre in the network. The sample with 100 % flocs has a large number of contact points in the flocs but the structure yields at a low strain.

RETENTION AND FORMATION

The papermaker needs controlled experiments on retention, formation and drainage. The purpose is often to optimise the process by using a new type of process chemical. In these cases the controlled experiments should preferably be run on the actual paper machine in the mill.

Research is also needed with controlled experiments on the interrelations between retention, formation and drainage. It is especially important to be able to link laboratory investigations to mill-scale experience. Allen and Yaraskavitch (144) point out the lack of published investigations on a mill-scale of the effect of retention and drainage aids. When studies have been made, experimental conditions are often so different that comparisons are difficult to make.

Effect of fibre flocculation on formation

It is well known that it is more difficult to produce a paper with good sheet formation from a stock which exhibits a strong fibre flocculation. The degree of fibre flocculation in a flowing suspension was measured in a laboratory flow loop (111) for a range of different kraft pulps at a concentration below that at which the fibres can form a continuous network. The pulps were also used in pilot experiments on the FEX fourdrinier unit (145, 146) and the formation of the paper was evaluated (147).

Fig. 26 shows the formation number as a function of the flocculation number. The formation shows a close relation to the degree of flocculation. The longer softwood (SW) fibres give more flocculation than the shorter hardwood (HW) fibres.

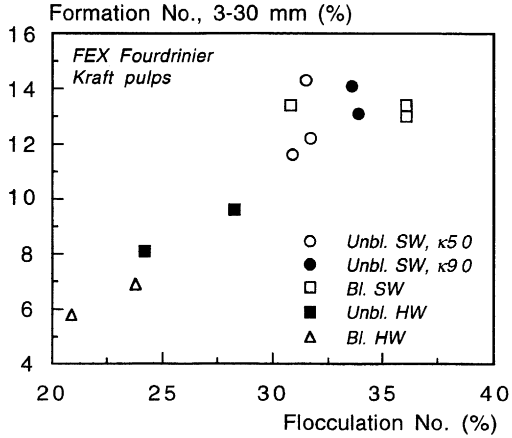

Fig. 26 The formation number, 3-30 mm (%) (FEX Fourdrinier, headbox consistency 0.5 %) as a function of the flocculation number (coefficient of variation of local concentration) measured at 0.15 % consistency for a range of different kraft pulps. A higher flocculation number means greater flocculation; a higher formation number means worse formation. From (148).

A correlation has also been found by e.g. Jokinen and co-workers (149, 150) between laboratory-scale flocculation measurements and formation in pilot paper machine experiments.

Longer fibres give a higher shear strength than shorter fibres. To demonstrate the influence of fibre network strength, the following experiments were carried out (148). The network strength (elastic shear modulus) in fibre suspensions was measured at the headbox consistency and the formation number was measured on the paper produced in a roll former on the FEX experimental paper machine. A number of pulps with different fibre lengths and different degrees of beating were used. Fig. 27 shows that the fibre network strength is one important parameter that influences the formation of the paper. The results agree with the opinion of Wahren (151) that the fibre network strength has a large effect on the forming.

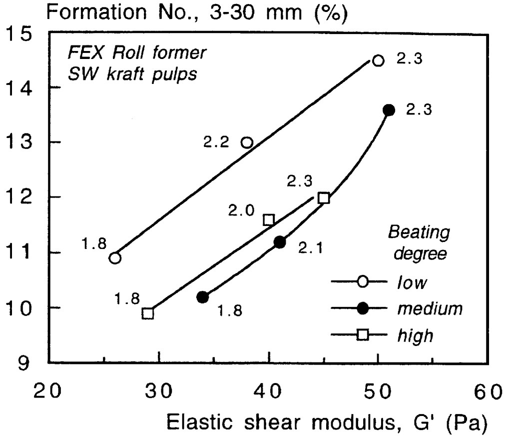

Fig. 27 The formation number, 3-30 mm (%) as a function of the elastic shear modulus for softwood pulp fibre suspensions of different fibre lengths (mm) and different degrees of beating. Paper produced on the FEX roll former. The numbers at each measuring point give the fibre length in mm (length-weighted average). The values of the shear modulus were interpolated to the headbox concentration of fibres used in the FEX experiments. From (148).

There are, of course, other factors such as dewatering conditions on the paper machine that affect the formation. The influence of the drainage conditions on the formation is however very difficult to simulate in laboratory experiments.

Nilsson (152) showed in pilot paper machine experiments that, if the network strength is high, i.e. with softwood fibres rather than hardwood fibres, a higher jet-to-wire speed difference in twin-wire forming is needed for good formation. It was also pointed out (152) that, because retention aids affect the fibre network strength, they should also affect the jet-to-wire speed difference necessary to achieve good formation.

Fig. 28 shows results from experiments with a stock consisting of 100 % softwood kraft pulp in the FEX roll-blade former (148, 153).

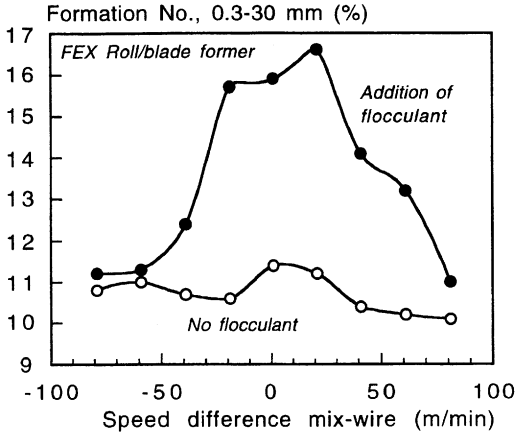

Fig. 28 Formation number, 0.3-30 mm (%) as a function of mix-to-wire speed difference during roll-blade forming of a softwood kraft pulp on the FEX paper machine. The machine speed was 900 m/min. The retention aid system was 500 g/ton of C-PAM and 2 kg/ton of bentonite clay. From (148).

When a retention aid is added to the stock, fibre flocculation and the fibre network strength increase and the region of inferior formation around zero mix-to-wire speed difference is wider. These results show a close analogy with results from network strength measurements (45, 48). A higher strain has to be applied to produce floc breakage if chemical flocculants have been added to the fibre suspension.

Retention versus formation

A multitude of studies have been reported on the effects of retention and drainage aids in laboratory investigations. The classical Britt jar (21, Tappi standard method T261 cm-90) or modifications of this equipment to better simulate actual flow conditions or to enable evaluation of dewatering, e.g. (154-156), has been used.

In laboratory investigations (157, 158), correlations between flocculation and fine material retention were found. A close relation between the flocculation and the formation of laboratory sheets with cationic polymer added has also been shown (159). Correlations between laboratory-scale measurements and mill-scale measurements of the filler retention have been reported (160).

Retention aids increase the adhesion of filler particles to the fibre surfaces. Pelton (161) and Hubbe (162) made laboratory experiments in which the adhesion strength in the presence of retention aids was investigated. Filler particles deposited on the walls of a glass tube (161) or a rotating disc (162) were subjected to well-defined shear forces. It was found that retention aids could indeed give sufficient adhesion to withstand most of the shear levels on a paper machine.

Kamiti and van de Ven (163) investigated the motion of single particles flocculated to a solid surface by bridging polymer subjected to a controlled shear and undergoing Brownian motion. From these experiments, a polymer bridge spring constant could be determined. This spring constant could be compared to a theoretical calculation based on the loss of entropy when a polymer chain is stretched. It was concluded that the polymer molecule made multiple attachments between filler particle and surface, as illustrated in Fig. 29.

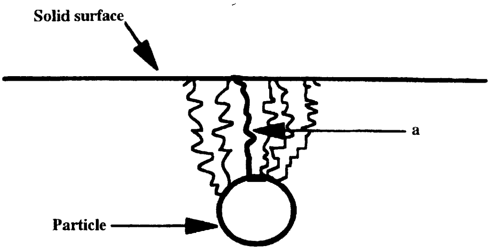

Fig. 29 Attachment model for polymer bonds in the flocculation of a particle to a solid surface. Segment "a" determines the maximum extension of the polymeric linkage. From (163).

Application of high shear to the particle causes the shorter polymer linkages to detach and the longer linkages to stretch. At higher shear levels, the particle would become detached and could carry polymer that had transferred from the surface to the particle (164).

Stratton and Miller (165) extended the polymer bridging concept to include a polymer tail expansion effect. Fig. 30 shows results of laboratory retention experiments.

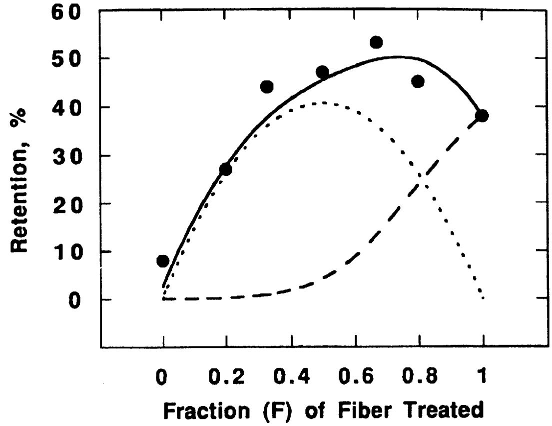

Fig. 30 The filler retention as a function of the fraction of fibre treated, showing the contribution of different effects on the overall retention effect. Dotted curve, interparticle bridging; dashed curve, polymer tail expansion. The experimental data are from Britt Jar retention experiments with latex particles as a model for filler particles. From (165).

By introducing the polymer tail expansion effect, a better prediction of the retention based on the added amount of polymer was possible. The description of polymer tail expansion was based on investigations of PEO adsorption. Charged polymers show a different behaviour in the expansion of the adsorbed layer as a function of the adsorbed amount (166). This behaviour was included in an expression for the flocculation efficiency (68) but no experimental data were available to support the influence of an increase in adsorbed layer thickness on the flocculation efficiency.

It is generally recognized among papermakers that a high retention level is often accompanied by an impaired formation. However, this is not necessarily true. Fig. 31 shows filler retention as a function of the formation number from a number of FEX experimental paper machine trials for the same type of former and papermaking stock but for different retention aid systems (32, 93). The diagram shows a large scatter indicating that there is no general relationship between retention and formation. It is for instance possible to have a very good formation (10 %) and almost no filler retention or a very acceptable 60 % filler retention.

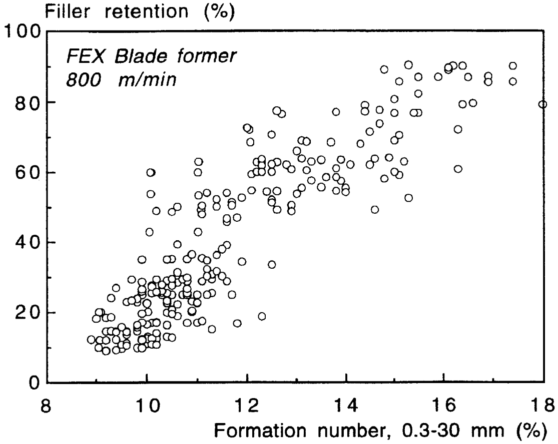

Fig. 31 Filler retention as a function of formation number (coefficient of variation of grammage, 0.3-30 mm wavelength interval). A twin-wire blade former was used with a fine paper stock containing 80 % softwood kraft pulp and 20 % $CaCO_3$. The amounts added and addition points of microparticle retention aid systems as well as the wire tension in the outer forming wire was altered. From (32, 93).

Even though there is no general relation between retention and formation, some rules of thumb can be given. If addition points, machine speed and other parameters are kept constant, the relation between retention and formation is often straightforward, as shown in Fig. 32.

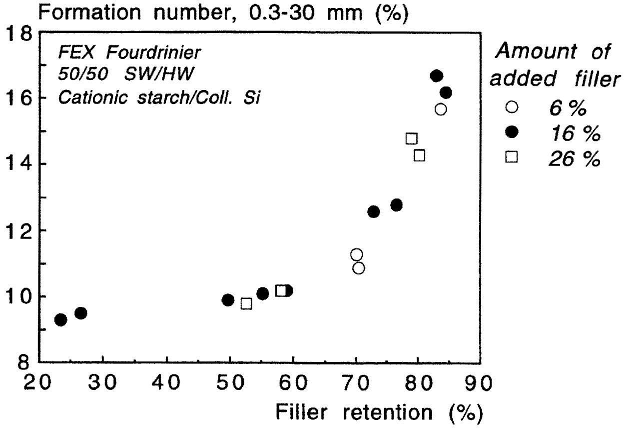

Fig. 32 Formation number (coefficient of variation of grammage, 0.3-30 mm wavelength interval) versus filler retention. The FEX Fourdrinier former was used with a fine paper stock containing 50/50 softwood/hardwood kraft pulp and 20 % $CaCO_3$ as filler. A microparticle system with cationic potato starch and anionic colloidal silica was used. The amounts of added cationic starch and colloidal silica were changed (FEX, unpublished results 1992).

At a certain retention level, the formation number starts to increase rapidly. The same trend was shown irrespective of the added amount of filler, so the explanation is most probably that strong fibre flocculation is induced at the high retention aid dosages required to give filler retention levels above 65-70 %.

One way to decrease the degree of fibre flocculation is to increase the shear during forming. This can however be accompanied by a loss of retention, as shown in Table 3 in which the wire retention is given for different machine speeds.

Machine speed (m/min)	Wire retention (%)
500	84
700	80
800	77

Table 3 Wire retention at different machine speed at the same discharge ratio. FEX Fourdrinier former. Fine paper stock with 50/50 softwood/hardwood pulp and calcium carbonate filler. From (167).

It is generally recognized that blade forming with pressure pulses during dewatering gives paper of better formation than the uniform dewatering during roll forming (168, 169). Fig. 33 shows a comparison of the retention/formation relation for these two types of twin-wire forming.

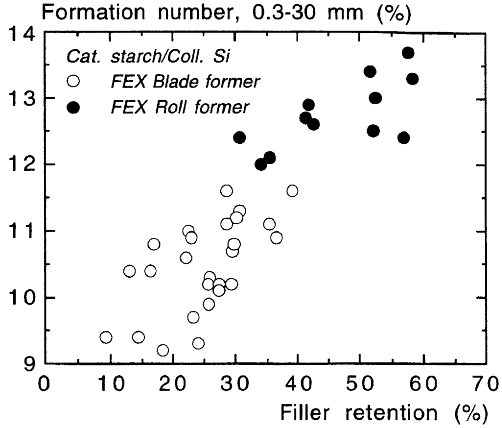

Fig. 33 Formation number, 0.3-30 mm (%) versus filler retention from FEX paper machine experiments. Fine paper stocks containing bleached kraft pulp and 20 % $CaCO_3$ filler. Different types of twin-wire formers were used: (○) blade forming and (●) roll forming with cationic starch/colloidal silica retention aid systems. Different retention levels were achieved by changing the amount of added retention aid. Data from (32, 87).

The blade forming gives a better formation than roll forming. The better formation using blade forming is achieved at the expense of a decreased retention. It is obvious that the retention aid system used is not strong enoung to withstand the high shear forces during blade forming. Roll/blade formers (168) have been developed to optimise the retention/formation relationship and it is, of course, important to optimise retention/formation also from a retention chemistry point of view.

One important machine parameter in twin-wire forming is the mix-to-wire speed difference (discharge ratio). It is generally recognized that the this speed difference has a large influence on paper formation (168) but the retention chemistry is also affected. It was shown in Fig. 28 that the degree of oriented shear during forming is also an important parameter for formation when retention aids are used. Fig. 34 shows the formation versus mix-to-wire speed difference for two cases, a stock containing 100 % softwood pulp flocculated by a microparticle system and a stock containing 80 % softwood pulp/20 % calcium carbonate filler flocculated by a microparticle system.

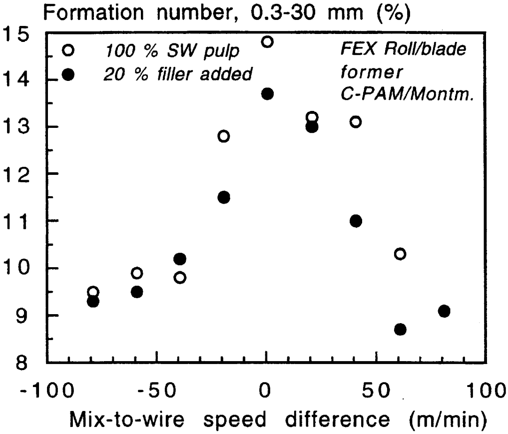

Fig. 34 Formation number, 0.3-30 mm (%) versus mix-to-wire speed difference in FEX paper machine experiments using a roll/blade former at 900 m/min: (○) 100 % softwood pulp and 500 g/ton C-PAM, (●) 80/20 softwood pulp/$CaCO_3$ filler and 1000 g/ton C-PAM. The addition of montmorillonite was 2 kg/ton in both cases. The speed difference was altered by changing the jet velocity. (Swerin, unpublished results, 1993).

The deterioration in formation was also great when filler was added. The filler retention was about 70 % at the most in these experiments. Increasing the mix-to-speed difference is obviously one way of improving formation. However, this is accompanied by an increase in the fibre anisotropy (153).

Fig. 35 shows the filler retention as a function of the mix-to-wire speed difference for different levels of added C-PAM in a microparticle system (153).

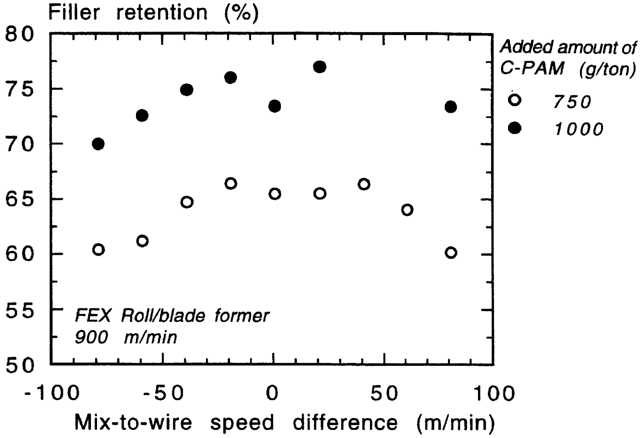

Fig. 35 Filler retention versus mix-to-wire speed difference on the roll during roll-blade forming of a softwood kraft pulp with 20 % ground calcium carbonate as filler in FEX paper machine experiments. The retention aid system consisted of C-PAM and 2 kg/ton of bentonite clay. From (153).

The filler retention shows a maximum at a zero mix-to-wire speed difference, at which the degree of oriented shear in the forming zone is at a minimum. This allows the mix to reflocculate and a higher filler retention is one result.

Further FEX experiments (32) have shown that the formation can be improved at a constant retention level. Fig. 36 shows the filler retention versus the formation number from experiments made in the FEX twin-wire blade former in experiments where the wire tension in the outer forming wire was changed.

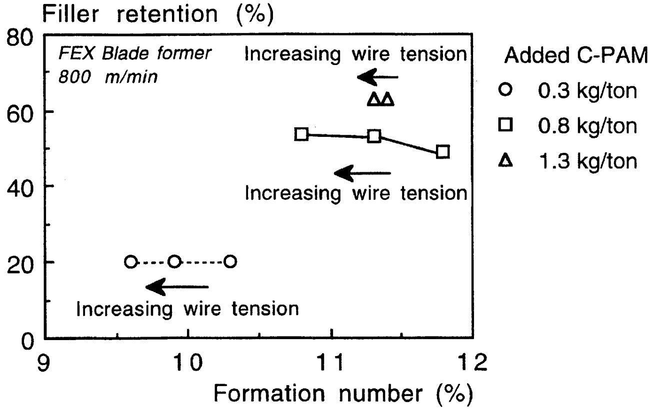

Fig. 36 Filler retention vs formation number, 0.3-30 mm (%) at different amounts of added cationic polyacrylamide, C-PAM, as retention aid. FEX twin-wire blade former with different wire tension in the outer wire (5.2, 7.8 and 10.4 kN/m). The stock contained 80 % softwood kraft pulp and 20 % calcium carbonate filler. From (32).

The increased wire tension during blade forming could in this case obviously rearrange flocs and break fibre flocs without major detachment of filler particles. It is seen that the effect of an improved formation at constant retention is high at low and moderate amounts of added retention aid. At the highest amount of added C-PAM (1.3 kg/ton) the floc strength is too high for the wire tension to give an improved formation.

SUMMARY AND CONCLUDING REMARKS

As an extremely condensed **summary** of this review, Table 4 presents the effect of shear and particle concentration on some processes involving retention aids. Typical time-scales for the processes are also given.

Process step	Effect of: Particle concentration	Shear	Typical time-scale
Mixing	–	+	seconds
Adsorption	++	++	0.1 s to minutes
Reconformation	–	?	1 s to minutes
Penetration into pores	–	0	10 s to days
Flocculation	++	+	0.1 s to minutes
Floc break-up	+?	+++	seconds
Transfer of paper chemicals	+	++	1 s to minutes
Reflocculation	++	+	0.1 s to minutes

Table 4 The effects of shear and particle concentration on different processes when retention aids are used. Adapted from Gregory (18).

Some **concluding remarks** should also be made. Although substantial progress has been made during recent years regarding the mechanism of retention aid systems, we are far from having a satisfactory knowledge. One reason why it is difficult to predict the effect of retention aids is that the real systems are difficult to define. The fibre surfaces are rough and porous, and the topography and the local chemical composition are not known in any detail. The polymers often have a broad molecular weight distribution. The hydrodynamic situation is furthermore often quite complex, with various degrees of turbulence. In almost all cases, the system is far from equilibrium, e.g. the polymer conformation is seldom an equilibrium conformation.

The only possible way for further research is, however, to work with well defined model systems. From the experimental results obtained with these systems, models should be constructed. These models should then be compared to practical experience on the paper machine. In these cases where the models fail, it is necessary to go back to the laboratory and find out what simplifications in the model were not justified.

Modern experimental techniques make possible new relevant model experiments. New possibilities are developed all the time. One new possibility is atomic force microscopy (AFM). If a filler particle is attached to the tip in the AFM microscope it should be possible to probe the interactions between the filler and a polymer coated surface. Such experiments have been performed with zirconia spheres (170). This could give more information about the strength of attachment of fillers to fiber surfaces. A new model surface for cellulose fibers has been developed using Langmuir-Blodgett techniques (171). This surface, unmodified and modified, has been used for studies of polymer adsorption by ellipsometry (172). This surface has also been used to study the interaction between a polymer-coated cellulose surface and an uncoated surface, using the surface force apparatus (173).

With regard to fibre flocculation, the work on friction between fibres (140) should be extended to include friction between polymer-coated fibres. The strength of flocs and fibre networks with and without chemical flocculants should be further investigated in various shear fields, e.g. elongational flow. The properties of flowing fibre suspensions flocculated by retention aids need further exploration. These studies should be done in various geometries, e.g. headboxes, flow distributors and mixing devices. New techniques such as combinations of video photography and laser-optical measurements (115) and NMR imaging techniques (119) should be used in detailed investigations. There is still a lack of knowledge about how flocculation is influenced by such basic parameters as fibre flexibility and fibre length even though progess has been made recently (138, 139).

The reversibility of flocculation by retention aid systems is an important property which needs further research. Several processes which can account for loss of reversibility in flocculation have been described in this review, such as reconformation and polymer chain cleavage. However, there is still a lack of knowledge of the importance of these processes, especially during realistic papermaking conditions.

Paper chemistry research should not, as has repeatedly been emphasized in this review, only be performed in the laboratory. There is a strong need for controlled experiments on pilot machines operating under realistic conditions. Some times it is also possible to make trials on production machines eventhough it can be difficult to control all parameters as accurately as one might want. All available and relevant information from production machines should, however, be used when trying to improve our knowledge on retention chemistry.

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Transcription of Discussion

Review Paper: Some Aspects of Retention Aids

Lars Ödberg, Vice President, Basic Research, STFI, Sweden

Dr Richard Bown, Research & Technology Director, EEC, UK: (Session Chairman)

Thank you for that very interesting summary and particularly for drawing attention to the kinetics and importance of size-scales in systems which are subjects quite often overlooked in simplistic discussions on what is happening in the paper furnish.

Bruce Lyne, Senior Manager, International Paper, USA

I was a little concerned that you are using G' the storage modulus from oscillatory rheometry experiments to characterise the integrity of the floc structure because if you simply add a small amount of long chain polymer to water you will increase G. I wonder if experiments should be done with the oscillation frequency in the same range as the relaxation time for flocs rather than for the relaxation time for stretching out polymers in flow (in other words much much lower frequencies).

Lars Ödberg

We did measure on fibre networks - not on a solution. These were integral fibre networks that we were examining.

Bruce Lyne

How do you distinguish the effect of the polymer itself on the water increasing G'

Lars Ödberg

All the polymer is adsorbed on the fibres in these experiments so there is no polymer in solution. The polymer is adsorbed on the fibres sitting partly where the fibres meet.

Bruce Lyne
Even in fairly intense shear conditions.

Lars Ödberg

Yes - but this was done in a rheometer with typical oscillation frequencies in the order of 1-10Hz. It is not at all papermaking conditions for these G' measurements. That is why I showed the NMR measurements.

Jonathan Phipps, ECC, UK

You have shown some good evidence of the increased reflocculation ability of the micro particle systems, but you have also quoted some data in your paper that shows similar effects with combinations of polymers. Do you think the same mechanism of action of microparticles can be achieved with polymers alone, or is some property of the particle important, such as a well defined surface?

Lars Ödberg

I think the presence of particles is essential because the reflocculation tendency could be easier with particles. You do not cleave the particles as easily as you do with polymers - this is one aspect.

Dr Theo van de Ven, Director, Paprican/McGill, Canada

Why in your model of the micro particulate retention aid system are some colloids more effective than others - we know that colloidal silica works well, bentonite works well but kaolin will not work - there are many other colloids which will not work. Why is that?

Lars Ödberg

I don't know. It is a simplistic model I have shown which covers some aspects of micro particle systems.

Richard Bown

I suggest it may be particle size - you need very small particles for these systems to work.

Dr Kari Ebeling, Director, UPM Kymmene Group, Finland

Congratulations Lars for a very thought provoking review. As a papermaker I am very pleased to see that STFI is using the FEX pilot paper machine efficiently to confirm the theoretical and lab scale results for us papermakers in real papermaking conditions which are important in retention.

Professor Gunter Gerischer, University of Stellenbosch, South Africa

In your excellent presentation I missed something on the micro particle system - the possibility of the co flocculation of fines and fillers as a future model in retention systems with the view of saving chemicals in the process.

Lars Ödberg

We have not looked into preflocculated fines and fillers but it is a possibility.