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SHEAR-INDUCED FLOCCULATION OF MICRO-CRYSTALLINE CELLULOSE WITH POLYACRYLAMIDE

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THE most widely used synthetic additives to improve drainage and fines retention during the formation of the fibrous mat are cationic polymers. These polymers are also frequently used to improve paper wet strength and internal bonding.(1) Their wide applicability is based on their preferential adsorption onto the anionic fibres and fines.

As the paper mills move towards a closed water system, the white water will contain increasing amounts of salt and anionic material originating from both the paper and pulp effluents.(2) With currently used polymers, this could result in an increased polymer demand as well as a decrease in retention. It thus becomes important to search for new polymers which will be less sensitive to salt as well as insensitive to dissolved anionic polymeric substances.

For our initial investigation, the flocculation characteristics of microcrystalline cellulose with polyacrylamide (PAM) was studied. Several parameters basic to flocculation, such as PH and ionic strength of the medium, as well as polymer molecular weight were evaluated. Studying the performance of this polymer may provide additional information on the flocculation mechanism of cationic polyacrylamides with cellulose. The cellulose used was fibrillar microcrystalline cellulose (2 500 Å × 150 Å) prepared by shearing Avicel PH 105 in a blender and using the nonsettling fraction.(3) This material, rather than paper fines, was used since the destabilisation of fines results in physical changes which are not easily identifiable. Furthermore, since the sol and the polymeric flocculant are in the same size range, interpretation of the flocculation kinetics in terms of polymer-particle interaction is more meaningful.

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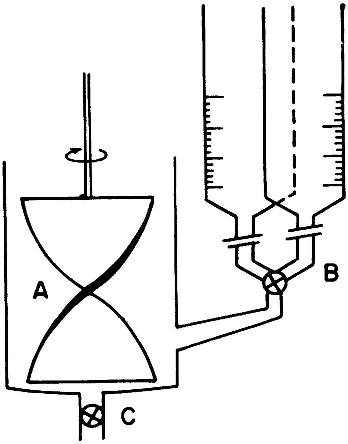

A = HELICAL STIRRER
B = MIXING CHAMBER
C = SAMPLE PORT

Fig. 1—Mixing apparatus to study the flocculation of microcrystalline cellulose with PAM

The cellulose sol was mixed with polymer in the arrangement shown in Fig. 1. Uniform stirring was obtained by a spiral-type stirrer, and the degree of flocculation was monitored by determining the solids content of the suspension by turbidity measurements.

Results and discussion

THE results of typical experiments on the monitoring of the flocculation of microcrystalline cellulose with PAM are shown in Fig. 2 where the degree of flocculation is plotted as a function of stirring time for different polymer concentrations. The relative extinctions of the supernatants were determined 20 hours after the stirring was stopped, during which time flocs settled out. Differences of one minute in stirring time result in large changes in turbidity after 20 hours' settling. This means that the flocculation by Brownian collision during 20 hours standing is negligible compared to the few minutes in the stirred reactor. Removal of flocs by centrifugation, directly after withdrawal from the reactor, gave turbidities of the supernatants similar to the turbidities of the samples after 20 hours' settling. Consequently, the flocculation was effectively stopped when the sample was withdrawn from the stirred reactor.

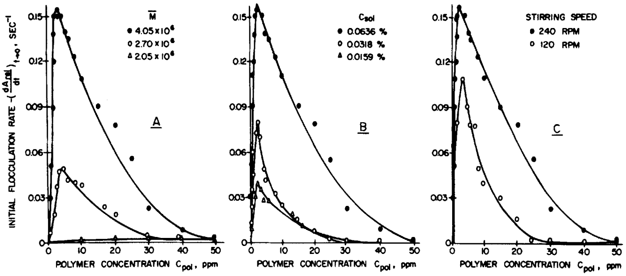

Fig. 2—The degree of flocculation of microcrystalline cellulose with PAM; $C_{sol} = 0{\cdot}0318$ per cent, pH = 6·0, 240 rpm, $\overline{M} = 4{\cdot}05 \times 10^6$

However, it is possible that flocculation occurs without shear but that the flocs are not sufficiently dense to sediment. To test this hypothesis, turbidity measurements were made directly on the cellulose sol flocculated with PAM. No changes in turbidity with time were observed, seemingly indicating the absence of flocculation. However, Kratohvil *et al.*(4) have previously reported that coagulation with electrolyte produced no change in turbidity, a result confirmed in this study. Consequently, turbidity measurements on the cellulose system cannot indicate the extent of particle aggregation but only the solids content. This light scattering anomaly is most likely related to the rod-shaped cellulose particles. Pending additional critical experiments, we shall assume at this point that the flocculation of microcrystalline cellulose with PAM is shear induced.

Fig. 2 shows that the most rapid increase in flocculation occurs at a polymer dosage of 3·2 ppm. At higher polymer dosages, the initial flocculation rates decline. At still higher polymer dosages, the flocculation curves shows an induction period. However, prolonged stirring (15 min) results in a greater flocculation at higher polymer dosages.

Initial flocculation rates as a function of polymer concentration were determined for the effect of molecular weight, particle concentration, and stirring speed. These results are shown in Fig. 3. The degree of flocculation after 15 minutes' stirring time for the same data is shown in Figs. 4 and 5. No maxima are observed in these curves since the stabilised particles are flocculated by the continued stirring.

The results in these figures can be partially explained by a classical bridging mechanism.(5-6) Polymer adsorption results in extension of the particle size by the polymer loops permitting interparticle bridging. With increasing polymer concentration, flocculation is enhanced until the surface coverage is such that the adsorbed polymer on one particle cannot find any free

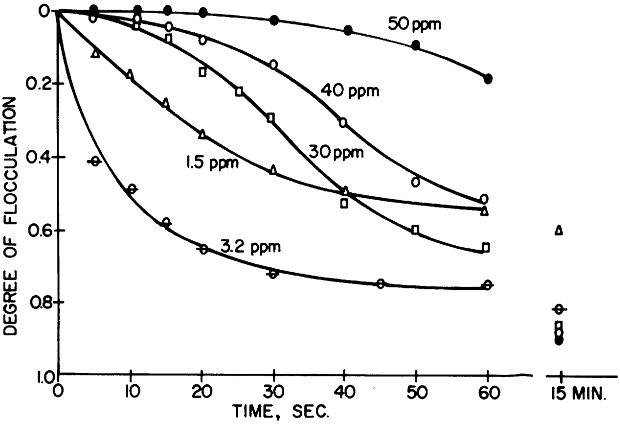

Fig. 3—Initial flocculation rates of microcrystalline cellulose as a function of PAM concentration

A. C_{sol} = 0·0636 per cent, pH = 6·0, 240 rpm
B. pH = 6·0, 240 rpm
C. pH = 6·0, C_{sol} = 0·0636 per cent

adsorption sites on neighbouring particles. At this point, flocculation is retarded. At sufficiently high polymer dosage, the particles may become completely stabilised. Increasing the molecular weight of the polymer facilitates bridging as does particle concentration. However, this picture is incomplete since Brownian motion does not provide the necessary energy for sedimentation. Only on shear does flocculation with settling occur. This suggests that additional factors are involved in the sedimentation process. First, experiments showed that the adsorption of polyacrylamide onto the cellulose surface is a low affinity adsorption. Even at the optimum polymer dosage of 3 ppm, residual polymer was present after 15 minutes' stirring, indicating that all polymer molecules are not involved in bridging.

A further analysis of the flocculation data (Fig. 3) shows that for the $\overline{M} = 4{\cdot}05 \times 10^6$ molecular weight sample at the optimum polymer dosage (OPD) of 3 ppm and at a solids concentration of 0·0636 per cent, the polymer: particle ratio is 1:15 and 1:1 in the stabilised zone. These flocculating conditions contrast sharply with other flocculation data where the polymer: particle ratio is $\sim 1 \times 10^5$.(7) These considerations suggest a unique flocculation mechanism for the PAM-cellulose system.

When PAM is added to microcrystalline cellulose, several cellulose particles may be loosely laced together by a single PAM molecule (Fig. 6). The formation of these large aggregates greatly reduces the relative Brownian motion

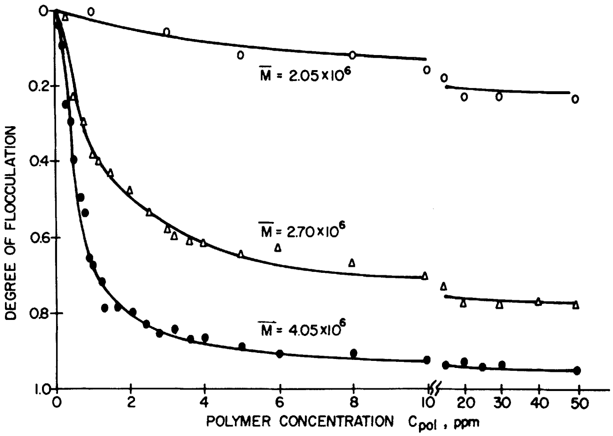

Fig. 4—Degree of flocculation of microcrystalline cellulose with PAM of different molecular weight; C_{sol} = 0·0636 per cent, pH = 6·0, 240 rpm

of the constituent particles. When shear is applied to this system, collisions occur between aggregates with simultaneous deformation. The shearing forces align the microfibrils and elongate these aggregates. This process increases their density, leading to settling. These denser microfibril structures may now settle out.

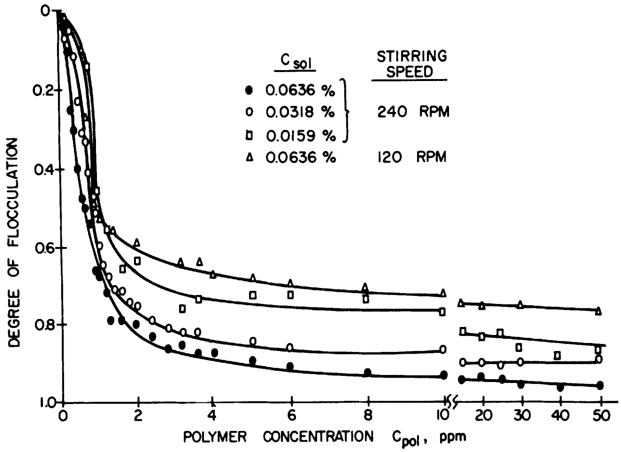

Fig. 5—Degree of flocculation of microcrystalline cellulose with PAM at different solids contents; pH = 6·0, $\overline{M}$ = $4{\cdot}05 \times 10^6$

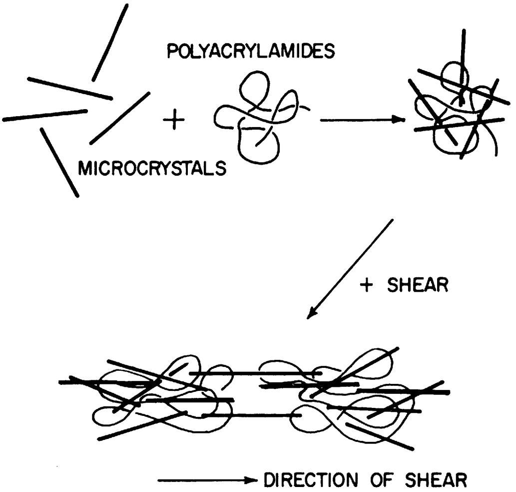

Fig. 6—Mechanism for flocculation of microcrystalline cellulose with PAM

The retardation in flocculation at high polymer dosage (Fig. 2) is a consequence of the low number of particles per polymer molecule (less dense aggregates). Hence, more extensive shearing is required to build up a fibrillar system which sediments. The floc morphology below the OPD is different from that above the OPD. This observation suggests that below the OPD, homoflocculation may be considered to occur between aggregates while above the OPD, heteroflocculation (i.e., aggregates and polymer) also occurs.

The critical dependence of molecular weight in the flocculation of the cellulose-PAM system can now be understood. For a given particle concentration, the higher molecular polymer molecule will interlace more microfibrils giving larger aggregates. In addition, the higher molecular weight samples will provide more contiguous length to better align the polymer with particles under shear. This is an essential requirement to build up dense flocs for sedimentation.

Fig. 3 shows that the flocculation rate and degree of flocculation are enhanced by an increase in solids concentration and stirring speed. These results are in agreement with the proposed mechanism of flocculation since both of these factors enhance aggregation.

Effect of double-layer modification on flocculation

THE DLVO theory(8) predicts that particle destabilisation is facilitated by reducing the surface potential of the particle by the addition of potential

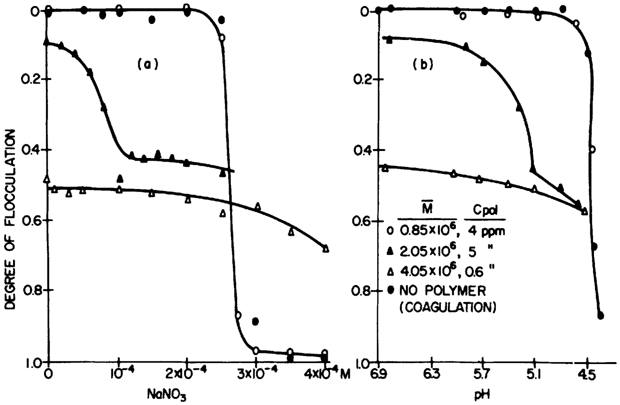

Fig. 7—Degree of flocculation of microcrystalline cellulose with PAM of different molecular weight as a function of

A. Ionic strength, and
B. pH
both at stirring speed of 240 rpm

determining ions (here H^+ ions) and increasing the ionic strength of the system whereby the 'thickness of the double layer' is reduced. As microcrystalline cellulose spontaneously coagulates at $pH < 4{\cdot}5$ and in 2×10^{-4} M $NaNO_3$ (pH 6), the range over which these two parameters can be investigated in the cellulose-PAM system is limited.

Fig. 7 shows the degree of flocculation of the cellulose-PAM system as a function of ionic strength and pH at three molecular weights. These experiments were made at polymer concentrations below the optimum dosages since at these concentrations, the particles are not restabilised, and thus the degree of flocculation and initial rate of flocculation are in qualitative agreement.

It is readily apparent from Fig. 7 that for the three polymers, decreasing the pH, i.e., decreasing the charge of the particle, runs parallel to decreasing the double layer thickness, i.e., ionic strength. It appears that the lowest and highest molecular weight samples are not significantly affected by the particle charge or double layer thickness. From this, it can be inferred that the loop length for the high molecular weight sample exceeds the double layer thickness under all experimental conditions. For the lowest molecular weight sample, it appears that the loop length is always smaller than the double layer thickness. In the former case, the degree of flocculation is constant, while for the latter case, the polymer plays no role in the coagulation process. In contrast, the flocculating ability of the $2{\cdot}05\times10^6$ molecular weight polymer sample improves with salt concentration and decreasing pH to a limiting value, indicating that under these conditions the loop length of this molecule weight sample is critical for bridging. Salt concentration and pH now determine whether the double layer thickness is greater or less than the extension of loops.

Acknowledgements

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Transcription of Discussion

Discussion

Dr R. H. Marchessault Have you taken X-ray diagrams of these fibres? The birefringence is often deceptive as to the degree of orientation in the crystallites.

Luner Not yet.

Marchessault Have you measured the mechanical properties, for example the initial modulus of these?

Luner No, when you dry these fibres they are extremely brittle and difficult to handle. We have tried to incorporate various types of polymers like polyvinylalcohol and we have achieved some success in giving it some handleability, but in the dry state it fractures rather easily.

Mr D. R. Cosper I have two questions. Could the adsorption of polyacrylamide be shear induced?

Luner I think it is a good possibility. Either you are transporting the particle to the polymer or vice versa and I am sure that you can look at it either way.

Cosper In your preprint I was curious about the ratio of polymer molecule to microcrystalline cellulose particles. The ratio seems quite low. For titanium dioxide containing furnishes, for example, the ratio would be three or four powers of ten higher than that. Just looking at your dosages I would have expected the ratio to be in the order of 100 rather than 0·1. I am questioning the calculation.

Luner We calculated the number of particles from the particle size that we determined. We know the molecular weight of the polyacrylamide and the dosage, so we know how many molecules are in the solution, and that is how

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we arrived at a ratio of particles to polymers either initially or at the optimum polymer dosage.

Dr H. G. Higgins The resolution of this question may depend on our definitions of strength and of fines. Would people argue for example that fines do not have an influence on extensibility properties? The effect on stress properties is probably much less.