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# Influence of flocculant molecular weight and anionic charge on flocculation behaviour and on the manufacture of fibre cement composites by the Hatschek process

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**Abstract**

Although in the industrial Hatschek process it is necessary to use flocculants to improve retention, dewatering and formation, the use of flocculants may also decrease the strength of the final product. This paper studies the influence of the molecular weight and the anionic charge of anionic polyacrylamides on the flocculation behaviour of fibre cement suspensions and on the bending strength of the final product. Flocculants influence the density of the final product and in-turn the lowering of the density results in strength reduction. Results showed that an increase in the flocculant molecular weight reduces the bending strength of the composites significantly due to its density reduction. However, an increase in flocculant anionic charge increases the bending strength of composites. Therefore, in order to optimise the fibre cement process, it is necessary to use flocculants with high anionic charge and medium molecular weight.


*Keywords:* Kinetics; Particle size distribution; Bending strength; Fibre-reinforcement; Flocculation

## 1. Introduction

The Hatschek machine is mostly used to produce flat or corrugated sheets of cellulose fibre cement composites. In this process a suspension of water, cement, other minerals and fibres is mixed and introduced into each one of the sieve cylinder vats of the machine. The rotating sieve cylinder collects a primary layer of the solid materials whilst most of the excess water passes through the wire mesh of the sieve cylinder. The thin layers of all the various sieve cylinders are collected on the felt, which runs over dewatering vacuum boxes to the accumulating forming roller. It is well known that the correct selection of flocculant is critical in the industrial manufacture of wood fibre cement composites by the Hatschek process due to its effect on mineral fines retention, dewatering and formation and, as a consequence, on the overall efficiency of the machine [1–7]. However, most work in this field has been carried out at mill sites and so no information is available. Most of the published basic work related to this topic comes from the paper industry. This paper fills that gap by providing a fundamental understanding of flocculant effect on the fibre cement suspension and the resultant composite properties.

In general, retention programs not only enhance retention but also improve the removal of water from the fibre cement suspension stock. However, flocculation can negatively affect the formation if big flocks are present in the suspension during the formation of the sheet [4,5]. The flock size and the flock properties are the key factors influencing retention, drainage and formation. These are controlled by the addition of chemicals, but are also dependent on the ability of flocks to resist degradation from shear forces, as well as turbulence in the chest and in the forming elements. Ideally a retention system needs to flocculate effectively at a minimum dosage level and to be somewhat shear resistant without adversely affecting sheet structure.

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Flocculation is a complex phenomenon because of the wide variety of available flocculants, the different properties of the flocks, according to the predominant flocculation mechanism, and the numerous interactions that may occur between the chemicals and the different components present in the fibre cement suspension. Therefore, a deeper knowledge of flocculation mechanisms is required to optimise the industrial manufacturing process.

Many fibre cement companies have difficulty controlling the optimal chemical dosages in real time which can cause flocculant overdoses. This phenomenon leads to product strength losses. The excess of flocculant affects the flocculation process and the flock properties. Therefore, the study of this effect is essential to understand and to predict possible problems.

Monitoring of flocculation is usually based on the electro-kinetic properties of the suspensions [5,8–10]. Colloidal titration, cationic demand and zeta potential measurements are commonly used at laboratory scale, e.g. in the paper industry. However, methods are not applicable in this case because of the high abrasion character of the fibre cement suspensions (it will damage the Teflon measuring cells), the colour of the suspension and the high solid content of the samples [8,9].

Another option is the use of a focused beam reflectance measurement (FBRM) probe, which allows the in situ measurement of chord length distribution over a wide range of solid concentrations. The significant advantage of this method is that sampling and dilution are not required. This is especially relevant for flocculation processes where any change in the suspension will alter the structure of the flocks [11,12].

The evolution of the particle chord size distribution was studied by monitoring the number of counts per second, namely the number of particles the sensor measures per second, and the mean of the chord size distribution (mean chord size).

The application of this laser technology to optimise flocculation was developed in the early 1990s for the paper industry. It has also been used to study the flocks resistance to shear forces by studying the flocculation, de-flocculation and re-flocculation processes from a kinetic point of view [13].

The kinetics of the flocculation, de-flocculation and re-flocculation processes was studied by following the Smoluchowski classical theory, based on the evolution of the particle number concentration. It can be considered that the evolution of the number of counts per second varies in the same way as that of the evolution of the particle number concentration. Then:

$$\frac{dn_c}{dt} = -k_{c1}n_c^2 + k_{c2}n_c \qquad (1)$$

where $n_c$ is the number of counts measured per second, $t$ is the time (s) and $k_{c1}$ and $k_{c2}$ are functions of the Smoluchowski's kinetic constants. This relationship allows us to compare the flocculation and the de-flocculation kinetics of different polymers. The relationship between both types of kinetics allows us to obtain the equilibrium situation towards which the system tends in each case. This methodology has been successfully applied in the paper industry and in this paper it is applied to study fibre cement suspensions [14–17].

## 2. Materials and method

### 2.1. Materials

Experiments were performed using a fibre cement suspension typical of the main process technologies for the production of fibre cement sheets in the air cured process. It is a mixture of highly refined *Pinus radiata* unbleached Kraft pulp, poly-vinyl-alcohol (PVA) fibres and silica fume on a matrix of ASTM Type II cement.

A wide selection of anionic polyacrylamides (A-PAM), with different charges and molecular weights supplied by Sachtleben Chemie (Germany), were chosen as flocculants. Fig. 1 shows their molecular weights and anionic charges.

### 2.2. Fibre cement specimen preparation

In order to study the effect of different flocculants on composite properties, 100 ppm of flocculant was added to the fibre cement suspension used to prepare the fibre cement specimens. The specimens were prepared using a 10 wt.% fibre cement suspension, following an internal standard developed by Uralita S.A. After mixing, a 1 L suspension was stirred for 45 s, in order to obtain a homogenous sample, then the flocculant was added. After 30 s, the mixture was poured into an evacuable casting box of 210×80 mm size and it was homogenously distributed over the sieve being used as a filter medium. A vacuum of 250 kPa was applied to dewater the sheet. An 11 kg mould weight was put over the sheet to simulate the pressure from the cylinder former in the Hatschek machine. Finally, the sheet was removed from the sieve and pressed for 5 s at 6.2 MPa. For each experiment, 6 different specimens were prepared in order to obtain representative values.

The specimens were stored between two steel plates inside a sealed plastic bag until the stacks of six samples were prepared. The specimens were then stored in a curing chamber with a water-saturated atmosphere for 24 h. Finally, they were cured in saturated water, with respect to cement, until the flexural test was carried out.

### 2.3. Property measurements

Two product properties, bending strength and density, were determined after 7 days curing. The test method follows the standard EN 492. Modules of rupture (MOR) were measured in centre point bending and six replications were carried out for each test.

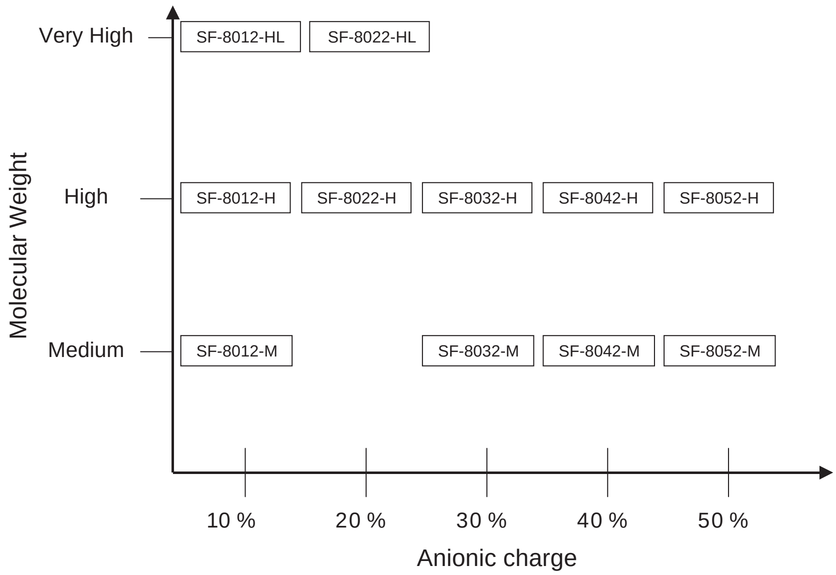


Fig. 1. Classification of anionic polyacrylamides: anionic charge density and molecular weight.

### 2.4. Flocculation studies

The effects of the different flocculants on the process were studied flocculating a 5% cement suspension with a polymer dosage of 100 ppm.

The flocculation process and the flock properties were studied using a FBRM probe M500L manufactured by Lasentec, Seattle, USA. The principle of the measurement and the details of the applied methodology have been described by the authors in a previous reference [13].

To study flock properties the following experimental sequence was carried out: flocculation at 300 rpm for 300 s, allowing the flocks to evolve, then increasing the stirring intensity to 800 rpm for 300 s, in order to de-flocculate the system and, finally, decreasing the stirring speed again to 300 rpm, in order to reflocculate the suspension. During all the experiments the behaviour of the suspended particles was monitored.

## 3. Results

### 3.1. Influence on composite properties

Figs. 2 and 3 show the bending strength and the density obtained for the different flocculants tested. Both flocculant

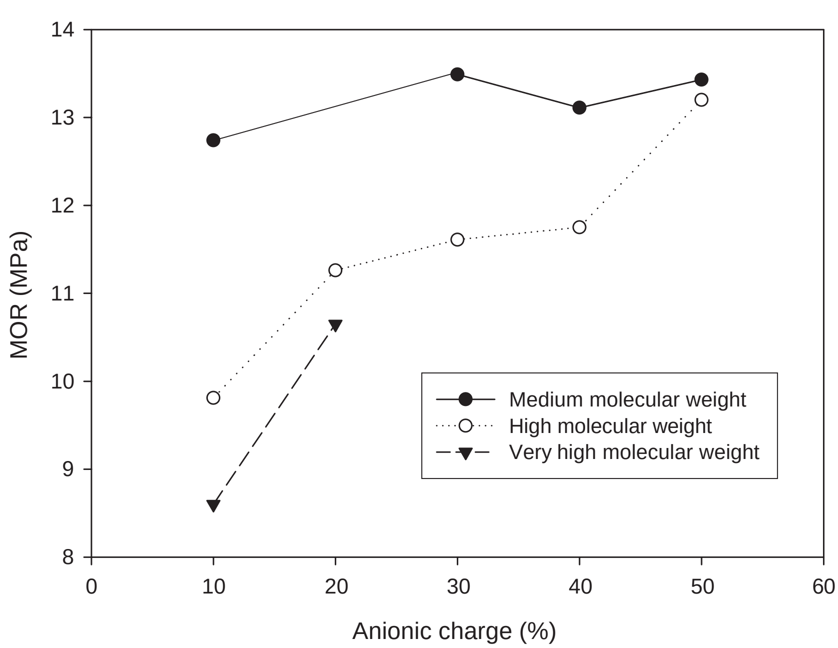


Fig. 2. Effect of molecular weight and charge density of the flocculant on the bending strength of the composites.

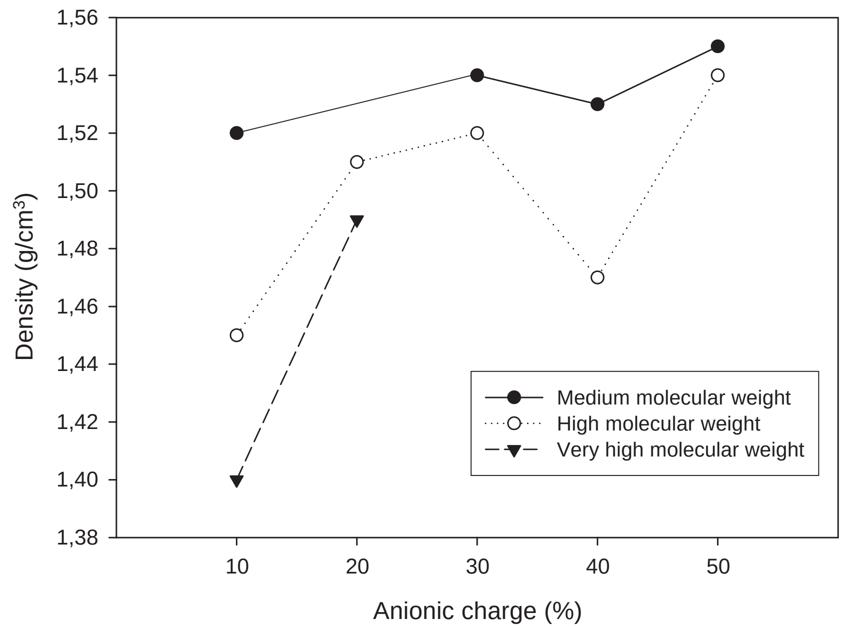


Fig. 3. Effect of molecular weight and charge density of the flocculant on the density of the composites.

properties (molecular weight and anionic charge) affect both product qualities (bending strength and density).

A flocculant molecular weight increase reduces both the density and in-turn the bending strength of the product significantly. This effect is more important for the lowest anionic charge. The influence of molecular weight can be explained because bigger flocks are formed when flocculant molecular weight increases. As a consequence, the water content inside the flock increases. Therefore, the air content in the sheet will be higher after curing and thus the density will be lower and hence a reduction in strength properties is expected. Another explanation could be proposed considering that a high molecular weight flocculant induces the production of big flocks and, therefore, the sheet formation in the sieve is poorer and that is why a strength reduction could be expected.

An increase in anionic charge increases the bending strength and the density. The explanation could be that when flocculant anionicity increases, more compact flocks are obtained because of there being more bonding groups to interact with the cement particles. As a consequence, the water in the flocks is lower and after the curing process the

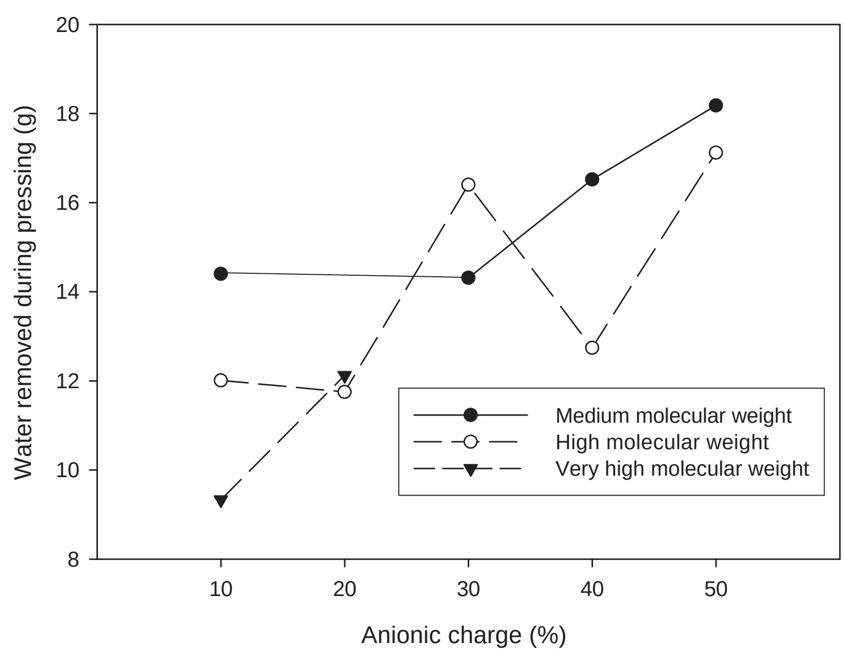


Fig. 4. Effect of molecular weight and charge density of the flocculant on the water removal during pressing.

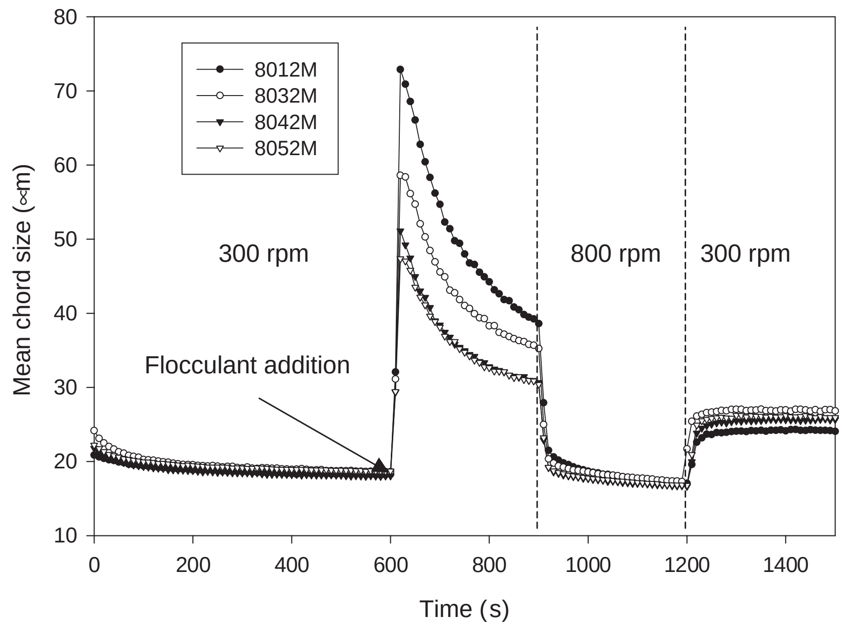


Fig. 5. Effect of the charge density on the evolution of the mean chord size.

air content of the sheet is lower, the density is higher and it leads to increases in the strength properties of such a product. The improvement in strength properties can also be explained as a consequence of the better formation obtained if smaller, compact flocks are formed when the flocculant anionicity increases.

Fig. 4 shows the amount of water removed during the pressing step for different specimens. The tendency corroborates the theories explained above concerning the different flock characteristics at low and high anionic charges and different molecular weights. In the obtained values there is one exception for the case of high molecular weight flocculant with 30% anionic charge that seems to be abnormally high.

According to these results, the optimum situation would be the use of a flocculant with medium molecular weight and high anionic charge. In order to confirm this hypothesis a more detailed study of flock behaviour was carried out.

### 3.2. Flocculation kinetics and flock properties

Figs. 5–7 show the evolution of the mean chord size during the trials. Fig. 5 shows the differences due to the charge density for the medium molecular weight flocculants.

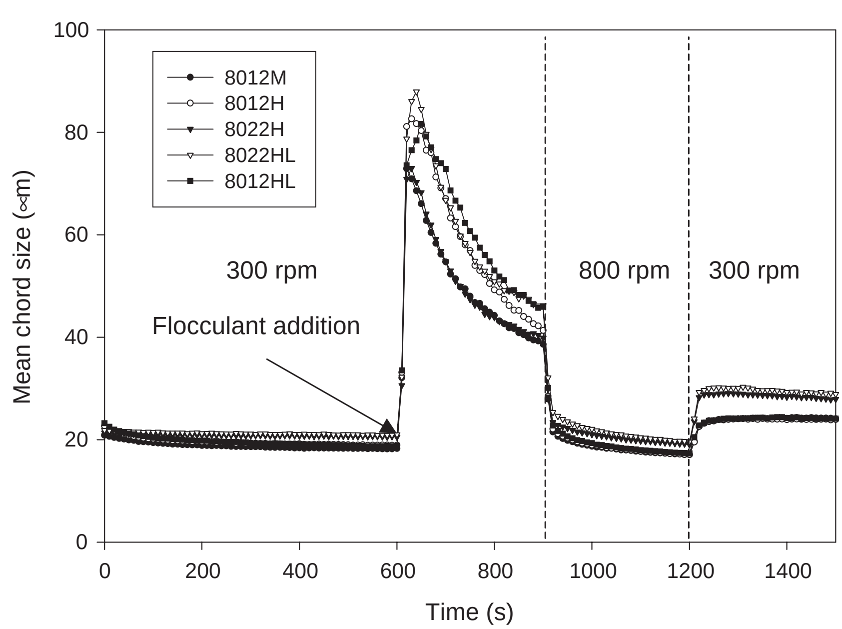


Fig. 6. Effect of the molecular weight on the evolution of the mean chord size at low charge density.

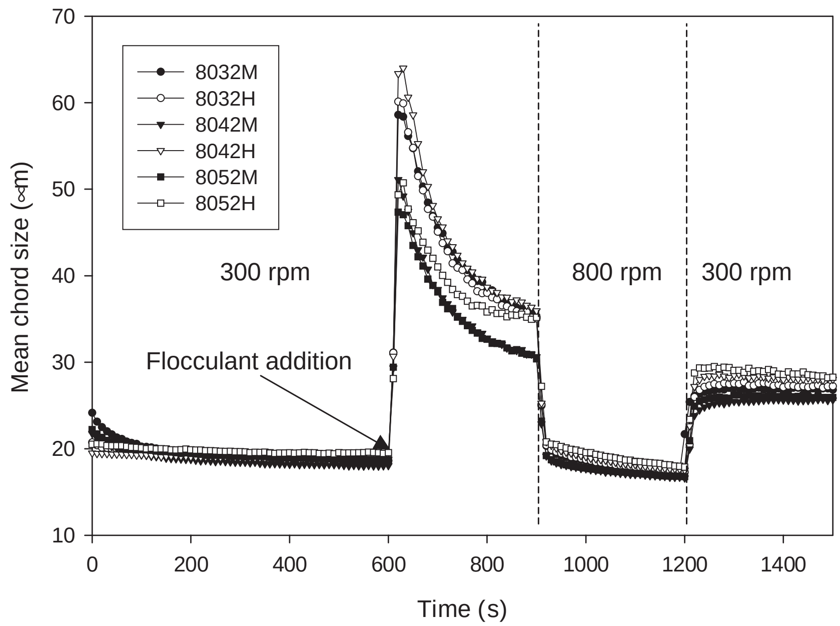


Fig. 7. Effect of the molecular weight on the evolution of the mean chord size at high charge density.

Figs. 6 and 7 show the effect of the molecular weight for the flocculants of low and high charge densities respectively. The first 600 s corresponds to the evolution of the cement suspension to simulate the residence time at industrial scale in the various mixing tanks prior to the machine. After that, the polyacrylamides were added and a fast flocculation occurs because of the bridge formation among the particles increasing the mean chord size. However, after reaching a maximum, the mean chord size decreases towards an equilibrium value. The explanation for this is that hydrodynamic forces start to break down the formed flocks and parts of the destroyed flocks are unable to aggregate again as the flattening of the adsorbed polymer chains avoids the formation of bridges.

When the stirring intensity increases to 800 rpm ($t=900$ s) flocks are completely destroyed but some particles aggregate again when the stirring intensity decreases ($t=1200$ s) indicating the reversible character of the flocks.

Fig. 8 shows that the flock size increases with the molecular weight of the flocculant and decreases when the anionic charge increases except for the very high molecular weight flocculants. Furthermore, the effect of the molecular weight on the flock size decreases at high anionic charge. These results confirm the hypothesis that the higher

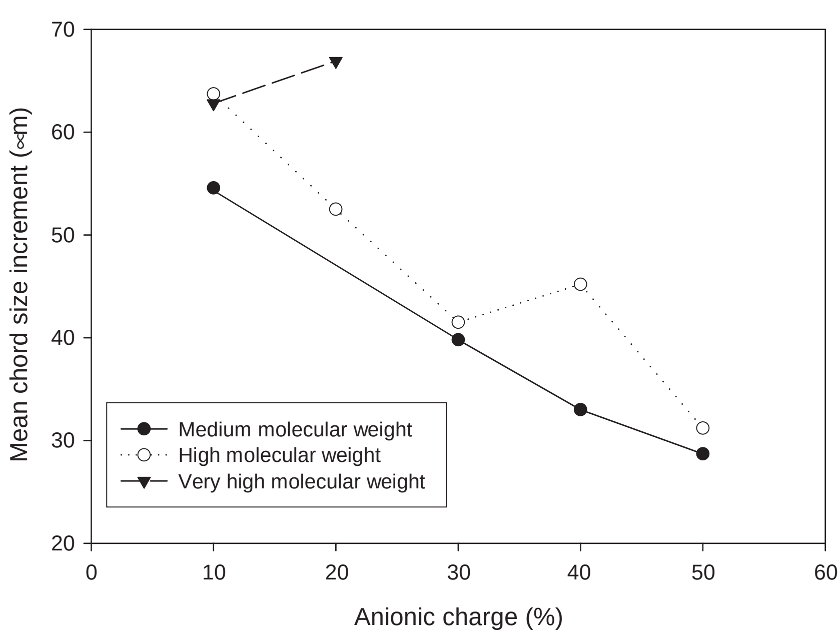


Fig. 8. Effect of molecular weight and charge density on the flock size.

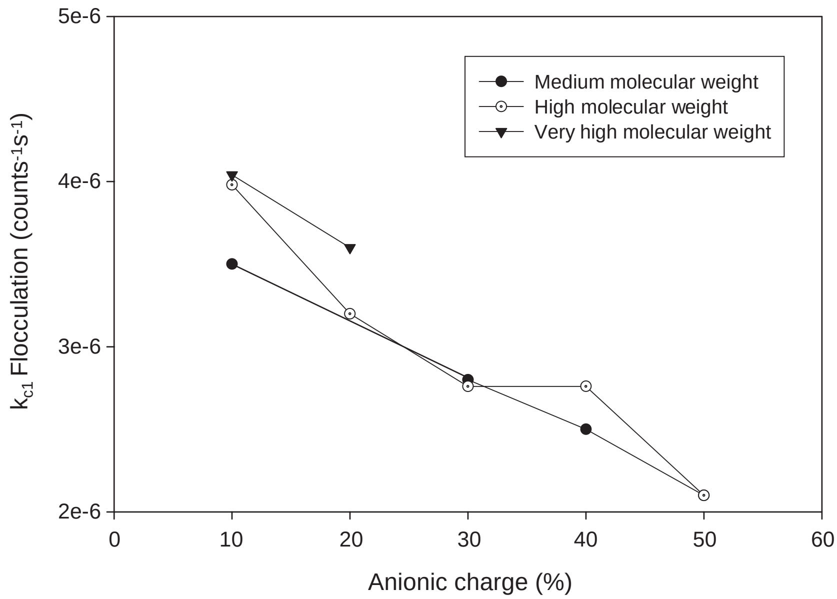


Fig. 9. Effect of molecular weight and charge density on the flocculation kinetic.

molecular weight polyacrylamides formed larger flocks and affected the formation negatively. Only two flocculants with very high molecular weight have been tested and, therefore, the effect on anionic charge cannot be properly studied in this case.

Fig. 9 shows the $k_{c1}$ values, obtained from Eq. (1), for the flocculation to reach the maximum mean chord size or the minimum number for particle concentration. The anionicity decreases the flocculation rate and the molecular weight does not have a significant effect on it. Dissolved calcium ions present in the medium interact with the anionic carboxylic groups of the polymers increasing the stiffness of the chains that evolve to a less extended conformation. The anionic charge density increases this interaction, decreasing the probability of extended conformation, and therefore each chain can join fewer particles and the formed flocks are smaller. This negative effect on the flocculation kinetics overcomes the adsorption improvement produced by the calcium–flocculant interaction.

During the evolution of the flocks there are two simultaneous processes: the flock breakage due to the hydrodynamic forces ($k_{c2}$) and the aggregation of the formed particles ($k_{c1}$), provided that the thickness of the adsorbed polymer chains overcomes the double electrostatic layer thickness to form bridges between particles. However,

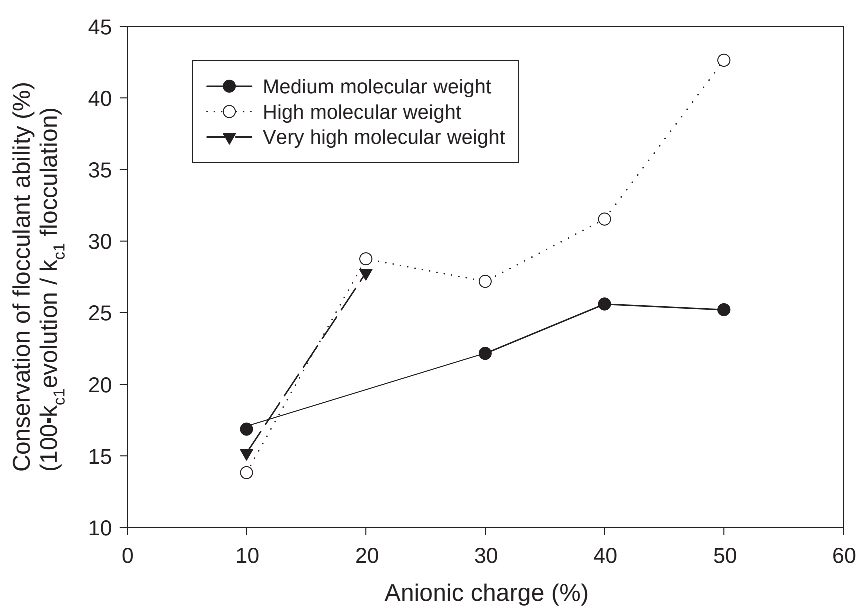


Fig. 10. Effect of molecular weight and charge density on the flattening.

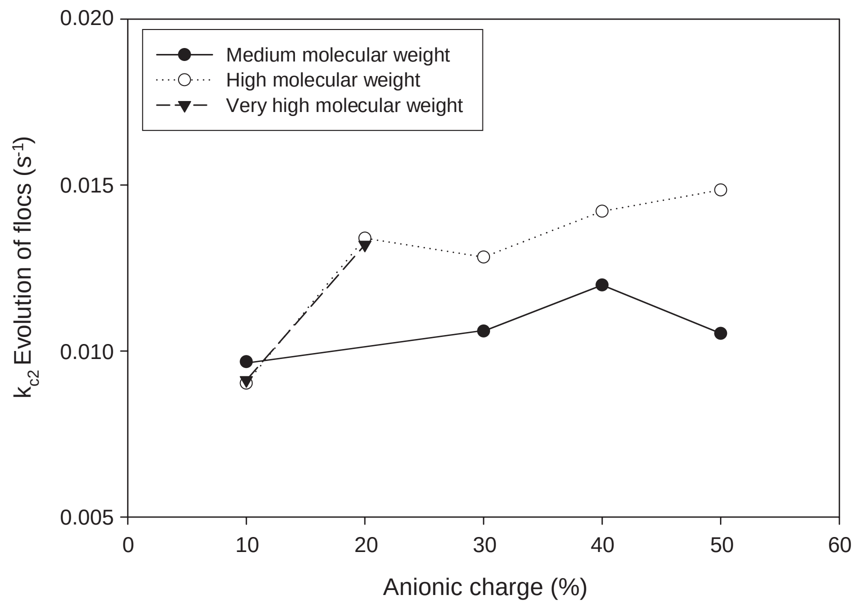


Fig. 11. Effect of molecular weight and charge density on the flock strength.

the conformation of the adsorbed polymer chains evolves towards a flat configuration and this flattening decreases the number of particles able to aggregate. Consequently, as Fig. 10 shows, the value of $k_{c1}$ decreases and the deflocculation rate overtakes the flocculation rate, decreasing the mean chord size. The increase of the anionic charge avoids the flattening of the adsorbed polymer, minimising the loss of flocculant efficiency (higher $k_{c1}$ conservation). The increase of molecular weight increases the conservation of flocculant ability, because it increases the adsorbed polymer layer thickness. However, it decreases the flock strength as shown in Fig. 11 (higher $k_{c2}$). This fact, and the effect of molecular weight on the mean chord size, confirms that the flocks formed by medium molecular weight polymers are more compact that the ones formed by high molecular weight polyacrylamides.

Fig. 12 shows that the reversibility of the flocks increases with the anionic charge which makes the flocculation process easier to control. The molecular weight has a negative effect on flock reversibility when the anionic charge is low.

In summary, the medium molecular weight polyacrylamides with high anionic charge induce slower flocculation, forming smaller, more compact, stable and reversible flocks.

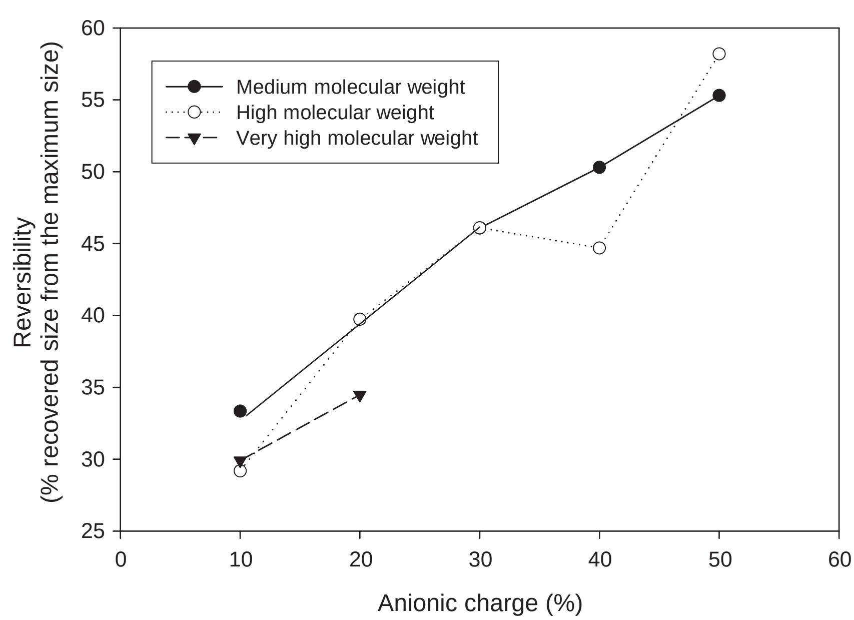


Fig. 12. Effect of molecular weight and charge density on the flock reversibility.

This leads to a better formation (higher strength of the product) and easier flocculation control.

## 4. Conclusions

The flocculant used in the manufacture of fibre cement not only improves the productivity but also has a strong influence on the final composite properties. Flocculants influence the density of the final product and this in-turn influences the final product strength, however this influence depends on flocculant properties. An increase in flocculant molecular weight reduces the bending strength of the composite significantly as it can interact with particles at greater distances and thus decreases the density of the flocks. On the contrary, an increase in flocculant anionic charge increases the bending strength of composites because it constrains the chain configuration, reducing the distance between the particles and, therefore, increase the density of the flocks. Furthermore, the reversibility of the flocks increases with the anionicity making the flocculation control easier. In order to optimise the fibre cement processes it is necessary to use a flocculant with high anionic charge and medium molecular weight.

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## References

[1] D. Eklund, T. Lindström, Paper Chemistry—An Introduction, DT Paper Science, Grankulla, Finland, 1991.
[2] X. Yu, P. Somasundaran, Kinetics of polymer conformational changes and its role in flocculation, J. Colloid. Interface. Sci. 178 (1996) 770–774.
[3] A. Yeung, A. Gibbs, R. Pelton, Effect of shear on the strength of polymer induced flocks, J. Colloid. Interface. Sci. 196 (1997) 113–115.
[4] A. Blanco, C. Negro, J. Tijero, Modelling drainage in the wire section of a Fourdrinier machine, PIRA International, Leatherhead, UK, 1997.
[5] A. Blanco, C. Negro, T. Tijero, Developments of Flocculation in papermaking, PIRA International, Leatherhead, UK, 2002.
[6] R.S.P. Coutts, M.D. Campbell, Coupling agents in wood fibre-reinforced cement composites, Composites 10 (1979) 228–232.
[7] A.J. Michell, Composite of commercial wood pulp fibres and cement, Appita J 33 (6) (1980) 461–463.
[8] E. Fuente, Mechanism and kinetic of flocculation process in the paper manufacture, PhD thesis, Madrid, Spain, Complutense University, 2003.
[9] M. Hubbe, Selecting and interpreting colloidal charge measurements, Proceedings of Scientific and Technical Advances in Wet-End Chemistry PIRA International Conference. Spain, June, 2000.
[10] A. Blanco, C. Negro, A. Hooimeijer, J. Tijero, Polymer optimization in papermills by means of a particle size analyser: an alternative to zeta potential measurements, Appita. J. 49 (2) (1996) 13–116.
[11] I. SanPío, Methodology to optimise flocculation in the manufacture of fibre-cement without asbestos, PhD thesis, Madrid, Spain, Complutense University, 2003.
[12] P. Barrett, Selecting in-process particle-size analysers, Chem. Eng. Prog. 99 (8) (2003) 26–32.
[13] A. Blanco, E. Fuente, C. Negro, J. Tijero, Flocculation monitoring: focused beam reflectance measurement as a measurement tool, Can. J. Chem. Eng. 80 (4) (2002) 734–740.
[14] M. Smoluhowski, Versuch einer mathematischen theorie der koagulationskinetik kolloider Lösungen, Z. Phys. Chem. 92 (1917) 129–168.
[15] B. Dobias, Coagulation and Flocculation. Theory and Applications, Marcel Dekker Inc., New york, 1993.
[16] D.N. Thomas, J. Judd, N. Fawcett, Flocculation modelling: a review, Water Res. 33 (7) (1999) 1579–1592.
[17] T.G.M. Van de Ven, Colloidal Hydrodynamics, Academic Press Inc., London, 1989.