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Effects of flocculants and sizing agents on bending strength of fiber cement composites

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Abstract

Wood fiber is used to replace asbestos in the manufacture of fiber cement due to its high availability, low cost and good reinforcement properties. The different chemical composition of the cellulose fibers makes its compatibility with the cement much more complex than that of asbestos fibers. In the Hatschek process a suitable flocculant is needed when using cellulose fibers. The right selection of the flocculant is crucial due to its effect on mineral fines retention, dewatering and formation and, as a consequence, on the overall efficiency of the machine. This paper shows how anionic poly-acryl-amides (A-PAM), the most common flocculants used in Hatschek machines, have a negative effect on the bending strength properties of fiber cement sheets. In order to overcome this problem fiber surface treatment, with sizing agents, is proposed in this paper. Sizing with styrene-acrylate copolymers and alkyl ketene dimer produces an increase in bending strength properties.

Keywords: Bending properties; Organic materials; Composite; Fiber reinforcement; Fiber surface treatments

1. Introduction

Over the last decades many research studies related to the substitution of asbestos by other raw materials have been published. These works are mainly focused on natural cellulose fibers and synthetic fibers, alone or as a mixture [1,2]. The group of studies related to natural cellulose fibers includes all types of wood pulps: mechanical, thermo-mechanical, chemical and semi-chemical from different softwood and hardwood species [3–5]. Also the utilization of recovered paper from different sources e.g. magazines, newsprint, office mix etc., has been studied [6–8].

Furthermore, fibers from non-wood raw materials have been proposed as substitutes in the literature. For example, suggested sources include sisal, banana, straw, bagasse, bamboo, jute, flax etc. [9–12]. Finally, steel, glass or polymeric synthetic fibers constitute another important group of studied fibers. The synthetic fibers include nylon, polyester, aramid, acrylic, polyethylene, polypropylene, etc. [1,2,13,14].

Out of all the sources considered softwood unbleached Kraft fibers are one of the fibers most widely used on an industrial scale because of their strength characteristics, their high availability and the relatively low price.

However, the main disadvantage of using this type of fibers is its vulnerability to chemical decomposition, of certain of the wood chemical constituents, in the alkaline environment of cement. There are many chemical constituents in wood fibers that inhibit cement setting during curing and this topic has been widely studied in the Refs. [15–18].

Another important aspect is that asbestos is a natural occurring fibrous silicate and the fiber's size, together with its chemical structure, makes asbestos very compatible with cement. However, the different chemical composition and the hygroscopic character of the cellulose fibers make the compatibility of the cellulose fibers with the cement much more complex and, therefore, new aspects have to be considered during the manufacturing process. For example, in the Hatschek process, because of the differences between these two fibers it is necessary to use a suitable flocculant.

The right selection of flocculant is crucial in the industrial process because of its effect on mineral fines

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retention, dewatering and formation and, as a consequence, on the overall efficiency of the machine. There are two important problems for the operator known informally as elephant skin appearance and delamination. These two problems can be controlled through proper flocculant selection. Most work in this field has been carried out at mill sites and no public information is available in the references since flocculant optimization is considered, at this moment, as a competitive key issue for this industry.

The most common flocculants used in the Hatschek machines is the group of A-PAMs. They are suitable for improving the productivity due to retention, dewatering and formation improvements. However, mill experiences show that problems in flocculant dosage could lead to a reduction in bending strength properties. The loss in bending strength was first attributed to variability of fiber supply and the inhibiting characteristic of the mentioned compounds e.g. extractives content and composition. However, a more detailed study has shown that the flocculant also affects bending strength properties, as will be explained in the experimental part of this paper.

Different alternatives to improve the mechanical properties of fiber cement composites are described in the references. The influence on mechanical properties of refining degree, fiber distribution in the sheet, presence of inhibitors, fiber length, fiber flexibility, etc. are well known [19–22].

Another approach proposed in the literature to improve mechanical properties of fiber cement composites is the surface chemical treatment of the fibers, with the aim of improving bonding between the fibers and the cement matrix. The first trial involved the use of inorganic compounds, mainly derivatives of titanium. Later, the use of many different inorganic compounds e.g. sodium silicate, potassium silicate, sodium water glass, silica sol, etc. was also proposed. Organic compounds such as acrylic emulsions, alkyl-silanes, etc. have also been reported in the Refs. [23–28].

A patent describing the improvement of fiber cement composites using sizing agents has been recently published. It focuses on the improvement of the fiber cement materials performance against humidity. However, there are no technical or scientific papers in the literature confirming this improvement [29].

Sizing is a common treatment in the papermaking industry used for different paper grades in which liquid penetration resistance is needed. The addition of hydrophobic chemicals to the papermaking furnish in order to reduce the rate of penetration of a liquid, usually water, into the paper structure is known as internal sizing. Surface treatments are also considered in papermaking.

The main sizing agents used on an industrial scale are alkenyl succinic anhydrides derivates (ASA), alkyl ketene dimer (AKD) and rosin. The choice between them is normally based on the limitations related to make-down equipment, retention, hydrolysis, deposition and curing requirements. In recent years polymeric sizing agents have been introduced to the market. They are made combining a latex based polymeric material, for example a styrene-acrylate (SAC) or styrene maleic anhydride (SMA) copolymer with a carrier to produce a product with a hydrophobic component [30–32].

The research described in this paper shows the suitability of using a sizing treatment to improve bending strength properties of fiber cement composites.

2. Experimental

2.1. Materials

Experiments were performed with two different fiber cement suspensions representing the two main process technologies for the production of fiber cement sheets:

- Air cured process: a mixture of highly refined *Pinus radiata* unbleached Kraft pulp, poly-vinyl-alcohol (PVA) fibers and silica fume on a matrix of ASTM Type II cement.
- Autoclave process: refined *Pinus radiata* unbleached Kraft pulp and standard ground silica on a matrix of ASTM Type II cement.

The flocculants selected for this research were three commercial anionic poly-acryl-amides (A-PAM) commonly used in the manufacture of fiber cement products. Table 1 shows their molecular weights and anionic charges.

Finally, the sizing agents were chosen from the most common chemicals used in the paper industry: 1 rosin, 5 styrene-acrylate copolymers (SAC) with different charges and viscosity and 2 alkyl ketene dimers (AKD). Table 2 summarizes their main properties.

2.2. Fiber cement specimen preparation

The specimens were prepared according to an internal standard developed by Uralita as follows. First, a 10 wt.% fiber cement suspension was prepared using different raw materials depending on process. For air cured process a mixture of highly refined *Pinus radiata* unbleached Kraft pulp (3%), poly-vinyl-alcohol fibers (2%) and silica fume (6%) on a matrix of ASTM Type II A cement (89%) was used. On the other hand, for the specimens corresponding with the autoclave process the mixture was 10% of refined *Pinus radiata* unbleached Kraft pulp, 39% of standard ground silica on a matrix of ASTM Type II cement (51%).

After mixing, 1 L suspension was stirred for 45 s in order to obtain a homogenous sample followed by flocculant

Table 1
Main characteristics of studied flocculants

Flocculant	Molecular weight (g/mol)	Anionic charge (meq/g)
A-PAM 1	$7.4 \cdot 10^6$	−1.6
A-PAM 2	$17 \cdot 10^6$	−2.3
A-PAM 3	$7.5 \cdot 10^6$	−0.6

Table 2
Main characteristics of tested sizing agents

	Active ingredient content, (%)	Viscosity, (mPa·s)	pH	Charge density
SAC 1	30	100*	3.7	Cationic
SAC 2	31	50*	5.0	Anionic
SAC 3	30	100*	5.0	Amphoteric
SAC 4	32	150*	3.5	Cationic
SAC 5	30	50*	4.5	Anionic
AKD 1**	16	<50***	3.7	Cationic
AKD 2****	18.5	<50***	3.8	Cationic
Rosin	30	<100	6.0	–

* Measured at 20 °C.
** The active ingredient is AKD-wax.
*** Measured at 25 °C.
**** The active ingredient is AKD-wax and modified rosin.

addition. After 30 s, the mixture was poured into an evacuable casting box of 210 × 80 mm size and evenly distributed over the sieve, used as a filter medium. A vacuum of 250 kPa was applied to dewater the sheet. Finally, an 11 kg weight mold 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 obtained in order to obtain representative values.

The specimens were stored between two steel plates inside a sealed plastic bag until stacks of six were prepared. Then the specimens were stored in a curing chamber with a water-saturated atmosphere for 24 h. Finally, depending on the fiber cement suspensions used specimens were cured in saturated water with respect to cement until the flexural test for the specimens corresponding with the air cured process or in an autoclave for 9 h, at 9 atm steam pressure and 180 °C previously to the time in saturated water for the specimens corresponding to the autoclave process.

To study the effect of the sizing agents, two different sequences were used: the pre-treatment of the cellulose fibers with the size products for 1 min or the addition of the sizing agent, as an additive, at the same time as the flocculant.

2.3. Property measurements

The bending strength and density were determined after 7 days curing. The test method follows the standard EN 494, modules of rupture (MOR) were measured in center point bending and six replications were used for each test.

3. Results and discussion

3.1. Influence of flocculant dosage

A first set of experiments was carried out in order to determine the effect of flocculant dosage on product properties. It was decided to study the effect of the flocculant used at the mill site, the A-PAM 1, at nine different dosages between 100 to 300 ppm, in order to cover a range wider than that used industrially.

Table 3
Results obtained at different A-PAM 1 dosages

A-PAM 1 dosage (ppm)	Density[a] (g/cm^3)	MOR[a] (MPa)	COD (ppm)
100	1.52 ± 0.01	11.3 ± 1.0	157
125	1.51 ± 0.02	11.1 ± 0.7	133
150	1.51 ± 0.03	11.6 ± 1.1	137
175	1.48 ± 0.03	9.3 ± 0.9	201
200	1.48 ± 0.02	9.2 ± 1.1	151
225	1.48 ± 0.04	9.7 ± 0.6	201
250	1.48 ± 0.03	8.9 ± 1.1	155
275	1.47 ± 0.01	9.4 ± 0.7	122
300	1.48 ± 0.02	9 ± 0.8	109

[a] Results obtained from the average of 6 test specimens.

Table 3 summarizes the obtained results. An important reduction of MOR values, around 20%, is observed for dosages higher than 150 ppm. A slight reduction in density values is also observed. The chemical oxygen demand (COD) from the filtrate water did not increase significantly with the flocculant dosage. This gives a clear indication of the high flocculant retention of the product being the cause of bending strength losses.

To explain the bending strength losses, analysis by infrared spectroscopy (FTRI) was performed on the flocculant in order to identify any potential functional groups that could alter the cement curing process. The infrared spectrum showed the presence of citric acid. This acid has been reported in the references as a retarding agent [33].

Therefore, a second set of tests was performed using 100 ppm of flocculant and different citric acid concentrations (50, 100, 150 and 200 ppm) in order to identify its influence. Results are shown in Fig. 1. As can be observed, the presence of citric acid significantly decreases the MOR values and a 20% reduction was obtained. According to these results the presence of citric acid could be one of the reasons for bending strength reduction.

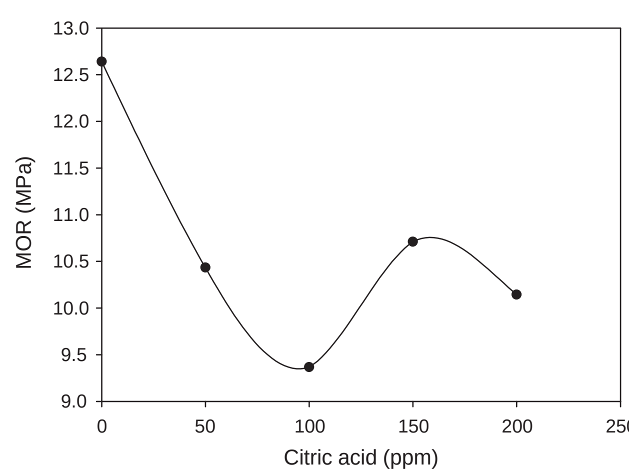

Fig. 1. Influence of citric acid concentration on bending strength properties.

Table 4
Influence of several A-PAM at different dosages

	Flocculant dosage (ppm)	Density[a] (g/cm^3)	MOR[a] (MPa)	COD (ppm)
A-PAM 1	0	1.51±0.02	13.1±0.8	122
	100	1.52±0.03	11.2±0.9	214
	200	1.42±0.01	9.4±1.3	99
	300	1.47±0.03	9.3±0.6	140
	400	1.47±0.02	9.3±0.6	99
	500	1.54±0.03	9.5±1.0	129
A-PAM 2	0	1.51±0.02	13.1±0.8	122
	100	1.54±0.03	13.1±0.7	233
	200	1.51±0.01	10.5±0.5	194
	300	1.52±0.02	10.1±0.7	131
	400	1.47±0.02	8.4±0.5	168
	500	1.47±0.01	8.6±0.6	159
A-PAM 3	0	1.51±0.02	13.1±0.8	122
	100	1.49±0.01	11.2±1.1	218
	200	1.48±0.02	9.8±1.5	151
	400	1.47±0.03	10.3±0.9	190

[a] Results obtained from the average of 6 test specimens.

3.2. Influence of flocculant type

In order to confirm the hypothesis a new set of experiments was performed with other A-PAMs also used in the mills which did not have citric acid in their compositions. Results are shown in Table 4. The main conclusion is that the three anionic poly-acryl-amides tested have a negative influence on bending strength properties. The effects at lower flocculant dosages are more important for the A-PAM 1, probably due to the presence of citric acid. However, a significant bending strength reduction is observed in all cases. This effect could be explained because of the presence of carboxylic groups (see Fig. 2) that give anionic character to the PAM and these functional groups could act as retarding agents.

According to the references hydroxy-carboxylic groups appear to be particularly active in producing retardation. A further analysis of the results obtained for the three tested flocculants justifies this fact, since the lower bending strength reduction is in correspondence with the use of A-PAM 3, being the one with lower charge density (see Table 1) and, therefore, with less carboxylic groups in its structure and consequently with less retardation effect. Higher dosages of A-PAM 2 induce the highest bending strength reduction and this could be justified because of its higher charge density and, as a consequence, the higher number of carboxylic groups [33 34].

However, in order to improve Hatschek machine productivity (retention, dewatering and formation) at industrial level, flocculants are needed but these negative effects should be minimized, avoiding flocculant over dosage through a good flocculation process control. Another alternative is to use new flocculant chemicals in order to overcome the drawback of the actual A-PAM used in the industry or to develop new methods to improve bending strength, e.g. fiber surface treatment.

3.3. Effect of sizing treatment

One solution to increase bending strength properties of fiber cement products is to treat the fibers and balance the negative effect of the usage of A-PAM.

A recently published patent proposes the use of sizing agents to overcome the problems due to the humidity sensitive nature of the fiber cement sheet. However, no scientific or technical papers are in the literature confirming this fact. Thus we decided to study the effect of different sizing agents for the bending strength properties. The main sizing agents used in the paper industry are rosin, alkyl ketene dimer (AKD), alkenyl succinic anhydride derivates (ASA) and copolymers. It was decided to test all of them except the ASA because of its high hydrolysis rate in alkaline medium.

These tests were performed using suspensions from both processes (air cure and autoclave). The results are summarized in Table 5. Comparing these with the reference values, it can be observed that the use of sizing agents can improve the bending strength properties. In general, better results are obtained when fibers are pre-treated with the sizing agents instead of using it as an additive with the flocculant.

For the two processes different sizing chemistry is optimal. The best results for the autoclaving process are obtained when AKD is used as the sizing agent. This fact can be explained by the high temperature in the autoclave which induced the cure needed for AKD sizing. AKD sizing is very slow at low temperatures and required a cure time at high temperature in order to develop sizing. At low temperatures the reaction between the AKD and the fibers is very slow and the sizing properties are not developed. This justifies that AKD does not have a positive influence when the air curing process is used.

On the contrary, polymeric size agents are more easily retained onto the fibers by a combination of electrostatic attraction and hydrogen bonding and they do not require thermal curing. Hence the best sizing agents for the air curing process were the styrene-acrylate copolymers. The best results were obtained for the sizing agents with the lower viscosity (SAC2 and SAC5) and with anionic charge.

Results obtained with rosin are not conclusive and further studies are needed in order to assess its potential suitability. This issue is outside the aim of this paper.

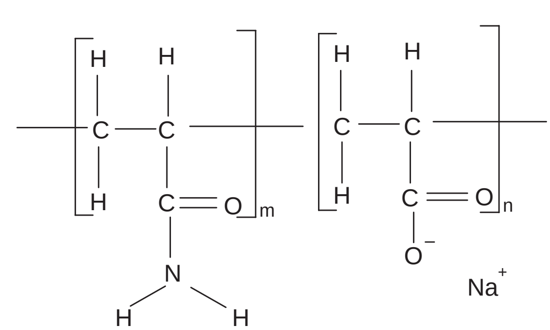

Fig. 2. Chemical structure of anionic poly-acryl-amides.

Table 5
Effects of different sizing agents

	Air curing process				Autoclaving process			
	Fiber pre-treatment		Additive		Fiber pre-treatment		Additive	
	MOR (MPa)	Density (g/cm^3)	MOR (MPa)	Density (g/cm^3)	MOR (MPa)	Density (g/cm^3)	MOR (MPa)	Density (g/cm^3)
Rosin	13.9±0.8	1.51±0.02	–	–	7.1±0.9	1.26±0.08	–	–
Styrene-acrylate copolymers								
SAC 1	12.9±0.3	1.46±0.01	12.5±0.8	1.50±0.02	6.5±0.4	1.22±0.01	6.72±0.09	1.19±0.01
SAC 2	**14.0±0.8**	1.50±0.02	12.4±0.2	1.47±0.02	7.4±0.1	1.20±0.01	6.2±0.3	1.20±0.01
SAC 3	11.8±0.3	1.44±0.03	12.3±0.3	1.45±0.01	6.8±0.4	1.25±0.01	6.2±0.5	1.24±0.01
SAC 4	12.3±0.4	1.53±0.03	12.2±0.2	1.54±0.02	6.1±0.4	1.23±0.02	6.9±0.4	1.22±0.01
SAC 5	**14.7±0.9**	1.52±0.02	14.1±0.2	1.53±0.01	6.6±0.3	1.24±0.01	6.6±0.2	1.24±0.01
Alkyl ketene dymer								
AKD 1	13.5±0.4	1.50±0.02	12±1	1.44±0.03	**7.6±0.5**	1.22±0.03	6.4±0.5	1.23±0.01
AKD 2	11.4±0.9	1.51±0.02	11.7±0.5	1.52±0.01	**7.6±0.1**	1.24±0.01	6.1±0.2	1.22±0.03

	Air curing process		Autoclaving process	
	MOR (MPa)	Density (g/cm^3)	MOR (MPa)	Density (g/cm^3)
Reference	13.1±0.8	1.51±0.02	6.5±0.4	1.23±0.03

Results obtained from the average of 6 test specimens.
Bold data are marked as the best results obtained.

These results open a fascinating line of research in which fiber sizing and cement chemistry for a given fiber type must be optimized in order to improve the strength properties of composites.

4. Conclusions

The anionic poly-acryl-amides used as flocculants in the fiber cement manufacture process with the standard Hatschek machine decrease the bending strength of the product when high flocculant dosages are used. The bending strength reduction is more important when the flocculant anionicity increases because of the higher number of carboxylic groups in the polymer structure. Consequently, new chemicals are needed to increase machine productivity without affecting product quality.

The use of sizing agents increases the flexural strength of fiber cement sheets significantly. The best sizing is different depending on the process technology. For the autoclaving process the use of AKD is recommended while for air cured products the use of styrene-acrylate copolymers gives better results.

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