Effect of kaolin on the performance of PVA reinforced fiber cement

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Abstract. The fiber cement industry can use a wide range of materials as fillers. These fillers are used mostly to reduce costs of the raw materials, but they also can be used to control relevant properties of the product and to facilitate the operation of the Hatschek machines. It is known that fillers may also affect mechanical properties as well as drying shrinkage. There is a large experience on the use of limestone, silica, and fly-ash as fillers. This paper aims at measuring the effect of kaolin on mechanical properties, drying shrinkage, and rheology of PVA reinforced fibrocement. Experimental results compare the reference composition (Portland cement, limestone, cellulose, and PVA fibers) with samples with various amount of kaolin, added as partial replacement of limestone filler. The samples were produced in laboratory using vacuum filtration, which emulates a Hatcheck machine. The rheological behavior of fresh mats was assessed by squeeze flow test. Porosity, drying shrinkage, and MOR were measured by conventional methods. The results show that kaolin increases the plastic deformation of the composite, making the conformation of the products easy. This may be attributed to the plate-like shape of its particles, high specific surface area, and surface charges. The use of kaolin does not change the mechanical properties of the fiber cement.

Introduction

The fiber cement industry can use a wide range of materials with a filling function. It can be used with filler, limestone, silica, fly ash, and other types of pozzolan. These fillers are used mostly to reduce costs of the raw materials, but they also can be used to control relevant properties of the product and to facilitate the operation of the Hatschek process.

It is known that fillers may also affect mechanical properties as well as drying shrinkage. For example, silica can increase flexure strength, but it can also increase shrinkage [1]. There is a large experience on the use of limestone, silica, and fly-ash as fillers in cementitious composites.

Kaolin is an ore that can be found in the nature, and its predominant mineral is the kaolinite (higher amount to 90%). This mineral belongs to the aluminosilicate group.

$$\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O} \xrightarrow{450-700°C} \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 + 2\text{H}_2\text{O}$$

(Eq. 1)

The triclinic crystalline system of the kaolin results in particles with plate geometry [2]. This quality makes a wide influence on the rheological properties of the fiber cement paste. The shape of kaolin particles is expressed in terms of the aspect ratio, which is defined as average diameter divided by thickness [2].

Adding kaolin to the fiber cement can change the parameters of the Hatschek process, such as the particle retention in the Sieve Cylinder, the compression efficiency of the fresh fiber cement, the fresh humidity, molding the corrugated sheets, etc. Besides improving the performance of the products, such as the aspect of corrugated sheets, alteration in hygroscopic movement, decrease of edge cracking [3], etc.
This paper aims at measuring the effect of kaolin on mechanical properties, drying shrinkage, and rheology of PVA reinforced fiber cement.

Methodology

Experimental results compare the reference composition (Portland cement, limestone, cellulose, and PVA fibers) with samples with 7% of kaolin, added as partial replacement of limestone filler. The samples were produced in laboratory using vacuum filtration, which emulates a Hatchek machine.

The ratio of the raw materials used on samples made in the laboratory is representative compared to fiber cement products industrially produced in Brazil, with 70.0% of cement, 25.1% of filler, and 4.9% of organic fibers (PVA and cellulose pulp). The samples were produced by the method suggested by Savastano [4], whose principle is the same as the one involved in the Hatschek manufacturing process, which is filtering a reactive suspension followed by compression (compression pressure: 1 MPa) (Fig. 1).

The rheological behavior of fresh mats was assessed by squeeze flow test. The squeeze flow test consists in compressing the sample fiber cement and applying a fixed load of 500 N in a puncture to 2.54 cm of diameter. This test measures the deformation in the compression. 20 measurements for each sample were made (5 measurements for specimen with 200x200 mm).

The kaolin effect on cement hydration kinetics was measured by isothermal calorimetry. This test was made at 23°C, with cement paste, limestone, kaolin, and water, with a 0.4 water/solids ratio. This equipment measures the heat released by chemical reactions in cement.
Porosity was determined by Archimedes’ principle, which determines the dry mass, immersed mass, and saturated mass of samples.

\[ P = \frac{m_{sat} - m_{dry}}{m_{sat} - m_{im}} \]  

(Eq. 2)

Where: P – porosity [%]; M_{sat} – saturated mass [g]; M_{dry} – dry mass [g]; and M_{im} – immersed mass[g].

Drying shrinkage was calculated by measuring the length and mass of samples when exposed in a controlled environment, with relative humidity of 50% and temperature of 23°C.

The mechanical performance of the fiber cement was measured by the flexural strength test. From this test, it was determined the modulus of rupture (MOR) and the limit of proportionality (LOP), which is the maximum load of the elastic period.

\[ MOR = \frac{P_{\text{máx.} \, L}}{b \cdot e^2} \]  

(Eq. 3)

\[ LOP = \frac{P_{\text{lop.} \, L}}{b \cdot e^2} \]  

(Eq. 4)
Where: \( P_{\text{max}} \) – maximum test load (N); \( L \) – distance between the supports (135 mm); \( b \) – width of the sample [mm]; and thickness of the sample [mm].

The raw materials were characterized by means of laser particle size distribution assays, BET specific area, and density of He gas pycnometry. Images were made from SEM to characterize the kaolin.

**Results**

**Materials characterization.** The materials used in this study were:

- Ordinary Portland Cement (OPC) \( \rightarrow \) Portland cement type CPII F-32 (according to the Brazilian standard NBR 11578 [6])
- Limestone filler
- Cellulose pulp
- PVA fiber

The cement chemical composition used is shown in **Erro! Fonte de referência não encontrada.**

<table>
<thead>
<tr>
<th>Material</th>
<th>( \text{SiO}_2 )</th>
<th>( \text{Al}_2\text{O}_3 )</th>
<th>( \text{Fe}_2\text{O}_3 )</th>
<th>( \text{CaO} )</th>
<th>( \text{MgO} )</th>
<th>( \text{SO}_3 )</th>
<th>( \text{Na}_2\text{O} )</th>
<th>( \text{K}_2\text{O} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPC</td>
<td>18.7</td>
<td>4.13</td>
<td>2.85</td>
<td>64.5</td>
<td>5.44</td>
<td>2.10</td>
<td>0.11</td>
<td>0.91</td>
</tr>
</tbody>
</table>

Among the materials that make up the cement matrix of fiber cement samples, limestone has a higher particle size (most frequent diameter of 55 \( \mu \)m). The cement has the most frequent diameter of 22 \( \mu \)m. The kaolin is the thinnest raw material, with the most frequent diameter of 3.6 \( \mu \)m (Fig. 5).

![Fig. 5. Particle size distribution of the raw materials.](image)

**Table 1. Chemical composition by XRF [%].**

<table>
<thead>
<tr>
<th>Material</th>
<th>( \gamma ) [g/cm(^3)]</th>
<th>( S_{\text{BET}} ) [m(^2)/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cement</td>
<td>3.154</td>
<td>1.59</td>
</tr>
<tr>
<td>Kaolin</td>
<td>2.613</td>
<td>8.91</td>
</tr>
<tr>
<td>Limestone</td>
<td>2.730</td>
<td>1.15</td>
</tr>
</tbody>
</table>

In addition to the smaller size particles, kaolin shows a surface area higher than other materials, with 8.91 m\(^2\)/g compared to 1.59 e 1.15 m\(^2\)/g of cement and limestone, respectively (**Erro! Fonte de referência não encontrada.**).

The large surface area comes from the geometry of kaolin, presenting plate format. The micrographs shown in Fig. 6 and Fig. 7 confirm this geometric aspect of kaolin. In Fig. 6, it is possible to observe agglomerates of kaolin particles having smaller thickness in one of its direction. Fig. 7 shows a SEM of limestone, when particles are larger and with geometry like cubes.
The results of thermogravimetry show that kaolin has 92.36% of kaolinite, because the loss of volatile (chemically combined) water at around 550°C was 12.89%.
Hydration kinetics. Being an aluminosilicate, the chemical composition of kaolin is compatible with a pozzolanic material. However, in order to react with cement, it is necessary that the kaolin not be 100% crystalline. To measure the reactivity of kaolin in the first hours of hydration, isothermal calorimetry tests were made in different kinds of pastes containing different amounts of kaolin in their composition (from 0% to 25.2% by mass).

The results shown in Fig. 9 indicate that there was no significant difference in the accumulated heat after 72 hours of hydration. The kaolin does not react chemically with the cement during the first hours of hydration. However, the pozzolanic reaction can occur over time, and it is possible that there be a chemical interaction between the kaolin and hydrated cement matrix.

The only change observed due to the addition of kaolin in the cement paste was a delay in the start of setting time, or early acceleration period (period of rapid precipitation of C-S-H and portlandite). At lower levels (up to 7%), the beginning of the acceleration period can take up to 13 minutes more to happen. In most kaolin content tested (25.2%), this time was 49 minutes (Fig. 10).

The precipitation of C-S-H and portlandite occurs when the reactive suspension reaches a supersaturation level of Ca$^{2+}$ ions. The addition of kaolin to replace limestone reduces the amount of calcium suspension, and it also reduces the pH, this way delaying the start of setting time.
Rheology properties. The kaolin has characteristics that strongly influence the rheological behavior of the pastes. The small particle size, the extensive surface area, and plate geometry make the pastes require more water to flow. The acting surface forces the adsorption of water between the particles, facilitating their movement.

A sample of cement with kaolin showed lower resistance load, with more deformation for an applied load of 500N. This result shows that fiber cement containing kaolin has lower viscosity at this shear rate level. The viscosity of the paste can be determined by the maximum strain or load relaxation. Fig. 12 shows the correlation between load relaxation and compressive extension, furthermore the sample with kaolin showed higher compressive extension and higher load relaxation.

The dispersion with kaolin was more difficult because this material tends to agglomerate due to its affinity with water. Therefore, the results with kaolin have shown more variability.
Shrinkage. The shrinkage is an important property of fiber cement, especially due to a recurring industrial problem, which is the differential shrinkage on the edge of the corrugated plates, generating cracking.

Studies show that the addition of fine materials in the cementitious matrix may increase the shrinkage \([1],[7]\). However, the results show that the kaolin did not change the shrinkage of fiber cement (Fig. 13).

Fig. 12. Correlation between load relaxation and compressive extension.

Fig. 13. Drying shrinkage results.

Fig. 14. Shrinkage susceptibility.
The relationship between shrinkage and mass loss during drying indicates susceptibility to shrinkage of fiber cement, i.e. it shows that for the same mass loss, two samples may have different shrinkage. Fig. 14 shows that the susceptibility to shrinkage of both samples is similar, indicating that the kaolin did not alter this property of the fiber cement.

The total shrinkage of the cement depends on the porosity and pore size distribution of the cement matrix [8]. This is because shrinkage is a function of the amount of water stored in the material, and function of the pore size distribution, since the shrinkage is caused by capillary pressure acting on pores smaller than 2 µm.

The total porosity of the cement sample was smaller in the sample with kaolin than in the reference sample, but this difference is small and within the range of the variation of results, as shown in Fig. 15.

The kaolin promoted a refinement of the fiber cement pores, with decrease in pore volume between 2 and 20 µm. However, these changes are not reflected in shrinkage, since the pores of this size do not suffer from capillary pressure drying.

![Fig. 15. Total porosity by Archimedes’ principle.](image1)

![Fig. 16. Mercury intrusion porosimetry.](image2)

**Flexural strength.** The mechanical strength of the fiber cements was measured by the flexural strength test. The modulus of rupture (MOR) and the limit of proportionality (LOP) were determined for this test.

The differences in flexural performance of the reference samples and kaolin were few, always within the standard deviation of the average range for the MOR, LOP and elastic modulus. However, it was observed that the kaolin has improved mechanical strength of fiber cement in all cases (Fig. 17 and Fig. 18).
The kaolin increased the rigidity of the matrix, with an increased modulus of elasticity. The paste strength also increased, indicated by the higher LOP sample containing kaolin. The maximum resistance indicated by the MOR was also higher in the sample with kaolin, indicating the potential of improving the mineral addition in fiber cement strength.

Fig. 17. Flexural performance of fiber cement REF (left) and fiber cement with kaolin (right).

Fig. 18. Flexural performance of fiber cement. MOR, LOP, and elastic modulus.

Conclusions

According to the results presented, it can be concluded that the use of kaolin fiber cement influences its rheological properties positively. It improves the flow conditions, which may be reflected in an improvement in the appearance of products, ease of conformation (reduction in longitudinal cracking), better efficiency in compression, and a decrease in the permeability of the products.

The kaolin did not significantly change the cement hydration kinetics. The increase in the setting time when using kaolin at 25% is 49 minutes. However, this added amount of kaolin is very high. In the lower content, benefits to the rheological properties have been achieved, and the change in hydration kinetics was minimal.

The shrinkage of the cement was not changed, although pore refinement was observed. This behavior occurred because changes in pore size distribution happened in the upper pores of the 2 µm range, and this pore range did not suffer capillary pressure drying.

The flexural strength increased with the addition of kaolin, due to the increased stiffness of the cementitious matrix, LOP, and MOR.
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**References**


