LATEST INSIGHTS TO INTEGRAL TREATMENT OF FIBERCEMENT WITH SILICONES

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ABSTRACT

Fibercement boards are globally used for a large variety of applications in the building industry. The replacement of asbestos by cellulose and synthetic fibers has led to higher process and formulation complexity and specific challenges, such as water permeability issues, due to the poorer adhesion between cement and the organic fibers.

Hydrophobic agents, especially silicones, have a proven track record to reduce the water absorption of fibercement boards and help to maintain the original product properties for a long period of time. Beyond the well-introduced surface treatment of the boards after production and curing, the integration of the water-repellent agent during the production process gains acceptance in the market, since the whole bulk of the board is treated, and no pre-curing or any post treatment at the job site is required. Being a complex material with both organic and inorganic components many different aspects need to be considered when an integral treatment in a fibercement production is put in place, especially the interaction between the silicone and the cement particles.

Recently new, tailor-made silicone-based chemicals for the integral treatment of fibercement boards have been developed and introduced into the market. The different aspects of integral treatments shall be discussed and key findings on silicone chemistry in fibercement processing shall be presented.

KEYWORDS:

Fibercement; Silicones; Integral treatment; Hydrophobic agents.

INTRODUCTION

Reinforcement of cementitious-based materials with fibers has been widely used in the construction industry worldwide for many years (Johnston, 2014). Asbestos was the dominant fiber in this field, especially for the fabrication of the so-called Fiber Reinforced Cement Boards and Corrugated Sheets (FRC), which contained around 10% of asbestos. However, by the end of the 20th century, asbestos has been banned in many countries due to its hazards to human health, leading to the development of modern technologies in the fabrication of FRC, which consisted in the use of natural (cellulose) and synthetic (PVA and PP, majorly) fibers as replacement of asbestos (Quang & Kien, 2010).

The successful introduction of these modern technologies lead to higher process and formulation complexity and also to challenges in the properties of the final boards. The increased porosity create a tendency for higher capillary water uptake, which is the major cause of pathologies such as salt efflorescence, reduced dimensional stability (due to swelling and shrinking cycles), reduced freeze/thaw resistance and even water leaking, in some critical cases.

Silicone chemistry is worldwide used since the beginning of 1960’s as the most effective chemistry in water uptake reduction. It is employed at several fields in the construction industry such as coatings, concrete, red-clay ceramic, cementitious mortars, insulation materials (mineral wool, perlite, aerated lightweight concrete, expanded clay), gypsum-based materials and also FRC (Tomanek, 1990). In FRC applications, silanes and siloxanes are used in diluted forms, either dissolved in solvent or as emulsion, and applied over the material surface as a topical treatment to reduce the water uptake. On the other hand, water repellent additives that can be added as an ingredient in the Fibercement slurry are not well stablished. When using such technology, process is simplified and also provides an improved protection system, as the whole bulk of the material is protected and not only its surface. This paper focuses on the development and the performance of a silicone resin called SILRES® BS 1703, especially designed to be used in FRC integral treatment.

SILICONE CHEMISTRY

Silanes are molecules based on one single silicon atom with four chemical substituents. Especially alkyl trialkoxy silanes are used in hydrophobic additives as they have good reactivity towards surfaces of many mineral substrates, as they are rich in silanol groups. The aliphatic alkyl group provides the hydrophobic character to the treated substrate. Longer alkyl chains, such as iso-octyl, helps providing excellent resistance to alkalinity. After hydrolysis and condensation, silanes create a silicon resin network, which is chemically bonded to the substrate, providing long lasting and outstanding water uptake protection performance (Pachaly et al, 2005). The structure after the reaction and its protection against water can be observed in Figure 1.

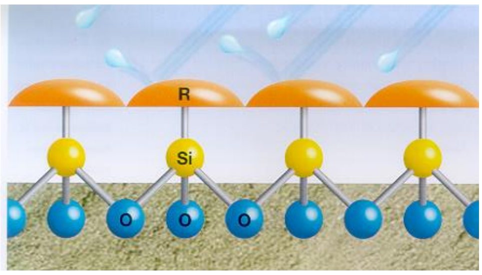

Figure 1 – Structure formed after the reaction between alkyl trialkoxy silanes and mineral substrates and the provided protection against water

Alkyl trialkoxy silanes also quickly react with water forming silanol groups, which will react within themselves, losing its capacity to react with the mineral substrate. Therefore, when used as an additive in a fiber-cement slurry, it tends not to provide the same expected performance as observed in topical treatment.

Silicone resins are obtained by a sequence of controlled hydrolysis and condensation reactions of silanes, creating branched siloxanes structures of increased molecular weight. These structures contain the same alkyl groups from the original silane, but a smaller amount of reactive alkoxy groups per silicon unit; therefore having a lower reactivity and lower susceptibility to react with water, being able to be used as a FRC integral treatment agent. A representation of a part of silicon resin structure, after hydrolysis and condensation of silanes, is described in Figure 2.

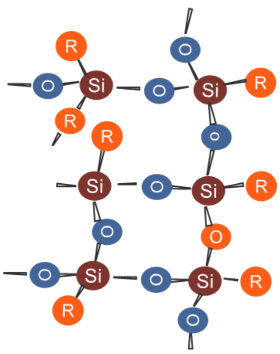

Figure 2 – Representation of a part of a silicon resin structure, after hydrolysis and condensation of silanes

To have the right silicone molecular structure is essential for an optimal usage in a FRC board integral treatment. Silanes tend to react fast with water, being less susceptible to react with the cementitious phase and allowing a concentration over time on the process water. Polymers of higher molecular weight does have a lower reactivity with water and provide a more efficient water uptake reduction, but deposits over the cement particles and impact its reaction with water, harming the mechanical properties of the FRC board.

IMPACT ON CEMENT SETTING

One of the main differences between a silicone for topical and integral treatment is that when used as an additive in the slurry, cement setting is in a very initial stage and therefore, any physical deposition over the cement particles will result in a delay on the cement hydration reaction.

The impact of the different additives over the cement setting was measured calorimetricly using an adiabatic calorimeter and cement pastes, containing OPC Type CP II-F-40 (in accordance to Brazilian Standard ABNT NBR 11578), which has between 6 and 10% of carbonate material as filler, and 40% water content (w/w). Silicone additives were added during the cement paste mixing in a 0,2% of silicone actives dosage (vs. cement dry weight). Reference material without any silicone additive was compared to a silicone emulsion widely used in surface treatment and 3 silicone resin products (Silicone Resin I, Silicone Resin II and Silicone Resin III) with different molecular weights (and therefore different reactivity due to the amount of reactive alkoxy groups). The composition of the Silicone Resins cannot be disclosed due to ongoing patenting process. Heat measurements over time are described in Figure 3 and Peak time results are described in Table 1.

Silicone Resin I did not affect significantly cement setting time, while the other 2 silicone resins and the silicone emulsion did so; Silicone Resin III did it in a minor way. The different silicon polymer composition in the 3 analyzed Silicone Resins and in the Silicone Emulsion, mainly catalyst and molecular weight distribution, can be mentioned as the cause of the delay in cement setting. In the case of the Silicone Emulsion, the emulsifier also contributes to this effect.

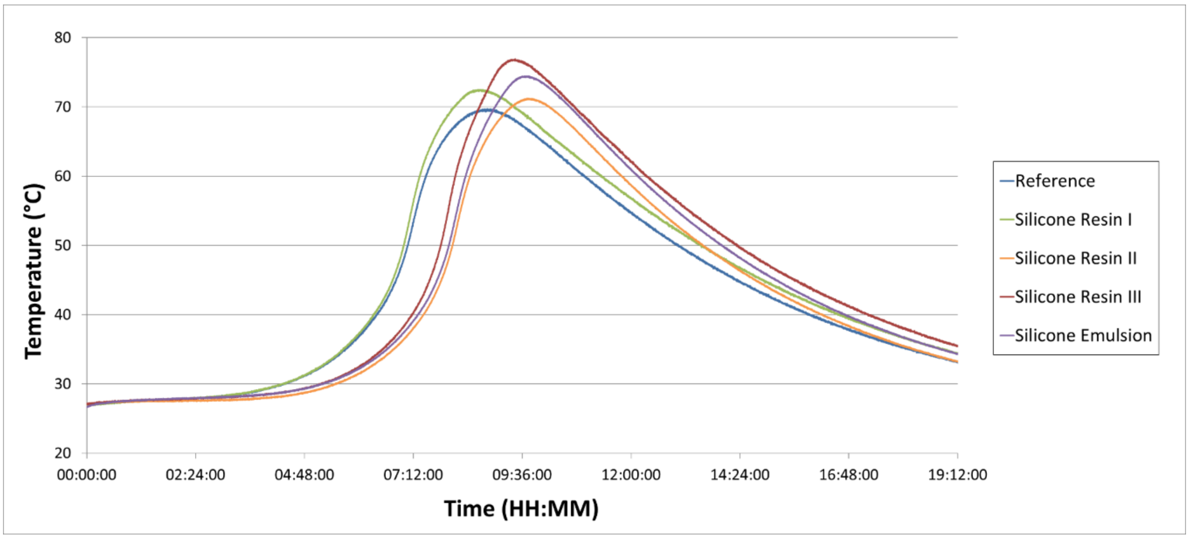

Figure 3 – Calorimetric Trials: Heat measurements over time for different silicon additives added to a cement slurry

Sample	Peak Time (HH:MM)
Reference	09:02
Silicone Resin I	08:45
Silicone Resin II	09:51
Silicone Resin III	09:36
Silicone Emulsion	09:50

Table 1 – Calorimetric Trials: Peak times for the different silicone additives added to a cement paste

EVALUATION ON FRC MINI-HATSCHEK PROCESS

Process and Method

Evaluation trials were conducted on a mini Hatschek Machine plant at Eternit Brasil.; curing conditions employed were typical air curing. Formulations were produced in a mixing tank and added to a storage tank, which feeds the mini Hatschek machine. Before any new formulation trial started, the content in the storage tank was drained and it was refilled with the new formulation, to avoid the need to wait for additive build-up in the formulation. Process measurements were done at constant intervals and corrections to the process were minimized to ensure comparative results. Initial FRC material produced in each batch were discarded until the machine produced stable layers. Samples of 250x250x6 mm were produced and wrapped with plastic films after production, only opened at the required test intervals of 7, 14 and 28 days.

Figure 4 reflects the process data for the different trials. Solids retention (in %), settling (in mL/1 L/3 min), green sheet density (in g/cm3) and moisture content (in %) were analyzed and are described in Figure 4.

From the collected data it is clear that the process parameters were all under control during the trials and that no significant changes were observed with the addition of the hydrophobic silicone additive.

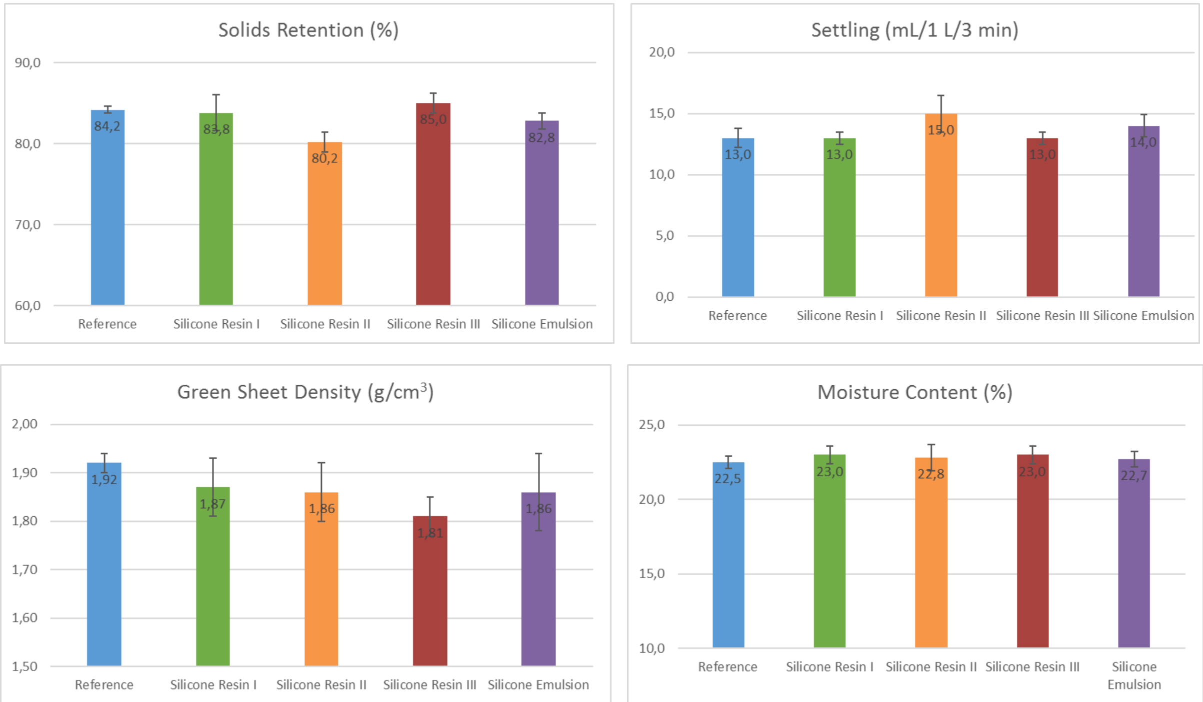

Figure 4 – Process data recorded during the production of FRC Boards in Mini-Hatschek machine

Water absorption

Water can penetrate a porous substrate by two different mechanisms: by forced ingression (commonly in heavy rains) and by capillarity (when substrate is wet, after rain or dew). Protection levels will be different depending on the mechanism evaluated. The FRC boards were cured for 28 days prior to the analysis. For forced ingression, a 4 mL Karsten tube was attached to the surface of the board and filled with water; volume of water absorbed was analyzed after 1, 4 and 24 hours exposure. For capillarity, a methodology similar to EN 1062-3 was applied, positioning the FRC board over a water saturated sponge and weighting it over time (after 1, 2, 3, 6 and 24 hours) in order to determine the amount of water that ingressed through the FRC pores. Figures 5 and 6 presents the water absorption results obtained for forced ingression and capillarity, respectively.

In forced ingression, there are 2 silicone resins that provide outstanding water uptake progression: Silicone Resins I and II, with results below 1 mL after 24 hours. In longer periods (24 hours), Silicone Resin III and Silicone Emulsion do not provide significant improvements in the water uptake, even if in shorter periods (lower than 4 hours) their effectiveness is good. In capillarity evaluations, there is a clear differentiation between the 4 analyzed silicone additives and a trend can be observed: Silicone Resin I being the most effective product in water uptake reduction, followed by Silicone Resin II, Silicone Resin III and Silicone Emulsion.

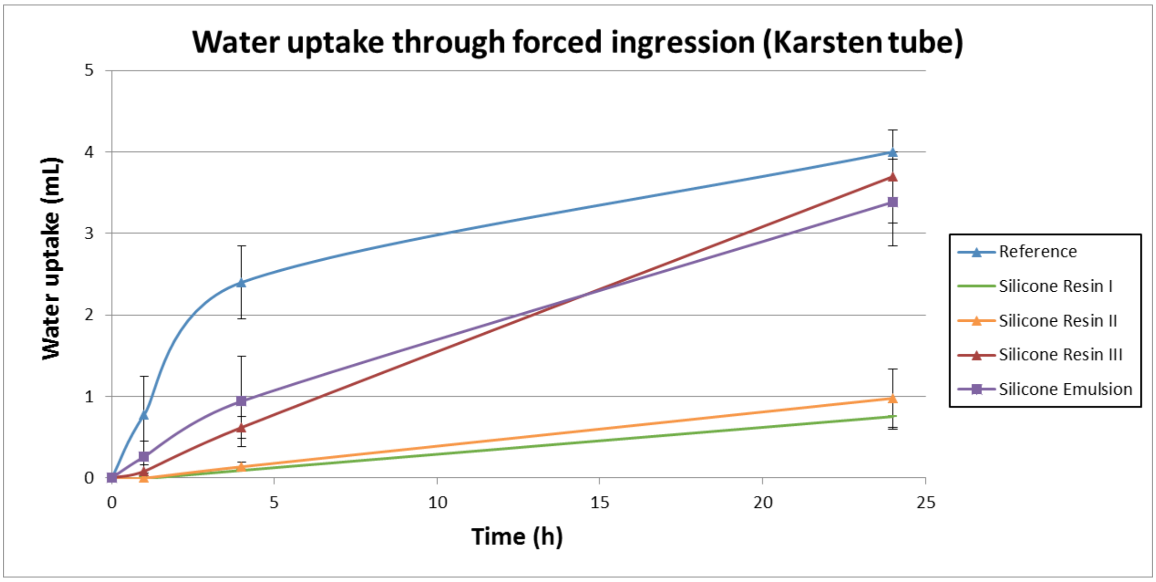

Figure 5 – Water uptake through forced ingression results

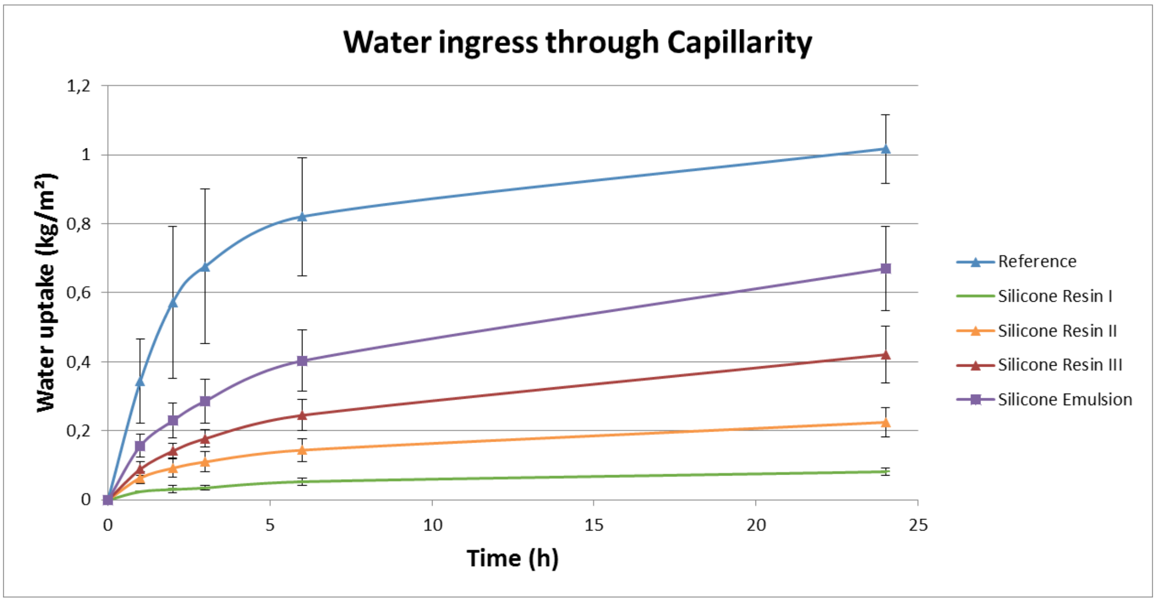

Figure 6 – Water uptake through capillarity

Flexural Strength

Flexural strength was measure in accordance to ABNT NBR 15498. The boards were totally immersed in water for 24 hours prior to the evaluation. The results of Module of Rupture build-up over increasing setting ages (7, 14 and 28 days) are described in Figure 7 and the Module of Rupture and Fracture Energy after 28 days curing are described in Figure 8.

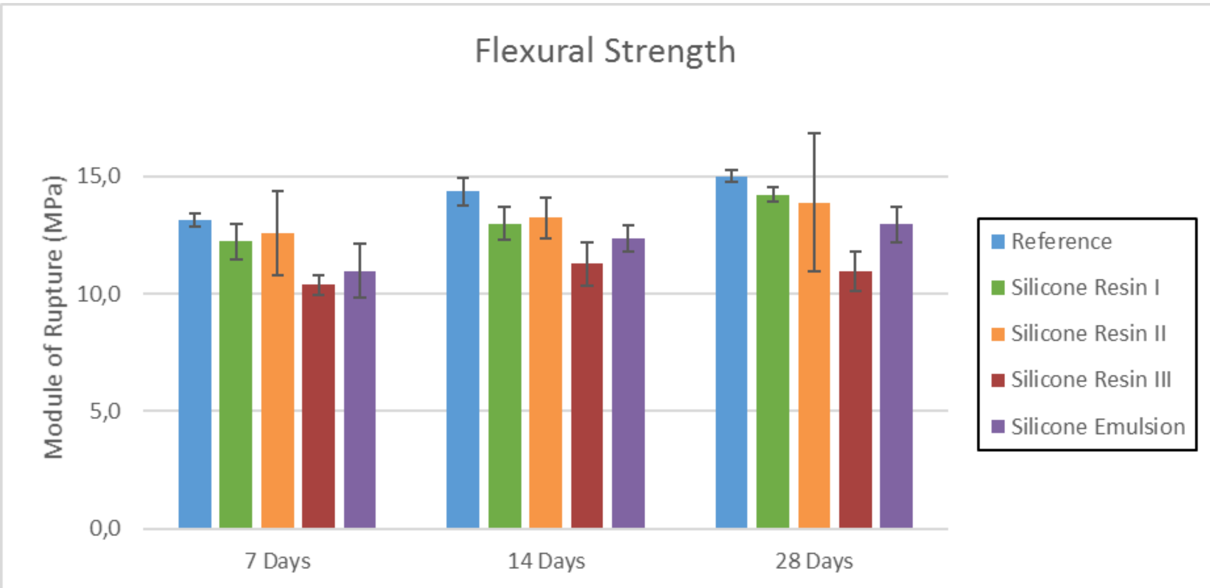

Figure 7 – Results of Module of Rupture obtained in different ages for the different silicone additives evaluated

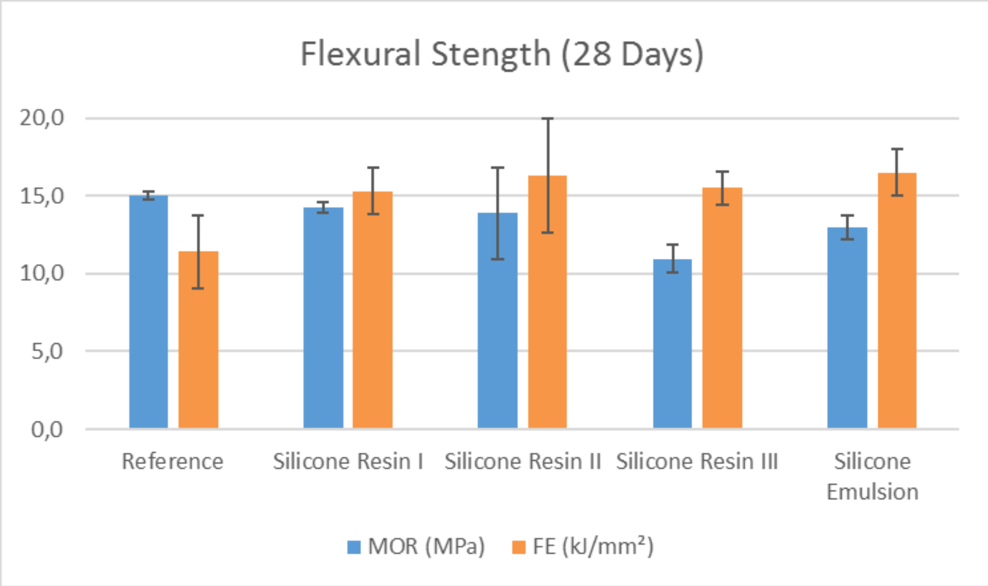

Figure 8 – Results of Module of Rupture and Fractural Energy obtained for the different silicone additives evaluated after 28 days curing

Silicone Resin I and Silicone Resin II impacted the flexural strength in a diminishment of less than 10%, while for Silicone Emulsion this impacted was in the level of 15% and for Silicone Resin III, it was in the level of 20%. This has a good correlation with the obtained results for cement setting impact, where the silicones additives that impacted more the cement setting time provided lower flexural strength resistance; the exception for this trend is for Silicones Resin II, which provided the biggest impact in cement setting but marginal impact on flexural strength. The increase in the results of fractural energy, in kJ/mm2, is an indication of the board increased toughness, where the addition of a silicone hydrophobic agent grants the FRC board the ability to absorb more energy before fracturing.

IMPACT OF SILICONE ADDITIVE DOSAGE VARIATION

The combined results of cement setting impact, Hatschek process variations, water uptake reduction and flexural strength impact allow us to define that Silicone Resin I is the most recommended product to be used as an additive for integral treatment of FRC boards and corrugated sheets. Therefore, a new study, considering a variation in the dosage of additive, has been conducted. Additive dosages varied from 0,1 to 0,3%. The results obtained for cement setting impact are described in Figure 9 and peak times are described in Table 2. Figures 10 and 11 presents the water absorption results obtained for forced ingression and capillarity, respectively. Finally, results of Module of Rupture build-up over increasing setting ages (7, 14 and 28 days) are described in Figure 12 and the Module of Rupture and Fracture Energy after 28 days curing are described in Figure 13.

Additionally in this second study, contact angle was measured, by using optical equipment Phoenix-I from SEO. Results obtained are described in Figure 14.

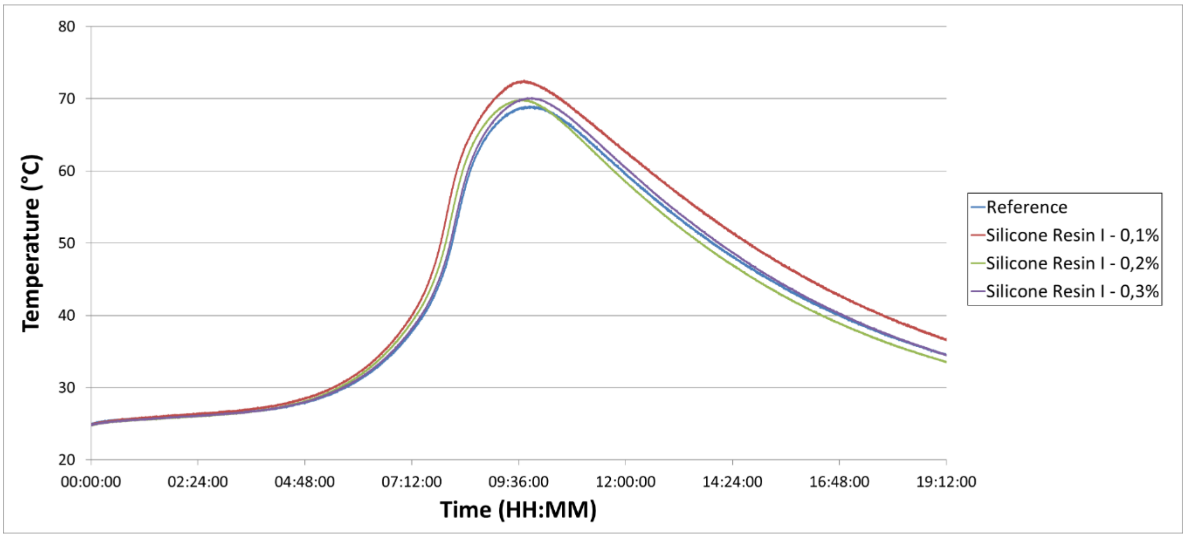

Figure 9 – Calorimetric Trials: Heat measurements over time for different dosages of Silicone Resin I added to a cement slurry

Sample	Peak Time (HH:MM)
Reference	09:50
Silicone Resin I – 0,1%	09:43
Silicone Resin I – 0,2%	09:44
Silicone Resin I – 0,3%	09:53

Table 2 – Calorimetric Trials: Peak times for the different dosages of Silicone Resin I added to a cement paste

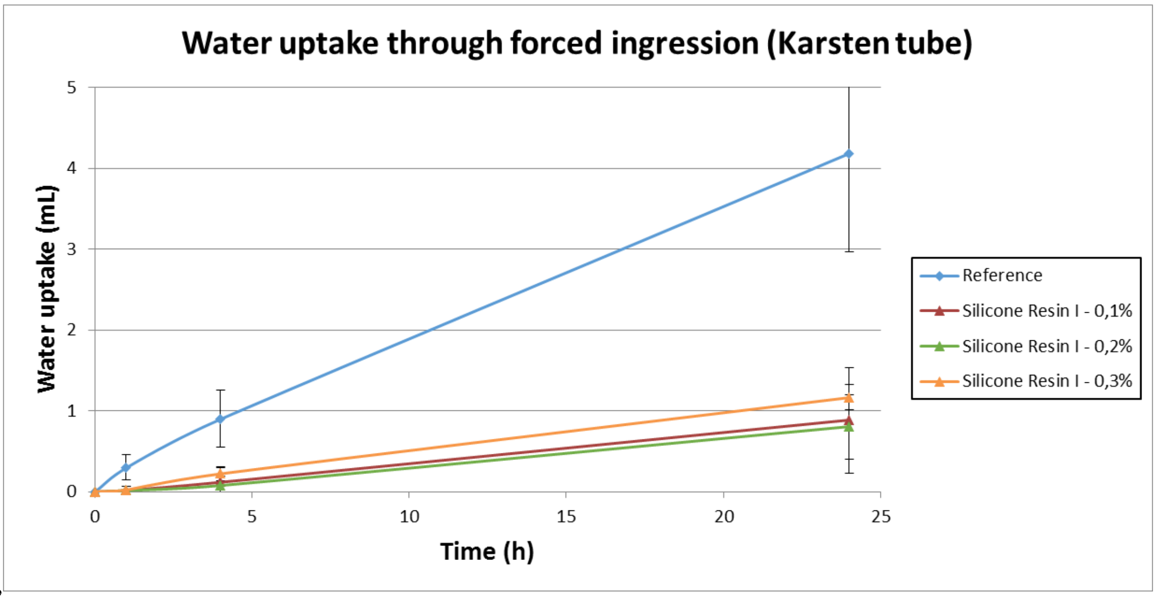

Figure 10 – Water uptake through forced ingression results for samples with different dosages of Silicone Resin I

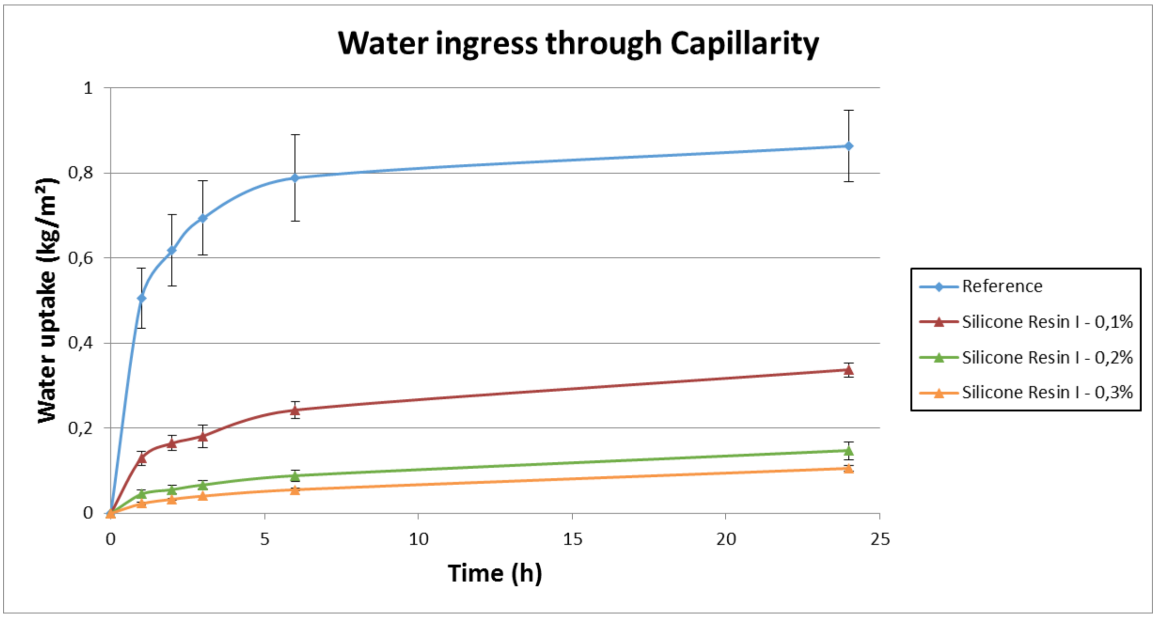

Figure 11 – Water uptake through capillarity with different dosages of Silicone Resin I

Dosage variations of Silicone Resin I did not impact the cement setting time, which indicates that this performance parameter is linked to the silicone additive chemistry type and not by its dosage. The same behavior of not majorly impacting the results have been observed also on the flexural strength. The dosage, on the other hand, performed a key role on the water uptake results, especially on water uptake through capillarity; dosages of 0,2% on weight or higher provided water uptake reduction of more than 90% compared to the blank reference, while 0,1% dosage only provided a 70% reduction. On forced water ingression, evaluated through Karsten tube, no difference was observed when varying dosages in the levels adopted. This indicates that, in order to chemically modify the big pore size structures in FRC boards in an effective way, a certain level of silicone addition should be reached, and over this level, no extra improvement is observed. In the formulation and Hatschek process parameters studied in this paper, the optimal dosage was 0,2% on weight over the total solids; to other formulations and process parameters, the optimal value will vary, but should be in the range of 0,1-0,5%.

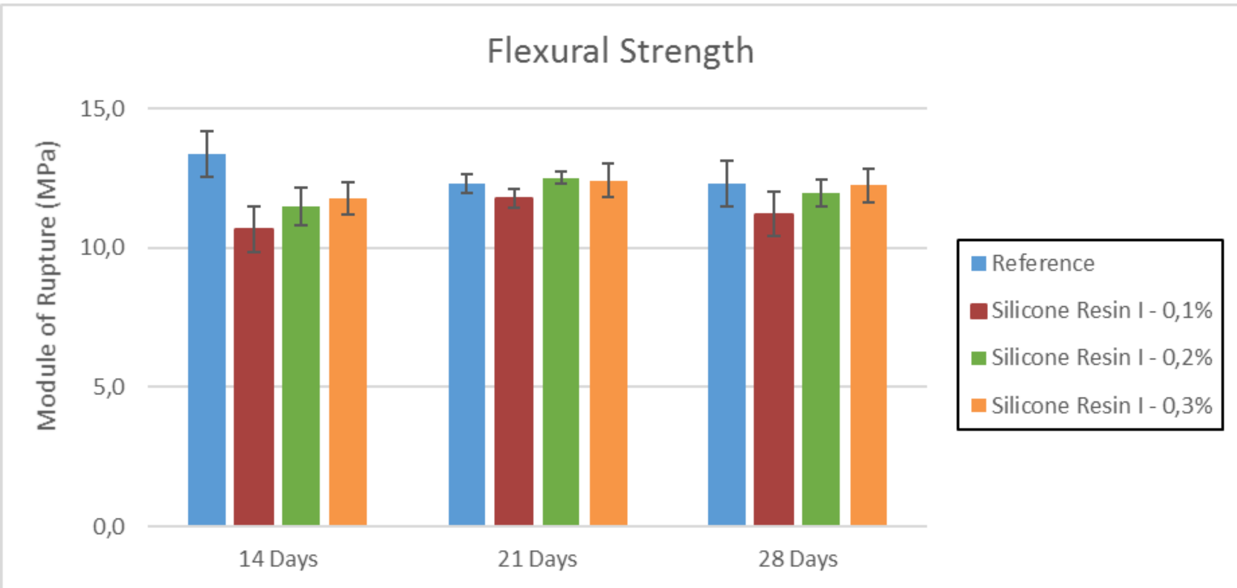

Figure 12 – Results of Module of Rupture obtained in different ages for the different dosages of Silicone Resin I evaluated

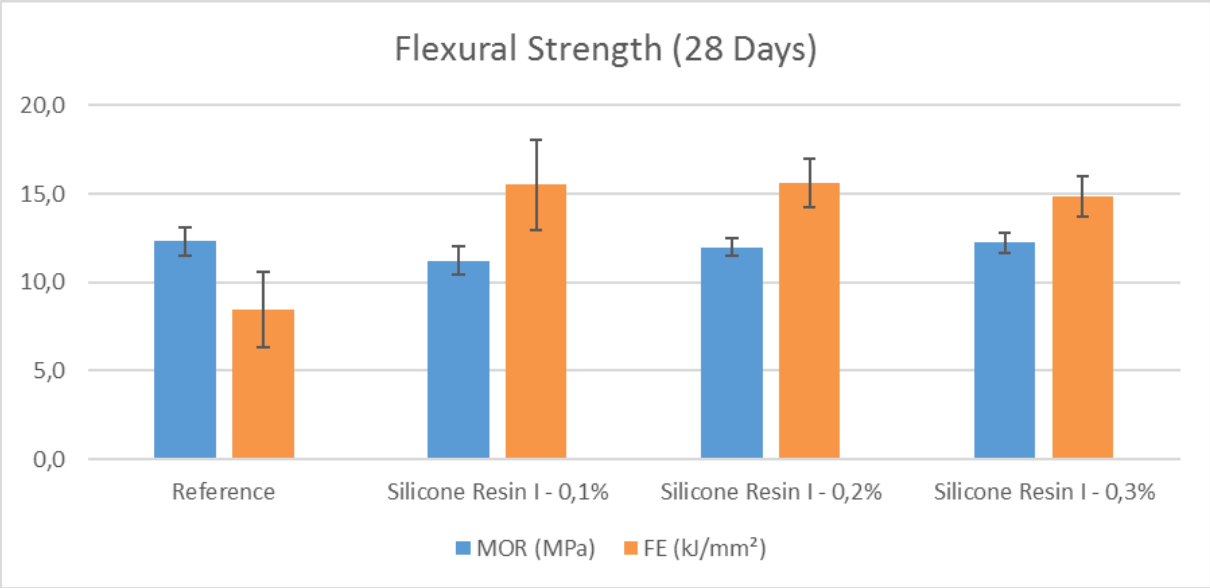

Figure 13 – Results of Module of Rupture and Fractural Energy obtained for the different dosages of Silicone Resin I evaluated after 28 days curing

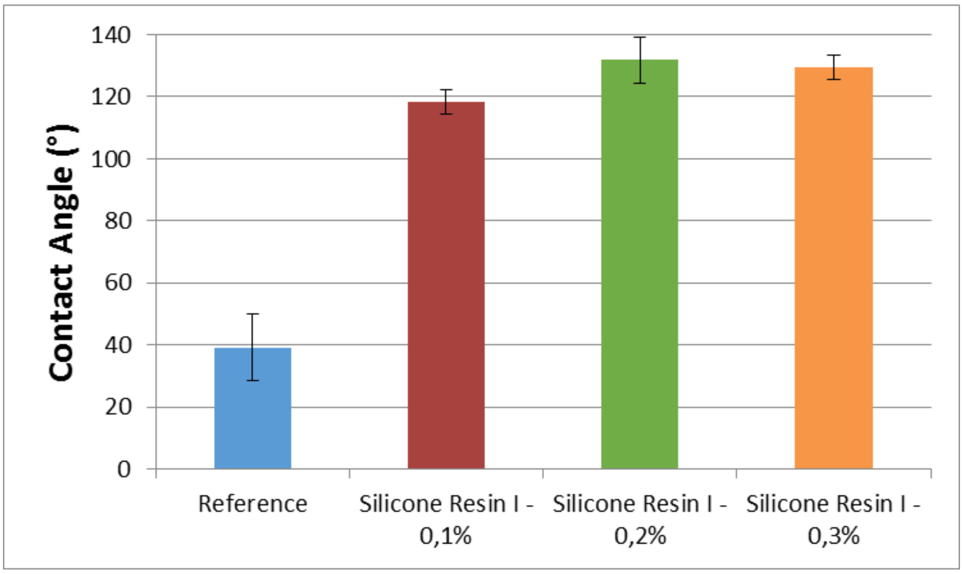

Figure 14 – Measurements of contact angle for FRC formulations with different dosages of Silicone Resin I

CONCLUSION

Silicone Resin I, now available under the product name SILRES® BS 1703, is a new silicone resin additive to be used as an integral treatment additive for FRC boards. It has been designed to have the right molecular weight distribution in order to balance its reactivity and water solubility, having minimum impact on the cement setting time and therefore on the mechanical strength of the modified FRC board. It is also stable under heat and pressurized conditions, being able to be used in either air or autoclaving curing processes.

It has been proved that the material has a chemical composition that enables an efficient chemical modification of the big pore size structures present in FRC in low dosages addition level, in the range of 0,1-0,5% on weight over total solids. This modification can provide a reduction in the water uptake of the FRC boards of more than 80% in comparison to the blank reference, which enhances the quality of these materials, by reducing the occurrence of efflorescence, improving the dimensional stability (by reduction in swelling and shrinkage cycles) and the freeze-thaw resistance, and also avoiding the occurrence of leakages, in some critical cases.

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