

1. Introduction

The use of Self-Compacting Concrete (SCC) requires a certain care in its mix design and production, demanding a strict control over the choice of materials and their variability during the process. It is important to include a high content of fines and/or the use of a viscosity modifier, which makes the mixture more stable and consequently less susceptible to segregation during the entire process of transport and casting.

Viscosity modifying admixtures (VMAs) are basically water-soluble polymers, which may be based on acrylic or glycol, cellulose, biopolymers and inorganic agents. Their function is to make the mixture more homogeneous and cohesive, replacing the fines of the concrete and reducing the discontinuities due to granulometric variations. The VMA increases the viscosity and the yield stress of the mixture by constructing a three-dimensional structure, consequence of the interaction of the functional groups of the molecules with the water and the surface of the fine materials (EFNARC, 2006). In this interaction, dispersion in water is the main mechanism. The VMA uses the effect of the superplasticizer of leaving more free water in the mixture, and its polymer chains bond in the free water to promote the viscosity increase.

When it comes to the flow properties of the cementitious materials, the yield stress is considered the main intrinsic parameter of the material that is associated with concrete workability, as well as its subsequent ability to maintain shape stability (ROUSSEL et al., 2012; MARCHON et al., 2018). Concerning cement paste, the flocculation due to attractive interaction between cement grains and the growth of hydration products at those grains' contact points are the main mechanisms responsible for yield stress. (REITER et al., 2018). It is also worth noting that the cementitious matrix must be cohesive to prevent segregation and bleeding during the flow (MARCHON et al., 2018). Thus, when choosing admixtures that act on the flow properties of the material, such as VMAs, it is of utmost importance to understand how the admixture will interact with the material and change those flow parameters.

Prior to the application in concrete, the development of a new admixture often begins with a compatibility study that is carried out in smaller scale. Generally it starts with a cement paste and

sometimes progress to the study in mortars before the application in concrete itself. James et al. (2016) made use of the Marsh's Cone test with cement pastes to investigate the compatibility of an admixture with different cement brands of varying chemical composition for SCC; Shrivastava and Kumar (2016) made use of the same test method with cement pastes to test the compatibility of different water reducing admixtures with different cement brands prior to implementation in concrete; von Daake and Stephan tested the kinetics of retarding admixtures for concretes starting with tests on cement pastes; Zuo et al. (2017) also started testing cement pastes to investigate the effects of a novel polymer-type shrinkage-reducing admixture.

Especially when discussing rheology, the tests with cement pastes seem to provide a good prediction of the behavior of the concrete. Barrak et al. (2009) demonstrated the existence of a good correlation in the performance of cement pastes and concrete with relation to the amount of admixtures and rheological properties. The author highlight that by studying the cement paste it is possible to understand the influence of different components on its flowability leading to an optimization in the production of concrete.

In terms of developing new materials, the current scenario of the construction industry demands for more eco-environmentally friendly solutions. In this regard, the use of natural polymers would have an added benefit. Its use provides a lower water consumption, since mixtures containing a smaller quantity of fines have a reduced surface area. They also form a kind of weave that supports the aggregates, thus improving the segregation and bleeding of concrete (TUTIKIAN and DAL MOLIN, 2008).

Additives based on biopolymers act on the free water of the mixture. They are not adsorbed by the fines of the mixture and do not interfere in the adsorption of superplasticizers, which makes them more recommended for concretes where better flowability and viscosity are expected, such as the self-compacting concrete (FIORENTIN, 2011). Biopolymers are polysaccharides produced from microorganisms or raw materials from renewable sources, such as sugar-cane and corn, usually obtained by fermentation processes. Even when at low concentrations, they can produce viscous solutions and gels in aqueous media. Their use has been growing in relation to the usual

polymers, due to the current environmental awareness, preservation of the limited resources and more rigid taxes to discard and recycle materials that are not biodegradable in nature, such as biopolymers (BRITO et al., 2011; SILVA et al., 2006). There are several classifications of the biopolymers according to the raw material and the biodegradability, among them, within the group of biopolymers of regenerable, biodegradable materials of animal origin, is the chitosan.

Chitosan is an amino polysaccharide derived from the deacetylation process of chitin, which constitutes the largest fraction of exoskeletons of insects and crustaceans, being thus assumed to be the second most abundant organic compound in nature (ASSIS & SILVA, 2003), leaving behind only cellulose. The waste from marine crustaceans, for example, has a large amount of chitin, around 20%, and it is estimated that the annual worldwide production of this substance is approximately 10^{10} - 10^{12} tons (GORTARI & HOURS, 2013), which illustrates the level of the positive environmental impact of reusing such residues.

The use of chitosan is very broad and has been increasing daily, being used as an auxiliary substance to slimming, in the treatment of water (removal of metal ions and reduction of odors), agriculture (fertilizer and defence mechanisms) and in the cosmetics industries (toothpaste and treating acnes), food (cholesterol reducer and preservative sauces), biomedical (surgical sutures and bone reconstruction) and biopharmaceutical (anticoagulant and antitumor) (Azevedo et al., 2007, Silva et al, 2006).

A few publications were found with the application of chitosan-based products in cementitious materials. TKEN-C (1982) possess a patent for a cationic polymer for spraying concrete or mortar, where the chitosan is used to increase viscosity without clogging spray pipe. Jeon et al. (2008) investigated the use of chitosan to avoid the recrystallization of de-icing salts. Duan et al. (2011) presented a process for the preparation of amphoteric chitosan as water reducing admixture for concrete.

Melo et al. (2006) studied a cementitious paste based on Portland cement and the powder form of chitosan and evaluated mechanical properties of this cement matrix to be used in operations

at elevated temperatures in oil production. They observed increments of up to approximately 40% of the compressive strength values and up to approximately 91% to the tensile strength in comparison to a reference paste without the chitosan.

Lasheras-Zubiate et al. (2011) used chitosan as a complexing agent for heavy metals and viscosity modifier agent and found that the highest molecular weight chitosan showed the greatest effectiveness in a combined role as heavy metal retainer and thickener.

Santos Filho et al. (2012, 2013) studied a chitosan-based composition as a corrosion inhibitor for reinforced concrete. They observed reductions of approximately 70% in the corrosion current in Tafel polarization tests, and an increase of about 70% in the value of the load transfer resistance, by the Impedance technique in tests on steel electrode, in a solution of saturated calcium hydroxide.

Vyšvail and Žižlavský (2017) also studied a chitosan composition and its effects on the flow behavior of cementitious mortars. The mortars with chitosan were plastic and thixotropic and had an increase in yield stress and consistency. Therefore they related the similarity of the viscosity enhancing effect to the utilization of starch ether.

In this context, this paper describes the production of a viscosity modifying agent based on chitosan solution and its efficiency, initially tested in cement pastes. The study represents the initial step into the production and optimization of a new composition to be used as a viscosity modifying agent for concrete.

2. Materials and Methods

Portland cement type CP-II-F-32 (contains 11-25% of limestone filler, in compliance with the Brazilian standard NBR 16697 (ABNT, 2018)) was used as binder, a polycarboxylate type superplasticizer (Glenium 51, solid content of 30%, BASF, Brazil) and an in-house developed biopolymer composition as the viscosity modifier agent (BP) were also used. The chemical composition of the cement, as determined by the producer, is shown in Table 1.

2.1. The viscosity modifier agent (BP)

The viscosity modifier was prepared by solubilizing the chitosan in a solution of acetic acid 0.5 M (LISBOA, 2011). The chitosan had a deacetylation degree of 98.18%. The acid acetic had a density of 1.05 g/ml, 99.7% purity and molar mass of 60.05 g/mol. For the preparation of 500 ml of BP, 15.06 g of acetic acid and 8.5 g of the chitosan were used. The final solution had a solid content of 1.67% and the total time for a single production was 24 hours.

2.2. Experimental program

Cement pastes were produced with a constant water-to-cement ratio of 0.5 and dosage of superplasticizer of 0.35% (over the mass of cement). The set of mixtures was composed by a reference mixture without BP and four other mixtures with increasing amounts of BP over the mass of cement (0.1%, 0.2%, 0.3% and 0.5%). The mixture compositions are detailed in Table 2. For all mixtures, the amount of mixing water was determined taking into account also the water content of both the superplasticizer and the chitosan solution. The dosages of both admixtures were calculated considering their solid content.

A planetary mortar mixer with vertical axis and maximum volume capacity of 2 L was used. The following mixing procedure was adopted:

- cement and 80% of the water – mixing in slow speed for 30 s;
- mixing in high speed for 1 min;
- resting for 3 min;
- addition of superplasticizer and the remaining water – mixing in high speed for 1 min.

The influences of the new admixture on the workability of cement pastes was evaluated by means of rheological and so-called traditional techniques. A viscometer with concentric cylinders (model DV III Ultra by BROOKFIELD ENGINEERING LABORATORIES) was used for the rheological measurements. The following test routine was applied:

- prior to the beginning of the tests, a pre-shearing was performed. A shear rate in the range from 0 to 65.1 s⁻¹ was applied during a time interval of 70 s;

- the first part of the experiment was performed under a crescent shear regime. The shear rate was applied in the range from 0 to 186 s⁻¹ with a variation of rotation speed of 5 rpm every 10 s, until a maximum rotation speed of 200 rpm;
- a resting time of 15 s during which the mixture remained under the action of the maximum shear rate;
- the last part consisted of a descending shear regime. The shear rate was reduced from its maximum value to zero following the same rate used in the crescent rate regime.

The values of plastic viscosity and yield stress were obtained based on the model of Bingham, also used by Paes Junior (2011) for studying the flow behaviour of similar cement paste mixtures. Tradition flow tests were also performed. The Marsh's Funnel was used to evaluate the flow time of the mixtures. The test consists of measuring the time for the flow of 500 ml from a 1000 ml cement paste specimen poured inside the Funnel. A size 9 nozzle was used at the end of the funnel, in compliance with the Brazilian standard NBR 7682 (ABNT, 1983).

The flow table test with a mini truncated cone was also performed. The truncated cone had a base with 80 mm diameter, a height of 40 mm and a top surface diameter of 70 mm. The test proceeds right after the filling of the mini truncated cone, with the slowly vertical removal and following flow of the mixture. After achieving a stable flow, the final spread diameter was measured in two perpendicular directions. The test followed and adaptation of the Brazilian standard NBR 13276 (ABNT, 2002). Similar methods have been also applied by Bouvet et al. (2010) and Tregger et al. (2008).

3. Results and discussion

The addition of BP caused an increase in the flow time of mixtures in comparison with the references. With the dosage of BP in the range between 0.1 and 0.3% the increase varied between 18% and 26%. With 0.5% of BP on the other hand, the increase was more relevant (157%). The plastic viscosity of the mixtures followed the same trend in behaviour, being even more pronounced with 0.5% of BP (Figure 1).

During the tests with the viscometer, the reference mixture and the one with 0.1% of BP presented a plastic viscosity and yield stress below the measurement range of the equipment, which is why the values are not shown in Figure 1 and Figure 2. The flow spread of the mixtures was reduced with the addition of the BP, which is also reflected by an increase in the yield stress (Figure 2).

The performance of BP can be compared with results of other materials found in literature. Figure 3 and Figure 4 show the effect of BP in comparison to the addition of a filler material to cement pastes studied by Tenorio Filho and Melo (2017) in terms of flow spread and Marsh's funnel tests. In their study the authors used powder of marble and granite as a filler material to control the segregation and improve the flow of fluid cement pastes. The filler material was added to the mixtures with the dosages of 43%, 67% and 100% in relation to the mass of cement. Those mixtures were produced with the same cement, same superplasticizer type (and dosage) and same w/c ratio as the ones in the current paper.

All mixtures with the addition of BP presented a high flowability with no indication of bleeding or segregation. The addition of mineral filler had a stronger effect on the viscosity of the mixtures in the range of dosage adopted by the authors. When comparing both materials one can conclude that until a dosage of 20% the addition of mineral filler is very effective as a viscosity modifying agent. However, for values above that threshold the increase in the flow time of mixtures is too high and leads to mixtures with a very discontinuous flow. On the other hand, the addition of BP until a dosage of 0.2% promoted the production of mixtures with a high flowability and stability.

Figure 5 compares the effects of BP pastes with chitosan etherified derivatives and two commercial VMAs studied by Laberas-Zubiate et al. (2012). The mixtures were produced with a w/c ratio of 0.5 and the references present a similar flowability in comparison to the one used in this study (201 mm and 226, respectively). The values in the graph represent the slump measured in comparison with the reference mixture of both studies. The chitosan derivatives used by Laberas-Zubiate et al. (2012) were hydroxypropylchitosan (HPCH) and hydroxyethylchitosan (HECH). The commercial VMAs were hydroxypropylmethylcellulose (HPMC, Hercules HPMC HK 15 M®) and hydroxypropyl guar gum (HPG, Lamberti Quimica S.A., ESACOL HS-30®).

The BP behaves in-between the commercial products for a dosage until 0.2%, having stronger effects on the flow spread for dosages above this value. In comparison with the chitosan derivatives, the native chitosan in the form of BP can be considered to be more efficient and less dosage dependent. Both HPCH and HECH showed an increase in the flow spread for dosages higher than 0.3%. For these same dosages the authors reported a reduction in the water retaining ability, which could lead to segregation.

4. Conclusions

A new polymeric solution based on the waste material of the fishing industry was presented as an alternative viscosity modifying agents. The use of both rheological and so-called traditional techniques applied proved to be suitable when combined for the assessment of the effects of BP in the cement pastes. The limitations of the equipment in the rheological tests were compensated by the other test methods and the results showed the same trend of behavior in both methods.

The addition of BP in the mixtures up to a dosage of 0.2% showed the expected behavior of a viscosity modifier. The increase in both plastic viscosity and yield stress are desirable features when one is referring to self-compacting concrete. This means that the BP could be especially beneficial for the production of very fluid and yet stable concrete compositions, also the amount of filler materials could be reduced. With dosages above 0.2%, the thickening effects were very pronounced if one aims for the production of a self-leveling mixture. However, the behavior presented in the mixtures with dosages of 0.3% and 0.5% (stronger reduction in the flow spread but yet not much change in the flow time) can be interesting when it comes to mixtures for pumping applications.

The next step in this research is to investigate the effects of BP in concrete compositions. The efficiency of the BP as a VMA is to be compared with commercially available products and its effects on mechanical properties and durability of the concrete are being evaluated. It has to be emphasized the relevance of the work in terms of innovation and contribution not only to the local concrete market but also for the local fishing market, that could benefit from turning its residue

into a valuable by-product. The results already obtained with the research provided input for a request of a patent with the national office of industrial and intellectual property in Brazil (registration number BR102015011030).

Data Availability Statement

All data, models, and code generated or used during the study appear in the submitted article.

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Figure captions

Fig. 1. Plastic viscosity and flow time of the paste mixtures for different amounts of BP.

Fig. 2. Yield stress and flow spread of the paste mixtures for different amounts of BP.

Fig. 3. Comparison of flow spread between mixtures containing the BP and a mineral filler.

Fig. 4. Comparison of flow time between mixtures containing the BP and a mineral filler.

Fig. 5. Flow spread of mixtures containing the BP and commercial VMAs in relation to reference mixtures without VMA.

Table 1. Chemical composition of the cement (as determined by the producer).

Al ₂ O ₃ (%)	SiO ₂ (%)	Fe ₂ O ₃ (%)	CaO (%)	MgO (%)	SO ₃ (%)
4.28	18.30	2.94	61.35	2.49	2.59

Table 2. Composition of the mixtures studied.

Mixture	Cement (kg/m ³)	Water (kg/m ³)	Superplasticizer (kg/m ³)	BP (kg/m ³)
REF1	1223.30	601.66	14.27	0
P1-0.1	1223.30	576.15	14.27	26.77

P1-0.2	1233.30	550.64	14.27	53.54
P1-0.3	1233.30	525.13	14.27	80.30
P1-0.5	1233.30	474.11	14.27	133.84

Figure 1

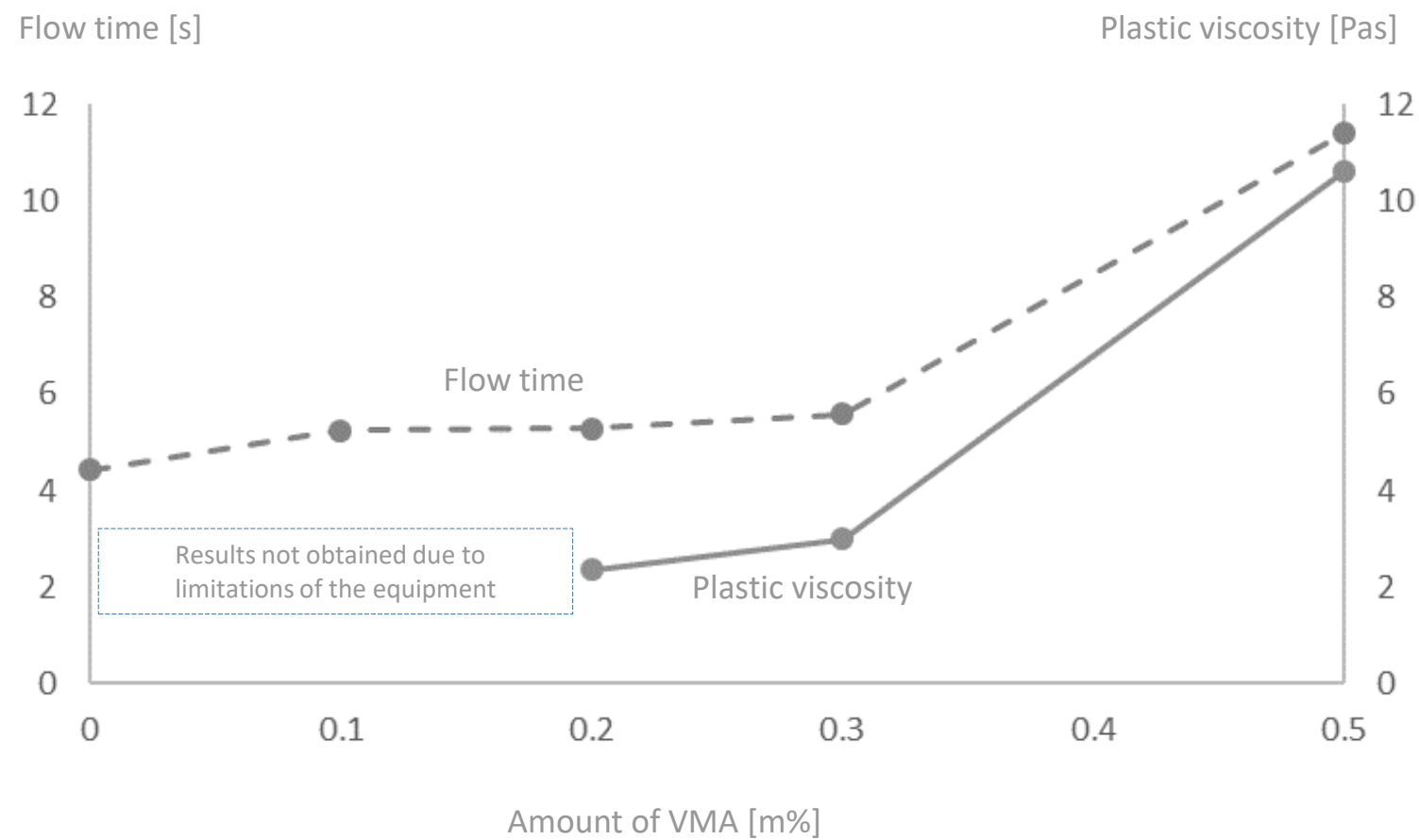
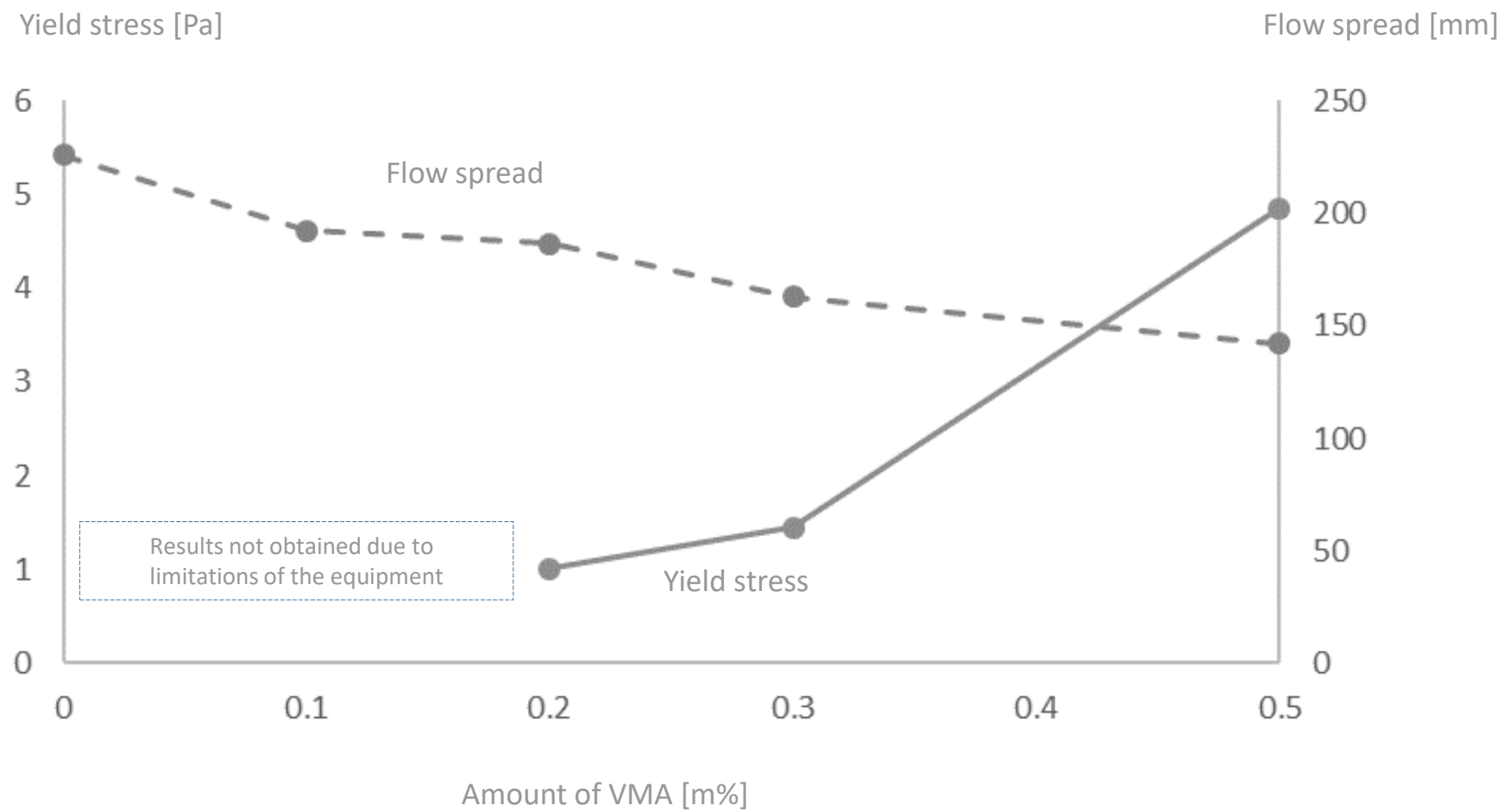
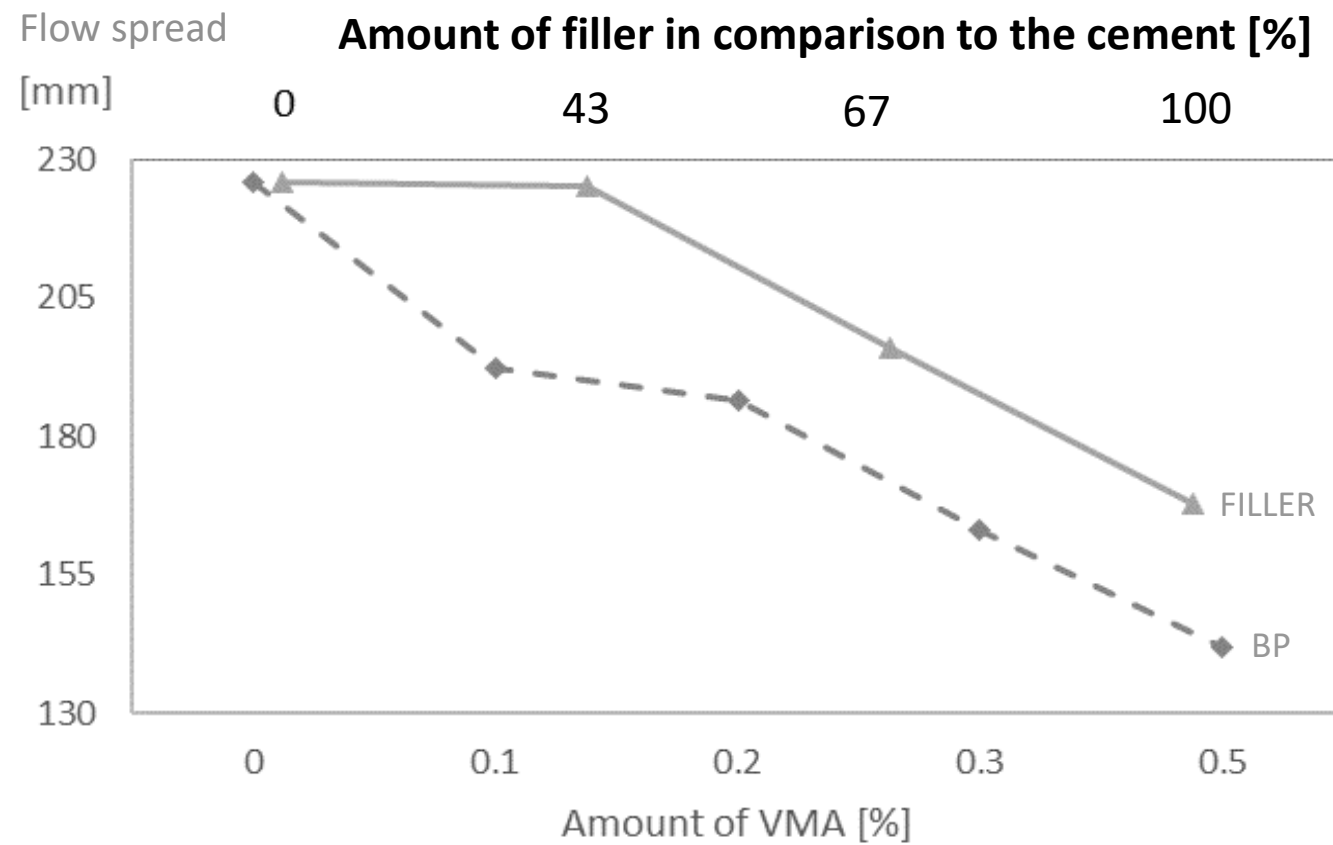


Figure 2





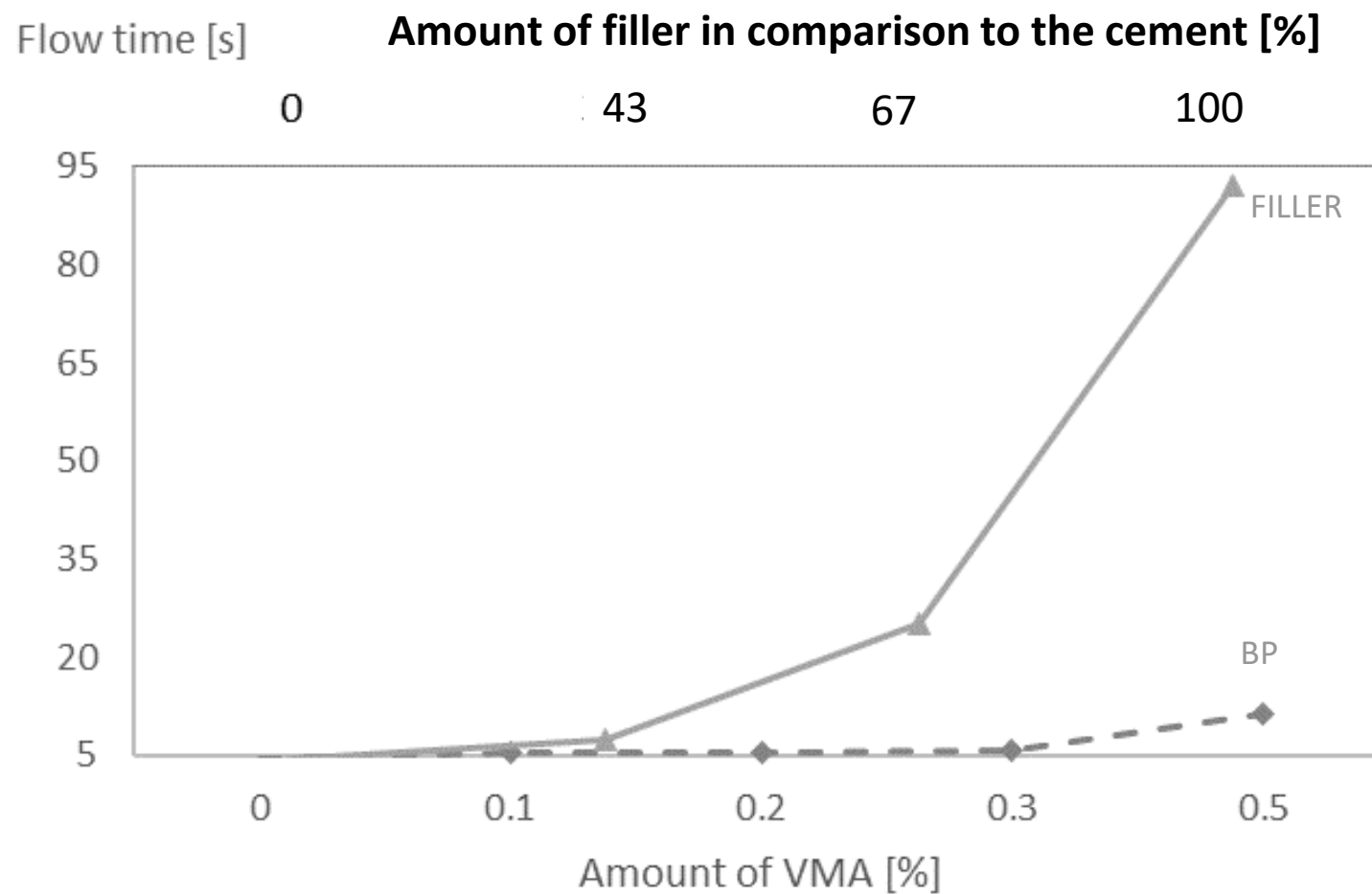


Figure 5

