EFFECT OF VISCOSITY MODIFIER ADMIXTURE ON PORTLAND CEMENT HYDRATION

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Abstract

Significant attention has been given to the development of materials and techniques employed on the additive manufacturing process or also called 3-dimensional printing (3D printing) applied on the construction market. This building technique extrudes cementitious composites to form the contour of the desired geometry. Together with a robotic arm and linked to the blueprints the material is extruded exactly as digitally designed. Therefore, making this building technique a progress on the automation process on the construction industry. In order to have the exact contour as designed for the building, the material used on this application must be developed respecting rigorous rheology parameters. To achieve such high viscosity in cementitious materials, usually viscosity modifiers admixtures (VMA) are employed. One of the commonly used chemical admixtures for this purpose is the hydroxypropyl methylcellulose. However, the consequences of using high content of this admixture in cementitious matrices is still not fully understood. This study characterized the influence of different VMA content on Portland cement paste, by means of a microstructure analysis. The hydration development was assessed, and the influence of the admixture was measured for different curing ages. Important negative side effects were found such as: VMA increasing the cement setting time, different distribution of hydration products on the bulk or increasing the void content. On the other hand, positive effects were also found such as: evidences of internal curing, higher degree of hydration and the lack of undesired hydration products.

1.   INTRODUCTION

A promising construction technique which has drawn notable attention in the past few years was the additive manufacturing (AM). This revolutionary technique is likely to open a new era on the construction industry, optimizing process and materials [1]. AM is a general classification for technologies which fabricates objects with the help of automated equipment, directly from a digital design technology [2], [3]. There are several different techniques to manufacture the objects developed based on AM, such as the powder bedding with an inkjet head [4] or the laser melting [5], and the counter craft technology which employs extrusion techniques to fabricate objects [6]. Both AM technologies builds the object through a layer by layer deposition process. The counter craft AM has drawn a lot of attention in the construction

market as its implementation looks feasible to be applied in large scale for this industry. It should be noted that materials with unique properties need to be developed to meet the mechanical and durability-related demands of a long-lasting and safe structure.

Recent investigations have shown the development of cementitious composites with different aggregate particle sizes. Concrete and mortars have been developed with printable characteristics. In some studies fibres have been incorporated to stabilize the mixture at fresh state or to minimize the occurrence of cracks due to shrinkage. However, the materials and printing methods have not yet delivered solutions to improve the composites hardened performance when loaded in tension [7], [8].

Moreover, researchers have addressed this problem developing a technique to produce mortar filaments through AM reinforced by a steel wire. Higher ductility was achieved with samples reinforced by the steel wire. Further, more research is needed to enhance the interface bond between the wire and the mortar [9].

Another strategy to increase the ductility of printed brittle materials is the incorporation of fibres. Great plastic deformations can be achieved on cementitious composites reinforced by fibres namely, strain hardening cementitious composites (SHCC), for instance. This type of composite can deliver high tensile strain, strength, higher frequency but smaller multiples cracks during tensile loads [10].

SHCCs are cementitious composites reinforced by high volume of fibres. Usually the reinforcement level is around 2% of the total composite's volume, which brings challenges regarding the flowability of such mix designs. An alternative often approached to enhance the fibre dispersion and even thought keep a high flowability is the employment of viscosity modifier admixtures (VMA) [11]. These admixtures are usually composed by a long organic chain with -OH ramifications, that "arrest" the free water on the mixture through hydrogen intermolecular bridge. One of the most used VMA is composed by Hydroxypropyl methylcellulose (HPMC) [12]. In addition, the use of VMA is also a key factor while developing a printable cementitious composite. The right tune of the amount of the chemical admixture, coupled with a good distribution of the grain size of the particles employed on the matrix, and optimum water-to-solid ratio may lead towards a material with the needed viscosity for printing.

Besides the fact that VMA can help on the controlling of the rheology properties of a solid suspension, the consequences on the microstructure of hydrated Portland cement is not yet fully understood. The influence of some water-soluble polymers on the microstructure development of Portland cement was investigated by [13]. They have shown a delay on the hydration process, formation of unusual minerals at early ages, a slightly lower $Ca(OH)_2$ content and a higher amount of chemically bound water. Furthermore, the cement hydration delay was explained with the influence that HPMC has on the precipitation of calcium hydroxide, the polymer's absorption capacity [14]–[16], and the methyl content [17]. Moreover, a study have also reported the influence of molecular weight on the rheology of cement paste modified by HPMC admixture and its potential to combine via intermolecular and intramolecular crosslinks with Ca^{+2} ions [18].

The present research aims to build a better understanding to the consequences of HPMC use in cement paste. This information together with the literature already available, contributes to a better understanding to the new generation of construction materials which are under development to be applied on 3D printing.

2. EXPERIMENTAL METHODS

Microstructure characterization of cement paste for different curing ages and VMA content were studied. Chemical composition of the Ordinary Portland Cement (OPC) CEM I 42,5N

and its loss on ignition (LOI) can be found on Table 1. They were assessed by X-ray fluorescence analysis (XRF) and thermogravimetric analysis (TGA) performed at 10°C/min under Argon atmosphere. The LOI was calculated using the loss of mass between 45 and 1000°C.

Table 1: Chemical composition of Portland Cement.

Compound	CaO	SiO_2	Fe_2O_3	Al_2O_3	SO_3	MgO	K_2O	TiO_2	P_2O_5	Rest	LOI
CEM I 42,5 N [wt. %]	69.53	15.6	3.84	3.09	2.6	1.67	0.55	0.31	0.14	0.53	2.14

VMA is composed by HPMC with viscosity 201000mPa.s was provided by Shanghai Ying Jia Industrial Development Co., Ltd. The samples were cast mixing a volume of 0.5 litres in a planetary mixer (HOBART) according to the following procedure:

- All dry materials were mixed for two minutes at speed 1;
- While mixing at speed 1, during approximately one minute, the water was added;
- The wet powders were steered for the next two minutes at speed 1. In this phase it is possible to observe a significant change in the mixture's viscosity. A dough like consistence is achieved;
- At speed 2, the dough like mixture is further mixed. At this phase the dough opens on the mixing bowl.

A reference cement paste with a water-to-cement ratio of 0.3 (REF) and three levels of VMA, 0.1, 0.3 and 1% of the cement weight, named 1M, 3M and 10M respectively were evaluated. The mixed paste was cast on plastic containers and sealed with the help of paraffin paper. Right after moulding they were left for 24 hours rotating around their own axis to ensure a homogenous material avoiding any segregation. With the exception of 10M samples, afterwards, they were demoulded and cut in slices of approximately 5mm and the followed curing time was done in a curing room at (20 ± 2)°C and relative humidity of (98 ± 2)%. 10M samples could be demoulded and cut only after 48 hours after the casting.

To stop cement hydration the cut slices were manually crushed in small particles and partially submerged on liquid nitrogen for 3 minutes and completely submerged for 5 minutes. Immediately after, crushed particles were conditioned on plastic bags with holes to allow the release of moisture from the samples and stored in a freeze drier for further drying. Those samples were used on the TGA tests. Stopping hydration employing liquid nitrogen was chosen for TGA tests, as [19] reported formation of carbonate like minerals at high temperatures in samples where solvent exchange technique was used. The small cut slices destined to electron microscopy observations, X-ray diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR) had their hydration arrested by solvent exchange procedure, employing ethanol.

3. RESULTS

Before the description of all results found for evaluated specimens it is important to show that the VMA employed was investigated under electron microscope, TGA and XRD. The results from these tests have demonstrated that the chemical admixture suffers of a small volume of sodium chloride impurity.

3.1 Isothermal calorimetry test

On Figure 1 the result from the isothermal calorimetry test is reported. The increasing volume of viscosity modifier on the cement paste, lead towards delaying Portland cement hydration. The greatest consequences were measured on pastes with 1% of VMA, where the dormant stage was prolonged up to 9 hours of hydration.
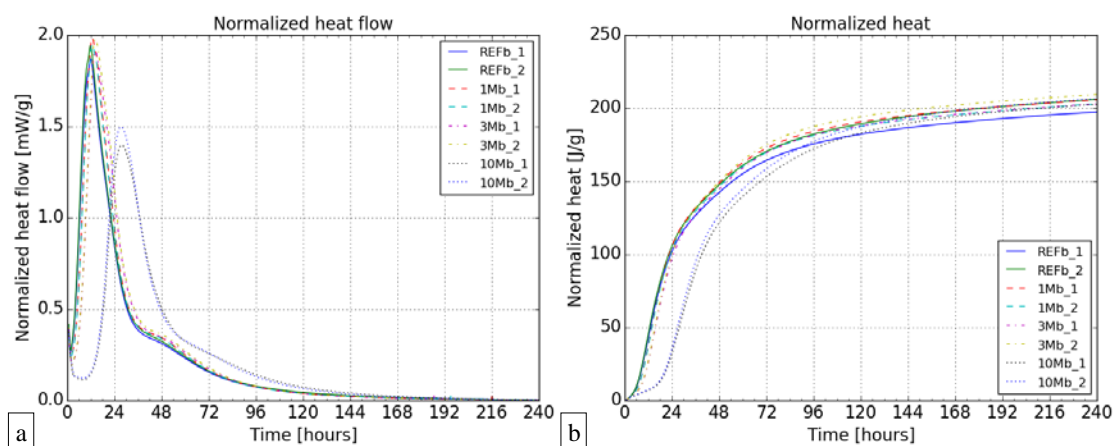

Figure 1: (a) normalized heat flow and normalized total heat released (b) results from isothermal calorimetry tests.

Specimens 1M and 3M had also their early age properties changed. Both had a slightly longer dormant period, then reference. However, the C_3S peak obtained for both were also slightly higher than reference samples, meaning that the hydration reactions were significantly accelerated. Other fact that shows this acceleration is the overlapping of the peak of heat generated by the hydration of C_3S and the renewed formation of ettringite [20]. On reference samples after about 10 hours the slope of the heat released decreases, followed by a reacceleration after some minutes. 1M samples the different slopes can also be noticed however, the second slope was shown only during the descending part of the curve, after approximately 10.5 hours. Specimens with 0.3% of VMA do not show these two slopes. The heat released by these clinker components overlay creating a wider peak.

On Figure 1b the total heat generated during the measurement period is plotted. Besides the fact that the employment of VMA delays the Portland cement hydration, after approximately 30 hours of hydration samples 1M and 3M had already a slightly higher total heat released. In general, samples with HPMC have released a higher amount of energy during the first 10 days of curing.

3.2   Thermogravimetry analysis

Thermogravimetry results were especially important to quantify the results found on this study. A summary with all results obtained with the test is give on Table 2. The influence of 1% VMA on the hydration delay of cement paste could also be noticed on the TGA results. Degree of hydration was calculated for all samples and the results show a significant loss on 1 day cured samples for 10M specimens. Moreover, a significant increase in α since the 1st day of hydration for 1M and 3M specimens was noticed. 10M specimens only develop higher degree of hydration after the 3rd day.

Table 2: Summary of properties measured using TGA technique.

	Age [days]	α	H$_2$O from 105 to 450°C [%]	Portlandite [%]	Calcium carbonate [%]
REF	1	0.2853	3.97	8.86	5.64
	2	0.3693	5.33	9.40	7.10
	3	0.4062	5.84	10.46	5.73
	29	0.6475	8.96	14.52	6.56
1M	1	0.3584	4.90	9.64	7.14
	2	0.4073	5.43	10.69	7.28
	3	0.4281	5.78	9.72	10.44
	7	0.5686	7.56	13.70	9.18
	29	0.7424	9.45	14.69	11.77
3M	1	0.3377	4.62	7.94	8.48
	2	0.4286	5.71	10.20	8.82
	3	0.4917	6.55	11.32	8.60
	7	0.6097	7.97	13.44	8.95
	29	0.8050	10.14	16.70	9.22
10M	1	0.1423	2.16	2.65	5.73
	2	0.3181	4.43	7.54	9.36
	3	0.4391	5.98	9.45	12.46
	7	0.5438	7.19	11.03	17.11
	29	0.7652	9.52	14.57	15.86

To explain the higher values found for samples with HPMC an understanding of how this chemical admixture changes the viscosity of solid solutions must be approached. The HPMC molecules can "arrest" water through hydrogen intermolecular interactions. These interactions decrease the availability of water during the first hours of cement hydration increasing significantly the viscosity of the water which surrounds OPC particles. As soon as pH values rise, the increasing availability of OH$^-$ ions decreases the capabilities of VMA in change the viscosity's solution. Gradually this phenomenon happens on the paste, and therefore gradually the water "arrested" on HPMC molecules are released to become available for hydration. This description is also found to explain the phenomena known as internal curing. Therefore, it is believed that the VMA does not only contributes for the viscosity modifying of the solid suspension, the chemical admixture can also contribute to improve OPC hydration.

The total loss of water from ettringite and CSH, as well as the total amount of calcium hydroxide is smaller for 10M samples only until the 3rd day of hydration. Nevertheless, with exception of 3M specimen, all 29 days cured samples have close values of calcium hydroxide content. As it was measured, the higher degree of hydration found on samples with VMA is coming mainly from the water lost from 105 until 450°C, corresponding to hydration products like ettringite, and C-S-H.

Another important characteristic from samples where the viscosity modifier was employed is the total amount of calcium carbonate. The proportions from this mineral rise with the increasing employment of the admixture. This phenomenon might be correlated with the large amount of entrapped air voids found on samples with HPMC. The high void content would increase the paste exposure therefore, perhaps increasing the carbonation speed.

3.3   X-ray diffraction

The delay of hydration caused using VMA, and the lack of distinguish of ettringite and C_3S heat release peaks might lead to a lack on the availability of some intermediate minerals for the cement hydration. Therefore, an investigation of the mineralogical properties was conducted to verify if the formation of the main crystals on samples with admixture followed the same trend as the reference. Besides the fact that formation of non-conventional minerals were reported by [21], the XRD patterns from all evaluated ages and different VMA content did not present formation or lack of mineral. Therefore, the employment of rheology modifier does not generate any hazardous minerals which could lead to a decrease on the durability or reliability of printed cementitious composites.

3.4 Fourier transform infrared spectroscopy

The band corresponding with presence of $Ca(OH)_2$ is found at $3645cm^{-1}$ and from 1635 to $3445cm^{-1}$ are bands due to the presence of calcium sulphate in the form of ettringite [21]. FTIR results corresponding the first 3 days of hydration emphasizes the bands corresponding to ettringite. Moreover, the bands measured during the test were also in accordance with the calorimetry tests, demonstrating that the employment of VMA delays hydration of Portland cement. 3M samples show higher transmittance bands, until the 3rd day of hydration. However, from the 7th hydration day 10M samples take over, as the reactions for those samples were significantly delayed, as reported with the calorimetry results. The FTIR results followed the same trend observed on TGA and calorimetry test results.

3.5 Electron scanning microscopy

The microstructure of 29 days samples was observed under scanning electron microscope and are exemplified on Figure 2. One of the first noticed differences was the number of voids on samples where the chemical admixture was employed. This might be caused due to the high viscosity achieved while mixing the paste, when air can be entrapped.

Besides that, around the voids found on samples with VMA a darker region is always found, leading to the conclusion that these are less dense than the bulk paste. This means that the voids found on these samples were perhaps filled or at least highly concentrated with water. This is an important result that is connected to the fact that the HPMC molecules can "arrest" part of the mixing water through its -OH ramifications. Progressing the hydration reactions this water is released, locally rising the water-to-cement ratio on these regions.

One other important observation is the location where portlandite is found. Usually, $Ca(OH)_2$ grows spread on the paste's bulk and eventually on the void or pore walls. However, samples with the chemical admixture had their voids progressively filled with portlandite, from 0.1 to 1 wt.% of VMA. Remarkably, voids from 10M samples were almost totally filled with portlandite.
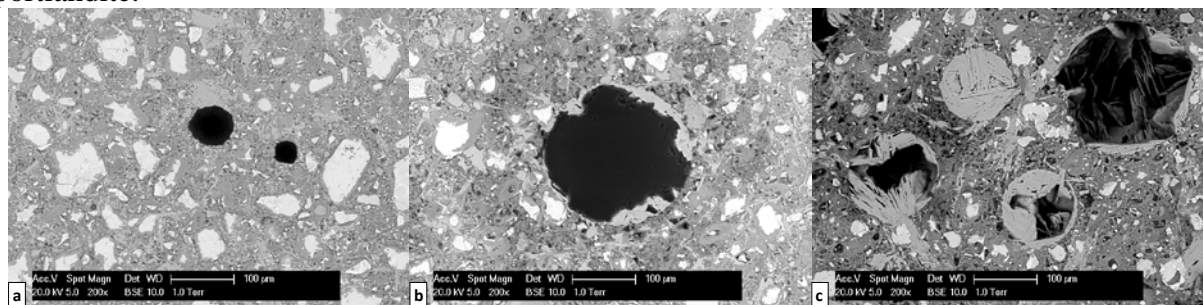

Figure 2: SEM pictures from REF samples (a), 1M (b) and 10M (c).

4.   CONCLUSIONS

The results obtained during this study are of fundamental importance for the understanding of the chemical admixture employed on the extrusion and nowadays additive manufacturing industries. Summarizing the main conclusions are:

- VMA concentration is of high importance on OPC hydration. Even small concentrations of the admixture lead to retardation of the initial hydration. 1 wt.% already leads to a large latent time of the Portland cement;
- The rheology modifier admixture "arrest" the available water with hydrogen bonds. The admixture only loses its preference for the water when the pH of the solution increases, making stronger connections with other ions;
- As demonstrated with the degree of hydration and the total heat released VMA can also be employed for internal curing purposes.
- Under electron microscope, it was possible to observe that air voids formed during mixing works also as water reservoir. As soon as the pH of the paste rises, the water released from VMA develops a region around theses voids with a higher water/cement ratio, in comparison with the rest of the matrix.
- To modify the rheology parameters of solid suspensions, the grain size distribution or the employment of viscosity modifier admixtures are usually employed. However, according with the manufacture specifications sheet the VMA employed on this study works within pH values 4 to 8. Therefore, solid suspensions which have high pH from the beginning of the mixing, like alkali activated materials, will be challenged to decrease the solution's pH or provide a well distributed particles grain size.

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