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Influence of hydroxypropylguars on rheological behavior of cement-based mortars

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ABSTRACT

Hydroxypropylguars (HPGs) are used as water retention agents in modern factory-made mortars. Nevertheless, these molecules can also impact the rheological behavior of cement-based materials. The influence of HPG and its dosage on mortar rheological properties was thus investigated thanks to a suitable measurement procedure. HPG allows keeping a positive yield stress value while the yield stress of hydroxypropyl methyl cellulose (HPMC) mortars was found to decrease with an increase in dosage. HPG increases the shear-thinning behavior and the consistency of mortars. The study of pore solution viscosity suggests that the entanglement of HPG coils beyond a threshold dosage is crucial to understand the rheological macroscopic behavior of HPG-admixed mortars. Nevertheless, the increase in mortar viscosity induced by HPG was lower than expected which reveals additional and specific repulsive forces induced by polysaccharides.

1. Introduction

Characterization and understanding of rheological properties of cement-based materials are crucial since they affect the properties and thus durability of hardened materials. Roussel et al. [1] have established the physical parameters which govern the steady state flow of fresh cement paste. According to the authors, cement-based materials can be represented as biphasic system consisting of suspended particles in a continuous fluid phase. This composition results in complex interplay between colloidal interactions, Brownian forces, hydrodynamic forces and direct contact forces between particles.

The stability of a cement paste results therefore from the balance between attractive and repulsive interactions. Because of adsorbed ions at the surface of the cement particles, there are repulsive electrostatic forces [2]. Otherwise cement particles tend also to agglomerate because of van der Waals attractive forces [3]. Nonat et al. [4–6] have highlighted these short-range attractive forces by means of optical microscopy observations and particle size measurements.

Natural polysaccharides or their derivatives are well-known to act as viscosity-enhancing admixtures (VEA) by modifying the rheological behavior of cementitious materials [7]. Concrete, mortar and cement grout with high fluidity (e.g. self-compacting concrete or self-leveling underlayment) have been developed in order to facilitate placement. However, the use of highly flowable mixtures may lead to segregation or excessive bleeding and subsequently, durability issues. The use of VEAs allows overcoming this problem by enhancing the sedimentation resistance while maintaining high fluidity [8–13]. The incorporation of VEA in shotcrete or render mortar is also very useful to ensure sagging resistance for thick application on vertical support, and allows sufficient fluidity for normal pumpability [10,14–17] by supplying shear thinning rheological behavior. Thus polysaccharides provide high yield stress and apparent viscosity at low shear rate but low resistance to flow at high shear rate [7].

Recent studies show that it is more complicated since results from literature are contradictory. For instance, the evolution of yield stress with the dosage of polysaccharide depends strongly on the kind of binder and polysaccharide studied. Khayat and Yahia [11] and Sonebi [12] report a steady increase in yield stress of cement grout by increasing dosage of welan gum. Leemann and Winnefeld [10] obtained similar results with starch derivatives incorporated in self-compacting mortar. In contrast, Cappellari et al. [17] obtained a reduction in yield stress of mortar with increasing dosage of hydroxyethyl methyl cellulose. The results of Paiva et al. [15] and Bouras et al. [18] show an initial decrease followed by an increase in mortar yield stress when the dosage of hydroxypropyl methyl cellulose and starch ether, respectively, increases. In addition, these trends can be amplified or modified when several polysaccharidic admixtures are blended, due to synergic effect and formation of interpolymer complexes [19].

Among the polysaccharidic VEAs, microbial-source polysaccharides such as welan gum [11–13,20,21] and cellulose ethers [14–17,22] are the most widely used and studied. Nevertheless, the hydroxypropylguar (HPG) are now well-established in the construction industry as water retention agent for mortars [23].

Guar gum is a natural polysaccharide extracted from the seeds of *Cyamopsis tetragonolobus*. It consists of a β(1-4)-linked

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D-mannopyranose backbone with random branchpoints of galactose via an α(1–6) linkage. Hydroxypropylguar is obtained from the native guar gum via an irreversible nucleophilic substitution, using propylene oxide in the presence of an alkaline catalyst. It is one of the most widely available derivatives of guar gum since it has application as thickener in many important industries, including hydraulic fracturing process, paper manufacturing, water treatment or textile printing [24–28].

The manufacture of HPG has the advantage of having a more reduced impact on the environment than cellulose derivatives. Indeed, guar gum exhibits a higher chemical reactivity and is soluble in cold water because of its branched-chain structure with a lot of hydroxyl groups. Thus, the chemical modification of the native guar gum requires normal reaction conditions of temperature and pressure, does not generate large quantity of by-products, and requires minimal purification procedure [23].

The efficiency of HPG as good water retention agent has been shown by several authors [17,29–31] but studies about their effect on rheological properties are very scarce. Izaguirre et al. [32] have worked with aerial lime-based mortars and Cappellari et al. [17] have characterized only one HPG. However, the formulation of modern factory-made mortars requires choosing a specific type and dosage of polysaccharide to obtain the desired water retention performance and rheological behavior suitable for the application. These requirements underscore the need to characterize and understand the influence of HPG on mortar rheological properties.

The aim of this paper is to characterize and understand the influence of HPG and its dosage on the rheological properties of cement-based mortars. This study will be divided into three parts. Firstly, the impact of HPG on mortar rheological behavior will be described using the parameters of the Herschel–Bulkley model. Then, the effect of HPG on pore solution viscosity will be presented. The pore solution was extracted from the mortar by means of centrifugation. Finally, the relationship between pore solution and mortar viscosities will be investigated.

2. Material and methods

2.1. Mineral and organic compounds

2.1.1. Mineral products

Mineral products used in this study consist in ordinary Portland cement, siliceous sand (DU 0.1/0.35, Sibelco) and limestone filler (BL 200, Omya).

Chemical and phase compositions of the cement used are given in Table 1. It is an ordinary Portland cement (OPC), classified CEM I 52.5 R CE CP2 NF type cement according to EN 197-1 and French NF P 15-318 standards. Phase composition was determined by Rietveld refinement method (Siroquant V2.5 software) after XRD analysis (D5000, Siemens). Oxide composition was quantified by means of X-ray fluorescence spectroscopy (SRS3400, Bruker-AXS).

The median particle diameters by volume (D_{50}%), determined by means of laser diffractometry with dry powder disperser, (Mastersizer 2000 and Scirocco dispersing unit, Malvern), are about 310, 12 and 6 μm for the sand, cement and filler, respectively.

2.1.2. Organic admixtures

Seven polysaccharidic water retention admixtures were investigated: five hydroxypropylguars (HPG 1, HPG 2, HPG 3, HPG 5 and HPG 6) and two hydroxypropyl methyl celluloses (HPMC 1 and HPMC 2) as references for comparison since they are widely used in industry. Fig. 1 shows the molecular structure of HPMC and HPG (substituent positions are arbitrary). Table 2 provides a qualitative description of the admixtures. The qualitative substitution degrees are provided by the manufacturers.

All the HPG samples, provided by *Lamberti S.p.A*, exhibit similar molecular weight, about 2.10^6 g·mol^{-1}. The molar substitution ratio (MS_{HP}) represents the number of moles of hydroxypropyl groups per mole of anhydroglucose unit and is less than 3 for the investigated HPG samples. It appears from Table 2 that the only difference between HPGs 1, 2 and 3 is the molar substitution ratio while HPGs 5 and 6 exhibit additional substitution (short or long alkyl chains).

The degree of substitution (DS_M) represents the amount of methoxy groups per anhydroglucose unit and is about 1.8 for HPMC 1 and HPMC 2. The molecular weights are about $0.25 \cdot 10^6$ and 1.10^6 g·mol^{-1} for HPMC 1 and HPMC 2 respectively, which constitute the only difference between these two samples.

2.2. Preparation of mortars

Admixtures were dissolved in deionized water. Polymer dosages in mortars varied from 0.1 to 1.6% by weight of cement (bwoc) by preparing polymer solutions of concentrations varying from 1 to 16 g·L^{-1}. Complete dissolution of all polymers was obtained by means of magnetic stirring for 24 h.

Mortars were prepared according to the following mixture proportions: 30 wt.% of cement, 65 wt.% of siliceous sand and 5 wt.% of limestone filler. Dry mixture (i.e. cement, sand and filler) was homogenized in a shaker (Turbula, Wab) with low shear forces for 15 min. Admixture solutions were then added in order to obtain a water to cement ratio W/C = 1. Dry mixture and admixture solution were mixed (MIx40, CAD Instruments) in accordance with EN 196-1 [33]. A control test was performed with a mortar without admixture.

Each mortar studied was divided into two parts after mixing. One part was used to study mortar rheological properties, while the other portion was centrifuged in order to determine pore solution viscosity.

It is worth noting that the mortar formulation with high W/C was adapted from the CEReM (European consortium for study and research on mortars) mixture design [34,35]. This work is part of a larger study that focuses on the influence of HPG on overall mortar properties at early age, including mortar water retention capacities. Regarding water retention, the high W/C ratio corresponds to extreme conditions which allow highlighting the effectiveness of HPG as water retention agent.

2.3. Rheological measurements

All the rheological measurements were obtained with Anton-Paar Rheometer MCR 302, thermostated at 20 °C because rheological properties are temperature-dependent.

Table 1
Chemical and phase compositions of the investigated cement.

Chemical composition (% wt)				Phase composition (% wt)			
Oxides	XRF	Oxides	XRF	Phases	XRD (Rietveld)	Phases	XRD (Rietveld)
CaO	66.9 ± 0.8	MgO	1.16 ± 0.01	C_3S	79.4 ± 0.5	Gypsum	1.3 ± 0.2
SiO_2	20.9 ± 0.2	TiO_2	0.32 ± 0.03	C_2S	8.2 ± 0.4	Anhydrite	3.2 ± 0.2
Al_2O_3	4.7 ± 0.1	P_2O_5	0.14 ± 0.01	C_3A	3.3 ± 0.2	Hemi-hydrate	0.8 ± 0.3
SO_3	2.4 ± 0.2	MnO	0.04 ± 0.01	C_4AF	4.1 ± 0.9	Free CaO	0.5 ± 0.2
Fe_2O_3	2.6 ± 0.1	K_2O	0.10 ± 0.01				
LOI	2.1 ± 0.1						