Cement and Concrete Research 70 (2015) 50–59

Contents lists available at ScienceDirect

Cement and Concrete Research

journal homepage: http://ees.elsevier.com/CEMCON/default.asp

Influence of the polysaccharide addition method on the properties of fresh mortars

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ARTICLE INFO

Article history:
Received 1 July 2014
Accepted 6 January 2015
Available online 21 January 2015

Keywords:
Polysaccharide (D)
Admixture (D)
Water retention (C)
Rheology (C)
Method of addition

ABSTRACT

This study focused on comparison of polysaccharide addition methods, either in powder form, or as a solute in the mixing water. The influence of the methods was assessed by measuring water retention and rheological properties with one cellulose ether and two guar ethers.

Polysaccharides were more efficient to enhance water retention and rheological properties when they are pre-dissolved in the mixing water. This is related to differences in polymer concentration in the pore solution of mortar. These differences are not stemming from a difference in dissolution kinetics, but from a difference in adsorption on growing hydrates. Being immediately available when it is pre-dissolved, the admixture slows down the nucleation and growth of hydrates limiting in turn the surface area for further adsorption. Consequently, more molecules are left in the interstitial solution and a lower dosage is required to achieve the overlapping of polymer coils, responsible for the effectiveness of polysaccharides.

1. Introduction

Polysaccharides, natural or derivatives, are commonly used as admixtures in modern factory-made mortars. They are able to improve the water retention capacity of cement-based mortars at fresh state [1–6]. Limiting the absorption of mixing water by the substrate allows enhancing mechanical and adhesive properties of the mortar [7,8]. Due to their thickening properties, polysaccharides improve also the mortars rheological properties since their use results in a highly shear thinning material [9]. This particular rheological behavior induced by polysaccharides ensures a high apparent viscosity at low shear rate in order to ensure sagging and sedimentation resistance, while maintaining a high fluidity because of low viscosity at high shear rate [10–16]. The major drawback of the use of polysaccharide in cement-based materials is the induced delay of cement hydration [17–22].

Most studies are devoted to the influence of cellulose derivatives since they represent the most widely industrially used polysaccharidic admixtures. Nevertheless, the use of hydroxypropylguars (HPGs) is of interest since the HPG manufacturing is less pollutant than cellulose ethers [23]. HPG is now well-established in the construction industry as water retention agent for mortars [23]. In previous studies, the influence of HPG on water retention capacity [24] and rheological properties [25] of cement-based mortars was investigated. In agreement with other authors [1,4,5], the importance of polymer coil overlapping for the efficiency of HPG as admixture was highlighted.

The influence of HPG on the early age hydration of cement has been also investigated [26]. It was assumed that the mechanism responsible for the hydration delay is a decrease in the hydrates growth rate because of HPG adsorption on hydrated phases via polar interactions. The influence of the HPG pre-dissolution in the liquid phase has been studied too. A higher hydration delay was noticed after pre-dissolution, especially for HPG with low substitution degree.

Method of chemical admixtures addition, and in particular the delayed addition, has been often investigated by researchers in order to improve the knowledge about the working mechanism of these molecules in the cement-based materials. Delayed addition of retarders such as sucrose, EDTA, calcium ligno-sulphonate, oxalic acid or organic acid has been studied [27–29]. It was found for example that delayed addition of sucrose leads to a greater percentage of sugar remaining in solution because less retarder is consumed in the initial reaction [29]. Therefore, sucrose retards further hydration when its addition is delayed. It is also well know that the fluidity and the fluidity loss of fresh cement-based materials are affected by the time of superplasticizers addition [30–33]. Flatt and Houst [34] have proposed a simplified view on the effects of superplasticizers in concrete. It appears that superplasticizers interact with the ongoing chemical reactions and hence these molecules can be consumed in an organo-mineral phase formed around cement particles. The delayed superplasticizer addition allowed confirming this hypothesis since the admixture is more effective to contribute to the dispersion because the polymer consumption is reduced.

The polysaccharide pre-dissolution in mixing water was useful to better understand the interaction between HPG and cement and its impact on cement hydration kinetics [26]. The aim of the current

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http://dx.doi.org/10.1016/j.cemconres.2015.01.004

paper is to reuse this simple method of investigation in order to examine the key properties of freshly-mixed mortars induced by polysaccharides: water retention capacity and rheological behavior.

These two properties will thus be characterized on mortars prepared with two methods of addition: (i) "dry addition", the common way where the polymer is added as dry powder and homogenized with all the solid phases before being put into contact with water and (ii) "pre-dissolved", where the polymer is first dissolved in the mixing water before being mixed with the dry mixture composed of sand and cement. The characterizations of dissolution kinetics and adsorption ability of polysaccharides will be useful to interpret the experimental data. Finally, a schematic representation of the interaction between polysaccharide and cement will be presented and its impact on mortar macroscopic properties will be discussed.

2. Materials

2.1. Cement

This study was conducted using a CEM I 52.5 R CE CP2 NF type cement according to the EN 197-1 and NF P 15-318 standards. Chemical and phase compositions of the cement used are presented in Table 1. Oxide composition was determined by X-ray fluorescence spectroscopy using a Bruker-AXS SRS3400 instrument. Phase composition was obtained by XRD using a Siemens D5000 instrument. Siroquant V2.5 software was employed to quantify the amounts of individual phases present in the cement by following Rietveld's method of refinement.

2.2. Organic admixtures

The description and comparison of the cellulose and guar chemistry were detailed in [35]. Guar gum is a polysaccharide extracted from the seed endosperm of *Cyamopsis tetragonolobus*, a native plant from India. This is a galactomannan consisting of a (1–4)-linked β-D-mannopyranose backbone, with random branchpoints of galactose via an α-(1–6) linkage. The ratio of mannose to galactose is about 1.8. HPGs are obtained from the native guar gum via an irreversible nucleophilic substitution, using propylene oxide in the presence of an alkaline catalyst. Cellulose is a polysaccharide composed of individual anhydroglucose units linked through β-(1–4) glycosidic bonds. Because of strong intermolecular hydrogen bridging bonds, cellulose is not soluble in water. Thereby, cellulose ethers are obtained by pretreating cellulose with base (alkali cellulose) in order to break hydrogen bonds and to make accessible the active groups for etherifying agents. In the present work, two HPG and one HMPC were studied. Table 2 presents the qualitative substitution degrees (provided by the manufacturer), the weight-average molecular mass (determined by size-exclusion chromatography, analyses were carried out on a Water apparatus) and the parameters characterizing the concentration dependence of zero-shear viscosity of admixtures dissolved in 20 mM lime solution (b_1 and b_2) as explained in Section 3.2.

The molar substitution ratio (MS_{HP}) is defined as the number of hydroxypropyl groups per anhydroglucose units and is less than 3 for our molecules. The degree of substitution, noted DS_M, represents the amount of substituent methoxyl groups on the anhydroglucose units of cellulose and is about 1.8 for HPMC 2 according to the manufacturer. The weight-average molecular mass is noted as Mw and the critical overlap concentration of polymer coils is noted as C^*.

Table 2
Description of the admixtures used.

	MS_{HP}	DS_M	Mw (10^3 g · mol^{-1})	C^*	b_1	b_2
HPG 1	Low	–	1700 ± 80	3.7	1.4	4.1
HPG 3	High	–	1800 ± 50	3.2	1.2	4.0
HPMC 2	Very low	Very high	950 ± 50	2.3	1.5	3.9

These three polysaccharidic admixtures were chosen since they exhibit strong (HPG 1), medium (HPG 3) and slight (HPMC 2) pre-dissolution effect regarding cement hydration kinetics [26].

3. Methods

All tests were carried out at controlled temperature because fresh mortar properties and dissolution kinetics are temperature-dependent. All the rheological measurements were carried out with Anton-Paar Rheometer MCR 302.

3.1. Freshly-mixed mortars properties

For a given formulation (i.e. kind and dosage of admixture), freshly-mixed mortars properties (i.e. water retention and rheological properties) and pore solution viscosity were determined on the same mortar which have been divided into three parts. Each test was repeated in order to ensure the reproducibility of the results. Moreover, the same procedure was performed with a mortar without admixture as a control test.

3.1.1. Preparation of mortars

In the case of pre-dissolved addition, admixtures were previously dissolved in deionized water. Complete dissolution of all polymers was obtained after strong stirring for 24 h by means of a magnetic stirrer. Polymer dosages in mortars varying from 0.1% to 0.66% by weight of cement (bwoc) by preparing polymer solutions of concentrations ranging from 1 to 6.66 g · L^{-1}.

Mortars were then prepared according to the following mixture proportions: 30 wt.% of cement, 65 wt.% of siliceous sand (DU 0.1/0.35, Sibelco) and 5 wt.% of limestone filler (BL 200, Omya). Particle size distribution of the solid phases given in Fig. 1, was determined employing a laser-based particle size analyzer with dry powder disperser (Mastersizer 2000 equipped with Scirocco dispersing unit, Malvern). The median particle diameter by volume (D_{50}%) are about 310, 12 and 6 μm for the sand, cement and filler respectively.

Dry mixture (*i.e.* cement, sand, filler, and polymer in the case of dry addition) was homogenized in a shaker (Turbula, Wab) for 15 min. Deionized water or admixture solution, according to the method of polymer introduction, was then added to the dry mixture in order to obtain a water to cement ratio $W/C = 1$. Mortars were mixed (MIx40, CAD Instruments) in accordance with EN 196-1 [36].

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	66.1 ± 1.2	TiO_2	0.24 ± 0.01	C_3S	73.0 ± 0.53	Gypsum	1.7 ± 0.15
SiO_2	20.2 ± 0.4	P_2O_5	0.05 ± 0.01	C_2S	12.7 ± 0.50	Anhydrite	2.3 ± 0.28
Al_2O_3	4.8 ± 0.1	MnO	0.04 ± 0.00	C_3A	4.2 ± 0.18	Hemi-hydrate	0.8 ± 0.30
SO_3	3.5 ± 0.2	K_2O	0.01 ± 0.01	C_4AF	6.1 ± 0.22	Free CaO	0.5 ± 0.13
Fe_2O_3	2.9 ± 0.1	LOI	2.2 ± 0.2				
MgO	1.11 ± 0.02						