

01 Feb 2022

## Viscosity Modifying Agents: Key Components of Advanced Cement-Based Materials with Adapted Rheology

Hela Bessaies-Bey

Kamal Khayat

Missouri University of Science and Technology, khayatk@mst.edu

Marta Palacios

Wolfram Schmidt

et. al. For a complete list of authors, see [https://scholarsmine.mst.edu/civarc\\_enveng\\_facwork/2365](https://scholarsmine.mst.edu/civarc_enveng_facwork/2365)

Follow this and additional works at: [https://scholarsmine.mst.edu/civarc\\_enveng\\_facwork](https://scholarsmine.mst.edu/civarc_enveng_facwork)



Part of the [Architecture Commons](#), and the [Civil and Environmental Engineering Commons](#)

---

### Recommended Citation

H. Bessaies-Bey et al., "Viscosity Modifying Agents: Key Components of Advanced Cement-Based Materials with Adapted Rheology," *Cement and Concrete Research*, vol. 152, article no. 106646, Elsevier, Feb 2022.

The definitive version is available at <https://doi.org/10.1016/j.cemconres.2021.106646>

This Article - Journal is brought to you for free and open access by Scholars' Mine. It has been accepted for inclusion in Civil, Architectural and Environmental Engineering Faculty Research & Creative Works by an authorized administrator of Scholars' Mine. This work is protected by U. S. Copyright Law. Unauthorized use including reproduction for redistribution requires the permission of the copyright holder. For more information, please contact [scholarsmine@mst.edu](mailto:scholarsmine@mst.edu).



Contents lists available at ScienceDirect

## Cement and Concrete Research

journal homepage: [www.elsevier.com/locate/cemconres](http://www.elsevier.com/locate/cemconres)

# Viscosity modifying agents: Key components of advanced cement-based materials with adapted rheology

Hela Bessaies-Bey<sup>a,\*</sup>, Kamal H. Khayat<sup>b</sup>, Marta Palacios<sup>c</sup>, Wolfram Schmidt<sup>d</sup>, Nicolas Roussel<sup>a</sup>

<sup>a</sup> Université Gustave Eiffel, France

<sup>b</sup> Center for Infrastructure Engineering Studies, Missouri S&T, Rolla, MO, USA

<sup>c</sup> Eduardo Torroja Institute for Construction Science (IETcc-CSIC), Madrid, Spain

<sup>d</sup> Bundesanstalt für Materialforschung und -prüfung (BAM), 12205 Berlin, Germany

## ARTICLE INFO

## Keywords:

Viscosity modifying agents  
Cement  
Stability  
Rheology  
Working mechanism  
Compatibility

## ABSTRACT

Viscosity modifying agents (VMAs) are essential ingredients for the production of flowable cement-based materials. This paper presents an overview of commonly used VMAs and attempts to shed some light on the underlying physics at the origin of their mechanisms of action. The main molecular parameters of VMA controlling the rheological properties of the cement pore solution are highlighted. As the mechanisms of action of VMAs in cement-based materials are closely related to their affinity with the surface of cement particles, the adsorption of the main VMA types is discussed. The effect of VMAs on flow properties and stability of cement-based materials is presented for VMAs added without any superplasticizer, and then in systems incorporating both VMAs and superplasticizers. Finally, the effect of VMAs in enhancing concrete properties to secure adequate performance of different construction applications, and perspectives for future developments of novel cement-based materials made with VMAs are showcased.

## 1. Introduction

For a long period of time, concrete has been a relatively simple construction material, where cement and water contents control the fresh and hardened properties of the material. However, over the course of the last couple of decades, performance specifications of cement-based materials have evolved towards the formulation of sophisticated materials with the potential for tailored and specified properties to satisfy a wide range of performance and casting processes. High-performance concrete with adapted rheology has been made possible due to ongoing innovation in the field of rheology modifying admixtures, first and foremost yield stress reducing admixtures, namely superplasticizers. Nevertheless, complex casting processes, such as grouting, pumping, self-consolidation, and 3D-printing have increased the level of demand on the rheological characteristics necessitating adjustment possibilities beyond yield stress modification. This can be achieved by the sole use or supplementary use of viscosity modifying agents (VMAs) where modifications of yield stress, viscosity, and thixotropy can be achieved, thus allowing a wide range of mixture proportioning at a given water-to-cement mass ratio. VMAs are also known as viscosity modifying admixtures, viscosity enhancing agents (VEAs),

anti-washout admixtures (AWAs), and stabilizing agents (SAs).

VMAs are mainly used for their ability to enhance the stability of cement-based materials when faced to destabilizing conditions, such as phase separation induced by gravity (i.e., segregation, bleeding) [1–4] or induced by the contact with a dry surface or a pressure gradient (i.e., water filtration, washout) [5–10]. They can also be used to enhance the yield stress of cement-based materials. This is critical for some applications, such as shotcrete or monolayer mortars that, after spraying, should exhibit high resistance to sagging and stay on the wall in thick layers [11,12]. Similarly, in an extruded layer during 3D printing, the deposited material should not deform under its own weight [13,14]. The use of VMA along with superplasticizer is critical in many applications necessitating the design of low yield stress and moderate to high viscosity, such as in the case of self-consolidating concrete (SCC) [1–4]. The use of VMA can also be useful in enhancing the robustness of cement-based materials, despite of their adequate stability levels, as discussed below.

Yet, the vast variety of mechanisms to stabilize cement-based systems makes it complex to provide a complete overview. Enhancing concrete stability can be secured through proper use of inorganic powder components, organic polymers, air entraining admixtures, or

\* Corresponding author.

E-mail address: [hela.bessaies-bey@univ-eiffel.fr](mailto:hela.bessaies-bey@univ-eiffel.fr) (H. Bessaies-Bey).

capillary forces. The effects of inorganic components such as nano silica or nano clay are discussed in [15–20] in this special issue and in [21]. The present paper concentrates on the organic VMAs. Although VMAs can affect the setting and hardening processes along with the hardened properties of cement-based materials, they are mainly applied to modify the rheology and stability of the materials in the fresh state.

In addition, for certain construction applications and with the need for novel binder compositions, maintaining consistent properties of the formulated material is key to successful processing and production. Thus, the relevance of VMAs to enhance stability and robustness will significantly increase in the future. A more fundamental understanding of their modes of action is required for efficient use of this unique class of chemical admixtures. Within this frame, this paper presents a comprehensive review of the relevant research findings pertaining to VMAs and attempts to offer some perspectives for research and developments in the relevant area of VMAs.

This paper discusses the mostly commonly used categories of VMAs. The main molecular parameters of VMAs that can control the rheological properties of cement pore solution are highlighted. The mechanisms of action of VMAs in cement paste are underlined. This includes the affinity of VMAs with the surface of cement particles and their effect on flow properties and stability of cement-based materials for systems proportioned with and without any superplasticizers. Finally, the effect of VMA on enhancing concrete performance intended for various construction applications is presented, and perspectives for future developments and applications of novel cement-based materials made with VMAs are highlighted.

## 2. VMA classification and overview of their “mechanisms of action”

### 2.1. VMA classification

The classification of the ample variety of chemistries of VMAs is not a straightforward issue. In fact, in literature, different categories of VMAs can be found based on the origin of the VMAs, their working mechanism, or their impact on the physical properties of the concrete incorporating the VMA. Probably, the classification done by Kawai et al. [22], that distinguishes three main types of VMAs according to their origin, is the one with the lowest complexity. However, this classification does not provide a physical or chemical meaning related to the specific effect of the VMA type on concrete properties. In particular, Kawai et al. classified organic VMAs as natural, semi-synthetic, and synthetic polymers. *Natural polymers* include microbial polysaccharide polymers, such as welan gum, diutan gum, and guar gum, cellulose, and starch. *Semi-synthetic polymers* include cellulose-ether derivatives, guar gum derivatives, and modified-starch. These polymers are mostly based on naturally occurring polymers that are partially modified by the addition of functional groups. *Synthetic polymers* are namely polyethylene oxide, polyvinyl alcohol, or polyacrylamides. These polymers have the main advantage that their molecular structure can be tailored to achieve the aimed properties of cementitious materials. The chemical composition of different types of VMAs was extensively described by Gelardi et al. [23]. In this review paper, the most relevant features of the molecular structure of different VMA types are briefly explained. Among them, Sphingans gum, cellulose ether, and modified starch are commonly used in cement-based materials.

#### 2.1.1. Microbial polysaccharides

Sphingans are microbial polysaccharides obtained by aerobic fermentation by Sphingomonas. Welan gum, diutan gum or gellan gum belong to this group. Welan gum and diutan gum are the sphingan gums that have been more extensively investigated in cementitious materials. They both have a linear tetrasaccharide backbone structure that contains L-mannose, L-rhamnose, D-glucose and D-glucuronic acid but different side chains [24]. The side chains in welan gum consists of L-

mannose or L-rhamnose in the C-3 of every glucose repeating unit, while two units of L-rhamnose are present in diutan gum (see Fig. 1a). For welan gum, the molar ratio of the L-mannose, L-rhamnose, D-glucose, and D-glucuronic is 1.0:4.5:3.1:2.3, and the D-glucuronic acid is around 11.6%–14.9% [24] (see Fig. 1b). The molecular weight of welan gum is significantly lower than that of diutan gum, with a value of around  $10^6$  g/mol in the former VMA and  $3\text{--}5 \cdot 10^6$  g/mol in the latter VMA [25,26]. Both polysaccharides contain a carboxylate group that provides them with an anionic charge and the ability to adsorb onto cement particles. The side chains shield the carboxylate group of the backbone in aqueous solution, and the polysaccharides adopt a double helix conformation. This provides the aqueous solution with high viscosity even at high concentrations of Calcium [27]. Welan gum and diutan gum are also chemically stable at 150 °C and high pH that makes them very interesting to work in the cement field and oil-well industry [28,29].

Xanthan gum is a microbial polysaccharide obtained by the fermentation of the bacterium *Xanthomonas campestris*. Its structure consists of a backbone made of glucose units and side chains of the trisaccharides alpha-D-mannose that contains an acetyl group, beta-D-glucuronic acid and a beta-D-mannose terminal unit, linked to a pyruvate group (see Fig. 1c). The presence of glucuronic acid in side chain provides the xanthan gum with an anionic characteristic. It has a molecular weight in the range of  $2 \cdot 10^6$  to  $20 \cdot 10^6$  g/mol, and it is stable at high salt concentrations (up to 150 g/l NaCl), temperature in water of up to 90 °C, and pH in the range of 2 to 11 [30].

#### 2.1.2. Cellulose and cellulose ether polymers

Such VMA types have a linear molecular structure based of up to thousands of D-glucose units. Their molecular weight is around  $10^5$  and  $10^6$  g/mol. The properties of cellulose polymers depend on:

- (1) Molecular mass: The increase of the molar mass decreases their solubility and increases the shear thinning behavior.
- (2) Degree of substitution (DS): This is the average number of hydroxyl groups per glucose unit that has been substituted by ether groups [31]. It varies from 0 to 3 and has a direct impact on the solubility of the cellulose polymer. Cellulose polymers with DS below 0.1 are insoluble, those with DS values of 0.2–0.5 are soluble in alkali solutions, while celluloses polymers with DS of 1.2–2.4 are soluble in water. Celluloses with DS values above 2.4 are only soluble in organic solvents [32,33].
- (3) Chemical composition of the substitution group: In the case of cellulose ether polymers (CE), the structure of cellulose is normally modified by introducing small groups such as hydroxypropyl methyl, hydroxyethyl methyl and hydroxyethyl in the hydroxyl groups of C-2, C-3 and C-6 (see Fig. 2).
- (4) Molar substitution (MS). MS is the molar fraction of substituents per glucose.

#### 2.1.3. Guar gum and guar gum derivative polymers

Guar gum is derived from the seeds of the guar plant *Cyanopsis tetragonolobus*, and it is a non-ionic branched polysaccharide with  $\beta$ -1,4-linked D-mannopyranose backbone with random branch points of galactose via an  $\alpha$ -1,6-linkage [34]. The ratio of mannose to galactose units varies from 1.6:1 to 1.8:1 depending on the source. Guar gum is one of the polysaccharides with the highest molecular weight that ranges from  $1.0 \cdot 10^6$  to  $2.0 \cdot 10^6$  g/mol [35].

Hydroxyl groups of the backbone can be replaced by different functional groups to overcome some limitations of guar gums, including viscosity reduction due to uncontrolled rate of hydration, turbidity, or susceptibility to microbial attack [35]. Hydroxypropylguar is the most commonly used derivative of guar gum (see Fig. 3) and, as in the case of CEs, its water retention properties depend on its molecular weight, degree of substitution, and molar substitution [8].

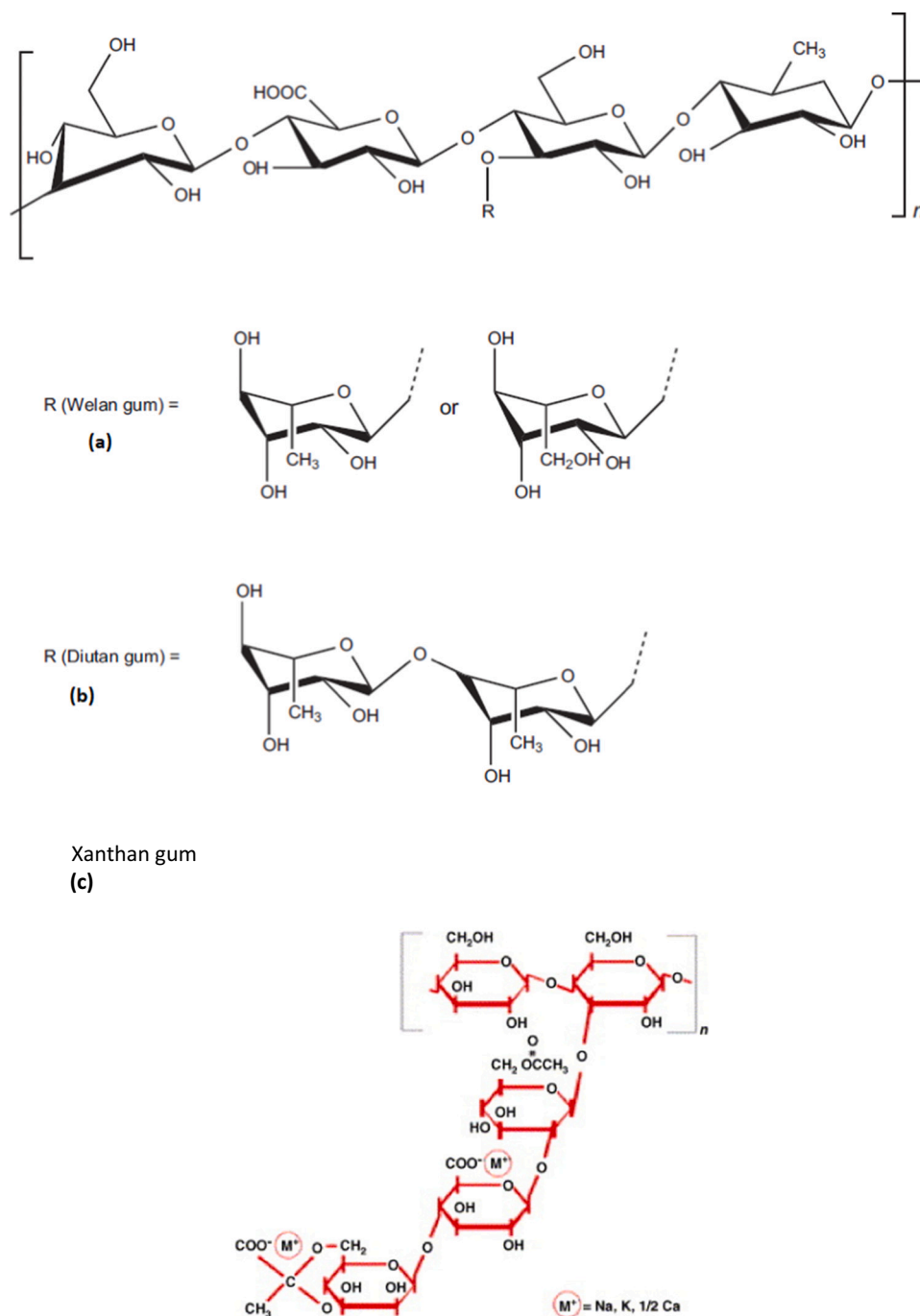


Fig. 1. Structure of (a) welan gum, (b) diutan gum and (c) xanthan gum Reproduced respectively from [23] and [30] with permission.

#### 2.1.4. Starch and modified starches

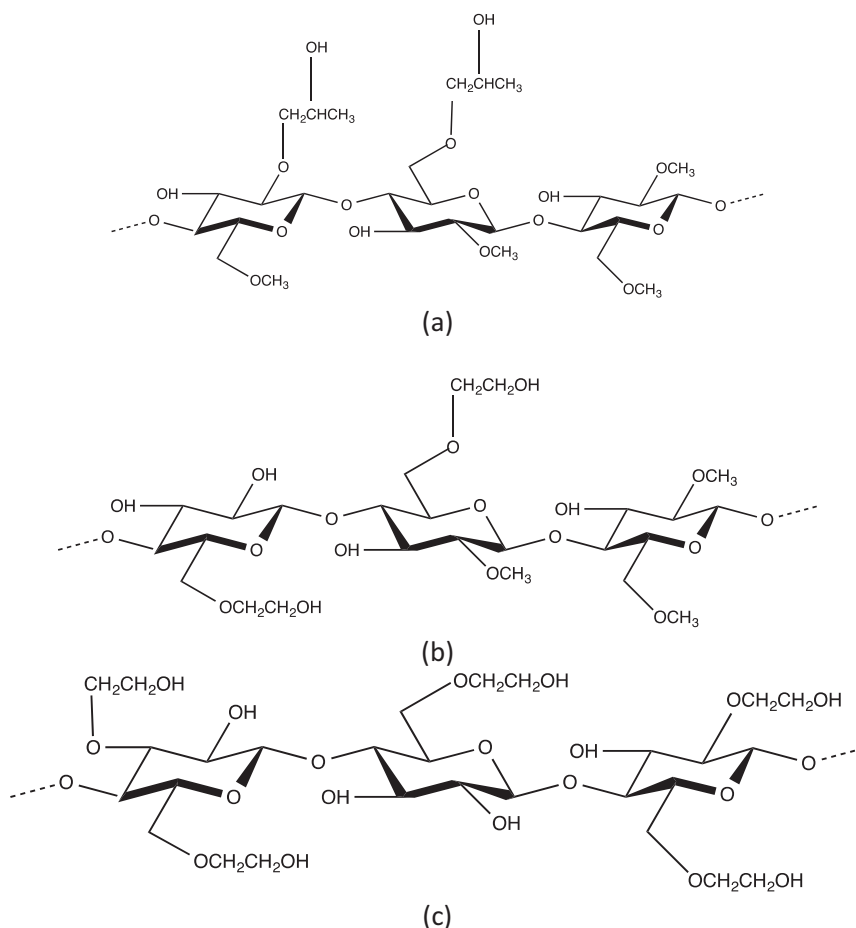
Starch is a polysaccharide composed of amylose and amylopectin (see Fig. 4), where amylose is mainly a long linear chain of  $\alpha$ -1,4 linked glucose units while amylopectin is a highly-branched molecule with shorter  $\alpha$ -1,4 linked glucose units and frequent  $\alpha$ -1,6 branches. Except for waxy starches, which contain 100% of amylopectin, the percentages of amylose and amylopectin vary with the source of the starch, but normally is around 20%–30% of amylose and 70%–80% amylopectin. Amylose is linear or sometimes partially branched, with a degree of polymerization up to 6000 and a molecular weight of  $10^5$  to  $10^6$  g/mol. Amylose chains can form single or double helices. Amylopectin is highly branched with an average degree of polymerization of 2 million and a molecular weight of  $10^7$ – $10^9$  g/mol [36]. Radius of gyration of amylose

and amylopectin from potato starch are approximately 50 nm and 50–500 nm, respectively [26,37–39].

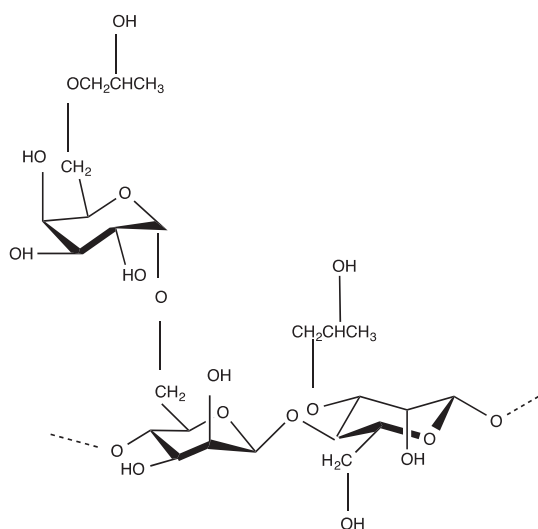
Starch is normally modified by esterification or etherification of the hydroxyl groups at C-2, C-3 and C-6 of each glucose unit, being the modified-starch soluble in water and stable at high pH. Hydroxypropyl starch are the most widely used modified starches in cementitious materials.

#### 2.1.5. Other VMAs

Polyethylene glycol (PEG), also called polyethylene oxide (PEO), is a linear non-ionic polymer with a wide molecular weight that ranges from 200 to 7.  $10^6$  g/mol. The chemical structure of its repeating unit is shown in Fig. 5a, with hydrophobic ethylene group and a hydrophilic



**Fig. 2.** Structure of cellulose ethers (a) HPMC; (b) HECM; (c) HEC. Reproduced from [23] with permission.



**Fig. 3.** Structure of hydroxypropylguar. Reproduced from [23] with permission.

oxygen [40].

Polyacrylamides (PAM) are linear non-ionic polymers with high molecular weight. Anionic PAMs (see Fig. 5b) obtained by the copolymerization with anionic salts such as carboxylates are normally used in the construction field [42]. Their molecular weight ranges from  $10^3$  to

over  $10^6$  g/mol.

Polyvinyl alcohol (PVA) admixtures are water-soluble polymers synthesized by the hydrolysis of polyvinyl acetate. PVA can be classified in fully and partially hydrolyzed PVA (see Fig. 5c). PVA products have different properties (molecular weight, flexibility or solubility) depending on the initial length of the vinyl acetate polymer and their hydrolysis conditions [41].

## 2.2. Overview: schematic representation and description of VMA mechanism of action

The main mechanism of actions of the different types of VMA are summarized in Fig. 6 [25,43,44].

### 2.2.1. Solvation and swelling

Polymer chains swell to increase the number of interactions with the solvent. The polymer size depends on the polymer molecular properties, on the environment of the polymer and on the applied shear rate (see Section 3.1).

### 2.2.2. Entanglement

Above a critical concentration and critical molar mass, polymer chains tend to entangle, and they cannot move without displacing or deforming their neighbors. The identity of a polymer is lost, and the representative element of the network becomes that of the mesh size (i. e., distance between two points of contact between polymers) (see Section 3.1).

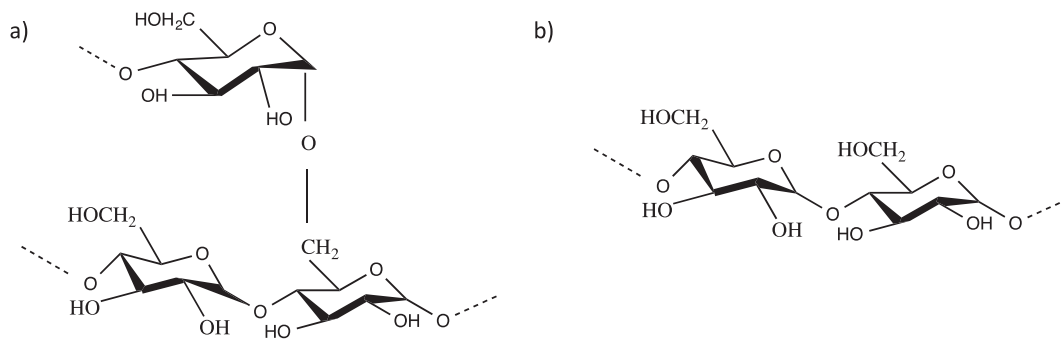


Fig. 4. Structure of (a) amylopectin and (b) amylose. Reproduced from [23] with permission.

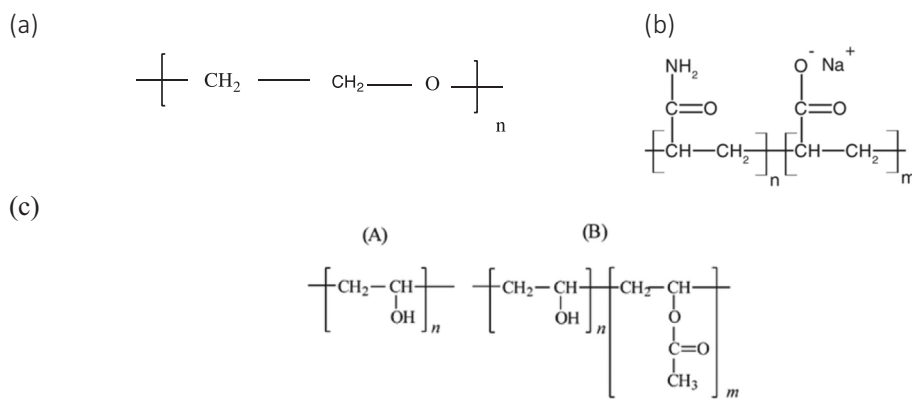


Fig. 5. Structure of repetitive unit of (a) PEO (b) anionic PAM and (c) PVA. Reproduced respectively from [42] and [41] with permission.

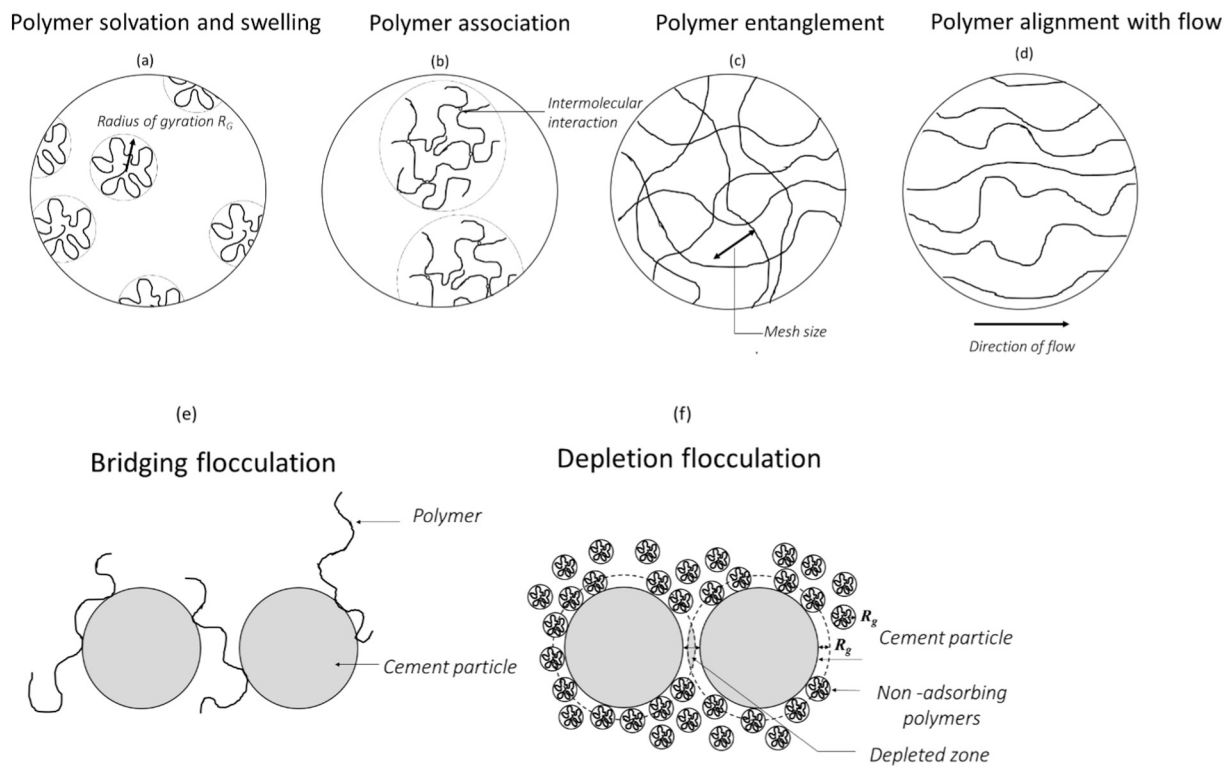


Fig. 6. The main mechanism of actions of the different types of VMA.

### 2.2.3. Association

Associative polymers are characterized by a high propensity for aggregation so as to minimize the contact between their hydrophobic part and the solvent (see Section 3.2).

### 2.2.4. Alignment under shear

Under shear, changes in the polymer structure could occur, the polymer chains align with the flow direction, stretch, and/or disentangle (see Section 3.3).

### 2.2.5. Depletion

The difference in non-adsorbed polymer concentration between bulk solution and depleted zones generates so-called attractive depletion forces, which may cause particle flocculation (see Section 4.2).

### 2.2.6. Bridging

High molar mass polymers are able to adsorb simultaneously at the surfaces of several cement particles at the same time (see Section 4.2).

## 3. VMA in cement pore solution

### 3.1. Conformation and concentration regime

The conformation (i.e., chain shape), molecular weight, and tendency for the VMA molecules to associate in cement pore solution have marked influence on the mechanism of action of the polymer and the rheological properties of cement pore solution and cement paste. The conformation of polymer depends on the polymer molecular properties (i.e., molecular weight, chain flexibility, intra and inter molecular interactions), on the environment of the polymer (i.e., interaction between polymer monomers and solvent, volume concentration of the polymers in solution) and on the applied shear rate [44–51]. In the dilute regime, the polymer chains are spaced apart and develop the same conformation as when they are alone in solution [51]. The size of polymer can be described by the radius of gyration  $R_G$  (see Fig. 6a). Above a critical volume concentration  $c^*$ , the semi dilute regime is reached. In the semi dilute non-entangled regime, the polymer chains are compressed to reduce their apparent volumes and the size of coil decreases with concentration. In the semi dilute entangled regime, the polymers are entangled and they cannot move without displacing or deforming their neighbors [51] (see Fig. 6c).

The critical concentrations, separating these regimes, has not been precisely defined in the literature. Their value differs according to the hypotheses of transition from one regime to the other. Assuming that deformable spheres occupy a volume  $\frac{4\pi}{3}R_G^3$ , the volume concentration of  $n$  spheres in solution is  $\varphi = \frac{4\pi}{3}nR_G^3$ .

Considering the approximation made on the shape of the polymer coils in solution, it is possible to consider that the maximum packing fraction of the polymer coils is  $\varphi_c=1$  [44]. Therefore, the critical concentration separating the diluted and semi-diluted regimes is  $c^* = \frac{M}{N_A \frac{4\pi}{3}R_G^3}$ , where  $M$  is the molar mass of the polymer, and  $N_A$  is the Avogadro number. For a VMA having a molar weight of 800 k g/mol and a hydrodynamic radius around 60 nm, the critical concentration is of the order of 0.15%. In practice, the critical concentration is identified by measuring the changes in the viscosity of solution (see Section 3.3). It should be kept in mind that this critical concentration could be affected by the formation of associates (see Sections 3.2 and 3.3).

In the concentrated regime, the monomers of the polymers are quite close to each other [51]. This situation is attained for highly concentrated solutions or melt polymers and is out scope of this paper.

The conformation of polymers in the dilute has extensively been studied in the literature [46,47,50]. Depending on the affinity of the monomers with the solvent, the polymer exhibits an expanded or contracted conformation. Repulsive electrostatic forces between the monomers of a polyelectrolyte in water leads to an expanded

conformation of the polymer. However, the addition of ionic species could screen these charges and lead to a more compact conformation. In some case, these ionic species could lead to a crosslinking of the polymer or even a precipitation.

It was observed in [42] that while anionic polyacrylamide (i.e., poly (acrylamide-co-sodium acrylate)) adopts an expanded conformation in water, the counterions present in cement pore solution (i.e.,  $Ca^{2+}$  or  $Mg^{2+}$ ) lead to polymer crosslinking and a dramatic decrease of the polymer size. It was shown in [52] that the conformation of carboxymethyl cellulose strongly depends on the Calcium ions in the solvent to the charged side groups of the polymer ratio and a precipitation, an expansion or contraction of the polymer could be observed.

Moreover, results obtained by Khayat et al. [25] suggest that for welan gum, conformation is not affected by the composition of the cement pore solution. According to [23], diutan gum and welan gum exhibit a double-helical conformation where the side chains screen the carboxylate groups of the backbone and prevent crosslinking by Calcium ions. Finally, it was shown in [7,53], that cellulose ether (HEC and HPMC) conformation is also almost the same in both distilled water and cement pore solution.

In the dilute regime and in the case of linear polymers, the relation between the radius of the coils and molar mass  $M$  of the polymer can be expressed as  $R_G = K_{RG}M^\nu$ , where  $K_{RG}$  and  $\nu$  are constants depending on the flexibility of the chain and the affinity of the polymer with the solvent, respectively.

As the radius of gyration, the intrinsic viscosity captures the size of the polymer in solution. The intrinsic viscosity  $[\eta]$  corresponds to the reduced viscosity (i.e., ratio of the specific viscosity  $\eta_{sp}$  to the dissolved polymer concentration  $c$ ) of an individual molecule at very low shear rate. Its dimension is therefore the inverse of a concentration. As stated earlier, the specific viscosity is defined as  $\eta_{sp} = \frac{\eta_0}{\eta_{00}} - 1$ , where  $\mu_0$  is the zero-shear viscosity of polymer solution and  $\eta_{00}$  is the viscosity of the solvent. The intrinsic viscosity parameter can then be computed from the molar mass  $M$  via the Mark-Houwink-Sakurada relationship  $[\eta] = K_\eta M^\alpha$ , where  $K_\eta$  and  $\alpha$  depend on the polymer and the solvent [54].

The above constants linking the molar mass to the radius and to the intrinsic viscosity respectively for polyethylene glycol, cellulose ether, xanthan gum and polyacrylamide in different solvents are summarized in Table 1. It should be kept in mind that these constants depend on polymer polydispersity and could be affected by other molecular parameters such as DS and MS of cellulose ethers or polymer anionicity.

As stated above the conformation of polymers in solution also depends on their intermolecular interaction, which will be discussed further in the next section.

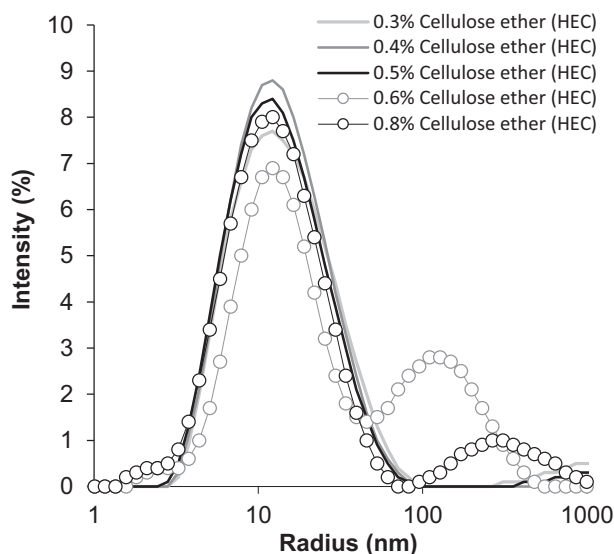
### 3.2. Associative polymers and formation of aggregates

Cellulose ethers' skeletons are grafted with hydrophobic groups, mainly alkyl or hydroxyalkyl chains. In an aqueous solution, these polymers are characterized by a strong propensity to combine in such a way as to minimize water contact between water and hydrophobic part of the polymers [5–7,57,58]. In dilute solution, intramolecular interactions are favored and at higher concentration they lead to the formation of polymer associates (i.e., aggregates, agglomerates) [59] (see Fig. 6b).

Fig. 7 shows the size distribution by intensity measured by dynamic light scattering of HEC in cement pore solution at different concentrations [53]. The main peak around 10 nm can be attributed to polymer coils. Above 0.5% of HEC, the apparition of polymer associates which were not observed at lower concentrations and which size is around hundreds of nanometers is noted. Similar results have been obtained in [5–7,57,58] and show that above a critical concentration, called in the following the overlapping concentration, cellulose ether polymers are able to form hydrophobic association which size is around few micrometers (i.e., order of magnitude of cement particle size).

**Table 1**  
R<sub>G</sub>-M and [η]-M relationship.

Polymer	Solvent	K <sub>RG</sub> (nm)	ν	a	K <sub>η</sub> (ml/g)	Reference
Polyethylene (PEG)	Cement pore solution	0.0375	0.53			[53]
	DI water	0.0343	0.53			[55]
Hydroxyethyl cellulose (HEC)	Cement pore solution	0.04	0.53			[53]
	DI water	0.026	0.59	0.73	4.1 × 10 <sup>-2</sup>	[52]
Hydroxypropyl cellulose (HPC)	DI water	0.025	0.56	0.68	4.2 × 10 <sup>-2</sup>	[52]
Hydroxyethylmethyl cellulose (HEMC)	DI water	0.038	0.53	0.6	1.7 × 10 <sup>-1</sup>	[52]
Hydroxypropylmethyl cellulose (HPMC)	DI water	0.047	0.51	0.53	3.6 × 10 <sup>-1</sup>	[52]
Hydrolyzed Polyacrylamide (HPAM)	Water	0.0076	0.62			[42]
Xanthan Gum	0.01 M NaCl			1.27	2.79 × 10 <sup>-3</sup>	[56]



**Fig. 7.** Relative contribution to the scattering light intensity as a function of the hydrodynamic diameter for Cellulose ether (HEC) in cement pore solution. Reproduced from [53].

It was shown in [8] that above a critical concentration, hydroxypropyl guar chains can also form associates. It is suggested that similarly to cellulose ether, the hydrophobic character of the alkyl side chains leads to strong intermolecular interactions and formation of associates. By comparing different hydroxypropyl guar polymers, they showed that additional substitution of alkyl side chains enhances the formation of associates at lower dosages. However, according to [60], for natural starches, associated polymers could not be observed in water and limewater.

It was shown in [61] that in the semi dilute regime, xanthan gum forms a microgel. According to [59], these microgels are not compact and are stable in good solvent and high ionic strength. It is suggested in [62] that hydrogen bonding between neighboring chains could lead to the formation of these associates. Finally, it should be kept in mind that low molar mass surfactant addition can strongly inhibit or enhance the formation of these associates. Clasen et al. [52] extensively studied the effect of the concentration of surfactant Sodium dodecyl sulfate on the formation of associates of HPC, HEMC, and HPMC.

To the best of our knowledge, the critical concentration (i.e., overlapping concentration) above which polymer associates form cannot be easily defined from the molecular properties of the polymers and experimental measurements are needed.

### 3.3. Viscosity and concentration regimes

Viscosity of cement pore solution has a marked influence on both the stability (see Section 4.3) and the viscosity of the cement-based material (see Section 4.2.2.). At low shear rates the higher is the viscosity of the

cement pore solution containing VMA, the more stable is the suspension. At high shear rates induced by mixing, pumping and casting concrete, shear thinning behavior of VMA solution maintain a relatively low resistance to flow [25].

It should be kept in mind that only non-adsorbed VMA increase the viscosity of cement pore solution. In this section we focus on the rheological behavior of aqueous VMA solution regardless of their affinity and adsorption on the surface of cement particles.

Depending on the concentration regime and polymer chain properties, polymer solution could behave as a Newtonian solution, as shown for cellulose ether below 0.4% in Fig. 8a, or exhibit a Newtonian behavior at low shear rates and a shear thinning behavior (i.e., viscosity decreases with shear rate) above a critical shear rate value, as shown for welan gum in Fig. 8b and for cellulose ether above 0.4% in Fig. 8a. The viscosity at the Newtonian plateau is called the zero-shear viscosity and has extensively been studied in literature.

Fig. 9a shows the evolution of the specific viscosity of cellulose ether and polyethylene glycol aqueous solution as a function of polymer concentration. At the same concentration, the specific viscosity depends on the polymer and increases with the polymer molar mass. Fig. 9b shows the evolution of the specific viscosity of cellulose ether, polyethylene glycol and xanthan gum aqueous solution as a function of the dimensionless number  $c[\eta]$  (which is proportional to the volume concentration of polymers in solution). As a first observation, the evolution of the viscosity of all these polymers follows the same master curve.

Below a critical concentration  $c^*$ , which seems to depend on the polymer family, the specific viscosity of these polymers is described by the same master curve with a gradient of 1. Above this concentration, a sudden change in slope 4.4 is observed.  $c[\eta]$  seems to well capture, at a first order, the effect of polymer conformation in solution and concentration on the viscosity of solution. For the VMA studied here, the critical concentration is between 0.1% and 1%.

We recall that the evolution of the zero-shear viscosity of a solution of a linear polymer as a function of the concentration can be described by the Huggins equation [64]:

$$\eta_{sp} = c[\eta] + k_H(c[\eta])^2 + B_n(c[\eta])^\alpha$$

where  $k_H$  is the Huggins coefficient,  $B_n$  is a constant dependent on polymer/solvent and  $\alpha > 2$  is a constant which will be discussed in detail below.

Depending on the polymer volume concentration (i.e., the concentration regime), one of the three terms of the Huggins equation dominates the specific viscosity.

In the dilute regime, when the polymer volume concentration is lower than few percent, polymers coils are sufficiently spaced to interact hydrodynamically and viscosity can be well predicted by Einstein equation. In this situation the specific viscosity is proportional to  $c$  and  $c[\eta]$  (see Fig. 9a and b).

In the dilute regime and beyond the range where polymer volume concentration is a few percent maximum, the flow disturbances induced by a polymer coil significantly affect the flow velocity field of the solvent around its neighbors. In this case, the viscosity can only be



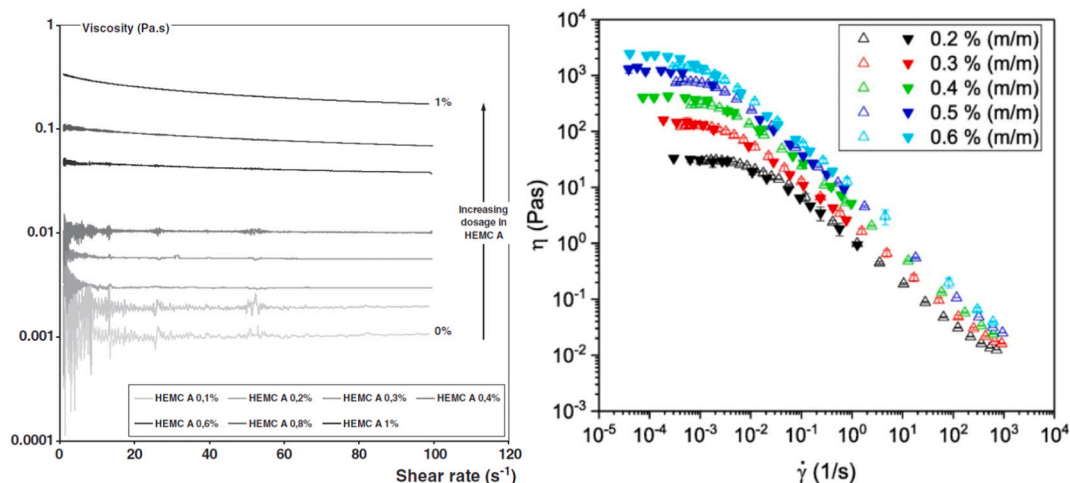


Fig. 8. Viscosity of (a) cellulose ether (HEMC). (b) welan gum in water for various dosages in polymer as a function of the shear rate. Reproduced respectively from [7,63] with permission.

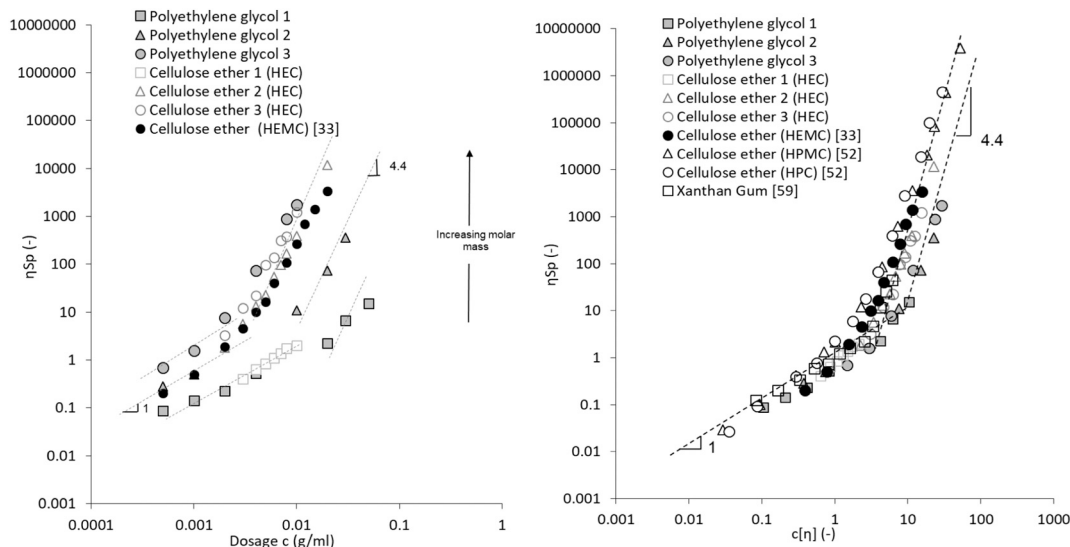


Fig. 9. Specific viscosity as a function of (a) polymer dosage (b)  $c[\eta]$ . Adapted from [53].

approximately described by the two first terms of Huggins equation which is  $c[\eta] + k_H(c[\eta])^2$ .

In the semi-dilute regime, intermolecular interactions between neighboring polymers begin to dominate the mechanical behavior of the solution. To decrease their apparent volume, polymers contract and above a critical molar mass their chains become entangled and play a very important role in increasing the viscosity of the solution. In this regime the specific viscosity is dominated by the last term of the Huggins equation  $(c[\eta])^\alpha$ . As shown in [65–67], an exponent  $\alpha$  equal to 4.4 suggests that the increase in viscosity observed for all the polymers studied here is mainly due to the hindrance of movement induced by their entanglement. This constant is obtained for linear polymers in good solvent. The above results are in agreement with the literature of polymer solution and suggest that at a first order, the zero-shear viscosity of aqueous VMA solution depends mainly on the volume concentration of the polymer in solution, no matter the specificities of the polymer.

However, the differences observed between the curves of associative polymers (i.e., cellulose ethers and xanthan gum) and non-associative polymers (i.e., polyethylene glycol) suggest that polymer association

and formation of aggregates is involved, along with chains entanglement, in the increase of viscosity.

Furthermore, Fig. 8b shows that at high shear rates, viscosity decreases when shear rate increases following a power law  $\mu \propto \dot{\gamma}^{-n}$ ,  $n$  is a called flow index and lies between 0 and 1. The shear thinning behavior could be owed to changes in the polymer structure, the polymer chains align, stretch, and/or disentangle [44] (see Fig. 6d). The higher the flow index, the more pronounced are these changes. It was shown in [52], that the flow index of aqueous cellulose ether solution only depends on polymer volume concentration and is independent on the polymer molar weight, and the DS an MS. It was shown in [68,69] that under the same conditions, aqueous welan gum solution exhibits a more pronounced shear thinning behavior (i.e., higher flow index  $n$ ) than aqueous cellulose derivatives. According to [44] the critical shear rate above which viscosity decreases with shear rate decreases with polymer molar mass and concentration. For the best of our knowledge, the polymer properties controlling the shear thinning behavior is still not fully understood. Further investigation is needed to control such rheological behavior.

### 3.4. Evolution of dissolution over time

Dissolution of soluble polymer powder in cementitious suspensions can be difficult and dramatically affect the mechanism of action of the polymer [5,70–72] (see Section 4.1.3).

It was shown in [5,72,73], that cellulose ether dissolution in water could be slowed by the formation of lumps which dissolution at gentle stirring and at room temperature, could take more than a week. It was shown in [70], that dissolution of hydroxypropyl guar in lime solution could take few hours (see Fig. 10). However, when incorporated to cement paste, strong shear induced by mixing leads to a total dissolution of cellulose ether and hydroxyl propyl guar within few minutes [70].

According to literature of soft matters, at a constant stirring conditions, the dissolution of soluble polymer powders depends on the osmotic pressure between the gel and the dilute solution and the permeability of the formed gel [74].

It is well known from literature that dissolution rate of polymers decreases when the molar mass increases [74–78] and when the dry grain size increase. For polyethylene glycol, it was shown in [74] that the dissolution time is proportional to  $M_w^{2/3}$ .

For polyelectrolytes, osmotic pressure between the solution and the gel is controlled by the ionic strength [79]. It was shown in [74] that when the solution ionic strength increases, osmotic pressure gradient decrease and dissolution rate of the polyelectrolyte (i.e., a bio fermented polysaccharide) decreases. Finally, it is obvious that stirring the gel efficiently enhances its dissolution and turns it into a polymer solution. It was shown in [74] that dissolution time is inversely proportional to the applied shear rate.

## 4. VMA in cement paste: adsorption and consequence on rheological properties

The working mechanisms of VMAs and their impact on the rheological properties will depend on if it fully remains in solution or, if in contrast, it partially adsorbs onto cement particles. In this section, the main limitations of the adsorption measurements in cement pastes containing VMAs and the origin of this adsorption are described. Afterwards the impact of the VMAs on the rheological parameters of concentrated suspensions, in relation with the adsorption or not of the polymer, have been summarized.

### 4.1. Adsorption

#### 4.1.1. Adsorption measurements

The ability of VMAs to adsorb onto the mineral surfaces mainly depends on the molecular structure of the polymer and the surface properties of the solid. However, the measurement of the polymer adsorption

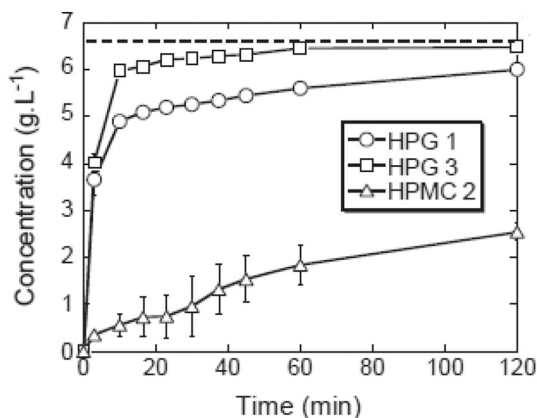


Fig. 10. Dissolution kinetics of admixture in lime solution ( $\text{Ca}(\text{OH})_2 = 20 \text{ mM}$ ). Reproduced from [70] with permission.

is not an easy task and it can involve some artefacts. In general, the depletion method is applied in which the amount of polymer adsorbed is determined from the difference between the initially added polymer and the remaining in the aqueous pore solution after certain time. At concentrations below the VMA polymer overlapping no great artefacts should be introduced if the pore solution is adequately extracted. However, in the case of cellulose ether VMAs and at dosages higher than the overlapping concentration, polymer associates are formed and they can be trapped in the porosity of the paste [6,7,80]. This could lead to an overestimation of the amount of polymer adsorbed.

The physical retention of non-ionic CEs between cement particles after centrifugation was systematically studied by Hurnaas and Plank [80]. This retention was concluded from the low amount of CE depleted, the fact that the amount of polymer depleted decreased with the increase of the water/cement ratio (W/C) and the absence of plateau value in the adsorption isotherm. Furthermore, when using silica flour as model system in synthetic cement pore solution, the addition of non-ionic CE did not modify the zeta potential of the suspension as expected if adsorption would take place. The authors also concluded that the amount of polymer retained depended on the number of polymer aggregates formed, that increased with the rise of the polymer concentration and the decrease of DS.

For all these reasons, the adsorption of VMA at concentrations above the critical concentration for the formation of polymer associates must be carefully interpreted.

#### 4.1.2. Origin of affinity: effect of molecular parameters

**4.1.2.1. Interaction of ionic VMAs with cement.** Polymers adsorb on surfaces by physical or chemical adsorption. Attractive electrostatic forces are responsible for the physical adsorption, while the latter involves the formation of chemical bonds. Anionic VMAs such as welan gum, diutan gum or anionic polyacrylamides can physically adsorb in lower or greater extent depending on their affinity by the mineral surface.

In cement pastes, up to 10-fold adsorption plateau values have been measured for welan gum with respect to polycarboxylate-based superplasticizers [81] (see Fig. 11) due to the higher specific anionic charge of welan gum. This has relevant implications in practice as competitive adsorption of both polymers could occur [43], something that we describe in more detail in Section 5.

The interaction of anionic PAMs with Calcium ions in solution leads to their crosslinking and the formation of microgels that can also adsorb onto the cement particles. An increase of the acrylate content of the PAM, and consequently their degree of anionicity, enhances the polymer adsorption [42].

**4.1.2.2. Interaction of non-ionic VMAs with cement.** Several studies [16,19,70] have measured the adsorption onto cement particles of non-ionic VMAs such as CEs, starch or guar gum admixtures including the modified one with non-ionic groups. To this respect, starch VMA have shown to adsorb in cement pastes although its affinity by the cement surface is significantly lower than PCE superplasticizers and welan-gum as shown in Fig. 6. However, the underlying adsorption mechanism of non-ionic VMAs still remains a matter of debate and further research on this topic is required. In the case of CEs (HEMC and HPMC), a decrease of DS leads to an increase of the adsorption [7,31,82] (see Fig. 12). Different adsorption mechanisms for polysaccharides onto surface minerals have been proposed such as (a) hydrogen bonding [83]; (b) hydrophobic interactions [84], (c) complexation between the hydroxyl groups of the polysaccharides and metal ions on the mineral surface [85], and (d) electrostatic attractive forces [86] between the charged surfaces of cement and hydrates and the polar hydroxyl groups of polysaccharides.

Several authors have investigated possible artefacts during the measurements that could contribute to the adsorption of non-ionic

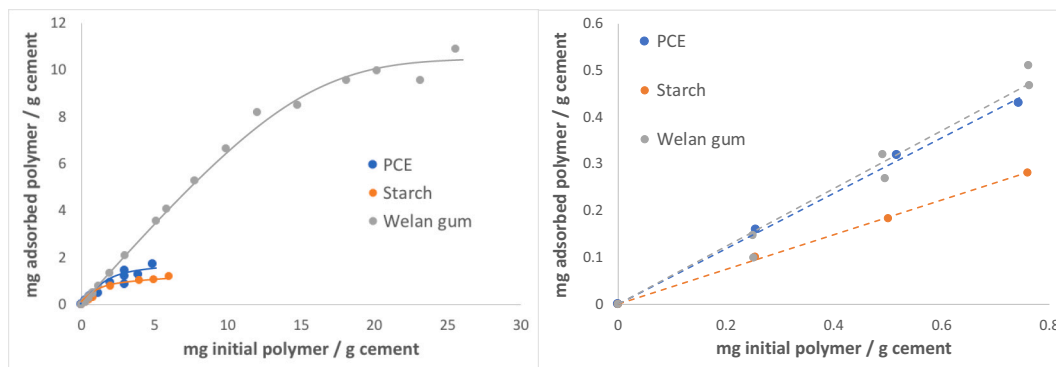


Fig. 11. Adsorption isotherms of PCEs and starch-based and welan gum VMAs. Reproduced from [81] with permission.

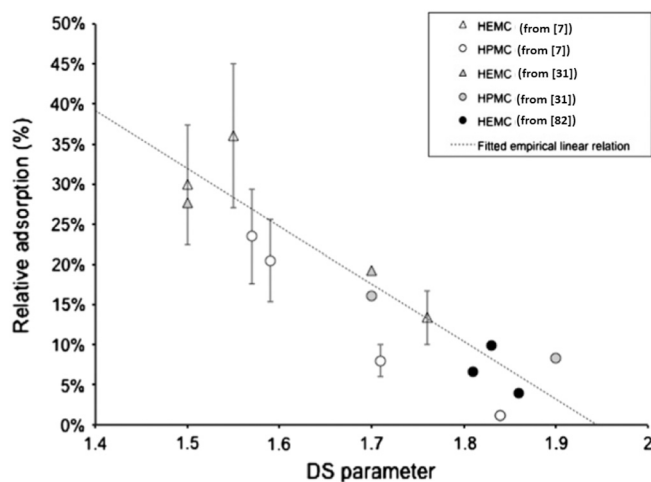


Fig. 12. Relative CE adsorption as a function of the DS for a CE dosage of 0.2% that it is below the overlapping concentration. Reproduced from [7] with permission.

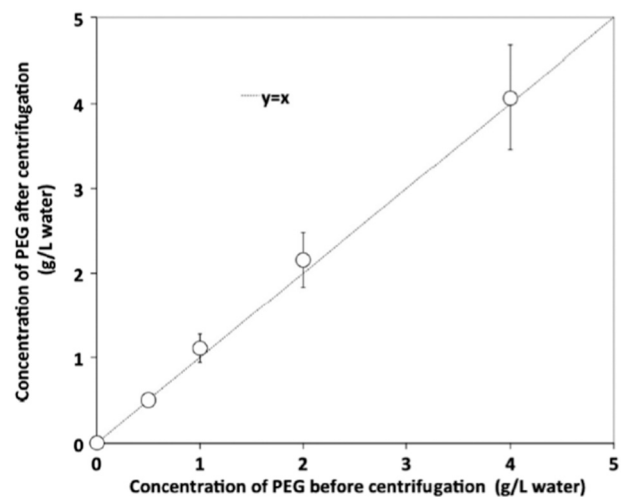


Fig. 13. PEG concentration in the filtrate after centrifugation as a function of the initial PEG concentration before and after contact with cement. Reproduced from [42] with permission.

VMAs. Bülischen et al. [6] explained the adsorption of CEs in base of the presence of anionic impurities. Müller [31] investigated the possible role of the degradation products of CEs in highly alkaline conditions to the adsorption, concluding their high stability by Size Exclusion Chromatography (SEC) measurements. Moreover, Hurnaus and Plank [80] established that the polymer was retained in the cement porosity during the extraction process of the pore solution and not adsorbed onto cement particles.

In contrast with non-ionic CEs and guar gum derivatives, PEGs do not adsorb onto cement and  $\text{CaCO}_3$  [87] particles and, as shown in [42], PEG with a molecular weight of  $4 \cdot 10^6$  g/mol and a hydrodynamic radius of 80 nm cannot be entrapped in cement porosity (Fig. 13).

#### 4.1.3. Effect of dry and predissolved addition of VMA

The mode of the VMA addition may play a relevant role on their interaction with the cement particles and consequently on their effect on the rheology of cementitious systems. Pointot et al. [70] showed that the addition of hydroxypropylguars (HPGs) and CEs pre-dissolved in water led to a higher water retention and viscosity with respect to the addition of these polymers in solid state. In particular, the pre-dissolution of HPG induced its faster adsorption onto cement hydrates and the inhibition of their growth. The lower specific surface area would explain the lower amount of polymer adsorbed and its higher content in cement pore solution to reach the overlapping of the polymer coils with respect to the addition of HPG and CEs in dry state (see Fig. 14).

## 4.2. Consequences on rheological properties

### 4.2.1. Effect on yield stress

The majority of cement-based materials exhibit a yield stress above which the material starts flowing and below which the materials stops flowing [88]. The desired yield stress depends on the application and can be affected by the use of VMA. While low yield stress is required for SCC which can be placed in congested reinforcement without vibration, high yield stress is necessary for shotcrete or monolayer mortars which, after spraying, should stay on the wall in thick layers [11,12]. In this section we focus on the main forces induced by VMA in cement-based materials and their consequences on the rheological behavior of cement paste. A better understanding of the microscopic mechanism of actions of VMA allows for an appropriate choice of VMA polymer and dosage and a better control of the material yield stress.

**4.2.1.1. Bridging forces.** The effect of VMA was studied using advanced rheometry in [12] in the case of CEs. The authors based their analysis on the fact that, as flow onset measurements screen various range of strains, they also screen the various interactions associated to these strains. For instance, strains lower than  $1E-3$  in Fig. 15 corresponds, for a cement paste, to extremely rigid interactions that only hydrate bridges between grains can provide [89]. Strains around a couple % correspond to the standard Van der Waals forces that dominate the fresh state behavior in typical cement pastes without admixtures. Using this frame of analysis,

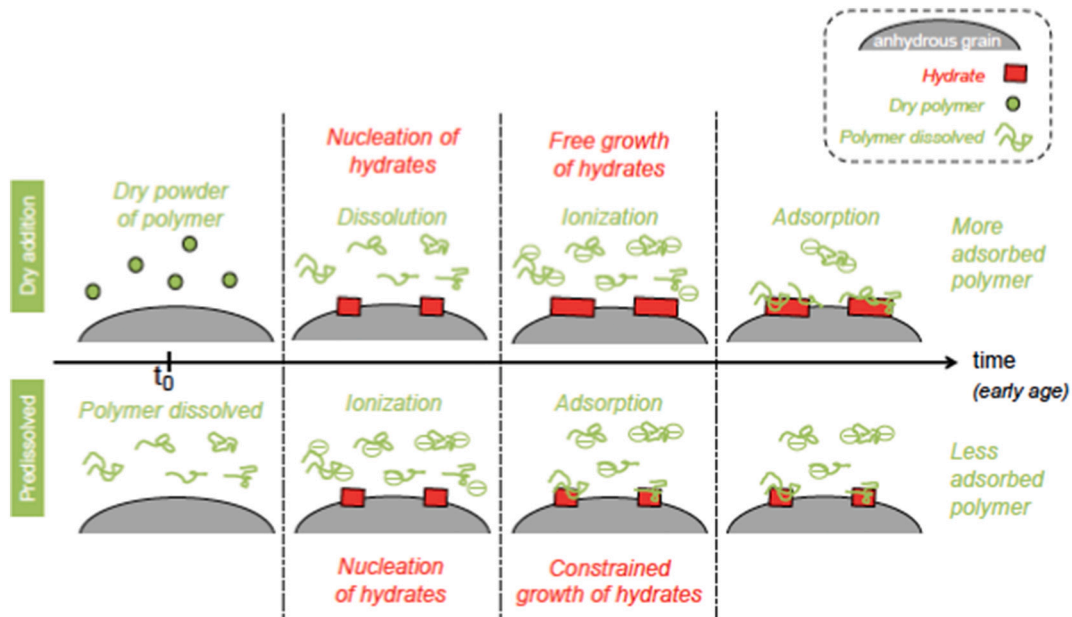


Fig. 14. Schematic representation of polysaccharide-cement interaction in relation to the addition method of the VMA. Reproduced from [70] with permission.

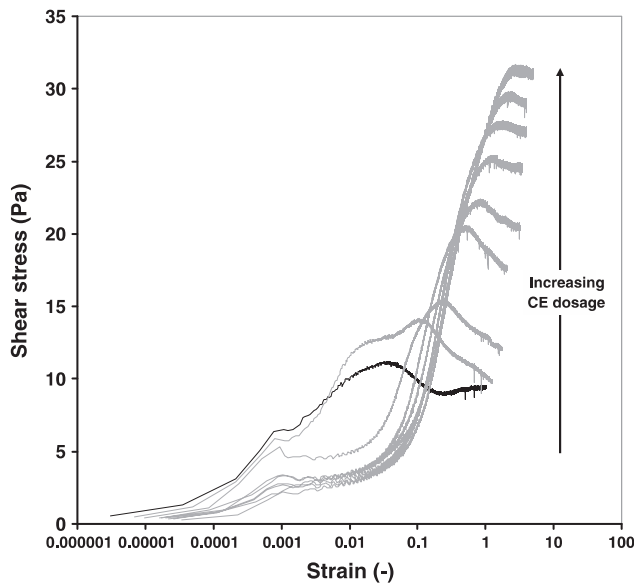


Fig. 15. Flow onset measurements for the reference cement paste (black curve) and for pastes containing 0.1, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2 and 1.5% of HEMC. Reproduced from [12] with permission.

it was shown in [12] that CE adsorption on cement grains is at the origin of a full collapse of the van der Waals attractive interaction network (Around 0.01 strain in Fig. 15). It was moreover suggested that the adsorbed CE molecules are at the origin of repulsive steric forces leading to this collapse similarly to what adsorbed superplasticizers do. Finally, it was suggested that adsorbed CEs are at the origin of the formation of a new interaction network in the paste. From dimensional inter-particle force analysis, the authors suggested that this network finds its origin in the bridging of cement grains by adsorbed ether molecules (see Fig. 6e). Flow onset occurs then through a desorption process, the energy of which can be assessed from adsorption isotherm measurements.

Furthermore, VMA efficiency in bridging particles depends on their molar mass (see Fig. 16). For high molar mass VMAs, the yield stress

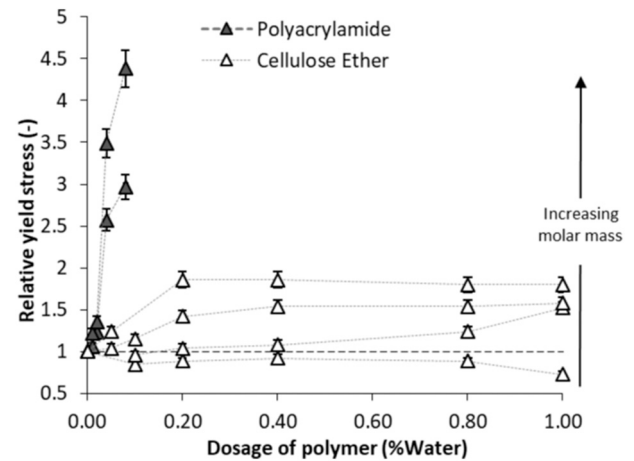


Fig. 16. Relative yield stress (i.e., the ratio between the yield stress of the paste with polymer and the yield stress of the reference paste) as a function of VMA dosage.

Adapted from [53].

increases when the molar mass increases. Low molecular weight VMAs are unable to adsorb on multiple particles and can be at the origin of a yield stress decrease through steric hindrance (see Fig. 16). Similar results have been obtained by Patural et al. [90,91].

It was moreover shown in literature that, the ability of polyacrylamide to bridge particles is sensitive to shear history and the suspension seems to progressively lose its ability to rebuild with each shearing or re-mixing cycle [42]. It was suggested that this feature could find its origin in the progressive flattening under shear of the adsorbed polymer at the surface of cement grains.

4.2.1.2. Depletion forces. From interparticle force calculations and rheological measurements, it was shown in [87] that Van der Waals attractive forces are the dominant flocculating mechanism in cement paste containing non-adsorbing VMA. In this case, attractive depletion forces resulting from non-adsorbing polymers are negligible and do not affect the yield stress of the suspension (see Fig. 17). In cement paste

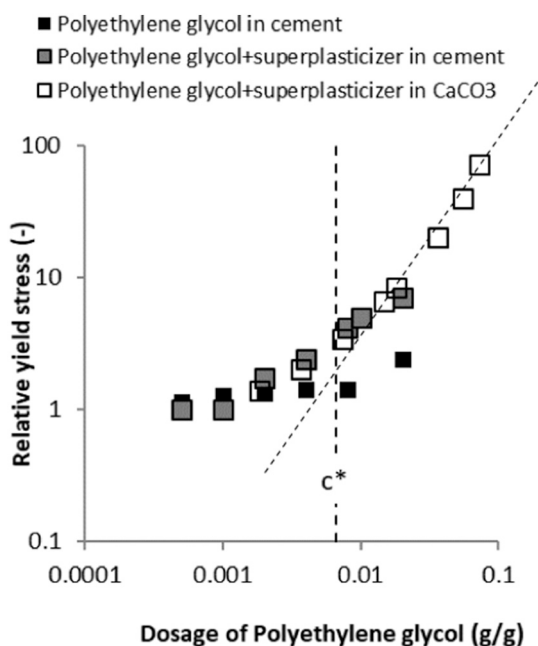


Fig. 17. Relative yield stress of cement pastes and calcite as a function of Polyethylene glycol dosage (g/g powder). The superplasticizer is a PCE. Its dosage is 1 g/l in cement and 5 g/l in CaCO<sub>3</sub> paste, W/Cement = 0.4 and W/CaCO<sub>3</sub> = 0.55. The relative yield stress is the ratio between the yield stress of the paste with Polyethylene glycol and the yield stress of the reference paste without Polyethylene glycol. The vertical dashed line corresponds to the critical polymer concentration  $c^*$  defined in the text. Reproduced from [87] with permission.

containing superplasticizers, the magnitude of the attractive van der Waals forces decreases, and the contribution of attractive depletion forces generated by non-adsorbing VMA to the flocculation mechanism become important (Fig. 6f). In this system, the addition of non-adsorbing polymers leads to an increase of relative yield stress (see Fig. 17).

Below a critical concentration which corresponds to the critical concentration  $c^*$  (i.e., in the dilute regime), a moderate increase in the relative yield stress is observed. At higher polymer concentrations, a rapid increase in the relative yield stress, scaling with  $c^{3/2}$ , is observed. This scaling is consistent with the magnitude of the computed depletion forces. From Fig. 17, it was noted that in the common industrial dosage range of VMA (i.e., of the order of few tens of %), the relative yield stress remains equal to 1 in the reference cement paste without PCE and vary between 1 and 3 in cement pastes containing PCE. This suggests that the combination of a superplasticizer and a VMA could lead to an increase of the yield stress which is in most cases considered inconvenient. However, it should be kept in mind that before VMA addition the yield stress of the reference cement paste containing superplasticizer is very low and any addition of VMA at a common industrial dosage will have a very moderate effect on the flowability of the suspension.

For differently modified starches and diutan gum depending upon PCE dosage and solid volume a similar increase of the relative yield stress is observed in cement and limestone filler paste [92].

#### 4.2.2. Effect on viscosity

The apparent viscosity is defined as the ratio between shear stress and shear rate. It depends on the suspension composition and the applied shear rate [88]. The rheological behavior at low and intermediate shear rates of cement pastes is often described by the Bingham type relation  $\tau = \tau_0 + \mu_p \dot{\gamma}$  where  $\tau$  is the stress,  $\tau_0$  is the yield stress,  $\mu_p$  is the plastic viscosity and  $\dot{\gamma}$  is the shear rate.

It was shown in [93–100] that VMA incorporation increases the plastic viscosity of cement paste. However, shear thinning behavior of

VMA solution maintains a relatively low resistance to flow during mixing, pumping and casting [25,98].

At low shear rates, colloidal attractive forces dominate the hydrodynamic forces and the cement paste displays a shear thinning behavior (i.e., decreasing apparent viscosity with shear rate). At intermediate shear rates, hydrodynamic forces govern the viscous dissipation and the suspension display a Newtonian behavior (i.e., constant apparent viscosity). At high shear rates, particle inertia leads to shear thickening behavior (i.e., increasing apparent viscosity with shear rate) [88]. In high solid volume fraction suspensions, the transition between shear thinning behavior and shear thickening behavior is direct and the Newtonian behavior is not observed.

According to literature, viscosity of cement paste at the Newtonian plateau is expected to scale with the product of the cement pore solution and another function of the solid volume fraction [101]. However, some results from literature [33,34,53,102] show that viscosity of cement paste containing VMA increases with the viscosity of cement pore solution but the increase is attenuated (i.e. not proportional to the viscosity of cement pore solution). According to [102], this behavior is owed to non-adsorbed polymers which, thanks to hydrodynamic lubrication, prevents direct contacts and reduces the overall energy dissipation. More explanations are given in literature which suggest that non adsorbing VMA could be at the origin of repulsive depletion forces [33] or repulsive steric forces [53] which lead to an increase of the interparticle distance and to the decrease of viscosity [103]. The origin of the attenuated viscosity in the presence of VMA is still a subject of debate. However, it should be kept in mind that it is very delicate to isolate the viscosity of cement paste which only results from hydrodynamic dissipation (i.e., Newtonian plateau) from the colloidal and inertial contributions [88,103]. To avoid misinterpretation, viscosity results from literature must therefore be carefully interpreted. Moreover, since in suspensions, the microscopic shear rate is higher than the macroscopic shear rate, for shear-thinning polymer solutions it is important to consider the viscosity of cement pore solution at high shear rates.

#### 4.2.3. Effect on thixotropy

Thixotropy has two origins in cement paste: flocculation (over time scales of the order of some minutes) and structuration due to hydrates nucleation (over time scales of the order of some tens of minutes) [89]. VMAs that do adsorb introduce in the system some bridging forces as described above. As such, they enhance the flocculation of the system and therefore the short time scales thixotropy. The material builds up its yield stress very quickly once it has stopped flowing. However, some of these macromolecules were reported to delay hydration and therefore slow down hydrates' nucleation [82,104–106]. As such, they decrease the kinetics and amplitude of the material structuration over long time scales, as shown in Fig. 15 where the stress level in the 1E-3 strain range drastically drops when CEs are added to the system.

#### 4.2.4. Effect of varying W/C

The yield stress of colloidal particles suspensions is expected to scale with the product of the interparticle force with a function of the solid volume fraction [107], while the viscosity is expected to scale with the product of cement pore solution viscosity and another function of the solid volume fraction [101].

Cement pastes are no exception, and this is expected to apply to systems containing VMAs. This means that, as VMAs are expected to modify interparticle forces and cement pore solution viscosity (as described above), their effects are not expected to depend on solid volume fraction.

Some caution should however be taken here. First, VMA mode of action depends on adsorption, which is itself expected to depend on concentration, which, in turn, depends on W/C when the VMA dosage is expressed as a function of the cement mass.

Moreover, W/C variations often lead to variations in PCE demand to maintain a constant yield stress. As PCEs and VMAs can compete for

adsorption sites (Cf. Section 5), a variation in W/C and related variations in PCE demand can induce variations in VMA adsorption and, in turns, the effect of VMA on fresh properties.

Finally, the variation of W/C modifies the ionic composition of cement pore solution and the hydrates at the surface of cement particles and can affect the mechanism of action of VMA [108,109]. This can also affect the conformation of VMA in solution (Cf. Section 3) and its adsorption.

#### 4.3. Effect on stability

As shown in Sections 3 and 4.1, the rheological behavior of cement pore solution can be correlated to the amount of non-adsorbed VMAs. Consequently, and as described in the previous section, the apparent viscosity of both cement pore solution and of the resulting cement-based suspension increases when the amount of non-adsorbed VMA increases. This has, however, some beneficial consequences on the material ability to retain some of its free water when faced to destabilizing conditions, such as the contact with a dry surface or pressure gradient (i.e., water filtration, washout) or simply the phase separation induced by gravity (i.e., segregation or bleeding). This feature was demonstrated in [7] in the case of CE effect on water retention. It was shown that, below overlapping concentration, water retention of mortars containing CE can be seen as a biphasic filtration process, in which the rheological properties of cement pore solution dictate the ability of water to resist migration under a pressure gradient whereas, above the overlapping concentration, the formation of some CE associates in the paste pore structures start to dominate water retention (see Fig. 18). The size of these associates could reach few micrometers which is the characteristic size of the porosity of the common pastes [88].

As suggested by [110], the viscosity of cement pore solution can control the rate of filtration but cannot govern alone the water retention. The formation of associates is needed to physically plug the filter cake porosity and therefore improve water retention. Similar results on the effect of the formation of CE associates [5–7,57,58] and hydroxypropyl guar associates [8] on water retention have been reported in literature.

However, the stability of grout or concrete constituent when submitted to gravity is expected to depend on the viscosity of cement pore solution and not on the formation of polymer associates. Although polymer associates enhance the viscosity of cement pore solution, their presence is not mandatory in this case. It should be kept in mind that the viscosity of cement pore solution can control the rate of constituent separation but cannot govern alone the stability of the suspension.

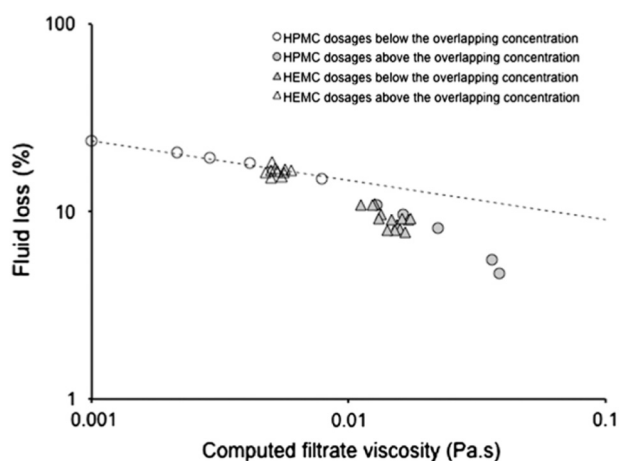


Fig. 18. Fluid loss as a function of the computed filtrate viscosity for 24 different HEMC(s) and different HPMC(s). The dashed line illustrates the correlation between fluid loss and filtrate viscosity below the overlapping concentration.

Reproduced from [7] with permission.

Constituents separation can be avoided when the yield stress of cement paste builds up very quickly thanks to hydrate nucleation and/or VMA induced flocculation (see Section 4.2.3) [111,112]. The yield stress of cement paste must be high enough to resist gravity forces applied on the flocculated cement particles and generated by the density difference between an individual coarse grain and the cement paste [88].

The effect of VMA on stability in various industrial applications is illustrated in Section 6.1.

#### 5. Viscosity modifying admixtures and superplasticizer compatibility

In some construction applications, such as SCC, the mixture design combines VMA and superplasticizer to secure adequate rheological properties and proper performance of the material. While superplasticizers enhance concrete flowability, the incorporation of VMA can increase yield stress and/or viscosity of the mixture leading to a flowable yet and stable system during processing and ideally until the onset of hardening. However, the blending of these chemical admixtures can generate some incompatibilities in cement pore solution or lead to competitive adsorption on surface sites of particles, which can influence the performance of the cement-based material.

Mikanovic et al. [113] observed that, while a cellulose ether (HPMC) acts as a VMA in water and in lime solution, it exhibits no significant viscosity enhancement in the presence of superplasticizer (i.e., Polynaphthalene Sulfonate (PNS)). These and related observations indicate that the erratic behavior (incompatibility) of some VMAs and superplasticizer couples can, in part, originate from solvation effects and polymer interactions occurring in the solution. Such interactions, as observed in this example can dramatically alter the combined action of these admixtures. On the other hand, Khayat et al. [4] reported good compatibility between diutan and PNS-based and two PCE-based superplasticizers used in SCC. The superplasticizer demand and workability characteristics of the SCC was shown to depend on the selected superplasticizer and dosage of the VMA.

Moreover, it was shown in [87] that in cement paste containing superplasticizers, depletion forces induced by non-adsorbing VMA become important and could contribute to the flocculation mechanism. More details on this mechanism of action are summarized in Section 4.2.1.

In cement paste, the mechanism of action of both an adsorbing VMA and superplasticizer is sensitive to their adsorption behavior onto cement particles. Competitive adsorption at the surface of cement particles can be an advantage leading to synergetic effects between adsorption species but, on the other hand, can in some cases reduce the desired performance [114].

It was observed in [114] that when surface saturation is attained, the adsorption of a PCE-based superplasticizer can lead to the gradual desorption of the VMA (see regime 2 in Fig. 19). The VMA is a cellulose ether (HEC). At relatively high superplasticizer dosage, cement particles can be completely covered by superplasticizer molecules, and the entire VMA polymer remains in the cement pore solution (see regime 3 in Fig. 19). The substitution of the VMA by superplasticizer occurs rapidly (i.e., within 15 min). However, it should be pointed out that the desorption of an already adsorbed polymer could be very slow process in some cases and can take hours, days or even years [115].

When the VMA is displaced by the superplasticizer, yield stress is governed by the adsorbed superplasticizer, while the residual viscosity is mainly dictated by the concentration of the VMA remaining in cement pore solution (see regime 3 in Fig. 20).

Similar results have been observed in [106] where a PCE-based superplasticizer is shown to hinder the adsorption of diutan gum and a modified starch and controlled the yield stress of the cement paste. In these cases, competitive adsorption enhances the efficiency of both the superplasticizer and the VMA. Further demonstration of the effect of competitive adsorption of superplasticizer and VMA was shown in [116]

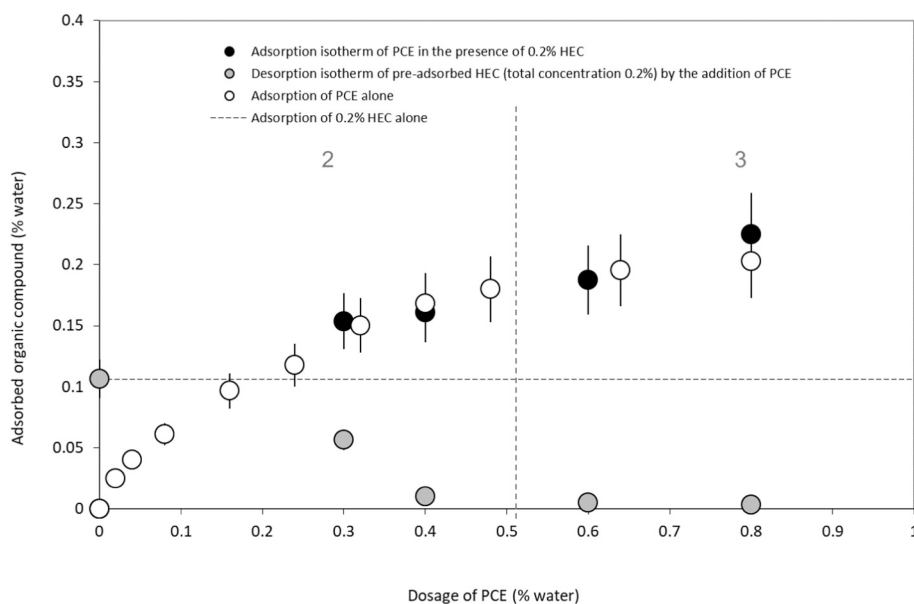


Fig. 19. Desorption isotherm of pre-adsorbed HEC (dosage 0.2%) by the addition of PCE and simultaneous adsorption isotherm of PCE. PCE and HEC adsorption when they are alone in the system are also plotted. (regime 2) Gradual displacement of the HEC from the surface and (regime 3) total displacement of the HEC. Reproduced from [114] with permission.

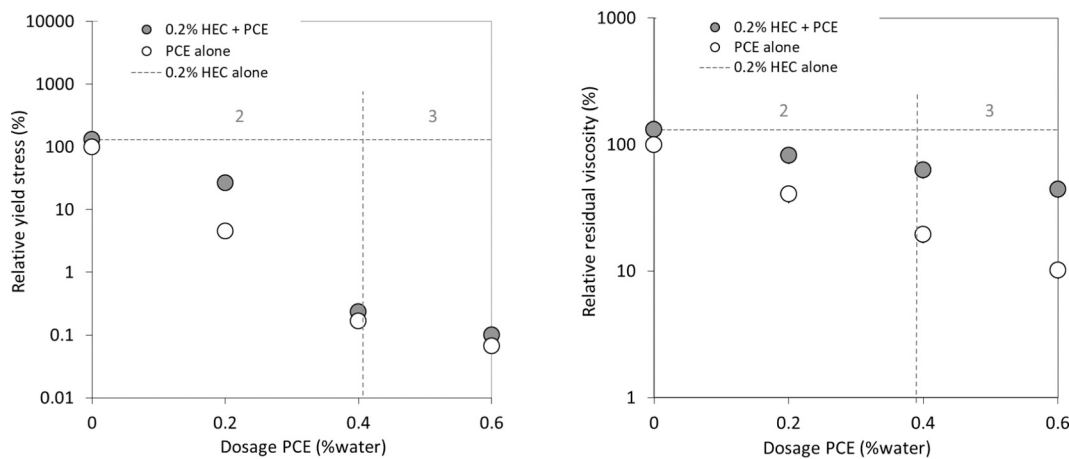


Fig. 20. Relative yield stress (i.e., ratio between yield stress of the paste with polymer and yield stress of the reference paste) as a function of PCE dosage (left). Relative residual viscosity (i.e., ratio between the residual viscosity at the plateau of the paste with polymer and the residual viscosity of the reference paste) as a function of PCE dosage (right). Reproduced from [114] with permission.

where lateral form pressure characteristics (initial pressure and pressure decay) exerted by SCC made are found to depend on the type, combination, and dosage rates of VMA and superplasticizer. Mixtures made with relatively low dosage of VMA polysaccharide- or cellulose-based VMA correlated well to thixotropy. Increased concentration of VMA led to considerably lower pressure decay given the increase in superplasticizer demand that can interfere with the rate of the development of cohesion and degree of restructuring of the material at rest. Moreover, it was observed in [106,117] that starch and diutan gum enhance the formation of ettringite and limit the effect of PCE on C-S-H growth. In fact, more PCE can be found adsorbed on ettringite, which causes earlier accelerated formation of C-S-H. These results suggest that in the presence of PCE these VMAs could enhance thixotropy of cement paste.

These results should be taken as an illustration rather than a general rule. It should, indeed, be kept in mind that the compatibility or incompatibility between these polymers cannot be extrapolated to all types of superplasticizers or VMAs. Any modification in the chemical

composition or structure of the admixtures could drastically change their behaviors.

## 6. Use of VMA in various construction applications

### 6.1. Stability

The incorporation of VMA can significantly enhance the performance of cement-based materials, especially when used in highly flowable systems (i.e., systems requiring low yield stress and moderate to high viscosity to ensure proper stability). This includes the design of grouts for post-tensioning applications, mortar and concrete for underwater placement and repair applications, as well as highly flowable concrete and SCC for precast and cast-in-place construction and repair applications. The use of VMA can enhance dynamic stability, which refers to the resistance of concrete to separation of constituents during transport, placement, and flow into place. It can also lead to greater

static stability to ensure homogeneous dispersion of cast material until the onset of hardening. Several studies have demonstrated the benefit of VMA to enhance stability of cement-based materials, which in turn affects the performance of the hardened system including impermeability and bond to embedded steel reinforcement [118–120].

Cement-based materials made with proper concentration of VMA can exhibit limited or no bleeding. The forced bleed test can be conducted to evaluate the ability of the paste to retain some of the free water in suspension given a certain hydraulic gradient. This property can be of interest when the material is subjected to pumping where water can migrate through the matrix of the skeleton leading to segregation and in grouts used for post-tensioning applications when mixing water in grout under overhead pressure can lead to water infiltration through closely spaced strands. Proper use of VMA and superplasticizer in such grout is shown to significantly enhance the resistance to forced bleeding (pressure filtration) compared to grout made with superplasticizer and no VMA. For example, compared to grout made with 0.40 W/C and 0.5% superplasticizer (PNS), the incorporation of 0.055% welan gum and 1.6% superplasticizer needed to achieve the same flowability was reported to reduce forced bleeding from 25% to 1% [1]. Similar benefits of reducing pressure filtration was reported for grouts made with cellulose-based VMAs [2].

As shown in Fig. 21 [3], regardless of the W/C and slump value of concrete, the incorporation of welan gum can significantly enhance the resistance to bleeding, segregation, and surface settlement. Concrete containing 0.07% VMA and no silica fume was shown to secure greater resistance to bleeding, segregation, and surface settlement than similar mixture made with 0.035% VMA and 8% silica fume. Such enhancement of stability is critical in SCC applications, especially when the concrete is proportioned with a W/C greater than 0.40 and low to moderate binder content.

In production of SCC, VMA is often used to secure high stability and passing ability and filling capacity of the formwork. As shown in Fig. 22 [4], the use of diutan gum in SCC can enhance the resistance to surface settlement and caisson filling capacity. The latter is dependent on high deformability and resistance to segregation and blockage. The investigated SCC was proportioned with 0.42 W/C. The resistance to surface settlement was shown to vary with superplasticizer type (PNS and two PCE) and diutan gum concentration and superplasticizer contents, the latter added to secure a slump flow of  $665 \pm 15$  mm.

### 6.2. Washout resistance for underwater casting

Because of their ability to retain water in the suspension described in the above sections, highly flowable cement-based materials (grout, mortar, and concrete) with fixed yield stress can exhibit considerably

greater washout resistance when an AWA is used. As shown in Fig. 23, the washout mass loss decreases with the increase on AWA in concrete with a fixed slump consistency [9]. These results are more accentuated with the increase in W/C and at relatively high concentration of AWA, as shown in Fig. 23 for concrete made with cellulose-based and welan gum-based AWAs. The investigated mixtures were prepared with powdered welan gum and a liquid-based cellulosic AWA. The latter had 40% solid content. A naphthalene-based superplasticizer was incorporated in mixtures containing welan gum and those without any AWA. A melamine-based superplasticizer was used in mixtures prepared with the cellulose-based AWA. The washout resistance determined using a standard basket dropped three times in a 1.7-m high water column [121] was found to vary with yield stress and plastic viscosity of the concrete.

Sonebi and Khayat [10] evaluated the effect of AWA on washout loss of concrete cast at different water velocities. As shown in Fig. 24, the increase in the dosage of welan gum from 0 to 0.07% and 0.15% resulted in net reduction in both the standard washout mass loss (Was.3 of 10.7%, 8.0%, and 5.9%, respectively) and washout mass loss determined by subjecting a freshly cast concrete sample in moving water.

### 6.3. Robustness of concrete

Robustness of concrete refers to the ability of the material to display the same properties when submitted to some variations in physical and chemical properties of the constituent materials, or some variations in the content of constituent materials [122–125]. Greater robustness refers to the ability of freshly mixed material to tolerate small changes in material characteristics without adverse effect on key properties, including workability. This includes changes in material temperature, sand humidity, sand fineness modulus, and dosage rate of chemical admixtures.

Robustness is, at first order, mostly a water effective dosage issue emerging from the sensitivity of the mixture to water content at low W/C and often originating from the difficulty in assessing the water content of sand stockpiles in practice. Studies have shown that VMAs are able to directly and indirectly improve the robustness of cement-based materials. Indeed, these molecules seems to intrinsically improve the robustness of low W/C concrete that already have proper resistance to bleeding and segregation.

Naji et al. [126] showed that the use of microbial anionic polysaccharide VMA can provide greater robustness than cellulose-based VMA in stable SCC mixtures proportioned with 0.37 W/C. The mixtures were prepared with W/C 0.35 and 0.39 to simulate different sand moisture contents that correspond to surface saturated dry (SSD) of  $-1\%$  and SSD of  $+1\%$ , respectively. Three powder-based microbial anionic polysaccharides milled to different fineness levels were used: PS1 and

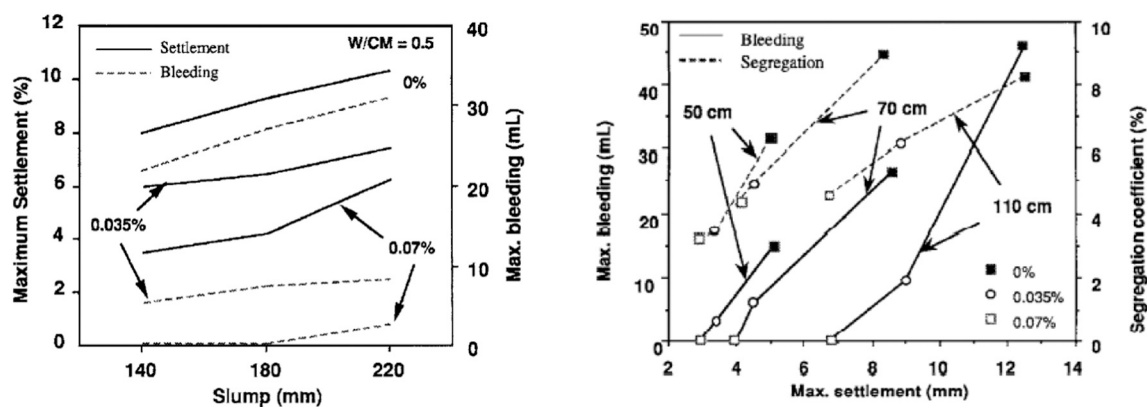


Fig. 21. (left) Effect of welan gum content on surface settlement and external bleeding determined for concrete proportioned at different slump values cast in 70-cm high columns; (right) variations of bleeding, segregation, and settlement with VMA content and column height. Reproduced from [3] with permission.



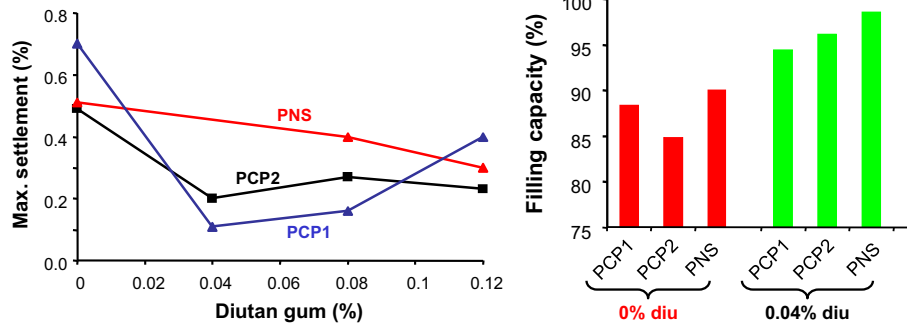


Fig. 22. Effect of diutan gum on surface settlement and caisson filling capacity of SCC prepared with different HRWR types. Reproduced from [4] with permission.

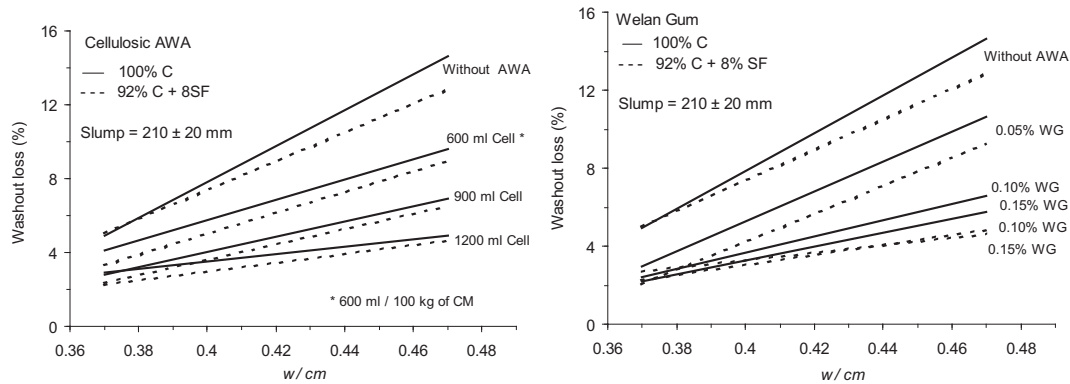


Fig. 23. Effect of W/C and binder composition on variations of washout loss for mixtures made with different dosages of cellulosic AWA and 210 ± 20 mm slump. Reproduced from [9] with permission.

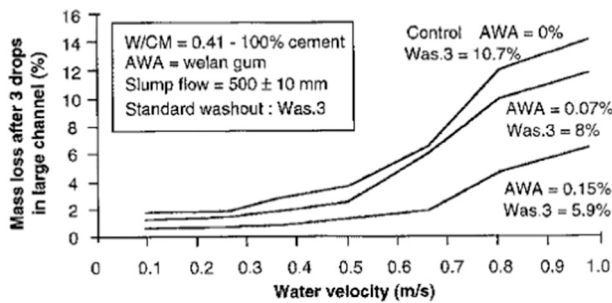


Fig. 24. Effect of welan gum content and water velocity on washout mass loss. Reproduced from [10] with permission.

PS2 representing diutan gum with maximum apparent diameter of 180 and 75 μm, respectively, and PS3 (welan gum) with a maximum apparent diameter of 180 μm. A cellulose-based derivative VMA (CEL) with a maximum apparent diameter less than 210 μm and a modified starch (MS) VMA were also investigated. PNS-based and PCE-based admixtures were used to ensure high fluidity. The tested mixtures were ranked in terms of robustness using the values of the coefficient of variation (COV) for 20 investigated properties of the fresh and hardened concrete. As shown in Table 2, SCC made with PNS-based superplasticizer and PS2 VMA had greater robustness than that made with PS1 VMA. This may be attributed to the higher fineness of the PS2 product. The PS2 was also more effective in terms of robustness than the PS3, which could be explained by the higher molecular weight and higher fineness of the PS2 VMA. The used PCE-CEL and PCE-No VMA led to the lowest robustness.

The variation of temperature affects the conformation of VMA, its

Table 2

Comparison of the effect of combination of superplasticizer and VMA on robustness of stable SCC [126].

Superplasticizer-VMA	Normalized sum of ranking (%)	Category	Robustness
PNS-PS2	100	I (75%–100%)	Very high
PNS-PS3	86		
PCE-PS1	71	II (50%–74%)	High
PCE-MS	71		
PNS-PS1	69		
PNS-No VEA	45	III (25%–49%)	Medium
PCE-CEL	24		
PCE-No VEA	0	IV (≤ 24%)	Low

adsorption and efficiency in cement-based materials. For SCC and flowable concrete, when PCE for ready-mixed applications (with a lower charge density) is used, it can be shown that VMA with a lower adsorption tendency can be particularly reasonable to absorb the effect of varying temperature. However, for pre-cast applications, where higher charge density PCE is used, a VMA, such as diutan gum with a stronger adsorption can support flow stability and rapid processing [26]. It was found that at cold temperatures (5 °C), when the stability of the cement paste is not amended by significant hydration progress, diutan gum provided much better robustness in comparison to starch based VMA, although at moderate temperatures (20 °C), both VMAs showed similar effects and slump retention. In return, diutan gum caused a more rapid loss of workability at high temperature (30 °C) than starch based VMA [26]. The incapability of starch VMA to stabilize concrete at low temperatures effectively was also reported before from field observations [127].

Furthermore, it was shown in [128,129] that for steady casting processes, where steady consistency is important, the inevitable scatter in the flow performance of concrete can be effectively adjusted by incorporating either superplasticizer, when the consistency is too stiff, or a VMA (here starch and diutan gum) if the consistency is too flowable. This adjustment worked well when an effective process observation and clear decision rules were applied, regardless of the root cause of the scatter, even if cement content, or water content varied up to  $\pm 10\%$ , gypsum was added, aggregates replaced or cement was replaced by limestone filler. These studies clearly showed that by using cusum along with v-mask decision making criteria [130,131] a constant rheological performance could be achieved by using VMA as a specific rheology control.

#### 6.4. Printability of 3D extruded layer

The incorporation of certain types of VMAs can significantly enhance the printability of cement-based materials. During mixing, pumping and extrusion, the incorporation of VMA can reduce the risk of bleeding and segregation of the 3D extruded layer [132–134].

Immediately after deposition, the incorporation of VMA can allow for a control of the shape stability through the increase of yield stress (see Section 4.2.1). It was shown in [135,136] that a 3D extruded layer containing VMA almost does not deform under its own weight and under the weight of successive layers. Moreover, it was shown in [16,137,138] that the incorporation of VMA can reduce the drying rate of the deposited layer, improve surface moisture and enhance the interlayer bond strength.

#### 7. Perspectives

Since polysaccharides occur in abundance and in wide variety in nature, they offer exhaustless potentials for innovation in concrete technology. Acacia gum, for example, has shown to be an effective retarder, superplasticizer, and VMA [139–142]. Whether the polymer acts as a VMA or a superplasticizer depends upon the polymer dosage as well as the solid particle volume fraction [142]. In combination with PCE, it can significantly increase the thixotropy of cement paste [140]. Further investigation is needed to understand the mechanism of action of Acacia gums. Another example of a polysaccharide found in nature is the easy water-soluble gum that acts as insect protection inside the bark of the *Triumfetta pendrata* A. Rich plant. It can significantly increase the thixotropy of cement paste when combined with PCE. Application tests have shown that cement pastes can become flowable for a few minutes after mixing and build up a stiff structure within the first 5 min after mixing [139]. The cement hydration is not affected by the presence of this gum, which makes it particularly interesting for additive manufacturing applications since no set-modifying admixture is required to promote the structural build-up [140].

Unmodified starches can also be interesting as VMA for cement-based materials. While they can exhibit a yield stress reducing effect, they can increase the overall viscosity [139]. Their effect is complex and depends upon multiple parameters [143], but based on the source, the ratio of amylopectin and amylose as well as the hydrodynamic diameters of the macromolecules varies [144], which offers a wide range for viscosity modification.

The novel use of polysaccharides, that have not been established in concrete technology to date, can therefore become an effective innovation driver. Furthermore, water soluble polysaccharides that can manipulate the rheological properties without complex industrial processing can become sustainable concrete constituents that help reducing cost and environmental impact of concrete construction and create livelihood potentials resulting from rapid urban growth [145–147]. Therefore, more attention should be given to the better understanding of polysaccharides in future research to design high performance concrete with adapted rheology.

Although VMA and superplasticizers compatibility has been extensively studied in literature, further investigations are needed to understand the interaction of VMA with other chemical admixtures. The incorporation of VMA can significantly affect the required dosage rate of certain chemical admixtures demand. As shown in [68], the increase in welan gum content reduces the free water in the solution that can be available to the air-entraining admixture (AEA), hence leading to a greater demand of the AEA to secure a given air volume. Other mechanisms associated with the increase in AEA demand are elaborated in [68]. As shown in [148], the addition of a shrinkage reducing admixture affects the stabilizing effects of VMA. More attention should be given in future to the better understanding of VMA and other chemical admixture incompatibilities to secure adequate rheological properties and proper performance of the material.

#### 8. Conclusion

VMAs are critically important to produce advanced cement-based materials for which stability and flow properties are fundamental to secure adequate performance. In this paper, commonly used VMAs are presented, and the underlying physics at the origin of the effect of VMA on cement-based materials is discussed. By highlighting the effect of VMA on cement-based flow properties and stability, this paper provides the knowledge to design highly stable materials and facilitates the use of a broader range of VMAs.

Non-adsorbing VMAs are shown to enhance the stability of the suspension through the increase of the zero-shear viscosity of cement pore solution and the formation of associates. The formation of associates is needed to physically plug the filter cake porosity and therefore improve water retention. The effect of non-adsorbed VMA on the zero-shear viscosity of cement pore solution depends mainly on their volume concentration in solution and concentration regime. The shear thinning behavior of aqueous VMA solution, which allows it to maintain a relatively low resistance to flow during mixing, pumping, and casting increases when the polymer volume concentration increases, and is dependent on the VMA molecule specificities. The polymer properties controlling the shear thinning behavior is still not fully understood, and further investigation is needed. Moreover, as shown in literature, some VMAs mainly enhance the yield stress of cement-based materials by adsorbing at the surface of adjacent cement particles and introducing bridging force in the system. Furthermore, the combined use of VMA and superplasticizer can generate some incompatibility in cement pore solution and can lead to competitive adsorption onto surface sites of particles, which can influence the performance of the cement-based materials. A number of examples of the effect of VMA on enhancing concrete properties in various construction applications are discussed to highlight the great benefit of using this unique family of chemical admixtures on the design of novel construction materials.

#### CRedit authorship contribution statement

**Hela Bessaies-Bey:** Writing - Review & Editing, Conceptualization.  
**Kamal H. Khayat:** Writing - Review & Editing, Conceptualization.  
**Marta Palacios:** Writing - Review & Editing, Conceptualization.  
**Wolfram Schmidt:** Writing - Review & Editing, Conceptualization.  
**Nicolas Roussel:** Writing - Review & Editing, Conceptualization.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## References

- [1] K.H. Khayat, M. Saric-Coric, in: *Effect of Welan Gum-Superplasticizer Combination on Properties of Cement Grouts* 195, ACI-Special Publication, 2000, pp. 249–268.
- [2] M. Saric-Coric, K.H. Khayat, A. Tagnit-Hamou, Performance characteristics of cement grouts made with various combinations of high-range water reducer and cellulose-based viscosity modifier, *Cem. Concr. Res.* 33 (2003) 1999–2008.
- [3] K.H. Khayat, Z. Guizani, Use of viscosity-modifying admixtures to enhance stability of fluid concrete, *ACI Mater. J.* 94 (1997) 332–340.
- [4] K.H. Khayat, A. Mechaymech, B. Skaggs, in: *Performance of Self-Consolidating Concrete Made With Diutan Gum* 239, ACI-Special Publication, 2006, pp. 545–566.
- [5] C. Marliere, E. Mabrouk, M. Lamblet, P. Coussot, How water retention in porous media with cellulose ethers works, *Cem. Concr. Res.* 42 (2012) 1501–1512.
- [6] D. Bülchen, J. Kainz, J. Plank, Working mechanism of methyl hydroxyethyl cellulose (MHEC) as water retention agent, *Cem. Concr. Res.* 42 (2012) 953–959.
- [7] C. Brumaud, H. Bessaies-Bey, C. Mohler, R. Baumann, M. Schmitz, M. Radler, N. Roussel, Cellulose ethers and water retention, *Cem. Concr. Res.* 53 (2013) 176–184.
- [8] T. Poinot, A. Govin, P. Grosseau, Importance of coil-overlapping for the effectiveness of hydroxypropylguars as water retention agent in cement-based mortars, *Cem. Concr. Res.* 56 (2013) 61–68.
- [9] K.H. Khayat, J. Assaad, Relationship between washout resistance and rheological properties of high-performance underwater concrete, *ACI Mater. J.* 100 (2003) 185–193.
- [10] M. Sonebi, K.H. Khayat, Effect of water velocity on the performance of underwater, self-consolidating concrete, *ACI Mater. J.* 96 (1999) 519–528.
- [11] M. Pfeuffer, W. Kusterle, Rheology and rebound behaviour of dry-mix shotcrete, *Cem. Concr. Res.* 31 (2001) 1619–1625.
- [12] C. Brumaud, R. Baumann, M. Schmitz, M. Radler, N. Roussel, Cellulose ethers and yield stress of cement pastes, *Cem. Concr. Res.* 55 (2014) 14–21.
- [13] D. Marchon, S. Kawashima, H. Bessaies-Bey, S. Mantellato, S. Ng, Hydration and rheology control of concrete for digital fabrication: potential admixtures and cement chemistry, *Cem. Concr. Res.* 112 (2018) 96–110.
- [14] N. Roussel, Rheological requirements for printable concretes, *Cem. Concr. Res.* 112 (2018) 76–85.
- [15] S. Kawashima K. Wang R. Ferron J.H. Kim N. Tregger S. Shah , A review of the effect of nanoclays on the fresh and hardened properties of cement-based materials, Under Review by Cement and Concrete Research Special Issue on Superplasticizers and Other Chemical Admixtures.
- [16] S. Ma, S. Kawashima, Investigating the working mechanisms of viscosity-modifying admixtures through rheological and water transport properties, *J. Mater. Civ. Eng.* 32 (2020).
- [17] S. Kawashima, J.H. Kim, D.J. Corr, S.P. Shah, Study of the mechanisms underlying the fresh-state response of cementitious materials modified with nanoclays, *Constr. Build. Mater.* 36 (2012) 749–757.
- [18] S. Ma, Y. Qian, S. Kawashima, Experimental and modeling study on the non-linear structural build-up of fresh cement pastes incorporating viscosity modifying admixtures, *Cem. Concr. Res.* 1–9 (2018).
- [19] Z. Quanji, G.R. Lomboy, K. Wang, Influence of nano-sized highly purified magnesium aluminosilicate clay on thixotropic behavior of fresh cement pastes, *Constr. Build. Mater.* 69 (2014) 295–300.
- [20] B. Panda, S. Ruan, C. Unluer, M.J. Tan, Improving the 3D printability of high volume fly ash mixtures via the use of nano attapulgite clay, *Composites Part B* 165 (2019) 75–83.
- [21] A. Leemann, F. Winnefeld, The effect of viscosity modifying agents on mortar and concrete, *Cem. Concr. Compos.* 29 (2007) 341–349.
- [22] T. Kawai, Non-dispersible underwater concrete using polymers, in: *Marine Concrete*, 1987, 3 p.
- [23] G. Gelardi, S. Mantellato, D. Marchon, M. Palacios, A. Eberhardt, R.J. Flatt, 9. Chemistry of chemical admixtures, in: P.-C. Aitcin, R.J. Flatt (Eds.), *Science and Technology of Concrete Admixtures*, Elsevier, 2016.
- [24] V. Kaur, M.B. Bera, P.S. Panesar, H. Kumar, J.F. Kennedy, Welan gum: microbial production, characterization, and applications, *Int. J. Biol. Macromol.* 65 (2014) 454–461.
- [25] K.H. Khayat, N. Mikanovic, Viscosity-enhancing admixtures and the rheology of cement, in: *Understanding the Rheology of Concrete*, Woodhead, 2012, pp. 209–228.
- [26] W. Schmidt, Design Concepts for the Robustness Improvement of Self-Compacting Concrete Effects of Admixtures and Mixture Components on the Rheology and Early Hydration at Varying Temperatures, Eindhoven University of Technology, the Netherlands, 2014. PhD Thesis.
- [27] E. Üzer, J. Plank, Impact of welan gum stabilizer on the dispersing performance of polycarboxylate superplasticizers, *Cem. Concr. Res.* 82 (2016) 100–106.
- [28] H. Li, H. Zhu, S. Sun, Z. Feng, Y. Sun, W. Zhou, Biological production of welan gum, *Phys. Sci. Rev.* 1 (2016).
- [29] R.C. Navarrete, J.M. Seheult, M.D. Coffey, New biopolymers for drilling, drill-in, completions, spacer fluids and coiled tubing applications, in: *Paper SPE 62790 Presented at the SPE International Symposium on Oilfield Chemistry*, Houston, Texas, 2000, pp. 13–16.
- [30] S. Rosalam, R. England, Review of xanthan gum production from unmodified starches by *Xanthomonas compestris* sp, *Enzym. Microb. Technol.* 39 (2006) 197–207.
- [31] I. Muller, Influence of Cellulose Ethers on the Kinetics of Early Portland Cement Hydration, University of Karlsruhe, 2006. Dissertation.
- [32] D.D. Nguyen, L.P. Devlin, P. Koshy, C.C. Sorrell, Impact of water-soluble cellulose ethers on polymer-modified mortars, *J. Mater. Sci.* 49 (2014) 923–951.
- [33] C. Brumaud, Origines microscopiques des conséquences rhéologiques de l'ajout d'éthers de cellulose dans une suspension cimentaire (PhD Thesis), Univ. Paris Est, 2011 (in French).
- [34] T. Poinot, A. Govin, P. Grosseau, Influence of hydroxypropylguars on rheological behavior of cement-based mortars, *Cem. Concr. Res.* 58 (2014) 161–168.
- [35] A.M.A. Hasan, M.E. Abdel-Rauf, Applications of guar gum and its derivatives in petroleum industry: a review, *Egypt. J. Pet.* 27 (2018) 1043–1050.
- [36] B. Valdez, Scientific, Health and Social Aspects of the Food Industry, BoD – Books on Demand, 2012.
- [37] J.J.M. Swinkels, Composition and properties of commercial native starches, *Starch – Stärke* 37 (1985) 1–5.
- [38] J.N. BeMiller, K.C. Huber, "Starch", *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA, 2000.
- [39] W. Burchard, Light scattering from polysaccharides, in: S. Dumitriu (Ed.), *Polysaccharides - Structural Diversity and Functional Versatility*, Second Edition, 2 ed, Marcel Dekker, New York, 2005, pp. 189–237.
- [40] Q. Zhang, Investigating Polymer Conformation in Poly (Ethylene Oxide) (PEO) Based Systems for Pharmaceutical Applications a Raman Spectroscopic Study of the Hydration Process, Chalmers University of Technology, 2011 (Master's thesis).
- [41] N.B. Halima, Poly(vinyl alcohol): review of its promising applications and insights into biodegradation, *RSC Adv.* 6 (2016) 39823–39832.
- [42] H. Bessaies-Bey, R. Baumann, M. Schmitz, M. Radler, N. Roussel, Effect of polyacrylamide on rheology of fresh cement pastes, *Cem. Concr. Res.* 76 (2015) 98–106.
- [43] M. Palacios, R.J. Flatt, 20 - working mechanism of viscosity-modifying admixtures (PhD Thesis), in: P.-C. Aitcin, R.J. Flatt (Eds.), *Science and Technology of Concrete Admixtures*, Woodhead Publishing, 2016, pp. 415–432 (in French).
- [44] P. Coussot, *Rheophysics – Matter in all its State*, Springer, Berlin, 2014 (Master's thesis).
- [45] W. Kuhn, *Kolloid Z.* 68 (1934) 2.
- [46] P.J. Flory, *Principles of Polymer Chemistry*, Cornell Univ. Press, Ithaca NY, 1953.
- [47] S.F. Edwards, *Proc. Phys. Soc.* 85 (1965) 613, 88 (1966) 265.
- [48] F. Reif, *Fundamentals of Statistical and Thermal Physics*, McGraw-Hill, 1965 chs. 12 and 15.
- [49] H. Yamakawa, *Modern Theory of Polymer Solutions*, Harper&Row, NY, 1971.
- [50] P.G.De Gennes, *Scaling Concepts in Polymer Physics*, Cornell University Press, Ithaca, NY, 1979.
- [51] W.W. Graessley, Polymer chain dimensions and the dependence of viscoelastic properties on concentration, molecular weight and solvent power, *Polymer* 2–11 (1980) 258.
- [52] C. Clasen, W.M. Kulicke, Determination of viscoelastic and rheo-optical material functions of water-soluble cellulose derivatives, *Prog. Polym. Sci.* 26 (9) (2001) 1839–1919.
- [53] H. Bessaies-Bey, *Polymères et propriétés rhéologiques d'une pâte de ciment: une approche physique générique* (PhD thesis), Univ. Paris Est, 2015 (In French).
- [54] C. Tanford, *Physical Chemistry of Macromolecules*, Wiley, NY, 1963.
- [55] M. Kurata, W.H. Stockmayer, *Fortschr. Hochpolym. Forsch.* 3 (1963) 196.
- [56] M.A. Masuelli, Mark-Houwink parameters for aqueous-soluble polymers and biopolymers at various temperatures, *J. Polym. Biopolymer Phys. Chem.* 2 (2014) 37–43.
- [57] D. Bulichen, J. Plank, Mechanistic study on carboxymethyl hydroxyethyl cellulose as fluid loss control additive in oil well cement, *J. Appl. Polym. Sci.* 124 (2012) 2340–2347.
- [58] D. Bulichen, J. Plank, Role of colloidal polymer associates for the effectiveness of hydroxyethyl cellulose as a fluid loss control additive in oil well cement, *J. Appl. Polym. Sci.* 126 (2012) E25–E34.
- [59] C. Esquet, *Propriétés structurales et dynamiques des solutions de polyélectrolytes rigides et semi-rigides et de polysaccharides associatifs*, Université Joseph Fourier, Grenoble, 2003. Thèse de doctorat.
- [60] W. Schmidt K.A. Olonade R. Mbugua F.J. Lenz I.L. Tchegnina Ngassam , Bio-based rheology modifiers for high performance concrete – possible modes of actions and case study for cassava starch in West Africa. In: W. P. Boshoff R. Combrinck V. Mechtcherine M. Wyrzykowski , eds. 3rd International Conference on the Application of Superabsorbent Polymers (SAP) and Other New Admixtures Towards Smart Concrete, 2019 Skukuza Camp, South Africa. RILEM S.A.R.L, 158–166.
- [61] V.J. Morris, D. Franklin, K. I'Anson, *Carbohydr. Res.* 121 (1983) 13–30.
- [62] T. Sun, H.E. King, *Macromolecules* 29 (9) (1996) 3175–3181.
- [63] J.A. Carmona, P. Ramírez, M.C. García, et al., Linear and non-linear flow behavior of welan gum solutions, *Rheol. Acta* 58 (2019) 1–8.
- [64] M.L. Huggins, Theory of solution of high polymers, *J. Am. Chem. Soc.* 64 (1942) 1712–1719.
- [65] M. Adam, M. Delsanti, *J. Phys. Paris* 43 (3) (1982) 549–557.
- [66] M. Adam, M. Delsanti, *J. Phys. Paris* 44 (10) (1983) 1185–1193.
- [67] Y. Takahashi, Y. Isono, I. Noda, M. Nagasawa, *Macromolecules* 18 (5) (1985) 1002–1008.
- [68] K.H. Khayat, Effects of anti-washout admixtures on fresh concrete properties, *ACI Mater. J.* 92 (1995) 164–171.
- [69] C.B. Skaggs, S.F. Whitaker, W.G. Rakitsky, Application of rheological modifiers and superplasticizers in cementitious systems, in: V.M. Malhotra (Ed.), *Proceeding of 4th CANMET/ACI International Conference on Superplasticizers*

- and Other Chemical Admixtures in Concrete, ACI SP-148, Montréal, 1994, pp. 189–207.
- [70] T. Poinot, M.C. Bartholin, A. Govin, P. Grosseau, Influence of the polysaccharide addition method on the properties of fresh mortars, *Cem. Concr. Res.* 70 (2015) 50–59.
- [71] T. Poinot, A. Govin, P. Grosseau, Impact of hydroxypropylguars on the early age hydration of Portland cement, *Cem. Concr. Res.* 44 (2013) 69–76.
- [72] C. Marlière, Étude des transferts hydriques en milieu poreux en présence de polymères réticulateurs d'eau : application au mortier (PhD Thesis), Univ. Paris Est, 2013 (in French).
- [73] B. Wittgren, B. Porsch, *Carbohydr. Polym.* 49 (2002) 457.
- [74] P. Valois, E. Verneuil, F. Lequeux, L. Talini, Understanding the role of molar mass and stirring in polymer dissolution, *Soft Matter* 12 (2016) 8143–8154.
- [75] B. Narasimhan, J.E.M. Snaar, R.W. Bowtell, S. Morgan, C.D. Melia, N.A. Peppas, *Macromolecules* 32 (1999) 704–710.
- [76] D.G. Bucknall, J.S. Higgins, S.A. Butler, *J. Polym. Sci. B Polym. Phys.* 42 (2004) 3267–3281.
- [77] S. Ugur, A.K. Dinc, Y. Kislak, *J. Polym. Res.* 19 (2012) 9943.
- [78] S. Abrahamsen-Alami, A. Korner, I. Nilsson, A. Larsson, *Int. J. Pharm.* 342 (2007) 105–114.
- [79] A. Dobrynin, R. Colby, M. Rubinstein, *Macromolecules* 28 (1995) 1859–1871.
- [80] T. Hurmaus, J. Plank, Adsorption of non-ionic cellulose ethers on cement revisited, *Constr. Build. Mater.* 195 (2019) 441–449, <https://doi.org/10.1016/j.conbuildmat.2018.11.020>.
- [81] M. Palacios, R.J. Flatt, F. Puertas, A. Sanchez-Herencia, Compatibility between polycarboxylate and viscosity-modifying admixtures in cement pastes, in: 10th International Conference on Superplasticizers and Other Chemical Admixtures in Concrete, Prague, 2012, pp. 29–42.
- [82] J. Pourchez, Aspects physico-chimiques de l'interaction des éthers de cellulose avec la matrice cimentaire, Ecole Nationale des Mines de Saint-Etienne, France, 2006 (PhD thesis).
- [83] J. Wang, P. Somasundaran, D.R. Nagaraj, Adsorption mechanism of guar gum at solid-liquid interfaces, *Miner. Eng.* 18 (2005) 77–81.
- [84] J.M. Wie, D.W. Fuerstenau, The effect of dextrin on surface properties and the flotation of molybdenite, *Int. J. Miner. Process.* 1 (1974) 17–32.
- [85] Q. Liu, J.S. Laskowski, The role of metal hydroxides at mineral surfaces in dextrin adsorption, I. Studies on modified quartz samples, *Int. J. Miner. Process.* 26 (1989) 297–316.
- [86] Z.H. Ou, B.G. Ma, S.W. Jian, Influence of cellulose ethers molecular parameters on hydration kinetics of Portland cement at early ages, *Constr. Build. Mater.* 33 (2012) 78–83.
- [87] H. Bessaies-Bey, M. Palacios, E. Pustovgar, M. Hanafi, R. Baumann, R.J. Flatt, N. Roussel, Non-adsorbing polymers and yield stress of cement paste: effect of depletion forces, *Cem. Concr. Res.* 111 (2018) 209–217.
- [88] N. Roussel, A. Lemaitre, R.J. Flatt, P. Coussot, Steady state flow of cement suspensions: a micromechanical state of the art, *Cem. Concr. Res.* 40 (2010) 77–84.
- [89] N. Roussel, G. Ovarlez, S. Garrault, C. Brumaud, The origins of thixotropy of fresh cement pastes, *Cem. Concr. Res.* 42 (2012) 148–157.
- [90] L. Patural, J.P. Korb, A. Govin, P. Grosseau, B. Ruot, O. Deves, Nuclear magnetic relaxation dispersion investigations of water retention mechanism by cellulose ethers in mortars, *Cem. Concr. Res.* 42 (2012) 1371–1378.
- [91] L. Patural, P. Marchal, A. Govin, P. Grosseau, B. Ruot, O. Deves, Cellulose ethers influence on water retention and consistency in cement-based mortars, *Cem. Concr. Res.* 41 (2011) 46–55.
- [92] W. Schmidt, S. Peters, H.C. Kühne, Effects of particle volume fraction and size on polysaccharide stabilizing agents, in: V.M. Malhotra (Ed.), -302 Eleventh International Conference on Superplasticizers and Other Chemical Admixtures in Concrete, 2015.
- [93] H. Okamura, M. Ouchi, Self-compacting concrete, *J. Adv. Concr. Technol.* 1 (1) (2003) 5–15.
- [94] V.A. Ghio, P.J.M. Monteiro, L.A. Demsetz, The rheology of fresh cement paste containing polysaccharide gums, *Cem. Concr. Res.* 24 (1994) 243–249.
- [95] M. Lachemi, K.M.A. Hossain, Y. Lmbros, P.-C. Nkinamumbanzi, N. Bouzoubaa, Performance of new viscosity-modifying admixtures in enhancing the rheological properties of cement paste, *Cem. Concr. Res.* 34 (2004) 185–193.
- [96] J. Kwasny, M. Sonebi, S.E. Taylor, Y. Bai, P.A.M. Basheer, The influence of different viscosity-modifying admixtures on the fresh properties of superplasticized cement-based grouts, in: Proceedings of 3rd International RILEM Symposium on Rheology of Cement Suspensions such as Fresh Concrete, Reykjavik, Iceland, 2009, pp. 208–218.
- [97] K.H. Khayat, A. Yahia, Effects of welan gum – high range water reducer combination on rheology of cement grout, *ACI Mater. J.* 94 (1997) 365–372.
- [98] M. Sonebi, Rheological properties of grouts with viscosity modifying agents as diutan gum and welan gum incorporating pulverised fly ash, *Cem. Concr. Res.* 36 (2006) 1609–1618.
- [99] M. Sonebi, M. Lachemi, K.M.A. Hossain, Optimisation of rheological parameters and mechanical properties of superplasticised cement grouts containing metakaolin and viscosity modifying admixture, *Constr. Build. Mater. J.* 38 (2013) 126–138.
- [100] M. Sonebi, W. Schmidt, J. Khatib, Influence of the type of viscosity-modifying admixtures and metakaolin on the rheology of grouts, *Chem. Mater. Res.* 5 (2013) 106–111.
- [101] I.M. Krieger, T.J. Dougherty, Mechanism for non-newtonian flow in suspensions of rigid spheres, *Trans. Soc. Rheol.* 3 (1959) 137–152.
- [102] H. Lombois-Burger, P. Colombet, J. Halary, H. Van Damme, On the frictional contribution to the viscosity of cement and silica pastes in the presence of adsorbing and non adsorbing polymers, *Cem. Concr. Res.* 38 (2008) 1306–1314.
- [103] J. Hot, H. Bessaies-Bey, C. Brumaud, M. Duc, C. Castella, N. Roussel, Adsorbing polymers and viscosity of cement pastes, *Cem. Concr. Res.* 63 (2014) 12–19.
- [104] J. Pourchez, A. Govin, P. Grosseau, R. Guyonnet, B. Guilhot, B. Ruot, Alkaline stability of cellulose ethers and impact of their degradation products on cement hydration, *Cem. Concr. Res.* 36 (2006) 1252–1256.
- [105] J. Pourchez, P. Grosseau, B. Ruot, Changes in C3S hydration in the presence of cellulose ethers, *Cem. Concr. Res.* 40 (2010) 179–188.
- [106] W. Schmidt, H.J.H. Brouwers, H.-C. Kühne, B. Meng, Interactions of polysaccharide stabilising agents with early cement hydration without and in the presence of superplasticizers, *Constr. Build. Mater.* 139 (2017) 584–593.
- [107] R.J. Flatt, P. Bowen, Yodel: a yield stress model for suspensions, *J. Am. Ceram. Soc.* 89 (2006) 1244–1256.
- [108] J. Stroh, M.C. Schlegel, W. Schmidt, Y.N. Thi, B. Meng, F. Emmerling, Time-resolved in situ investigation of Portland cement hydration influenced by chemical admixtures (in English), *Constr. Build. Mater.* 106 (2016) 18–26.
- [109] W. Schmidt, S. Leinitz, H.C. Kühne, Effects of particle volume fraction and size on polysaccharide stabilizing agents, in: V.M. Malhotra, P.R. Gupta, T.C. Holland (Eds.), 11th International Conference on Superplasticizers and Other Chemical Admixtures in Concrete, 2015, pp. 39–52.
- [110] L. Patural, P. Porion, H. Van Damme, A. Govin, P. Grosseau, B. Ruot, O. Deves, A pulsed-field gradient and NMR imaging investigations of the water retention mechanism by cellulose ethers in mortars, *Cem. Concr. Res.* 40 (9) (2010) 1378–1385.
- [111] W. Schmidt, H.J.H. Brouwers, H.-C. Kuehne, B. Meng, Influence of temperature on stabilizing agents in presence of superplasticizers, in: Tenth International Conference on Superplasticizers and Other Chemical Admixtures in Concrete, Prague, Czech Republic, 2012.
- [112] W. Schmidt, H.J.H. Brouwers, H.C. Kuehne, B. Meng, Influence of environmental temperatures on the performance of polymeric stabilising agent in fresh cementitious materials, *Key Eng. Mater.* 466 (2011) 97–104.
- [113] N. Mikanovic, J. Sharman, C. Jolicoeur, K.H. Khayat, M. Page, in: Compatibility of Viscosity-Enhancing Agents and Superplasticizers in Cementitious and Model Systems: Rheology, Bleeding, and Segregation 262, ACI-Special Publication, 2009, pp. 67–84.
- [114] H. Bessaies-Bey, R. Baumann, M. Schmitz, M. Radler, N. Roussel, Organic admixtures and cement particles: competitive adsorption and its macroscopic rheological consequences, *Cem. Concr. Res.* 80 (2016) 1–9.
- [115] J.A. Kling, H.J. Ploehn, Desorption of adsorbed poly (ethylene oxide) from colloidal polystyrene particles, *J. Colloid Interface Sci.* 198 (1998) 241.
- [116] J. Assaad, K.H. Khayat, Effect of viscosity-enhancing admixtures on formwork pressure and thixotropy of self-consolidating concrete, *ACI Mater. J.* 103 (4) (2006) 280–287.
- [117] J. Stroh, M.C. Schlegel, W. Schmidt, T.Y. Nguyen, B. Meng, F. Emmerling, Time-resolved in situ investigation of Portland cement hydration influenced by chemical admixtures, *Constr. Build. Mater.* (2016) 18–26.
- [118] K.H. Khayat, Use of viscosity-modifying admixture to reduce top-Bar effect of anchored bars cast with fluid concrete, *ACI Mater. J.* 95 (2) (1998) 158–167.
- [119] K.H. Khayat, E. Attiogbe, H. See, in: Effect of Admixture Combination on Top-Bar Effect in Highly Flowable and Self-Consolidating Concrete, ACI-SP247 (Publication No 247-4), 2007, pp. 33–44.
- [120] N. Petrov, K.H. Khayat, A. Tagnit-Hanou, in: K. Ozawa, M. Ouchi (Eds.), Effect of Stability of Self-Consolidating Concrete on the Distribution of Steel Corrosion Characteristics along Experimental Wall Elements, Proc., 2nd Inter. Symp. on Self-Compacting Concrete, Tokyo, Japan, 2001, pp. 441–450.
- [121] CRD C91-89A, Test method for determining the resistance of freshly-mixed concrete to washing out in water, in: US Army Experiment Station, Handbook for Concrete, Vicksburg, Mississippi, 1989, 3 p.
- [122] W. Zuo, H. Bessaies Bey, Q. Tian, C. Miao, N. Roussel, Robustness of cement-based materials: from dosage variations to yield stress fluctuations, *Cem. Concr. Res.* 139 (2021), 106260.
- [123] P. Billberg, Increase of SCC robustness to varying aggregate moisture content using VMA, in: Proceedings of the 2nd International Symposium on Design, Performance, and Use of Self-Consolidating Concrete, China, 2009, pp. 473–493.
- [124] S. Nunes, H. Figueiras, O.P. Milheiro, J.S. Coutinho, J. Figueiras, A methodology to assess robustness of SCC mixtures, *Cem. Concr. Res.* 36 (2006) 2115–2122.
- [125] K.H. Khayat, G. De Schutter, in: Mechanical Properties of Self-Compacting Concrete, RILEM State-of-the-Art Reports, @RILEM, 2014, p. 14, [https://doi.org/10.1007/978-3-319-03245-0\\_1](https://doi.org/10.1007/978-3-319-03245-0_1). ISSN 0008-8846.
- [126] S. Naji, S.D. Hwang, K.H. Khayat, Robustness of self-consolidating concrete incorporating different viscosity-enhancing admixtures, *ACI Mater. J.* 108 (4) (2011) 432–438.
- [127] W. Schmidt, H.C. Kuehne, D. Rosignoli, B. Meng, Development and application of a novel ready-made compound including additions and admixtures for the easy production of SCC, in: *Conc. Plant + Precast Tech.*, No. 3, 2008, pp. 4–11.
- [128] W. Schmidt, Application of a cusum control system for enhanced robustness of the flow properties of self-compacting concrete, 21.11.2016, in: H. Beushausen (Ed.), fib Symposium 2016 - Performance-Based Approaches for Concrete Structures, Cape Town, South Africa, dération internationale du béton (fib), 2016, 106-1-106-10.
- [129] W. Schmidt, H.-C. Kühne, Cusum charts for the control of the slump flow of self-compacting concrete in a steady production process, in: K.H. Khayat (Ed.), Proceedings of the 8th RILEM Symposium on Self-Compacting Concrete, Washington, USA 2016, RILEM Publications S.A.R.L., 2016, pp. 283–294.

- [130] W. Schmidt, H.C. Kuhne, F. Haamkens, Shewhart and CUSUM control charts for simultaneous process control and conformity assessment - new conformity verification methods for the upcoming EN 206, *Beton- Stahlbetonbau* 109 (6) (Jun 2014) 417–427.
- [131] R. Caspeepele, L. Taerwe, Combined production and conformity control of concrete with acceptance cusum control charts, in: *Proceedings of the 7th International Probabilistic Workshop*, Dresden, Germany, 2009.
- [132] M. Rubio, M. Sonebi, S. Amziane, Fresh and rheological properties of 3D printing bio-cement-based materials, in: *Proceedings of 2nd ICBBM (PRO 119)*, Clermont-Ferrand, 2017, pp. 491–499 (PhD thesis).
- [133] M. Rubio, M. Sonebi, S. Amziane, 3D printing of fibre cement-based materials: fresh and rheological performances, in: *Proceedings of 2nd ICBBM (PRO 119)*, Clermont-Ferrand, 21–23 June 2017, pp. 284–291.
- [134] D. Marchon, S. Kawashima, H. Bessaies-Bey, S. Mantellato, S. Ng, Hydration and rheology control of concrete for digital fabrication: potential admixtures and cement chemistry, *Cem. Concr. Res.* 112 (2018) 96–110.
- [135] Y. Chen, S.Chaves Figueiredo, Ç. Yalçinkaya, O. Çopuroğlu, F. Veer, E. Schlangen, The effect of viscosity-modifying admixture on the extrudability of limestone and calcined clay-based cementitious material for extrusion-based 3D concrete printing, *Cem. Concr. Res.* 132 (17) (2020), 106040.
- [136] Y. Chen, S.Chaves Figueiredo, Z. Li, Z. Chang, K. Jansen, O. Çopuroğlu, E. Schlangen, Improving printability of limestone-calcined clay-based cementitious materials by using viscosity-modifying admixture, *Cem. Concr. Res.* 132 (2020), 106040. ISSN 0008-8846.
- [137] E. Keita H. Bessaies-Bey W. Zuo P. Belin N. Roussel, Weak bond strength between successive layers in extrusion-based additive manufacturing: measurement and physical origin, *Cem. Concr. Res.* 123, 105787.
- [138] E. Keita, Y. Rifaai, P. Belin, N. Roussel, Influence of non-adsorbing polymers on drying of fresh mortars, *Cem. Concr. Res.* 116 (2019) 38–44.
- [139] W. Schmidt, I.Tchetgna Ngassam, K. Olonade, R. Mbugua, H.-C. Kühne, Plant based chemical admixtures – potentials and effects on the performance of cementitious materials, 21.11.2016, in: *RILEM Technical Letters* 3, 2019, pp. 124–128, 106-1-106-10.
- [140] W. Schmidt, K.A. Olonade, R. Mbugua, F.J. Lenz, I.L.Tchetgna Ngassam, Bio-based rheology modifiers for high performance concrete – possible modes of actions and case study for Cassava Starch in West Africa, in: W.P. Boshoff, R. Combrinck, V. Mechtcherine, M. Wyrzykowski (Eds.), *3rd International Conference on the Application of Superabsorbent Polymers (SAP) and Other New Admixtures Towards Smart Concrete*, Skukuza Camp, South Africa, RILEM S.A.R.L., 2019, pp. 158–166.
- [141] R. Mbugua, R. Salim, J. Ndambuki, Utilisation of Gum Acacia Karoo as Set-retarding Water-reducing Admixture in Cement Mortar and Concrete at Optimum Dosage, in: N.S. Msinjili Tanzania, W. Schmidt (Eds.), *1st Symposium on Knowledge Exchange for Young Scientists (KEYS) - Sub-Saharan African Standards for Cement and Concrete Research and Raw Materials, Quality Control and Maintenance of Cementitious Products*, BAM, 2015, pp. 97–101.
- [142] W. Schmidt, SCC for Sub-Saharan Africa based on local raw materials – material development, optimisation, and application concept, in: V. Mechtcherine, K. H. Khayat, E. Secrieru (Eds.), *Rheology and Processing of Construction Materials*, 23 ed.RILEM Bookseries, 2019.
- [143] E. Vasiliou, W. Schmidt, M. Stefanidou, H.-C. Kühne, A. Rogge, Effectiveness of starch ethers as rheology modifying admixtures for cement based systems, in: S. Amziane, M. Sonebi, K. Charlet (Eds.), *RILEM Proceedings PRO 119*, Paris, France 2017, RILEM S.A.R.L., 2017, pp. 81–85.
- [144] J.J.M. Swinkels, Composition and properties of commercial native starches, *Starch - Stärke* 37 (1) (1985) 1–5.
- [145] W. Schmidt, Specific materials challenges and innovation potentials for mineral bound construction materials in Africa, in: *RILEM Technical Letters* vol. 4, 2020 p. submitted.
- [146] W. Schmidt, Challenges, opportunities and potential solution strategies for environmentally and socially responsible urban development of megacities in Africa, in: *3RD RILEM Spring Convention 2020 - Ambitioning a Sustainable Future for Built Environment: Comprehensive Strategies for Unprecedented Challenges*, RILEM, Guimaraes, Portugal, 2020.
- [147] W. Schmidt, K. Olonade, N. Radebe, F. Zando, V. Ssekamatte, Rural employment perspectives from sustainable, green construction materials for urban development, *Rural* 21 (2/20) (2020) 36–38.
- [148] W. Schmidt, H.J.H. Brouwers, H.-C. Kühne, B. Meng, Influences of superplasticizer modification and mixture composition on the performance of self-compacting concrete at varied ambient temperatures, *Cem. Concr. Compos.* 49 (2014) 111–126.