Fluidizing efficiency of comb-like superplasticizers: The effect of the anionic function, the side chain length and the grafting degree

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ABSTRACT

Superplasticizers and especially polycarboxylate grafted polyethylene oxide (PCE) demonstrated their efficiency to fluidify concrete. The aim of this work is to investigate the evolution of the fluidity as a function of adsorption in a sulfated solution with a wide variety of comb-like superplasticizers and at incomplete adsorption rate. Polymers with various side chain lengths, grafting ratios and also with modified anionic functions (carboxylate, dicarboxylate and phosphate) were synthesized. Inert calcite suspensions were used to mimic early age cementitious materials avoiding the cement hydration. Models of polymer conformation and yield stress prediction have been tested. But the most appropriate parameter which captures the fluidity/adsorption relationship is the mass of adsorbed polymer. A unique relationship "log(yield stress) vs. adsorbed mass of PCE" has been highlighted whatever the classical carboxylate PCE structure. The modification of the anionic function does not enhance the fluidizing efficiency. Each PCE has roughly the same fluidizing efficiency when it manages to adsorb in these ionic conditions.

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1. Introduction

Nowadays cement and concrete industry is subjected to two long-term constraints: environmental, by reducing the emission of greenhouse gases, and technological, by increasing the mechanical strengths and the durability of hardened concrete. There is also a short-term constraint to achieve a good workability necessary for the placement of the fresh concrete. To overcome these issues, organic admixtures are used as so-called normal and high range water reducing admixtures (WR/HRWRA) or superplasticizers. The last generation is made of a polyanionic (mainly methacrylate) backbone partially esterified with neutral side chains of polyethylene oxide (PEO). These comb-like copolymers are referred to hereafter by the acronym PCE. As the cost of admixtures is high, the current challenge lies in a comprehension and improvement of fluidizing efficiency for a certain added amount.

Upon addition to cement slurry PCE dispersant may be distributed in three possible states. (i) Because of the alkaline pH of the cement suspension (pH > 12), the non-esterified anionic groups are ionized. Thus these groups adsorb on mineral surfaces which are positively charged, either because of their intrinsic positive charge or as a consequence of the strong affinity of the Ca^{2+} ions with the surface. The adsorbed polymers generate steric repulsive forces that overcome the attractive interparticle forces causing the flocculation [1,2]. The repulsive force and its extent depend on the layer thickness of the adsorbed polymer linked to the density

and length of PCE side chains. (ii) A part of the added amount remains in the pore solution. The PCE structure and the ionic conditions, in particular calcium and sulfate ions, control the proportion of adsorbed PCE [3,4]. The polymer adsorption is very sensitive to the concentration of divalent anions like sulfate ions as a consequence of their competitive adsorption [4]. (iii) In a more anecdotal manner, the interaction of PCE for the formation of organo-mineral phases will render a small fraction of the admixture inactive for dispersion [5,6].

Several studies report the effect of the side chain length of comb-like polymers on cement slurry [7–10]. The fluidizing efficiency, i.e. the slope of the fluidity/adsorption relationship, results from a combination between backbone charge density and the adsorbed layer thickness. The increase of the side chain density or length leads to thicken or densify the adsorbed layer rising the repulsive steric forces as shown by AFM studies [11,12] or theoretical calculations [13]. Theoretical models which are validated by experimental data can help to tackle the rheology of cement paste such as the conformation model for PCE [12] or the model for predicting the yield stress of a suspension called Yodel [14, 15]. Most of these studies focused on the particular case of a full surface coverage (at high adsorption amount) i.e. with homogeneous interparticle forces between all surfaces. We decided to challenge the fluidity/adsorption relationship on the complex case, but more realistic for a cement paste, of the incomplete surface coverage i.e. at a low adsorption amount with a wide variety of PCE. We changed the microstructural parameters of comb-like polymers: the side chain density and length and in a more original way the anionic function (carboxylate, dicarboxylate and phosphate). The main objective is to study the influence of the

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superplasticizer structure on the fluidizing efficiency thanks to an inert calcite system to avoid the time dependent chemical evolution of cement. First the theoretical models proposed in literature to predict the yield stress and the layer thickness of the adsorbed polymer are described. Then experimental data obtained with model polymers are confronted to these theoretical models to select the best parameter governing the fluidizing efficiency. Finally we conclude about the microstructural parameter effect of comb-like polymers on the fluidity/adsorption relationship.

2. Theoretical models

2.1. The surface conformation model of comb-like superplasticizers

A comb-like polymer can be described as the assemblage of n repeating structural units, each containing N monomers in the backbone and one side chain of P monomers [16]. Based on the minimization of the Flory free energy (sum of the elastic energy for the backbone and the side chains and the excluded volume energy of the side chains), Flatt [12] has shown that it is possible to elucidate the unknown polymer surface conformation from its known molecular structure. This work was established on Gay and Raphael study [16] which predicts a conformation diagram of non-ionic comb homopolymers in the solution. As a first hypothesis both models derived within a Flory scaling law and so cannot provide a very quantitative prediction. Then the main assumptions of Flatt conformation model are the following. (i) The model of Gay and Raphael is also valid for a comb copolymer with different monomer sizes (backbone and side chains). (ii) The polymer should be in the Flexible Backbone Worm (FBW) domain i.e. the comb copolymer behaves in solution as a chain of spherical cores (also called blobs). (iii) Once adsorbed on a mineral surface, the polymer behaves as a chain of hemispheres (equivalent to the cores or blobs in solution), each of radius R_{ac}. (iv) The contributions of the excluded volume effect and the adsorption energy for the backbone have been neglected. According to those assumptions, the radius of one adsorbed blob is [12]:

$$R_{ac} = \left(2\sqrt{2}(1-2\chi)\frac{a_P}{a_N} \right)^{1/5} a_P P^{7/10} N^{-1/10}. \qquad (1)$$

Where χ is the Flory parameters of the side chains (0.37 for PEO in water at 25 °C), a_N is the size of the backbone unit, a_P is the size of the side chain unit, P and N have been defined previously. Another assumption has been done by choosing a constant Flory parameter χ. This value was measured in pure water in the semi-dilute regime [17]. AFM experiments on C–S–H substrate at full surface coverage have shown the good predictive character of the conformation model regarding the polymer layer thickness. A few studies have tried to correlate the values obtained by this model to experimental data with success as Giraudeau [6] to check the intercalation of polycarboxylate in AFM phases or to quantify the influence of sulfate ions on the yield stress [18,19].

However some experimental results show that a few assumptions should be considered with caution. The side chains represent an important weight fraction (>70%) of a PCE, so a slight modification of it can induce a big effect on the conformation with the one-fifth power for χ and the seven-tenth power for P in Eq. (1). The influence of the ionic conditions and strength on the hydrodynamic radius R_h of PCE is always under discussion in the literature. Depending on the authors, R_h of PCE can be unaffected [20] or decreased [7,21] by an increase of the ionic strength and sulfate concentration. One can imagine a false prediction of the model if the Flory parameter is not well chosen or if it varies from the solution to the adsorbed state. In fact the ionic concentrations, e.g. sulfate, in the double layer are far away from the ionic conditions in the bulk solution. According to Borget [20], a PCE is in a good solvent in a classical pore solution but only when the sulfate concentration is not really high, obviously not the case near the interface because of the charge balance of the positive (or apparently) charge of the surface. The model

also makes the hypothesis that the conformation and R_{ac} is independent of the surface saturation. As evoked in [20], the solubility of PCE is not only governed by the PEO side chains, but also by the molar mass, the local concentration and molecular environment of PCE which can evolve once adsorbed. In that case the conformation and layer thickness can be modified with the increase of the surface adsorption rate and lead to change the efficiency of the steric repulsion [22]. These two remarks pointed out the more global question about the validity of transposing a model designed for the solution behavior to a model at the surface where the ionic conditions and the dilution regime of the polymer can change. Finally the model neglects the contribution of the adsorption energy. However this enthalpic (electrostatic or specific) interaction contributes to the adsorption. To challenge this strong assumption, the case of the linear polyacrylates can be put in light. Their "loops and tails" conformation is governed by the charge density of the backbone and the interactions with the opposite charged surface. Consequently it is reasonable to think that the grafting degree or the nature of the anionic function can induce a modification of the polymer conformation.

2.2. The Yodel

Predicting the rheology of concrete is a complex issue for several reasons. The size of particles varies from tens of nanometers for C–S–H to 20 mm for the biggest aggregates. Various interactions interplay between these polydisperse particles: gravity, surface forces (colloidal interactions), Brownian forces, hydrodynamic forces and various contact forces. Some models have been developed on defined scales. Particularly recent progress in the prediction of yield stress for colloidal suspension has come from Bowen and Flatt [14,15] who linked it to two contributions: the interparticle forces through non-contact interactions and the number of interacting particles through volume fractions of solids and particle size. According to the assumptions of this model (called the Yodel), cement particles interact via attractive forces at short distance described by Van der Waals type forces. Also the electric double layer repulsive forces have a short range and become negligible compared to the steric hindrance generated by the adsorbed polymer layer of several nanometers [13,23]. Thus the magnitude of these interparticle forces depends primarily on their separation distance. According to the Yodel, the yield stress is written as:

$$\tau_0 \cong m \frac{A_0 a^*}{d^2 H^2} \times \frac{\phi^2 \left(\phi - \phi_{perc} \right)}{\phi_m (\phi_m - \phi)}. \qquad (2)$$

Where m is a pre-factor, which depends on the particle size distribution and shape, A_0 is the nonretarded Hamaker constant, a^* is the radius of curvature of the contact points, d is the particle average diameter, H is the surface to surface separation distance at contact points, ϕ is the solid volume fraction, ϕ_{perc} is the percolation volume fraction and ϕ_m is the maximum packing fraction of the powder. The percolation volume fraction is the critical solid fraction above which a network of colloidal interactions appears in the suspension [23]. Eq. (2) separates the contribution of the interparticle forces (first term) and the contribution of the number of interacting particles (second term) depending on the solid volume fraction. This second part is described in Eq. (2) by $f(\Phi)$ with

$$f(\phi) = \frac{\phi^2 \left(\phi - \phi_{perc} \right)}{\phi_m (\phi_m - \phi)}. \qquad (3)$$

In the case of a defined paste formulation without admixture (especially plasticizer or superplasticizer) at constant volume fraction, the yield stress should thus only depend on the inverse square of the separation distance ($\tau_0 \approx 1/H^2$). A strong assumption has been done on the choice of the interparticle forces. In fact in the case of cement paste, the cohesion was attributed to the interaction between highly charged particles in the presence of divalent calcium counterions which is strongly