Relating the Molecular Structure of Comb-Type Superplastizicers to the Compression Rheology of MgO Suspensions

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ABSTRACT

The compression rheology behavior of concentrated MgO suspensions could be related to the estimated thickness of the adsorbed superplasticizers and an attempt was made to quantitatively assess the importance of the length of the grafted PEO-chains on the magnitude of the interparticle bond strength.

INTRODUCTION

Superplasticizers are able to reduce the porosity of the hardened concrete by allowing the fresh material to become workable with less water. This greatly enhances the durability and also makes it possible to substitute substantial volumes of cement with industrial waste materials, e.g. slag and fly ash[1]. The first generations of superplasticizers, e.g. sulphonated naphthalene formaldehyde (SNF) and modified lignosulphonates (LS), resulted in significant improvements of the properties of fresh concrete and they are still widely used. Increasing demands on workability, high strength and enhanced durability spurred the development of new types of synthetic superplasticizers with improved performance[2,3]. These new generation superplasticizers are comb-type copolymers with an anionic backbone, commonly having carboxylic and/or sulphonate groups that can render the polymer a negative charge, and un-charged poly(ethylene oxide (PEO))- based chains of variable length grafted onto the anionic backbone at regular intervals.

Numerous studies have investigated the mode of action of superplasticizers. Overall, it is believed that the superplasticizers adsorb at the solid-liquid interface, imparting a repulsive inter-particle force of electrostatic or steric origin that reduces or eliminates the adhesion between particles at close proximity. Their relative importance of the double-layer and the polymer-induced contributions in reducing the degree of flocculation has been an issue of several studies. The high ionic strength and the relatively low surface charge densities in cementitious systems suggest that the steric repulsion should be dominating, in particular for the new comb-type copolymers[4-6]. However, there are also studies suggesting that non-adsorbed polymers may play an important role, either through depletion interactions[7] or nucleation inhibition[8].

Unfortunately, there is a lack of experimental studies, relating the rheological properties to the polymer architecture, that corroborate the theoretical predictions based on calculations on inter-particle forces[5,9] on cementitious systems.

Systematic studies have been restricted by a limited access to a range of well-characterised polymers and also faced problems with quantification that are related to the very low yield stresses that the comb-type superplasticizers usually infer at full surface coverage. Hence, previous work has mainly reflected how the adsorbed amount at sub-monolayer coverage is related to the flow and rheology. Yamada and Hanehra[10] showed that competitive adsorption of sulfates decreases adsorption and thereby flow. Schober and Mäder[11] found that the spread of cement paste dispersed with various comb-type polymers varied linearly with the adsorbed amount regardless of the length of the grafted side chains.

This study aims for a more fundamental understanding of the stabilisation mechanism of comb-type superplasticizers. We have related the rheological behaviour to the conformation of the adsorbed superplasticizers. Inert suspensions of MgO in an ionic solution, representing that of an ordinary Portland cement paste (OPC, measured on a paste with w/c=0.5 after 30 minutes), were used as a model system for cement. We have used a range of comb-type superplasticizers with a systematic variation in the length of the grafted polyethylene oxide side chains. The study was performed by centrifugal consolidation, also known as compressive rheology, which exploits rather then suffers from the tendency of a dispersed or weakly flocculated suspension to sediment.

EXPERIMENTALS
Superplasticizers
We have used six different comb-type superplasticizers (noted PC 1-4 and A-B) in the study (Fig. 1). All the polymers are composed of a polymethacrylic (PMA) backbone and grafted side chains of polyethylene glycol (PEG) and the length of the backbone and the grafted side chains have been systematically varied.
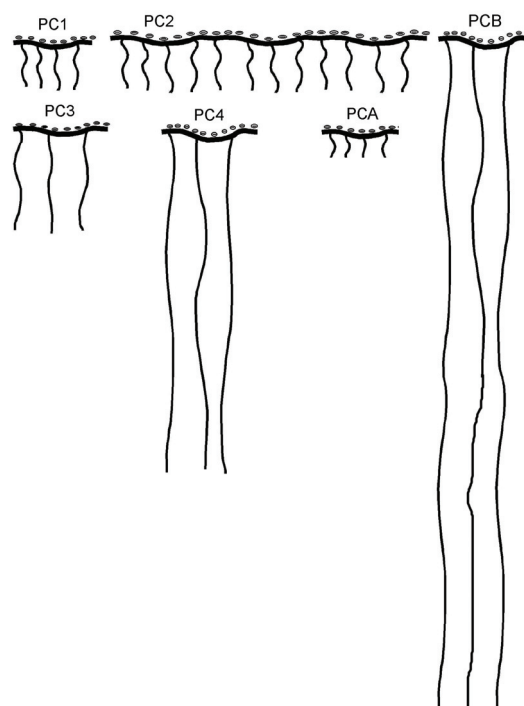

Figure 1. Schematic illustration of the molecular structure comb-type copolymers with a negatively charged polycarboxylate backbone with grafted polyethyleneoxide side chains of different length.

Suspension preparation and centrifugation
Concentrated MgO-suspensions at solids concentration of 20 vol% were prepared by mixing the MgO powder with the electrolyte solution YS. The MgO suspension was ultrasonicated in an ultrasonic bath for 5 minutes and then left with magnetic stirring for 30 minutes until the initial hydrolysis period had been completed. The polymers were added and the suspension was equilibrated for 30 minutes under magnetic stirring. We added an amount of polymer of 6 mg of polymer/g of the MgO powder, which ensures that the MgO surface is saturated by the polymer. One set of experiments was also performed at sub-monolayer coverage where the polymer PC 1 was added at a lower dosage; 0.41, 0.98, 2.00 and 4.00 mg polymer/g powder, respectively.

The polymer-containing suspensions were transferred into a polyallomer tube with dimension ø 25 mm and length 89 mm. The bottom of the tubes had been made flat with an epoxy/lead ball mix, to minimise the radial stress gradient on the suspension and the resulting particle cake. The suspensions were centrifuged in a Mistral 2000 Small Capacity Bench centrifuge at 400 rpm for approximately 3 hours. The centrifugation was terminated when the consolidation process had reached steady state, as determined from the variation in the cake height during centrifugation. The consolidation cake was cut into slices of a thickness of 2-3 mm following a modification of the procedure described by Meeten[12]. The water content, and thus the solids volume fraction of the slices (henceforth known as volume fraction), was determined by measuring the weight loss after drying at 105°C. All experiments were repeated between 2 and 4 times and showed a variation in the volume fraction between 1 and 5% with a mean of 2%.

RESULTS AND DISCUSSION

The rheological properties of a suspension are normally investigated by subjecting the system to a shear field. This can be done in several modes and give information about e.g. the steady shear viscosity as a function of shear rate or the shear yield stress. The yield stress is a very important parameter that is of profound importance for the flow properties of cementitious systems[13,14]. Concentrated suspensions can develop a yield stress when the particles are flocculated resulting in the formation of a continuous particle network, which can support a stress up to a critical value, the yield stress. Weakly flocculated suspensions with relatively coarse particles, typical for cementitious systems with added comb-type superplasticizers, are very difficult to characterise using shear rheology as the particle gels are very fragile and unstable. Preliminary work on the MgO suspensions showed that it was not possible to obtain a reliable measure of the shear yield stress when the comb-type superplasticizers had been added. However, it is also possible to determine the yield stress of a particle network that is subjected to a compressive stress gradient[14,15]. The compressive yield stress is typically two orders of magnitude greater than the shear yield stress and thus more sensitive to small variations in the degree of flocculation also in weakly flocculated systems[15].

Fig. 2 illustrates how the compressive yield properties can be determined by a simple centrifugation experiment. The centrifugal acceleration infer a force to the particles that results in a settling or consolidation of the particle network. The consolidation proceeds until the stress gradient that is developed in the particle network is balanced by the strength of the particle network. When consolidation has reached steady state, the stress on the particle network must be balanced; hence we can assume that the compressive yield stress, P_y, equals the applied stress at all levels and positions in the particle network. Determining the solids volume fraction profile of the centrifuged cakes thus gives information on the compressibility and strength of the particle networks as the stress on the particle network increases towards the bottom of the cake. Sedimentation experiments, although under normal gravity, have in fact been used not only to study early hydration kinetics of cement but also to infer the dispersing character of lignosulfonate type superplasticizers in cement suspensions.

Compressive yield behaviour

Fig. 3 shows that the addition of comb-type superplasticizers to the MgO suspensions has a significant effect on the steady-state volume fraction profiles at a centrifugal speed of 400 rpm. All the suspensions displayed a compressible behavior with an increasing volume fraction towards the bottom of the centrifuge tube (increasing distance from the rotor centre).
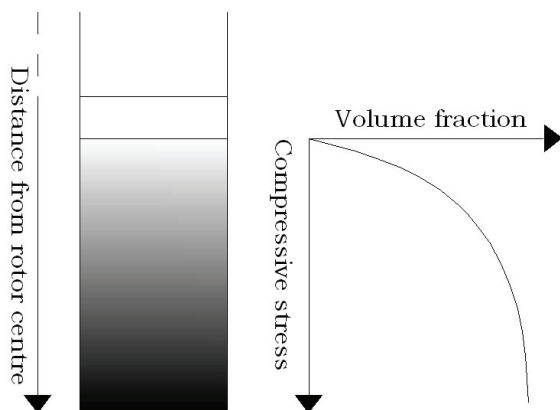
Figure 2. Schematic illustration of a consolidated particle network with the associated compressive stress curve. The volume fraction of the centrifuged cake increase towards the bottom of the tube as the compressive stress increases with distance from the rotor centre and with the accumulated weight of the particle network.
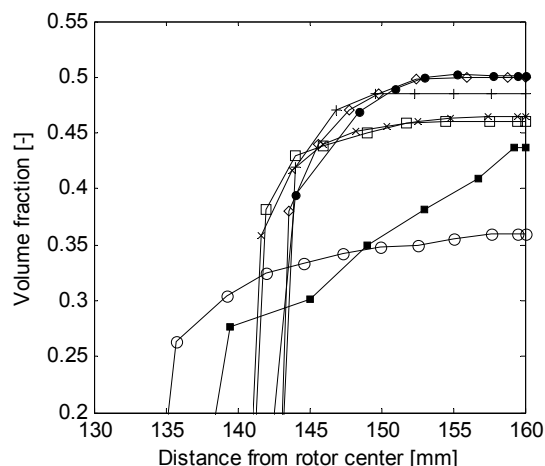

Figure 3. Volume fraction profiles at steady state for MgO suspensions with different comb-type superplasticizers added. The suspensions were centrifuged at 400 rpm for 3 hours.

This behavior is typical for flocculated particle networks since a fully stable suspension is expected to display an essentially incompressible consolidation behaviour[16]. The MgO suspension without addition of any superplasticizer forms a particle network that attains a low volume fraction in the applied centrifugal force field (Fig. 3). This implies that the compressive yield stress is high and that the maximum stress that is applied at the bottom of the cake at a rotational speed of 400 rpm (approximately 6 kPa) only consolidates the MgO particle network to a volume fraction of $\Phi \approx 0.36$. Additions of superplasticizers result in an increase of the volume fraction at the bottom of the tubes, $\Phi \approx 0.43$-0.50, which shows that adsorption of the comb-type superplasticizers significantly reduces the compressive yield stress of these particle networks.

The consolidation study at full surface coverage indicates that the volume fraction and thus also the compressive yield stress depends on the molecular structure of the comb-type superplasticizers. Fig. 4 shows that the volume fraction obtained at the bottom of the tubes increases with PEG length towards a maximum value. This indicates that the degree of flocculation decreases with increased layer thickness. We have made an attempt to estimate the thickness of the adsorbed polymers at the surface of the MgO particles and rationalize how the polymers control the degree of flocculation.

Fig. 5 shows that the maximum volume fraction of the consolidated particle networks scales with the inverse of the estimated layer thickness. The layer thickness is estimated in arbitrary units as the absolute number of monomers is unknown. The simple relation clearly corroborates the importance of the grafted PEO-side chains in imparting a steric repulsion that controls the consolidation of the particle network. The inverse scaling could also be used in future work and assist in the design of optimal architectures of new types of superplasticizers.
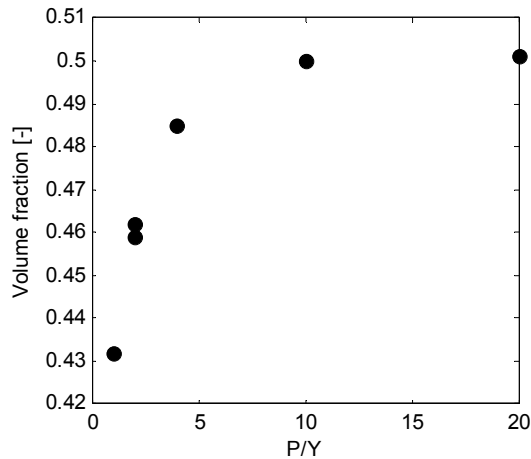
Figure 4. The highest attained volume fraction after centrifugation at 400 rpm, as a function of the relative length, P/Y, of the polyethylene oxide side-chains on the superplasticizers.
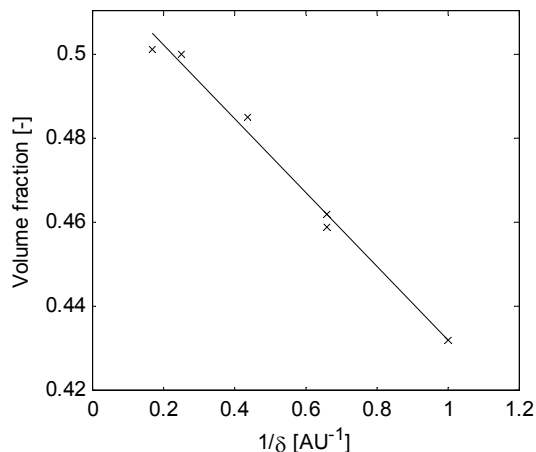

Figure 5. The highest attained volume fraction after centrifugation at 400 rpm, as a function of the inverse of the estimated adsorbed layer thickness, $1/\delta$.

SUMMARY AND CONCLUSIONS

The use of a compression rheology approach based on the analysis of centrifugally consolidated suspensions of MgO particles offers a novel tool to study and quantify the effect of the molecular structure of comb-type superplasticizers on the rheological properties. This simple experimental approach by-passes the issue of sedimentation and poor sensitivity that has been a common problem on steady-shear investigations.

We found that an increased length of the grafted ethylene-oxide side chains of the adsorbed comb-type superplasticizers reduces the strength of the flocculated particle network and results in an increased volume fraction when the suspensions are consolidated at moderate rotational speeds. This is consistent with an increase in the range of the polymer-induced steric repulsion which reduces the degree of flocculation and thus also the compressive yield stress.

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