

NEW POLY-PHOSPHONIC SUPERPLASTICIZERS PARTICULARLY SUITED FOR THE MANUFACTURE OF HIGH PERFORMANCE SCC

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ABSTRACT

The design of Self-compacting concrete (SCC) is essentially an empirical procedure, and the resulting concrete is sensitive to minor variations of the constituents. Moreover, especially for high performance SCC concretes with low water-to cement (w/c) ratio, the consistency is often “sticky”, i.e. concrete retains a relatively high viscosity at shear rates in the range of mild stirring, while having a low yield stress to flow under gravity. In this work we present a novel poly-phosphonic superplasticizer (Ph) which, while achieving a high water reduction, reduces the high-shear viscosity of SCC thus reducing its “stickiness”. Also the robustness of SCC is improved and its sensitivity to small variations of w/c is reduced. We hypothesize a mechanism to explain this behavior, based on rheological measurements on the concrete mortar and paste.

Keywords: rheology; stability; shear-thinning; superplasticizer;

INTRODUCTION

Self-compacting concrete (SCC) does not require vibration for placing and compaction. It flows under its own weight and completely fills the formworks even in the presence of highly congested reinforcements. The technological advantages connected to its use include fast concrete placement and construction times, a high level of homogeneity, minimal concrete voids and gravel nests, superior surface aspect and the potential for a less porous and more durable structure. These characteristics stem from its composition and its properties in the fresh state: compared to traditional concrete SCC has a higher volume of paste, usually comprised between 300 l/m³ and 380 l/m³, and

a high solids volume fraction of the paste, usually ranging within 0,48 and 0,55 [1]. The volume of paste must be high enough to transport the large aggregate fraction without segregation, even in the occurrence of sudden changes of direction or velocity. The viscosity of the paste must be high enough to avoid dynamic segregation of the large aggregates, while its yield stress must be low enough to allow flow under gravity. Static segregation of the aggregates is limited by the tixotropy of the paste [2-4].

The properties of SCC in its fresh state are dictated by the rheological characteristics of paste, these being determined by its solids volume fraction and microstructure [5]. The microstructure of cement paste is a function of mechanisms and kinetics of the gelation of the slurry [6,7], occurring immediately after mixing cement and water at virtually zero hydration [8-10]. The presence of superplasticizers affects the coagulation of cement particles [11] by interacting with the hydroxylated surfaces and the tightly adsorbed Ca^{2+} counterions and thus modifying the particle interaction potential [12]. In this paper we present a novel poly-phosphonate (Ph) based superplasticizer, with a comb-type polymer architecture similar to PCE but with phosphonic groups replacing carboxylic ones. The use of such a superplasticizer replacing a PCE in an already optimized SCC concrete results in a product which is less viscous and more robust. Rheological measurements on the mortar and paste of this SCC concrete reveal differences in the shear thinning characteristics as well as in the onset of shear thickening. Also, the scaling relation of the yield stress on the solids volume fraction of the paste is different for the different superplasticizers, pointing to a different microstructure of the particle agglomerates constituting the paste [13].

EXPERIMENTAL

For the present study we have selected a SCC concrete of strength class C 35/45 used in a prefabrication factory of small non-structural elements. The cement used is CEM II/A-M (LL-S) 42,5 R and the filler is limestone. The composition of the concrete mixture is reported in Tab. 1. The moisture content of the sand and aggregates has been measured and accounted for. This composition results in a volume of paste of 362 l/m^3 , in a solids volume fraction of the paste of 0,48 and in a ratio of sand over all aggregates of 0,50.

Table 1. SCC concrete mix design.

Component	kg/m³
cement CEM II/A-M (LL-S) 42,5 R	429
limestone filler	90
sand 0/2 mm	860
aggregate 4/8 mm (crushed aggregate)	264
aggregate 8/16 mm (crushed aggregate)	605
Water	189

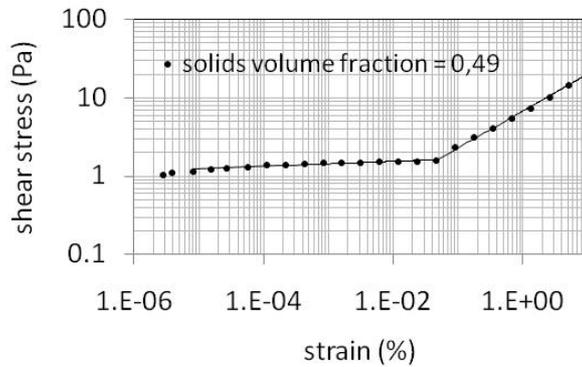
Two different superplasticizers have been used, a PCE and a poly-phosphonic polymer (Ph). The PCE used is a commercial superplasticizer from TKK Srpenica d.d., routinely used for the manufacture of SCC precast concretes. The Ph is a poly-phosphonic polymer constituted by ethylene oxide side chains grafted onto a backbone carrying phosphonic groups. The average molecular weight of the polymer is $\langle M_w \rangle = 3000$ Da and the charge density of the polymer is 4,30 meq/g. Both PCE and Ph have equal side chains, with about 23 ethylene oxide repeating units, but they differ in molecular weight, Ph being about 10 times smaller than PCE, and in the chemical nature of the anionic groups, carboxylic for the PCE and phosphonic for the Ph.

The amount of superplasticizer used has been selected in order to have a slump flow of 700 mm. For the PCE this resulted in a dosage of 3,66 kg/m³ of a 24% solution, equivalent to 0,17% by weight of dry matter content over the weight of powder (cement + filler). For the Ph the required dosage was 6,41 kg/m³ of a 30% solution, equivalent to 0,37% by weight of dry matter content over the weight of powder. Finally also a blend of PCE and Ph has been used, composed of 36% of the PCE 24% solution and 64% of the Ph 30% solution, equivalent to 31% PCE dry matter and 69% Ph dry matter. The required dosage of this blend was 5,04 kg/m³, equivalent to 0,27% by weight of dry matter content over the weight of powder.

The different SCC concretes have been tested for the slump flow and T_{500} time, the V-funnel efflux time and the 3-bar L-box passing ability. In addition to the SCC concrete, experiments have been carried out on the mortar and on the paste issued from it. The mortar of this SCC, used in rheometric flow measurements, is composed by cement, filler, sand 0/2 mm, water and superplasticizers in the same ratio as used for the concrete, excluding the aggregates. The paste has been used to measure the yield stress and flow curves in a plate-plate rheometer. It is constituted by cement and filler in the same ratio as for the concrete. Measurements on the paste have been carried out both without and with superplasticizers at various water-to-powder ratios, ranging from 0,44 to 0,53 for the paste without superplasticizers, and from 0,53 to 0,61 for the paste with superplasticizers. The superplasticizers, where used, have been dosed at the same ratio to the powder than in the concrete.

The flow curves on the mortar have been measured with a Viskomat NT rheometer with the Vogel type measuring body. The mortar has been mixed in a Hobart mixer, and a preshear was allowed prior to the measurement of the flow curve, from high to low shear rates. The rheological characteristics of the paste have been measured with a MCR 301 rheometer from Physica. The paste has been mixed in a high speed mixer, and loaded in the measuring system constituted by serrated plates of 25 mm diameter, with the gap set to 1 mm. A preshear was allowed prior to the measurement, which started with the measurement of the yield stress, followed by a flow curve measured from high to low shear rates, taking care at each experimental point to have reached the stationary viscosity. The yield stress has been measured via a strain sweep, as shown in Fig. 1, the values of yield stress τ_0 and yield strain γ_0 being defined by the slope change. The entire procedure was repeated three times but in the following only the initial results will be described. Each strain sweep lasted 3 minutes.

Figure 1. Direct measurement of the yield strain γ_0 and yield stress τ_0 exemplified for the paste at solids volume fraction $\varphi = 0,49$ without superplasticizer.



RESULTS AND DISCUSSION

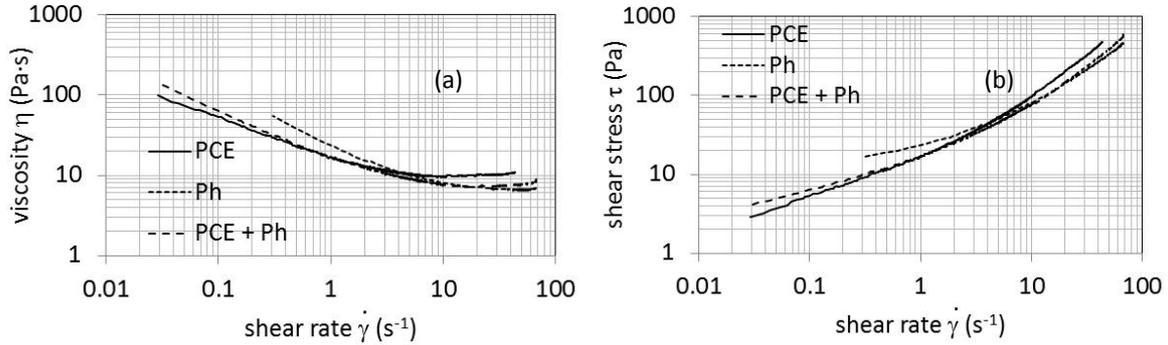
The properties of the concretes mixed with the different superplasticizers are shown in Tab. 2. It appears that the use of the Ph superplasticizer, either alone or in combination with the PCE significantly decreases concrete viscosity and improves its passing ability. These results are obtained starting from a concrete that has already been optimized, and is presently in industrial use. The cohesion of concrete is not affected: the concrete mixed with the Ph superplasticizer after testing has been remixed adding 8,5 kg/m³ water without showing any tendency to segregation.

Table 2. Characteristics of the SCC concretes.

property	PCE	Ph	PCE + Ph
slump flow (mm)	700	700	715
T ₅₀₀ (s)	3,3	2,9	2,6
V-funnel flow time (s)	8,5	6,3	6,5
L-box passing ratio	0,73	0,75	0,80

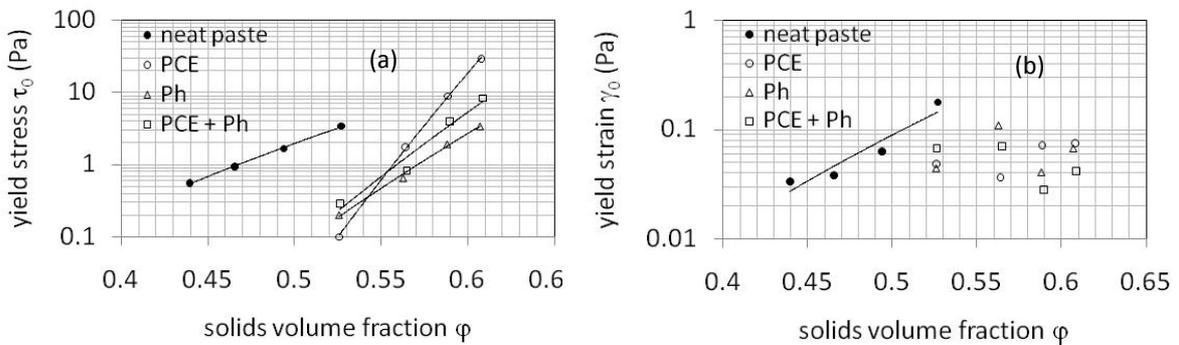
To investigate the origin of this different behavior, the rheology of the mortar and of the paste has been investigated. The flow curves of the different mortars are shown in Fig. 2. The mortar mixed with the PCE superplasticizer has a significantly higher viscosity at shear rates higher than 10 s⁻¹, and its viscosity begins leveling off at lower shear rates. This leveling of viscosity is shown in Fig. 2(b) as a change in the slope of the shear stress – shear rate curve. It has been shown by Lootens [14] that in the case of concentrated suspensions of silica, 1 μm in diameter, the change in slope shifts towards lower shear rates on increasing the solids volume fraction. Also, the slope in the low shear rate region is shown to increase on increasing the particle dimensions. In these measurements the solids volume fraction of the mortars is constant and the shift might be attributed to a different microstructure of the solid suspended phase.

Figure 2. Flow curves of the mortars mixed with the different superplasticizers: viscosity (a) and shear stress (b).



It has been observed that the microstructure of cement paste has fractal characteristics [15,16]. We do not want to imply here any fractal scaling of the microstructure, and we will use in the following the term fractal only to designate the power-law variation of the volume fraction of the agglomerates with their diameter: $\varphi_a \sim r^{3-d}$, d being the fractal dimension of the agglomerates. Within this frame, the data shown are consistent with the hypothesis of the paste within the mortar being constituted by agglomerates which undergo fragmentation in the hydrodynamic shear field [7,19] thus showing a shear thinning behaviour. In the presence of different superplasticizers, these agglomerates have different microstructure, porosity and size, thus resulting in different shear thinning behaviour of the mortar.

Figure 3. Yield stress (a) and yield strain (b) for the paste mixed with the various superplasticizers at different solids volume fractions.



The measurements of yield stress and yield strain of the paste at different solids volume fraction are shown in Fig. 3. The yield stress shows a power-law scaling to the solids volume fraction. Such a scaling is frequently observed for yield stress, elastic modulus and compressive strength of diverse systems such as colloidal gels, aggregate networks and concentrated pastes [13,17,18]. The scaling exponents for both yield stress and yield strain are shown in Tab. 3. We observe a difference among the trends for the paste without superplasticizer and the paste with superplasticizers. The first one shows a smaller scaling exponent for the yield stress, and a positive scaling exponent for the yield strain, while the paste with the superplasticizers shows a larger scaling exponent for the yield stress and no clear trends for the yield strain.

Table 3. scaling exponents for yield stress and yield strain.

Paste	neat	PCE	Ph	PCE + Ph
yield stress scaling exponent	9,98	39,1	20,0	23,6
yield strain scaling exponent	9,21	≈ 0	≈ 0	≈ 0

According to [13] this difference may be interpreted as a different structure of the cement particle agglomerates. Two limiting conditions are identified: strong-link and weak-link regimes. In the strong-link regime the elasticity of the system is dictated by the elasticity of the agglomerates themselves which are not stronger than the links among them. On the contrary in the weak-link regime the elasticity of the system is dictated by the elasticity of the inter-agglomerate links, the agglomerates themselves behaving as rigid bodies. Trying to make this description more intuitive, we may call the strong-link regime as “soft agglomerated regime”, and the weak-link regime as “strong agglomerated regime”. In the soft agglomerated regime the scaling of the elastic constant K and of the yield strain is respectively $K \sim \phi^{(3+x)/(3-d)}$ and $\gamma_0 \sim \phi^{-(1+x)/(3-d)}$, while in the strong agglomerated regime the scaling is $K \sim \phi^{1/(3-d)}$ and $\gamma_0 \sim \phi^{1/(3-d)}$. In the above formulas x is the backbone fractal dimension of the flocs, i.e. the tortuosity of the effective chain of stress transduction within a cluster of particles yielding under an externally applied stress, and d is the fractal dimension of the flocs. The parameter x is difficult to estimate, and it is usually assumed to be in the range $(1 \div 1,3)$. Within this frame the paste without superplasticizer is in the strong agglomerated regime, with agglomerates which are stronger than the link between them and a high fractal dimension $d \approx 2,9$: a value close to what has been previously reported [19]. The paste with the superplasticizers on the contrary is in the transition zone between the strong and soft agglomerated regimes, and shows a slightly different fractal dimension depending on the superplasticizer used, with d increasing from $\approx 2,8$ for Ph and PCE+Ph to $\approx 2,9$ for PCE, arbitrarily assuming $x = 1,2$. The PCE superplasticizer shows a higher scaling exponent and a slightly higher fractal dimension than the Ph superplasticizer, pointing to a more compact microstructure constituted by larger agglomerates, as can be deduced by considering that denser agglomerates with higher fractal dimension must grow larger to fill up the space compared to less compact ones.

From the data above we may hypothesize that the presence of the superplasticizers, by changing the particle interaction potential, modifies the microstructure of the particle agglomerates and their elasticity, thus affecting their response to the hydrodynamic shear field and their shear thinning behaviour. The chemical nature and molecular structure of the superplasticizers has an effect on the rheological behaviour, and the different performance of the PCE and Ph superplasticizers may be due to their different adsorption characteristics and different influence on the particle interaction potential brought about by their different molecular weight and chemical nature.

The flow curves of the paste show similar trends to what discussed above for the mortar, and additionally the likely occurrence of shear banding at low shear rates, with the shear stress passing through a minimum on decreasing the shear rate [20].

CONCLUSION

A novel poly-phosphonic superplasticizer is introduced, which shows significant advantages in the manufacture of SCC. It results in concretes which are less viscous at intermediate shear rates, and more robust with regards to minor variations in the constituents. The lower viscosity of concrete, without loss of cohesion, increases its passing ability, and decreases the feeling of stickiness typically shown by high performance, low w/c self-compacting concretes.

Differences are observed in the flow curves of the concrete mortar, with the PCE showing higher viscosity in the $\dot{\gamma}$ range between 10 s^{-1} and 100 s^{-1} . The differences observed in the rheological response are attributed to differences in the microstructure of the paste, which shows a different elasticity in the yield stress and yield strain variation with the solids volume fraction. The PCE seems to result in larger and more compact particle agglomerates, possibly as a result of its different influence on the particle interaction potential.

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