Towards Tailored Superplasticizers

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ABSTRACT. Superplasticizers (SP) of the “new generation” are essentially polycarboxylate polymers. Polymers of this family can be produced with almost infinite variations in their chemical structure, which allow the fulfilment of specific (tailored) properties. These polymers are more efficient for water reduction and for keeping concrete workability for longer periods. Another class of superplasticizer also available essentially for extreme specifications, is poly(oxyethylen) phosphonates. A few years ago, one objective of superplasticizer development was to produce very robust SPs usable in all types of concrete with limited incompatibilities. It seems now that such a product will probably never exist due to the underlying complexity and variability of cement. More versatile SPs can, however, be obtained by blending different polymers. As the interactions cement/superplasticizer are better understood, tailored SPs for given applications are becoming more readily available. This paper aims at highlighting some key structure-property relationships of these different SPs. The role of the polymer fraction that does not get adsorb onto cement particles is also mentioned.

Keywords: Superplasticizers, Polycarboxylates, Lignosulfonates, Poly(oxyethelen) phosphonates, Adsorption, Interactions, Model systems.

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INTRODUCTION

The use of superplasticizers is actually very common for many concretes [1-4]. Efficient products like polynaphtalene (PNS) or polymelamine (PMS) sulfonates are still the main types used for most current concretes. This is essentially due to the large experience that concrete producers have accumulated during the last decades and to the relatively low cost of these superplasticizers. From the 1990's, novel superplasticizers were proposed to reduce the drawback of a more or less rapid loss of workability and common cement /superplasticizer incompatibility. These superplasticizers, generally of the polycarboxylate polymer type (PCP), are designed essentially for their high dispersing ability and their high workability retention with a minimal setting retardation. These products have permitted the development of very high strength concrete. For extreme specifications, poly(oxyethylen) phosphonates are available [5]. The recent development of sugar-free modified lignosulfonates (MLS) has allowed these polymers to begin to compete with traditional superplasticitzers like PNS and PMS [6]. All these superplasticizers have led to major progress in concrete technology with the incorporation of more or less large amounts of fly ash and silica fume. More recently, they have allowed the use of self-compacting concrete on a large scale.

The development of commercial superplasticizers is closely linked to the research works carried out essentially since the end of the 1970's, which have themselves benefited from the development of colloidal theories and polymer chemistry. A few hundred papers dealing with scientific aspects of superplasticizers have been published during the last 25 years. The causes of incompatibilities between cement and superplasticizers, which have been often reported, are now much better understood and thus can be prevented more efficiently.

The main role of (super)plasticizers has been known for a long time. First, they disperse cement particles, which are strongly agglomerated (flocculated) when cement is contacted with water. This action is closely linked to the adsorption of the polymers onto cement surfaces [1]. Second, the polymers remaining in solution may have different effects. However, it seems reasonably well established that they also lubricate contacts between cement particles [7,8]. The more recent polymers are synthesised in order to disperse cements predominantly by the steric effect. The main advantage of the steric effect is that, contrary to the electrostatic effect, it is less likely to be influenced by the ions in the interstitial solution, i.e. by the cement composition. The understanding of the detailed mechanisms through which superplasticizers act, is a key factor for the development of new superplasticizers, to become more efficient and robust. This means that we should be able to understand and explain the structure-property relationship between the polymer structure and the improved fluidity. In the following sections, we will try to describe these relationships for some superplasticizers of the latest generation. We intend to show how the structure of the superplasticizer molecules influences their dispersing properties using data available in the literature.

INTERACTIONS CEMENT/SUPERPLASTICIZERS

Forces Acting Between Particles in Suspension

The forces acting between particles in suspension have been presented in the previous Congress of this series [9]. At small separation distances, the so-called dispersive force (F_{Disp}) is attractive for similar isotropic cement particles. Electrostatic forces (F_{ES}) can be either repulsive between particles of identical charges or attractive between particles of opposite charge. As a negative charge is induced by the adsorption of anionic superplasticizers, a repulsive force is resulting. The adsorption of superplasticizers also leads to a steric force (F_{Ster}). The total interacting force (F_{Tot}) is the sum of these three forces and can be written as:

$$F_{Tot} = F_{Disp} + F_{ES} + F_{Ster} \qquad (1)$$

The intergranular friction between particles has been found to be important in the rheology of cementitious systems. The lubrication of contacts by superplasticizers has been recently highlighted [8]. It has been shown that PNS polymers confer shear thinning properties to cement slurries in the flow conditions used in practice and that polycarboxylates polymers with PEO side chains induce shear thickening behaviour for the same slurries in the same conditions. This behaviour is attributed to a better lubrication effect of PNS [7] and is probably due to differences in the molecular conformation at the particle – liquid interface.

Superplasticizers

PCP's, which can be produced with almost infinite variations in their chemical structure, represent the most novel superplasticizers. It is the reason for which we give here a more detailed description of these polymers, often called comb-type polymers. Schematically, these polymers have a backbone chain with ionic groups (fully dissociated at high pH as found in the interstitial cement solution) and grafted side chains mainly of poly(ethylenoxide) (PEO) with a length varying between 10 and 130 PEO units. PEO chains are in a good solvent (water) and tend to extend into the solution. It has been also proposed to graft short and long side chains on the same backbone [10,11]. Typical structures of these polymers assumed to act essentially through the steric effect are given in Figure 1. Polymers of another type with one or two adsorbing groups at one of their ends are also available [5].

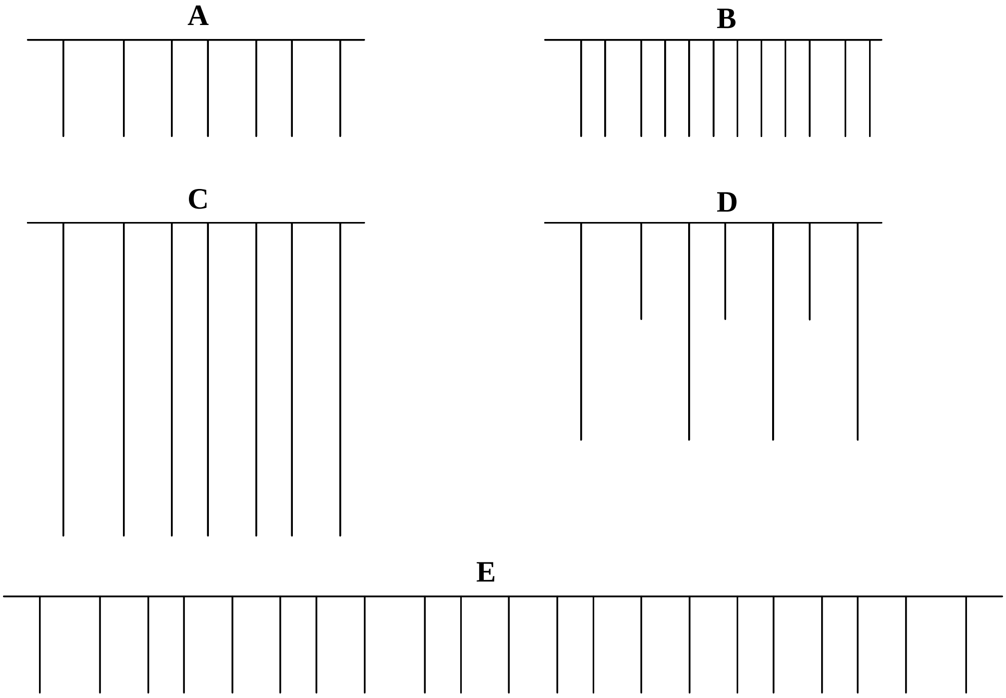

Figure 1 Typical variations of molecular parameters of polycarboxylate type superplasticizers: spacing of side chains (A-B), side chain length (C - D), backbone length (A,B,C,D - E).

The structure of comb-like polymers in solution can be modelled according to existing theories as described in [12]. Basic characteristics like the radius of gyration can be determined experimentally for instance by viscosimetry. The radius of gyration of the side chain can be measured on the PEO alone.

In a suspension, the adsorbed polymers may have two different regimes according to the degree of surface coverage. This has been demonstrated theoretically and experimentally. At low surface coverage, adsorbed polymers are independent of each other and we have the so-called *mushroom regime,* like in a dilute solution where the polymers have a coil conformation). When the surface coverage increases, the polymers overlap and a *brush regime* establishes. The conformation of the adsorbed polymers is thus like in a semi-dilute solution at high surface coverage. However, such a regime can be expected for polymers with very long side chains and relatively short backbone chain. The probability of this transition between the two regimes can be evaluated by using the Gay and Raphaël approach [12], which takes into account the polymer architecture and polymer – solvent interactions. Atomic force microscopy (AFM) can help evaluate the thickness of adsorbed polymer molecules [13]. This is a very important parameter since it defines the distance at which the steric repulsion starts to influence interparticle interactions, and allows comparison of computed theoretical layer thickness and experiment as discussed in more detail later in this article.

Adsorption Isotherms

The most common way to study the adsorption of superplasticizers is to put in contact a solution of polymers with a powder. After, a given period of time the solid is separated by filtration or centrifugation and the amount in polymer in supernatant determined. Several concentrations in polymer allow the representation of the adsorption isotherm. This method also allows the study of the kinetics of adsorption by varying the time of contact. When brought in contact with water, cement reacts quickly and releases ions into the solution (essentially Na^+, K^+, Ca^{++}, SO_4^{--} and OH^-. Thus, a complex system evolves over time and the influence of the different parameters cannot be separately studied. For this reason a model powder is often used instead of cement. From our point of view, the best of the model powders is *dead burned* magnesium oxide (MgO) which is relatively inert after a certain time of contact with water and has a surface charge similar to cement at pH 12-13 [14]. Magnesium hydroxide can also be used if an adequate powder is found. Calcium carbonate (calcite) has also been used. However, its main drawback is to have an isoelectric point at pH = 9.6 instead of 12.45 for MgO. The surface MgO hydrates to give $Mg(OH)_2$. An example of adsorption isotherms on MgO is given in Figure 2. One can see that lignosulfonates LS-1 and LS-2 adsorb a higher amount than PCPs for any quantity of SP added. This is certainly due to the more compact shape of the adsorbed molecule.

The forces attaching superplasticizers on the surface of cement particles can be of different origins. Superplasticizers are ionic water soluble polymers which can form complexes with cations of the surface: $-Ca^+$ with calcite and cement, $-Mg^+$ with MgO and also other cations with cement). The complexation phenomenon has been studied on calcite [15] and should be similar with $Mg(OH)_2$ and cement. The interstitial cement solution has a pH between 12 and 13 and the surface charge of cement particles is low or even negative. This is not favourable to electrostatic binding since superplasticizers are also negatively charged. However, even if a surface has an overall negative charge, it carries positively charged sites. This has been demonstrated for calcite [15]. Van der Waals forces can also have a minor role through the interaction of a negatively charged surface and induced dipoles in the polymer molecules. However, it seems that surface complexation, which does not depend on the overall surface charge, is the main mechanism binding polycarboxylates to a surface. Geffroy et al. [15]

demonstrated this by using different n-di-carboxylic ligands forming ring structures. However, the complexation of ions and cationic surface sites by superplasticizers has still to be studied in more detail. Also identification of types of adsorption sites on a heterogeneous solid surface for both model powders and real cement systems, is a great challenge for the future tailoring of SPs.

The adsorption isotherms of Figure 2 can be approximated first by a straight line and then by a hyperbolic function. The linear part corresponds to the *mushroom regime* described above (the adsorbed polymer increases linearly with its concentration in solution) and the hyperbolic part may correspond to the *brush regime* when it exists. The adsorption curve tends towards a plateau. At the plateau, one may assume that all the available surface is occupied by polymer molecules. This is the most frequent situation with superplasticizers and the plateau value corresponds roughly to the minimum of viscosity [16]. Additions of superplasticizers below the plateau can be critical in practice because a small variation of surface coverage may lead to large variations of workability. The presence of a plateau depends on several factors among which the molar mass distribution is important. If the adsorption depends on the molar mass of the molecules, there is generally no plateau. The slope of the linear region of the isotherm is called the affinity and is a qualitative measure of the adsorption free energy. The affinity is strong for superplasticizers like MLS, PNS, PMS, POEP, and lower for PCP. An example of the affinity of different superplasticizers for MgO is given in Figure 3. It has been shown with superplasticizers such as poly(ethylene) di-phosphonates, that the transition between the *mushroom* regime and the *brush regime* corresponds to the minimum amount of polymer that is required to get a full surface coverage. This corresponds also to the minimum amount of polymer to stabilise and fluidise a calcite suspension [17].

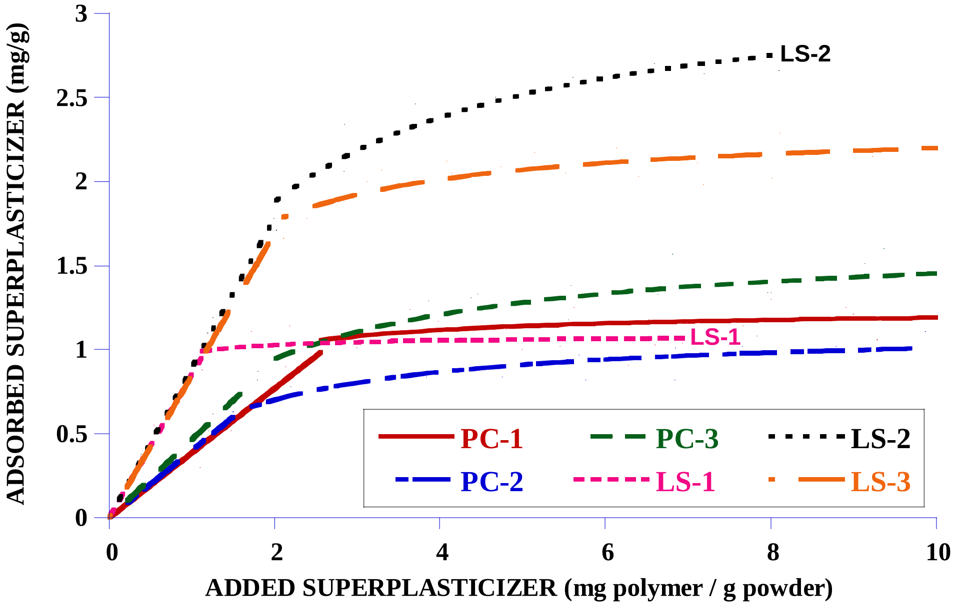

Figure 2 Adsorption isotherms of three different PCPs and two LSs. The adsorption isotherms are approximated with a linear and a hyperbolic function (adapted from [18]).

Adsorbed Layer Thickness

Different models allow the evaluation of a polymer molecule size in solution. It is more complex for adsorbed molecules. However, atomic force microscopy (AFM) developed for measuring surface forces can help in evaluating the thickness of adsorbed polymer molecules [19]. Dynamic light scattering (DLS) is another possible technique for particles with a narrow size distribution, ideally spherical and monodispersed. The method measures the hydrodynamic radius of particles of a few tens of nanometers with and without an adsorbed polymer layer. The difference between both measurements provides the adsorbed layer thickness. Other techniques can also be used to obtain this difference such as filter pressing [20]. The adsorbed layer thickness is a key parameter for the prediction of superplasticized concrete rheology [21].

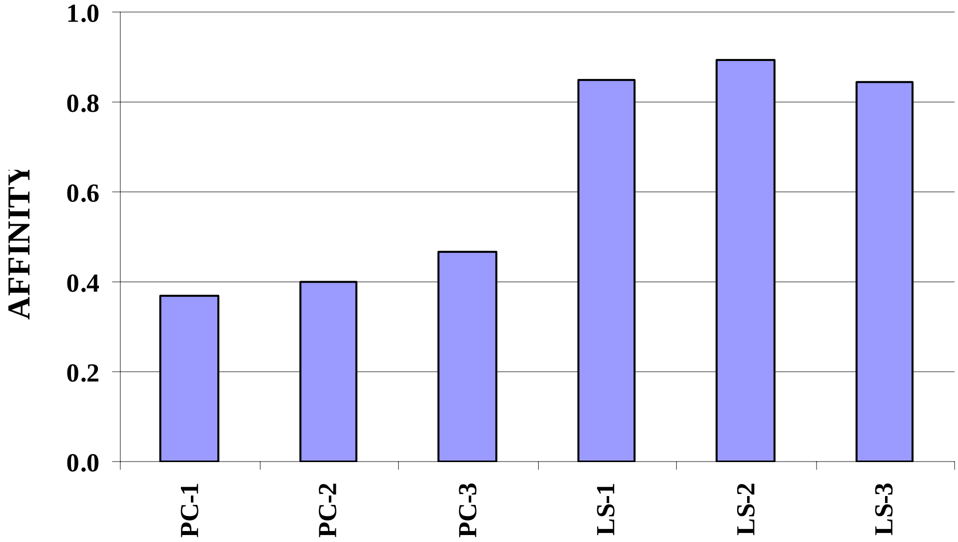

Figure 3 Affinity of the PCPs and LSs calculated from Figure 2. It is the slope of the straight line of figure 2.

MAIN MOLECULAR PARAMETER INFLUENCING PERFORMANCE

Numerous results, which have been achieved on very different cementitious systems, are often inconsistent. This is not surprising since the interactions between cement and superplasticizers are strongly influenced by the chemical and mineralogical compositions of the solids and of the liquid phase [22]. The influence of the molecular structure on the properties is always accentuated for cement paste and concrete of low water/cement ratio. The time of the superplasticizer addition (direct or delayed) is known to be of high importance. High concentrations of ionic functional groups in solution delay the setting time. The terminology and experimental determinations and procedures vary greatly between different studies rendering comparisons difficult. Furthermore, the commercial impact of superplasticizers tends to limit the number of details of some important characteristics that are provided in the literature. Commercial superplasticizers do not contain only the active polymer, but they are formulated and contain at least a defoamer. However, some general trends on the effects of the molecular make up can be discerned for the active polymers.

Measurements carried out on MgO have shown that both a longer main chain and a longer side chain lead to an increase of the adsorbed superplasticizer amount [23]. The same trend has been observed on cement pastes [24]. The higher the adsorption value, the higher the paste fluidity for polymers that have an adsorption plateau.

Polymers with longer PEO side chains show higher fluidity, a larger fluidity decrease with time and a shorter setting time [25].

As already mentioned above, polymers with two different lengths of PEO side chains have been tested [10,11]. Such a configuration intends to avoid the drawback of long side chains (fluidity decrease with time) and to benefit from the advantage of these long chains (high steric repulsion). The intercalation of short side chains permits the repulsion of the longer side chains, which extend into the solution, increasing the effective layer thickness. The hybrid superplasticizer gives better results than a blend of polymers with long and short side chains [10].

Ohta et al. [26] have stated some semi-quantitative structure/dispersibility relationships which are summarised in Table 1. They also propose polymers with long backbones, which can be hydrolysed by hydroxyl ions (OH^-), to produce shorter molecules fulfilling the required time dependent properties and reacting quickly, i.e. a long backbone at early stages giving way to short backbones for long dispersability retention.

Table 1 Structural factors influencing dispersability and dispersability retention [26].

STRUCTURAL FACTOR/ DISPERSIBILITY	RELATIVE CHAIN LENGTH OF BACKBONE	RELATIVE SIDE CHAIN LENGTH	RELATIVE NUMBER OF SIDE CHAINS
Low dispersability & short dispersability retention	Long	Short	Large
High dispersability	Short	Long	Small
Long dispersability retention	Shorter	Long	Large

It should still be mentioned that numerous polymers are not simple polycarboxylate polymers, but contain additional groups like sulfonate or styrene. Finally commercial polymers are often blended to confer special properties like short setting time or long fluidity retention.

Recently, a novel LS was introduced [6]. This product is much more effective in terms of workability of the concrete as a function of the dosage compared to the performance of the best commercially available MLS and PNS. However, the set retardation is the same as traditional LSs which retard more than PNSs. Despite large efforts, the structure/properties relationship could not be clearly established because of the high complexity of lignosulfonate molecules linked to their natural origin.

A very particular superplasticizer is commercially available especially for extreme applications: the ethoxylated di-phosphonate. The molecule consists of a di-phosphonate group fixed at one end of a PEO chain. This molecule adsorbs on surfaces according to the two regimes described above, i.e. mushroom or brush. The molecule is fixed at the surface by the di-phosphonate groups. Due to the absence of charged groups in the chain, the stabilisation of particles is essentially steric with little dependence on the cement and the composition of the interstitial solution, more particularly on sulfates. This superplasticizer has a lower affinity and adsorption capacity, presumably due to a limited number of specific adsorption sites. This allows more superplasticizer to remain in solution and to then retain the capacity to adsorb and disperse cement particles for longer periods, even when the surface is covered by the later formed hydration products. This superplasticizer is particularly adapted for extreme concreting conditions like hot weather, long workability requirements such as long distance pumping [5].

CONCLUSIONS

The progress in the science and technology of polymers, as well as the application of colloidal theories to cementitious systems have led to a good understanding of the relationships between structure and properties over the last few decades. The use of model powders for cement has allowed us to overcome a part of the complexity of cementitious systems that evolve over time. This actually allows us to envisage the development of tailored superplasticizers for specific applications while having fewer incompatibilities. This may be achieved by modification of polymer backbone functional groups to give more specific adsorption for specific applications, e.g. by creating complexing groups for specific surface sites. Towards this goal the types of adsorption sites that dominate cement particle surfaces at different ageing times need to be further investigated. Model heterogeneous surfaces should contribute significantly in this area. However, traditional superplasticizers like PNS, PMS, LS will still be used for current applications where a great deal of experience has been obtained.

ACKNOLEDGEMENTS

The authors would like to thank all partners of the Superplast project [27], who have contributed to provide us with a larger view of the interactions cement superplasticizers through many fruitful discussions. The *Superplast* project was funded by the 5Th European Framework Programme (Contract G5RD-CT-2001-00435). It also received funding from Vinnova in Sweden and from the Swiss Federal Office for Education and Science (contract No 00.273-1).

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