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Recent Developments in Superplasticizers

by M. Collepardi and M. Valente

Synopsis: Superplasticizers are considered to be the most important chemical admixtures in cement mixtures due to their influence on the hardened concrete properties (related to the water-cement ratio) as well as on those of the concrete in the fresh state (workability and workability loss).

During the last decade a new family of polymers based on polycarboxylate as the main polymer chain and polyether as side graft chains have been developed. This new family of products appear to be in general more effective in terms of higher water reduction, lower slump loss and lower retarding effect at very early ages.

More recently these performances have been enhanced in view of some specific applications: a) in precast concrete structures, the very early strength (such as at 12-16 hours) can be increased even in cold climates and in the absence of steam curing; this effect depends on the number and length of the polyether graft chain which are responsible for the dispersion effect related to the steric hindrance; b) in ready-mixed concrete mixtures, the slump maintenance behavior can be designed as a function of the transport time and placing temperatures, so that fresh superplasticized concrete mixtures can be transported from the batching plant to the job site without any slump loss even in summer times; this effect depends on the gradual liberation of special molecular groups which are responsible for the adsorption of these polymers on the surface cement grains; c) a new series of polycarboxylate polymers has been synthesized in which functional chemical groups, acting as shrinkage-reducing admixtures, again are gradually liberated by the superplasticizer polymer as a function of the pH of the aqueous phase related to the cement hydration.

Keywords: adsorption; polycarboxylate; polyether; shrinkage; slump loss; steric hindrance; superplasticizer; water-reduction; zeta potential

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INTRODUCTION

Superplasticizers are unanimously considered to be the most important chemical admixtures for concrete. This is due to the numerous properties of concrete which can be improved by using superplasticizers. When superplasticizers are used without any change in the mixture composition they really act as admixture-enhancing fresh concrete workability. On the other hand, when they are used at given workability and cement content, they can act as high-range water reducers and then they can increase both early and later strength as well as improve durability and water-tightness. These admixtures can also reduce drying shrinkage and thermal stress of concretes when they are used at given workability and water-cement ratio (w/c) because of the higher aggregate/cement ratio.

Moreover, special high-performance concretes can be manufactured by combining superplasticizers with mineral additions such as silica fume (high strength concrete), fly ash (high volume fly ash concrete for mass concrete structures) or granulated ground blast-furnace slag (chloride-resistant concrete).

DEVELOPMENT OF NEW SUPERPLASTICIZERS

During the last three decades [1-2] the main ingredients of the superplasticizers were synthetic water-soluble polymers such as sulfonated melamine formaldehyde (SMF) condensate and sulfonated naphthalene formaldehyde (SNF) condensate. These admixtures are polymers based on a single repeating unit (sulfonated naphthalene or melamine molecule) which do not allow for much variation of the molecular structure. Advances in superplasticizers, containing alternative water soluble synthetic products, have been proposed in the last decade to reduce the slump-loss drawback [3-17]. More recently, these new superplasticizers - all based on the family of polycarboxylate polymers (PC) - have been deeply investigated, and numerous papers on these admixtures have been presented at the CANMET-ACI International Conferences on "Superplasticizers and Other Chemical Admixtures" [18-24]. Polycarboxylate superplasticizers are based on two or more structural groups that provide for more diversity in possible molecular structures with respect to those based on SNF or MSF [25]: for example, by changing the number of carboxylic groups per polyether unit, the adsorption of polymers on the cement surface can be significantly changed; moreover, the molecular weight of polyether molecule can be adequately adjusted to form polymers

with different performance characteristics in terms of reduction in mixing water or retarding effect on the early cement hydration.

DISPERSION MECHANISMS OF CEMENT AGGLOMERATES

Superplasticizers cause dispersion of particles of coarse agglomerates which predominate in the cement paste of the concrete [26]. Due to the dispersion effect, there is a fluidity increase in the cement mixture (Fig. 1). In the past, the dispersion effect was ascribed only to the development of the same electrostatic (negative) charge on the cement particles. The electrostatic attractive forces, existing among cement particles and causing agglomeration, would be neutralized by the adsorption of anionic polymers negatively charged, such as SNF or SMF, for the presence of SO_3^- groups on the surface of cement particles. The dispersion of cement particles (Fig. 2) would be related with the electrical repulsion produced by the negatively charged groups (SO_3^-) on the other side of the main polymer chain [27].

The electrostatic repulsion of cement particles was determined through zeta potential measurements. Additional available experimental results did not confirm this mechanism for the superplasticizing action of the polycarboxylate polymers. These results would indicate that the dispersion of cement particles, responsible for the fluidity increase caused by superplasticizer, is not necessarily related to the electrostatic repulsion associated with zeta potential measurements.

The dispersion mechanism performed by the PC-based superplasticizers (Fig. 3) is related more to a steric hindrance effect produced by the presence of pendant ethylene oxide (EO) side graft chains, rather than to the presence of negatively charged anionic groups (COO^-) which are responsible for the adsorption of the polymers on the surface of cement particles. In other words, the pendant graft chains of the polymer molecules adsorbed on the surface of cement would hinder by themselves from flocculating into large and irregular agglomerates of cement particles (Fig. 3).

SLUMP RETENTION

Slump loss appears to be the most serious problem at least for ready mixed concrete industries. When a concrete mixture must be transported for a long time, particularly in hot weather, it should keep as far as possible at its initial slump level to avoid the practice of redosing the concrete with water above and beyond that required in the mixture proportion. Results of investigations of retempered concrete indicate that many of the properties of the hardened concrete (strength, durability, abrasion resistance, etc.) are significantly affected, since retempered concrete does not perform as well as concrete which has not been retempered [28]. However, slump loss is un-avoidable because of the intrinsic requirement for concrete mixtures which should set and harden in a relatively short time. Therefore, a right and proper compromise would be a zero-slump-loss concrete mixture for about 1 hour. By using superplasticizers based on SNF or SMF polymers it is not easy to achieve this target, because in general slump loss is higher in superplasticized concrete with respect to the corresponding plain mix at given initial

slump (Fig. 4). The lower the w/c, the higher is the slump loss for the same initial slump level. It seems that the lower w/c in superplasticized concrete and the consequent smaller distance among cement particles (Fig. 5) cause a more significant slump loss when the same amount of water is lost through evaporation or by reaction with cement during the transportation time.

Several methods have been adopted to control the rate of slump loss. One method is to add the superplasticizer at the point of discharge but there are some practical problems associated with this approach. For instance, the concrete into the truck-mixer before the superplasticizer addition would be too stiff when a high-quality concrete, (with low w/c), should be produced. Moreover, dosing the superplasticizer at the work site is too time consuming and does not allow an accurate control of the final slump and admixture dosage.

Other methods to control slump loss include adding a higher than normal dosage of superplasticizer or using some type of retarding admixture in the formulation. However, there are some limits in this approach, because sometimes the final effect is to produce concrete with un-acceptable low early strength or, surprisingly, to aggravate more seriously slump loss. For instance, slump loss accompanied by a surprisingly quick set may sometimes occur by using retarders such as sugar, sucrose, corn syrup or calcium lignosulfonate [29]. The cement content, as well as the chemical and mineralogical composition of cement, play an important role in determining such a singular slump loss although the detailed mechanism is not clear: it seems that the content of C_3A , gypsum and alkali, as well as the form of calcium sulfate used as set regulator, can affect the rate of slump-loss.

Also redosing the superplasticizer at different intervals of time has been suggested [30] to reduce slump-loss, but this method appears to be not always easy to be adopted in practice. Moreover, the total dosage of superplasticizer, as well as the relative cost, cannot be kept under control according to a given plan.

Therefore a superplasticizer is required which by itself is capable to maintain the slump for a long period of time independently of the temperature or the type and content of cement. Collepari et al. [13] studied the effects of a PC-based superplasticizer on the properties of ready-mixed concrete mixtures. This admixture acts as both an immediate superplasticizer and a slump loss reducing agent, and appears to be more effective than that based on SNF. Although the PC-based superplasticizer has been used at a lower content of active polymer (0.30% versus 0.40%), it was more effective than that based on SNF for the water reducing capability (w/c = 0.43 versus 0.47) as well as for the maintainance of the initial slump level (Fig. 6).

Tanaka et al. [17] studied the effect of a CLAP-based superplasticizer (Cross Linked Acrylic Polymer) on the slump-loss of concrete mixtures. This superplasticizer is a partially cross-linked copolymer of acrylic acid and polyethylene glycol mono-alkyl ether (Fig. 7). According to Tanaka and co-workers the cross-linked polymer is hydrolyzed by the alkaline water phase of the cement paste and then converted into a PC-based polymer (Fig. 8). The negative carboxylic groups due to the alkaline hydrolysis would be adsorbed on cement surface of cement particles and then would be responsible for the dispersion of cement particles and the fluidizing action of the admixture. The low slump-loss effect of this superplasticizer should be related with increasing number of the protruding side

chains of the acrylic polymer which would prolong the dispersion of hydrated cement particles through a steric hindrance effect.

Hamada et al. [22] developed a new family of acrylic polymers based on the following changes with respect to the traditional PC-based superplasticizer:

- a new superplasticizer, called PE because of the much longer side chains of ethylene oxide (EO): 130 moles of EO instead of 10-25 moles as in traditional PC-based superplasticizer (Fig. 9); this change, combined with a lower number of carboxylic groups (COO^-), produces a lower adsorption speed and reduces the typical retarding effect related to the early adsorption;
- a modified PE-based superplasticizer where a great number of carboxylic groups are replaced by a slump-loss controlling agent (SLCA) to achieve a still higher slump retention with minimal setting retardation: indeed, due to the relatively low number of carboxylic groups in SLCA (Fig. 10) the initial adsorption and the dispersing effect are negligible as well as the setting retardation; however, subsequently due to the hydrolytic effect related with the OH^- presence in the aqueous phase of the cement paste, the number of carboxylic units increases (Fig. 11) and the slump can still increase by prolonging the mixing time due to the increasing adsorption of the polymer on the surface of the cement particles.

The behavior of fresh concrete in the presence of PC and SLCA-based superplasticizers is schematically shown in Fig. 12.

Figure 13 schematically shows the heat of cement hydration and Figure 14 shows the concrete hardening in the absence and in the presence of PC or PE acrylic superplasticizers.

Sugiyama et al. [32] synthesized a new series of superplasticizers in which functional groups called EPBE acting as shrinkage reducing agent (SRA), capable of reducing surface tension, were attached to the structure of various polycarboxylate polymers (Fig. 15). Figure 16 shows the drying shrinkage behavior of concretes with PC-based superplasticizer or modified EPBE-PC-based admixture: the drying shrinkage of the latter is lower than that of the former.

Nakanishi et al. [24] invented another multi-function and multi-purpose admixture incorporating a shrinkage reducing group (based on diethylene glycol monobutyl ether) acting as SRA on the PC chain acting as a water reducing agent.

CONCLUSIONS

Superplasticizers are able to enhance the placing characteristics of concrete mixtures by increasing the workability level at a given w/c. Therefore they allow to make easy placement of concrete mixtures even with low w/c as required by strength or durability reasons.

The main drawback of superplasticized concrete mixtures with sulphonated polymer-based admixtures is the slump-loss. This can reduce the advantage of using these superplasticizers particularly in hot weather, with long transportation times and reactive cements.

A new family of superplasticizers based on acrylic polymers is available with improved placing characteristics: a) flowing concretes can be produced at lower w/c with

respect to concrete mixtures containing sulphonated superplasticizers; b) the slump-loss is much more reduced with respect to concrete mixes with sulphonated superplasticizers; c) multi-purpose superplasticizers with shrinkage reducing properties have been invented by incorporating special functional groups on the PC chain.

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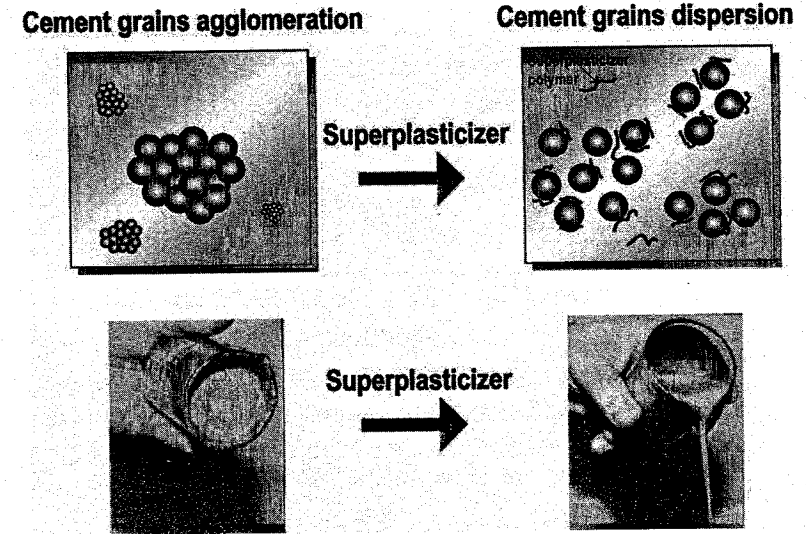


Fig. 1 – Relationship between cement grains dispersion and fluidifying effect on the cement.

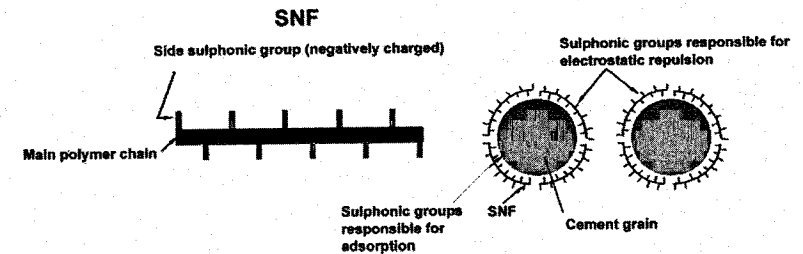


Fig. 2 – Schematic picture of sulfonated polymer (SNF) and its electrostatic repulsion effect on the dispersion of cement particles.

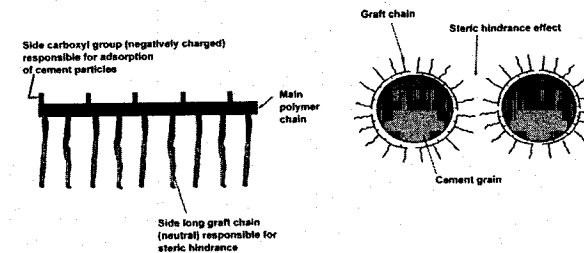


Fig. 3 – Schematic picture of the polycarboxylate (PC) superplasticizer and its steric hindrance effect on the dispersion of cement particles.

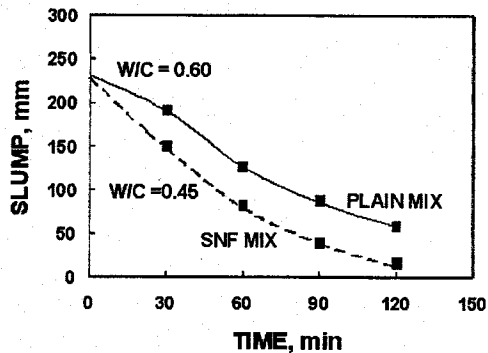


Fig. 4 – Slump loss at 20 °C for plain and superplasticized mixes at the same initial slump. Superplasticizer: 0.4% as dry SNF polymer by weight of cement.

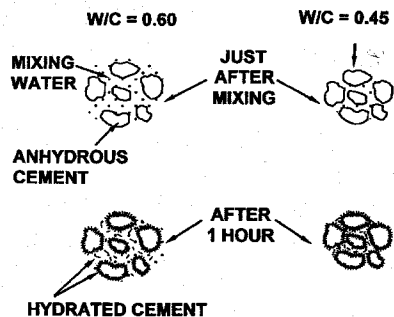


Fig. 5 – Schematic picture of cement paste in a plain ($w/c = 0.60$) and superplasticized concrete ($w/c = 0.45$).

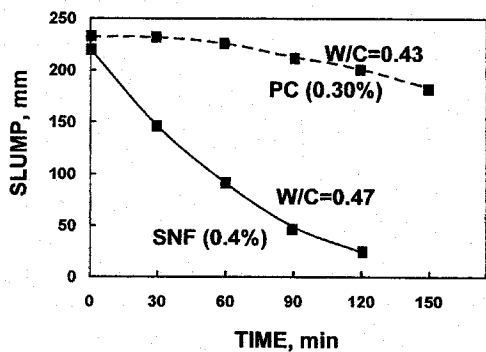


Fig. 6 – Slump loss of superplasticized concretes at 20 °C with PC or SNF polymer based admixtures [13]. Percentages on the curves refer to dry polymer.

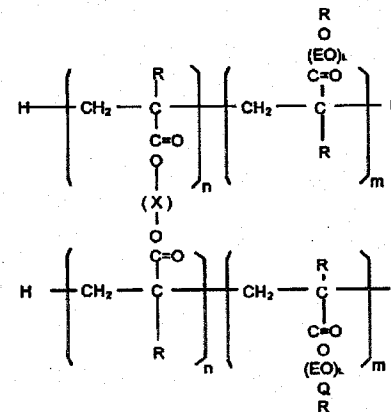


Fig. 7 – Chemical Structure of CLAP (cross-linked acrylic polymers). X is the cross linking group.

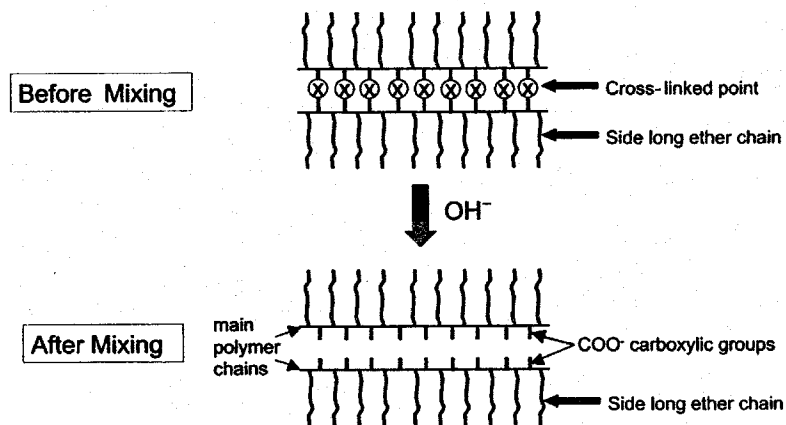


Fig. 8 – CLAP-based superplasticizer hydrolyzed by the alkaline water of cement paste: the number of COO⁻ progressively increases with time and this is responsible for the low slump loss.

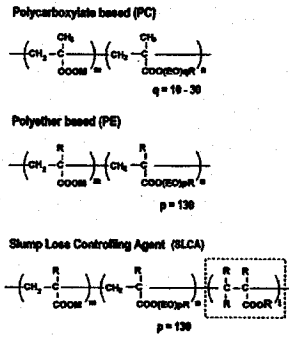


Fig. 9 – The chemical structure of polycarboxylate type (PC), polyether type (PE), and slump-loss-controlling agent superplasticizer (SLCA); q and p are the number of moles of EO in PC and PE or SLCA polymers [22].

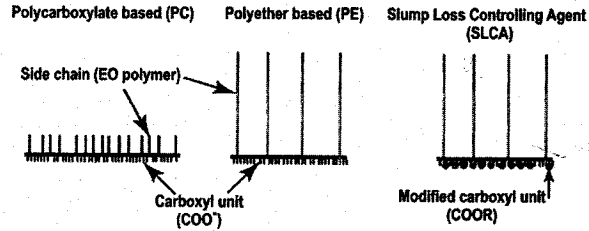


Fig. 10 – The schematic molecular structure of polycarboxylate type (PC), polyether type (PE) and slump-loss-controlling agent superplasticizer (SLCA) (adapted from Reference 22).

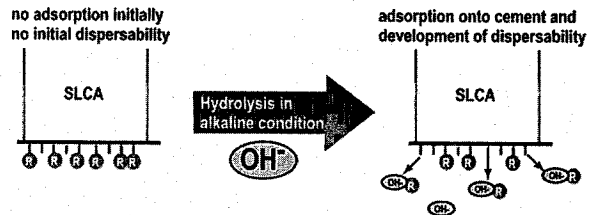


Fig. 11 – The mechanism and the hydrolysis reaction of SLCA in alkaline condition of cement paste (adapted from Reference 22).

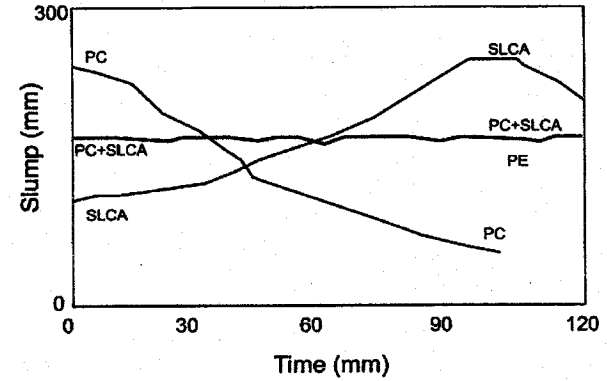


Fig. 12 – Schematic trend in the slump loss behavior with different acrylic superplasticizers (PC, PE, SLCA, PE+SLCA) in concrete mixtures with CEM II A/L 32.5R (340 kg/m^3), $w/c = 0.45$.

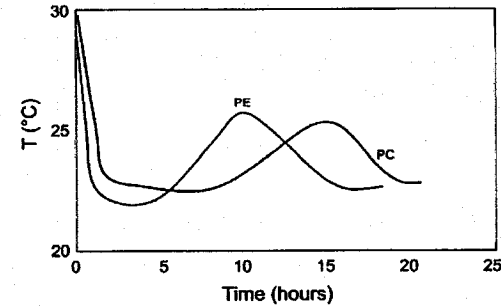


Fig. 13 – Heat development in portland cement pastes with PE or PC polymers.

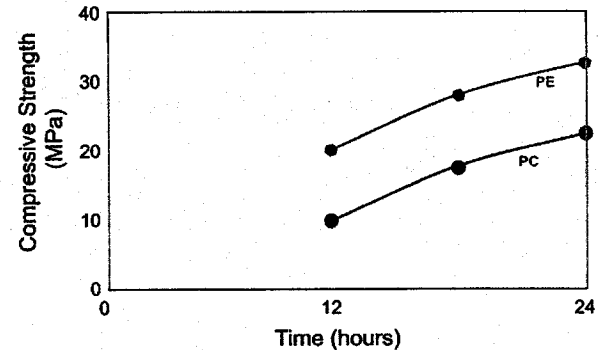


Fig. 14 – Compressive strength development of concrete with PE or PC.

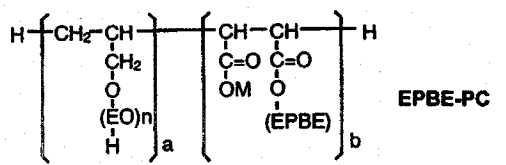
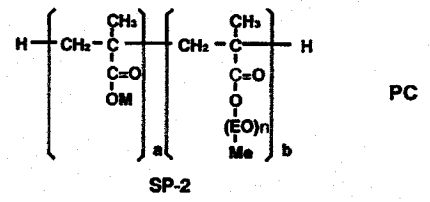


Fig. 15 – Chemical structures of PC and EPBE-PC [32].

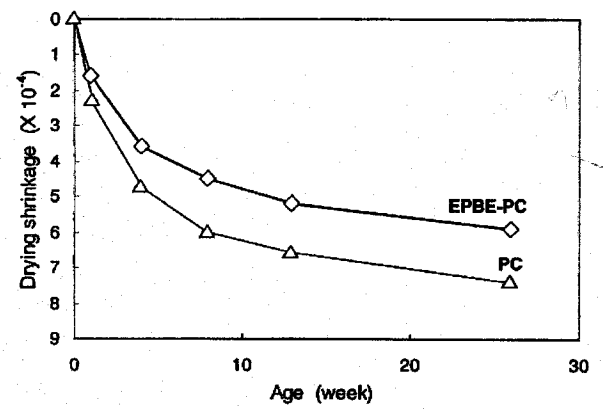


Fig. 16 – Shrinkage of concretes with PC-based superplasticizer or modified PC-based superplasticizer by EPBE groups [32].