New Trends in the Development of High-Range Water-Reducing Admixtures

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Chemical admixtures, in addition to cement, sand, gravel and water, are a primary component of concrete. High-range water reducers, also known as superplasticizers, are one of the most important chemical admixtures. The different kinds of superplasticizers possess specific advantages, but also drawbacks. Therefore, new chemical structures for advanced superplasticizers need to be tried. This paper presents new trends in the development of superplasticizers.

Key words: superplasticizer, admixtures, cement, hyperbranched polymers

Introduction

Concrete is a composite material in which aggregate grains (gravel and sand) are bound by hydrated cement paste. The amount of water required for the reaction of hydration represents about 25% of the mass of cement. However, in order to obtain flowing concrete mix, which can be either cast or pumped, much more water is required (about double). In the long term, this excess water evaporates, leaving voids in the concrete. The associated porosity decreases both the mechanical strength and durability. Such concrete does not reach the optimum properties it could have if it was produced as a more compact material [1]. This is why water reducing admixtures are of interest.

The curve of concrete development (Fig. 1) shows that progress in concrete technology, driven by the decreasing of the water-binder ratio, would have not been possible without the impressive achievements in improving the efficiency of plasticizing admixtures for concrete mixes [2].

Dispersing admixtures fall into two groups which, for standards purposes [3], are divided by their water-reducing ability. There are the water reducing admixtures (plasticizers) and the high range water reducers (superplasticizers). Standard [3] stipulates that the water reduction must be greater than 5%. A water reduction more than 12% can be obtained through the use of superplasticizers.

Superplasticizers can be used for three different purposes, namely to increase workability without changing the mixture composition, to reduce the amount of mixing water in order to reduce the water-to-cement ratio and then to increase strength and/or improve durability, and to reduce both water and cement in order to reduce cost in addition to reducing creep, shrinkage and thermal strains caused by heat of cement hydration.

High range water reducers are polymeric dispersants, which are added in small amounts to concrete (typically less than 0.5% of the mass of cement). In the 1980s, polycarboxylate superplasticizers (PC) were introduced as a new generation of concrete admixtures. Generally, PC are composed of lateral polyethylene oxide (PEO) side chains grafted onto an anionic polymer backbone (Fig. 2). Polycarboxylate superplasticizers are effective at lower dosages, and specific molecular structures provide excellent slump retention. Polycarboxylate-type superplasticizers are very efficient in the formulation of high performance concrete due to their excellent water reducing capacity. Although PC have more advantages than traditional superplasticizers,

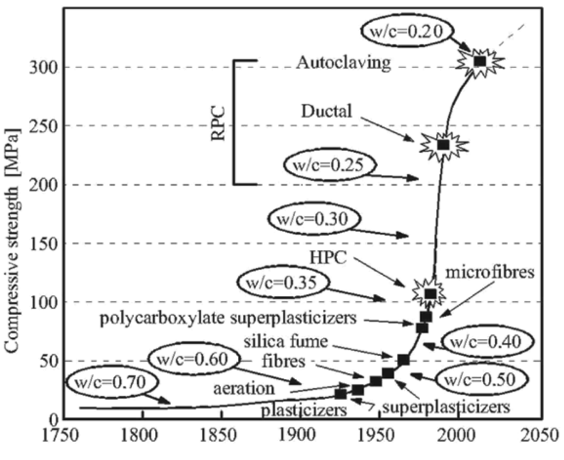

Fig. 1. Generalized curve of concrete development [2]

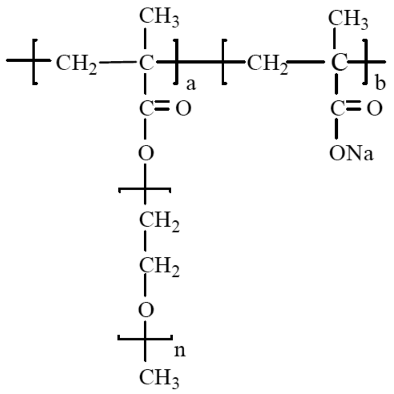

Fig. 2: Chemical structure of polycarboxylate-based (PC) superplasticizer [6]

they also have some limitations, such as increasing of tendency of the concrete mix to bleed and segregate and being sensitive to muddy aggregate. Moreover, PC cause excessive foaming which needs to be controlled by the addition of defoamers. It is thus hard to control or to predict the concrete workability with these particular superplasticizers [4, 5].

The molecular structure of PC have a close relationship with their performance in cement system. In the field of water-reducing admixtures, the research and development of newer polymers is being undertaken utilizing tailored superplasticizers. At present, several research groups are investigating the chemical compounds as potential new superplasticizers.

Potential new superplasticizers

The research by Lei and Plank [4] presented a novel type of superplasticizer – a high molecular weight ($M_W \approx 220\,000$ g/mol) polycondensate from cyclohexanone, formaldehyde and sulfite (CFS) (Fig. 3). Advantages of this cycloaliphatic superplasticizer are simple preparation method, effectiveness at low water-to-cement ratio, huge water reducing capability and stable performance in the presence of clay.

New melamine superplasticizer can be synthesized by the reaction among melamine, formaldehyde, and sulfonated glucose (Fig. 4). According to Wang et al. [7] this type of superplasticizers have the potential to be used as a kind of high performance water-reducing admixture in concrete.

Modification of biopolymers is one of the new trends in the development of high-range water-reducing admixtures. Casein, the principal protein found in bovine milk, is anionic polyelectrolyte. The anionic phosphate groups present in casein can easily chelate calcium ions on the adsorbed surface of cement. This way, adsorption of casein superplasticizer on cement is improved, and hence its dispersing effect is achieved [8,9]. Chitosan is a polysaccharide which is made by treating shrimp and other crustacean shells with the alkali sodium hydroxide. A sulfonated chitosan superplasticizer (SCS) has many advantages and may replace PC. The characteristic of SCS is that it allows for better maintenance for cement paste fluidity and concrete slump. SCS macromolecules adsorb on cement particle surface by interaction between various functional groups in the ring of SCS (Fig. 5). This study demonstrates that a high-performance superplasticizer may be synthesized using a renewable natural polymer and simple synthesis methods, which will be a trend for the future [10,11].

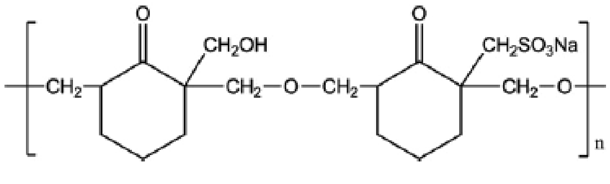

Fig. 3: Example of molecular structure of CFS [4]

β-cyclodextrin is a 7-membered sugar ring molecule with a hydrophobic cavity and a hydrophilic wall (Fig. 6). Lv et al. [12,13] prepared a poly-carboxymethyl-β-cyclodextrin (PCM-β-CD) superplasticizer (Fig. 7) and β-cyclodextrin-modified polycarboxylate (MPC). The PCM-β-CD superplasticizer showed retardation of fluidity loss and setting time for cement paste and concrete depending on its dosage. The dispersion and retarding performance of MPC was closely related to the number of β-CD side chains. An increase in the number of β-CD side chains led to increases in the initial fluidity and prolonged the setting times of the cement pastes, whereas excessive numbers of β-CD side chains led to serious retardation.

A new class of organosilane-modified polycarboxylate superplasticizers has been studied by Fan et al. [14] (Fig. 8). A partial substitution of carboxyl groups by trialkoxysilane in the polymer makes them more resistant to sulfate ions.

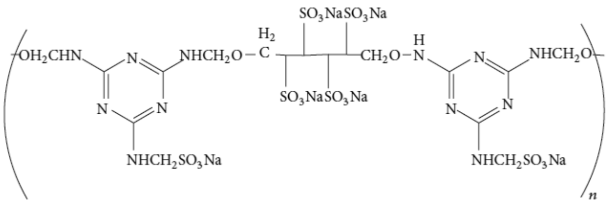

Fig. 4. Example of melamine superplasticizer [7]

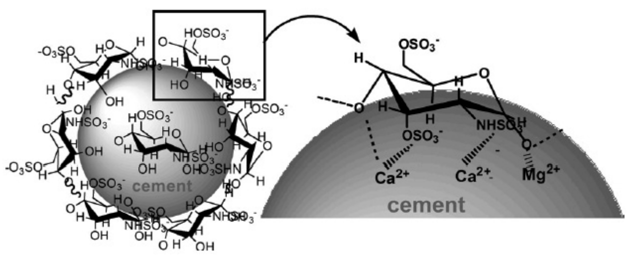

Fig. 5: Schematic diagram of adsorption mechanism of SCS on cement particles surface [10]

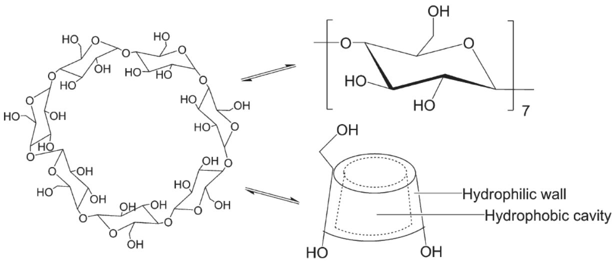

Fig. 6: Molecular structure of β-cyclodextrin [13]

Another example of modification of polycarboxylate is synthesis a 2-acrylamide-2-methyl propylene sodium sulfonic (AMPS)-modified polyacrylic acid superplasticizer [15].

Hamada et al. [16] predicts that the future of high range water reducers belongs to New Hyper-Branched Polymers (NHBP). Hyperbranched polymers represent a new class of polymeric compounds. Because of their unique features such as high solubility, low viscosity, high concentration of reactive groups they find many applications in material sciences.

Summary

Because superplasticizers are one of the most important ingredients used in concrete, the research and development of new superplasticizer are still drawing much attention. Chemical admixtures are necessary for adding new functions to concrete. The mechanism of interaction between superplasticizer molecules and the major mineral components in cement suspensions depending on the chemical nature of admixture. With polycarboxylate-based superplasticizers many types of polymers can be synthesized.

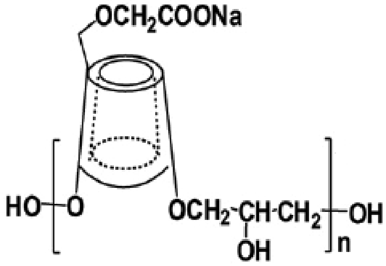

Fig. 7. Poly-carboxymethyl-β-cyclodextrin [12]

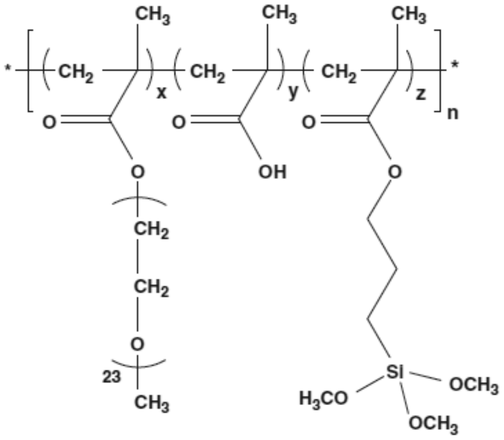

Fig. 8. Example of organosilane-modified polycarboxylate superplasticizer [14]

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