The New Variety of Polycarboxylate Dispersants

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Polycarboxylate admixtures (PCs) were introduced in Japan in the early 1980s.Since then they have come a long way through their molecular design in polymer technology for tailor made market oriented applications for different conditions and then engineered molecules to achieve that result.

ASTM covers the use of chemical admixtures for the production of flowing concrete in ASTM C 1017. In this standard, the focus is on treating a concrete mixture with a chemical admixture for the express purpose of producing high-slump concrete while not reducing any of the mix water. In most cases admixtures classified as C 494 Type F or G also would be used in the manner prescribed by ASTM C 1017. These high-range water-reducing admixtures do more than simply reduce water; they disperse cement particles. This dispersive action then allows one to either reduce water, to generate higher slump, or both. Therefore, more flexibility and value is available than the name implies.

Polycarboxylate dispersants

Significant advances in dispersant chemistry have been made in the last decade. This includes the introduction and use of polycarboxylate dispersants across all segments of the concrete industry. Prior to that, most dispersant chemistries had limitations with respect to making modifications to the molecule. However, the introduction of polycarboxylate dispersants has paved the way for developing molecules that will influence performance in specific and tailored ways. This is a tremendous technological advancement for the concrete industry as this enables the use of molecules developed for the sole purpose of dispersing Portland cement, whereas previous dispersants were mainly byproducts of other industries.

Dealing with molecules designed for concrete applications has real advantages for concrete producers. Considering the architecture of a polycarboxlyate molecule allows one to better understand why there is so much promise and flexibility in their application to the concrete industry. First, polycarboxylates are classified as being comb polymers (Figure 1).The name itself implies much about the structure of these molecules in that they are characterized as consisting of a backbone having pendant side chains, much like the teeth of a comb. For these molecules to be effective as dispersants, they must be attracted to the surface of a cement particle. The backbone of the polycarboxylate molecules typically serves two functions: as the location of binding sites (to the surface of the cement particle) and to provide anchoring sites for the side chains of the molecule. The pendant side chains serve as a steric, or physical, impediment to reagglomeration of the dispersed cement grains.

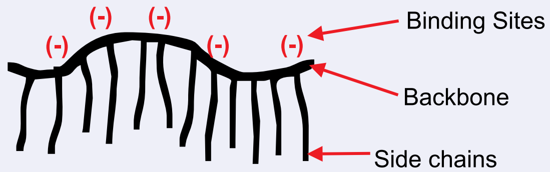

Figure 1 : Comb like molecular structure of PC

Due to the nature of the processes used to manufacture early synthetic dispersants, a chemist's ability to manipulate their structure was limited. Typically, the structures obtained were complex and the processes were relatively difficult to control from a molecular design point of view.

However, the nature of the chemistry that leads to polycarboxylates is rich with possibilities. It allows a chemist to design a dispersant that is an excellent water reducer versus a dispersant that may maintain high levels of workability over longer periods of time. However, the powerfully flexible chemistry behind polycarboxylates is helpful only if one truly understands the nuances of the other materials in the concrete mixture. Ultimately, differences seen in concrete behavior often can be traced back to mineralogical differences in the cements and aggregates. This opens up the door for chemists to optimize a dispersant's performance based on the predominant mineralogies found in a given material. The design of these next generation dispersants may be based on careful and intelligent manipulation of any of the design parameters for polycarboxylates, or through customized formulations, or both. One thing is for certain–game changing performance is often the result. The various properties of PCs which play an important role in concrete are discussed below.

Rheology

PCs is an anionic surfactant, when adsorbed on cement particles becomes negatively charged causing a repulsive effect with each other, consequently its fluidity increases; in addition, the side chains preserve water molecules in contact via hydrogen bonding creating osmotic pressure which increases the movement of these cement particles. PCs improve the fluidity of cement pastes by the dispersion of cement particles. The adsorption of PCs superplasticizer molecules on the cement particles hinders their flocculation as a result of the electrostatic repulsion forces and/or through steric hindrance. Consequently, the particles are homogenously distributed in the aqueous solution, minimizing the amount of water needed for then to be dispersed, which leads to the higher fluidity and workability of cement pastes.

Initial setting time

Figure 2 shows the effect of PCs on initial setting time of cement pastes. PCs forms a complex with Ca^{2+} ions liberated on the surface of C-S-H gel or Ca $(OH)_2$ crystals; the interweaved net structure consists of ion bonded large molecular system bridged by means of Ca $(OH)_2$. In the presence of PCs, it appears that only a few number of Ca^{2+} ions go into the solution and do not becomes supersaturated with respect to Ca $(OH)_2$, i.e. PCs inhibits the growth of hydrates, leading to retard of the setting. Initial setting time of OPC paste extended as the dosage of PCs increases. Adding silica fume with the paste setting time increases upto 40% as PCs content increases up to 0.75%. Also setting times decrease by 5% at higher dosages of PCs.

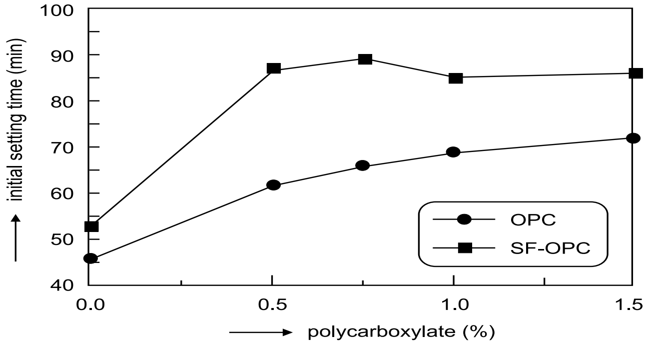

Figure 2 : Effect of PC on initial setting time

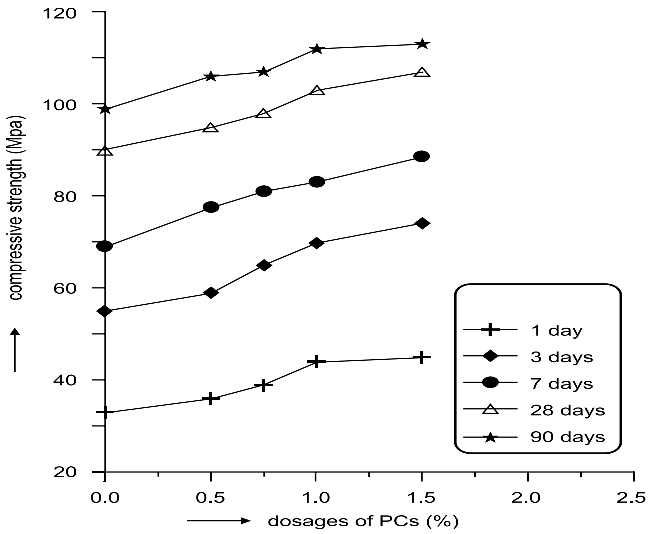

Figure 3 : Compressive Strength of OPC cement paste

Porosity and Compressive strength

The increase of the dosages of PCs causes reduction of total porosity. As the porosity decreases, the compressive strength increases and electrical conductivity decreases. The compressive strength of all cement pastes increases with curing time. As the dosages of PCs increases upto a maximum of 1.5%, the compressive strength of all samples increases but an over dosages beyond 1.5% causes a reduction of strength (figure 3). This is mainly due to decrease of the total porosity that affects positively the compressive strength of the cement pastes.

Effect on self-compactability

The effect of PC-based SPs on self-compactability of concrete mixtures depends on dosages of PC and water/powder (W/P) ratios. A dosage of 0.8% to 1.5% along with a mix proportion is sufficient to pass the flow tests by U-flow, slum-flow and funnel tests. The various formulaes available can be used to establish a rational method for adjusting the water-powder ratio and superplasticizer dosages to achieve appropriate deformability and viscosity which are known as the index for the dispersing effect by superplasticizer.

The requirements for super plasticizer in self-compacting concrete are given below

- High dispersing effect of low water/powder (cement) ratio : less than approx. 100% by volume
- Maintenance of the dispersing effect for at least two hours after the mixing
- Less sensitivity to temperature changes

There have been many examples of the development of new type of superplasticizer for self-compacting concrete. Characterization of the dispersing effect of superplasticizer independent of the effect of water flow is indispensable for self-compacting concrete.

Figure: 4 Use of PCs in self-compacting concrete in Delhi Metro

The next generation

The latest generation of polycarboxylate admixtures is based on this cutting-edge molecular design and synthesis. One can now take into consideration a significant number of factors and create a dispersant molecule that is custom designed for that scenario. As has been previously mentioned, the concept of these polycarboxylate dispersants being labeled simply as "water reducers" is somewhat outdated. Polycarboxylates do reduce water; however, additional performance characteristics that benefit the concrete construction process also are possible via molecular design. These additional benefits include previously unreachable levels of slump retention, which can result in significant material and production efficiencies for the concrete producer and the contractor. Figure 5 shows the slump retention comparison between three polycarboxylates tailor made for specific applications.

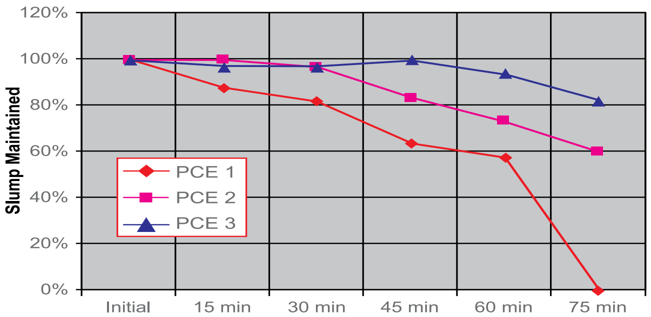

Figure 5 : Slump retention comparisons of three different types of PCs

Impressive levels of high early compressive strength also can be achieved, which will impact production efficiencies for contractors, as well as precast concrete producers. Some of these new molecules provide combinations of the previously mentioned characteristics resulting in never before seen concrete performance. For example, a molecule has been developed that will provide slump retention for 45 to 60 minutes while still providing high early strength. Historically, some level of retardation was required to provide slump retention to high early strength concrete mixtures, however, too much retardation would negatively impact the early compressive strength. Because of this need to balance retardation and strength gain, a compromise twas required that would not allow one to capture the full benefits of both slump retention and early compressive strength.

Figures 6 and 7 compare a first generation high early strength polycarboxylate molecule coupled with a retarder (for slump retention) versus a next generation polycarboxylate designed specifically for slump retention and high early strength without a retarder. The figures show slump retention, rate of hardening, and 14-hour compressive strength respectively.

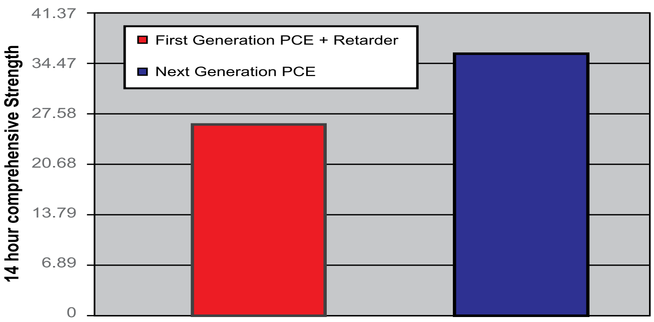

Figure 6 : Compressive Strength (MPa) of two different types of PCs after 14 hour.

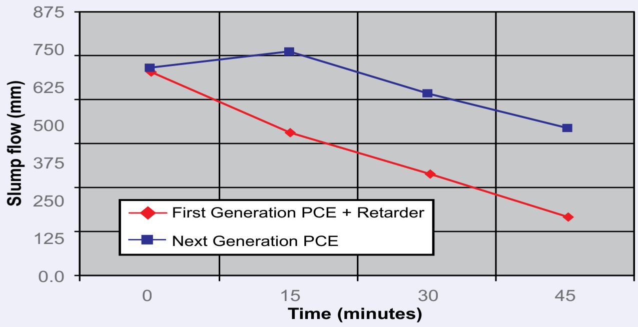

Figure 7 : Slump Flow vs. Time of two different types of PC

These new performance combinations provide significantly greater value to the concrete producer and contractor than previous dispersants. In considering the concrete performance, one must take the next step and relate that to actual value for the industry. Performance characteristics, such as slump retention, can provide the following benefits:

- Eliminate or reduce retempering at the jobsite allowing for more consistent and efficient concrete placement
- Improved surface aesthetics due to consistent workability resulting in a reduction in surface patching
- Overall more consistent and higher quality concrete

The sensible lower cement contents and a consequent reduction in the risk of thermal cracking and higher concrete consistency as standard at lower cost are other benefits to the end-user. PCs are compatible with air entrainment in concrete, and have no adverse impact on freezing and thawing durability and also compatible with other mineral admixtures such as GGBS and Silica Fume.

These well engineered mixtures are being used in a variety of concrete applications and the new polycarboxylates have become an important component in these mixtures. Additionally, several large precast concrete producers have begun using the high early strength/slump retaining polycarboxylates to facilitate the placement of high-performing SCC mixtures. This results in more consistent concrete production as well as further improvements to the surface finish of the elements cast with concrete.

This next generation of polycarboxylate superplasticizers is being recognized as more than just a high-range water-reducing admixture. They are being recognized as "performance admixtures." The incredible feat of this technology is to allow concrete producers to find new ways of producing concrete as well as creating concrete mixtures with new levels of performance. This is perfect timing for an industry moving towards performance-based concrete. One thing is for sure—this is just the beginning.

Comparing the properties of superplasticizers in terms of dosage and effectiveness, -OH terminated poly (ethylene glycol) methacrylate macro monomers offer an attractive alternative to –OMe terminated methacrylates. However, by using appropriate polymerization technique, superplasticizers of high quality can be synthesized.