STUDY OF THE SYNTHESIS OF POLYCARBOXYLATE PLASTICIZERS USED TO OBTAIN CONCRETE PRODUCTS AND FACTORS AFFECTING THE SYNTHESIS PROCESSES

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The modern construction industry makes higher demands on building materials every year. In pursuit of new progressive technologies available to society, the concrete we are used to is also changing. Today, the delivery of ready-mixed concrete to a customer can take more than four hours, while the concrete does not lose its physical and mechanical characteristics. House-building factories are able to produce a sufficient amount of reinforced concrete products for the construction of a seventeen-story building in three months.

Superplasticizers are the most important admixtures enhancing concrete performance. The development of new superplasticizers during the last decades has determined the most important progress in the field of concrete structures in terms of higher strength, longer durability, lower shrinkage and safer placement particularly in elements with very congested reinforcement [1].

In Finland, elevated air contents have been reported in air entrained concrete. The highest air contents determined from samples drilled from structures have exceeded 15% and significant deficiencies in compressive strength of the concrete have been reported. Some indications of elevated air contents have been seen during the last years, for example the railroad bridge in Kemijärvi [2] and the Turku University Hospital [3]. Concrete composition and consistency have been noticed to affect the air entrainment [4]. In addition, one critical factor could be the use of combination of air entraining agent (AEA) and the third generation polycarboxylate ether (PCE)- based superplasticizers admixtures.

1H spin-lattice relaxometry (T1, longitudinal) of cement pastes with 0 to 0.18 wt % polycarboxylate superplasticizers (PCEs) at intervals of 0.06 wt % from 10 min to 1210 min was investigated. Results showed that the main peak in T1 relaxometry of cement pastes was shorter and lower along with the hydration times. PCEs delayed and lowered this main peak in T1 relaxometry of cement pastes at 10 min, 605 min and 1210 min, which was highly correlated to its dosages. In contrast, PCEs increased the total signal intensity of T1 of cement pastes at these three times, which still correlated to its dosages. Both changes of the main peak in T1 relaxometry and the total signal intensity of T1 revealed interferences on evaporable water during cement hydration by dispersion mechanisms of PCEs. The time-dependent evolution of weighted average T1 of cement pastes with different PCEs between 10 min and 1210 min was found regular to the four-stage hydration mechanism of tricalcium silicate (Fig-1) [5].

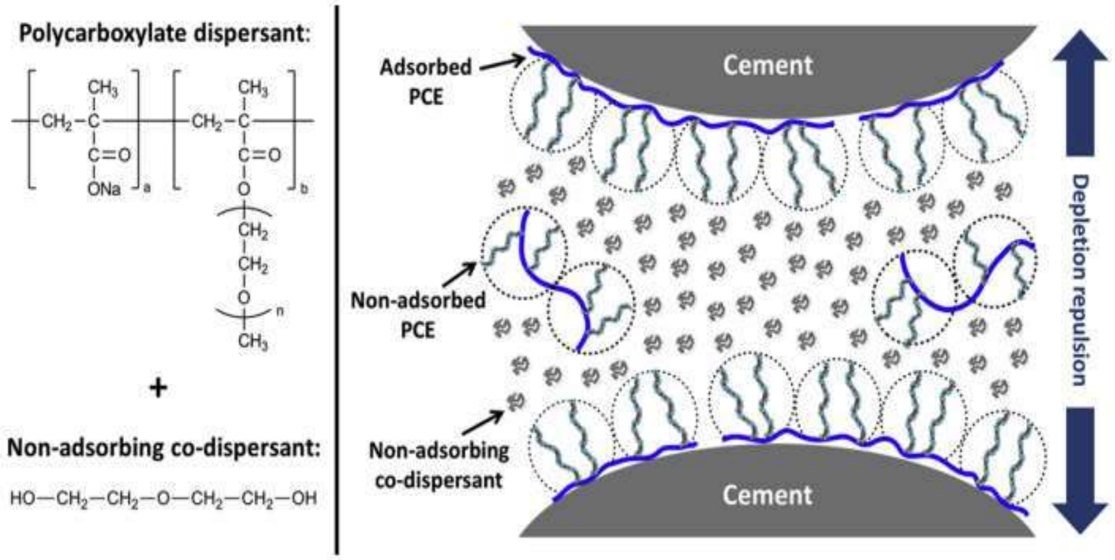

Fig 1. Four-stage mechanism of hydration of tricalcium silicate.

The dispersing ability of polycarboxylate superplasticizers (PCEs) can be ascribed to the electrostatic and steric stabilization of cement suspensions. For this purpose, PCEs need to adsorb on the cement particle surface to become effctive at all. In this study, it is demonstrated that at low water to cement ratios ≤ 0.30, even nonionic molecules like diethylene glycol or 2-methyl-2,4-pentanediol which do not adsorb on cement, but remain dissolved in the interstitial pore solution, can greatly enhance cement dispersion when combined with PCEs such as conventional methacrylate ester based comb copolymers. Their effct as codispersant is particularly pronounced for PCEs possessing a low side chain density and long side chain length. Relative to the co-dispersants it was found that especially non-polar small molecules like neopentyl glycol greatly enhance the paste flidity. These molecules signifiantly reduce the surface tension of the pore solution and thus increase the wettability of cement. Based on results from spread flw tests, adsorption measurements and pendant drop tensiometry it is concluded that in cementitious systems formulated at low w/c ratios, non-adsorbing molecules with a molecular weight of ≤ 1000 g/mol induce repulsive depletion forces which prevent cement particles from agglomeration. This way, such small molecules act as auxiliary or co-dispersant when combined with PCEs [6].

The prerequisite to synthesize PCE was to prepare new macromonomers with controlled molecular mass, adjustable hydrophiliclipophilic groups, long-chain alkyl groups, and large terminal hydroxyl groups as well. Structural modifications in the molecular scale of polycarboxylate superplasticizer (PCE) would lead to changes in properties of dispersion and water retention as well as enhancement in the compatibility of Portland cement and so on. This paper reviewed recent developments from synthetic methods of macromonomers as the initial step of production of PCE, PCE at room and elevated temperatures, and relationships between structure and properties of PCE. Through the analysis of references, it was found that PCE synthesized at room temperature had the same performance with PCE synthesized at elevated temperature in terms of conversion rate and initial dispersion in cement but broader molecular weight distribution. Conclusively, the dispersion of PCE in cement might be explained by multiple theories rather than a single one based on development trends as discussed in this paper [7].

Certain types of the new generation superplasticizers (SP) cause the rise of excessive air content in self compacting concrete (SCC). The influence of different type of SP on air-content in cement paste and fresh SCC are tested in the paper. The qualitative methods (foam ability and stability index), which serves the best choice of SP not showing the side-effect in the form of an excessive SCC air-entrainment are presented. The surface tension of SP solutions is also analyzed. The results of tests show that we can predict the influence of SP on air-content of SCC by measuring the surface tension of SP solution, foam ability and stability index of cement paste [8].

After analyzing the above evidence, we can say that the plasticizers used to produce concrete products in the construction industry are of great importance, at the same time, specific requirements are imposed on them. The zeta potential indicator is important in the synthesis of plasticizers and their use. Polycarboxylate plasticizers exhibit polyelectrolytic properties in water and create an electrostatic barrier on cement particles. As a result, the mutual attraction of particles decreases and the fluidity of the cement paste increases, which is realized due to the zeta potential of the polyelectrolyte and the lyophilic and hydrophilic groups of the plasticizer.

In the synthesis of polycarboxylate plasticizers, the ratio of initial monomers and the amount of initiator are of great importance. With an increase in the amount of acrylic monomer during the synthesis, gelation of the removable plasticizer in water will occur, which will lead to an increase in water demand in the preparation of the cement mixture. An increase in the molecular weight of the polycarboxylate macromolecule reduces the solubility of the plasticizer in water and reduces the plasticizing properties.

In the synthesis of plasticizers, temperature and reaction time are important factors. This causes an increase in the reaction temperature and an expansion of the molecular distribution curve. As a result, polycarboxylate molecules of various molecular weights are formed. Different molecular weights reduce the plasticizing properties of the resulting plasticizer. The rapid implementation of the reaction leads to the formation of a network structure of the molecule and, as a result, reduces the solubility of the resulting plasticizer in water.

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