INFLUENCE OF POLYCARBOXYLATE-BASED SUPERPLASTICIZER ON THE MICROSTRUCTURE OF CONCRETE

Changwen Miao, Qian Tian, Qianping Ran, Jiaping Liu

Jiangsu Academy of Building Science Co., Ltd, Nanjing, China

Abstract

This paper elaborates the mechanism of polycarboxylate-based superplasticizer on cement concrete and, in particular, describes the effect of this type of admixture on pore structure and interface state of cement based materials. Experimental results demonstrate that the effect of polycarboxylate-based superplasticizer on concrete microstructure is largely influenced by its molecular structure, graft group and graft quality. Using the polycarboxylate-based superplasticizer with superior performance can effectively optimize the pore structure of cement concrete.

1. INTRODUCTION

It is commonly recognized that admixture has become the necessary important component for high performance concrete. The new generation of polycarboxylic admixture emerges as the times require with the development of the concrete technology. However, due to the variation of their molecular structure, grafting group and the grafting quality, the effect of this kind of admixtures on the microstructure and macro properties of concrete could have large difference.

2. ACTION MECHANISM OF POLYCARBOXYLATE-BASED SUPERPLASTICIZER ON CONCRETE

The action mechanism of traditional condensation polymerized admixture on concrete is mainly attributed to electrostatic repulsion. Cement belongs to ionic compound. Cement particle will adsorb anionic superplasticizer directionally when contacts with water and carry electrical charge, form electrical double layer and produce electrostatic repulsion. The higher the density of the electric charge in the main chain (i.e. the higher the $\zeta$-potential), the better the dispersion effect of admixture is (as shown in Fig.1(a)). The magnitude of the water reduction of condensation polymerized admixture mainly depends on the $\zeta$-potential of cement paste. However, increasing $\zeta$-potential can enhance the water reduction but bring
forward the problem of rapid slump loss of concrete, which makes the pumping construction of concrete difficult.

The new generation of polycarboxylate-based superplasticizer adopts the technique of grafting in the molecular design by introducing long side chain on the main chain and produces steric repulsion. When the admixture is adsorbed on the surface of cement particle, the large amount of long side chains in the graft copolymer generate bulky spacial adsorption structure, by which the adsorption efficiency increases and the ζ-potential still maintains at a relatively low level. Therefore, the slump retention capability of concrete improves efficiently (as shown in Fig.1(b)).

For a cement particle with adsorption layer on its surface, its steric energy can be expressed as follows:

\[
E^c_r = \frac{4\pi r^2 (\delta - \frac{H}{2})}{S(r + \delta)} \beta T \ln(\frac{2\delta}{H})
\]  

(1)

Where S is the area of the cement particle surface occupied by each polymer adsorption, \( S = \frac{M}{L} \), \( \Gamma \) is the adsorption amount of the dispersion agent at the concentration, L is Avagadro constant, M is the molecular weight, \( \beta \) is Boltzmann constant, T is the absolute temperature, r is the particle radius, \( \delta \) is the thickness of adsorption layer, H is the minimum distance between particles.
As for $E_R^S$, when the two particles adsorbed with polymer come closer till their adsorption layer contact each other, two cases will happen, as shown in Fig.2. One case is that the adsorption layers are compressed and do not penetrate each other (as shown in Fig.2(a)). If the polymer molecule has the shape of rigid rod, the polymer molecule will lose structural property and produce entropy repulsion force ($E_R^e$) in their inter-action zone. The magnitude of the repulsion force existing between the particles depends on the length of their molecular chain of adsorbed polymer. If the polymer molecule is elastic in stead of rigid, the adsorption layer produces elastic repulsive steric energy($E_R^e$). Another case is that the adsorption layers superpose and penetrate each other, as given in Fig.2(b). The concentration of the polymer in superposition zone increases, generates osmosis pressure and “solution condensation”, and produces osmosis repulsive steric energy($E_R^0$) and enthalpy repulsive steric energy($E_R^H$).

Therefore, $E_R^S$ can be written as:

$$E_R^S = E_R^e + E_R^e + E_R^0 + E_R^H$$  \hspace{1cm} (2)

It can be observed from the molecular structure of polycarboxylate-based graft copolymer that it is constituted with two major parts. One part is the anchoring group, which can be tightly adsorbed on the surface of cement particles and prevent desorption of admixtures. This type of groups are generally taken on by high polarity groups, such as $-\text{COOH}$, $-\text{COO}^-$, $-\text{SO}_3^-$ and $-\text{OH}$ etc., which generate strong inter-action with the cement particle by hydrogen bond, covalent bond and Van der Wall force etc., and produce adsorption. The adsorption on cement particle surface is influenced by the surface area, surface energy, surface chemical structure and surface polarity of cement particles. The other part is the long chain that can be inter-dissolved with the solvent molecule, i.e. salvation chain. It has well consistence with dispersion and can form enough thickness on cement particle surface, acting as the protection layer. When the cement particles adsorbed by graft polymer come closer, they will flick and cannot contact each other due to the compression of the long chain in the protection layer and exert steric repulsion.

The actual mechanism of polycarboxylate-based superplasticizer on concrete is the co-action of steric repulsion and electrostatic repulsion, which provides sound base for optimizing the microstructure of concrete and improve concrete performance by reasonable use of this kind of material.
3. EFFECT OF THE POLY CARBOXYLIC ADMIXTURE ON THE SURFACE TENSION OF THE PORE SOLUTION IN THE PASTE

According to theory of capillary tension, if admixture can effectively lower the surface tension of pore fluid, the capillary force acting on the pore wall decreases and thus the shrinkage of concrete diminishes. Fig.3 gives the influence of admixtures with different concentration on the surface tension of solution. Experimental results illustrates that JM-PCA (IV) admixture, which has graft group of shrinkage reducing function, can lower the surface tension of pore solution efficiently. Even at a very low concentration ($10^{-5}$g/L) its solution still maintains low surface tension. Therefore, even if the admixture is absorbed by cement particles to a large extent, due to cement hydration the amount of free water decreases, and thus the concentration of admixture is still big enough to maintain a lower level of surface tension of pore solution and leads to a decreased concrete shrinkage. While naphthalene based superplasticizer (FDN) has much higher surface tension compared with JM-PCA (IV). The surface tension of its solution is more than 50 nM/m even at a higher concentration (5.0%). Shrinkage reducing admixture (SRA) reduces the surface tension of pore solution effectively when its concentration is up to 5%. However, the surface tension of its solution is more than 50 nM/m when its concentration drops to 1.25%, which indicates that SRA may have little shrinkage reducing effect at low dosage.

The reduction of the surface tension leads to a decrease of capillary depression. Therefore, at the same level of water evaporation under drying condition, or water consumption under sealed condition, the resulted macro shrinkage stress decreases and leads to a lower shrinkage. This can be described by Laplace equation.

$$\Delta p = p_g - p_w = \frac{2\sigma}{r} \cos \theta$$

Where $\Delta p$ is the meniscus depression, $p_g$ is the saturated steam pressure of planar water; $p_w$ is the saturated steam pressure of curved water, $\sigma$ is the surface tension of pore water, $\theta$ is the contact angle, $r$ is the critical pore radius.
Fig. 4 illustrates the relationship between the meniscus depression and the surface tension. It can be observed that the under pressure across the meniscus decreases with the surface tension, which leads to a lower macro shrinkage stress. The reducing effect is more obvious for small pores, especially for those pores with radius less than 20nm. Assuming that the mixing parameters are the same and the admixture does not influence hydration process and paste pore structure, i.e. the course of water consumption and water transportation can be kept at the same speed, the shrinkage should be proportional to the reduction of surface tension and the reduction of drying shrinkage should be equal to that of autogenous shrinkage. However, the absorption of admixture on cement particle surface not only changes cement hydration process but also changes paste pore structure.

4. ADSORPTION OF POLY CARBOXYLIC ADMIXTURE

The experimental research on structure-properties relationship of admixture indicates that the ratio between the adsorption group and the ester group in copolymer (CA/CE) has great influence on shrinkage behaviour, which demonstrates that the adsorption capacity of copolymer on the interface influences shrinkage of concrete. Fig. 5 illustrates the effect of Mol ratio of CA/CE on adsorption performance. The copolymer exhibits a relatively weak adsorption tendency at a lower CA/CE. When CA/CE increases a stronger adsorption tendency of the copolymer towards the surface of cement particles is observed and results in a higher shrinkage reduction ability. It should be noted that the adsorption rate is up to 95% when CA/CE is 6.0, while the shrinkage reduction capacity decreases on the contrary, which was represented by the higher surface tension measured with the pore solution centrifuged from paste. Too many adsorption groups leads to extremely strong adsorption, thus increases the water affinity and surface tension of the copolymer and decreases its content of shrinkage reducing component correspondingly.

![Fig.5: Effect of CA/CE mol ratio on adsorption behaviour](image-url)
Experimental results show that the adsorption capability of shrinkage reducing admixture is very weak, less than 20%. While JM-PCA(IV) can be easily adsorbed onto the surface of cement particles and so efficiently lower the surface tension of pore solution in cement paste. The surface tension maintains very low even at a very low concentration ($10^{-5}$g/L), as shown in Fig.6. However, the shrinkage reducing effect of JM-PCA(IV) does not increase but decrease at a higher dosage, which need further investigation.

5. PORE STRUCTURE ANALYSIS

Fig.7 gives the pore size distribution of the hardened paste with different admixtures at the age of 3 days. In this figure, No 1 represents pure cement paste, No 2 is cement paste with 0.5% FDN, No 3 with 0.5% FDN and 0.05% JM-PCA(III), No 4 with 0.2% JM-PCA(I), and No 5 with 0.3% JM-PCA(II). All of the specimens are cured at standard condition for 3 days and 28 days, respectively.

Fig.7: Density distribution of pore size for the paste at 3 days
Fig. 8: Volume fraction of the four ranges of pore size for the paste at 3 days

At the age of 3 days, the evolution of the pore structure can be represented clearly by the amount of harmful pores (with diameter in the range of 100~200nm) and minor-harmful pores (with diameter in the range of 20~100nm). For pure cement paste, the most probable pore size is 58nm, which is in the range of harmful pore size; its density distribution curve is relatively broader compare with the other curves, which also indicates a higher amount of harmful pores within the pure cement paste. For the cement paste with FDN, the pore size distribution changes and the most probable pore size decreases to 40nm. For the paste incorporated with FDN superplasticizer and JM-PCA(III) slump retention composite, although its most probable pore size is close to that of the reference pure cement paste, a narrower density distribution curve is observed, which indicates a lower amount of harmful pores. Similar behaviour is observed for the paste with JM-PCA(I) except its density distribution curve is keener compare with that of the paste with FDN and JM-PCA(III) and exhibits a denser pore structure. In all the specimens the best pore structure is observed with the paste incorporated with JM-PCA(II). Its most probable pore size is only 35 nm, and its density distribution curve is the keenest. Based on the above analysis it can be concluded that the addition of a certain amount of JM-PCA(II) efficiently improves the pore structure of cement paste, while JM-PCA(I) superplasticizer and JM-PCA(III) slump retention admixture only have minor effect on early-age pore structure.

Fig. 8 gives the fraction of the four ranges of pore size for the specimens at 3 days. It can be also observed that the paste incorporated with JM-PCA(II) has the least amount of harmful as well as minor-harmful pores and the highest amount of harm-free pores. The experimental results indicate that the adsorption of JM-PCA(II) on the surface of cement particles releases free water, strengthens inter-particle bondness as well as improves workability of concrete, reduces the amount of harmful pores and thus improves durability of concrete.
Fig.9 gives the pore size distribution of the hardened paste with different admixtures at the age of 28 days. It can be observed that the most probable pore size decreases obviously compared with that of the specimens at 3 days. For the reference specimen the most probable pore size drops to 45 nm. For the paste with FDN no distinct reduction is observed compared with 3 days, similar behaviour is observed with the paste with JM-PCA(I) superplasticizer. The fraction of the harm-free pores and minor-harmful pores increases for the paste incorporated with FDN superplasticizer and JM-PCA(III) slump retention composite. The pore structure of the paste with JM-PCA(II) gets further densification and almost no harmful pores are observed after 28 days of standard curing, which helps to improve durability, especially the impermeability of concrete.
From Fig.10 it can be also observed that the fraction of the harmful pores within paste decrease obviously at the age of 28 days. The behaviour of the paste with JM-PCA(I) is similar with the case of the paste with FDN. The densification with age is strongest in the case of admixture composed with FDN superplasticizer and JM-PCA(III) slump retention agent. However, the pore size distribution is the best for the paste with 0.3% JM-PCA(II).

![Fig.11: Evolution of pore size distribution with curing time](image1)

![Fig.12: Evolution of the sinuosity of pores with curing time](image2)

Fig.11 compares the pore size distribution of the paste at the age of 3 days and 28 days. It gives a more distinct view that the pore structure of the paste is densified along with the curing time.

Fig.12 shows the evolution of the sinuosity of pores with curing time. The sinuosity of pores represents the connectivity of pores. The higher the sinuosity the lower the connectivity is and results in a better impermeability of concrete. According to Fig.12 the sinuosity of pores increases substantively with curing time.
6. CONCLUSIONS

- The action mechanism of polycarboxylate-based superplasticizer on cement concrete is the co-action of electrostatic repulsion and steric repulsion, in which the latter is the domain mechanism.
- The incorporation of JM-PCA(IV) grafted with shrinkage reducing group in cement concrete helps to decrease the surface tension of capillary and lower the shrinkage of concrete. Within a specific range the increasing of the Mol ratio of CA/CE leads to a higher adsorption capability and shrinkage reducing effect. However, too many adsorption groups and extremely strong adsorption may leads to an increases in the surface tension of pore solution in concrete and thus lower the shrinkage reducing efficiency.
- The polycarboxylate-based superplasticizer generally improves the pore structure of concrete. However, such kind of optimization effect depends on the form of graft to a large extent.

REFERENCES