第五届全国混凝土外加剂应用技术专业委员会年会

聚羧酸系高性能减水剂及其应用技术新进展

New Development of Polycarboxylate Superplasticizer and Application Technology

◎中国建筑学会建材分会混凝土外加剂应用技术专业委员会 编

北京理工大学出版社
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前　　言

近几年，我国聚羧酸系高性能减水剂及其应用技术的发展突飞猛进，聚羧酸系高性能减水剂对保证混凝土工程质量发挥了十分重要的作用，取得了显著的成绩。如今外加剂行业迎来了聚羧酸系高性能减水剂及其应用技术发展进程又一新的起点。

混凝土外加剂应用技术专业委员会于2005年与2007年先后两届全国“聚羧酸系高性能减水剂及其应用技术交流大会”的成功举办，在我国混凝土及外加剂领域引起了强烈的反响，并大大促进了聚羧酸系高性能减水剂研究的技术创新，加快了这一新技术、新产品的推广应用，对引导行业发展起到了重要的作用。为及时交流外加剂行业的前沿技术，总结近几年聚羧酸系高性能减水剂最新研究成果与工程应用经验，促进行业技术水平进一步的提高，顺应业内广大技术人员的要求，“第三届全国聚羧酸系高性能减水剂及其应用技术交流会”于2011年6月在北京举行。本届大会组委会专门为会议征集并出版了会议论文集，其中收录了经过专家评审的60余篇相关学术论文，涉及聚羧酸系高性能减水剂的综述与理论研究、合成与复配技术、应用技术、检测技术等内容。这些论文可以使读者充分了解我国近几年聚羧酸系高性能减水剂在工业化生产、复配技术、工程应用中遇到的各种问题，以及解决的方法与途径。我们衷心希望这本论文集能够为读者带来收获。

由于时间及水平有限，论文集中难免有错误之处，恳请广大读者批评指正。

混凝土外加剂应用技术专业委员会

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综述与理论研究

Current Status of Advanced Superplasticizers Development in Japan and Asia Pacific

Akira Ohta, Qiuling Feng

Abstract: In Japan, advanced superplasticizers that exhibit excellent slump (fluidity) retention, viscosity control and air entrainment control, as well as greater water reduction than conventional superplasticizers, have been marketed for more than 15 years. During this time, these advanced superplasticizers have become indispensable in the production of ultra high-strength and high-fluidity concretes. Admixture companies have striven to develop and improve new functional materials.

Polycarboxylate-based materials have become the main raw material for advanced superplasticizers, since these possess a molecular structure that can be easily manipulated to impart new functions.

In this paper, the authors outline the current status and future trend of this technology.

Keywords: chemical admixture; polycarboxylate; superplasticizer

1 INTRODUCTION

In the past years, chemical admixtures such as water reducers and superplasticizers (SPs) have contributed to the improvement in the durability of concrete. Among these admixtures, polycarboxylate (PC) -based SPs in particular, have been found to have a high potential, since their performance can be easily modified by changing the combined monomers. Concrete admixture companies have competed and developed various admixtures according to demands of users. On the other hand, many researchers have been studying their role in the dispersing mechanism and their effects on the hydration chemistry.

In the social environment in Japan, much higher strength and durability have been required for concrete structures. In order to realize a high strength concrete, it is necessary to mix concrete with a large amount of binder. Having a high dispersing capacity, PC-based SPs have made it possible to mix such concrete. However, their actual application posed additional problems. The high binder content led to high viscosity concrete and high autogeneous shrinkage.

The authors have been involved in the development of PC-based admixtures to overcome these

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issues. The background of PC-based SPs development, mechanism of the dispersing effect and advanced PC-based SPs specialized for good slump retention, shrinkage reduction and stickiness reduction are described in this paper.

2 CURRENT ADVANCED PC ADMIXTURES STUDY

Many types of PC-based polymers have been developed to date and commercialized into the market. Several representing chemical structures are shown in Fig. 1. There is a great difference between the molecular structures of the first generation PC-based SPs (Figs. 1 (a) and (b)) and the later ones. Regardless of the chemical species, advanced PC-based SPs have graft chains

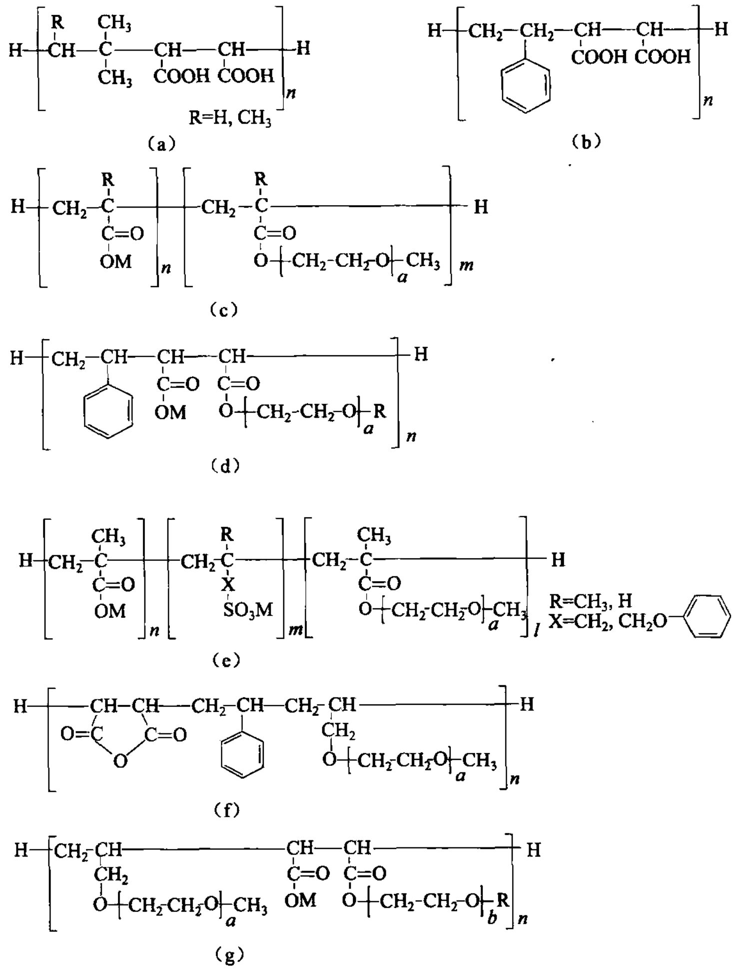

Fig. 1 Chemical structures of polycarboxylates for superplasticizer

(a) Olefine-maleic acid copolymer; (b) Stylene-maleic acid copolymer;

(c) (meth) acrylic acid- (EO) (meth) acrylate copolymer; (d) Stylene- (EO) maleate copolymer;

(e) Methacrylic acid-methacrylic (EO) ester (sulfonate including) copolymer;

(f) Allyl (EO) ether-maleic anhydrate-stylene copolymer; (g) Allyl (EO) ether- (EO) maleate copolymer composed of ethylene oxide. The specific "comb-like structure" affects the dispersibility of inorganic particles. Although the DLVO theory well explains the phenomena of dispersion and cohesion of particles, it is not applicable to the behavior of comb-like polymers (Comparisons between beta-naphtalene sulfonate and PC in the measurement of zeta-potential and flowability are shown in Figs. 2 (a) and (b), respectively). The authors have proposed the steric repulsive force as an explanation for the dispersion by the graft chains besides the electric potential theory. This proposal has been proven appropriate by later studies for explaining the role of PC on the dispersing effects.

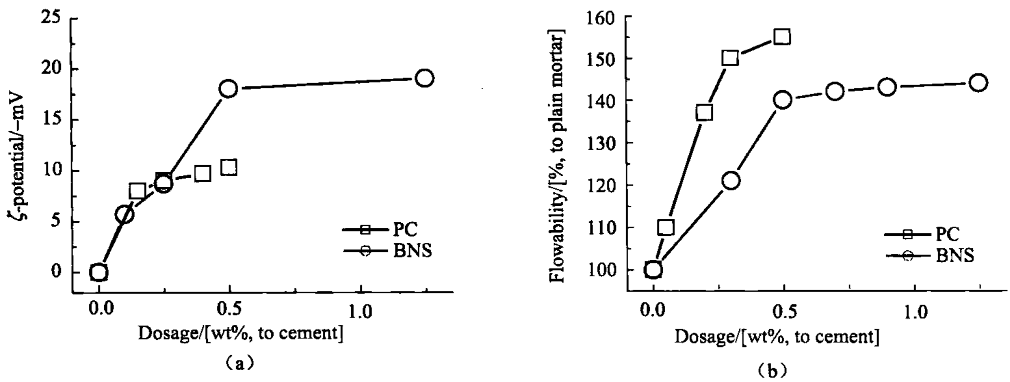

Fig. 2 Comparison between PC and beta-naphthalene sulfonate (BNS) in zeta-potential and flowability measurements

(a) zeta-potential; (b) flowability

2.1 Slow-releasing SPs for slump retention control

The slump retention of PC-based SPs is relatively better than the other SPs including beta-naphthalene Sulfonate (BNS). However, a much longer slump retention has been desired to enhance the production capacity of ready-mixed concrete plants, since the heavy traffic conditions in urban areas require good workability retention over time.

The authors noticed the hydrolysis reaction of ester bond in PC chemicals. The highly alkaline conditions during the hydration of cement may have been effective for the hydrolysis of this chemical. On the basis of this chemical reaction, a specialized PC polymer for long slump retention has thus been developed with a cross-linking chemical structure. Its molecular structure is shown in Fig. 3.

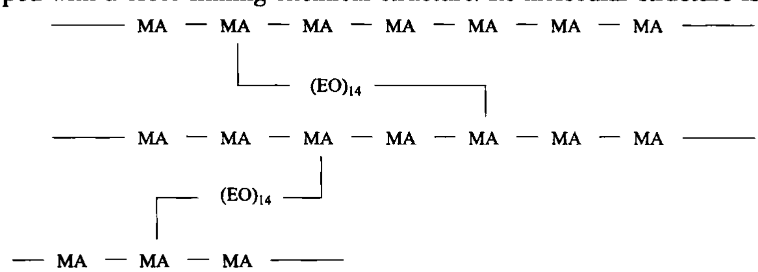

Fig. 3 Schematic figure of the cross-linking polymer

(MA: carboxylic acid monomer, EO: ethyleneoxide)

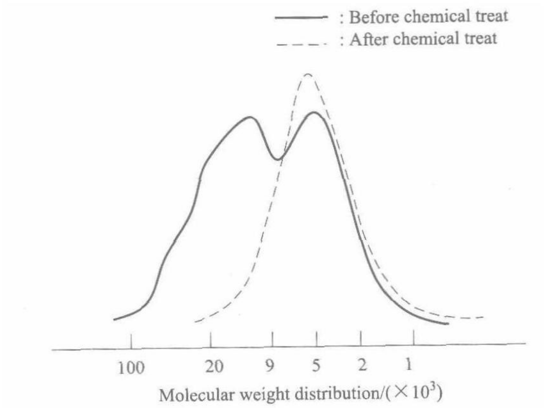

Fig. 4 GPC measurement results (the solid line represents the cross-linking polymer; the dotted line represents the cross-linking polymer treated with a pore solution of cement paste)

The cross-linked polymer breaks by cement alkaline into smaller pieces which are effective in dispersing cement particles in the high pH value conditions resulting from cement hydration. Before the breaking of the cross-linking ester bond, the molecular weight of this polymer is excessively high for working as a dispersant. This system has realized good slump retention for a long time.

The reaction process was confirmed by the analysis with GPC and ^{13}C-NMR. The GPC measurement results are shown in Fig. 4. These results reveal that the cross-linking polymer generated another polymer which acts as a cement dispersant. In addition, a typical chemical shift due to the hydrolysis reaction was found in the ^{13}C-NMR results.

This type of polymer was developed as a slump retainer. Therefore some kinds of polymers which work as dispersants are combined for actual use as concrete admixtures.

2.2 Shrinkage reducing type SP

Drying shrinkage has been known as a major negative aspect of hardened concrete for a long time. In addition, autogeneous shrinkage has recently become well known as a difficult problem about (ultra) high strength concrete.

The drying shrinkage mechanism of cementitious materials has been explained by several theories. Among them the capillary tension model based upon Kelvin's equation is widely accepted as a reasonable model. The authors have studied the relationship between the surface tension of aqueous solutions of a model chemical (diethylene glycol dipropylene glycol monobutyl ether; EPBE, shown in Fig. 5 (a)) and their drying shrinkage-reducing effect. One of the major advantages of PC-based SPs is that it provides a chance for functionalization by changing the combined monomers and/or chemical modification after polymerization. EPBE was inserted into PC-based polymers (Figs. 5 (b) and (c)) and found to successfully reduce the drying shrinkage of concrete even with a lower dosage than a typical shrinkage reducing agent (Fig. 6).

2.3 Ultra high strength concrete type SP

A concrete with a compressive strength of over 100 MPa is often used in structures in Japan. Such an ultra high strength concrete provides the construction with high durability and permits large heights and wide spans, while it means we have to mix concrete containing a relatively higher content of binder (cement, silica fume, fly ash and so on) with water at a water-to-powder ratio below 0.20. To realize such a concrete, the authors have developed an advanced PC-based SP which

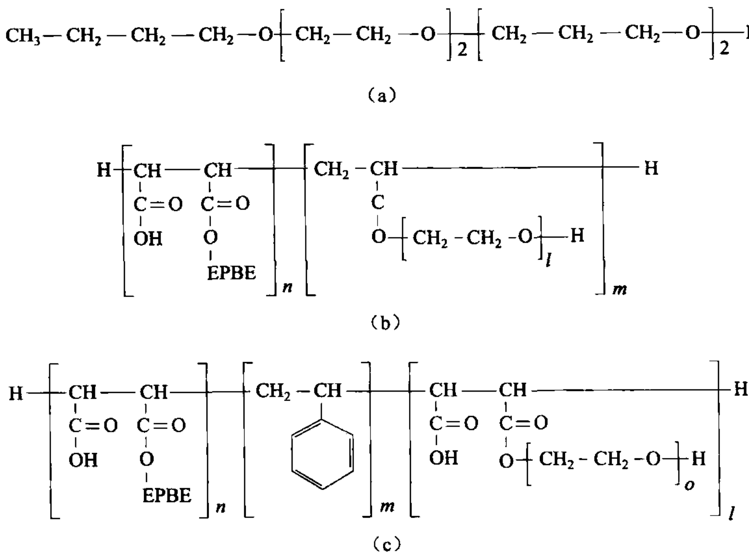

Fig. 5 Chemical structures of model compound (a) and advanced PC polymers ((b) and (c))

(a) Chemical structure of EPBE; (b) NSP-1; (c) NSP-2

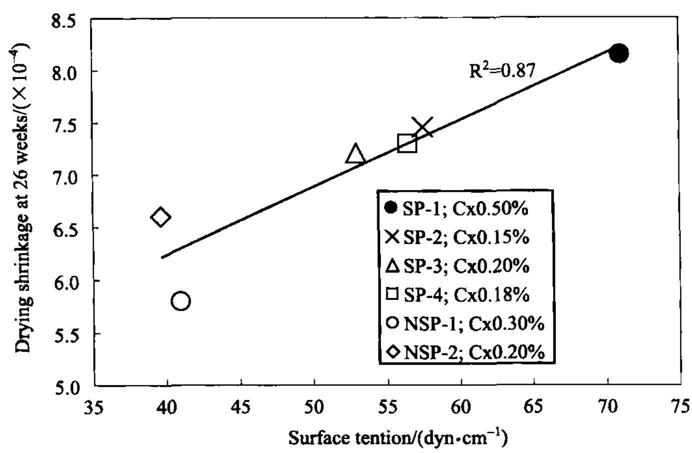

Fig. 6 Relationship between surface tension and drying shrinkage of concrete

(SP-1: beta-naphtalene sulfonate, SP-2, -3 and -4: polycarboxylate,

NSP-1 and -2: polycarboxylate with chemically attached EPBE)

can be used with a W/C as low as 0.12. As the W/C decreases, the viscosity of concrete increases. In other words, such a low W/C causes difficulty in placing, pumping and so on, of the concrete. The advanced PC-based SP has been designed to reduce the viscosity of concrete by combining a new monomer. The T50 (flow spreading time to 50 cm) value of concrete containing this SP is shown in Fig. 7. The advanced PC-based SP effectively suppressed the increasing viscosity with the lowering W/C. The newly developed SP was used for SLIM-crete bridge and achieved a compressive strength of over 180 N/mm^2 at the normal temperature hardened-high toughness -high strength mortar.

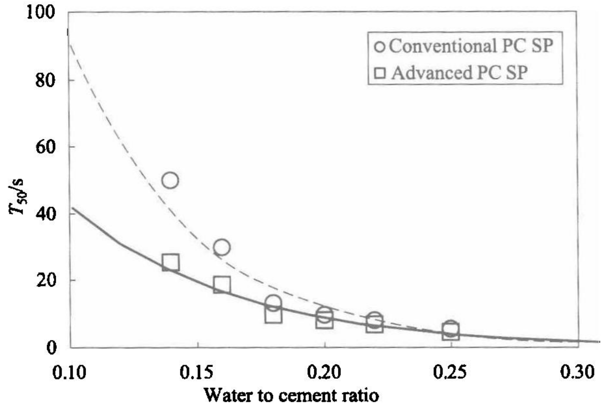

Fig. 7 Flow spreading time to 50 cm with various W/C's

2.4 Low stickiness type SP

PC-based SPs have been able to control the fluidity and slump loss of ready-mixed concrete responding to the demand of users. However, customers also need rheological control of stickiness and viscosity. A stickiness-reducing-type admixture composed of advanced PC with a "multi-ion" concept has been developed (a schematic figure of this structure is shown in Fig. 8). As one of the stickiness factors, the spread speed of concrete by L-box testing was measured (Table 1). The concrete with newly developed PC-based SP showed a faster spreading speed than the conventional PC-based SP. It is therefore inferred that the new PC-based SP lowered the stickiness of concrete. In order to prove the stickiness reduction, the pumpability of concrete containing this admixture was studied (Fig. 9 and Fig. 10). The results showed the advanced PC-based SP reduced approximately 20% of the pressure generated by pumped concrete inside the tube. The advanced PC-based SP can reduce the stickiness and increase the fluidity of concrete.

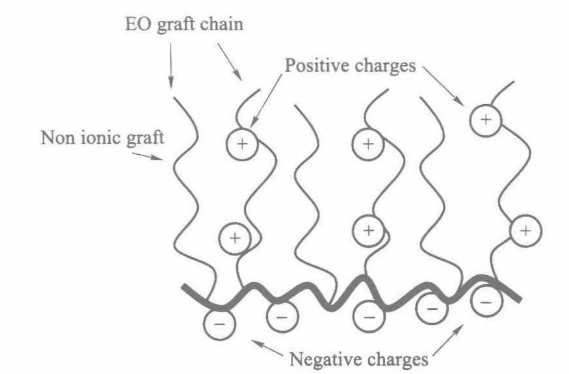

Fig. 8 Schematic figure of advanced polycarboxylate polymer

Table 1 L-box flow spreading time measurement results

Admixture	Dosage /%	Slump /cm	Slump Flow /cm	Air /%	L-box spread test		
					Flow /cm	Flowing Time /s	Speed /(cm · s^{-1})
Conventional PC SP	1.1	21.5	37.0	2.1	38.0	10.5	3.6
Advanced PC SP	1.0	21.5	36.5	2.0	38.5	6.5	5.9

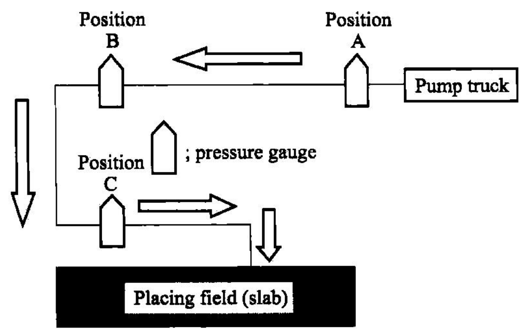

Fig. 9 Schematic diagram for the pumpability test (a piston-type pump was used, approx. 95 m actual length of tube and 4B diameter, approx. 110 m as horizontally (straight) converted)

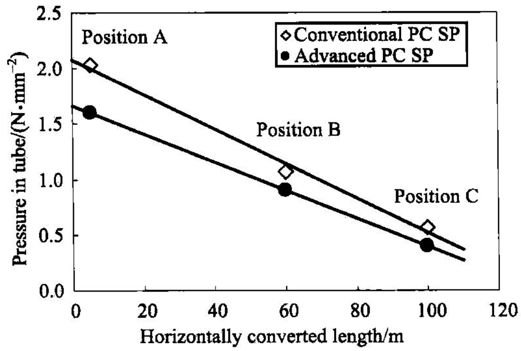

Fig. 10 Pumpability test results

2.5 Low-cost self-compacting concrete

Penetration of existing self-compacting concrete was late in Japanese market because it had a high binding material content and more expensive than normal weight concrete.

Smart dynamic concrete (SDC) concrete that is less expensive than existing one and has a simple production process was developed. It contains same level of cement for normal weight concrete; from 350 kg/m^3 to 400 kg/m^3 and special know-how for mix design is not necessary.

It is formulated to prevent segregation by the combined use of special viscosity enhancer (Fig. 11) and specialized superplasticizer regardless of high fluidity.

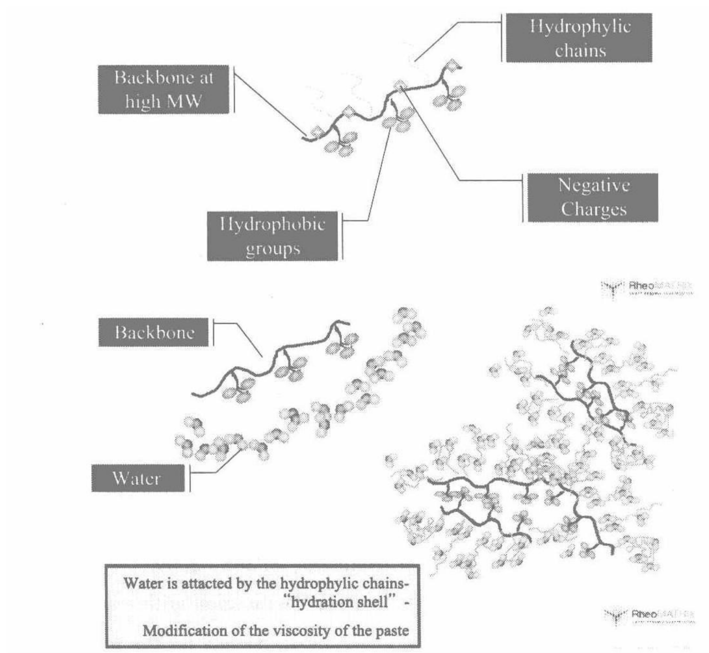

Fig. 11 Novel polymer for modifying concrete viscosity

By using "Smart dynamic concrete (SDC)", self-compacting concrete with high fluidity and without compacting, reduced the amount of time for slab foundation of Shanghai Tower under construction in China.

2.6 Future study

As described in the beginning of this report, Japan in the near future will face the effects of its declining birthrate and increasing proportion of elderly people. Japanese society has to refrain from mass production, mass consumption, and mass disposal and shift toward a recycling society.

Future chemical admixtures should contribute to sustainability of concrete under these circumstances. Durability improvement is a key issue for future innovative concrete admixtures.

3 CONCLUSION

The background of PC-based SP development and advanced PC-based SP development have been described. In this study, several types of advanced PC-based SPs have been developed and their performance discussed. The flexibility of polycarboxylate chemicals allows design to meet users' demands.

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K_2SO_4 对聚羧酸减水剂作用效果的影响机理研究

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摘要：水泥中的 K_2SO_4 含量对聚羧酸减水剂作用效果有重要的影响。本研究使用两种不同甲基丙烯酸（MAA）/甲基丙烯酸－聚乙二醇酯（PMAA-MPEG）物质的量之比的聚羧酸减水剂，通过测量水泥浆体的流动度变化、减水剂在水泥颗粒表面的吸附量、水泥浆体Zeta电位的变化、减水剂分子在水泥浆体中的直径变化，讨论了水泥中的 K_2SO_4 含量对聚羧酸减水剂作用效果的影响规律及其微观机理。研究结果表明：K_2SO_4 会显著降低聚羧酸减水剂在水泥浆体中的作用效果，表现为水泥浆体的流动度明显降低，聚羧酸减水剂在水泥颗粒表面的吸附量下降。聚羧酸减水剂与 K_2SO_4 溶出的硫酸根离子存在竞争吸附关系。竞争吸附降低了聚羧酸减水剂在水泥颗粒表面的吸附量，从而降低了聚羧酸减水剂增加流动度的效果。主链电荷密度较大的聚羧酸减水剂在竞争吸附中受到的影响较小，增加流动度的效果降低也较少。当使用聚羧酸减水剂配制高流动度混凝土时，需要尽量控制水泥浆体中 K_2SO_4 的含量，避免对聚羧酸减水剂作用效果产生过大影响。对于高 K_2SO_4 含量的水泥产品，应尽量选用减水剂主链电荷密度较大的聚羧酸减水剂，以减少 K_2SO_4 对减水剂作用效果的影响。

关键词：K_2SO_4 含量；聚羧酸减水剂；流动度；Zeta电位；竞争吸附

1　引言

聚羧酸减水剂已经被广泛应用于混凝土和建筑砂浆的生产过程中，聚羧酸减水剂能够大幅增加新拌混凝土的工作性，减少拌和用水，提高建筑材料的强度。聚羧酸减水剂更是配制高性能混凝土（UHPC）必不可少的化学外加剂，其在水泥浆体中的作用效果高于传统的三聚氰胺系减水剂（PMS）和萘系减水剂（BNS）。

聚羧酸减水剂是一种由带负电荷的甲基丙烯酸聚合而成的主链和聚乙二醇分子侧链构成的梳状聚合物。在水泥浆体中加入聚羧酸减水剂，带有负电荷的主链会吸附在水化水泥颗粒的表面，侧链则伸展在水泥浆体溶液中。关于聚羧酸系减水剂的作用机理，目前已经有较多的研究和讨论。研究结果认为聚乙二醇的分子侧链越长，越有利于水泥粒子的分散，原因是吸附减水剂的水泥粒子之间的空间排斥力加强。侧链的空间位阻作用提供了水泥颗粒之间的

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