

Superplasticizers and Other Chemical Admixtures in Concrete

Proceedings
Twelfth International Conference
Beijing, China

October 2018

**Jiaping Liu
Ziming Wang
Terence C. Holland
Jing Huang
Johann Plank**



American Concrete Institute

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Preface

In May 1978, the Canada Centre for Mineral and Energy Technology (CANMET), in association with the American Concrete Institute (ACI) sponsored a three-day conference in Ottawa, ON, Canada on the use of superplasticizers in concrete. Selected papers from the conference were published as ACI SP-62.

In 1981, CANMET again in association with the ACI, sponsored a second three-day International conference in Ottawa on the use of the superplasticizers in concrete. Proceedings of the conference were published as ACI SP-68. The purpose of the third international conference in Ottawa in 1989 was to review the progress made since the meetings in 1978 and 1981, and to bring together representatives of the chemical admixtures, cement, and concrete industries to exchange information and delineate new areas of needed research. The scope of this conference was expanded to include chemical admixtures other than superplasticizers. Proceedings of the conference were published as ACI SP-119.

In October 1994, CANMET in association with the ACI and several other organizations sponsored the fourth conference in Montreal, QC. Canada. The objective of this conference was to bring attention to new developments in chemical admixture since the last conference in 1989. Proceedings of the conference were published as ACI SP-148.

In October 1997, the Committee for the Organization of CANMET/ACI International Conference, (ACI Council), in association with the ACI and several cement and concrete organizations in Italy, sponsored the fifth conference in Rome, Italy. The conference was aimed at transferring technology in the fast -moving field of chemical admixtures. The proceedings of the conference were published as ACI SP-173.

In October 2000, Committee for the Organization of CANMET/ACI International Conferences, (ACI Council), in association with several organizations in Canada and France, sponsored the sixth conference in Nice, France. More than 50 papers from more than 20 countries were received and reviewed by the ACI review panel, and 37 were accepted for publication in the proceedings of the conference. The proceedings were published as ACI SP-195

In October 2003, The Committee for the Organization of CANMET/ACI International Conferences (ACI Council) in association with several organizations in Canada and Germany, sponsored the seventh conference in Berlin, Germany. The conference attracted more than 275 delegates and proceedings of the conference consisting of 39 papers, were published as ACI SP-217.

In October 2006, the Committee for the Organization of CANMET/ACI International Conferences, (ACI Council), sponsored the eighth conferences in Sorrento, Italy. More than 60 papers from more than 25 countries were received, and peer reviewed by the CANMET/ACI review panel in Budapest, and 36 were accepted for publication as ACI SP-239.

In October 2009, the Committee for the Organization of International Conferences (COIC) (formerly CANMET/ACI International Conferences) sponsored the ninth ACI International Conference in Seville, Spain. More than 50 papers from more than 20 countries were received and peer reviewed, and 35 were accepted for publication in the proceedings of the conference. The proceedings were published as ACI SP-262.

In October 28 to 31 2012, COIC sponsored the Tenth International Conference on Superplasticizers and Other Chemical Admixtures in Concrete in Prague, Czech Republic. More than 70 papers from all over the world were peer reviewed, and 33 were accepted

for publication in the proceedings of the conference. The proceedings were published as ACI SP-288.

In July 10-13, 2015, the COIC in association with ACI sponsored the Eleventh International Conference on Superplasticizers and Other Chemical Admixtures in concrete in Ottawa, Canada. More than 60 papers from the world over were peer reviewed, and 28 were accepted for publication in the proceedings of the conference. Also, additional papers were presented at the conference that were published in the Supplementary Papers Volume.

In October 28-31, 2018, the Chinese Ceramic Society and the China Academy of Building Research (CABR), Beijing China, in association with ACI, sponsored the Twelfth International Conference on Superplasticizers and other Chemical Admixtures in Concrete in Beijing China. More than 80 papers from all over the world were received and peer reviewed. A total of 36 refereed papers were accepted for publication in the proceedings of the conference. The proceedings were published by the ACI as SP 329. Also, 54 additional papers were presented at the conference, and were published in the Supplementary Papers Volume.

The organizers of the conference were the Chinese Ceramic Society, Beijing and the Committee for the Organization of International Conferences (formerly CANMET/ACI Conferences).

Thanks are extended to the members of the technical papers review panel that met in Hainan island, China from March 4 to 10, 2018. The panel members were selected from Canada, China, Italy, Norway, Switzerland, the U.K. and the U.S.A. Without their dedicated effort and work, it would not have been possible to publish the proceedings for distribution at the conference. Co-operation of the authors in accepting the reviewers' suggestions and in revising the draft manuscripts accordingly are greatly appreciated.

Guidance and great support for organization of the conference from Dr. V. M. Malhotra, Prof. Changwen Miao, the Honorary Chairpersons of the conference, are sincerely appreciated.

The support of CABR for the administrative work associated with the review of the papers, and the conference is gratefully acknowledged. Also, acknowledged is their support for the publication of the proceedings (ACI SP 329).

Prof. Ziming Wang, Secretary General of the Conference

Prof. Jiaping Liu and Prof. Johann Plank, Chairpersons, Scientific Committee of the Conference

Dr. Terence C. Holland, Chairperson, Paper Review Panel

Prof. Jing Huang, Vice Director of the Organizing Committee

Editors

The Twelfth International Conference on Superplasticizers and Other Chemicals Admixtures, Beijing, China, October 28-31, 2018.

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Influences of Star-Shaped Polycarboxylate Superplasticizers with Different Arm Lengths on Their Performances in Cement Paste

by Xiao Liu, Guanghong Lai, Qian Xu, Jianan Guan, Ziming Wang, and Huiqun Li

A series of star-shaped polycarboxylate superplasticizers (SPCEs) possessing different arm lengths were synthesized by changing the amount of chain transfer agent in the polymerization stage. The molecular structure information was determined by ^1H Nuclear Magnetic Resonance (^1H NMR) and gel permeation chromatography (GPC). The effects of arm length on the adsorption behavior in cement pastes, and the rheological properties, zeta potential and hydration heat of cement pastes were also evaluated. SPCE with moderate arm length exhibited prominent dispersing capacity, low surface tension, strong adsorption; the arm length was directly proportional to hydration delay and reduction. Furthermore, the moderate arm length exactly corresponded to strong hydrophilicity, suggesting that the high-performance superplasticizer was designed towards as hydrophilic as possible. The aim of this study is to provide a theoretical guidance from viewpoint of surface-interface physicochemistry in designing a superplasticizer with great potential applications in concrete engineering requiring good workability and other performances.

Keywords: polycarboxylate superplasticizer; molecular design; star-shape; arm length; cement paste; dispersion; adsorption; interface.

INTRODUCTION

Nowadays, the demands for the application of concrete admixture have increased due to the development of high-performance concrete, and thus, the researchers have devoted their efforts to exploring excellent concrete admixtures which can significantly improve the workability, strength and durability of concrete.¹ Polycarboxylate superplasticizer (PCE), a novel admixture invented in 1980s, are widely applied in concrete engineering by advantages of high water-reducing capability, good slump retention, environmentally friendly production and adjustable molecular structure.²⁻⁴

With the development of researches in the field of PCE, some researchers found that the performances of PCE are closely related to its molecular structure. Consequently, it is of great significance to probe structure-property relationship of PCE by the molecular

structure design of PCE. Generally, the structural parameters of conventional comb-shaped PCE include backbone length, side chain length and side chain density, etc., and thus a series of PCEs synthesized by altering one of these structural parameters can be used to get some universal characteristics. Zingg⁵ investigated the effects of side chain length and side chain density of PCE on the performances of cement pastes containing different C_3A amounts. Yamada⁶ investigated the effects of side chain length, backbone length and functional groups of PCE on the dispersing power in cement pastes, and the optimum molecular structure was accordingly suggested. Furthermore, the change of molecular structure can bring the enhancements of dispersing and interfacial properties. Houst⁷ showed the important structural features of the macromolecules that lead to a good adsorption behavior and rheological properties by specifically designing PCEs with varied architectures.

There are also some requirements on the molecular structure diversification in the field of PCE. It is important to innovatively explore novel structure by molecular structure design to achieve some extraordinary performances. Liu⁸ synthesized an “octopus-like” PCE with star-shaped structure, presenting better rheological properties and adsorption capacity compared with conventional PCE possessing comb-shape structure. This new type of PCE possessing special molecular structure may exhibit attractive prospect, signifying that the PCE researches should not be limited to focus on the comb-shaped PCE. However, there were no studies reported on the structure-property relationship of novel synthesized star-shaped PCE from the innovative viewpoints of interfacial chemistry.

In this study, a series of SPCEs possessing different arm lengths were successfully synthesized by altering the amount of chain transfer agent in the polymerization stage. Moreover, the effects of arm length of SPCE on the dispersing capacity and adsorption behavior, the interfacial properties, namely surface tension and hydrophilic-lipophilic balance (HLB), and hydration heat of cement pastes were probed. The optimum structural parameter was suggested based on the comparative analysis of performances from the point of hydrophilic/hydrophobic characters. This research can provide an avenue of guiding molecular design and performance optimization for PCE, giving a useful enrichment to the theories of structure-property and surface activity of PCE.

RESEARCH SIGNIFICANCE

The investigation on the relationship between structure and property of PCE especially novel type of PCE is an important subject for PCE researchers to guide the molecular design and performance optimization. The dispersing capacity is closely related to the surface-interface characters of the star-shaped PCE, which performances and effectiveness are essentially dependent on the arm length. Hence, this research attracts researchers' attentions to how to obtain excellent performances by molecular design. These findings can enrich the theory of structure-property for PCE, and further provide a simple method to design and synthesize high-performance PCE.

EXPERIMENTAL INVESTIGATION

Materials

Acrylic acid (AA), ammonium persulfate (APS), thioglycolic acid (TGA) and sodium hydroxide (NaOH) were purchased from Tianjin Fuchen Chemical Reagents Factory (Tianjin, China). Methyl allyl polyethylene glycol (MAPEG, $M_w=2400$ g/mol) was

Table 1—Chemical and mineral compositions of reference cement

Composition	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃
Content, %	22.93	4.29	2.89	66.23	1.92	0.35
Composition	Na ₂ O	f-CaO	C ₃ S	C ₂ S	C ₃ A	C ₄ AF
Content, %	0.70	0.64	58.78	21.38	6.49	8.77

provided by Liaoning Oxiranchem, Inc (Liaoning, China). Star core was self-synthesized from our laboratory, described in detail in our patent.⁹ Reference cement P.I.42.5 was supplied by China Building Materials Research Academy (Beijing, China), which chemical and mineral compositions are illustrated in **Table 1**.

Synthesis

The MAPEG and star core were diluted in a four-neck round-bottom flask with a stirrer placed in a bath at $65 \pm 1^\circ\text{C}$ with stirring, and then AA, APS and TGA solutions were dropwise added within 3 hours, followed by retaining the heating and stirring for 2 hours. Thereafter, the polymer solution was neutralized by NaOH solution to adjust pH value to 7 followed by cooling to room temperature, thus yielding the final product. The obtained products were placed in a dialysis bag (MWCO 5000), in which the water was changed every 4–6 hours for lasting 3 days to remove the unconverted reactants. The molar ratio of star core: APS: AA: MAPEG is 0.05:0.28:4:1, and the SPCE samples 1–6 are identified according to the TGA/MAPEG ratio of 0.05:1, 0.10:1, 0.15:1, 0.20:1, 0.25:1 and 0.30:1, respectively. The structural sketch of the synthesis process of SPCE is shown in **Fig. 1**.

Items of investigation

¹H NMR spectra of SPCEs were recorded on an ARX-400 spectrometer (Bruker Co., Germany) and the chemical shift values were expressed in δ values (ppm), relative to tetramethylsilane (TMS) as an internal standard and deuterated water (D₂O) as internal reference.

The polydispersity (PD), number average molecular weight (Mn), weight average molecular weight (Mw) of samples were determined on a Waters PL-GPC50 (Polymer Laboratories, UK) equipped with a PL aquaql-OH MIXED 8- μm chromatographic column. The mobile phase was aqueous solution of sodium azide with an injection volume of 100 mL and a flow rate of 1 mL/min.

The fluidities of cement pastes containing SPCE were tested according to the standard method GB/T 8077-2012¹⁰ described in the National Standards of the People's Republic of China at a water-cement ratio (W/C) of 0.29 and a dosage of 0.2% by weight of cement (bwoc). The fluidity retentions were examined every 60 min within a total period of 120 min. The mixture proportions of the cement pastes tested is shown in **Table 2**.

The apparent viscosities of cement pastes containing SPCE (SPCE dosage=0.2% bwoc, W/C=0.29) were measured using a RheoPlus QC coaxial cylinder rotary rheometer. The rheological curves of pastes were tested at 5 min after mixing at $25 \pm 2^\circ\text{C}$.

The hydration heat and hydration exothermic rate of cement pastes with or without SPCE (SPCE dosage=0.2% bwoc, W/C=0.5) were measured by using a TAM AIR-08 Thermostat (Thermometric, Järfälla, Sweden), according to the reported method.⁵

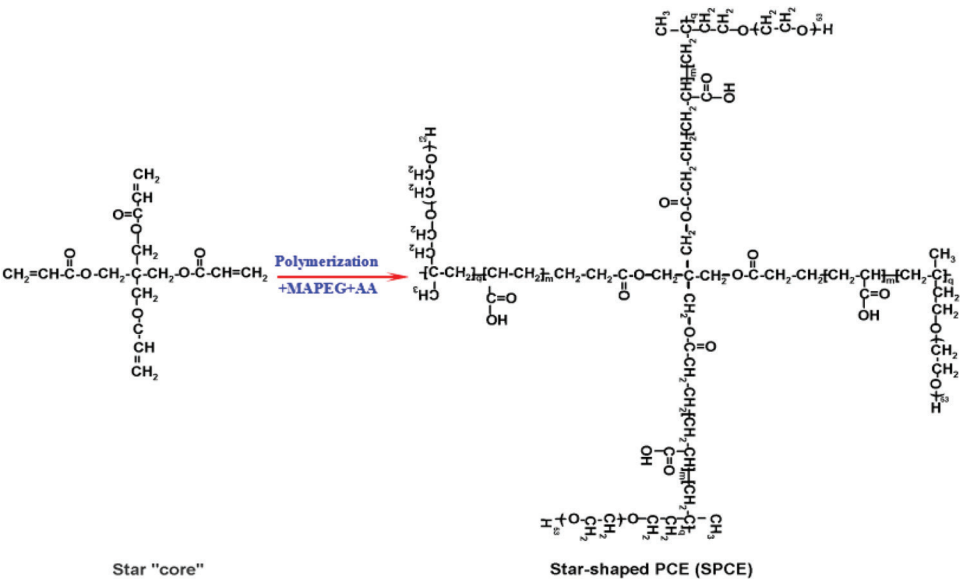


Fig. 1– Structural sketch of the synthesis process of SPCE.

Table 2 – Mixture proportions of the cement paste tested

Composition	Cement	Water	SPCE (Solid content)
Content, g	300	87	0.6

Adsorption amounts of SPCE on the surfaces of cement particles were evaluated according to the reported method¹¹ by analyzing the total organic carbon (TOC) content of the solution, determined on a Vario TOC Cube instrument (Elementar Analysensysteme GmbH, Germany). Measurements were generally repeated three times and the average was reported as the final adsorption amount.

Zeta potentials of cement pastes containing SPCE (SPCE dosage=0.2% bwoc, W/C=0.5) were determined on a Nano ZS90 Zeta potential analyzer (Malvern Instruments Ltd., UK). Measurements were generally repeated three times and the mean value was reported as the zeta potential.

Surface tensions of SPCE solutions were measured by a BZY-1 Surface or interface tension apparatus (Shanghai Hengping Instrument Factory, China). The cooled platinum plate after heating was submersed in the surfactant solutions and then the measured value was recorded.

HLB values of SPCEs were calculated according to Griffin’s method¹²

$$HLB = 20 \times M_h/M$$

Where

M_h = the molecular mass of the hydrophilic portion of the macromolecule, and

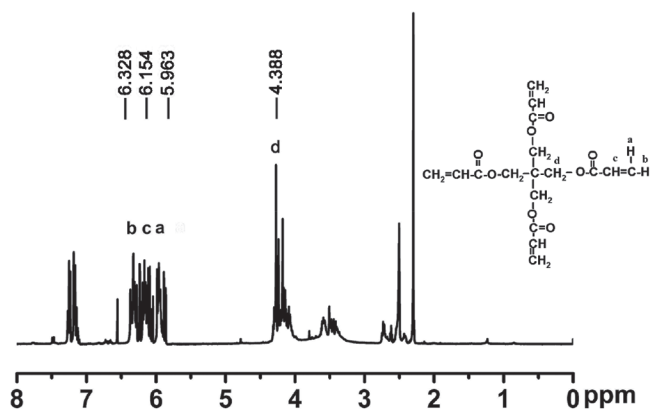


Fig. 2– ^1H NMR spectrum of star core.

M = the molecular mass of the entire macromolecule.

Contact angles were measured on the surface of SPCE film at 25°C using an OCA 20 Contact angle system (Dataphysics Instruments GmbH, Germany). A $2\ \mu\text{L}$ drop of distilled water was dispensed on the flat surface of the film. Each angle reported here was the average of 2 different drop deposition measurements, and at least 3 measurements for each deposition.

EXPERIMENTAL RESULTS AND DISCUSSION

Molecular characterization of SPCEs

^1H NMR analysis of star core

Fig. 2 shows the ^1H NMR spectrum of the star core, which was analyzed by means of the reported chemistry book.¹³ From Fig. 2, the primary characteristic peaks of the star core appear at 5.963 ppm, 6.154 ppm and 6.328 ppm, which correspond to the three H atoms of $-\text{CH}=\text{CH}_2$ bonds linked to ester groups. Furthermore, peak at 4.388 ppm correspond to the H atoms of methylenes of pentaerythritol, confirming the molecular structure of the star core.

^1H NMR analysis of star-shaped superplasticizer

The ^1H NMR spectra of the SPCEs are shown in Fig. 3, analyzed by the reported literature.¹³

From Fig. 3, the peaks at 3.3–3.8 ppm and 4.5–5.0 ppm corresponding to the H atoms of polyethylene glycol in the side chains of SPCE are distinctly higher than other peaks. It also can be seen that peak at around 4.30 ppm corresponds to the H atoms of methylenes of star core. It is well-known that this peak will not be displayed at this position if the star core does not polymerize with other monomers or forms other products. Furthermore, the large integral area of these characteristic peaks implies substantial formation of star-shaped structure, confirming the polymerization reaction and the as-expected star structures for the synthesized SPCEs.

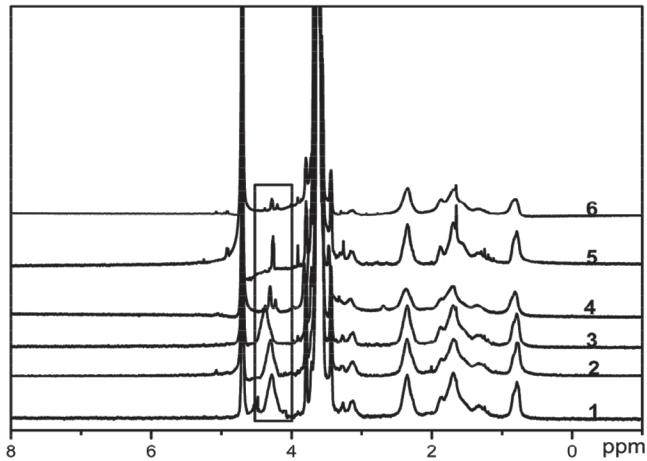


Fig. 3– ¹H NMR spectra of the synthesized SPCEs.

Table 3–Molecular properties of SPCEs

Sample	Mw, g/mol	Mn, g/mol	PD
1	108495	66972	1.62
2	82581	56562	1.46
3	61260	47123	1.30
4	55332	36644	1.51
5	34332	23842	1.44
6	27527	19662	1.40

Molecular properties

The molecular properties of the synthesized SPCEs are listed in **Table 3**. All of the synthesized SPCEs possessing different arm lengths show the relatively narrow molecular weight distribution (PD < 2), manifesting as quite uniform macromolecule composition. It also can be clearly seen that under a constant side chain density for the arm of SPCE, the molecular weight regularly decreases with the increase of TGA/MAPEG ratio, signifying that the arm length of SPCE is inversely proportional to the TGA/MAPEG ratio. The reason is that, the process of chain growth from four polymerizable points on star core is significantly inhibited due to the increased chain transfer power. This result proves the successful synthesis for a series of SPCEs possessing different arm lengths.

Rheological properties of cement pastes containing SPCE

Fluidity

The fluidities at 0, 1 and 2 hours of cement pastes containing SPCEs with different arm lengths are shown in **Fig. 4**. The fluidities and retentions exhibit a trend of first increase and then decrease with the decrease of arm length, implying too long or too short arm cause poor performances in fluidity.

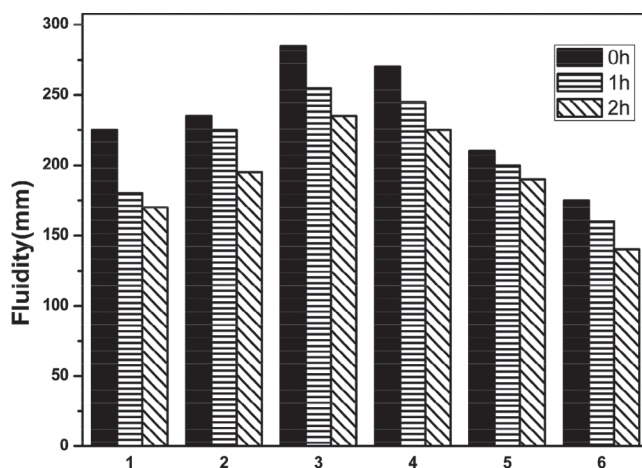


Fig. 4— Fluidities of cement pastes containing SPCEs with different arm lengths.

As reported, the dispersing mechanism of SPCE can be described via the model of adsorption-dispersion.¹⁴ The dispersing capacity is mainly dependent on the adsorption and steric hindrance, determined by the structural parameters such as arm length, side chain length and side chain density. Based on this, with regard to our synthesized SPCEs possessing different arm lengths, the possible reason for the fluidity trend displayed in **Fig. 4** is that, too long arm length may enhance steric hindrance whereas the adsorption on the surfaces of cement particles is less. The shorter arm length causes poor steric hindrance to lower the dispersing capacity to cement particles. A moderate arm length may synergistically perform well in both adsorption and steric hindrance. To verify the effects of adsorption behavior on the dispersing capacity, it will be discussed in detail below.

Apparent viscosity

The apparent viscosities of cement pastes containing SPCEs with different arm lengths are shown in **Fig. 5**. The apparent viscosities of cement pastes decrease sharply under a low shear rate ($0-10s^{-1}$), and then decrease slowly to a constant with the increase of shear rate ($10-50s^{-1}$). Compared with the blank sample, the samples containing SPCE show lower apparent viscosity, mainly because SPCE can disperse the cement particles to lessen the flocculation structure, which is in line with other reported literature.¹⁵ It is interesting that the samples containing SPCE with moderate arm length exhibit lower apparent viscosity, consisting with the results of paste fluidity. This also implies that inappropriate arm length goes against the elimination of flocculation structure of cement particles.

Hydration kinetics of cement pastes containing SPCE

The hydration heat evolvments from cement pastes in absence or presence of SPCEs with different arm lengths are shown in **Fig. 6**. For the samples containing SPCE compared with blank sample, the delayed hydration process (i.e. a later hydration heat peak appeared) and the reduced hydration heat (i.e. a smaller integral area of hydration heat peak appeared)

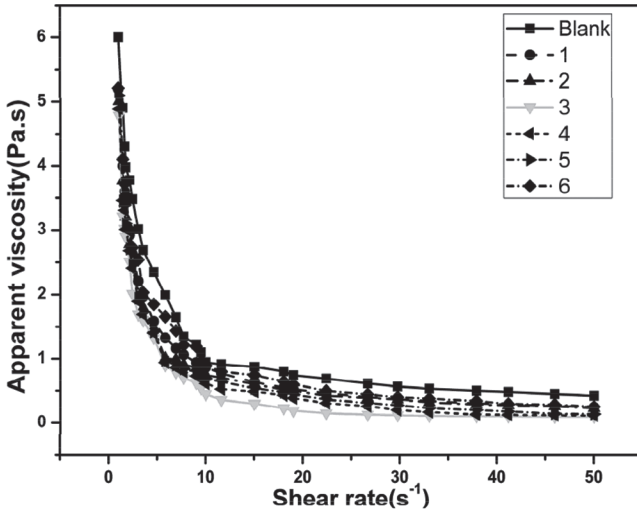


Fig. 5– Apparent viscosities of cement pastes containing SPCEs with different arm lengths.

can be observed, consistent with other reports.¹⁶ The main reason is that the formation of the complexes from -COOH of SPCE and Ca^{2+} in pore solution leads to the reduction of Ca^{2+} concentration and further the inhibition of nucleation and growth of the hydration products such as C-S-H and Ca(OH)_2 .¹⁷ This inhibition effect is directly proportional to the arm length of SPCE. This is probably because more anchored carboxyl groups for the SPCE possessing longer arm length can simultaneously adsorb on several cement particles, resulting in the particle agglomeration and further the delay of hydration process.¹⁸

Adsorption behavior and potential characteristic

Adsorption on cement particles

In the cement paste system, the adsorption behavior of SPCE closely related to dispersion capacity depends on its molecular structure. The adsorption amounts of SPCEs on the surfaces of cement particles as a function of time are shown in **Fig. 7**. All the samples exhibit a similar trend that the adsorption amount increases within 90 min and then remains constant over time, conforming to Langmuir adsorption isotherm.¹⁹ Also from **Fig. 7**, sample 3 exhibits the highest adsorption amount; both sample 1 and sample 6 exhibit lower adsorption amounts. This signifies that too long or too short arm length cannot contribute good adsorption behavior. The short arm implies fewer carboxyl groups, and likewise, the long arm is apt to be curled to wrap a part of carboxyl groups. On the other hand, the macromolecule possessing moderate arm length can make an effort to avoid the adsorbed groups being enveloped, thus achieving the highest adsorption effectiveness, which quite agrees with other research reported by Yamada.⁶ It can be concluded that moderate arm length is helpful to obtain good adsorption performance, which is similar to the fluidity results.

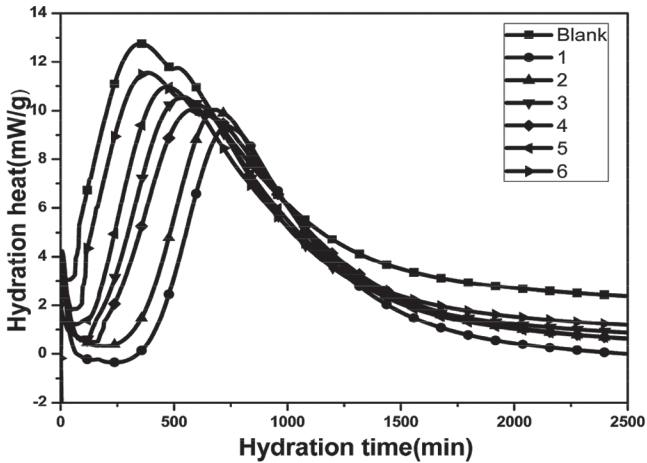


Fig. 6– Hydration heat of cement pastes in absence or presence of SPCE.

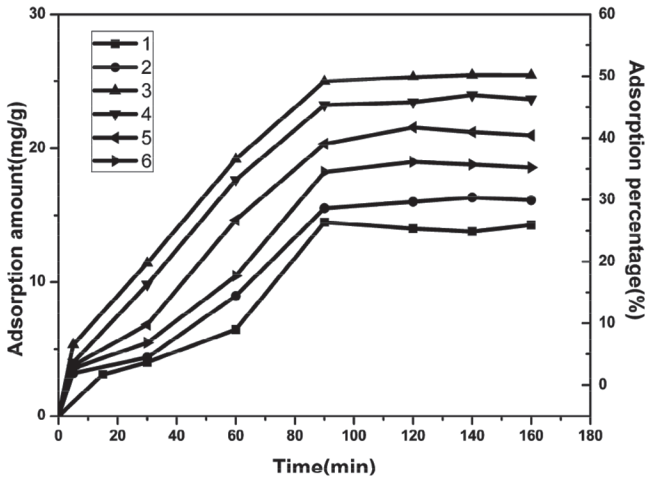


Fig. 7– Adsorption amounts for SPCEs with different arm lengths in cement pastes.

Zeta potential

The zeta potentials of cement pastes in absence or presence of SPCE as a function of SPCE dosage are shown in Fig. 8. The zeta potentials of cement paste initially show positive values mainly due to the faster hydration rate for clinker minerals,^{20,21} and then change to negative values after mixing with SPCE, mainly due to the adsorption of anionic groups of SPCE on the surfaces of cement particles. As the hydration process continues, a part of the precipitation of Ca^{2+} leads to the increase of $\text{SO}_4^{2-}/\text{Ca}^{2+}$ ratio, behaving as increased negative zeta potentials. With the SPCE dosage increases, the negative zeta potentials

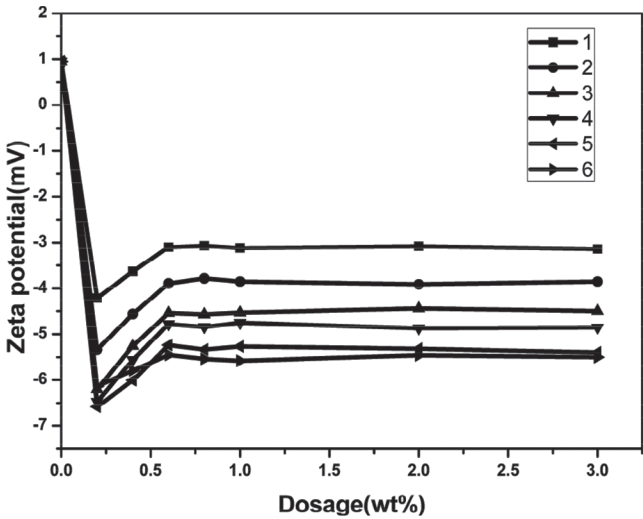


Fig. 8– Zeta potentials of cement pastes containing SPCEs with different arm lengths.

slightly decrease, owing to a partial replacement of COO^- to high-valent anions such as SO_4^{2-} . Also from **Fig. 8**, the negative zeta potential is inversely proportional to the arm length of SPCE. The main reason is that, long arm corresponds to more COO^- replacement to high-valent anions,^{22,23} showing a low negative zeta potential; short arm corresponds to thin adsorption layer, based on the double layer theory, thus resulting in a close distance between slipping plane on the surfaces of cement particles, presenting a high negative zeta potential.²⁴

Interfacial properties

Surface tension

The surface tensions of solutions of SPCEs (0.4g/mL) with different arm lengths were measured, as shown in **Fig. 9**, according to Gibbs Adsorption Isotherm expressed by equation as follows²⁵

$$\Gamma = -\frac{1}{nRT} \left(\frac{d\gamma}{d \ln C} \right)$$

Where

γ = the surface tension of surfactant solution (mN/m);

C = the bulk concentration of surfactant (μM);

R = the constant value ($8.314\text{J/mol}\cdot\text{K}$);

T = the temperature of solution (K),

Γ = the excess surface concentration ($\mu\text{mol/m}^2$); and

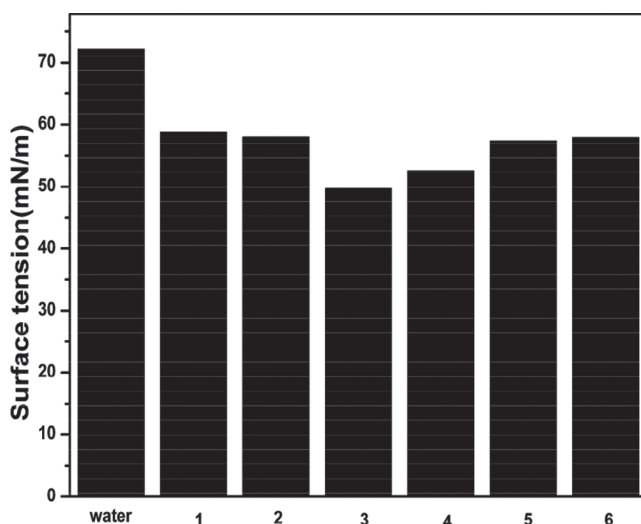


Fig. 9– Surface tensions of solutions of SPCEs with different arm lengths.

n = the number of solute species whose concentration at the interface changes with the change of C value, which is considered to be 1 for nonionic or anionic surfactant with presence of an excess concentration of electrolyte and 2 for anionic surfactant system without added electrolyte.

From **Fig. 9**, all the surface tensions of SPCE aqueous solutions (SPCE concentration is 0.4g/mL) are lower than that of pure water, implying that SPCE has an apparent surfactivity characteristic. Also from **Fig. 9**, sample 3 possessing moderate arm length exhibits the lowest surface tension, presenting as the strongest surfactivity; however, sample 1 and 6 exhibit higher surface tension, demonstrating that immoderate arm length for SPCE generally presents high surface tension.

It can be interestingly concluded that the surface tension is inversely proportional to the equilibrium surfactant adsorption density at the air/water interface. The probable reason is that an increase in arm length increases the repulsive force of molecules, causing a decrease in SPCEs adsorption density in gas-liquid interface and a reduction in surface activity, leading to high surface tension. For moderate arm length, the result is more related to the conformation of SPCEs during film-foaming process. The moderate arm length allows more hydrophobic and hydrophilic group reach gas-liquid interface due to the more mobility and flexibility of the molecules.

HLB value

The HLB value is an important interface parameter to express hydrophilicity and hydrophobicity. It ranges from 0 corresponding to hydrophobic components to 20 describing a purely hydrophilic polymer. The HLB values of SPCEs with different arm lengths are shown in **Fig. 10**. All of the HLB values exceeds 14.5, manifesting as good hydrophilicity. Besides, sample 3 exhibits the highest HLB value; sample 5 and 6 exhibit lower HLB

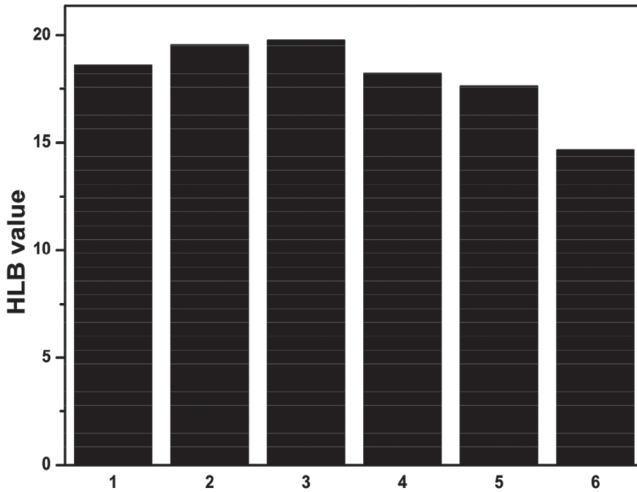


Fig. 10– HLB values of SPCEs with different arm lengths.

values. Combined with the above-mentioned rheological results, it is worth noting that the HLB values are directly proportional to the results of fluidity and apparent viscosity, implying a good correlation between rheological properties and hydrophilicity/hydrophobicity. Factually, HLB value affects the rheological properties via individual adsorption capacity, that is to say, under the condition of low HLB value, a great number of hydrophobic groups remove to the gas-liquid interfaces so that the hydrophilic groups adsorb on the surfaces of cement particles are reduced, behaving poor dispersing capacity to cement particles.

Contact angle

The contact angles of SPCEs with different arm lengths were measured, as shown in **Table 4**. The lower the contact angle is, the better hydrophilicity and wettability it exhibits.²⁶ All the samples exhibit relatively low contact angles in the range of 10°-60°, manifesting as good hydrophilicity. This is due to abundant hydrophilic groups such as carboxyl and ether in the molecular structure. Also, sample 3 shows the lowest contact angle, namely the best hydrophilicity and wettability, mainly because the strong hydrogen bonds formed by hydroxyl groups and water molecules result in good spreading of water droplet on the surface of polymer.²⁷ Sample 6 shows the highest contact angle, signifying that smaller M_w allows more $-CH_2$ reach surface can weaken the hydrophilicity. As for sample 1, the long arms are so flexible that a part of the hydrophilic carboxyl groups are wrapped to show a shielding effect, presenting a little poorer hydrophilicity than sample 3.

It is noteworthy that the contact angle results are closely related to the rheological performances of cement paste. The SPCE showing good hydrophilicity displays a stretched conformation in pore solution, which helps to improve the possibility of the interaction with cement particles and further enhance the rheological properties of cement paste. Therefore, we can conclude that the superplasticizer possessing stronger hydrophilicity

Table 4–Contact angle values of SPCEs with different arm lengths

Sample	1	2	3	4	5	6
Contact angle, °	21.3	22.5	13.0	28.0	39.2	55.3

should be endeavored to synthesize if there is a requirement of high fluidity for cement paste. This is somewhat similar to that reported by Plank.²⁸

Influencing mechanism of arm length of SPCE

To reveal the influencing mechanism of arm length of SPCE, all the experimental results are summarized from the viewpoint of the impact of molecular structure on performance.

When the arm length of SPCE is too long, the degree of spatial curliness of macromolecules increases so as to shield a part of the functional groups, resulting in a declined efficiency for each SPCE macromolecule; moreover, the large dimension is likely to cause the linkage of cement particles via the adsorption of SPCE on different cement particles, thus increasing the flocculation structures of cement particles and further bringing down the dispersing effectiveness.

When the arm length of SPCE is too short, the low adsorption amount leads to the lessening of SPCE-cement interaction. Besides, the small dimension significantly reduces the likelihood of full stretch of arms in pore solution, resulting in a relatively thin adsorption layer. Accordingly, each macromolecule exhibits weak steric hindrance effect and repulsion energy,^{29,30} thus enhancing the odds of particle aggregation and further impairing the dispersing capacity to cement particles.

From the above experimental results, too long or too short arm length corresponds to higher surface tension which causes higher capillary pressure, further leading to increased drying shrinkage for cement matrix to bring detrimental effect in engineering application. Therefore, the excellent adsorption behavior, interfacial properties and dispersing capacity to cement particles can be achieved only by employing moderate arm length for SPCE, namely 4 to 5 repeated units (AA-AA-AA-AA-MAPEG) for an average of each arm, according to the calculation from the molecular weight data. It is physicochemically proposed that the SPCE requiring high performance should be synthesized towards as hydrophilic as possible, which also exactly corresponds to have a structural characteristic of moderate arm length. This study gives a theoretical guidance to SPCE's potential applications in concrete engineering requiring good workability and other performances.

CONCLUSIONS

1. A series of SPCEs with different arm lengths were successfully designed and synthesized via varying the amount of chain transfer agent during the polymerization process. The expected star-shaped structures and uniformly distributed macromolecule compositions for the polymerization products were obtained.

2. Good rheological properties cannot be acquired by employing SPCE with too long or too short arm; on the other hand, SPCE with moderate arm length (4~5 AA₄-MAPEG units for average a arm) shows good dispersing capacity to eliminate the flocculation structure of cement particles, presenting good fluidities and low apparent viscosities of cement pastes.

3. The addition of SPCE is beneficial to the delay of hydration process and the reduction of hydration heat, and furthermore, this trend becomes prominent with the increase of arm

length of SPCE, due to more and more formation of complexes produced from -COOH of SPCE and Ca^{2+} in pore solution.

4. SPCE with moderate arm length presents low surface tension and strong adsorption on the surfaces of cement particles, as a direct reason of good rheological properties. Good performances can be achieved at a balance between electrostatic repulsion and steric hindrance, but not for the sample such as SPCE with the shortest arm length only exhibiting the strongest electrostatic repulsion.

5. The highest HLB value and the lowest contact angle occur at a moderated arm length for SPCE, giving a useful proposal that during our design in PCE, a superplasticizer having strong hydrophilicity helps to achieve good performances in cement-based materials. This finding provides a general design direction for obtaining a high-performance superplasticizer with great potential applications in practical concrete engineering.

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Investigation on Water Retention Property and Microstructure of Fresh State Cement Mortars Using ^1H Low-Field NMR

by Yanliang Ji, Zhenping Sun, and Xiaoxing Jiang

This paper presents important insights into the microstructure of the fresh cement based mortar and developed an original method for evaluation of water-retention capacity of the mortars based on ^1H Low-field NMR. Influence parameters, such as cement types, types and amounts of water retention agents, on water-retention properties were investigated. Results showed that the water retention capacity can be clearly identified by comparing the T_2 distribution before and after the traditional water-retention tests. Moreover, the paramagnetic substance may have impacts on the NMR effects of water insides the fresh mortars. The water retention property depicted by the proposed method is consistent with the conventional method (linearity up to 0.914). The results suggest that utilization of ^1H Low-field NMR on water-migration mechanism is objective and accurate.

Keywords: water retention capacity; microstructure; fresh mortar; ^1H Low-field NMR.

INTRODUCTION

Building mortar has the advantages of homogeneity of quality, using convenience and good physical and chemical properties.^{1,2} However, the building mortars in the fresh state suffer a drying process caused by the demand of inner hydration and absorption or by evaporation to the atmosphere in practical engineering.³ These water-migration phenomena not only affects the performance of mortars in plastic stage, such as rheological behavior,⁴ adhesive force⁵ and workability maintenance,⁶ but also determines the mortars' final properties in the hardened state.⁷ Thus, actually different types of water retaining agents may be involved in mix-design of the mortars to improve the water retaining capacity, and meet the requirements related to placement processing, hardening properties and long-time behavior.

Although many studies focusing on cement mortars have been devoted to study influence factors on water retention capacity, the recognition and characterization of the water migration process in the microstructure of the fresh mortars still remains in the hypothetical stage.⁸⁻¹¹ Therefore, objective and novel insights concerning microstructure in fresh state of mortars are essential to recognizing the mechanism of influencing factors on water

retention capacity, and associating with the scientific instructions of cement-based mortar design. For cement based mortars, the low-field nuclear magnetic resonance (NMR) by measuring only the proton NMR response (relaxation behavior) coming from the mixing water is neither invasive nor destructive.¹² This method is sensitive to the water molecules in fresh cement paste, gives a vivid scenario of microstructural variation and provides crucial insights into mechanism of water migration.¹³⁻¹⁵ The present study was designed to investigate the water retention property of fresh mortars based on technology of ¹H low-field NMR. In this study, characterization of different types of water retention agent was discussed by low-field NMR. Under identical consistency, water retention capacity of the mortars prepared with three different types of cement was evaluated by the proposed method. In addition, by analyzing the peaks in T2 distribution, the influence of parameters on water retention capacity and microstructure development in fresh mortars were also investigated. The correlation between the conventional method and proposed method for evaluation on water retention capacity was also discussed in this paper.

RESEARCH SIGNIFICANCE

NMR method can provide important insights into the microstructure of the fresh cement paste.

Through analyzing the peaks in T_2 distribution, this study improve the understanding about the influence mechanism of parameters on water retention capacity and microstructure development in fresh mortars. The correlation between the conventional method and proposed method for evaluation on water retention capacity evidence that the NMR method can be alternative way for evaluating water retention property. The authors believe that the method used in this paper has exhibited its superiority on the water retention capacity and microstructure of the fresh state mortar. In further investigations, it should be interesting to extend this study to permeability of the mortar.

EXPERIMENTAL INVESTIGATION

Methods and characterization

The consistency test carried out according to the standard JGJ/T70-2009.¹⁶ Test apparatus included mortar consistency tester which consists of a testing cone, a vessel and a bearing. The consistency will be reported as the average value of two experimental results and the extract value will be accurate to 1 mm. The method¹⁶ suggested by JGJ 70-2009 standard can be utilized to obtain the water retention capacity of freshly-mixed mortar rapidly, and the apparatus is described in Fig. 1. The water retention capacity of the fresh mortar can be evaluated after capillary action from the specified numbers of filter papers (pore size is 30 μ m-50 μ m). In order to prevent loss of mortars, the fresh sample was insulated by a metal filtering net under the filter papers. In the test, the fresh mortar was poured into the ring, and the top of the mortar was smoothed by a scraping knife. Then, the metal filtering net, filter papers, impermeable plate and ballast (weighted 2 kg) were successively placed on the surface of the mortar, and water-absorption time on the mortars was kept at 2 mins. The water retention capacity of fresh mortars can be calculated by Eq. (1).

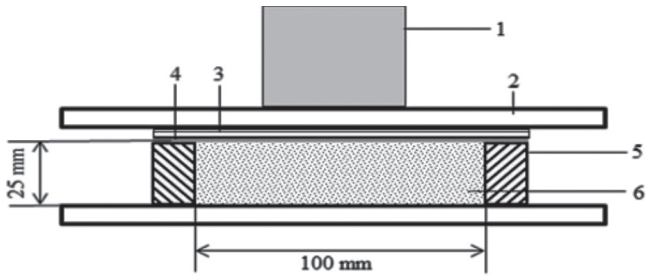


Fig. 1—JGJ 70-2009 test arrangement for determining the water retention of freshly mixed mortars(1: Ballast; 2: impermeable plates; 3: filter papers; 4: metal filtering net; 5: cylindrical metallic ring; 6: mortar)

Table 1—Parameter setting of low-field NMR

Parameters	TW/ms	SW/KHZ	TE/ms	TD	NECH	NS	PRG
Values	18000	250	0.450	2025050	18000	6	3

$$WR(\%) = \left[1 - \frac{m_{fp}}{\alpha \times m_t} \right] \times 100 \quad (1)$$

where, m_{fp} is the quantity of water retained by the filter papers, m_t is the quantity of the mortar inside the ring, and α is the water content of fresh mortars which is determined by the weight difference of the parallel sample after drying to constant weight at $105 \pm 5^\circ\text{C}$.

¹H Low-field NMR

The instrument (MICROMR12-040V; Niumag Electric Corporation, Su Zhou, China) operates at 11.794 MHz, with a constant magnetic field of 0.3 T. In comparison of the NMR instrument involved in previous study,¹³ the diameter of the magnet coil was 40 mm which allows more samples to be detected by this study. In addition, considering its sensitivity, the fresh mortars may be easily affected by environmental factors such as temperature difference between inside and outside of the NMR instrument and the vibration induced by movement of samples. Hence, reducing testing time in the instrument and avoiding unnecessary vibration are also advised. Parameter setting of the NMR equipment was adjusted on the basis of previous experiment results by trial and error, including repeated sampling waiting time(TW), sampling rate(SW), echo time(TE), sampling points(TD), echo number(NECH), number of scans(NS) and pre-amp gain(PRG). The optimized results are shown in Table 1.

The prepared sample (after mixing) was slightly poured into a glass tube with a height ranging from 25 mm to 30 mm (approximately 35 g- 40 g) after debugging of the instrument, then the whole was inserted in the NMR probe. It should be pointed out that, after the water-absorbing regime in Section 2.2.1, the mortar samples should be extracted from the centre of the plate from top to the bottom carefully without unnecessary vibration. The transverse relaxation curve was fitted to a multi-exponential curve by means of the inverse

Laplace transform algorithm used by the Multi-Exp Inv Analysis software provided by the Niumag Electric Corporation. Generally, the transverse magnetization decay containing the full information of proton relaxation in the sample, and it can be described by the superposition of exponential decays leading to the Eq. (2). The inversion of low-field NMR relaxation signals was conducted by the built-in computing method of SIRT (multi-component mode) to obtain the density function of proton distribution, also known as the T2 distribution. The peak position was obtained by the weighting method based on the relative amplitude and T2 distribution.

$$M(t) = M_0 \sum_i P_i \cdot \exp\left(-\frac{t}{T_{2i}}\right) \quad (2)$$

where, M_0 is the constant value (initial magnetization), P_i is the relaxation time probability density, T_{2i} is the transverse relaxation time for the component i . Based on the premise of ignoring the impact of bulk fluid relaxation rate, the adaption of the fast exchange model on pore microstructure is mostly affected by diffusion relaxation of samples caused by homogeneity of magnet field.¹⁷ The NMR instrument with a low average gradient (less than 73.0 ppm) of the magnetic field can efficiently reduce the impact of the diffusion relaxation to transverse relaxation rate of 1H protons. In addition, transverse relaxation time, T_2 , was measured using Carr-Purcell-Meiboom-Gill sequence. As a result, the signal attenuation caused by the heterogeneous magnetic field can be weakened by each application of the 180° pulse in the sequence. Therefore, transverse relaxation time (T_2) can be defined by Eq. (3).

$$T_2 = T_{2,surf} = \rho_2 \frac{V}{S} \quad (3)$$

Therefore, it is assumed that transverse relaxation time (T_2) correlates with distance between the particles including the fine aggregate, cement and hydrates, and a single pore decayed mono-exponentially (0.08-121.23 ms) in T_2 distribution generated by the signals suggests that the transverse relaxation time is weighted average of adsorbed water.

Materials

Portland cement (called Cem-0) with an initial setting time 105 min, manufactured by Onoda, was mainly used. Two other different types of commercial cements (Cem-1 and Cem-2) were also used for comparison analysis. In addition, the distribution of particle size of the cements are shown in Fig. 2. Bentonite and sepiolite as mineral admixtures for improving water-retention property of mortars, supplied by Changxing Lei Xiang Chemical Co., LTD and Shijiazhuang Yaxing Coating Factory, were also used in this study. The detail chemical composition and physical properties of the three kinds of cement and the mineral admixtures are shown in Table 2. The organic water retention admixtures was cellulose methyl-hydroxypropyl (MHPC) based compound with viscosity of 40000 (MHPC-1) and 70000 mPa·s (HPMC-2) (measured by Viscometer (Brookfield RV) with 20 RPM, and the sample solution for the test is 2.0%). Before using the inorganic water-retention, they were

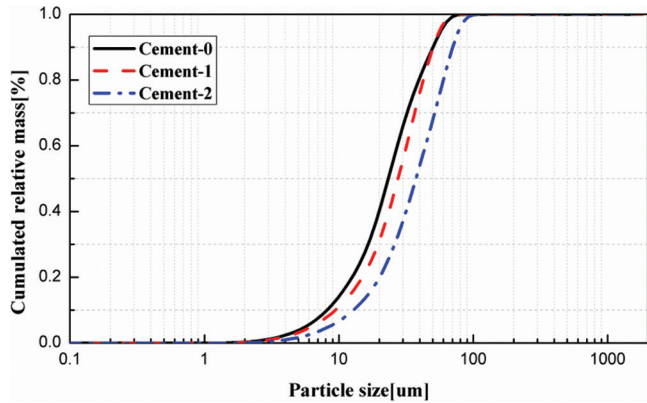


Fig. 2—Particle size distribution of cements

Table 2—Chemical composition /wt% and physical properties of cement and inorganic water-retention materials

	Cem-0	Cem-1	Cem-2	Bentonite	Attapulgite
SiO ₂	20.00%	22.60%	23.11%	60.8%	60.5%
Al ₂ O ₃	4.45%	2.72%	10.0%	14.4%	8.60%
Fe ₂ O ₃	1.28%	0.27%	4.54%	5.80%	5.82%
CaO	64.20%	64.90%	57.1%	0.30%	2.18%
MgO	0.73%	2.49%	0.83%	0.35%	10.1%
SO ₃	2.64%	2.68%	1.62%	0.25%	0.13%
K ₂ O	0.74%	0.44%	0.84%	1.39%	1.23%
Blaine [m ² /kg]	394	389	444	—	—
Specific weight [g/cm ³]	3.10	3.26	3.37	2.94	2.74
Water absorbency	—	—	—	0.65	3.43

dried to constant weight at 105°C in this study, and unless otherwise noted, the cement used for preparing mortar samples was all referred to the Cem-0. Mortars were prepared in a standard rotary blade mixer according to the mixture proportions shown in Table 3, and the cement to sand ratio of the mortars was kept at 0.30. Mixing procedure was in accordance with EN 196-1.

EXPERIMENTAL RESULTS AND DISCUSSION

Determination of water retention property by low-field NMR

The transverse relaxation time(T2) of the mortar samples prepared with Cement-0, Cement-1 and Cement-2 before and after the water retention test was depicted in Fig. 3. It can be seen that different cements in the mortar can generate various T2 distribution curves before the water retention test. The M-0 express that T2 peak mainly distribute between 0.881ms to 30ms, and the peak position (8.21 ms) was closer to the left in the relaxation graph compared with the M-1 and M-2. This was mainly due to the fact that the cement-0 is finer which results in more water being attached on the cement particles as well as a dense

Table 3—Mix design of the mortars for every patch

	Formulations				
	Bentonite (%)	Attapulgit (%)	HPMC-1(%)	HPMC-2(%)	W/C
M-0	0	0	0	0	0.52
M-1	0	0	0	0	0.59
M-2	0	0	0	0	0.55
MB	0.2-1.0	0	0	0	0.55
MA	0	0.2-1.0	0	0	0.55
MC ₁	0	0	0.02-0.1	0	0.55
MC ₂	0	0	0	0.02-0.1	0.55

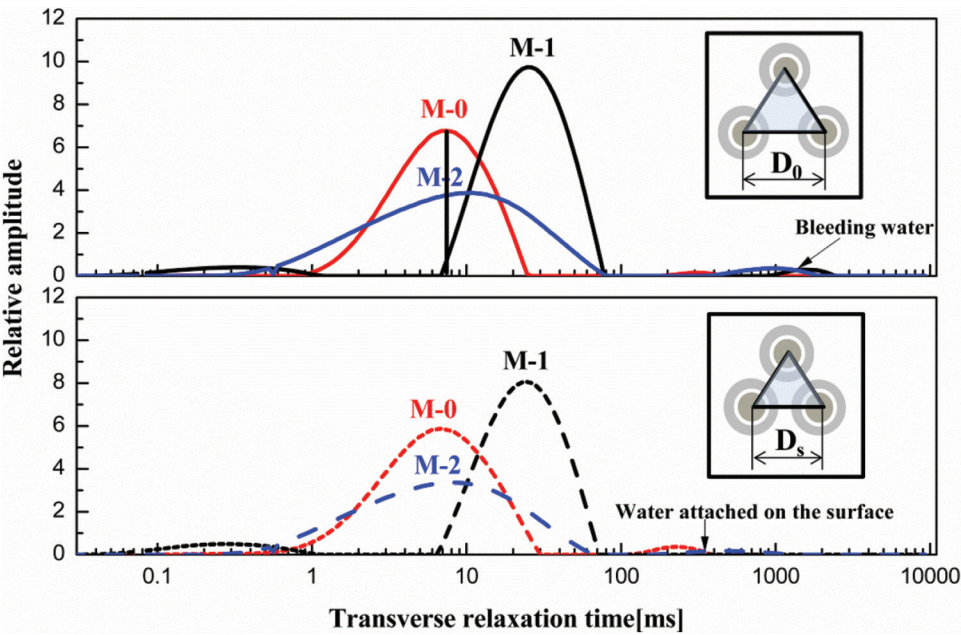


Fig. 3—Transverse relaxation time of mortars prepared with three kinds of cements before and after the water retention test (insert picture indicated the variation of distance between the solid particles

structure. The finer particles will also hydrate faster and this would also lead to a denser structure, at least initially. In addition, the paramagnetic species (Fe_2O_3 , etc.) present in the Cement-0 (Fe_2O_3 : 1.28%) also accelerate the time of transverse relaxation which contributes to forming a small T2 value. These conclusions have been drawn by others in the literatures,^{13,17} and it is obvious that the T2 peak of M-2 has a relative large range from 0.05 ms to 78.21 ms because the Cement-2 has a high content of Fe_2O_3 (4.54%). This probably greatly overwhelms the H^+ proton (mainly exists in the water molecules) to relax to its initial state in the NMR experiments. Besides, a small peak (500 ms-100000 ms) generated by a minor amounts of bleeding water was also found in the Fig 3. After the water

Table 4—Water retention rate of the three kinds of mortar

	M-0	M-1	M-2
Water retention capacity (JGJ/T70-2009)	90.66	89.54	91.26
Standard deviation/%	1.51	1.72	1.86
$W(R)$ (Low field NMR)/%	92.81	91.31	94.08
Standard deviation /%	0.44	0.35	0.93

retention test, it can be clearly identified that the T2 peaks all shifted to the left which was resulted from both the draining out water and the compression of the mortar by the ballast (described in Fig. 2). Also, a minor peak formed by the water attached on the surface of the mortar can also be found in the T2 distribution. The author believes that the water retention property can be evaluated by contrast between T2 distribution of sample the before and after the water retention test. Therefore, Eq. (4) based on the data of the T2 distribution was founded by this paper.

$$W(R) = \frac{S_A(T) + S_A(P) + S_A(S)}{S_{T=0}} \times 100 \quad (4)$$

where, $S_A(T)$ is the peak area of water in flocculation; $S_A(T)$ I'd the peak area of water between solid parties; $S_A(s)$ is the peak area of water attached on the surface of mortar; $S_{T=0}$ is the peak areas of all peaks founded in the T_2 distribution before the water retention test. The results of water retention rate ($W(R)$) or capacity calculated by the Eq. (4) and parallel test (JGJ/T70-2009) results is summarized in the Table 4.

Table 4 shows that the results achieved by the conventional method and the proposed method all confirm that M-2 has the highest water retention rate and M-0 has a higher water retention capacity than M-1. Moreover, the results shown in Table 4 indicate that the method proposed in this paper is more precise (a lower standard deviation) than the conventional method which suggests that the proposed method based on low-field NMR has a good stability and excellent repetition for bleeding test, and the standard deviation for the M-0 is 0.9% which is higher than that of the M-1 and M-2. This suggests the paramagnetic species in the cement indeed influence the accuracy of the proposed method for determination of the water retention capacity. Unlike the method suggested in the JGJ/T700-2009, our proposed method is efficient to detect water in the mortar without damage to the sample. Thus, artificial errors could be avoided because reducing unnecessary procedure are not needed. Simultaneously, the peak of T2 distribution (generally 0.80ms-150.13ms) associated with the microstructure of mortars which provides us a hard-won access to the spacing between solid particles for the further research on water retention capacity.

Influence of admixture on the water retention property

From the proposed method in this study, the water retention of the fresh state cement based mortar can be determined. Fig. 4(a) and Fig. 5(a) shows the evolution of water retention rate as a function of the dosage of water retention agent introduced. As expected, the water retention of the fresh state cement based mortars all increases, when increasing the water retention agent. In Fig. 4(a), the non-admixture containing sample exhibits a low

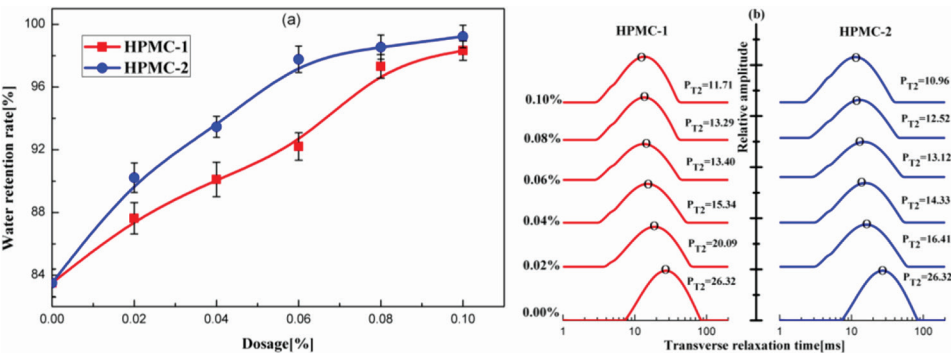


Fig. 4—Water retention property (a) and transverse relaxation time distribution (b) of the mortars containing different amounts of organic water retention agents (HPMC1 and HPMC, from 0.0% to 0.1%)

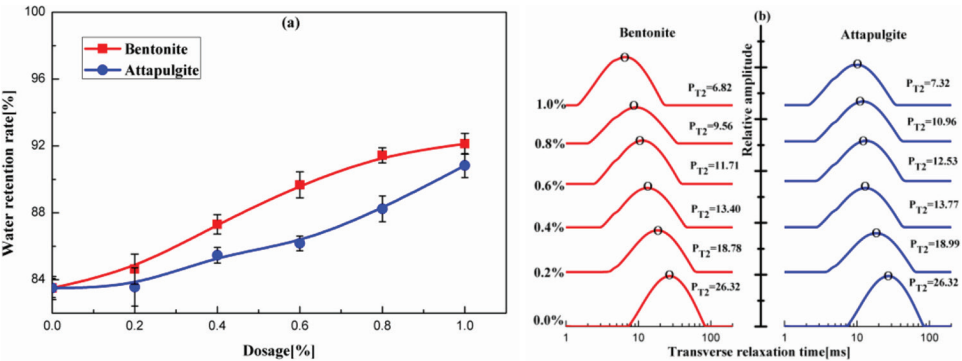


Fig. 5—Water retention property (a) and transverse relaxation time distribution (b) of the mortars containing different amounts of mineral water retention agents (bentonite and attapulgite from 0.0% to 1.0%)

water retention capacity of about $83.5\% \pm 0.6\%$. Then, the water retention increases with the use of HPMC-1 and with increasing polymer dosage,^{8,9} until reaching a plateau with very high WR values ($> 99.23\%$), and the water retention rate of the mortars mixing with the HPMC-2 is higher than that of the mortar which added HPMC-1 when the dosage are same. Additionally, in Fig. 5(a), it was found that the water retention increases with the use of bentonite and with increasing the dosage to the 1.0% of the cement content, the WR values is up to 92%, and the water retention rate of the mortars mixing with the bentonite is higher than that of the mortar which added attapulgite when the dosage are same.

Comparison results in Fig. 4(a) highlight the positive impact of molecular weight of HPMC on WR values of mortars. Indeed, the water retention is strongly improved by the use of HPMC-1 compared to HPMC-2, even at low dosages. It was believed^{5,8} that the soluble molecules of HPMC can distributes inside the mortar, meanwhile the solid particles are surrounded by forming molecular films, and the water in the mortar is confined in

both the macromolecular and the space between the solid particles. Fig. 4 (b) provides the insight into the microstructure of the mortars containing different amounts of organic water retention agents. It can be seen that T_2 peak position of the mortars all shifted to the left (HPMC-1: from 26.32 ms to 11.71 ms, and HPMC-2: from 26.32 ms to 10.96 ms) by increasing the amount of the organic water retention agents, and the T_2 peak position of mortars mixed with HPMC-2 was more sensitive to the amount of the organic water retention agent. Fast exchange theory¹³⁻¹⁵ concerning the NMR relaxation of water molecules in the porous medium considered that the T_2 value correlates with distance between solid particle surfaces. This accounts for the difference of water retention capacity of the mortars in Fig. 4(a).

The bentonite particles can form a network structure (usually called thixotropic gels) which hold water inside the body, and the volume expansion could be 30 times its own volume. Attapulgite clays used in this study also can absorb water to a certain extent, however the adsorption of attapulgite efficiency is too low to be applied in the mortars compared to the bentonite. Thus, it was observed in Fig. 5(b) that the transverse relaxation time distribution of the mortars containing different amounts of mineral water retention agents. It was observed that T_2 value of the mortars all decrease with the increasing bentonite and attapulgite, and compared with attapulgite, the bentonite was better able to change the microstructure of the mortars (T_2 position from 26.32 ms to 6.82 ms). Certainly, paramagnetic species (Fe_2O_3 , etc) also contribute to accelerating the relaxation rate of the water in the mortars. Even though the bentonite and attapulgite have almost identical iron content (5.80% for bentonite and 5.82% for attapulgite), mortars prepared with bentonite exhibit shorter T_2 values than attapulgite containing sample under the same admixture amount. This suggests that bentonite was better able to reform the microstructure of the mortars compared with attapulgite.

Relationship between the water retention property and microstructure

Without damage to the sample, the method based on NMR technology proposed in this study can both obtain the amounts of water (expressed as relative amplitude) and the water distribution inside the mortar. Fig. 6 shows the correlation between WR (water retention rate) measured by conventional method (JGJ/T70-2009) and water retention rate by low field NMR. Because of the sensitivity to the water molecules, low-field NMR can obtain the amount of water as well as the distribution of the water in the mortars,¹⁸ and it can be seen that the method proposed in this paper are suitable to detect the water retention property of mortars. In addition, it is found that the WR of the samples determined by NMR are linearly correlated with the results of the conventional method (JGJ/T70-2009). Even though the paramagnetic substance may have impacts on the NMR effects of water inside the fresh mortars, the linearity of up to 0.914 suggests that the water retention property depicted by the proposed method is consistent with the conventional method, and the analysis on results mentioned above is reasonable.

CONCLUSIONS

1. The method proposed in this paper can rapidly and precisely obtain the water retention capacity, and has a unique superiority on study of microstructure of fresh state cement based mortar. Results confirmed the cements in mortars could keep different water retention

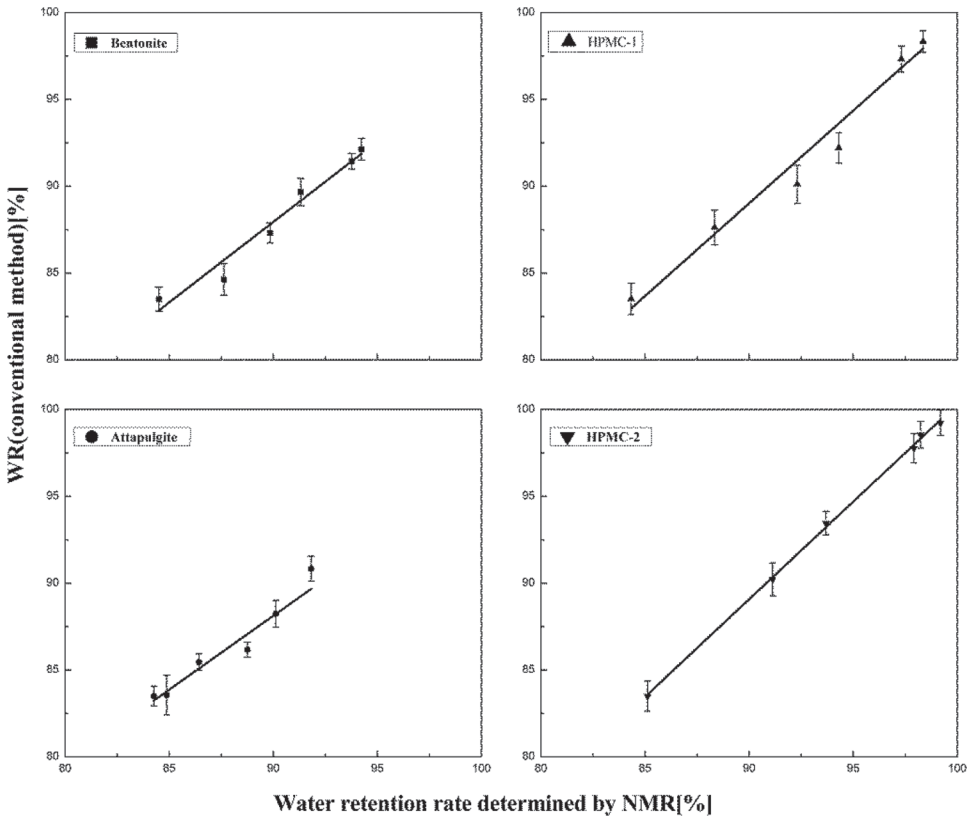


Fig. 6—Relations between water retention rate measured by NMR and WR determined by conventional method (JGJ/T70-2009)

tion capacity under same water absorbing regime which was consistent with results with the conventional method.

2. The addition of water retention agents can reform the microstructure of the fresh mortars(T2 values shift to the left) which increases the water retention capacity. Under same water absorbing regime, water retention capacity of the mortars is increased by the amount of the water retention agents.

3. The paramagnetic substance may have impacts on the NMR effects of water insides the fresh mortars, the linearity is more than 0.914, which suggests that the water retention property depicted by the proposed method is consistent with the conventional method.

The method used in this paper has exhibited its superiority on studying the water retention capacity and microstructure of fresh state mortars. In further investigations, it should be interesting to extend this study to permeability of the mortars. Also, the evolution of mortar microstructure of the mortar should be studied by using complimentary methods and the results should be compared with the method involved in this paper.

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Study on Polycarboxylate Superplasticizer with Slump Retention Capacity

by Zhenping Sun, Lelin Wu, Yanliang Ji, Xu Yang,
Yuansong Sun, and Chao Chen

The synthesis and performance of slump retention type polycarboxylate superplasticizer using different functional monomers are shown. These polycarboxylate superplasticizers are synthesized using methyl acrylate, hydroxyethyl acrylate, hydroxypropyl acrylate respectively. The best molar proportion of different monomers for synthesis is tested. Properties of these polycarboxylate superplasticizers are compared according to the fluidity of cement paste and their slump retention of concrete. The compositions of these polycarboxylate superplasticizers are described by IR and GPC. From these comparisons, polycarboxylate superplasticizers using hydroxypropyl acrylate have the best properties. Relatively better reaction conditions are determined as: 45°C (113°F) as reaction temperature, 3 hours as dropping time and 1% H₂O₂/0.15% ascorbic acid as initiator, 0.35% TGA as chain transfer agent. According to the results, polycarboxylate superplasticizers with higher slump retention capacity would be able to produce.

Keywords: polycarboxylate superplasticizer; slump retention; synthesis.

INTRODUCTION

With the developments of the construction industry in the recent years, the command of the performance of concrete has increased greatly. Nowadays, among the chemical admixtures, water reducing agent has become the indispensable part of concretes. In modern engineering, the water to cement ratio of concrete is getting lower due to the requirements of high strength. In this case, concretes with the capacity to maintain its slump for a longer time are needed. Besides, as concrete industry became commercialized, the construction sites of concrete are far away from its production sites, which calls for concretes with longer sustained slump as well. As a third-generation high performance concrete admixture, polycarboxylate superplasticizer (PCE) has been widely used in engineering construction at home and abroad due to its high water reducing rate, good slump retaining capacity and convenient molecular design.¹⁻⁵

In order to obtain a polycarboxylate superplasticizer with better slump retention, numerous scholars have carried researches on the synthesis. The researches were carried on several aspects including molecular weight, side chain length, species and proportion

of monomers and so on. The study of molecular weight and side chain length showed that the molecular structure of polycarboxylate superplasticizer mainly affected the adsorption capacity and steric hindrance effect of polycarboxylate superplasticizer.⁶⁻¹⁰ He Yan¹¹ studied on the adsorption performance and dispersion capacity of polycarboxylate superplasticizers with different functional groups. Her research showed that the polycarboxylate superplasticizers with amide groups lowered the fluidity of cement paste, while the adsorption performance of polycarboxylate superplasticizer containing sulfonic group was enhanced. A large number of studies have proved that ester groups and other functional groups have a great influence on the slump retention capacity of polycarboxylate superplasticizer. Tan Hongbo¹² studied the effect of ester monomers on polycarboxylate superplasticizer. The study showed that the introduction of ester group reduced the initial adsorption capacity of polycarboxylate superplasticizer, but improved its adsorption and dispersion properties in the following time. At present, there are three main methods to improve the slump retention capacity of polycarboxylate superplasticizer: carboxyl group protection, crosslinking synthesis of polycarboxylate superplasticizer and synthesis of amphoteric polycarboxylate superplasticizer.^{13,14}

This study focused on the types and proportion of functional monomers, using methyl acrylate, ethyl acrylate and hydroxypropyl methacrylate as functional monomer to synthesize polycarboxylate superplasticizers with slump retention capacity. The effect of different products on slump retention was compared, and the products with better performance were compared.

RESEARCH SIGNIFICANCE

The relationship between structure and performance of polycarboxylate superplasticizer has been the key and difficult point of the synthesis of polycarboxylate superplasticizer. This research may provide some help for revealing the structure-performance relationship of polycarboxylate superplasticizer.

EXPERIMENTAL

Materials

The main materials and reagents used in this experiment are: Methyl allyl polyoxyethylene ether, of which molecular weight is 2400(HPEG); acrylic acid (AA); methyl acrylate (MA); hydroxyethyl acrylate (HEA); hydroxypropyl acrylate (HPA); hydrogen peroxide (H_2O_2), 30%; mercaptoacetic acid (TGA); ascorbic acid; P.O.42.5 Portland cement.

Specimens

Polycarboxylate superplasticizer tested was synthesized by solution free radical copolymerization method. Firstly, put a certain amount of HPEG and deionized water into a round bottom flask and heat the solution to 45°C (113°F). The solution A was prepared with the reducing component of initiator, chain transfer agent and deionized water, the solution B was prepared with monomers weighing in proportion and deionized water. In the reaction, the oxidation component of initiator was added into the HPEG solution at one time, then solution A and B were added in accordance with the dropping rate of A solution 3.5h/B solution 3h, and the time of heat preservation was 0.5h.

Table 1-Synthesis plan

Functional monomers	Test number	mole ratio n(HPEG):n(AA):n(ester)
MA	MA3.0	1:2.0:3.0
	MA3.2	1:1.8:3.2
	MA3.4	1:1.6:3.4
	MA3.6	1:1.4:3.6
	MA3.8	1:1.2:3.8
	MA4.0	1:1.0:4.0
HEA	HEA3.0	1:2.0:3.0
	HEA3.2	1:1.8:3.2
	HEA3.4	1:1.6:3.4
	HEA3.6	1:1.4:3.6
	HEA3.8	1:1.2:3.8
	HEA4.0	1:1.0:4.0
HPA	HPA3.0	1:2.0:3.0
	HPA3.2	1:1.8:3.2
	HPA3.4	1:1.6:3.4
	HPA3.6	1:1.4:3.6
	HPA3.8	1:1.2:3.8
	HPA4.0	1:1.0:4.0

The cement pastes were prepared by using a low-speed mixer with a water/cement (w/c) ratio of 0.29, with 0.12% of polycarboxylate superplasticizer. On the basis of previous experiments, it was found beneficial to improve the slump retention performance of polycarboxylate superplasticizer when the molar proportion (against HPEG) of esters increased over 3. Therefore, the molar proportion of ester was set over 3. The test plan was shown in **table 1**.

The specimens for infrared spectrum were prepared by KBr method.

Items of investigation

Fourier transform infrared spectrometer (FTIR-650) was used, and the functional groups in the polycarboxylate superplasticizers were analyzed.

The cement pastes were determined referring to GB/T8077-2012.¹⁵ Methods for testing uniformity of concrete admixture”, the fluidity of cement paste of 1h, 2h and 3h were tested respectively.

The concrete was tested referring to GB8076-2008¹⁶ concrete admixture, in which concrete slump of reference concrete and concrete with polycarboxylate superplasticizer was controlled at (210±10 mm [8.26±0.39 in.]).

The molecular weight distribution of polycarboxylate superplasticizer was obtained by the gel permeation chromatography analysis.

EXPERIMENTAL RESULTS AND DISCUSSION

Fluidity of cement paste

In **Fig. 1**, the fluidity of cement paste with different polycarboxylate superplasticizers was compared. It could be seen that MA 3.8 and HEA 3.8 had the weakest performance among

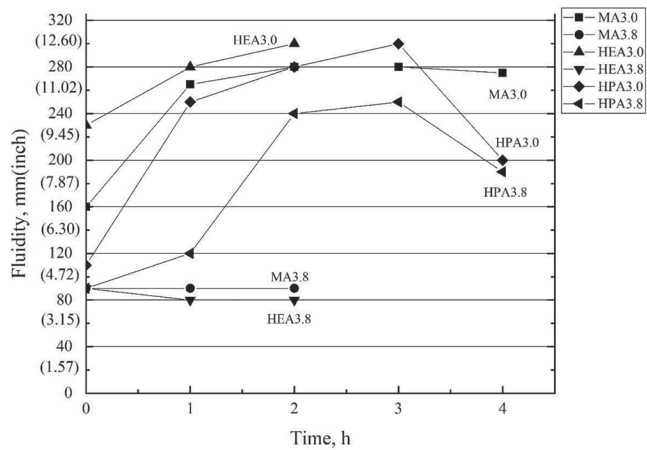


Fig 1-The fluidity of cement paste (w/c ratio = 0.29)

the six superplasticizers. The cement pastes initial fluidity were both less than 100 mm (3.94 in.), and they didn't increase with time passing by. The cement paste with HEA 3.0 has an initial fluidity of 230 mm (9.06 in.), then its fluidity obviously increased, however, serious segregation occurred at the time of 2 hour, its lower layer had begun to set. Cement paste with MA 3.0 had initial fluidity of 160 mm (6.30 in.) second to cement paste with HEA 3.0. Its fluidity increased in the following three hours and reached a maximum of 280 mm (11.02 in.), and then its fluidity started to decrease. As for the HPA group, cement paste with the two samples had lower initial fluidity than MA 3.0 and HEA 3.0. But their fluidity continued to increase until the third hour, and the maximum of them were 300 mm (11.81 in.) and 250 mm (9.84 in.) respectively.

Slump of concrete

After mixing concrete with the polycarboxylate superplasticizer containing methyl methacrylate group, the slump loss was serious within 10 min - 60 min respectively. The effect of using methyl acrylate to improve slump loss was not satisfying.

As shown in Fig. 2, with the molar proportion of HEA increased, the samples showed better long-term slump retention performance in concrete. HEA 3.0 and HEA 3.2 was weak in the concrete slump retention capacity. They both lost slump at the time of 1 hour. HEA 3.4 and HEA 3.6 lost slump slightly at the time of 1 hour, while HEA 3.8 and HEA 4.0 kept the slump for 2 hours. But even HEA 4.0, the best sample, had a little slump loss at the time of 2 hour.

In Fig. 3, with the molar proportion of HPA increased, the slump loss of polycarboxylate superplasticizer decreased. HPA 3.0 and HPA 3.2 lost their slump at the time of 1 hour. HPA3.4 kept its slump for 1 hour successfully, but couldn't kept it for 2 hours. HPA3.6 kept the 2-hour slump, and the slump lost at the third hour. The slump retention capacity of HPA 3.8 and HPA 4.0 were the best in this group. They were able to maintain the 3-hour slump. And at the time of 4 hour, the slump loss of concrete with HPA 4.0 was more than that with HPA3.8.

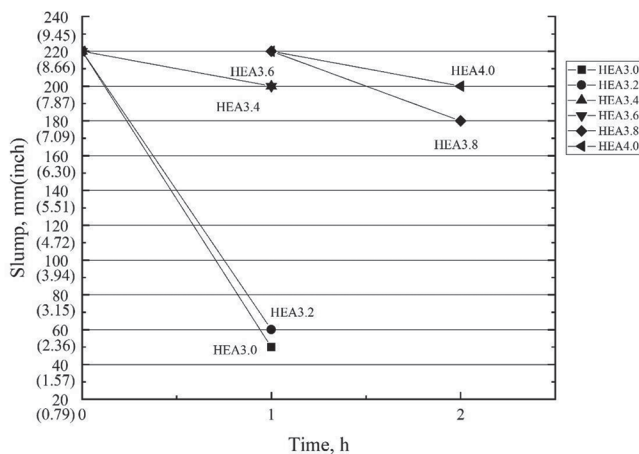


Fig 2-The slump of concrete using PCEs containing HEA (w/c ratio = 0.45)

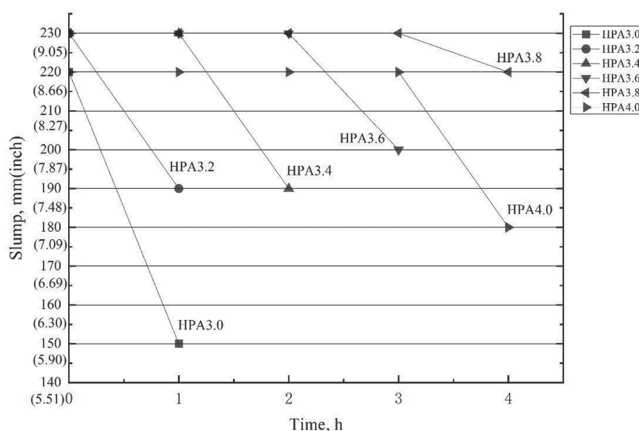


Fig 3-The slump of concrete using PCEs containing HPA (w/c ratio = 0.45)

The results of the three kinds of esters showed that ester monomers may improve the slump retention capacity of polycarboxylate superplasticizers to a certain degree, and with the increase of the molar proportion of esters, slump retention properties of polycarboxylate superplasticizer can be further improved. At the same time, different kinds of esters had different effects on improving the slump retention capacity of polycarboxylate superplasticizer.

Infrared spectrum and GPC analysis

According to the results of slump test, the samples of HEA3.0, HEA3.8 and HPA3.0, HPA3.8 were selected for infrared spectrum test and GPC, and the test results were shown in Fig. 4 and Table 2. From the infrared spectra of four samples it can be seen that in the

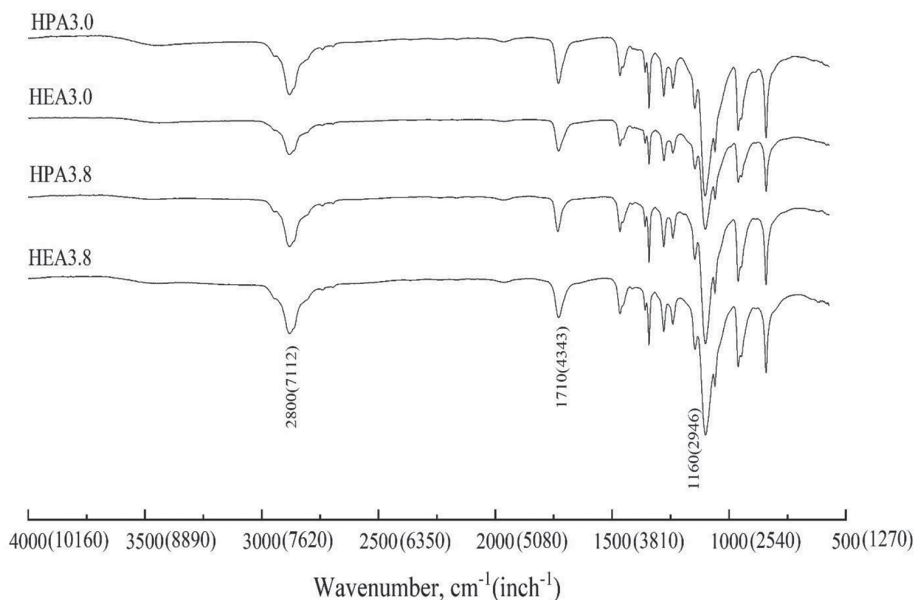


Fig 4-Infrared spectrum of samples

vicinity of 2800cm⁻¹(7112 inch⁻¹) there were methylene (-CH₂-) absorption peaks, and in the vicinity of 1160 cm⁻¹(2946.4 inch⁻¹) there were absorption peaks of ether (-C-O-C-), indicating that the HPEG monomers were successfully introduced into the four groups of samples. There were carbonyl (-C=O) stretching vibration peaks near 1710 cm⁻¹(4343.4 inch⁻¹), which showed that the four groups of samples were successfully introduced with acrylic acid and ester monomers. The analysis showed that the synthesized conditions could introduce the monomers into the polycarboxylate superplasticizer. What's more, from the GPC result it can be seen that the conversion rates of all samples tested were over 85%. Samples tested were synthesized by the monomers.

Discussion

In this experiment, the results of cement paste were different from that of concrete slump. The water/ cement ratio of cement paste was far lower than that of concrete, so the paste needed a polycarboxylate superplasticizer with higher dispersing performance to reach high initial fluidity in the cement paste needing. And the amounts of carboxyl groups in the MA 3.0, HEA 3.0, HPA 3.0 were higher than other three samples, so they had higher fluidity than other three samples. Cement pastes with MA 3.8 and HEA 3.8 set in the early times because of the poor initial adsorption of polycarboxylate superplasticizers, so that the fluidity in the later hours didn't increase.

Carboxyl protection is one of the mechanisms of how polycarboxylate superplasticizers help to reduce slump loss. By introducing hydrolysable groups, the effective action time of polycarboxylate superplasticizer is prolonged, that is to say, the slump retention capacity of polycarboxylate superplasticizer is improved. Infrared spectrum analysis showed that

Table 2- GPC results

Test number	M _w , g/mol (ounce/mol)	M _n , g/mol (ounce/mol)	PDI	Conversion rate, %
HEA3.0	46714 (1650.7)	31424 (1110.4)	1.49	87.5
HEA3.8	43655 (1542.6)	29056 (1026.7)	1.50	86.4
HPA3.0	50124 (1771.2)	35542 (1255.9)	1.41	89.6
HPA3.8	41852 (1478.9)	31255 (1104.4)	1.34	87.8

the synthesis successfully introduced MA, HEA and HPA into polycarboxylate superplasticizer with slump retention capacity. With the increase of the molar proportion of esters, the amount of carboxyl group on the main chain of polycarboxylate superplasticizer decreased. This lowered the initial adsorption performance of polycarboxylate superplasticizer, so that the amount of dissociative water reducing agents increased. With the passage of time, the ester groups hydrolyzed when exposed to the alkaline environment in cement paste. And the adsorption capacity of dissociative polycarboxylate superplasticizer increased, the water reducing agents were able to adsorb to the surface of unhydrated cement particles and hydration products. That's why the introduced ester group may prolong the effect time of polycarboxylate superplasticizer. The concrete test results showed that with higher ester proportion during the synthesis, the polycarboxylate superplasticizer would have a better slump retention capacity. For HPA, the improvement on slump retention performance of polycarboxylate superplasticizer reached a peak when molar proportion of HPA is 3.8, the performance of slump retention started to get worse when the HPA proportion continued to increase. This may be caused by different hydrolysis velocity.¹⁷ HPA 4.0 may hydrolyze faster than HPA 3.8 for its higher molar proportion of ester. In the experiments, at the time of 4 hour, the consumed HPA 4.0 may be more than HPA 3.8, so that the dispersion performance of HPA 4.0 was worse than that of HPA3.8.

FURTHER RESEARCH

It is desirable to test specimens made of other different kinds of ester groups, and efforts should be made to find out the relation between the ester groups and the performances of polycarboxylate superplasticizers.

CONCLUSIONS

Based on the results of this experimental investigation under normal environment, the following conclusions are drawn:

1. The introduction of esters into polycarboxylate superplasticizer can improve its slump retention performance, and different ester groups show different effects with respect to slump retention. In terms of MA, HEA and HPA, HPA is the best for the improvement of the slump retention capacity of polycarboxylate superplasticizer.

2. For the same kind of monomeric esters, it showed a positive correlation between ester proportion and the improvement of slump retention capacity for polycarboxylate superplasticizer.

plasticizer generally, but for HPA, when the molar proportion of ester increased to 3.8, the improvement on slump retention performance of polycarboxylate superplasticizer reached a peak, and when the proportion of ester continued to rise, performance of slump retention started to get worse. This may be caused by the different velocity of hydrolysis.

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