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Shrinkage reduction of cement-based materials containing polycarboxylate superplasticiser

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The purpose of this study was to investigate how the addition of shrinkage-reducing polycarboxylate superplasticiser (SRPC) affected the shrinkage of cement-based materials (CBMs). SRPCs can significantly reduce the surface tension of cement solutions. In this work, a new molecular structure of SRPC was synthesised; its surface tension was reduced to 34.1 mN/m, which is lower than that of ordinary polycarboxylate superplasticisers (PCEs). Compared with mortars without additives, the shrinkage-reducing ratios of mortars containing SRPC at 7 and 49 d were about 33 and 22%, respectively, for an SRPC dosage of 0.2% by mass of cement. The results showed that the SRPC reduced the shrinkage of CBMs more effectively than an ordinary PCE. Furthermore, the shrinkage mechanism of CBMs containing SRPC was assessed regarding three aspects: the change in the pore size distribution of the cement pastes with pore size below 50 nm, the reduction of the capillary pore pressure in the hardened cement pastes after the addition of a low-surface-tension SRPC and the reduction in the evaporation rate of moisture through SRPC aggregation on the gas–liquid interface in cement pastes.

Notation

A	area
D	pore diameter
L_0	inner length of mould (250 mm)
L_1	initial length of mortar
L_i	length of mortar after i days
M_n	number-average molecular weight
M_w	weight-average molecular weight
m_0	initial mass of solution
m_t	mass of solution after t hours
r	menisci curvature radius
R_i	shrinkage-reducing ratio of shrinkage-reducing polycarboxylate superplasticiser (SRPC) mortar and polycarboxylate superplasticiser (PCE) mortar relative to blank mortar (cement-based sample without admixture) after i days
S_i	shrinkage ratio after i days
S_{iB}	shrinkage ratio of blank mortar after i days
S_{is}	shrinkage ratio of SRPC and PCE mortar after i days
s	area of evaporating dish
t	evaporation time
V	volume intruded
γ_{LV}	surface tension of pore solution

θ	contact angle
μ	evaporation rate of solution
π	surface pressure
σ	capillary pressure

Introduction

Polycarboxylate superplasticisers (PCEs) are often used in large-scale concrete projects because of their remarkable water-reducing effect. However, PCEs cannot suppress concrete shrinkage and self-shrinkage in low-humidity environments, and even cause serious shrinkage on their own (Qian *et al.*, 2004; Wang and Zheng, 2008). Concrete cracking due to drying-induced shrinkage is a common phenomenon that threatens the durability and service safety of concrete structures. It has been extensively investigated and relevant theories have been proposed (Bentur *et al.*, 1979; Hung and Hui, 1997; Miu, 2018). As shrinkage is caused by moisture escaping from cement gel pores, capillary tension theory is very important when describing this process. When the free water in the capillary pores of cement-based materials (CBMs) escapes, the capillary tension causes drying shrinkage. Based on this, low molecular weight shrinkage-reducing agents (SRAs) with low

surface tensions have been used to reduce the shrinkage of concrete products (ACI, 2010; Rongbing and Jian, 2005). However, SRAs have been reported to have some negative effects on the mechanical properties and elastic modulus of concrete (Rajabipour *et al.*, 2008; Whiting *et al.*, 2000; Yoo *et al.*, 2015; Zhan and He, 2019). Additionally, they often have poor compatibility with PCE, which further deteriorates the performance of the mortar (Ma *et al.*, 2006; Wen and Yang, 2002; Yang, 2003).

Therefore, a new class of polymers – called shrinkage-reducing polycarboxylate superplasticisers (SRPCs) – has been synthesised to act as shrinkage- and water-reducing agents. An important feature of SRPCs is their low surface tension and, unlike PCEs, SRPCs generally contain a shrinkage-reducing monomer. When designing the shrinkage-reducing monomer, it is necessary to select an alcohol or ether with a specific structure, with low surface tension. Then, esterification of the alcohol or ether is performed using an acid to obtain the shrinkage-reducing monomer. The shrinkage-reducing monomer, the macromonomer and other co-monomers are copolymerised into the molecular structure of the PCE (Lu, 2013; Zhang, 2012). The surface tension of solutions containing 20–40% SRPC is generally between 45 mN/m and 32 mN/m. When the amount of SRPC is around 0.15–0.30% of the cement content, the long-term (>49 d) shrinkage ratio of the mortar is reduced by 15–25% compared with mortars without SRPC and its superplasticity is retained (Gu *et al.*, 2013; Lu and Xiong, 2014; Wang *et al.*, 2012; Zhou *et al.*, 2015).

Previous studies have shown that SRPCs can reduce the drying shrinkage of mortars, but there are still concerns about how SRPCs actually accomplish this. To address the above issues, a new SRPC was polymerised from a shrinkage-reducing monomer and other monomers. The shrinkage-reducing monomers that were copolymerised into the SRPC were formed by esterification of commercially available ethers and anhydrides. The structure of the SRPC was characterised using infrared spectroscopy and the shrinkage of the mortars containing SRPC was also tested. Then, an analysis was performed to determine the mechanism by which the SRPC reduces mortar shrinkage. The drying shrinkage of CBMs is closely related to their pore structure and the surface tension of the pore solution. In addition, moisture evaporation in the internal pores is a major cause of shrinkage when the relative humidity (RH) of the external environment is low. Therefore, the shrinkage mechanism of the SRPC was investigated with regard to three aspects: the change in pore size and its distribution, the change in pore pressure and the water evaporation rate.

Research significance

When formulated at low percentages, SRPCs can reduce the shrinkage in CBMs and maintain a good water-reducing effect.

The focus of this study was to determine how SRPCs suppress the shrinkage of CBMs. The findings provide theoretical results to facilitate future SRPC research.

Experimental materials and methods

Materials

Maleic anhydride (MA), anhydrous acrylic acid (AA), diethylene glycol monobutyl ether (DB), sodium methacrylate (MAS), *p*-toluenesulfonic acid (*p*-TSA) monohydrate, methyl allyl polyoxyethylene ether (TPEG, $M_w = 2400$ g/mol), ammonium persulfate (APS) and toluene were used as-received (all >98% purity). Sodium hydroxide (NaOH) and potassium hydroxide (KOH) were used to prepare a salt solution. Anhydrous ethanol was used to terminate cement hydration. A cellulose ester semi-permeable membrane (MD44-7) with a nominal molecular weight cut-off of 7000 Da was used to purify polymers. Reference cement and ISO standard sand were used for property evaluations. The chemical and mineral composition of the cement is provided in Table 1. The particle size distribution of the sand is shown in Table 2. Deionised water was used throughout, including polymer synthesis and the preparation of cementitious mixtures.

Synthesis of the shrinkage-reducing monomer

The shrinkage-reducing monomer with a low surface tension, called MA-22, was synthesised by esterification of *p*-TSA as a catalyst, MA and DB. DB and MA in a molar ratio of 1:1.5, *p*-TSA and toluene were sequentially added to a four-

Table 1. Chemical and mineral composition of reference cement

	Composition: %
Silicon dioxide (SiO ₂)	22.93
Aluminium oxide (Al ₂ O ₃)	4.29
Ferric oxide (Fe ₂ O ₃)	2.89
Calcium oxide (CaO)	66.23
Magnesium oxide (MgO)	1.92
Sulfur trioxide (SO ₃)	0.35
Sodium oxide (Na ₂ O)	0.70
Free calcium oxide	0.64
Tricalcium silicate (C ₃ S)	58.78
Dicalcium silicate (C ₂ S)	21.38
Tricalcium aluminate (C ₃ A)	6.49
Tetracalcium aluminoferrite (C ₄ AF)	8.77

Table 2. ISO standard sand particle distribution

Sieve size: mm	Accumulated sieve residue: %
2.0	0
1.6	7 ± 5
1.0	33 ± 5
0.5	67 ± 5
0.16	87 ± 5
0.08	99 ± 1

necked round-bottomed flask, followed by heating at 120°C with stirring. The esterification reaction was allowed to proceed for 7 h and the water produced during the reaction was removed by reflux of toluene. After reaction completion, excess MA and toluene were removed by vacuum distillation.

Synthesis of the SRPC

MA, AA, TPEG and MA-22 were used as co-monomers, APS as the initiator and MAS as the chain transfer agent copolymerised into SRPC. TPEG, MA-22 and MA were diluted with distilled water in a four-necked round-bottomed flask that was placed in a constant temperature bath at $60 \pm 1^\circ\text{C}$, and then AA, APS and MAS aqueous solutions were added to the flask dropwise while stirring over a period of 3 h, followed by a reaction time of 2 h. The molar ratio of the reactants was TPEG:MA-22:MA:AA:MAS = 0.75:0.25:1:3:0.5. The APS amount was 1% of the sum of the mass of monomers. Similar to PCE, SRPC is a comb-shaped polymer. PCE was synthesised as a reference sample for infrared spectroscopy measurements. The PCE polymerisation process was identical to that of the SRPC, except that the MA-22 monomer was replaced by TPEG.

Characterisation of the SRPC

Size exclusion chromatography (SEC)

The number-average molecular weight (M_n), weight-average molecular weight (M_w) and the polydispersity index ($\text{PDI} = M_w/M_n$) of PCE and SRPC samples were determined at 30°C using a Waters PL-GPC50 instrument (Polymer Laboratories, UK) equipped with a PL Aquagel-OH Mixed 8 μm chromatographic column fitted with differential refractive index, laser light scattering and capillary viscometer detectors. The laser light scattering detector and refractive index detector were used to determine M_w , M_n and the PDI of the prepared polymers.

All samples were dissolved in water at a concentration of 0.1 m/m%, and filtered through a 0.45 μm polyethersulfone filter to avoid column plugging by solids or other insoluble impurities. Prepared samples with approximate masses of 4 g were injected using a PL-AS RT GPC auto-sampler. The mobile phase was deionised water with an injection volume of 100 ml and a flow rate of 1 ml/min. Polyethylene glycol standards with narrow PDIs were used to construct a calibration curve and used to obtain the molecular weights and polydispersity indices of the SRPC and PCE (Table 3).

Table 3. Molecular weights of PCE and SRPC and spread diameters of corresponding cement pastes

	M_w	M_n	PDI	Spread diameter: mm
PCE	42 653	23 564	1.81	280
SRPC	46 082	19 863	2.32	270

Purification of synthesised SRPC

The polymer synthesis did not reach 100% conversion, and the SRPC product mixture contained fractions of polymer, oligomer, unreacted macromonomer, low molecular weight monomers and a tiny amount of salts from decomposition of the initiator. For infrared spectroscopy measurements, the SRPC was purified using a cellulose ester semi-permeable membrane (MD44-7) with a nominal molecular weight cut-off of 7000 Da (Zhang *et al.*, 2015). The PCE, which was used as the reference sample for the infrared spectrum, was purified in the same manner as the SRPC.

Fourier transform infrared (FTIR) analysis

The solid SRPC, MA-22 and PCE samples were mixed with potassium bromide (KBr) (1 mg solid-state PCE, 200 mg potassium bromide) and pressed into pellets prior to FTIR measurements. The FTIR spectra of the SRPC and PCE were detected using a Vertex 70 FTIR spectrometer (Bruker Co., Germany) at 25°C by scanning the sample pellets. In all cases, 32 scans in transmission mode were used to obtain the spectra, with a scanning range of 4000–450 cm^{-1} and a resolution of 4 cm^{-1} .

Experimental methods

Spread diameter of cement pastes

The spread diameter of fresh cement pastes containing SRPC and PCE was tested according to the Chinese standard GB/T 8077-2012 (SAC, 2012). The water-to-cement (w/c) ratio was fixed at 0.29 and the agent dosage was 0.2% by mass of cement.

Mortar shrinkage measurements

Since cement pastes are rarely applied directly in practical engineering, the shrinkage of mortars was investigated. Preparation and curing of the mortars were carried out according to the Chinese standard JC/T 603-2004 (SAC, 2004). Following this standard, the mass ratio of cement to standard sand was set at 0.5. The SRPC and PCE dosage was 0.2% of the mass of cement. The spread diameters of the samples were 130–140 mm. Compared with the mortars without admixture, the water consumption of the mortars containing SRPC and PCE decreased by 20.5% and 22.1%, respectively.

Moulds of size 25 mm $\times$ 25 mm $\times$ 280 mm were used to prepare samples. The specimens were cured for 24 h at a temperature of $20^\circ\text{C} \pm 1^\circ\text{C}$ and RH of $\geq 90\%$ and they were then demoulded and stored in water for 48 h in an air-conditioned room at 25°C. Drying shrinkage experiments were conducted immediately after the samples were removed from water, with their initial lengths recorded. The sample curing conditions were $20 \pm 1^\circ\text{C}$ and RH = $55 \pm 5\%$, and changes in the sample lengths were measured for 49 d using a comparator. The shrinkage ratio of the mortar specimens was calculated using

$$1. \quad S_i = \frac{L_1 - L_i}{L_0} \times 100$$

where S_i is the shrinkage ratio after i days (in %), L_1 is the initial length of the mortar (mm), L_i is the length of the mortar after i days (mm) and L_0 is the inner length of the mould (250 mm).

Surface tension of SRPC and PCE in salt solution

The M solution (0.05 mol/l sodium hydroxide + 0.35 mol/l potassium hydroxide) had a pH value identical to that of the cement pore solution. The surface tension of the SRPC and PCE in the M liquid phase was measured at room temperature using a JZHY-180 surface tension meter. Each sample was tested three times and the average value was used for analysis.

Contact angle of SRPC and PCE solutions on cement paste block surface

The contact angles of the SRPC and PCE solutions (40 m/m%) on cement paste blocks were tested at 25°C using an LXS-II hole contact angle meter. The cement block was prepared by polishing the surface of the cement pastes after 7 d hydration. The length, width and height of the samples were 5 mm, 5 mm and 3 mm, respectively. Measurements were repeated three times and the average value was taken as the contact angle.

The polishing process of the cement blocks was as follows.

- 600#, 800# and 1500# metallographic sandpapers and 2000# green silicon carbide sandpapers were used to polish samples. For each change of sandpaper, the sample was rotated 90° to remove scratches left by the last polishing.
- The surface of the primary polished sample was polished with a synthetic diamond abrasive paste diluted with a mixture of glycerol and distilled water (volume ratio = 1 : 1).
- Samples were rinsed and cleaned with ethanol for 2 min and then dried.

Pore structure of cement pastes

The pore structure of the cement pastes was determined using mercury porosimetry (MIP). The dosage of SRPC and PCE was 0.2% by mass of cement, with a w/c mass ratio of 0.29, 0.21 and 0.20 for the blank sample, the SRPC and PCE, respectively. After the cement pastes were cured to a specific age, the samples were crushed into particles of about 3–5 mm in diameter and cement hydration was terminated using anhydrous ethanol. The samples were then vacuum-dried for 24 h.

Samples were prepared with identical spread diameters since PCE is often used to improve the dispersion of cement to reduce water usage in practical engineering applications. Thus, samples with the same spread diameters would more closely reflect pore structure changes than those with the same water consumption.

Evaporation rate of SRPC and PCE in M solution

Different amounts of SRPC and PCE were added to deionised water and the M solution to prepare a series of solutions with different concentrations. Fifty grams of the prepared solution was transferred to an evaporating dish with a diameter of 105 mm, which was placed in an oven at a constant temperature of 65°C. After standing for 10 h, the mass of the solution was measured with an analytical balance (accuracy of 0.0001 g) and the evaporation rate was calculated using

$$2. \quad \mu = \frac{m_0 - m_t}{st}$$

where μ is the evaporation rate of the solution (g/cm² h), m_0 is the initial mass of the solution (g), m_t is the mass of the solution after t hours (g), s is the area of the evaporating dish (cm²) and t is the evaporation time (h).

Surface pressure–area isotherm measurements

The film of SRPC and PCE that formed at the gas–liquid interface was tested at 25°C with a prototype KSV Minitrough LB developed by KSV Chemicals (Helsinki, Finland). A monolayer was obtained by spreading the SRPC and PCE solutions on sodium chloride (NaCl) (1 mol/l) aqueous solution with an injection volume of 30 µl. The surface pressure–area (π – A) isotherms of solutions containing different concentrations of agents were recorded during compression.

Results and discussion

Structural characterisation of SRPC

The M_w , M_n and PDI of the SRPC and PCE were measured using SEC. As shown in Table 3, the PDIs of the SRPC and PCE were 2.32 and 1.81, respectively, indicating a relatively narrow molecular weight distribution. The refractive index curves of the purified SRPC and PCE are shown in Figure 1.

Figure 1. Refractive index SEC spectra of purified SRPC

As shown in Figure 2, the peak at 2912 cm^{-1} was attributed to the C–H absorption vibration peak of $-\text{CH}_3$ and $-\text{CH}_2$. The broad peak just above 3300 cm^{-1} in the PCE and SRPC was assigned to O–H stretching bands. The peak at 1634 cm^{-1} in the SRPC spectrum was assigned to the overlap of C=O in the AA repeating units and MA units. In addition, SRPC and PCE both showed a weak peak around 940 cm^{-1} , indicating that sulfonic ions were polymerised. Moreover, a characteristic band of TPEG also appeared at 1081 cm^{-1} in the SRPC and PCE for the C–O–C asymmetric stretch. In the spectra of MA-22, the 1713 cm^{-1} peak was attributed to the C=O elastic stretching peak in the ester bond. It is worth noting that there was a very faint saturated ether C–O–C vibration peak near 1100 cm^{-1} in the MA-22 spectrum, indicating that the

monobutyl ether was esterified. In the SRPC spectrum, the C=O vibration peak in the ester bonds of MA-22 also appeared at 1713 cm^{-1} , indicating that MA-22 was attached to the SRPC. However, it did not appear in the PCE spectrum since no MA-22 was present in the PCE. The presence of these characteristic peaks in the FTIR spectra demonstrates the successful copolymerisation of monomers into the SRPC.

Shrinkage of mortars

The drying shrinkage ratio of mortars at different curing ages is shown in Figure 4, where blank means a mortar without admixture and SRR indicates the shrinkage-reducing ratio results. To compare the shrinkage of the SRPC mortars and the blanks, Equation 3 was used to convert the shrinkage ratio of mortars to the shrinkage-reducing ratio relative to the blanks

$$3. \quad R_i = \frac{S_{iB} - S_{is}}{S_{iB}}$$

where R_i is the shrinkage-reducing ratio of the SRPC or PCE mortar relative to the blank mortar after i days, S_{iB} is the shrinkage ratio of the blank mortar after i days and S_{is} is the shrinkage ratio of the SRPC or PCE mortar after i days.

As shown in Figure 4, the shrinkage of the mortars showed a rapid change during the early ageing period. One significant contribution to early shrinkage is the self-desiccation and autogenous deformation that occurs at an early age. In addition, the hydration reaction of mortar in the initial stage is quick, meaning that moisture is quickly consumed, resulting in quicker shrinkage of mortars. The shrinkage-reducing ratios of the SRPC and PCE mortars were calculated using Equation 3 and the curves of shrinkage-reducing ratio with curing age are also shown in Figure 4. The shrinkage-reducing ratio of mortars containing SRPC was 33.7% at 7 d and 22.8% at 49 d, which were higher than that of the PCE mortar. Compared with the blank mortars, the shrinkage-reducing ability of the SRPC mortars was significantly higher.

Figure 4. Shrinkage of mortars at different hydration ages

These results indicate that the SRPC-dosed mortars had lower shrinkage, although the w/c ratio of the blank mortars was greater than that of the SRPC and PCE mortar. If only water consumption is considered, the blank mortar showed the smallest shrinkage (Gao *et al.*, 2013). Therefore, the shrinkage-reduction mechanism of SRPC was further assessed.

Analysis of the shrinkage-reduction mechanism of CBM containing SRPC

Effect of SRPC on pore size distribution

The drying-induced shrinkage of a CBM is closely related to its internal pore size distribution, especially capillary pores with diameters of 2–50 nm when the RH is below 50% (Collins and Sanjayan, 2000). The pore structure and pore size distribution of cement pastes were tested using MIP. The cumulative mercury intrusions of the cement pastes at 3 d and 28 d are shown in Figure 5 and the calculated pore size

Figure 5. Cumulative mercury intrusion of cement pastes at (a) 3 d and (b) 28 d

Table 4. Pore structure and size distribution of cement pastes

	Hydration time: d	Total pore volume: ml/g	Porosity: %	Pore size distribution: %	
				<50 nm	>50 nm
Blank paste	3	0.0859	20.2341	83.1626	16.8374
	28	0.0853	17.3156	61.1539	38.8461
PCE paste	3	0.0882	17.9901	76.5258	23.4742
	28	0.0806	16.5134	70.6386	29.3614
SRPC paste	3	0.1168	24.9765	47.4029	52.5971
	28	0.1019	20.0143	47.6615	52.3385

distribution and porosity values are shown in Table 4. The pastes containing PCE had the lowest porosity, which was attributed to their low w/c ratio. In addition, the dispersion of cement particles by PCE also made the pore distribution uniform (Huang *et al.*, 2016).

Interestingly, the SRPC pastes had a higher cumulative mercury intrusion and porosity than the blank and PCE pastes, especially at 3 d. There was a significant increase in the proportion of pores >50 nm in the SRPC pastes, as shown in Table 4, indicating that SRPC can lead to air entrainment in cement pastes. This is a result of the ability of MA-22 in the molecular structure to reduce the surface tension of SRPC, which facilitates the generation and stabilisation of air bubbles. Moreover, there were significantly fewer <50 nm pores in the SRPC pastes compared with the PCE and blank pastes, regardless of the pore size distribution ratio or pore content. A lower content of <50 nm pores in the SRPC paste contributed to a reduction in shrinkage.

The pore size distributions of the cement pastes are shown in Figure 6. The corresponding pore of each peak is the most probable pore diameter, which represents the highest probability of occurrence in cement pastes. As shown in Figure 6, the blank and PCE pastes appeared to have one most probable pore diameter at 3 d and 28 d, while the SRPC paste appeared to have two most probable pore diameters with the second pore peak disappearing at 28 d. This was attributed to the introduction of the MA-22 monomer, which allowed the SRPC to entrain air and thus change the pore structure and pore distribution of the cement paste. The disappearance of the second pore size peak in SRPC at 28 d was attributed to the fact that hydration products are more likely to grow in the pore walls, so that the voids were gradually filled as the hydration reaction of the cement paste proceeded. As a result, the macro-pores became smaller, lowering the porosity.

Effect of SRPC surface tension on capillary pore pressure

The surface tensions of SRPC and PCE at different concentrations in the M liquid phase are shown in Figure 7. The figure shows that the surface tension decreased as the concentration increased and then stabilised after reaching a certain concentration, defined as the critical concentration. The critical concentrations of SRPC and PCE in M solution were about 6 g/l and

Figure 6. Differential curve of the pore size distribution of cement pastes at (a) 3 d and (b) 28 d

10 g/l, respectively. At concentrations greater than the critical concentration, the surface tensions of SRPC and PCE showed only slight changes upon further superplasticiser addition.

Capillary tension theory has been widely used to explain and predict the shrinkage of concrete when the environmental RH exceeds 50%, and the pore structure of concrete is a key parameter used for this prediction (Fisher and Israelachvili, 1981;

Figure 7. Surface tension of SRPC and PCE at different concentrations in M liquid phase

Huang *et al.*, 2019; Yue and Li, 2014). Capillary pressure can be calculated using the Laplace equation (Equation 4), in which the capillary pressure is proportional to the surface tension γ and inversely proportional to the menisci curvature radius, r

$$4. \quad \sigma = -2\gamma_{LV} \cos \theta / r$$

In this equation, σ is the capillary pressure (Pa), r is the menisci curvature radius (m), γ_{LV} is the surface tension of the pore solution (N/m) and θ is the contact angle.

The pressures of the corresponding individual capillaries were calculated by substituting the most probable pore sizes from Figure 6 into Equation 4, and the results are shown in Table 5. For the freshly prepared cement pastes, the concentration of SRPC or PCE (0.2% dosage of cement by mass) was about 6.8 g/l. The concentration exceeds the critical concentration as cement pastes are hydrated and therefore the surface tension at the critical concentrations of SRPC or PCE was selected to simplify the calculation. Since the surface tension and contact angle of the SRPC are much smaller than those of water, the pressure of the inward contraction of individual capillary pores in the SRPC pastes was much smaller than that of the blank

paste, as shown in Table 5. Using the same most probable diameter, the single capillary pressure of the SRPC paste with a surface tension of 34.1 mN/m was reduced by 25.2% compared with the PCE paste with a surface tension of 45.6 mN/m. This indicates that surface tension significantly affects the capillary pore pressure.

The pore pressure of pores <50 nm was calculated by substituting the pore size, surface tension and contact angle into Equation 4. The results (Figure 8) show that the pore pressure increased sharply as the pore size decreased, regardless of the hydration duration, which indicates that the internal pore pressure is very sensitive to the pore size. According to capillary tension theory, the main driving force of concrete shrinkage is the capillary pressure in the concrete pore walls when water is absorbed by the pores. The capillary pressure varies as the pore structure changes, which results in different concrete shrinkage characteristics. Therefore, changes in the pore size distribution, the content of <50 nm pores and surface tension of the pore solution greatly influence the shrinkage of CBMs.

Effect of SRPC on the evaporation rate of moisture

The evaporation of moisture in internal pores causes shrinkage in CBMs in a low-RH external environment (Jensen and Hansen, 2001). The moisture evaporation rates of the SRPC and PCE in pure water and M solution are shown in Figure 9. The moisture evaporation curves in the M solution and pure water showed consistent trends. The curves of evaporation in the M solution were lower than those for water, which indicates that the M solution produced a slower rate of water evaporation because the partial pressure of the water in solution M was lower.

At low concentrations, the evaporation rate accelerated as the concentration of SRPC or PCE increased. This is because the addition of SRPC or PCE reduced the surface tension of the solution, meaning that intermolecular forces at the solution surface were weakened, making it easier for water molecules to escape. The evaporation rates of the SRPC and PCE in the M solution reached their maximum values at concentrations of 2 and 6 g/l, respectively, as shown in Figure 9, and a further increase in concentration decreased the evaporation rate.

Table 5. Most probable pore diameters and single pore pressures of cement pastes

	Hydration time: d	Most probable pore diameter: nm		Surface tension: mN/m	Contact angle, θ : degrees	Calculated single pore pressure: MPa	
		Peak 1	Peak 2			Pressure 1	Pressure 2
Blank paste	3	26.5136	—	72.1	32.7	−9.2246	—
	28	21.4725	—			−11.3902	—
PCE paste	3	26.0796	—	45.6	18.5	−6.6325	—
	28	21.8223	—			−7.9265	—
SRPC paste	3	26.5142	24.318.7731	34.1	9.2	−5.0782	−5.3824 × 10 ^{−3}
	28	26.6995	—			−5.0429	—

Figure 8. Calculated pore pressure of pastes with <50 nm pores at (a) 3 d and (b) 28 d

Figure 9. Moisture evaporation rates of SRPC and PCE in pure water and in M solution

The evaporation rate was lower than that of the unmodified solution (containing no PCE or SRPC) when the SRPC concentration was above 8 g/l, and the corresponding value for the PCE concentration was 12 g/l. This occurred because some of the SRPC and PCE molecules spontaneously migrated to the gas–liquid interface, which prevented water escaping as the concentration increased. In addition, the SRPC prevented

Figure 10. Surface pressure–area (π –A) isotherms of SRPC and PCE in M solution

water evaporation better than the PCE as the concentration increased.

In the freshly prepared cement pastes, the SRPC and PCE concentrations were both about 6.8 g/l, which further increased with cement hydration. The concentration of SRPC and PCE generally exceeded 10 g/l in the internal pore solution of the CBMs, which suppressed moisture evaporation. Bentz *et al.* (2001) and Weiss *et al.* (2008) showed that a higher internal RH reduced shrinkage.

The fact that SRPC accumulated at the gas–liquid interface to form a molecular film is demonstrated by the results of the surface pressure–area (π –A) isotherms. Figure 10 shows the relationship between the surface area and membrane pressure of SRPC and PCE solutions at concentrations of 2 g/l and 10 g/l.

As shown in Figure 10, at a concentration of 2 g/l, a change in membrane pressure was not observed when the surface area decreased, indicating that the SRPC and PCE molecules did not form a film on the solution surface. However, at a concentration of 10 g/l, the membrane pressure increased when the surface area decreased, meaning that the SRPC and PCE formed films due to the accumulation of more molecules on the surface. In addition, the membrane pressure of the SRPC was higher than that of the PCE at the same surface area at a concentration of 10 g/l, meaning that the SRPC molecules more easily aggregated at the gas–liquid interface than did the PCE molecules, which prevented moisture evaporation.

Mechanism of action of SRPC in reducing the shrinkage of CBMs

A schematic diagram illustrating how SRPC reduces the shrinkage of CBMs is shown in Figure 11. The SRPC has an

Figure 11. Schematic diagram of the mechanism of SRPC on the shrinkage reduction of CBMs

effect due to three aspects: (a) SRPC will change the void ratio and capillary diameter of the CBM, which reduces the proportion of capillary pores smaller than 50 nm; (b) SRPC reduces the surface tension of the pore solution in the CBM, thereby reducing the contraction pressure of the capillary; (c) SRPC aggregates at the gas-liquid interface, which suppresses the evaporation of free water present in the pores of the CBM, thereby reducing shrinkage.

Conclusions

A PCE with a low surface tension was synthesised and its effect on the shrinkage of CBMs was investigated. The following experimental results were obtained.

- The surface tension of the SRPC was effectively decreased when copolymerised with a shrinkage-reducing monomer, synthesised by esterification of DGME and MA. In addition, the surface tension of the SRPC solution at its critical concentration was 34.1 mN/m.
- SRPC reduced mortar shrinkage effectively. Compared with blank mortars without additives, the shrinkage-reducing ratio of the SRPC mortars was 33.7% at 7 d and 22.1% at 49 d, for an SRPC dosage of 0.2% by mass of cement.
- The shrinkage-reduction mechanism of the SRPC was discussed in terms of three aspects. Firstly, the SRPC containing the shrinkage-reducing monomer changed the pore size distribution of the cement paste, which

contributed to a reduction in drying shrinkage. Secondly, the low surface tension of SRPC significantly decreased the pressure of the capillary pores. Thirdly, the SRPC typically gathered at the gas-liquid interface to form a monomolecular film, which suppressed moisture evaporation and maintained the RH inside the cement and thereby reduced the shrinkage.

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REFERENCES

- ACI (American Concrete Institute) (2010) *ACI 231-R10: Report on Early-Age Cracking Cause, Measurement, and Mitigation*. ACI, Farmington Hills, MI, USA.
- Bentur A, Milestone NB, Young JF and Mindess S (1979) Creep and drying shrinkage of calcium silicate pastes IV. Effects of accelerated curing. *Cement and Concrete Research* **9**(2): 161–169.
- Bentz DP, Geiker MR and Hansen KK (2001) Shrinkage-reducing admixtures and early-age desiccation in cement pastes and mortars. *Cement and Concrete Research* **31**(7): 1075–1085.
- Collins F and Sanjayan JG (2000) Effect of pore size distribution on drying shrinking of alkali-activated slag concrete. *Cement and Concrete Research* **30**(9): 1401–1406.
- Fisher LR and Israelachvili JN (1981) Experimental studies on the applicability of the Kelvin equation to highly curved concave menisci. *Journal of Colloid and Interface Science* **80**(2): 528–541.

- Gao YL, Zhang HL, Tang S and Liu H (2013) Study on early autogenous shrinkage and crack resistance of fly ash high-strength lightweight aggregate concrete. *Magazine of Concrete Research* **65**(15): 906–913, <https://doi.org/10.1680/mac.13.00004>.
- Gu Y, He Y, Zhao LB and Jiang YQ (2013) Synthesis and properties of shrinkage-reducing polycarboxylate superplasticizer. *Science, Technology and Engineering* **13**(10): 2887–2890.
- Huang H, Qian C, Zhao F et al. (2016) Improvement on microstructure of concrete by polycarboxylate superplasticizer (PCE) and its influence on durability of concrete. *Construction and Building Materials* **110**: 293–299.
- Huang LP, Hua JM, Kang M, Zhou F and Luo Q (2019) Capillary tension theory for predicting shrinkage of concrete restrained by reinforcement bar in early age. *Construction and Building Materials* **210**: 63–70.
- Hung GX and Hui RY (1997) *Shrinkage of Concrete*. China Railway Publishing House, Beijing, China.
- Jensen OM and Hansen PF (2001) Autogenous deformation and RH-change in perspective. *Cement and Concrete Research* **31**(12): 1859–1865.
- Lu F (2013) *The Preparation and Action Mechanism of the Shrinkage-Reducing Polycarboxylate Based Superplasticizer*. Masters thesis, Beijing University of Technology, Beijing, China.
- Lu F and Xiong WF (2014) Effect of shrinkage-reducing polycarboxylate superplasticizer on the shrinkage performance of cement-based materials. *Concrete* **5**: 91–92.
- Ma BG, Xu YH, Dong RZ and Tan HB (2006) Influence of shrinkage-reducing agent on cement paste structural formation with chemical admixtures. *Journal of Yangtze River Scientific Research Institute* **23**(3): 40–42, 46.
- Miu CW (2018) Early shrinkage crack of modern concrete and its control technology. *Journal of Xuzhou Institute of Engineering – Natural Science Edition* **33**(3): 1–8.
- Qian XQ, Zhan SL and Fang MH (2004) The negative effect of water reducer on shrinkage and cracking of concrete. *Journal of Railway Science and Engineering* **1**(2): 19–25.
- Rajabipour F, Sant G and Weiss J (2008) Interactions between shrinkage reducing admixtures (SRA) and cement paste's pore solution. *Cement and Concrete Research* **38**(5): 606–615.
- Rongbing B and Jian S (2005) Synthesis and evaluation of shrinkage-reducing admixture for cementitious materials. *Cement and Concrete Research* **35**(3): 445–448.
- SAC (Standardisation Administration of China) (2004) JC/T 603-2004: Standard test method for drying shrinkage of mortar. China Standard Publishing House, Beijing, China.
- SAC (2012) GB/T 8077-2012: Method for testing uniformity of concrete admixture. China Standard Publishing House, Beijing, China.
- Wang XF and Zheng JF (2008) Influence of slump and superplasticizer on early cracking of concrete. *Journal of Xiamen University – Natural Science Edition* **47**(5): 681–685.
- Wang JH, Jia JT, Zhang M, Zhang PL and Wang HZ (2012) Synthesis research shrinkage reducing polycarboxylate superplasticizer. *New Building Materials* **39**(8): 22–24.
- Weiss J, Lura P, Rajabipour F and Sant G (2008) Performance of shrinkage reducing admixtures at different humidities and at early ages. *ACI Materials Journal* **105**(5): 478–486.
- Wen ZY and Yang YB (2002) Effects of chemical and mineral admixtures on drying shrinkage and cracking of mortar. In *Proceedings of the Chinese Materials Conference 2002, Beijing, China*. Chinese Materials Research Society, Beijing, China, pp. 1338–1347.
- Whiting DA, Detwiler RJ and Lagergren ES (2000) Cracking tendency and drying shrinkage of silica fume concrete for bridge deck applications. *ACI Structural Journal* **97**(1): 71–77.
- Yang YB (2003) The problem of compatibility between shrinkage reduce agent and superplasticizer. *Chemical Building Materials* **19**(5): 44–49.
- Yoo DY, Kim J, Zi G and Yoon YS (2015) Effect of shrinkage-reducing admixture on biaxial flexural behavior of ultra-high-performance fiber-reinforced concrete. *Construction and Building Materials* **89**: 67–75.
- Yue L and Li J (2014) Capillary tension theory for prediction of early autogenous shrinkage of self-consolidating concrete. *Construction and Building Materials* **53**(3): 511–516.
- Zhan PM and He ZH (2019) Application of shrinkage reducing admixture in concrete: a review. *Construction and Building Materials* **201**: 676–690.
- Zhang N (2012) *Research on Synthesis and Reaction Mechanism of Shrinkage-Reducing Polycarboxylate Superplasticizer*. Masters thesis, South China University of Technology, Guangzhou, China.
- Zhang YR, Kong XM, Lu ZC, Lu ZB and Hou SS (2015) Effects of the charge characteristics of polycarboxylate superplasticizers on the adsorption and the retardation in cement pastes. *Cement and Concrete Research* **67**: 184–196.
- Zhou W, Yan LL and You Q (2015) Study on anti-cracking performance and mechanism of shrinkage-reducing polycarboxylate superplasticizer. *New Building Materials* **42**(4): 69–72.

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