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Synthesis and evaluation of shrinkage-reducing admixture for cementitious materials

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Abstract

This paper describes a chemical process called ethoxylation to synthesize a shrinkage-reducing admixture (SRA). Using 2-butoxy ethanol and ethylene oxide (EO) or propylene oxide (PO), SRA was synthesized in a laboratory. SRA has a great reducing effect on the surface tension of its solution. Reduced free drying shrinkage (FDS) rate can be measured with the increment of dosage for both mortar and concrete. At 2% dosage, free drying shrinkage can be decreased by 30–40% for both mortar and concrete specimens at 60 days. It also reduces autogenous shrinkage for mortar about 20–30% at 90 days with 2% dosage. Comparing with expansive admixture, SRA performance was better than expansive admixture when no water curing is undertaken.

Keywords: Shrinkage-reducing admixture; Synthesis; Concrete; Shrinkage; Evaluation

1. Introduction

It is well known that the dry shrinkage of concrete is due to the evaporation of water from concrete and causes volume contraction. The measuring time for drying shrinkage is initiated after 7 days that a concrete specimen was immersed in water. Typically, concrete specimen is exposed to an environment with low humidity and high temperature. A major disadvantage of cement mortar and concrete has been that they tend to crack on drying due to their considerable drying shrinkage and low tensile strength. For this reason, a concrete which will dry with a minimum of contraction has been desired. To counteract drying shrinkage, expansive admixture or expansive cement has been used extensively in practice for many years. In recent years, new shrinkage-reducing admixtures (SRAs) appeared in concrete engineering. According to some reports, SRA can reduce plastic shrinkage [1], autogenous shrinkage [2], and especially drying shrinkage [3].The mechanism of SRA of reducing shrinkage is quite disputable. Our recent research indicated that, adding SRA, the weight loss of mortar is less than the plain specimen in the drying condition; some researchers [4] believe that SRA lowers the surface tension of water in capillary pores. The driving force for water to evaporate outside is the lower surrounding humidity. As water-filled pores in the size range 2.5–50 nm lose moisture, curved menisci are formed, and the surface tension of water pulls the walls of the pores. With the reduced surface tension of water, the force pulling in on the walls of the pores is reduced, and the resultant shrinkage strain is reduced. Tazawa and Miyazawa [5] have noted that the observed percentage decrease in autogenous shrinkage basically corresponds to the percentage decrease in the solution surface tension. In this paper, we focus on the synthesis and test of SRA for cementitious materials.

2. Experimental

2.1. Chemicals for synthesis of SRA

The following chemicals were used for synthesis: (1) 2-butoxy ethanol, purity 99.5%, Jiangyin Yida Chemical,

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Table 1
Materials and mix proportion for mortar and concrete test

Usage	Materials	Mix proportion (kg/m^3)
Length change for mortar	Portland cement	540
	Standard sand	1350
	Water	238
	SRA	10.8 or 16.2
Length change for concrete	Portland cement	465
	Sand	671
	5–10 cm Crushed limestone	328
	10–25 cm Crushed limestone	766
	Superplasticizer	2.325
	Water	170
	SRA	9.3 or 13.95

China; (2) ethylene oxide and propylene oxides (EO and PO, respectively), No 2 Jingling Petrochemical, China; (3) potassium hydroxide, Nanjing Chemical Plant, China; (4) Ettringite Expansive Admixture, Jiangsu Bote New Materials, China; and (5) Superplasticizer, Mighty 100, sulfonated naphthalene formaldehyde condensate from Kao Cor., Shanghai.

2.2. Synthesis of SRA

SRAs are regarded as nonionic surface-active agents. They are composed of two parts in their molecular structure, one is the hydrophobic group and the other is a hydrophilic group. Both 2-butoxy ethanol and ethylene or propylene oxide were used to synthesize SRA; at the same time, a catalyst was used for this reaction. The reaction of alkylene oxide with alcohols is called ethoxylation. Stockburger [6] does much research on the ethoxylation of alcohols. The ethoxylation was carried out in a stainless-steel jacket reactor equipped with a magnetic stirrer and cooling coil. In each process, the reactor was charged with an alcohol substrate and weighted amount of catalyst. The reactor was then closed, vented with nitrogen, and heated to the reaction temperature. After the preheating, ethylene or propylene oxide was admitted to the reactor from a high-pressure bottle, which was pressurized with nitrogen at 0.5 MPa. When the temperature arrived at 130–135 °C, the ethylene oxide (EO) or propylene oxide (PO) pressure was kept constant at 0.1–0.4 MPa by opening or closing the micrometric valve. When the EO or PO was used in the reaction, the pressure in the reactor will drop; more EO or PO is needed to add to the reactor to keep the reaction going on. To put the needed amount of EO or PO, an electric digital reading scale was put under the bottle to measure the needed amount of EO or PO. After all EO is added to the reaction vessel, the reaction will last for another 1 h for further reaction. When the pressure lowered to the atmosphere pressure, let the jacket reactor connect to the atmosphere. Then liquid product was taken from the discharge valve.

2.3. Test of mortar and concrete

The materials and mixture proportions of the mortar and concrete used are listed in Table 1. Normal Portland cement was used for the tests, and Mighty 100 was used as superplasticizer. Mortar and concrete were mixed in the laboratory according the Chinese National Test Method GB751-81 “Method of Testing for Length Change of Mortar and Concrete”. Free drying shrinkage (FDS) was conducted by evaluating the length change of mortars and concrete, the mortar specimen is prism, with three dimensions, 2.5×2.5×28 cm. The dimension of the concrete prism is 10×10×51.5 cm. The prism specimens were taken out of the moulds the next day and immersed in 20-°C water until the age of 7 days. The specimens were left in a room at 20 °C and 60% RH; the length changes were measured at specified ages until the final test at 90 days. The compressive strengths of concrete were tested using 10-cm cubic specimens, at the age of 3, 7 and 28 days according the Chinese National Standard GBJ81-85 “Method of Test for Compressive Strength of Concrete”.

3. Results and discussion

3.1. Chemical structure of SRA

Through careful comparing, optimizing, and chemical analyzing, the best shrinkage-reducing performance SRA is by such reaction that one molecule 2-butoxy ethanol with four molecules addition. The average molecular weight is 250. Comparing n-butyl alcohol and 2-butoxy ethanol in our research, the boiling point for 2-butoxy ethanol is much high than that of n-butyl alcohol. It will be quite easy for us to remove water from the reaction mixture before addition. Another reason for using 2-butoxy ethanol for starting alcohol is its high reactivity to EO than that of n-butyl alcohol.

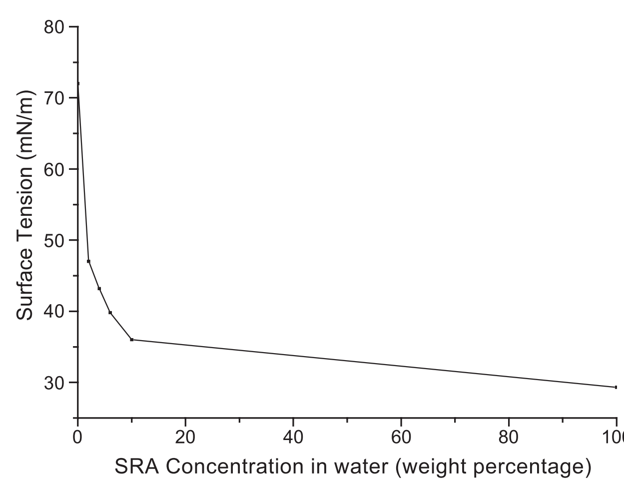

Fig. 1. Surface tension and SRA concentration.

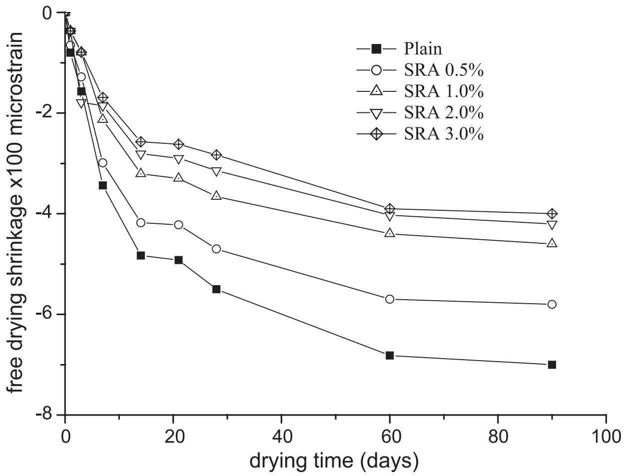

Fig. 2. Relationship between SRA dosage and free drying shrinkage of mortar.

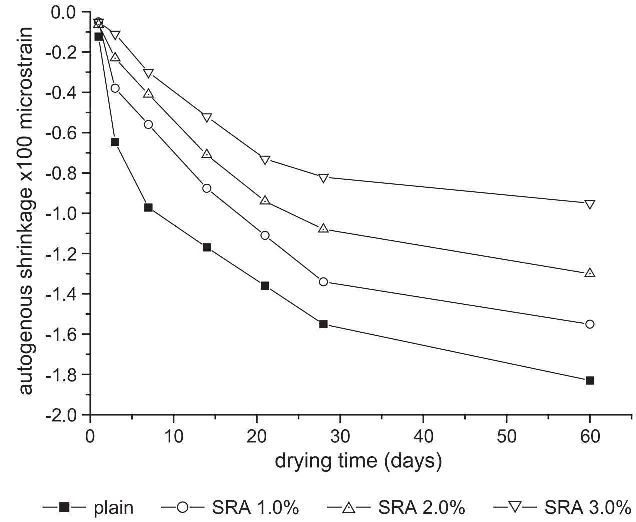

Fig. 3. Relationship between SRA dosage and autogenous shrinkage.

3.2. The surface tension of SRA

Pure water as reference and at temperature at 25 °C, the surface tension for SRA solution was measured. From Fig. 1, we can conclude that with the addition of SRA to water, the surface tension was reduced dramatically. Fig. 1 shows the surface tension of the solution as a function of SRA concentration in water. In the real hydrated mix, as water participates in the hydration, the concentration of SRA in the pore solution is likely to increase to a higher value than the in initial concentration [6].

3.3. The effect of SRA dosage on free drying shrinkage of mortar and concrete

SRA were added into mortar and concrete with different dosages, within 0–3.0%. The free drying shrinkage was measured using an advanced laser length change equipment with an accuracy within 0.001 mm. From Fig. 2 and Table 2, with increment of SRA dosage, the free drying shrinkage-reducing rates were increased. After 90 days drying, the free drying shrinkage-reducing rate for concrete specimens reached 21.9%, 28.1%, and 44.2%, respectively. Although the mechanisms of drying shrinkage are not fully understood, the literature [7] suggests that several mechanisms are dominant in different ranges of internal pore humidities. When considering concrete shrinkage in the 45–90% relative humility range, capillary stress appears to be predominant mechanism. When pore water evaporates from capillary pores in hardened concrete during drying, tension in the liquid is transferred to the walls, resulting in shrinkage. For a given pore structure, the internal stress generated upon evaporation is proportional to the surface tension of the pore water solution. SRA reduce drying shrinkage by lowering the surface tension of pore water in concrete.

3.4. Autogenous shrinkage and SRA

SRA can reduce autogenous shrinkage for cementitious materials [2]. To verify their conclusion, we used SRA from our research to test autogenous shrinkage. Mortar specimen was cast in the same size as in the drying shrinkage test. After 12-h setting, we used adhesive aluminum foil to wrap up all the specimen and seal the length detector with butyl rubber. We started to measure the length change 12 h after mixing. Our test results are displayed in Fig. 3. Comparing with other research's data, our data do not include the initial length change because of limited measuring conditions, but we can still find that SRA can reduce the autogenous shrinkage dramatically. For the dosages 1%, 2%, and 3%, after 60 days sealed curing, autogenous shrinkage was reduced to 15.3%, 29.0%, and 48.1%, respectively. Autogenous shrinkage should be measured from the mixing water and cement; their data measured from the initial setting should be bigger than ours because autogenous shrinkage is increased with time. This is why our data for autogenous shrinkage are smaller than their test results.

Table 2
SRA dosage and drying shrinkage of concrete

Test run	SRA dosage (%)	FDS of 28 days ($\times 10^6$)	FDY of 60 days ($\times 10^6$)	FDY of 90 days	FDY reducing rate of 28 days	FDY reducing rate of 60 days	FDY reducing rate of 90 days
1	0	191.0	251.8	312.2	0	0	0
2	1.0	137.0	193.8	243.7	28.2	23.0	21.9
3	2.0	130.4	173.8	224.6	36.6	31.0	28.1
4	3.0	102.7	122.0	174.1	52.8	51.5	44.2

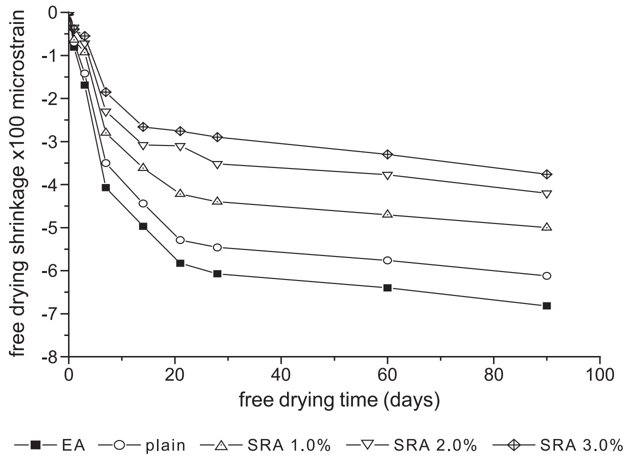

Fig. 4. Free drying shrinkage of mortar with EA and SRA.

3.5. Difference between expansive admixture and SRA on drying shrinkage on mortar

We test free drying shrinkage for mortar specimens added with expansive admixture and SRA on the condition that all specimens were cured in the drying condition with RH 60±1% and temperature 20±1 °C. Results are displayed in Fig. 4 At 90 days, the drying shrinkage for EA and SRA was totally different. The EA specimen shrunk 11.5% more than the plain specimen did; on the other hand, the SRA specimens shrunk 26.5–37.7% less than the plain specimen did. Expansive admixture or expansive cement was used to compensate the drying shrinkage in concrete for many years. Because of the large amount of ettringite formation in the early hydration stage, proper early water curing and designed amount of restraint must be provided for concrete. When no sufficient water curing can be provided, EA cannot provide any expansive for compensation for shrinkage because ettringite formation is impossible during early hydration without water. SRA can function very well on such drying condition, it still reduced the drying shrinkage to a favourable amount.

4. Conclusions

Shrinkage-reducing admixture was made successfully in our laboratory. Research data indicated that SRA can cause a significant reduction of surface tension of the SRA water solution. With the increment dosage of SRA, better free drying shrinkage and autogenous shrinkage can be observed. If no water curing can be supplied for mortar specimen after demoulding; specimens with EA had more free drying shrinkage. On the other hand, SRA still performed very well on such conditions. Therefore, SRA is very superior on such occasion where no water can present on the specimens.

Acknowledgments

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