Effects of novel polymer-type shrinkage-reducing admixture on early age autogenous deformation of cement pastes

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ABSTRACT

This study aims to investigate the autogenous shrinkage-reducing mechanisms of the novel polymer-type shrinkage-reducing admixture (SRA) with water-reducing function. For comparison, the traditional polyether-type SRA was also used. The development of autogenous deformation, hydration rate, internal relative humidity (RH), electrical resistivity, ions and SRAs concentration in pore solutions and crystal content of cement pastes were comprehensively investigated. Unlike the polyether-type SRA mixture which has an expansion period at early age, a relatively slow and monotonous evolution of shrinkage was observed for the polymer-type SRA mixture. It is concluded that the delay and regulation effects on cement hydration of the novel SRA obviously influence the microstructure development and the evolutions of various performances of cement pastes comparing to the polyether-type SRA. Furthermore, both the self-desiccation status induced capillary pressure and the crystallization pressure induced expansion stress contribute to the shrinkage-reducing behaviors of SRAs on the autogenous deformation of the cement pastes.

1. Introduction

Shrinkage is a common phenomenon in modern concrete and if not handled properly, it may lead to serious problems such as cracking and failure of the structure. Especially in high-performance concrete, the low water-to-cement ratios can result in an obvious autogenous shrinkage during the hydration of cement even under sealed conditions [1–5]. In recent decades, numerous experimental studies have been done to investigate various properties of cement-based materials with the addition of SRA, such as autogenous and drying shrinkage [6–10], plastic shrinkage [11–13], mechanics and hydration behaviors [14–15] as well as the moisture evaporation and capillary suction [5,16] of cementitious materials, etc.

As a special type of organic chemical admixtures, SRA had been introduced to mitigate shrinkage and control crack of cement-based materials since 1980s [4]. And it is considered as one of the most effective methods to reduce the shrinkage of concrete especially the autogenous and drying shrinkage [5–10]. Although the shrinkage-reducing mechanism of SRA is still not fully understood, most studies, however, hold the view that by adding SRA into cementitious systems, the surface tension of the pore solution in capillary pores is significantly

lowered [4,8,10]. According to the Young-Laplace equation (Eq.(1)) and Kelvin equation (Eq.(2)), under sealed condition, after the formation of the solid microstructure, the lower surface tension in turn can reduce the capillary pressure and maintain the internal RH in a higher level [3,14]:

$$\sigma_{cap} = -2\gamma_{LV}cos\theta/r \tag{1}$$

$$ln(RH) = -V_m/RT \cdot 2\gamma_{LV}cos\theta/r \tag{2}$$

where σ_{cap} is the capillary pressure (MPa), r is the menisci curvature radius (m), γ_{LV} is the surface tension of the pore solution (N/m), θ is the contact angle, V_m is the molar volume of the pore solutions (assumed to be water, 18.02 cm^3/mol), R is the gas constant (8.314 J/kmol), and T is the absolute temperature (293.15 K). Therefore, the macroscopic shrinkage stress of cementitious materials drops under the condition of moisture consumption.

Besides, the addition of SRA can reduce the concentration of Na$^+$ and K$^+$ in the pore solutions, which decreases the concentration of the counterbalancing anion such as SO$_4^{2-}$ and OH$^-$ comparing to the plain mixture, in turn increase the concentration of Ca^{2+} (common ion effect) and the oversaturation of portlandite and ettringite [4], especially

Table 1
Chemical and mineral composition of the cement.

Chemical composition (% by mass)							
SiO_2	Al_2O_3	CaO	MgO	Fe_2O_3	SO_3	NA_2O_{eq}	Ignition loss
21.08	4.29	62.68	1.55	3.94	2.55	0.48	2.31

Mineral composition (% by mass)			
C_3S	C_2S	C_3A	C_4AF
52.50	21.40	6.40	13.10

the crystallization of portlandite. Therefore, an early age expansion usually occurs which also plays an important role to compensate shrinkage stress partially [9,17–18].

Besides the investigations of the shrinkage-reducing mechanisms, recently, an increasing number of studies also focus on the development of new type of multifunctional chemical admixtures, among which the polymeric water-reducing type of SRA has been designed and investigated [19–21] which provides a vast space for the application of the concrete SRA. While possessing an excellent shrinkage-reducing effect on the cementitious materials, the novel type of water-reducing SRA also has a significant function of water-reducing which seems to be more economical and efficient. However, the specialized study on the mechanism of the novel type of SRA is seldom found [22].

In this paper, the impacts of a traditional polyether-type SRA (SRA1) and a novel polymer-type SRA (SRA2) on the early age autogenous deformation of cement pastes are investigated. The performance of mixtures with SRAs on autogenous deformation, hydration rate and dynamic elastic modulus were compared to the plain mixture. Finally, mechanisms of shrinkage reducing of different types of SRA at early age of cement pastes are revealed.

2. Materials, mix proportion and experimental procedures

2.1. Materials

Portland cement with strength grade of 52.5 MPa obtained from Xiao Yetian Cement Co., Ltd. (Jiangsu, China) was used. The apparent density of cement is 3060 kg/m^3, and the chemical and mineral compositions are listed in Table 1, which are obtained by the X-ray fluorescence spectrometer and X-ray diffractometer, respectively.

The tap water was used. The polycarboxylate-type of water-reducing agent (SP) was used as admixture with the solid content of 10% and the water-reducing ratio at around 35%. Two types of SRAs with different molecular structure were used and their basic physicochemical properties as well as the molecular structures are shown in Table 2 and Fig. 1, respectively. It should be noted that the SRA1 is the commonly used low molecular polyether [7–9] while SRA2 is a novel polymer-type SRA synthesized by unsaturated polyether monomer and acrylic acid through free radical copolymerization and the water-reducing ratio of SRA2 is around 25%.

2.2. Mix proportion

Three groups of cement pastes were prepared in this study (see Table 3). They are plain cement paste and cement pastes with 2.0% dosage (by cement mass) of SRA1 and SRA2, respectively. Small quantities of superplasticizer were added into the plain mixture and SRA1 mixture to obtain a similar workability of the SRA2 mixtures, since SRA2 possesses a function water-reducing. The mixtures were prepared by a planetary mixer and the experiments were conducted at the temperature of 20 ± 2 °C.

2.3. Experimental procedures

2.3.1. Autogenous deformation

The autogenous deformation of early age of the cement pastes were measured by corrugated tubes with length and diameter of 340 mm and 30 mm, respectively. The advantages of this measurement as well as the testing principle can be found in former studies [9,23]. Each of the tubes was sealed on both ends and placed horizontally on a rigid metal frame with one side fixed in the frame. And the non-contact electric eddy transducer was used to measure the displacement of the other end of the tube.

The final set time obtained by Vicat test (ASTM C191) was regarded as the starting point of the deformation of the corrugated tubes [24]. For comparison, the JD18 Universal Projection Length Measuring Instrument was also used to test the autogenous deformation of the mixtures. The sizes of the samples were 25 mm × 25 mm × 280 mm with copper head on both sides of the samples. The samples were demolded at 24 h since the contact of cement and water and covered by the plastic wrap as well as the aluminum foil to prevent the moisture evaporation. Further, the original length was measured immediately after the samples were sealed and then cured at the temperature of 20 ± 3 °C.
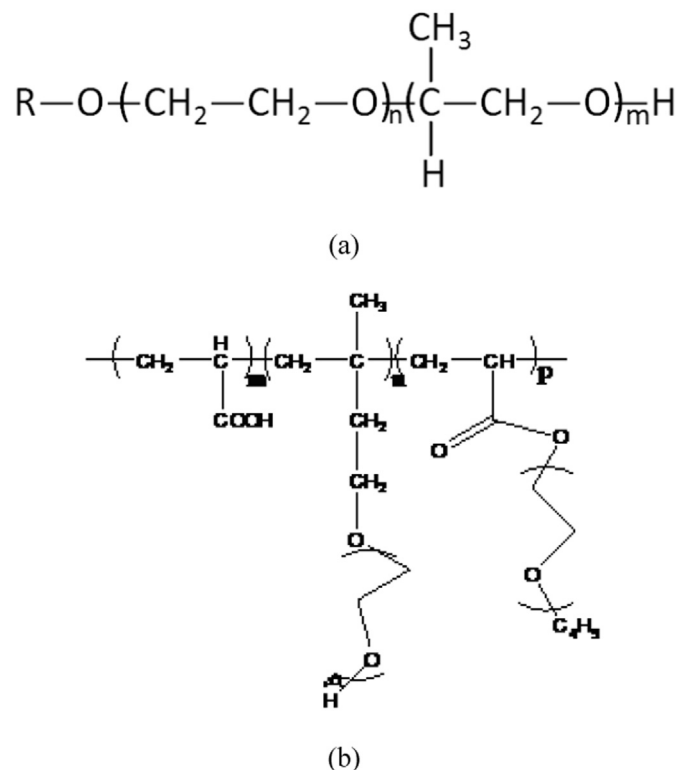

(a)

(b)

Fig. 1. Molecular structure of the two types of SRA: (a) SRA1; (b) SRA2.