- Technical Paper -

EFFECTS OF SUPERABSORBENT PLYMERS ON EXPANSIVE BEHAVIOR OF MORTARS AT EARLY AGES

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ABSTRACT

It has been noticed that the mixtures with superabsorbent polymer (SAP) frequently exhibit an expansion at early ages. In this study, the expansion in mixtures with SAP was investigated in relation to the hydration process of cement at early age. It is suggested that the internal water released from SAP may contribute to increase the expansion and that SAP may affect the evolution of microstructure even before the initial setting time. Differences in the subsequent expansive behaviors are related to the initial distribution of water released from SAP.

Keywords: superabsorbent polymer, shrinkage deformation, expansion, electrical resistivity, plastic viscosity, degree of hydration

1. INTRODUCTION

With the advent of high strength concretes with low water to cement ratios, occurrence with greater frequency of early age shrinkage cracking of concrete has been of great interest. Early age cracking, which primarily due to autogenous shrinkage, may affect the durability of the concrete. On the other hand, some methods to reduce autogenous deformation have been proposed. For example, it is well known that shrinkage reducing admixtures can greatly reduce the shrinkage[1, 2]. The other method to mitigate autogenous shrinkage is internal curing. Lightweight aggregate and superabsorbent polymers (SAP) have been used as internal curing material[3, 4]. In particular, SAP has various functions with respect to water control. Therefore, nowadays it is considered as an promising admixture which can be used for further new applications[5].

When SAP particles are used as internal water reservoirs in concrete, it has been noticed that the addition of SAP sometimes results in large expansion at early ages[6]. The impact of the expansion in mitigating autogenous shrinkage is considerable since differences in the initial expansion are reflected to subsequent differences in shrinkage at longer ages[7]. It should be noted that the expansion is often followed by considerable shrinkage. Mechanism of the expansion is not fully understood. Three primarily reasons have been proposed for the expansion[8-10]: (1) thermal dilation, (2) deposition of hydration products and (3) uptake of bleed water after setting time. For example, Mohr and Hood[11] have recently pointed out that reabsorption of bleed water is the dominant mechanism of the expansion and that effects of thermal dilation and ettringile formation are minimal.

With regard to bleed water, it is also important to clarify how SAP addition affects fresh properties of concrete since the internal curing water released form SAP can be regarded as internal bleed water. Rheological properties of fresh concrete are related to hydration process and chemical interactions in the cement paste system at a plastic state. Taking account of the purposeful water absorption and/or water release from SAP in fresh and hardened concrete, the rheological properties are also influenced by the addition of SAP. Mechtcherine et al.[12] have shown that the major factor that governs the rheological properties of fresh mortar is the distinct kinetics of water uptake inherent in the SAP samples, as governed by their particular chemical structures. Those changes in rheological properties may also affect evolution of microstructure in concrete. As mentioned above, the released water may be involved in the hydration process of cement[13].

In order to investigate the evolution of microstructure immediately after placing concrete, electrical conductivity testing may be a useful way since electrical conduction occurs primarily due to ion transport through the pore solution in a cement-based system. Then it is strongly dependent on pore solution conductivity, porosity and pore connectivity [14]. They are influenced by some factors such as water/cement ratios, cement types, chemical admixtures, and degree of hydration[15]. Therefore, electrical resistivity measurements on fresh cementitous materials are expected to provide useful information on characteristics of microstructure in concrete at early ages[16].

The objective of this study is to investigate the

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relationship between SAP addition and the autogenous deformation behaviors at very early ages. Experimental studies were carried out, in which the degree of hydration, electrical resistivity and rheological properties of mortars were measured. The evolution of microstructure in mortars with SAP was discussed in relation to expansion at early ages.

2. EXPERIMENTAL

2.1 Materials and mixture proportion

Ordinary Portland cement with a Blaine fineness value of 3310cm^2/g was used. A commercial product of silica fume with density and specific surface area of 2.20g/cm^3 and 20m^2/g, respectively, was used. The fine aggregate was siliceous sand of which density and absorption were 2.62g/cm^3 and 0.40%, respectively. A polycarboxylic acid type superplasticizer was used. Two types of SAP (A and B) were used. SAP-A is produced by aqueous polymerization while SAP-B is obtained by inverse suspension polymerization. As shown in Fig.1, SAP-A is irregular in shape and contains greater particles while SAP-B is almost a mono-sized spherical powder. Their absorption capacity in cement pastes are 10.0g/g and 13.3g/g of dry mass, respectively. The SAP was sieved to obtain two particle size distributions, large (300~600μm) and small (150~300μm). These properties of SAPs are summarized with notation of each SAP in Table 1. Using the equation proposed by Jensen and Hansen[4], the amounts of SAP for the internal curing at W/B of 0.28 were determined. Mixture proportion of mortars is given in Table 2.

2.2 Experimental procedures

(1) Length change test

Length change of mortars was measured by the corrugated tube method (Fig.2) in accordance with ASTMC1698-09[17]. Mortar specimens using corrugated plastic molds were placed in a room at 20℃. Length changes of the specimens were measured by laser displacement maters and digital gauges.

In a preliminary test, the initial setting time was determined using cement pastes with the same W/B as the mortar. The initial setting time determined by Vicat needle penetration was used as the origin of length change.

(2) Electrical resistivity test

The electrical resistivity was measured by the four electrodes method in accordance with JSCE-K 562-2008[18]. Mortars were directly placed into a cylindrical mold shown in Fig.3. Changes in the resistivity were continuously recorded up to twelve hours

Using the following equation, electrical resistivity ρ (Ω·m) was calculated:

$$\rho = \frac{V \cdot A}{I \cdot L} \qquad (1)$$

Where V(V) is the potential difference between two current probes, A(m^2) is the sectional area of the mold, I(A) is current, L(m) is the distance between two current probes.

(3) Rheology test

Plastic viscosity of mortars was measured with a commercial rheometer (Fig.4). The fresh mortars were tested with every 10 minutes after the water addition. After 1 hour, the fresh mortars were tested every 30 minutes until losing proper workability. Before each measurement, the mortar was agitated using a metal bar in order to reduce the effect of possible sedimentation.

The measurement is based on the continuous shear rate controlled test. Changes in shear stress are a function of shear rate and subsequent derivation of plastic viscosity values according to the Bingham model. To obtain the Bingham parameters, the descending branch of the shear stress-shear strain curve was approximated by using linear regression analysis. The intersection of the linear regression line with the slope of the line provided the value of the plastic viscosity.

(4) Degree of hydration

The degree of hydration was determined from non-evapolable water. Based on the Powers and Brownyard model[19], it was assumed that the ratio of the amount of non-evapolable water to the degree of hydration was constant at 0.23. Cement paste specimens with the same W/B of 0.28 were prepared

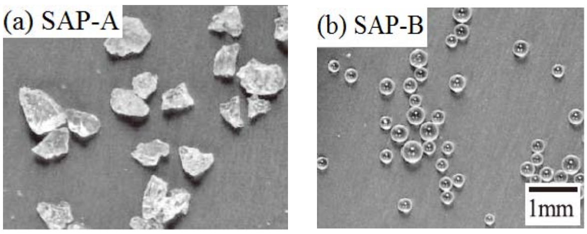


Fig.1 SAP particles at dry state

Table 1 Properties of SAP

SAP	Absorption capacity (g/g)	Particle diameter range (μm)
SAP-AL	10.0	300~600
SAP-AS		150~300
SAP-BL	13.3	300~600
SAP-BS		150~300

Table 2 Mixture proportion of mortars (mass fraction)

Mixes	W/B	C	SF	S	SP	SAP
Control	0.28	1	0.094	1.89	0.017	-
SAP	0.28	1	0.094	1.89	0.017	0.003

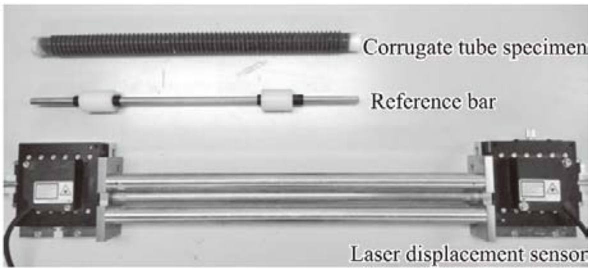
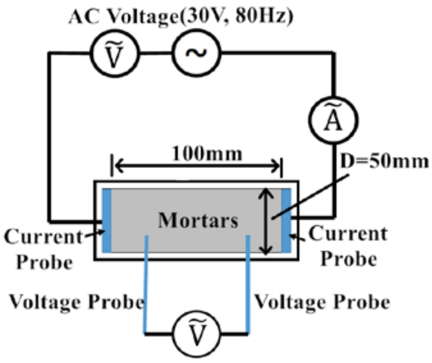
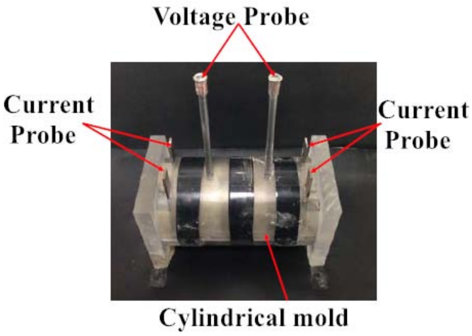


Fig.2 Measuring instruments



(a) Electrical circuit diagram



(b) Cylindrical mold for the test

Fig.3 Schematic drawing of testing apparatus for the four electrodes method

for the test at the prescribed ages of 6, 12 and 24 hours. Its non-evapolable water content w_n was determined by the loss on ignition. The degree of hydration α was calculated by the following equation[20]:

$$\alpha = \frac{w_n}{0.23} = \frac{(w_{105} - w_{1000})/w_{1000}}{0.23} \tag{2}$$

Where w_{105}(g) and w_{1000}(g) are the masses of the sample after drying at 105℃ and 1000℃, respectively.

(5) Absorption capacity test of SAP

Water absorption capacity of SAP was evaluated by a tea-bag method in accordance with JIS K 7223. Saturated solution of calcium hydroxide was used instead of deionized water. The absorption capacity of SAP was calculated by the following equation:

$$W = \frac{M_3 - M_2 - M_1}{M_1} \tag{3}$$

Where W(g/g) is water absorption capacity of SAP, M_1(g) is the mass of SAP under dry condition , M_2(g) is the mass of the tea-bag which had been pre-wetted in the saturated solution, M_3(g) is the mass of the tea-bag with the SAP which is hung in a beaker filled with the saturated solution of calcium hydroxide for a prescribed time.

3. RESULTS AND DISCUSSION

3.1 Effect of SAP addition on autogenous shrinkage

Autogenous deformation behavior of mortars using each SAP is shown in Fig.5. The control mortars showed pronounced deformations due to shrinkage after the initial setting to 1 day. After 1 day, the

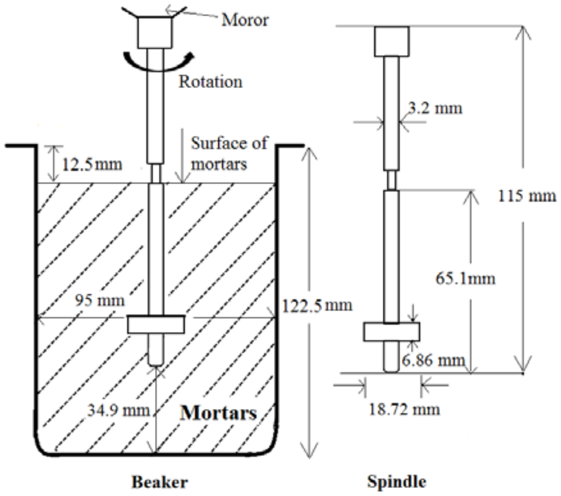


Fig.4 Schematic drawing of testing apparatus for the rheology test

hydration may slow down and effects of chemical shrinkage on the length change are reduced due to the formation of internal solid skeleton[21]. In contrast to the control mortars, mixtures with SAP exhibited expansion from the beginning to 1 day. It is clearly found from Fig.5 that the early age expansion is related to the presence of internal water. The large particles of SAP-AL and SAP-BL resulted in greater initial expansion than those with the small particles of SAP-AS and SAP-BS. Periods of the expansion continued longer when the large SAPs were used. The addition of SAP greatly reduced subsequent shrinkage. The magnitude of the expansion and the extent of shrinkage reduction depend on the size of SAPs. Differences in the initial expansion were reflected to subsequent differences in shrinkage at longer ages. A large part of the reduction in autogenous shrinkage resulted from the initial expansion.

In view of the autogenous deformation curves for the mortars with the SAPs, the internal curing by SAP was only effective at an early stage. Then the autogenous shrinkage of the SAP mixtures developed nearly parallel to the control without SAP after the initial expansion. The autogenous shrinkage behaviors of mortars with SAP should be discussed in relation with the time when the internal water is released from the SAP. Most of the SAPs produced as internal curing materials release the absorbed alkaline water to the surrounding cement matrix at very early ages[12]. This occurs irrespective of self-desiccation of the surrounding matrix. It may be an intrinsic property of SAP[12].

Changes in absorption capacity of SAPs with time of immersion are shown in Fig.6. After they were dipped into saturated calcium hydroxide solution for ten minutes, all the SAPs exhibited their maximum absorption capacity. It is consistent with the common understanding that the absorption of pore solution in the SAP is rapid and takes place in several minutes after mixing[22]. However, when they were immersed into the solution for a longer time, their absorption capacity decreased quickly. The absorption capacity at 1 hour

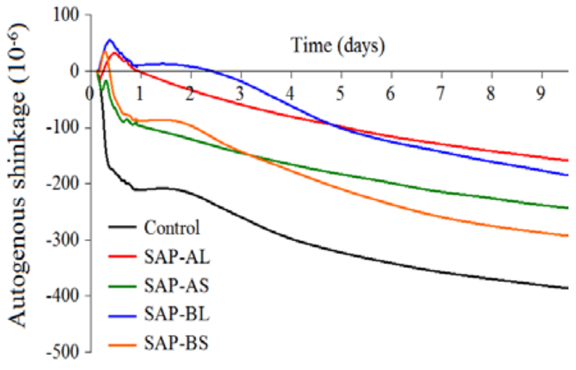


Fig.5 Autogenous deformation of mortars

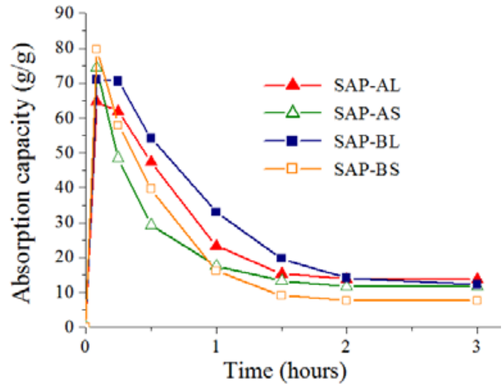


Fig.6 Change in absorption capacity with time

was less than a half of the initial capacity for all the SAPs. The smaller SAPs, the earlier decrease in absorption capacity was observed. Therefore, the small SAP in the actual mortars could also release the internal water at very early ages whereas the environmental condition in the mortars was different from that of the tea-bag method. Then the release of the internal water from the large SAPs takes place slowly compared to small SAP (Fig.6). The released water from SAP affects the expansion at very early ages since it is regarded as be internal bleed water[10]. Eventually, when the internal curing water is consumed or confined, its effect on the expansion decreases so that an apparently change from expansion to shrinkage is observed. Then the increase in autogenous shrinkage of the SAP mortars proceeded at the same rate as that of the control mortars (Fig.5). As for the mortars with large SAPs, expansion continued longer. This behavior may be related to the desorption rate of SAP. When the large SAPs were used, it exhibited a smaller rate of desorption, which affected the longer period of expansion (Fig.6).

3.2 Effect of SAP addition on electrical resistivity

The electrical resistivities of mortars are shown in Fig.7. All the mixtures exhibited a similar tendency in electrical resistivity with time. The electrical resistivity slowly dropped at first and then gradually increased with time. At the beginning, the control mortars showed a greater electrical resistivity than the SAP mortars, but a slow rise with time led it to be overtaken by the mortars with the large particles of SAP. The electrical resistivity of the mortars with the large SAPs was greater than that of the mortars with the small ones at 10 hours. It should be noted that the times when the resistivity began to increase in the SAP mortars were about 1 hour earlier than the control mortars. Setting times are also shown in Fig.7. The times when the resistivity of the SAP mixtures started increasing were almost the same as the initial setting time while it was between the initial and final setting for the control mixtures. The initial seeting time is close to the end of the dormant period. In this study, effect of pore solution composition on electrical resistivity is not considered since all the mixtures have the same W/B. However the electrical resistivity development with time still reflects the hydration process and evolution of capillary pores networks in mortars[23]. At the acceleration period after the initial setting time, chemical shrinkage and reabsorption of bleed water by hydration products occur simultaneously. Internal relative humidity was kept high by internal curing. Effects of the internal water from the SAPs were dominant so that the expansion was observed in the SAP mortars. Thus the hydration of cement can proceed so that internal solid skeleton is expected to be formed

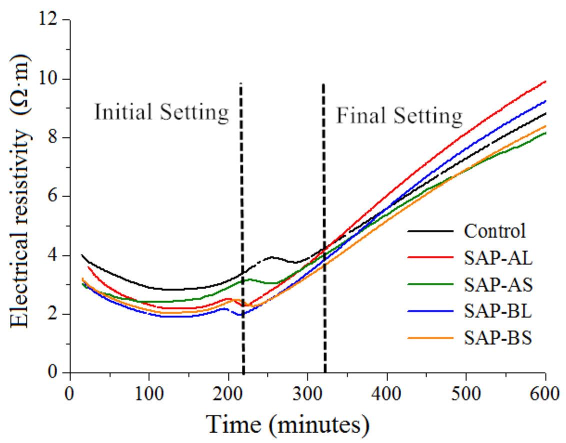


Fig.7 Development of electrical resistivity in mortars with SAPs

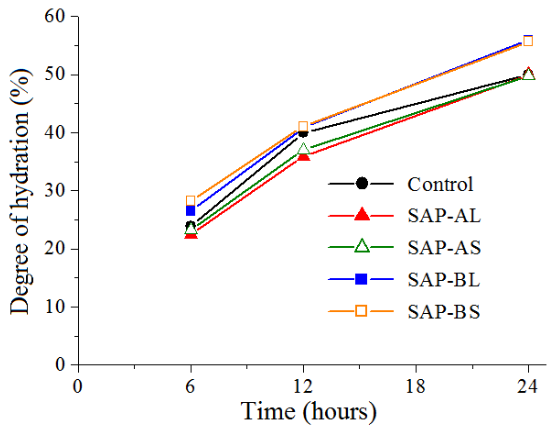


Fig.8 Changes in the degree of hydration of cement in mortars with SAPs

earlier in the SAP system. This results in the early increases in electrical resistivity (Fig.7).

Fig.8 shows the degree of hydration. Mixtures with SAP-B showed higher degrees of hydration than that for the control mixtures. For the mixtures with SAP-A, the degree of hydration was comparable to the control mixtures. However, differences in the degree between the mixtures are relatively small on the whole, nevertheless electrical resistivities in the SAP mortars start to increase earlier than the control (Fig.7). This fact suggests that autogenous shrinkage behaviors and the development of electrical resistivity in the SAP mortars cannot be explained simply from the amount of hydration products and their uptake of bleed water. In addition to the uptake of bleed water by hydration products, some other factors to change expansive behaviors in the SAP mortars should be taken into account.

3.4 Effect of SAP addition on plastic viscosity of fresh mortars

Fig. 9 shows time-dependent changes in plastic viscosity of fresh mortars with and without SAP. At first they kept a stable value of plastic viscosity, then started increasing rapidly. The control mortars exhibited a little higher plastic viscosity right from the beginning of the measurements. When SAP was used, the time at which plastic viscosity started increasing was delayed. The mortars with SAP-B showed a remarkable increase in plastic viscosity at 120 minutes. In contrast to this, gradual increase was observed for the mortars with other SAPs. Furthermore, the plastic viscosity in the mortars with SAP-B depends on its particle size whereas there is no difference in the viscosity between the mortars with SAP-AL and SAP-AS. It should be noted that these changes in the plastic viscosity were recorded before the initial setting time. In fact, they were observed in the periods when the internal water of SAP had released already. In particular, it should be also noted that SAP-BL absorbs water as quick as other SAPs, but it keeps it longer than the others(Fig.6).

Fig. 9 clearly suggests that there must be some differences in the microstructure between the mixtures with different SAPs even if it is in the dormant period in the hydration of cement. Basically, plastic viscosity reflects internal friction of a material. Therefore those differences in the internal friction result from the released water from SAP since it occurs during such a very early age. All the SAP mortars in this study have almost the same amount of internal water. However, the numbers of SAP particles are different among the mortars since the particle sizes of SAP are different. Therefore, their spatial distribution, in other words, the number densities of internal water reservoirs are different among the specimens. Thus when the internal water is released at very early ages before the initial setting time, the initial distributions of moisture are also different among the specimens. The particle sizes of SAP and the differences in the moisture distributions[24] could affect the initial evolution of internal friction. This may result in the differences in the subsequent expansive behaviors in mortars. Further study is needed to understand development of internal friction and its effect on movement of water at very early ages before the setting.·

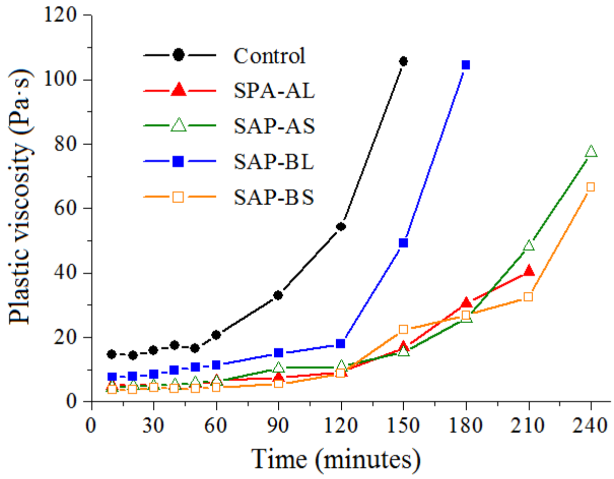


Fig.9 Development of plastic viscosity at early age

4. CONCLUSIONS

Expansive behavior of internally cured mortars with different SAPs was investigated. Major results obtained in this study are as follows:

(1) Early age expansion of the mortars with SAP is contributed from the internal water released from the SAP.

(2) The magnitude of the expansion and the extent of shrinkage reduction depend on the size of SAPs. The larger SAPs, the greater and the longer period of expansion.

(3) The absorption capacities of SAP are related to the transition periods of autogenous deformation from expansion to shrinkage. The smaller desorption rate, the longer expansion continued.

(4) When SAP was used as an internal curing material, the electrical resistivity began to increase earlier than that in the control.

(5) Even if the amounts of hydration products were almost the same, different expansive behaviors were seen in mortars with SAP. Expansive behavior of SAP mortars cannot be simply explained only by reabsorption of the internal bleed waters.

(6) The addition of SAP affects the development of the plastic viscosity.

(7) Difference in expansive behavior of mortars with SAPs may be related to differences in the initial moisture distribution at the very early ages before the setting of cement.

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