- Technical Paper -

COMPARISON OF ABSORPTION CAPACITY OF SUPERABSORBENT POLYMERS MEASURED BY DIFFERENT METHODS

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ABSTRACT

It is important to determine absorption capacity of superabsorbent polymer (SAP) by a proper method. In this study, the test results of the modified tea bag method are compared to those of the filtration method. It is suggested that the results of tea bag method is prone to be affected by agglomeration of SAP particles, which lead to insufficient swollen SAP. As a result, the absorption capacity in the tea bag method is smaller than that by the filtration method. The large increase in absorption capacity during the test period seems to result from the retention of interparticle liquid in the tea bag method.

Keywords: superabsorbent polymer, absorption capacity, de-ionized water, cement slurry filtrate, modified tea bag method, filtration method, plastic viscosity, interparticle liquid

1. INTRODUCTION

Superabsorbent polymer (SAP) has been considered as a promising and multifunctional admixture since Jensen and Hansen [1] used it as internal water reservoir. Nowadays, new application of SAP in concrete technology has been of a great interest, especially as additives for water control such as rheology modification. Therefore, it is essential to estimate SAP characters by certain measurement techniques before SAP is used for cement-based materials. However, practical and simple tests on SAP for concrete have not been standardized yet. More recently, RILEM has established a Technical Committee, RILEM TC 260-RSC "Recommendations for Use of Superabsorbent Polymers in Concrete Construction" (Chair: Prof. V. Mechtcherine, TU Dresden). Its main concern is to study a simple pre-test on SAP to disclose fundamental properties towards application in cement-based construction materials.

SAPs are a group of cross-linked polymeric materials that have the ability to absorb a significant amount water from the surrounding and to retain water within their structure without dissolving [1]. The kinetics and sorption capacity of SAP are key aspects on their effects and performance in cement-based construction materials. The kinetics and sorption capacity of SAP depend on properties of the SAP, and its exposure environment [2]. In particular, the kinetics and sorption capacity of SAP in a highly alkaline solution are significant since pore solution in concrete has a quite high pH value.

Appropriate selection of exposure fluid is particularly important to determine the kinetics and sorption capacity with respect to the use of SAP in cement-based construction materials. De-ionized water and synthesized pore solution are usually employed as the exposure fluid [3]. In de-ionized water, the inherent ability of SAP, which may be relevant for potential incorporation with cement-based matrix, can be observed. The synthesized pore solution is a reproduction of the liquid phase of a cement pore solution that contains characteristic ions. To obtain the synthesized pore solution requires accurate calculation of concentrations of some ions in pore solution at early ages [4]. However, practically, it is difficult to determine the concentration for the test since it depends on many factors such as types of cements and time. Instead of synthesized pore solution, cement slurry filtrate seems promising because of its simple preparation and similarity to the pore solution [5].

Several methods have been proposed to measure water absorption capacity of SAP. The tea bag method is frequently used to give a fast response of water absorption capacity of SAP. The absorption capacity evaluated by tea bag method is based on the mass of dry SAP in relation to the mass gain of the filled tea bag after it is removed from solution and drops off excess water by gravity. However, it is postulated that this method strongly depends on interparticle water. The water held by capillary forces between SAP particles cannot be totally removed. As an easy and alternative method, Jensen [2] has proposed a new method that uses a graduated cylinder. The method consists in measuring the volume change of a certain mass of loosely packed SAP as it absorbs water. The graduated cylinder method is considered as a useful way to evaluate water absorption capacity of SAP in cement environment [4]. However, it is sometimes difficult to see a rise in SAP height through the glass cylinder. On the other hand, in order to assess the possible sealing capacity of SAP particles, Snoeck [5] has proposed a filtration method to calculate water absorption capacity from the volume increase between the vacuum dried

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state and the saturated state. He also has confirmed that the test result is not affected by the interparticle water. Therefore filtration method is considered as a promising technique to obtain a realistic value of absorption [6].

This study focuses on comparison of absorption capacity of SAP measured by the tea bag method and the filtration method using de-ionized water and cement slurry filtrate. The comparison between the results of absorption capacities is discussed from the viewpoint of retention of interparticle liquid on SAP particles during the test period. Furthermore, rheological behavior of fresh mortars with SAP is discussed in relation to the kinetics and sorption capacity of SAP.

2. MATERIALS AND EXPERIMENTAL METHODS

2.1 Materials and mixture proportion

Ordinary Portland cement with a Blaine fineness value of 3310cm^2/g was used. The fine aggregate was siliceous sand of which density and absorption were 2.62g/cm^3 and 0.40%, respectively. Three types of SAP (1, 2 and 3) were used. SAP-1 and 2 are produced by aqueous polymerization, SAP-3 is obtained by inverse suspension polymerization. As shown in Fig.1, SAP-1 and 2 are irregular in shape. SAP-3 is spherical powder. Tiny particles of SAP-3 are gathered around large particles due to a surfactant. Their nominal absorption capacities in alkaline solution are 46.6g/g, 60.8g/g and 13.3g/g of dry mass, respectively. SAP-1 and 2 were sieved to obtain two particle size ranges, large (200~500μm) and small (<200μm). SAP-1 and 2 of the original grading were also used. Those properties of SAPs are summarized with their notations in Table 1. The water to cement ratio of mortar was 0.65. Dosage of SAP was determined to absorb 7.7% of mixing water. Therefore, the effective water to cement ratio in cement paste matrix was smaller than 0.65. Mixture proportion of mortars is given in Table 2.

2.2 Experimental procedures

(1) Modified tea bag method

Water absorption capacity of SAP was evaluated by the tea bag method, which is modified by RILEM TC-260-RSC. In that procedure, excess water is removed by wiping with clothes, instead of hanging the tea bag. The absorption capacity was measured when SAP was immersed in test fluids for 1, 5, 10, 30, 60 and 180 minutes. The absorption capacity of SAP was calculated by the following equation:

$$W = \frac{M_3 - M_2 - M_1}{M_1} \tag{1}$$

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 testing solution, M_3(g) is the mass of the tea bag with the SAP which is hung in a beaker filled with the test liquid for a prescribed time.

(2) Filtration method [5]

Dry SAP and test fluid of 100ml were added in a beaker. The swollen SAP and the test fluid were filtered after SAP immersion for the same prescribed time of 1, 5, 10, 30, 60 and 180 minutes as the tea bag method (Fig.2). The filter paper was saturated with the fluid before filtration, in order to ensure there was no influence of the filter paper. Filtration was continued until no drops are visible any more. The maximum filtration time is decided for a quarter of an hour to control the overall filtration, according the advice by RILEM TC260-RSC. The filtration time is excluded in the total time. The tests is carried out in the laboratory at a temperature of 20±2℃ and relative humidity of 60±5%, which is as the same as tea bag method. The absorption capacity of SAP is calculated by the following equation:

$$K = \frac{m_2 - m_3}{m_1} \tag{2}$$

Where K(g/g) is water absorption capacity of SAP, m_1(g) is the mass of dry SAP sample, m_2(g) is the mass of test fluid added, which is approximately 100g. m_3(g) is the mass of filtered fluid (Fig.2).

(3) Test fluids

As mentioned above, kinetics and sorption capacity of SAP depend on the solutions used. The measurements were performed with two test fluids. One

Table 1 Properties of SAP

SAP	Absorption capacity (g/g)	Particle size (μm)
SAP-1S SAP-1L SAP-1N	46.6	<200 200~500 Not sieved
SAP-2S SAP-2L SAP-2N	60.8	<200 200~500 Not sieved
SAP-3	13.3	Not sieved

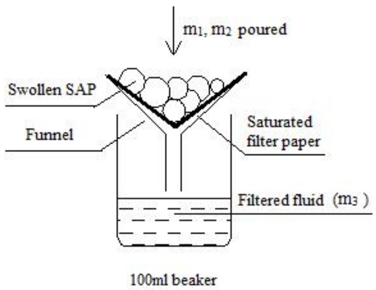


Fig.2 Procedure of the filtration method

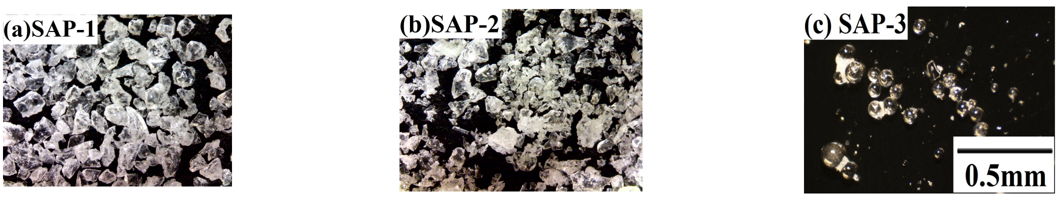


Fig.1 SAP particles at dry state

Table 2 Mixture proportion of mortars (mass fraction)

Mixes	W/C	W_e/C	C	S	W_e	W_{SAP}	SAP	Flow
REF-0.65	0.65	0.65	1	2	0.65	-	-	262
REF-0.60	0.60	0.60	1	2	0.60	-	-	221
SAP-1S(7.7%W)	0.65	0.60	1	2	0.60	0.050	0.001072	246
SAP-1L(7.7%W)	0.65	0.60	1	2	0.60	0.050	0.001072	255
SAP-1N(7.7%W)	0.65	0.60	1	2	0.60	0.050	0.001072	245
SAP-3(7.7%W)	0.65	0.60	1	2	0.60	0.050	0.003759	224

was de-ionized water, the other was cement slurry filtrate. Cement slurry filtrate was obtained by mixing ordinary Portland cement in de-ionized water and immersed 24 hours with continuous automated stirring. The suspension was subsequently filtered to remove residual solid cement particles. The water to cement ratio of cement slurry was 4.3, taking account of the current activity RILEM TC 260-RSC. The pH-value of the cement slurry filtrate is approximately 11.7, while that of de-ionized water is about 6.9.

(4) Rheology test

Plastic viscosity of mortars were measured with a commercial rheometer (Fig.3). It is common understanding that the absorption of pore solution by SAP is rapid and takes place in several minutes after mixing [7]. Mechtcherine et al. [8] have reported that the particle size distribution of SAP has exhibited a considerable effect on the plastic viscosity at the first point of time measured of 10 minutes after water addition to the mortars. Therefore, the fresh mortars were tested at 10 minutes after water addition. Before the measurement, the mortar was agitated (i.e. pre-sheared) 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 τ are a function of shear rate $\dot{\gamma}$ 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 rate 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 μ [8].

3. RESULTS AND DISCUSSION

3.1 Swelling behavior of SAP evaluated by the modified tea bag method

Fig.5 shows changes in absorption capacity of SAPs. After they were dipped for 10 minutes, all the SAPs exhibited rapid development of absorption

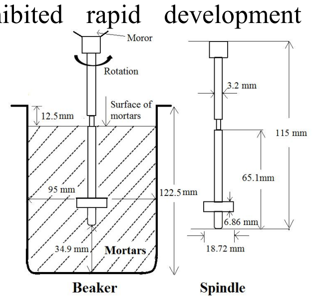


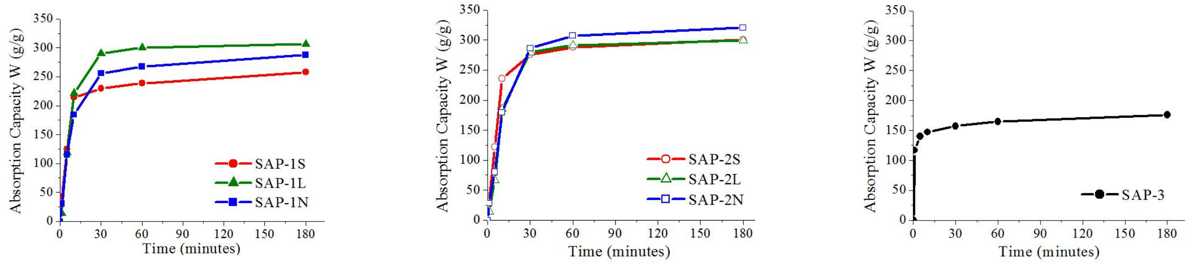
Fig.3 Schematic drawing of testing apparatus for the rheology test

capacities. When SAPs were immersed into de-ionized water (Fig.5 (a)), the maximum absorption capacity were observed at about 30 minutes and then changed little. When SAPs were immersed into the cement slurry filtrate (Fig.5 (b)), the maximum absorption capacity of any SAP sample was quite smaller than that in de-ionized water. The results are consistent with that measured by Snoeck [5]. The cations K^+, Na^+, Mg^+ and Ca^{2+} in cement slurry filtrate clearly results in the charge screening effect. Osmotic pressure which results from the relative lower concentration of ions within the SAP polymer network compared to the external environment, leads to a reduced swelling of the SAP.

In view of the results obtained by the tea bag method, SAP-3 with spherical shape showed relatively consistent values of absorption capacity even if different solutions were used. They may be related to surface properties of SAP-3 particles that are produced by inverse suspension polymerization. All the particles with different sizes are produced from the solution. Effect of this process will be discussed later. Contrary to this, there are appreciable differences in absorption capacities between particle sizes in SAP-1. In spite of the same production method as SAP-1, little differences between the sizes were seen in SAP-2. Effect of particle sizes on absorption capacity depends on the products even if the same method was used to produce SAPs [3].

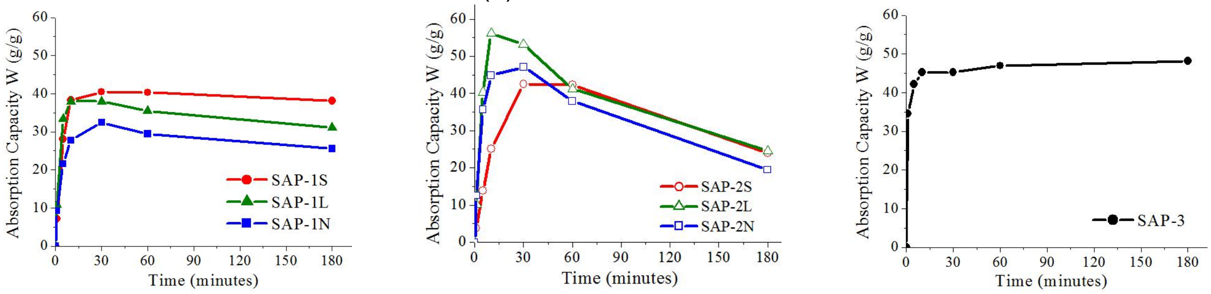
3.2 Swelling behavior of SAP evaluated by the filtration method

Fig.6 shows changes in absorption capacity of SAPs measured by the filtration method. When SAP was immersed into de-ionized water (Fig.6 (a)), a similar trend was observed in SAP-1 and SAP-2. SAP-1N of the original grading showed a greater absorption capacity than those of the large and small particles. Differences in the absorption behaviors were clearly seen in SAP-2 whereas little differences were present in the tea bag method (Fig.5 (a) (ii)). The sensitivity of particles size of SAP also be related to the measurement technique. Thus, the absorption property of SAP must be interpreted carefully not only from the data provided by the manufacture, but also by the proper measurement technical for the use in cement environment. Therefore, when SAP was immersed in cement slurry filtrate (Fig.6 (b)), decreases in the absorption capacity were observed in SAP-1L, SAP-2N and SAP-3. A significant decrease in absorption capacity of SAP-2 (Fig.5 (b) (ii)) was also observed. As mentioned above [9], the desorption from saturated SAP is mainly due to the diffusion of ions in the cement slurry filtrate of alkali solution.



i) SAP-1 ii) SAP-2 iii) SAP-3

(a) De-ionized water



i) SAP-1 ii) SAP-2 iii) SAP-3

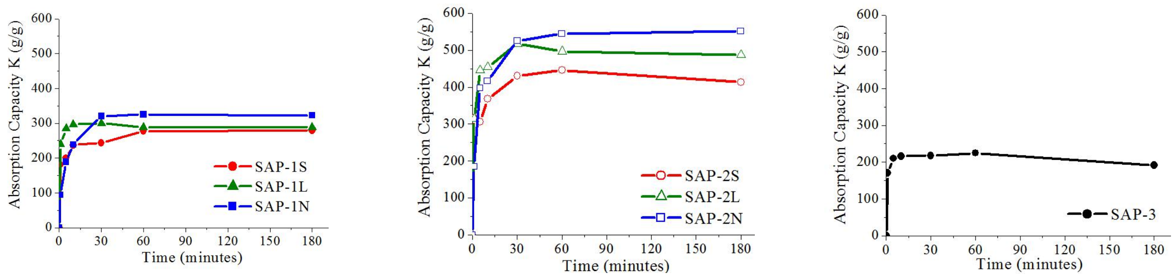
(b) Cement slurry filtrate

Fig.5 Change in absorption capacity measured by the tea bag method

In view of the results obtained by the filtration method, SAP-3 always showed the smallest value of absorption capacity, and SAP-2 has the largest value of absorption capacity. This result is consistent with the properties provided in Table 1. Furthermore, it also corresponds to the result in Fig.5.

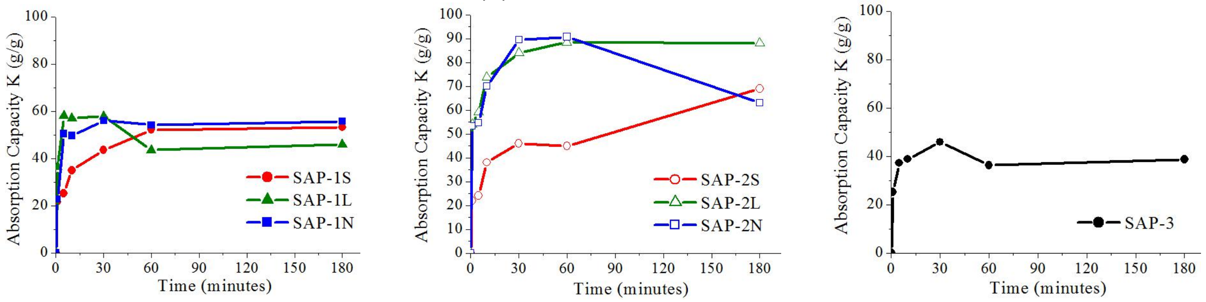
As found in Fig.5 also, SAP-3 with spherical shape that was produced by inverse suspension polymerization always showed a relatively stable absorption capacity than SAP-1 and 2. SAP of aqueous polymerization is macro-porous mass, which is produced by drying and pulverizing a gel-like elastic product. Dissolving reactants in water at desired concentrations, a fast exothermic reaction yields the gel-like elastic product with a large surface [10]. In the process of pulverization, the gel-like elastic product was pulverized and more new surfaces from its internal structure were exposed. This may be related to the difference in absorption capacity between particle sizes. In the process of inverse suspension polymerization, unique flowing properties of particles were provided [10]. This makes a better control of regulation of particle-size distribution. As a result of the process, SAP-3 particles could be less sensitive to the test fluid and the test methods.

3.3 Comparison of absorption capacity measured by two methods



i) SAP-1 ii) SAP-2 iii) SAP-3

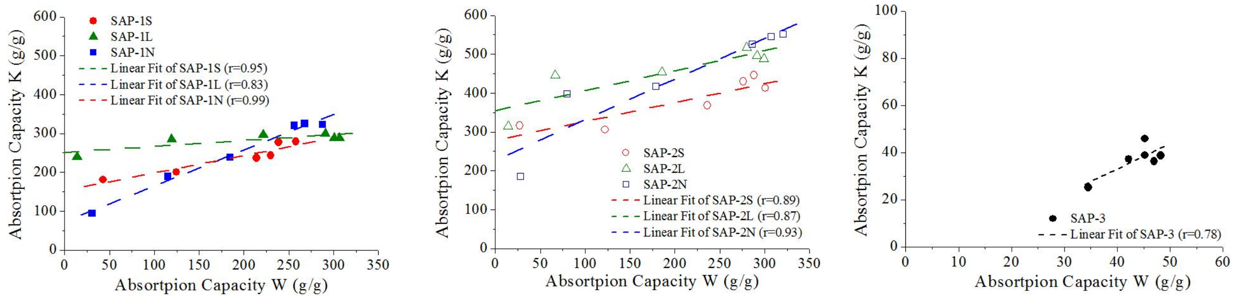
(a) De-ionized water



i) SAP-1 ii) SAP-2 iii) SAP-3

(b) Cement slurry filtrate

Fig.6 Change in absorption capacity measured by the filtration method



i) SAP-1 ii) SAP-2 iii) SAP-3

(a) De-ionized water

i) SAP-1 ii) SAP-2 iii) SAP-3

(b) Filtered cement slurry (w/c=4.3)

Fig.7 Correlation of absorption capacities measured the two methods

Fig.7 shows the relationship between absorption capacities measured by the two methods. The regression lines of linear fitting and correlation coefficients were given. When SAP is immersed into de-ionized water (Fig.7 (a)), it can be seen that the absorption capacities of SAP-1 obtained from the two different methods are well correlated, and the regression lines had high correlation coefficients. This indicates that the tea bag method and the filtration method give very similar information about the absorption capacity of SAP-1 immersed into de-ionized water. Compared with SAP-1, there were greater variation from linear regression in SAP-2 and SAP-3. At the same time, the absorption capacity K measured by the filtration method is always appreciably greater than the absorption capacity W. SAP particles were easy to form agglomeration on the corner of a tea bag, which caused an obviously reduction in the contacting area of SAP particles and test fluid[11]. In practice, insufficient swollen SAP was observed in the tea bag. The insufficient swollen SAP may affect the smaller value of absorption capacity obtained by the tea bag method.

In addition, the increase in absorption capacity W for the testing period (ΔW) was obviously greater than that in absorption capacity K (ΔK) for SAP-1S and SAP-1L, while ΔW and ΔK were very close for SAP-1N. The similar trend was also observed in SAP-2. The SAP that was not sieved showed a stable increase in absorption capacity than others. For SAP-3, the rate of increase in absorption capacity W to that in K was almost the same as SAP-1S and SAP-1L. Surfaces between SAP particles became larger with swelling. The larger particles, the more capillary water. The water between small particles was less since the packing of small SAP was denser than that of large SAP. The dense packing made a narrow channel to reduce capillary water. The water held by capillary forces between SAP particles cannot be totally removed by the tea bag method, while almost excess water dropped off in the filtration method. Therefore, these tendencies may results in a large increase in absorption capacity during the test period measured by the tea bag method. In short, the increase in absorption capacity W during the test period seems to be contributed by the retention of interparticle liquid.

When SAP immersed into cement slurry filtrate (Fig.7 (b)), there were significant variations from linear regressions for SAP-1 and 2 in contrast to that immersed into de-ionized water. However, for each SAP, the time-dependent change of absorption capacity showed a similar variation tendency whether SAP was immersed into de-ionized water or cement slurry filtrate. Thus, the tests with de-ionized water may be used for simple comparison of absorption capacity in cement environment while the absolute absorption capacity is quite different between the water and the cement slurry filtrate.

3.4 Effect of SAP addition on plastic viscosity of mortars

Fig.8 shows values of plastic viscosity. As seen in REF-0.65 and REF-0.60, mortars with lower water to cement ratio exhibit significant greater values of plastic viscosity. The low content of solid cement particles in a mortar with the high water to cement ration loosens the suspension, which intensifies the flow ability of the material (Table 2). When SAP was used, the freely available water in mortars was less than that in REF-0.65, thus the value of plastic viscosity of mortars with SAP was higher than that of REF-0.65.

One the other hands, with SAP addition led the

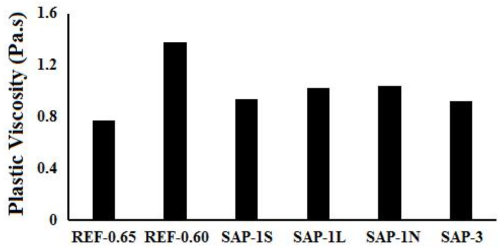


Fig.8 Comparison of plastic viscosity of mortars with different SAPs

effective water to cement ratio to similar to the reference specimens of REF-0.60, the plastic viscosity of mortars with SAP were lower than that of REF-0.60. This seems to be a logical case. When SAP was placed in hydraulically active suspensions, the absorption rate of SAP decreased since SAP must compete for water with cement and other fine solid particles.

However, differences of plastic viscosity between the mortars with SAPs are not as great as a whole. The results in this study do not agree with the result of Mechtcherine et al. [8]. All the SAPs reduce the internal friction of the mortar as gel-like water. Incorporation of different types of SAP does not lead to a great difference in plastic viscosity in mortars at the first time. However, as mentioned above, absorption and desorption properties depend on the types of SAP and time-dependent changes are expected. Therefore, it should be noted that the workability at 10 minutes after adding water could not be used for judging casting concrete at site if there is a time lag between the initial mixing and casting.

4. CONCLUSIONS

The kinetics and sorption capacity of SAPs were investigated. Major results obtained in this study are as follows：

(1) Evaluation of absorption capacity measured by the tea bag method is smaller than that by the filtration method. The results of tea bag method is easier to be affected by agglomeration of SAP particles, which seems to lead to insufficient swollen SAP.

(2) The increase in absorption capacity during the test period by the tea bag method seems to be contributed by the retention of interparticle liquid.

(3) A similar variation tendency was observed between the two methods when SAP was immersed in de-ionized water and cement slurry filtrate. De-ionized water may be used as a simple exposure fluid for preliminary test to compare SAP intrinsic properties in cement environment.

(4) SAPs produced by inverse suspension polymerization showed a relatively consistent behavior of absorption capacity than SAPs produced by aqueous polymerization.

(5) Differences of plastic viscosity at 10 minutes between the mortars with SAPs are not as great as a whole. It should be noted that the workability at 10 minutes after adding water could not be used for judging casting concrete at site.

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