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# Influence of Superplasticizers on Early Age Drying Shrinkage of Cement Paste with the Same Consistency

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**Abstract:** The influence of superplasticizer (SP) on the early age drying shrinkage of cement paste with the same consistency was investigated. To conduct the test, which lasted for 72 hours, three paste mixtures were used for comparison. The 72 hours early age drying shrinkage starting from the initial setting time was measured by a clock gauge. The pore size distribution was measured by Mercury Intrusion Method. The surface tension of capillary simulation liquid and mass loss of paste were also measured. The experimental results showed that the addition of SP increased the early drying shrinkage greatly. The ratios of water evaporation and the total free water in mixtures added with SPs showed great differences. SPs fined the capillary pores of paste, and the volume of pore with diameter within 50 nm was well consistent with shrinkage rate. The addition of SPs did not raise the capillary liquid surface tension. It showed that with the volume of pore with diameter within 50 nm and the ratio of water evaporation and the total free water a tolerable shrinkage result of paste added with SP could be predicted, and the elastic modulus could have an influence on the early shrinkage. These results have never been proposed before.

**Key words:** superplasticizer; early age drying shrinkage; paste; water evaporation; pore size distribution

## 1 Introduction

Superplasticizers are able to enhance the placing characteristics of concrete mixtures by increasing the workability level at a given  $w/c$ , which makes an easier placement of concrete mixtures, even with low  $w/c$  required for strength or durability<sup>[1]</sup>. The influence of SPs on the shrinkage (both autogenous shrinkage and drying shrinkage) of concrete is widely studied by investigators. The autogenous shrinkage is slightly reduced by SP, and the differences of different types of SPs and dosages are small<sup>[2]</sup>. And plain and silica fume cement concretes experiments indicate that SPs have a beneficial effect on reducing plastic shrinkage cracking<sup>[3]</sup>. However, there are still many investigators holding reversed opinions. Brook concludes that the addition of plasticizers and superplasticizers brings a

general increase in drying shrinkage between 3 and 130%<sup>[4]</sup>. And when keeping both the  $W/B$  ration and the content of cement paste constant, SP could increase free shrinkage, and further increase it if the dosage of SP is larger<sup>[5]</sup>. Erika Holt attributes the great shrinkage to improved cement dispersion and faster rate of hydration<sup>[6]</sup> while Yang and Wen attributes it to the fined capillary pore-pore volume with diameter from 3.2 nm to 25nm distinctly increased in mortars with SP<sup>[7]</sup>. Researches in the Ref.[8] provide a good understanding of the influence of superplasticizers on concrete and paste.

Superplasticizers not only increase the workability of the concrete with a constant  $w/c$  ratio, but also increase the compressive strength of it with same slump. And the fact is that in practical engineering, workability and compressive strength are the most important factors of cement paste. To guarantee the compaction and uniform of concrete, some special limits of the concrete slump on specific structural elements in concrete placement shall be satisfied. Otherwise, the shrinkage of concrete will be affected by the stability of mix and paste rheology. Previous studies were mainly on the influence of SP on the shrinkage

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by keeping the  $w/c$  ration constant, which increased the workability of concrete immensely. Obviously, the stability of mix and paste rheology changes with the addition of SP, and these properties can influence the shrinkage of concrete a lot. But there are few studies focusing on the shrinkage of concrete with the same slump.

This paper studied the influence of SP on early age drying shrinkage of mixtures with the same workability but different  $w/c$  ratios, which was close to the practical engineering. It is known that shrinkage of concrete is caused by the shrinkage of cement matrix, and aggregates restrain the shrinkage<sup>[6]</sup>. This paper ruled out the influences of aggregates by making paste mixtures so as to provide a better understanding of the laws and the mechanism of early drying shrinkage influenced by SP. Two different  $w/c$  ratios were used, 0.27 and 0.22. Two different kinds of SPs were also used in lower  $w/c$  ratio mixtures to get the same consistency with the control one. The early age drying shrinkage of each paste mixture was measured, and the water loss of each mixture was also studied. Besides, Mercury Intrusion Method was used to inspect and verify the mechanism of the superplasticizer's influence on the pore size distribution. At last, capillary liquid in cement paste was simulated to measure the capillary surface tension. Experimental results were presented thereafter.

## 2 Experimental

### 2.1 Materials and mix proportions

Table 1 Mix design of paste

Type	BC	FDN	PS
$w/c$	0.27	0.22	0.22
Cement/(kg/m <sup>3</sup> )	1 657	1 709	1 523
Water/(kg/m <sup>3</sup> )	449	371	330
Type of SP	None	Naphthalene	Polycarboxylate
Dosage of SP/(kg/m <sup>3</sup> )	None	15.38 (0.9%) <sup>1</sup>	6.85 (0.45%) <sup>1</sup>
Apparent density/(g/cm <sup>3</sup> )	2.11	2.09	1.86 <sup>2</sup>
Initial setting time	101min	160 min	151 min
1 day compressive strength/(N/mm <sup>2</sup> )	21.5	31.5	27.5

<sup>1</sup>The percentage in brackets refers to the ratio of SP against the quality of cement

<sup>2</sup>The polycarboxylate used in the experiments has a good air-entraining effect, so the apparent density of mixture PS is much smaller

The P•O 42.5 portland cement and two types of SPs were used in the experiments: ZWL-V naphthalene

SP from Zhejiang Wulong Chemical Co., Ltd., and JL-PCEP-I polycarboxylate SP (the solid content being 25%) from Shangyu Jielong Chemical Building Materials Co., Ltd. Table 1 shows the mix proportions.

### 2.2 Methods and equipment

Practical engineering shows that the shrinkage starting from initial setting is an important reason for concrete cracks. The curing is often neglected in the period from the initial setting to the final setting in practical engineering, when the cracks often appear. We started to measure the drying shrinkage at the time of initial setting because of the difficulties to measure the shrinkage accurately as the concrete is still in plastic condition and very poor in strength before the initial setting time. We started to measure the drying shrinkage right at the initial setting time when all mixtures had the same strength to resist shrinkage. Also starting measurement at this time could provide a better understanding of the influence of SP on early age drying shrinkage.

All mixtures were sealed before that time to ensure that there is no drying shrinkage before measurement. At the initial setting time, all specimens were opened at the right point when drying shrinkage arose and the measurement began.

Fig.1 shows the experimental equipment for shrinkage measurement in detail. The size of each specimen was 50 mm×50 mm×300 mm. 1 mm Teflon plate and a layer of plastic film were put at the bottom of concrete specimens for decreasing the frictional resistance respectively. Furthermore, Teflon plate and plastic film were also set around paste specimens to prevent the paste leakage when casting and vibrating. The Teflon plate was drawn off the moment when measurement started. Detachable probes, which were in contact with clock gauges fixed at the both ends of modules, were buried in specimens respectively in advance. Rods of detachable probes were separated from the modules walls during the operation, so that free shrinkage could be measured by clock gauge.

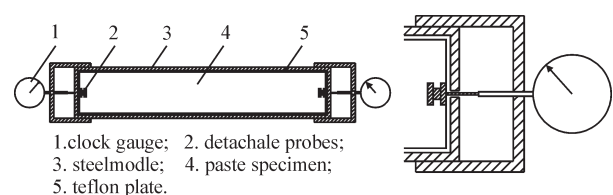


Fig.1 Full (left) and part (right) figures of paste shrinkage measurement equipment

The paste cube size used for compressive strength measurement was 2 mm×2 mm, and the testing

machine was electronic universal testing machine made by Julong Computer Testing Machine Co., Ltd. The pore size distribution was determined by using a Micromeritics Auto Pore IV 9500, and the capillary surface tension was measured by Automatic surface tension meter, BZY series, produced by Shanghai Fangrui Instrument Co., Ltd. Hereby a method was designed for measuring the surface tension of capillary liquid in paste and the result could be referred to in this paper. Furthermore, two kinds of liquids were prepared for the measurement. The first one was made by adding SPs directly into water according to the original mixtures shown in Table 1, functioning as a control group. The second one was prepared as follows: cement paste of each mixture was mixed and divided into a number of small pieces after the initial setting time. Then the pieces were soaked in water (at least 30% of the specimen needed to immerse the pieces) for 2 hours. At last such liquid was poured into a breaker, and stirred for 3 minutes. The second kind of liquid functioned as a simulation of capillary liquid in cement paste.

### 2.3 Specimen preparation and measurement

The setting time and consistency of paste were measured according to the Chinese Standard (GB/T 50080-2002). Plastic film was used to shield the specimens immediately after placement, then all specimens were placed into the curing room with a temperature of  $20 \pm 2$  °C and a humidity of  $65\% \pm 5\%$  RH. Before the initial setting time all the specimens were sealed. But after that all specimens were exposed to air with one surface while the other surfaces were still covered with plastic films. There were two specimens of each group prepared to measure the mass loss of specimens. We had the shrinkage curves starting from the initial setting time and lasting 3 hours studied.

## 3 Results and discussion

### 3.1 The early age drying shrinkage of cement paste

The shrinkage increases with the  $w/c$  ratio<sup>[9]</sup>. Brooks<sup>[4]</sup> confirmed that the drying shrinkage of cement paste was proportional to  $w/c$  ratio when the  $w/c$  ratio was between 0.2-0.6. According to Brooks, the mixture FDN and PS ( $w/c=0.22$ ) should have had smaller shrinkage than that of BC ( $w/c=0.27$ ) if there were no addition of SPs.

The results of the 3 days drying shrinkage of paste starting from the initial setting time are shown in Fig.2. From the shrinkage curves it can be seen that the

shrinkage rate in the first 5 hours after the initial setting time is very high, but then experiences a phase of relatively slow growth, which means a lower shrinkage rate. The shrinkage rate of mixture added with polycarboxylate SP is the highest (PS), followed by that of the mixture added with naphthalene SP (FDN). Both mixtures added with SP have larger shrinkage than that of the control group (BC). The differences of the three groups are significant in the first 5 hours, and it could be calculated that the shrinkage rate of FDN was 2.49 times that of BC, and the rate of PS was 2.76 times that of BC, group PS and group FDN possessing much higher shrinkage rates than BC. But 1 day later, the shrinkage rate (slope of shrinkage curve) of BC is close to that of PS, and the shrinkage rate of FDN is the lowest, which is different from that in the first 5 hours. We draw a conclusion that the total early drying shrinkage of paste is determined by the first 5 hours shrinkage rate and that overall the addition of SP increases the early age drying shrinkage intensely.

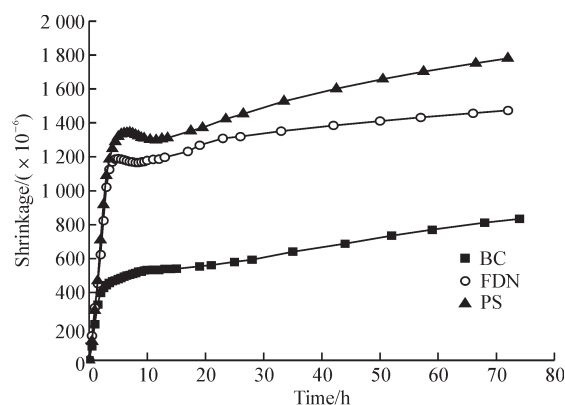


Fig.2 Early age drying shrinkage of cement paste

### 3.2 The evaporation of water in paste mixtures

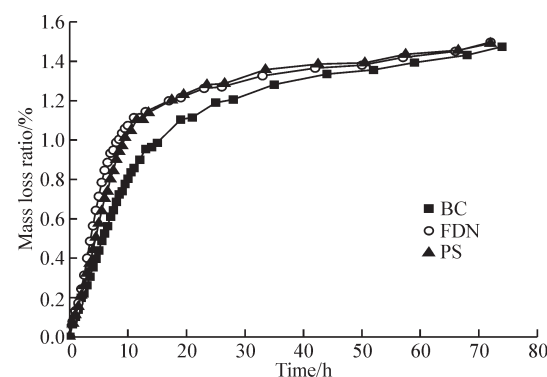


Fig.3 Mass loss ratio of cement paste

In this paper, mass loss ratio of paste is defined as mass loss (water evaporation) divided by the total mass of the cement paste. Fig.3 shows the mass loss ratio of paste starting from the initial setting time.

All specimens were sealed before the initial

setting time, which meant there was no water loss, so that the mass loss ratios could be compared scientifically. From Fig.3, it can be observed that the evaporation rate is very high in the first 15 hours but tends to be stable later. The evaporation rates of mixtures FDN and PS are similar, while the control group (BC) without SP seems relatively low. But 72 hours later, the mass loss ratios of all mixtures tend to be close to each other.

The curves shown in Fig.3 are the absolute evaporation of water. However, when coming to the relative evaporation of water, namely, the ratio of evaporation and total water used in each specimen, the curves are much different. The results of the relative evaporation of water are shown in Fig.4. The value of BC is about 6.9% in 72 hours, and the values of FDN and PS are closed to 8.4%. Obviously, this is not a small gap. But the discrepancy mainly occurs in the first 15 hours like that of the absolute evaporation of water.

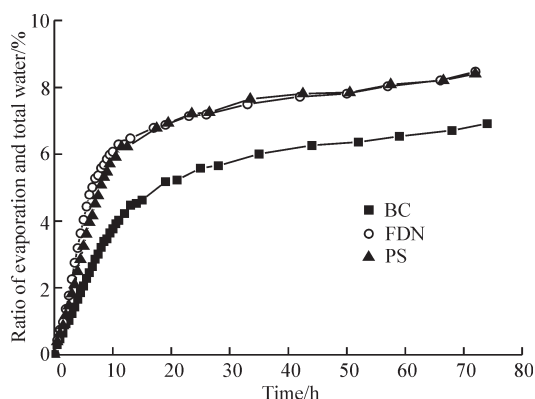


Fig.4 The ratio of evaporation and total water

Neville<sup>[9]</sup> believes the nonevaporable water content increasing with the cement hydration. Lea<sup>[10]</sup> holds that nonevaporable water content accounts for 23% of the quality of cement in completely hydrated cement. The degree of hydration in 72 hours almost accounts for 50% of the completely hydrated cement<sup>[11]</sup>. Figure in the Ref.[12] shows that the 3 days ignition losses of paste added with polycarboxylate or naphthalene SP are similar with that of blank control mixture. That is to say, the degree of hydration is not significantly influenced by the addition of polycarboxylate or naphthalene SPs. Based on such theory, the degree of neat cement hydration can be calculated using the following formula<sup>[13]</sup>:

$$\alpha_c = Wn_t / Wn_{\infty} \quad (1)$$

where,  $Wn_t$  is the quantity of chemically bonded water at time  $t$ , and  $Wn_{\infty}$  is the quantity of chemically bonded

water for complete hydration. As mentioned above, chemically bonded water content accounts for about 23% of the quality of cement in completely hydrated cement, so the formula can be expressed as:

$$\alpha_c = Wn_t / 0.23 \quad (2)$$

where,  $Wn_t$  is considered as the ignition losses in the range of 150-900 °C<sup>[14]</sup>. The chemically bonded water content of pastes mixture in this paper was measured by the methods mentioned in reference<sup>[14]</sup>, and the result of hydration degree of each mixture is shown in Fig.5.

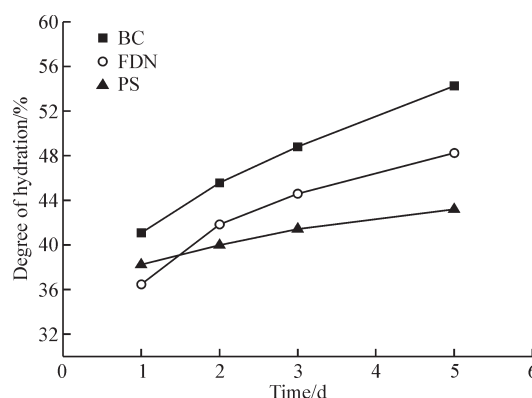


Fig.5 Hydration degree of each mixture

The size of every specimen is 50 mm×50 mm×300 mm, so the mass of water in each specimen can be calculated according to the apparent density of each mixture (shown in Table 1).The water mass is 336 g in BC, 277 g in FDN and 248 g in PS respectively.

The hydration degree of each mixture in 72 hours was measured. Results show that the hydration degree of BC is 48.8%, FDN 44.59% and PS 41.43%. Then the water needed for hydration in 72 hours of each group can be calculated. Water needed for hydration in 72 hours is 164 g for BC, 124 g for FDN and 103 g for PS, so the total free water of each mixture after 72 hours is 172 g, 153 g and 145 g, respectively, including evaporation and the free water left in paste after 72 hours. Thereafter, the ratio of the evaporation and the total free water is calculated, and the results are shown in Fig.6.

It can be found from the figure that the ratios of evaporation and the total free water of mixtures with SPs (FDN and PS) are up to 11.6% and 10.5% respectively in first 10 hours after the initial setting time, which are much bigger than that of BC whose ratio is just 6.4%. The ratios of evaporation and the total free water of paste mixture with SP are significantly bigger than that of the blank control paste. The ratios of evaporation and the total free water or the ratio of evaporation and the total water

can reflect the shrinkage well. In order to find the numerical relationship between shrinkage and the ratio of evaporation and the total free water, the ratios of each mixture in the first 5 hours are compared. We find out that the ratio of PS is 1.66 times that of BC and the ratio of FDN is 2.19 times that of BC.

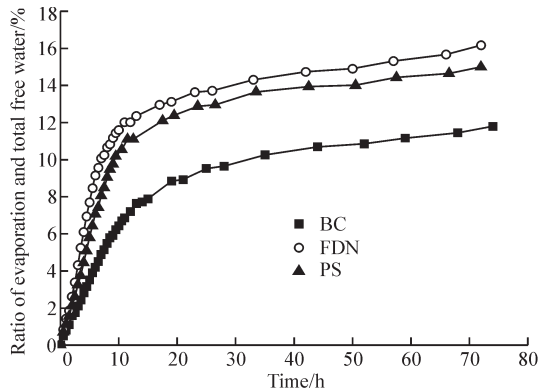


Fig.6 The ratio of the evaporation and the total free water

### 3.3 Surface tension of capillary liquid

Table 2 Capillary liquid surface tension/( $\times 10^{-3}$  N/m)

	FDN	PS	Control	Water
Water added with SP directly	70.9	61.8	none	72.0
Capillary liquid simulation	66.5	67.7	72.2	72.3

The result of surface tension of capillary in cement paste is shown in Table 2.

From Table 2 it can be observed that the addition of SPs does not raise the capillary liquid surface tension. In contrast, the capillary liquid surface tension in mixture added with SP is even lower than that of control mixture, which is consistent with the research in the Ref.[2].

### 3.4 Mechanism analysis

#### 3.4.1 The differences in relative evaporation of paste mixtures

The main reason for the emergence of pressure leading to shrinkage is the physical process but not the chemical causes which are not dominant in such early age<sup>[15]</sup>. Water evaporation is faster than the bleeding of paste in the initial hours after casting, resulting in a water loss of paste surface. Meniscus formed between solid particles which induce tensile stress on the pores walls can be attributed to the water loss. While the radius of capillary meniscus keeps decreasing with the evaporation of water, the pressure on the pore walls keeps increasing which leads to more shrinkage.

Furthermore, if we do not take the effect of SPs on the paste capillary pores into consideration (namely the pore size distribution of mixtures with and without

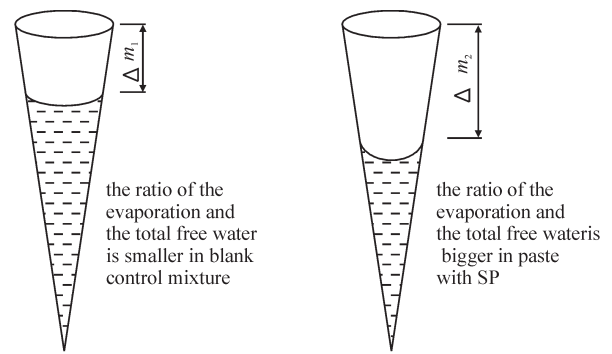


Fig.7 The influence of relative evaporation on early drying shrinkage of paste

SPs assumed similar), it can be inferred from Fig.4 that the ratio of evaporation and total free water of mixture without SP is smaller. That is to say, the change of the meniscus curvature is not such rapid, which can be seen from Fig.7. But for paste added with SPs, the ratios of evaporation and total free water are high. That may lead to more notable changes in the curvature of capillary pores, resulting in a smaller radius of meniscus curvature and a smaller contact angle of the interface between solid and liquid phases<sup>[16]</sup>, which are in accordance with the results shown in reference<sup>[17]</sup>. According to Laplace equation, a smaller contact angle leads to a greater capillary tensile force on pore walls as follows:

$$p_G - p_L = \frac{2\gamma}{r_s} \cos\theta \quad (3)$$

where,  $P_G$  is the pressure of the gas phase (Pa),  $P_L$  is the pressure of the liquid phase (Pa),  $r_s$  is the curvature of the interface (= radius of capillary) (m),  $\gamma$  is the surface tensile force of liquid water (N/m), and  $\theta$  is the contact angle.

From such result it can be found out that relative water evaporation makes a significant difference on the early age drying shrinkage of paste.

#### 3.4.2 The changes in pore size distribution of paste mixtures

The pore size distribution of each mixture was determined by Mercury Intrusion Method. The samples were cured in the same way as the paste mixtures. Results are shown in Figs.8-9.

From the results of pore size distribution of each mixture, it can be observed that the use of SPs not only disperses the cement particles but also makes capillary pores of cement paste finer, whether in 1 day or 3 days. According to Laplace equation, the finer the pore size, the bigger the shrinkage stress.

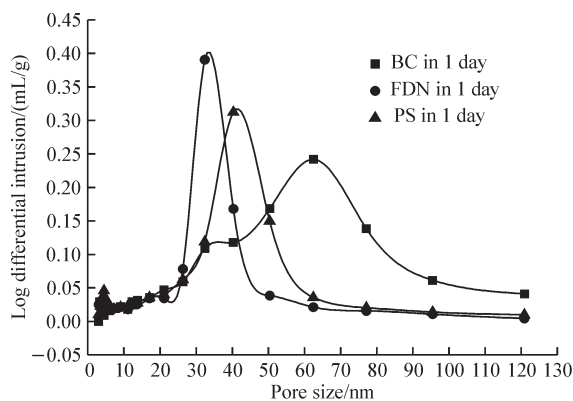


Fig.8 Pore size distribution of mixtures in the first day

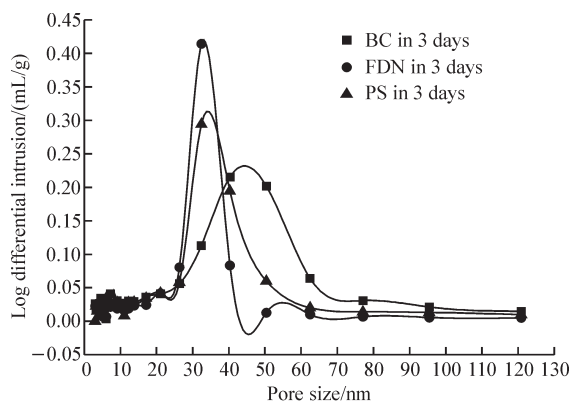


Fig.9 Pore size distribution of mixtures in 3 days

Mehta<sup>[18]</sup> found out that the pore size greater than 50 nm mainly influences the strength and permeability, and pore size smaller than 50 nm mainly affects the drying shrinking and creep. From the experiment we get the results that the pore volume within 50 nm in the first day was 0.066 mL/g of BC, 0.086 mL/g of FDN, and 0.087 mL/g of PS. The pore volumes within 50 nm of mixture FDN and PS are much larger than that of BC. When compared to the shrinkage result, which shows that the increase of shrinkage in mixtures added with SPs mainly occurs in the first day, we can see that the greater the pore content within 50nm, the greater the early drying shrinkage rate. It could be calculated that the pore volume of diameter within 50 nm of PS is 1.32 times that of BC, and the pore volume of FDN is 1.30 times that of BC.

Results from surface tension test show that the surface tension does not increase with the addition of SP. That is to say, the difference in capillary liquid surface tension caused by SP does not have an influence on shrinkage. But the pore volume of diameter within 50 nm and the ratio of evaporation and the total free water do have. If we take the influences of both pore volume of diameter within 50 nm and the ratio of evaporation and the total free water into consideration,

it can be calculated that the FDN increases by 1.32(multiples of pore volume of diameter within 50 nm)  $\times$  2.19(multiples of the ratio of evaporation and the total free water) = 2.85 times of shrinkage than BC, and mixture PS increases 1.3(multiples of pore volume of diameter within 50 nm)  $\times$  1.66(multiples of the ratio of evaporation and the total free water) = 2.2 times of shrinkage than that of BC. Compared with the actual shrinkage ratio of and FDN (2.49 times) and PS (2.76 times), there is still a gap, *i.e.*, the PS' actual shrinkage is much bigger than 2.2. But this result can still to some extent reflect that the shrinkage increases by the addition of SPs. The reason is that the elastic modulus of PS is smaller. Table 1 shows that the PS has a smaller density and smaller compressive strength than that of FDN, which leads to a smaller elastic modulus and a larger shrinkage under the same shrinkage stress of PS. But the specific relationship among elastic modulus, density and compressive strength still needs further research.

## 4 Conclusions

a) The shrinkage rate of paste reaches its top in first 5 hours after initial setting time. The differences between mixtures added with different SPs and blank mixture appear in the first 5 hours, and the shrinkage has a little increase 5 hours later. Shrinkage of paste with polycarboxylate SP is the largest, followed by paste with naphthalene SP. But both pastes added with SP have much more shrinkage than the control group.

b) The evaporation rate is very high in 15 hours after the initial setting time but slows down later. The evaporation rates of group FDN and group PS are similar, and that of the control group is relatively slow. But if we take into consideration of the ratio of the evaporation and the total free water of each specimen, the values of mixtures added with SPs are much bigger than that of the control mixture, as well as much more curvature radius change in capillary meniscus.

c) The addition of SPs fines the capillary pores of paste, which leads to a bigger pressure on pore walls. The pore volume within 50 nm is well consistent with early age drying shrinkage. The more pores within 50 nm, the more early age drying shrinkage.

d) The addition of SPs does not increase the surface tension of capillary liquid in paste.

e) By calculation, the change of pore volume of diameter within 50nm and the ratio of evaporation and the total free water are able to reflect the shrinkage

increased by the addition of SP, and we speculate that the elastic modulus would have an important impact on early age drying shrinkage.

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