Effects of Storage Temperature on the Performance of Sulfonated Scetone-formaldehyde Superplasticizers

Zunyu LIU
KZJ New Materials Group Henan Co. Ltd., Xinxiang, Henan 453731, China
owen@xmabr-kzj.com
*Corresponding author, E-mail: 524598417@qq.com

Abstract. Taking temperature as the research object, the effects of different storage temperatures on the performance of sulfonated acetone-formaldehyde superplasticizers (SAF) were studied. The molecular weight of the SAF were characterized by GPC, and disperse performance were evaluated by cement paste fluidity test. The results showed that when the temperature was higher than 40°C, the relative molecular weight of the SAF increased during storage process, and its disperse performance became worse. The influence of storage temperature on the disperse performance of the SAF can be weakened by adding the chain terminator.

1. Introduction
SAF is a kind of polymer concrete admixture obtained by sulfonation and polycondensation with acetone, formaldehyde and sulfonating agent as main raw materials[1]. SAF has the advantages of high water reducing ratio, good adaptability to sand and gravel, and high cost performance. It is widely used in commercial concrete. At present, the research on SAF focuses on optimization of synthetic formula and improvement of production process[2-4]. However, there is almost no research on the influence of storage conditions on the performance of SAF.

In this paper, the storage temperature is used as a controlling factor for the storage of SAF. The influence of different storage temperatures on the dispersion performance of SAF is studied. At the same time the relative molecular weight of SAF are further explored by adding chain terminator.

2. Test

2.1. Materials
Acetone, formaldehyde, caustic soda solution, sulfonating agent A, chain terminator B, Meng Dian P.O 42.5 cement.

2.2. Synthetic method of SAF
(1) Add sulfonating agent (sodium bisulfite, sodium sulfite or sodium metabisulfite) and water into the reaction flask, heat to the specified temperature for hydrolyze for 30 minutes, adjust pH with caustic soda solution.

(2) Simultaneously add formaldehyde, acetone and sulfonating agent into the beaker and mix at 40°C.

(3) After the solid components are dissolved, add the mixture dropwise to the reaction flask within...
the specified time. Raise the temperature to about 95°C, keep it for 4h, stop heating, cool naturally, and stop stirring when the temperature drops to 50-60°C. Cool to room temperature to obtain an aliphatic superplasticizer product.

2.3. Storage test of SAF
Store the SAF in water baths at 70°C, 60°C, 50°C, 40°C and 30°C. The chain terminator B is added to SAF at a mass ratio of 1%, 3% and 5%, and the storage test is performed under the same conditions.

2.4. Performance test methods

2.4.1. Gel permeation chromatography (GPC).
The US Waters 2414 gel permeation chromatograph is used. The chromatographic column consists of Ultrahydragel TM250 and Ultrahydragel TM500 in series. Test conditions: column temperature 40°C, differential detector temperature 40°C, mobile phase flow rate 0.8Ml/min.

2.4.2. Cement paste fluidity.
Cement paste fluidity test according to GB/T 8077-2012“concrete admixture uniformity test method” implementation. The cement paste fluidity is used to characterize the disperse performance of SAF.

3. Experimental results and discussion

3.1. Influence of storage temperature on the performance of SAF
The SAF were stored in water baths at 70°C, 60°C, 50°C, 40°C and 30°C. The cement paste fluidity were tested at a frequency of every 1 day to obtain the storage period of SAF. The experimental results are shown figure 1, figure 2.

Figure 1. The results of initial cement paste fluidity

It can be seen from Figure 1 that when SAF were stored at 70°C and 60°C for 3 days, their disperse performance begin to deteriorate. Then SAF continued to be stored for 11 days, the disperse performance was lost basically; when SAF were stored at 50°C, their disperse performance gradually deteriorated with the storage time. But when SAF were stored for 13 days, their disperse performance deteriorated sharply; when SAF were stored for 13 days, their disperse performance began to deteriorate; when SAF were stored at 30°C for 15 days, their disperse performance didn’t change obviously.
It can be seen from Figure 2 that when SAF were stored at 70°C and 60°C for 3 days, their disperse performance after 30mins began to deteriorate. Then SAF continued to be stored for 6 days, and the disperse performance was lost basically after 30mins; when the SAF were stored at 50°C, their disperse performance after 30mins gradually deteriorated with the storage time. But when SAF were stored for 9 days, their disperse performance deteriorated sharply; when SAF were stored at 40°C for 13 days, their disperse performance after 30mins began to deteriorate; when SAF were stored at 30°C for 15 days, their disperse performance after 30mins didn’t change obviously.

The disperse performance of SAF needs to be comprehensively analyzed for the initial and 30min cement slurry fluidity. So when SAF is stored at 70°C and 60°C for 3 days, its disperse performance becomes poor. When SAF is stored at 50°C for 9 days, its disperse performance becomes worse. When SAF is stored at 40°C for 11 days, its dispersing performance becomes poor. When SAF is Stored at 30°C for 15 days, its dispersion performance don’t change obviously.

### 3.2. Influence of chain terminator on the performance of SAF

The chain terminator B was added to SAF at a mass ratio of 1%, 3%, and 5%, and the SAF were stored in water baths at 70°C, 60°C, 50°C, 40°C and 30°C. The cement paste fluidity is tested at a frequency of every 1 day. The experimental results are shown figure 3-figure 8.

![Figure 3. The results of initial cement paste fluidity of 1% chain terminator](image)
The results show that when the content of chain terminator B was 1% and 3%, the initial cement paste fluidity of SAF were less affected. When the content of chain terminator was 5%, the initial cement paste fluidity of SAF decreased by about 10%. That it, water reducing ratio of SAF decreased. The chain terminator is a low-concentration liquid. So When the content of the chain transfer is higher, it will dilute the concentration of SAF and reduce the water reducing ratio of SAF.

When the content of the chain terminator B was 1%, SAF were stored at 70°C and 60°C for 3 days, the initial cement paste fluidity began to decrease. That is, the disperse performance of SAF began to deteriorate. Then SAF continued to be stored for 11 days, and they had no disperse performance basically; when SAF were stored at 50°C for 3 days, the initial cement paste fluidity began to decrease, but the initial cement paste fluidity did not change significantly as the storage time increased; when SAF were stored at 40°C and 30°C for 15 days, the initial cement paste fluidity didn’t decrease significantly, and the disperse performance of SAF didn’t decrease significantly.

When the content of the chain terminator B was 3% and 5%, SAF were stored at 70°C, 60°C, 50°C, 40°C and 30°C for 15 days, the initial cement paste fluidity didn’t decrease significantly, and the disperse performance of SAF didn’t decrease significantly.
The results show that when the content of the chain terminator B was 1%, SAF were stored at 70°C for 5 days, the cement paste fluidity decreased sharply after 30mins, and the disperse performance of SAF were basically lost after 30mins; when SAF were stored at 60°C for 5 days, the cement paste fluidity decreased gradually after 30mins, and the disperse performance of SAF deteriorated gradually after 30mins; when SAF were stored at 50°C for 11 days, the cement paste fluidity decreased gradually after 30mins, and the disperse performance of SAF began to deteriorate gradually after 30mins; when SAF was stored at 40°C and 30°C for 15 days, cement paste fluidity didn’t decrease significantly after 30mins, and the disperse performance of SAF didn’t decrease significantly after 30mins.

When the content of the chain terminator B was 3%, SAF were stored at 70°C, 60°C, 50°C, 40°C and 30°C for 15 days, the cement paste fluidity didn’t decrease significantly after 30mins, and the
disperse performance of SAF didn’t decrease significantly after 30mins.
when the content of the chain terminator B was 5%, SAF were stored at 70°C for 9 days, the cement paste fluidity decreased gradually after 30mins, and the disperse performance of SAF began to deteriorate gradually after 30mins; when SAF were stored at 60°C for 11 days, the cement paste fluidity decreased gradually after 30mins, and the disperse performance of SAF began to deteriorate gradually after 30mins; when SAF were stored at 50°C, 40°C and 30°C for 15 days, the cement paste fluidity didn’t decrease significantly after 30mins, and the disperse performance of SAF didn’t decrease significantly after 30mins.

3.3. GPC test of SAF

The relative molecular weight of SAF is affected by the ratio of raw materials, and its relative molecular weight increases with the increase of polymerization concentration[5-7]. The chain terminator B was added to SAF at a mass ratio of 1%, 3%, and 5%, and the SAF were stored in water baths at 70°C, 60°C, 50°C, 40°C and 30°C for 15 days. Use GPC to test relative molecular weight of SAF. The experimental results are shown figure 9.

![Figure 9. The number average molecular weight of SAF](image)

It can be seen from figure 9, when the content of the chain terminator B was 1%, SAF were stored at 30°C and 40°C for 15 days, the relative molecular weight of the SAF remains within the normal range; when SAF were stored at 50°C, 60°C and 70°C for 15 days the relative molecular weight of the SAF increases significantly. Correspondingly, the viscosity of SAF increases, and the cement paste fluidity decreases significantly. When the content of the chain terminator B was 3% and 5%, SAF were stored at 70°C, 60°C, 50°C, 40°C and 30°C for 15 days, the relative molecular weight of the SAF remains within the normal range. Correspondingly, the viscosity of SAF is normal, and the cement paste fluidity has no obvious change. The disperse performance of water reducing agent is determined by its adsorption efficiency and electrostatic repulsion on the cement particles. As the relative molecular weight of SAF increases, the increase in the corresponding cross-linked products will make the disperse performance of SAF worse. This may be due to the conformation of the polymer molecules which have cross-linked structure into a curled state, which reduces the adsorption efficiency of the water reducing agent[8-11]. The use of chain terminator effectively delays the condensation reaction of SAF during storage process and maintains its molecular weight in a normal range. The chain terminator can ensure that SAF has a relatively stable water-reducing rate.

4. Conclusions

In this paper, the influence of different storage temperatures on the dispersion performance of SAF is studied. At the same time the relative molecular weight of SAF are further explored by adding chain terminator. Through the study, the main conclusions are as follows:

(1) Storage temperature is an important factor affecting the performance of SAF. When the temperature is higher than 30°C, the disperse performance of SAF will deteriorate and the water-reducing rate of SAF will decrease with storage time.
(2) The chain terminator can delay the condensation reaction of SAF during storage process. The influence of storage temperature on the disperse performance of the SAF can be weakened by adding the chain terminator.

References
[1] Wang Z H, Fan Y Q, Chen D L. (1990) Synthesis and performance of sulphonated acetone-formaldehyde polycondensates as dispersant for cement slurries. Oilfield Chemistry, 7(2):129-133.
[2] Huang S M. (2009) Study on synthesis and process optimization of aliphatic superplasticizer. Xi’an, Xi’an University of Architecture and Technology.
[3] Zhang H L, Lin B S, Sun S H, et al. (2004) Study on the synthesis and performance of modified aliphatic superplasticizer. Concrete, 6:72-73.
[4] Wang J M, Liu Y S. (2007) Study on the production of aliphatic superplasticizer by heat-free method. Chemical building materials, 23(6):43-46.
[5] Zhang Z, Yang D J, Yi C H. (2009) Effect of synthesizing technology of sulfonated acetone formaldehyde polycondensate on its dispersing performance. New building materials, 7:79-82.
[6] You J, Xu H F, Chen X Q, et al, translation. (2013) Principles of polymerization. Machinery industry press, Beijing.
[7] Qiao M, Shen Q M, Liu G N, et al. (2017) Effects of molecular weight on the performance of sulfonated acetone-formaldehyde superplasticizers. New building materials, 2:28-30.
[8] Pang J X, Zhang C C, Xiong Y, et al. (2004) Study on synthesizing mechanism and dispensing property of SAF. Journal of Wuhan University of Technology, 24(6):29-31.
[9] Li S, Yu Q J, W J X, et al. (2011) Effects of molecular mass and its distribution on adsorption behavior of polycarboxylate water reducers. Journal of the Chinese Ceramic Society, 39(1):80-86.
[10] Wang H Q, Yang X F, Xiong W F, et al. (2015) Study on the performance of a kind of cross linked polycarboxylate superplasticizer. New building materials, 11:37-40.
[11] Zhang H B. (2010) Effect of molecular weight on the adsorption characteristics and dispersion performance of superplasticizers. Guangzhou, South China University of Technology.