The role and interaction of superplasticizer and emulsifier in fresh cement asphalt emulsion paste through rheology study

Jian Ouyang^{a,*}, Baoguo Han^b, Yu Cao^b, Wenjie Zhou^b, Wengui Li^c, Surendra P. Shah^d

^a *School of Transportation and Logistics, Dalian University of Technology, Dalian, China*

^b *School of Civil Engineering, Dalian University of Technology, Dalian, China*

^c *Centre for Built Infrastructure Research, School of Civil & Environmental Engineering, University of Technology Sydney, Sydney, NSW 2007, Australia*

^d *Center for Advanced Cement Based Materials, Northwestern University, Evanston, IL, USA*

Abstract

The workability and mechanical properties of cement asphalt emulsion (CA) mortar are unstable due to the complex interaction between cement and asphalt emulsion. To reveal the interaction between cement and asphalt emulsion, the effect of emulsifier and superplasticizer on the rheology of cement paste and asphalt emulsion is investigated, respectively, and the effect of the interaction between emulsifier and superplasticizer on the rheology of cement paste is studied in this paper as well. Results show that the apparent viscosity and yield stress of asphalt emulsion increase with superplasticizer and emulsifier dosage. Emulsifier can change the yield stress and apparent viscosity of cement paste, and its effect on cement paste differs greatly with the type and dosage of emulsifier. Some emulsifiers can increase the yield stress of cement paste, but some emulsifiers can decrease the yield stress of cement paste. Emulsifier has interaction with superplasticizer, thus affecting the reducing water effect of superplasticizer on cement paste. There is a competition relationship between emulsifier and superplasticizer when they are adsorbed by cement particles. The mixing method, in which superplasticizer is mixed with cement before emulsifier added, is beneficial to obtain a lower apparent viscosity of cement paste for all tested emulsifiers.

Keywords: Cement asphalt emulsion paste, Rheology, Emulsifier, Asphalt emulsion, Interaction.

1 Introduction

Currently, the high-speed rail network is in a continuous process of growth in the world. Most of the current high-speed railway tracks prefer non-ballast slab track due to its series of advantages such as low maintenance, low structure height, high availability, and so on[1]. **Fig.1 shows a typical non-ballast slab track.** The non-ballast

* Corresponding author. Tel: +86-18840957910(J Ouyang).

Email address: ouyangjian87@126.com, ouyangjian@dlut.edu.cn

slab track is composed of reinforced pre-stressed concrete slab, concrete roadbed, and cement asphalt emulsion mortar (CA mortar), in which CA mortar acts as elastic absorber and even-adjusting layer between concrete slab and concrete roadbed. For these reasons, CA mortar plays a key role in slab track.

Fig.1. Structure of slab track

CA mortar is grouted into the chamber between slab track and concrete base in placement. Therefore, a good and stable workability is a key for the successful application of CA mortar. However, it is difficult to control the workability and mechanical properties of CA mortar due to the complex interaction between cement and asphalt emulsion. In the view of asphalt emulsion, the demulsifying rate is accelerated and the formation process of asphalt membrane is affected by cement hydration [2-5]. As for cement, both the rheology and hydration rate of cement are affected by asphalt emulsion [6,7]. Any effect on cement and asphalt emulsion results in a change of workability, and furthermore affects the mechanical properties of hardened CA mortar. Revealing the interaction between cement and asphalt emulsion is very vital to control the unstable properties of CA mortar.

CA mortar consists of cement, asphalt emulsion, fine aggregate (sand), water, superplasticizer, and other chemical admixtures. There are at least two particles (asphalt droplets and cement particles) and two surfactants (emulsifier and superplasticizer) in CA paste. Although many studies focusing the effect of every ingredient in CA paste on the rheological behavior of CA paste as well as the corresponding mechanism have been published [3-16], few of them can reveal the complex interaction between cement and asphalt emulsion. Besides, there are two types of CA mortar in non-ballast slab track. One is high-strength CA mortar, in which anionic emulsion is used and asphalt emulsion to cement ratio (AE/C) is low. The other is low-strength CA mortar, in which cationic emulsion is used and AE/C is high. The rheological properties of CA mortar differ greatly when changing the

employed asphalt emulsions, emulsion dosage, and the mixing method [6, 11, 15, 16]. Surfactants play an important role in the properties of fresh CA paste. To reveal the complex interaction between cement and asphalt emulsion, it should be understood both the individual and joint effect of emulsifier and superplasticizer on asphalt droplets and cement particles. Different emulsions have different emulsifiers, thus their interactions with cement and superplasticizer vary greatly. The complex interaction between cement and asphalt emulsion in fresh CA paste includes essentially the effect of emulsifier and superplasticizer and their interaction in CA paste. Revealing it is very vital to control the unstable properties of CA mortar.

Because the rheological properties of suspension can not only reveal the inherent properties of suspension system, such as colloidal forces, thixotropy, particles interaction, and particles morphology [20], but also be relevant with the workability. The flow time of a cone flow test is related to apparent viscosity [21-24]. The flowability of cement paste can be improved by decreasing its apparent viscosity. The segregation resistance of coarse particles is dependent on both the yield stress and apparent viscosity of paste [25, 26]. Therefore, the rheological properties can be used to investigate the workability of paste and the particles interaction in suspension.

This paper aims to study the effect of emulsifier and superplasticizer and their interaction in CA paste through rheology study. To achieve the goal, the effect of superplasticizer on the rheology of cement paste and asphalt emulsion is firstly studied, respectively. Secondly, the effect of emulsifier on the rheology of cement and asphalt emulsion is investigated, respectively. Thirdly, the effect of the interaction between emulsifier and superplasticizer on the rheology of cement paste is explored. Finally, a method is proposed to improve the interaction between emulsifier and superplasticizer.

2. Experimental program

2.1. Materials and mix proportions

Tap water, ordinary Portland cement P.O42.5R, polycarboxylate-based superplasticizer, and organic silicon defoaming agent are used in the experiment. The chemical and mineral components of P.O42.5R cement are shown in Table 1 and Table 2, respectively. Two commercial anionic emulsifiers (A1, A2) and two commercial cationic emulsifiers (C1, C2) are employed in the experiment. A1 and C1 are provided by Jinyang road material technology development Co., Ltd. in Jiangsu, China. A2 and C2 are provided by Meadwestvaco Co. in Shanghai, China. The four emulsifiers are all slow-setting emulsifier. Three slow-setting anionic asphalt

emulsions and three slow-setting cationic asphalt emulsions are manufactured by A1 and C1, respectively. The mix proportions for manufacturing these asphalt emulsions are shown in Table 3. The emulsifier dosages are respectively 3%, 3.5%, and 4.5% in the three anionic emulsions and three cationic emulsions. The asphalt emulsions in Table 3 are used to study the effect of emulsifier on the rheology of asphalt emulsion.

The mix proportions of cement pastes in Table 4 are to study the effect of superplasticizer (SP) on the rheology of cement paste. Cement pastes with five superplasticizer dosages (i.e. 0, 0.5%, 1.0%, 1.5%, and 2.0% of superplasticizer to cement ratio by weight) are prepared.

The mix proportions of asphalt emulsions in Table 5 are to study the effect of superplasticizer on the rheology of asphalt emulsion, asphalt emulsions with three superplasticizer dosages (i.e. 0, 1.0%, and 2.0% of superplasticizer to asphalt emulsion ratio by weight) are prepared. The employed emulsions are cationic emulsion with 3.5% emulsifier (C1) and anionic emulsion with 3.5% emulsifier (A1).

The mix proportions of cement pastes in Table 6 are to study the effect of emulsifier on the rheology of cement paste. Cement pastes with five emulsifier dosages (i.e. 0, 0.5%, 1.5%, 3%, and 5% of emulsifier to cement ratio by weight) are prepared. The emulsifier dosages are chosen according to the practice of CA mortar. The asphalt emulsion to cement ratio by weight is ranging from 0.2 to 1.6 [30]. The emulsifier to asphalt emulsion ratio by weight is about 3-4% if the asphalt emulsion can be used in CA mortar [31]. The tested emulsifier dosage range can cover the emulsifier to cement ratios of CA mortar with different ratios of asphalt emulsion to cement in construction. Because emulsifier may introduce many air bubbles into cement paste during the mixing, organic silicon defoaming agent is used in cement paste with emulsifier. Two cationic emulsifiers (C1 and C2) and two anionic emulsifiers (A1 and A2) are employed in the pastes.

The mix proportions of cement pastes in Table 7 are to study the effect of emulsifier on the rheology of cement paste with superplasticizer. Cement pastes with five emulsifier dosages (i.e. 0, 0.5%, 1.5%, 3%, and 5%) are prepared.

Table 1 Chemical components of P·O42.5R cement

Chemical composition	CaO	SiO ₂	Al ₂ O ₃	MgO	SO ₃	Na ₂ O
Wt.%	61.13	21.45	5.24	2.08	2.05	0.77

Table 2 Mineral components of P·O42.5R cement

Mineral Composition	C3S	C2S	C3A	C4AF
Wt.%	46.62	26.32	8.99	8.78

Table 3 Mix proportions for manufacturing asphalt emulsions

Emulsifier type	Asphalt content (%)	Water content (%)	Emulsifier dosage (%)
C1	60	37.0	3.0
C1	60	36.5	3.5
C1	60	35.5	4.5
A1	60	37.0	3.0
A1	60	36.5	3.5
A1	60	35.5	4.5

Table 4 Mix design for cement pastes with only superplasticizer

Mix	cement	water	Superplasticizer dosage (%)				
Cement paste with SP	1	0.35	0	0.5	1	1.5	2

Table 5 Mix design for asphalt emulsions with superplasticizer

Mix	Asphalt emulsion	water	Superplasticizer dosage (%)				
Asphalt emulsion C1 with SP	1	0.35	0	1	2		
Asphalt emulsion A1 with SP	1	0.35	0	1	2		

Table 6 Mix design for cement pastes with only emulsifier

Mix	Cement	Water	Defoaming agent (%)	Emulsifier dosage (%)				
Cement paste with C1	1	0.35	0.1	0	0.5	1.5	3	5
Cement paste with C2	1	0.35	0.1	0	0.5	1.5	3	5
Cement paste with A1	1	0.35	0.1	0	0.5	1.5	3	5
Cement paste with A2	1	0.35	0.1	0	0.5	1.5	3	5

Table 7 Mix design for cement pastes with both superplasticizer and emulsifier

Mix	Cement	Water	Defoaming agent (%)	Superplasticizer dosage (%)	Emulsifier dosage (%)				
Cement paste with SP and C1	1	0.35	0.1	1	0	0.5	1.5	3	5
Cement paste with SP and C2	1	0.35	0.1	1	0	0.5	1.5	3	5
Cement paste with SP and A1	1	0.35	0.1	1	0	0.5	1.5	3	5
Cement paste with SP and A2	1	0.35	0.1	1	0	0.5	1.5	3	5

2.2 Mixing methods

For cement pastes with only superplasticizer or emulsifier, water and surfactant are firstly mixed, and then cement is added for mixing of 4 minutes. For cement pastes with both superplasticizer and emulsifier, two mixing methods are employed to prepare cement paste. One is called mixing method 1, in which all ingredients are

mixed for 4 minutes. The other is called mixing method 2, in which cement, water, and superplasticizer are mixed firstly for 2 minutes, and then emulsifier and defoaming agent are added for the following mixing of 2 minutes. For asphalt emulsion with superplasticizer, superplasticizer is added to asphalt emulsion for mixing of 2 minutes.

2.3 Rheology method

After mixing, the flow curves of samples are measured immediately using a coaxial cylinder rheometer at a controlled temperature of $22\pm0.1\text{ }^{\circ}\text{C}$ as shown in Fig.2(a). The diameter of the used rotor is 26.657mm. The gap between the rotor and cylinder is 1.13mm. The shear processes as shown in Fig. 2(b) is performed in the rheology test. First, a 2 min pre-shear at 300 s^{-1} and 1 min rest are intended to create uniform condition before testing. Then, 9 steps, in which shear rate is decreased from 100 s^{-1} to 1 s^{-1} , are performed to get the flow curve at steady state. **Three samples are tested for each mix.**

(a) The employed rheometer and rotor

(b) Shear process

Fig.2 Rheology test about samples

3 Results and discussions

3.1 Effect of superplasticizer on cement paste

Figs. 3 and 4 show the effect of superplasticizer on the rheological behavior of cement paste. It can be seen that cement paste without superplasticizer has large value of shear stress and apparent viscosity at any tested shear rate. However, the value is significantly decreased after superplasticizer added, which indicates that superplasticizer **influences** the flocculation structure of cement paste and makes it more fluid. The shear stress and apparent viscosity of cement paste decrease **slightly** with superplasticizer dosage from 0.5% to 1%, and then increase **slightly** from 1% to 2%. **Therefore, superplasticizer has pronounced effect on decreasing the apparent**

viscosity of cement paste without superplasticizer. However, the rheological properties of cement paste change little when superplasticizer dosage is from 0.5% to 2%.

Fig.3 Flow curves of cement pastes with superplasticizer

Fig.4 Apparent viscosity of cement pastes with superplasticizer

According to the experimental data, Herschel-Bulkley model can be employed to fit the flow curves of cement paste with superplasticizer:

$$\tau = \tau_0 + k\dot{\gamma}^n \quad (2)$$

where τ is the shear stress (Pa); $\dot{\gamma}$ is the shear strain rate (1/s); k is the consistency, and n is the flow behavior index. The apparent viscosity of cement paste without superplasticizer as shown in Fig.4 decreases gradually with shear rate, therefore, the n value of cement paste without superplasticizer is smaller than 1. However, the n value of cement paste with superplasticizer is more than 1 because the apparent viscosity of cement paste with superplasticizer increases with shear rate. Because superplasticizer has very strong effect on the flocculation structure of cement paste, the n value can

reach above 1.5 and the yield stress of cement paste nearly decreases to 0. As a result, cement paste with superplasticizer does not have shear thinning behavior. In the following, almost all cement pastes have nearly zero yield stress if superplasticizer is added. Therefore, it is **not necessary** to discuss the yield stress of cement pastes with superplasticizer.

3.2 Effect of superplasticizer on asphalt emulsion

Fig.5 shows the effect of superplasticizer on the rheological behavior of asphalt emulsion manufactured by emulsifier C1 and A1. It can be seen that both the shear stress and apparent viscosity of asphalt emulsion significantly increase with superplasticizer dosage. Herschel-Bulkley model is employed to fit the flow curves of asphalt emulsion, and the calculated yield stress of asphalt emulsion is shown in Fig.6. It can be seen that the yield stress of both cationic and anionic asphalt emulsion increases with superplasticizer dosage. The n values of all emulsions are below 1, thus there is no plastic viscosity. **In study of the rheology of suspension, the apparent viscosity at high shear rate is related to particles size distribution, particles morphology, and the interparticle force of particles [20, 27]. The yield stress is an indication of the interparticle force of particles [20, 28]. The increasing apparent viscosity and yield stress of asphalt emulsion due to the addition of superplasticizer indicate that superplasticizer leads to a significant change about the structure of asphalt emulsion.** There are two probable reasons for the change of asphalt emulsion: ① the addition of superplasticizer can suddenly change the surface tension of emulsion system, which leads to the flocculation and coalescence of asphalt droplets; ② superplasticizer may have adverse interaction with emulsifier, which increases the interparticle force of asphalt droplets.

It is reported in many previous studies that superplasticizer can retard the demulsification process of asphalt emulsion in CA mortar and prolong the working time of fresh CA mortar [2, 4, 17]. However, superplasticizer has no good effect on pure asphalt emulsion from the above results. The reason why superplasticizer can retard the demulsification process of asphalt emulsion in CA mortar may be due to its effect on cement. Superplasticizer can prevent cement particles from flocculation and

have retarding effect on cement hydration [29], thus it slows down the structure rebuild rate of CA paste [18]. Because of the two effects, superplasticizer slows down the demulsifying rate of asphalt emulsion in CA mortar.

Fig.5 Effect of superplasticizer on asphalt emulsion

Fig. 6 Effect of superplasticizer on the yield stress of asphalt emulsion

3.3 Effect of emulsifier on asphalt emulsion

Figs.7 and 8 show the effect of emulsifier dosage on the rheological behavior of asphalt emulsion. It can be seen that the shear stress and apparent viscosity of both emulsions significantly increase with emulsifier dosage. The yield stress of emulsions is fitted by Herschel-Bulkley model, as shown in Fig.9. It can be found that the yield stress of both cationic and anionic asphalt emulsion increases with emulsifier dosage.

It is an interesting phenomenon that asphalt emulsion can become thickening with the increasing emulsifier dosage. The function of emulsifier is to emulsify asphalt and prevent asphalt droplets from flocculation and coalescence [19]. Therefore, the repulsive force of asphalt droplets should become stronger and the apparent viscosity

of asphalt emulsion should decrease with more emulsifier. However, the experimental results have an **opposite** trend. So there should be other changes in asphalt emulsion with the increasing emulsifier. The probable reason for the increasing apparent viscosity is that asphalt droplets can become smaller with more emulsifier in the manufacture process of asphalt emulsion [17]. At the same particle concentration, the smaller size means the increasing number of asphalt droplets, which increases the interaction among asphalt droplets. Therefore, asphalt emulsion with smaller asphalt droplets can be more viscous.

It should be noted that the rheological behavior of cationic asphalt emulsion (C1) is different from anionic asphalt emulsion (A1) at the same solid content and emulsifier dosage. This indicates that asphalt emulsions manufactured with different types of emulsifier can have different rheological behaviors.

Fig.7 Effect of emulsifier C1 on the rheological behavior of cationic asphalt emulsion

Fig.8 Effect of emulsifier A1 on the rheological behavior of anionic asphalt emulsion

Fig. 9 Effect of emulsifier dosage on the yield stress of asphalt emulsion

3.4 Effect of emulsifier on cement paste

Two cationic emulsifiers (C1 and C2) and two anionic emulsifiers (A1 and A2) are employed to study the emulsifier on cement paste. Tables.8-11 show the effect of emulsifier C1, A1, C2, and A2 on the apparent viscosity of cement paste, respectively.

It can be seen from Tables 8 and 9 that emulsifiers C1 and A1 increase the apparent viscosity of pure cement paste at low shear rate ($<10 \text{ s}^{-1}$). Expect the point of emulsifier A1 at 0.5%, the apparent viscosity at low shear rate of cement paste with C1 and A1 increases with emulsifier dosage. However, the apparent viscosity of cement paste with C1 and A1 at high shear rate ($>70 \text{ s}^{-1}$) does not have the same trend. The apparent viscosity of cement paste with C1 and A1 increases with the increasing emulsifier from 0 to 0.5%, decreases from 0.5% to 1.5%, and at last increases above 1.5%. Overall, C1 and A1 do not greatly change the apparent viscosity at high shear rate of cement paste when emulsifier dosage is from 0.5% to 3%, but they significantly increase the apparent viscosity at low shear rate of cement paste. Besides, A1 has more pronounced effect on increasing the apparent viscosity of cement paste than C1 when emulsifier dosage is 5%.

The effect of C2 and A2 on the apparent viscosity of cement paste is significantly different from C1 and A1. Unlike C1 and A1, it can be seen from Tables 10 and 11 that C2 and A2 can significantly decrease the apparent viscosity of cement paste. For cement paste with C2, the apparent viscosity decreases with the increasing emulsifier dosage from 0 to 1.5%, and then increases from 1.5% to 5% at the tested shear rate

range. For cement paste with A2, the apparent viscosity and shear stress at low shear rate ($<10 \text{ s}^{-1}$) decrease with emulsifier dosage from 0 to 3%, and then increase from 3% to 5%. At high shear rate ($>30 \text{ s}^{-1}$), the apparent viscosity of cement paste with A2 decreases with emulsifier dosage from 0 to 1.5%, and then increases from 1.5% to 5%.

Table 8 Effect of emulsifier C1 on the apparent viscosity of cement paste

Shear rate (1/s)	Apparent viscosity (Pa·s)				
	0% E	0.5% E	1.5% E	3% E	5% E
1	4.39	6.91	7.39	8.77	13.04
3	2.49	3.45	4.00	4.95	6.63
5	2.08	2.73	3.15	3.92	4.86
7	1.86	2.38	2.78	3.20	3.82
10	1.69	2.14	2.47	2.63	2.89
30	1.33	1.57	1.45	1.52	1.59
50	1.14	1.30	1.19	1.19	1.31
70	1.03	1.17	1.03	1.03	1.18
100	0.94	1.06	0.89	0.91	1.11

Note: E is abbreviation of emulsifier.

Table 9 Effect of emulsifier A1 on the apparent viscosity of cement paste

Shear rate (1/s)	Apparent viscosity (Pa·s)				
	0% E	0.5% E	1.5% E	3% E	5% E
1	4.39	7.21	6.13	7.25	17.64
3	2.49	3.64	3.46	3.91	8.77
5	2.08	2.87	2.78	2.88	6.06
7	1.86	2.52	2.39	2.37	4.57
10	1.69	2.28	2.02	1.93	3.40
30	1.33	1.63	1.21	1.19	1.92
50	1.14	1.34	0.96	1.03	1.63
70	1.03	1.20	0.84	0.96	1.50
100	0.94	1.08	0.79	0.90	1.41

Table 10 Effect of emulsifier C2 on the apparent viscosity of cement paste

Shear rate (1/s)	Apparent viscosity (Pa·s)				
	0% E	0.5% E	1.5% E	3% E	5% E
1	4.39	4.05	2.55	3.01	4.29
3	2.49	2.01	1.37	1.65	2.38
5	2.08	1.52	1.14	1.40	2.04
7	1.86	1.34	1.03	1.28	1.88
10	1.69	1.19	0.98	1.19	1.76
30	1.33	0.90	0.83	0.95	1.35
50	1.14	0.77	0.72	0.84	1.15
70	1.03	0.69	0.68	0.77	1.02

100	0.94	0.62	0.63	0.70	0.91
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Table 11 Effect of emulsifier A2 on the apparent viscosity of cement paste

Shear rate (1/s)	Apparent viscosity (Pa·s)				
	0% E	0.5% E	1.5% E	3% E	5% E
1	4.39	3.95	1.64	0.71	1.02
3	2.49	1.97	0.85	0.53	0.80
5	2.08	1.48	0.64	0.50	0.74
7	1.86	1.30	0.54	0.48	0.71
10	1.69	1.16	0.47	0.47	0.68
30	1.33	0.76	0.38	0.42	0.61
50	1.14	0.65	0.36	0.41	0.58
70	1.03	0.58	0.35	0.40	0.57
100	0.94	0.52	0.34	0.40	0.56

The effect of different emulsifiers on the yield stress of cement paste is fitted by Herschel-Bulkley model, which is shown in Figs.10 and 11. It can be seen from Fig.10 that the yield stress of cement pastes with C1 and A1 increases sharply with emulsifier dosage from 0 to 0.5%, and then changes slightly from 0.5% to 3%, and at last increases significantly above 3%. When emulsifier dosage is smaller than 3%, the yield stress of cement paste with A1 shows little differences with cement paste with C1. However, the yield stress of cement paste with A1 is much larger than that of cement paste with C1 when the emulsifier dosage is 5%. Unlike C1 and A1, C2 and A2 can decrease the yield stress of cement paste. As can be seen from Fig.11, the yield stress of cement paste with C2 decreases with emulsifier dosage from 0% to 1.5%, and then increases from 1.5% to 5%. Similarly, the yield stress of cement paste with A2 decreases with emulsifier dosage from 0% to 3%, and then increases from 3% to 5%. Compared to cement paste with C2, cement paste with A2 has smaller yield stress at the same emulsifier dosage.

Fig. 10 Effect of emulsifier C1 and A1 on the yield stress of cement paste

Fig.11 Effect of emulsifier C2 and A2 on the yield stress of cement paste

The apparent viscosity and yield stress of cement paste is related to the flocculation structure of cement particles and the suspending media. Therefore, the different phenomenon about the effect of four emulsifiers on cement paste can be explained as follows. Emulsifier is essentially a specific surfactant for asphalt droplets which has a hydrophilic group and a lipophilic carbon chain. The hydrocarbon chain can be penetrated into asphalt droplets, and the hydrophilic group outside asphalt droplets contains charge to prevent asphalt droplets from flocculation and coalescence [19]. This molecular structure may also provide repulsive force for cement particles. However, different emulsifier has significantly different chemical properties, thus the effect of different emulsifier on cement differs greatly. With the addition of C2 and A2, the flocculation structure of cement particles is significantly decreased. Therefore, the apparent viscosity and yield stress of cement paste decreases significantly. However, emulsifiers C1 and A1 do not provide pronounced repulsive force for cement particles,

thus the flocculation structure of cement particles is little decreased by C1 and A1. To the contrary, emulsifiers C1 and A1 may be as water-soluble polymer to affect the viscosity of suspending media. The water-soluble polymer chains in emulsifier molecules can intertwine and entangle at rest, and this intertwining structure easily disaggregates at high shear rate. Therefore, C1 and A1 can significantly increase the apparent viscosity at low shear rate and the yield stress of cement paste, but do not greatly change the apparent viscosity at high shear rate of cement paste when emulsifier dosage is below 3%. However, when emulsifier dosage is very high (for instance 5%), the effect of emulsifier on the viscosity of suspending media is pronounced. Therefore, emulsifiers C1 and A1 significantly increase the apparent viscosity at high shear rate of cement paste when emulsifier dosage is 5%.

The flowability of cement paste increases with the decreasing apparent viscosity [23, 24]. The shear rate corresponding practical grouting is below 20 s^{-1} [13]. Therefore, it can be induced that C2 and A2 are beneficial to the flowability of cement paste. The optimum emulsifier dosage for C2 and A2 is approximately between 1.5% and 3%. The rheological properties of cement paste can be degraded with emulsifier dosage after the optimum dosage. A1 and C1 are as thickener for cement paste, which are not helpful for the flowability of cement paste. Because emulsifier is a surfactant, it is generally believed in previous publications that emulsifier should be acted as plasticizer for cement paste because the yield stress of CA paste is smaller than that of cement paste [6, 14]. This viewpoint is not accurate. Whether emulsifier is acted as plasticizer or thickener is dependent on emulsifier type. Different emulsifiers have significantly different compositions, so their effect on the rheological behavior of cement paste differs greatly. That may be the reason why CA pastes with different emulsions have significantly different rheological properties.

3.5 Effect of emulsifier on cement paste with superplasticizer

Emulsifier and superplasticizer are two important surfactants in the grouting CA paste. The joint effect of emulsifier and superplasticizer on asphalt emulsion has been studied in the Section 3.2. This section is to study the joint effect of emulsifier and superplasticizer on cement paste. Because the rheological properties of cement paste

differ little when superplasticizer dosage is from 0.5% to 2% in the Section 3.1, a constant superplasticizer dosage of 1% is chosen for all cement paste in this section. Besides, all samples in this section are mixed by using the mixing method 1, in which all ingredients are mixed together for 4 minutes.

Figs.12-15 show the effect of different emulsifiers on the apparent viscosity of cement paste with superplasticizer. It can be seen from Figs.12 and 13 that the apparent viscosity of cement paste with superplasticizer increases with emulsifier dosage for C1 and A1. The increasing apparent viscosity indicates that A1 and C1 **act as** thickeners for cement paste with superplasticizer. As mentioned previously, A1 and C1 increase the yield stress of cement paste without superplasticizer. It is reasonable that A1 and C1 can **act as** thickeners for cement paste with superplasticizer.

It can be seen from Fig.14 that the apparent viscosity of cement paste with superplasticizer firstly decreases with C2 dosage from 0 to 1.5%, and then increases from 1.5% to 5%. It can be seen from Fig.15 that the apparent viscosity of cement paste with superplasticizer increases with A2 dosage from 0 to 0.5%, and then decreases from 0.5% to 1.5%, and at last increases from 1.5% to 5%. If ignoring the point of emulsifier dosage at 0, the apparent viscosity of two types of cement pastes with superplasticizer decreases firstly, and then increases with emulsifier dosage. Compared to the effect of C1 and A1, C2 and A2 do not greatly increase the apparent viscosity of cement paste with superplasticizer. Moreover, C2 and A2 can decrease the apparent viscosity if the dosage is near 1.5%.

Fig. 12 Effect of C1 on the apparent viscosity of cement paste with superplasticizer

Fig. 13 Effect of A1 on the apparent viscosity of cement paste with superplasticizer

Fig. 14 Effect of C2 on the apparent viscosity of cement paste with superplasticizer

Fig. 15 Effect of A2 on the apparent viscosity of cement paste with superplasticizer

In comparison of the results in Tables 8-11 and Figs.12-15, it can be noted that the effect of superplasticizer on cement paste is affected by emulsifier no matter whether it can be acted as plasticizer for pure cement paste or not. C1 and A1 have no bad effect on the apparent viscosity of cement paste without superplasticizer at high shear rate when emulsifier dosage is from 1.5% to 3%. C2 and A2 can decrease the

apparent viscosity of cement paste without superplasticizer for all the tested emulsifier dosage. However, the apparent viscosity of cement paste with superplasticizer is increased by the addition of C1 and A1, and it is also increased by the addition of C2 and A2 if the emulsifier dosage is above 3%. In comparison of the results in Fig.4 and Figs.14-15, the apparent viscosity of cement paste with superplasticizer changes slightly when superplasticizer dosage is from 0.5% to 2%. However, the apparent viscosity of cement paste with superplasticizer decreases greatly when 1.5% of C2 or A2 is added. Therefore, emulsifier may have interaction with superplasticizer in cement paste. This interaction can be explained as follows. When cement, superplasticizer, and emulsifier are mixed together, cement particles can adsorb superplasticizer and emulsifier on their surface. If the surface of cement particles is surrounded by emulsifier, the emulsifier membrane can prevent cement particles from adsorbing superplasticizer, which affects the water reducing effect of superplasticizer on cement paste. When emulsifier dosage is small, this shielding effect of emulsifier on superplasticizer is not pronounced, and C2 and A2 can be acted as strong plasticizer if emulsifier dosage is 1.5%. In this condition, emulsifier can be as a supplement for the water reducing effect of superplasticizer. Thus, the apparent viscosity of cement paste with superplasticizer is decreased in the aid of emulsifier. However, when emulsifier dosage is high, the shielding effect of emulsifier on superplasticizer is very pronounced, thus the effect of superplasticizer on cement paste is weakened and the apparent viscosity of cement paste is increased. Besides, emulsifier is a soluble macromolecule material. It can affect the viscosity of suspending medium when its dosage is high.

3.6 Improving the interaction between emulsifier and superplasticizer by changing mixing method

The results in the section 3.5 show that emulsifier has interaction with superplasticizer and affects the water reducing effect of superplasticizer on cement paste. There may be a competition relationship between emulsifier and superplasticizer when they are adsorbed by cement particles. If this hypothesis is correct, the effect of emulsifier on cement paste with superplasticizer should be

improved if cement is firstly mixed with superplasticizer. To confirm this hypothesis, the effect of different mixing methods on the rheological properties of cement paste with superplasticizer and emulsifier is studied, which is shown in Figs.16-19. In these figures, the mixing method 2 is that cement, water, and superplasticizer are mixed firstly for 2 min, and then emulsifier and defoaming agent are added for the following 2 min mixing.

For C1 and A1, as can be seen from Figs.16 and 17 that emulsifier increases the apparent viscosity of cement paste with superplasticizer under the mixing method 1 when emulsifier dosage is 1.5%. However, emulsifier reduces the apparent viscosity of cement paste with superplasticizer under the mixing method 2. When emulsifier dosage is 5%, the apparent viscosity of cement paste with superplasticizer and emulsifier fabricated by using the mixing method 2 is larger compared to cement paste with superplasticizer, but it is still smaller than cement paste with superplasticizer and emulsifier fabricated by using the mixing method 1. For C2, as can be seen from Fig.18 that cement paste with superplasticizer and emulsifier under the mixing method 2 has slightly smaller apparent viscosity than that under the mixing method 1 when emulsifier dosage is 1.5%. For A2, as can be seen from Fig.19, the mixing method 2 is more beneficial to decrease the apparent viscosity of cement paste with two surfactants than the mixing method 1 when emulsifier dosage is 1.5%. C2 and A2 are both beneficial to decrease the apparent viscosity of cement paste with superplasticizer under the two mixing methods when emulsifier dosage is 1.5%. When emulsifier dosage is 5%, compared to the mixing method 1, the mixing method 2 can also reduce the apparent viscosity of cement paste with superplasticizer and emulsifier.

Fig. 16 Effect of mixing method on cement paste with superplasticizer and C1 (1.5% and 5%)

Fig. 17 Effect of mixing method on cement paste with superplasticizer and A1 (1.5% and 5%)

Fig. 18 Effect of mixing method on cement paste with superplasticizer and C2 (1.5% and 5%)

Fig. 19 Effect of mixing method on cement paste with superplasticizer and A2 (1.5% and 5%)

The above results indicate that the mixing method 2, in which cement particles firstly adsorb superplasticizer and then adsorb emulsifier, is helpful to the rheological properties of cement paste. The results also confirm that there may be a competition relationship between emulsifier and superplasticizer when they are adsorbed by cement particles. Because the water reducing effect of superplasticizer on cement paste is stronger than emulsifier, when superplasticizer is firstly adsorbed by cement particles, the shielding effect of emulsifier on superplasticizer is weakened. It should be noted that emulsifier can further greatly decrease the apparent viscosity of cement paste with superplasticizer fabricated by using the mixing method 2 no matter what emulsifier is used when emulsifier dosage is 1.5%. This indicates that emulsifier can be as a supplement for the plasticizing effect of superplasticizer at low dosage if emulsifier has little shielding effect on superplasticizer. Although the shielding effect of emulsifier on superplasticizer is very weak under the mixing method 2, the viscosity of suspending medium may be greatly increased by the high dosage (5%) of emulsifier. Therefore, the apparent viscosity of cement paste with superplasticizer and emulsifier is still larger than cement paste with only superplasticizer. It is recommended to moderately decrease emulsifier dosage when fabricating CA mortar with high emulsifier to cement ratio in construction industry. However, the mixing stability of asphalt emulsion with cement should be guaranteed when using this method.

From the above results, it can be noted that the difference between cement paste

with superplasticizer and emulsifier under different mixing methods differs greatly when different types of emulsifier are employed. For instance, the apparent viscosity of cement paste with superplasticizer and C2 differs little under the two mixing method, but the apparent viscosity of cement paste with superplasticizer and A2 differs greatly with different mixing methods. It can be deduced that the properties of fresh CA mortar may be little affected by mixing method for some asphalt emulsions, but it may be highly dependent on mixing method for some emulsions. Overall, the mixing method 2, in which cement and superplasticizer are mixed firstly and then emulsifier or emulsion is added, is better for the flowability of fresh CA mortar.

4. Conclusions

In the paper, the effect of emulsifier and superplasticizer on the rheology of cement paste and asphalt emulsion was studied, respectively. The interaction between emulsifier and superplasticizer on the rheology of cement paste was studied. Four emulsifiers and six asphalt emulsions were employed in the experiment. Based on the results and discussions, the following conclusions can be draw **about the tested materials**:

(1) The apparent viscosity and yield stress of asphalt emulsion increase with superplasticizer dosage, which indicate that superplasticizer has adverse effect on asphalt emulsion.

(2) The apparent viscosity and yield stress of asphalt emulsion increase with emulsifier dosage. The probable reason for the increasing apparent viscosity is that asphalt droplets can become smaller with more emulsifier in the manufacture process of asphalt emulsion.

(3) Emulsifier can affect the yield stress and apparent viscosity of cement paste, and the effect of emulsifier on cement paste differs greatly with emulsifier type and dosage. Some emulsifiers (C1 and A1) can increase the yield stress of cement paste. However, some emulsifiers (C2 and A2) can decrease the yield stress and apparent viscosity of cement paste. **Because the flowability of cement paste increases with the decreasing apparent viscosity, using emulsifiers like C2 and A2 is beneficial to the flowability of cement paste.**

(4) Emulsifier has interaction with superplasticizer and affects the water reducing effect of superplasticizer on cement paste. The effect of emulsifier on the apparent viscosity of cement paste with superplasticizer is dependent on mixing method,

emulsifier type and dosage. There is a competition relationship between emulsifier and superplasticizer when they are adsorbed by cement particles. The mixing method 2, which superplasticizer is mixed with cement before emulsifier added, is beneficial to obtain a lower apparent viscosity of cement paste than the mixing method 1 which superplasticizer and emulsifier are mixed together with cement. Therefore, the mixing method 2 is a better mixing method for the flowability of CA paste.

(5) The apparent viscosity of cement paste with superplasticizer increases with emulsifier dosage when emulsifier dosage is high no matter which mixing method is employed. Therefore, it is recommended to moderately decrease emulsifier dosage when fabricating CA mortar with high emulsifier to cement ratio. However, the mixing stability of asphalt emulsion with cement should be guaranteed if using this method.

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