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Effect of polycarboxylate ether superplasticizer (PCE) on dynamic yield stress, thixotropy and flocculation state of fresh cement pastes in consideration of the Critical Micelle Concentration (CMC)

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ABSTRACT

Polycarboxylate ether surperplasticizer (PCE) has been commonly used and studied to enhance flowability of cementitious materials. However, the effect of PCE addition on thixotropy and flocculation state has not gained enough attention. In this study, Focused Beam Reflectance Measurement (FBRM)-rheometer is coupled. The coupled setup could simultaneously measure both flocculation states in terms of chord length distribution of cement particles/agglomerates and rheological properties including dynamic yield stress and thixotropy. The effect of various PCE additions is explored, firstly by measuring the adsorption of PCE surfactants and the concentration of PCE surfactants in cement pore solution. It is found that the effect of PCE addition on dynamic yield stress, thixotropy and chord length distribution of paste particles/agglomerates are all bi-fold. The turning point is the Critical Micelle Concentration in cement pore solution. Results of more agglomerated flocculation states at low PCE addition are measured for the first time and further discussed.

1. Introduction

Surperplasticizers are indispensable in modern concrete. To decrease w/c ratio and increase strength and durability, water reducing agent is largely used to enhance flowability. Polycarboxylate ether superplasticizer (PCE) is an effective and popular type of superplasticizer. They are composed of comb copolymers with an adsorbing backbone and non-adsorbing side chains [1]. They are known to adsorb on cement particles and induce steric hindrance, thus reducing attractive interparticle forces [2]. Dynamic yield stress of cementitious materials under effect of PCE has been commonly studied to meet the requirement of bleeding and pumping, etc. [3–5].

Both static and dynamic yield stresses are critical for many field applications [6]. For example, the dynamic yield stress of SCC is preferably small for pumping, while the static yield stress is preferably high for lower formwork pressure and high stability [7–9]. In this case, not only the absolute values of the yield stresses, but also the relationship between the static and dynamic yield stress is of critical importance. Studies [10,11] have tied thixotropy to the discrepancy between the static and dynamic yield stress. Nevertheless, the influence of superplasticizers on thixotropy has not received appropriate attention yet.

Thixotropy is defined as a decrease in viscosity under shear, followed by an increase upon removal of shear. Several methods have been proposed to measure thixotropy, for example, hysteresis loop [12] and energy or area deduced hysteresis loop [13–15], shear rate decay method [16], yield stress growth rate A_{thix} [6], etc. Among these methods, shear stress decay under constant shear rate has been well studied [6,17,18].

The idealized shear stress response of a fresh cement-based suspension under a constant intermediate shear rate can be described as follows: an initial increase to a peak value, followed by a decay until steady-state is reached. The shear stress decay from the peak value to the equilibrium value captures the process of structural breakdown/destructuration process and is related to the thixotropy of the material.

Empirically, Tattersall [19], Papo [20] and Lapasin et al. [21] measured the difference between the maximum shear stress, τ_i, needed to initiate flow and the steady-state equilibrium value, τ_e, at constant shear rates. They found out that the stress decay curve of cement paste fits well by an exponential curve. Coussot et al. [22] and Roussel [6,17] also proposed thixotropic models and obtained exponential decrease of shear stress decay over shearing time.

From there a simplified stress decay and destructuration model is found to be:

$$\tau = \tau_e + (\tau_i - \tau_e)e^{-\alpha\dot{\gamma}t} \quad (1)$$

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where τ_i and τ_e are peak and equilibrium of the stress decay, respecively; α is a constant depending on the shear rate $\dot{\gamma}$ and the material.

The characteristic time of the destructuration equals to $1/(\alpha\dot{\gamma})$. The shorter the characteristic time, the faster the rate of destructuration.

From Eq. (1), Ouyang et al. [23] define the structure parameter to evaluate the thixotropy as

$$\lambda_0 = (\tau_i - \tau_e)/\tau_e \tag{2}$$

Qian et al. [10] explored the physical meanings of dynamic and static yield stress and tied the discrepancy between dynamic and static yield stress with thixotropy, which are related to τ_i and τ_e. Here, the ratio between τ_i and τ_e is defined as thixotropic index.

$$I_{thix} = \tau_i/\tau_e \tag{3}$$

This thixotropic index depicts the relationship between static and dynamic yield stress. The higher the thixotropic index, the higher the thixotropy.

From a microstructural point of view, thixotropy could be described as paste deflocculation and breaking down of CSH bridges under flow, and flocculation and formation of CSH bridges over time at rest [24]. Under constant shear rate, the gradual stress decay is related to the deflocculation process of cement pastes [17,25]. It is assumed that bigger agglomerates are broken down to smaller particles/agglomerates [26]. Thus, thixotropy is closely related to flocculation state of cement particles/agglomerates.

One method to measure the flocculation state is by measuring the chord length distribution of particles/agglomerates. Focused Beam Reflectance Measurement (FBRM) has proved to be an efficient tool. For cement pastes, no dilution is needed, thus in-situ measurement of the chord length distribution of paste particles/agglomerates is possible. Ferron et al. have used FBRM to measure the aggregation and breaking down kinetics of cement paste [26], and the effect of mixing method and intensity [27,28], in terms of mean chord length. Meanwhile, chord length distribution of the particles/agglomerates under various shear rates are also measured by FBRM [29,30].

In this study, a coupled FBRM-rheometer set-up is developed. The FBRM test is applied to study the chord length distribution of agglomerates of cement pastes under various PCE additions. Meanwhile, the rheometer measures the dynamic yield stress and thixotropy of cement pastes. The adsorption of PCE on cement paste and the concentration of PCE surfactants in cement pore solution are also obtained. Thus, the effect of PCE addition is correlated to the dynamic yield stress, thixotropy and the flocculation state measured by FBRM in consideration of the adsorption and concentration of PCE surfactants in cement pore solution.

2. Materials and methodology

2.1. Materials and mixing procedure

CEM I 42.5 N Portland cement is used in all mixtures. According to EN 196-1 and EN 196-6, its compressive strength at 28 days is averaged at 54 MPa, the Blaine fineness is 279.5 m^2/kg and the chemical constituents are summarized in Table 1.

Table 1
Cement chemical constituents.

Constituents	% by mass
SiO_2	19.6
Al_2O_3	4.88
Fe_2O_3	3.14
CaO	63.2
MgO	1.8
SO_3	2.9

All mixes have a water-to-cement ratio (W/C) of 0.4 by mass. As a parameter, the amount of PCE superplaticizer addition varies from 0, 0.05, 0.1, 0.15, 0.2, 0.25 to 0.3% by mass of cement. The polycarboxylate ether superplasticizer (PCE) used in this study is a commercial product commonly used in European market (MasterGlenium 51). In this study, the mass of PCE is the mass in liquid form sold by the supplier. The solid content of PCE surfactants is 35% over the total mass in liquid form. The recommended dosage for concrete by the supplier is between 0.5% and 1.6% of PCE in liquid form over cement by mass. It is noted that in this study, bleeding occurs for cement paste with over 0.3% of PCE addition. However, the recommended dosage is higher than 0.3%. It could be reasoned that in real concrete, fine and coarse aggregates also adsorb or consume PCE surfactants. Thus, the recommended dosage in concrete is higher than in cement paste in this study.

Interactions between superplasticizers and early hydration of cement could greatly affect the rheology and hydration of cement pastes [31–37]. Studies show that superplasticizers have retardation effects on cement hydration, possibly due to adsorption of polymers on the surface of cement particles [38]. Flatt and Houst [31] reasoned that superplasticizer consumption in fresh cement paste could fall into three categories: consumption by chemical reaction and formation of an organo-mineral phase (OMP); adsorption onto the surface of cement particles and early hydrates; and remaining in the aqueous suspension. Hot et al. [39] used delayed addition of superplasticizers and confirmed that 20 min delay addition helps to obtain repeatable results of rheological tests and adsorption isotherms. In this study, similar protocols as applied by Hot et al. [39] are used. To alleviate the effect of chemical reactions between superplasticizers and early cement hydrations, thus getting repeatable rheological and colloidal properties, superplasticizers are added 20 min after the first contact between cement powder and water.

De-ionized water is used in all the samples. The designated water is divided into two parts. 90% of water is mixed with cement in the beginning, the remaining 10% is mixed with PCE superplasticizer. The cement powder is slowly added into 90% of water and mixed at a speed of 4000 rpm for 1 min. After resting for 19 min, the PCE superplasticizer with 10% of water is added into cement paste and mixed at a speed of 4000 rpm for another 1 min. After resting for 10 min, the fresh cement paste is poured into the rheometer.

2.2. Rheometer and rheological tests

A commercial rheometer (Anton-Paar MCR 102) is used in this study. The coaxial cylinder bob-cup geometry is developed manually in the lab. The radius of the bob is 20 mm and the gap between the bob and cup is 12.5 mm. The height of the bob is 60 mm and the gap between the bottom of the bob and that of the cup is 5 mm. The bob is covered with sand paper with a roughness of 150 μm. The surface of the cup was sand blasted to a roughness of around 150 μm to prevent wall slip.

The Focused Beam Reflectance Measurement (FBRM) probe is slightly inserted into the gap between the bob and cup and fixed in the position during the tests. The window surface is 6 mm away from the surface of the bob. The FBRM-Rheometer set up is shown schematically in Fig. 1. It is noted that FBRM might affect the flow of materials in the geometry, especially in the vicinity of the FBRM window. However, results show that at both 300 and 600 rpm are showing the same trends. So FBRM insertion in the geometry doesn't seem to affect much the results or conclusions.

After mixing and 10 min resting, the fresh cement paste is poured into the cup. Before each test, the material is hand tampered for 1 min using a small whisk. Then the bob is quickly put in position and lowered to the designated position. The shearing protocol used in this study is simple: either steps down from 600, to 500, 400, 300, 200 and 100 rpm for 1 min each; or constant angular velocity at 600, 300 or 100 rpm for