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In-situ measurement of viscoelastic properties of fresh cement paste by a microrheology analyzer

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ABSTRACT

A microrheology analyzer was adapted to *in-situ* follow the development of viscoelastic properties of fresh cement pastes (FCPs) for the first time. It enables a non-disturbing measurement on the FCPs through monitoring the mean square displacement of cement particles, which gives an insight into the elastic and viscous properties of materials from a microstructural point of view. Various parameters including elastic index, macroscopic viscosity index, storage modulus, loss modulus and Maxwell parameters were obtained to quantitatively analyze the viscoelastic properties of FCPs. Results indicate that these parameters show a progressive increase with time at first and then stay stable. The incorporation of superplasticizer significantly decreases these parameters and their growth rates. Moreover, superplasticizer could evidently weaken the elastic feature of the FCP due to its effects of improving the dispersion of cement grains and retarding cement hydration. The effects of superplasticizer are more pronounced at lower water to cement ratio.

1. Introduction

Fresh cement paste (FCP) is considered as a viscoelastic material, because it responds to external forces in a manner intermediately between an elastic solid and a viscous fluid [1,2]. Viscoelastic properties not only play important roles in affecting the fluidity, consistence and workability of FCP, but also have effects on the volume stability of hardened cement paste (HCP) [3]. Generally speaking, the viscoelastic behavior of FCP is primarily determined by the physical condition of the solid cementitious particles in the suspension system which is related to the dispersion of the particles, the hydration process of cement and the addition of chemical admixtures [3]. Therefore, from an academic perspective, monitoring the development of viscoelastic properties of FCP is beneficial to explore the microstructural development resulting from the cement hydration and from the particle interactions in cement paste, and to further clarify the working mechanisms of chemical admixtures on the properties of FCPs.

Currently, various techniques have been employed to investigate the viscoelastic properties of FCPs, such as dynamic rheometer [1,2,4–7], electrical or ultrasonic reflection [3,8–20]. However, many of those methods have their intrinsic limitations and drawbacks. Special attention has been paid to oscillatory shear tests (dynamic rheometer) in low frequency by several researchers to study the rheology of cement paste [1,2,4–7]. On the premise of limiting the value of oscillatory shear strain and the frequency within the linear viscoelastic region of the material, the elastic and viscous behaviors of cement paste can be characterized by directly measuring the loss and storage moduli using this technique. In addition, this method is capable of providing useful information concerning structure or inter-particle forces [5]. However, in most cases, to ensure that the measurements are performed within the linear viscoelastic region is usually not an easy task. Electrical measurements barely establish any direct relationship with the mechanical properties despite the resistivity and capacitance of FCPs during cement hydration were recorded [8–10]. By monitoring shear wave reflected at normal incidence from an interface between a buffer material and the targeted material, ultrasonic reflection techniques were used to measure the viscoelastic properties of cement paste [11–19]. Nevertheless, the accuracy of this technique in the application of cement paste at the very early stage has remained a challenge [20].

In this study, a microrheology analyzer (Rheolaser LAB6™) was adapted to *in-situ* follow the development of the viscoelastic properties of FCPs in the presence of superplasticizer during the early hours after mixing. This method is based on the measurement of the mean square displacement of cement grains by laser scattering, which gives an insight into the elastic and viscous properties of the suspension system from a microstructural point of view. Various parameters including elastic index (EI), macroscopic viscosity index (MVI), storage modulus G', loss modulus G'', and Maxwell parameters, the viscosity of dashpot η and the elastic modulus of spring G, were extracted to quantitatively

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analyze the viscoelastic properties. On the basis of the results obtained from this technique, insightful information about cement hydration and the functions of superplasticizer could be also acquired.

2. Theory background

2.1. Microrheology

Microrheology is a new domain of rheology to study the viscoelastic behavior of a multi-phase system such as emulsion, suspension, gel or colloidal dispersion at a micron length scale [21]. It refers to measure the local deformation of a sample originated from an applied stress or thermal energy, which is directly correlated to the elastic and viscous properties of materials [22]. In this study, measurement of fresh cement pastes was performed using a microrheology analyzer that measures the displacement of particles based on diffusing wave spectroscopy (DWS) [23]. This technology uses a multi speckle diffusing wave spectroscopy (MS-DWS) set-up in a backscattering configuration with video camera detection. The scheme of the apparatus is depicted in Fig. 1 and the principle of DWS measurement is shown in Fig. 2. Unlike the traditional rheology testing methods in which a shear force and shear strain are usually involved, this method enables a non-disturbing measurement without any disturbance to the sample, and the same sample can be continuously monitored versus elapsed time. After the sample is placed in a cell, a fixed coherent laser beam (wavelength 658 nm) is incident upon the sample which contains scaterrers (cement grains here). The laser is multiply scattered many times by the particles into the sample, which leads to the interfering backscattering waves. An interference image called a "speckle image" is detected by a multi-pixel detector. In dynamic mode, particle motion induces spot movements of the speckle image [24]. The particle mobility in terms of speed and displacement is closely related with the viscoelastic properties of the whole system, so is the deformation of the speckle image (Fig. 2). Fast motion of particles results in fast deformation of speckle image and slow motion of the particles leads to a slow deformation of the speckle image. Based on the speckle image, a patented algorithm was used to quantitatively characterize the deformation rate of the speckle image and further plot the curve of the mean square displacement (MSD) of the scatterers versus decorrelation time t_{dec} [25].

For a single measurement of a stable colloid system, the decorrelation time t_{dec} is the measurement time, which is used to follow the change of the speckle image [25]. From the MSD curve with respect to the decorrelation time, one can calculate the viscoelastic moduli G' and G'' using the generalized Stokes-Einstein relation [26]:

$$\tilde{G}(s) = \frac{k_B T}{\pi a s \left\langle \Delta \tilde{r}^2(s) \right\rangle} = G' + iG'' \qquad (1)$$

where k_B is Boltzmann constant, T is temperature in kelvin, s is the Laplace frequency, which is proportional to $1/t_{\text{dec}}$, a represents the radius of the tracer, and $\langle \Delta \tilde{r}^2(s) \rangle$ denotes the Laplace transform of the MSD.

Samples with different microstructures possess different viscoelastic properties, thereby presenting varied MSD curves. From the shapes of MSD curves as shown in Fig. 3, viscoelastic properties of samples could be analyzed qualitatively [21]. In the case of a purely viscous sample, the MSD grows linearly with the decorrelation time as the particles are completely free to move in the sample and the slope of the MSD curve is associated with the viscosity of the sample. With respect to a viscoelastic sample, particles in the sample are not free to move but constrained in a "cage" or "network structure" formed by the neighboring particles. Smaller size of "cage" or "network structure" brings about a stronger constraining effect, which is indicated by the more pronounced elasticity of the sample. Overall, the MSD curve of a viscoelastic sample could be divided into three periods with respect to the decorrelation time. At the very initial decorrelation time, the particles are free to move in the continuous medium phase, so the MSD curve develops linearly and the slope is mostly related to the viscosity of the dispersant medium. Then, they are blocked by their neighbors, and the slope of MSD curve decreases and finally the MSD reaches a plateau. This is a characteristic of the elasticity of the sample. A lower plateau means a "cage" with smaller size and stronger elasticity. Thus, the height of the plateau characterizes the elastic modulus of the sample. At longer decorrelation time, the particles are able to find a way to escape from the "cage" and the MSD grows linearly again, which is a characteristic of the macroscopic viscosity as it corresponds to the moving speed of the particles in the sample. The longer time needed by the particles to finish a displacement implies the lower particle mobility and the higher macroscopic viscosity.

The following parameters extracted from MSD curves enable to characterize the viscoelastic properties of samples [21].

- Elasticity index (EI) is computed from the elastic plateau value, which corresponds to the inverse of the height of the MSD plateau.
- Macroscopic viscosity index (MVI) is a global computation and corresponds to a viscosity index at zero shear rate, which is the inverse of the slope of MSD curve in later linear scale.
- The storage modulus G', which represents the elastic behavior or the energy storage of the material, and the loss modulus G'', which signifies the viscous behavior or energy dissipation of the material, can be calculated using the generalized Stokes–Einstein relation [26]. For an elastic solid, the storage modulus dominates in the material and the loss modulus is low. For a viscous liquid, the loss modulus dominates. Thus, a material can be readily identified as an elastic solid or a viscous liquid by comparing the values of G' and G''.
- When the viscoelastic properties of the sample are described by the Maxwell model, the elastic modulus of a Hookean spring G and the viscosity of a Newtonian dashpot η could be obtained.

2.2. Microstructure of fresh cement paste

As well known, FCP is a reactive solid–liquid dispersion system. After the contact of cement with water, various ions are quickly dissolved from the mineral phases of cement grains into the aqueous phase, consequently developing a heterogeneous charge distribution on the surface of hydrating cement grains. This mosaic structure results in the formation of flocculated cement grains that entrap a large quantity of mixing water. Fig. 4(a) presents the schematic illustration of the initial "cage" or "network structure" in FCP. In the first minutes of cement–water contact, massive needle-like ettringite crystals are produced and cause a bridging effect among the cement grains, as shown in Fig. 4(b). With the progressing cement hydration, more newly formed hydrates are produced which create new links among cement grains and strengthen the inter-particle crosslinking, thus leading to a stronger "network structure", as shown in Fig. 4(c). Because of the change of the microstructure of FCP, the rheological properties of FCP continually evolve over hydration time.

At higher W/C, the distance between the cement grains is larger, namely the size of "cage" is larger. Thus, the "network structure" of FCP is relatively weaker during the cement hydration, as illustrated in Fig. 4(d)–(f).

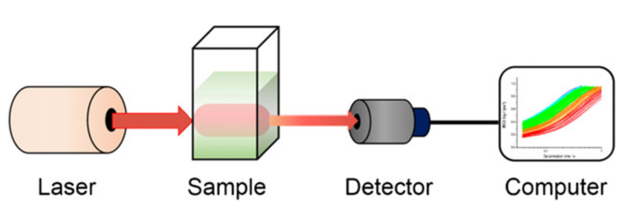

Fig. 1. Schematic representation of the experimental microrheometer.