Cement and Concrete Research 40 (2010) 384–391

Contents lists available at ScienceDirect

Cement and Concrete Research

journal homepage: http://ees.elsevier.com/CEMCON/default.asp

Influence of clays on the rheology of cement pastes

Nathan A. Tregger *, Margaret E. Pakula, Surendra P. Shah

Northwestern University, Civil and Environmental Engineering, 2145 Sheridan Road, Evanston, IL 60208, USA

ARTICLE INFO

Article history:
Received 12 July 2008
Accepted 9 November 2009

Keywords:
Clay
Fresh concrete
Rheology
Cement paste
Flocculation

ABSTRACT

The fresh state of concrete is becoming increasingly important in furthering the types of applications of today's construction world. Processing techniques have resulted in technologies such as self-consolidating concrete and depend on the microstructural changes that take place during and immediately after mixing and placing. These changes to the microstructure reflect the flocculation behavior between the particles in suspension. The ability to modify this behavior allows control over the balance among flowability and shape-stability of concrete. This study investigates how clay admixtures affect the microstructure of cement pastes from a rheological stand point. Shear and compressive rheology techniques are used to measure how the solids volume fraction of suspensions with different admixtures evolves with stress. Based on these relationships, the effectiveness of clays on the balance between flowability and shape-stability is measured. Results are consistent with green strength tests performed on concrete mixes derived from the cement paste mixes.

1. Introduction

The fresh state of concrete is becoming increasingly important in advancing the types of applications of today's construction world. Processing techniques have resulted in technologies such as self-consolidating concrete (SCC) and depend on the microstructural changes within concrete during the first hours after mixing and placing. The ability to modify the microstructure has led to high-performance concretes such as SCCs with reduced formwork pressure [1], and minimal-compaction energy concrete for slipform paving applications [2,3]. Minimal-compaction energy concrete requires sufficient flowability in order to consolidate without the use of internal vibration. However, this concrete must also gain sufficient shape-stability in order to keep its shape immediately after slipform paving; a process which involves consolidation and extrusion. It has been demonstrated for minimal-compaction energy concrete that small additions of clays (less than 1% by mass of cement) have made substantial improvements on the shape-stability. Similarly, clays have also been shown to improve the cohesiveness of cement-based extruded materials at very low dosages [4,5].

The purpose of this study is to quantify how clay admixtures affect the strength of the microstructure from a rheological stand point. Shear and compressive rheology techniques are used to measure how the solids volume fraction of cement suspensions with different admixtures evolves with stress. Based on these relationships, the effectiveness that clays and other admixtures have on the balance between flowability and shape-stability can be measured. A shear rheology method [6] is used to investigate how the maximum solids volume fraction of the flocs changes under shear stress, while a compressive rheology method [7] is used to determine changes in the local solids volume fraction (solids volume fraction of the sediment region) under compressive stress. Results are consistent with green strength tests performed on concrete mixes derived from the cement paste mixes investigated.

2. Background

When water and cement are combined in typical proportions, the inherent high solids concentration of the paste leads to the rapid formation of flocs rapidly due to the increase in the frequency of particle collisions [8]. During mixing, there is a constant formation and breakage of flocs. For a constant mixing speed, the floc size will reach an equilibrium that is a function of the flocculation strength; higher flocculation strengths can sustain larger flocs [9]. At sufficiently high mixing rates, the microstructure will reach a maximum solids volume fraction or maximum packing density that is a function of the flocculation strength as well as the particle size distribution and shape [10]. For suspensions with similar particle size distributions and shapes, stronger floc strengths lead to lower maximum packing densities.

Once mixing is complete, the flocs are free to grow, forming a space-filling network capable of supporting stress. The rate at which this occurs depends on both the rate of successful collisions, and the rate of breakage due to particle movement arising from Brownian motion and settling action [11].

The fresh cement paste microstructure can sustain shear stresses elastically up to the yield stress. The yield stress is dependent on both the flocculation strength and structure of the suspension [12]. When the shear stress exceeds the yield stress, flow is initiated and flocs

* Corresponding author. 2145 Sheridan Road, Suite A130, Evanston IL, 60208. Tel.: +1 847 491 7161.
E-mail address: n.tregger@u.northwestern.edu (N.A. Tregger).

0008-8846/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.cemconres.2009.11.001

begin to break down into smaller flocs. This microstructural process releases entrapped liquid within the flocs, increasing the liquid available for lubrication between particles. As a result, the viscosity decreases with increased shear, which explains the shear-thinning behavior of suspensions such as cement pastes [13,14].

Cement paste responds in a thixotropic manner when shear stresses are applied and removed; flocs break apart under stress, leading to a decrease in viscosity, but rebuild over time once the stress is removed, subsequently increasing the viscosity [15]. This reversible property is essential to the fresh state of concrete and has garnered much research in recent years [16–21]. Thixotropy is especially convenient for applications such as formwork pressure, where the increase in viscosity over time leads to a decrease in formwork pressure [22–24]. The influence of clays on thixotropy will be assessed in future work, but is not investigated here; the main focus is the effect of clays on floc strength.

The concept of a yield stress exists in suspensions subjected to compression just like suspensions subjected to shear stress. Below the yield stress, a suspension will deform elastically, and when the yield stress is exceeded, the microstructure will irreversibly collapse, where flocs break apart in order to rearrange into a denser configuration. As the flocs break apart, entrapped liquid is released, and the slow migration of water through the dense microstructure results in a viscoelastic response [25]. This new, denser configuration will in turn have a higher yield stress, since more particles must rearrange themselves to allow for further consolidation.

3. Theoretical background for data analysis

3.1. Shear rheology test method

In studies by Soua et al. and Liu [6,9], methods were developed to estimate the relative floc size of highly-concentrated suspensions for a given shear stress. For non-flocculated suspensions, the well-known Krieger and Dougherty model [26] relates the viscosity of a suspension to the volume fraction by Eq. (1):

$$\frac{\eta}{\eta_0} = \left(1-\frac{\phi}{\phi_m}\right)^{-K}, \tag{1}$$

where η is the viscosity of the suspension, η_0 is the viscosity of the suspending medium, ϕ is the volume fraction, ϕ_m is the maximum packing density and K is a fitting parameter, usually taken as 2, determined from experiments. Stuble and Sun [27] demonstrated that the Krieger and Dougherty model could be fitted for cement pastes, even if the parameters in Eq. (1) do not take on the same physical meanings as those for a non-flocculated, suspensions [27,28]. This model implies that an increase in viscosity is due to an increase in solids volume, and furthermore, as $\phi \rightarrow \phi_m$, $\eta \rightarrow \infty$. A convenience of having K fixed as 2 is that the maximum packing fraction can be determined by fitting a straight line to $1-(\eta/\eta_0)^{-1/2}$ versus ϕ; when $1-(\eta/\eta_0)^{-1/2}$ approaches 1, ϕ_m is achieved. However, flexibility is lost in the ability to fit the data to experiments. In order to increase the flexibility, Liu [10] added an adjusting parameter to yield Eq. (2):

$$\frac{\eta}{\eta_0} = \left[b\left(1-\frac{\phi}{\phi_m}\right)\right]^{-2} = [a(\phi_m-\phi)]^{-2}, \tag{2}$$

where the adjusting factor $a = b/\phi_m$. Soua et al. extend this concept to account for flocculated suspensions (in a similar fashion to a study by Liu [9]) [6]. As flocs form, they begin to trap water, reducing the amount of free water available to lubricate the system. As a result, the viscosity of the suspension increases. Furthermore, Eq. (2) does not hold, and the relationship between viscosity and volume fraction becomes a relationship between viscosity and effective volume fraction (floc volume fraction). This effective volume fraction accounts for the increase of entrapped water. Similarly, the maximum packing fraction varies with stress for a given floc size.

As the evolving flocs are subjected to increasing shear stress, the flocs will break down in size and continue to do so until the individual particles are achieved. Fig. 1 demonstrates how the maximum packing density of the flocs (ϕ_{fm}) evolves with stress. As the stress increases, the flocs begin to break down and release entrapped water resulting in a decrease in viscosity. In addition, particles can realign within the flow field to form a tighter configuration [6]. When the stress is sufficiently larger than the yield stress, ϕ_m is approached and all the entrapped water from the flocs is released. As a result, Eq. (2) now becomes Eq. (3) according to Soua et al. [6]:

$$\frac{\eta}{\eta_0} = \left[b\left(1-\frac{\phi_f}{\phi_{fm}}\right)\right]^{-2} = [a'(\phi_{fm}-\phi_f)]^{-2} \quad \text{for } \tau > \tau_y, \tag{3}$$

where ϕ_f is the volume fraction of the flocs, ϕ_{fm} is the maximum packing density of the flocs and $a' = b/\phi_{fm}$, τ is the shear stress and τ_y is the yield stress of the suspension. Note that for $\tau >> \tau_y$, Eq. (3) becomes Eq. (4) [similar to Eq. (2)]:

$$\frac{\eta}{\eta_0} = [a(\phi_m-\phi)]^{-2} \quad \text{for} \quad \tau \gg \tau_y. \tag{4}$$

In order to determine ϕ_{fm} and ϕ_m, a method developed by Liu can be implemented [10]. Flow curves are obtained for different initial volume fractions. For each stress value of each curve, the apparent viscosity, η, is calculated by taking the slope (stress / strain rate), shown in Fig. 2, marked by the circles for an example stress of 68 Pa. Then, for each stress value, the value $1-(\eta/\eta_0)^{-1/2}$ is plotted against the corresponding volume fraction. A linear fit is then applied and when $1-(\eta/\eta_0)^{-1/2} = 1$, the ϕ_{fm} is achieved for that given stress value, as shown in Fig. 3. Repeated for each stress value gives a ϕ_{fm}–τ curve. Finally, ϕ_m is the ϕ_{fm} value for $\tau >> \tau_y$ of the curve. For example, Fig. 4 shows ϕ_{fm}/ϕ_y versus τ/τ_y (where ϕ_y is ϕ_{fm} at τ_y), for a plain cement paste representing a flocculated suspension and a cement paste containing a high-range water-reducer representing a deflocculated suspension. Although ϕ_m is primarily dependent on the particle size distribution and shape, a flocculated suspension typically shows a lower ϕ_m when compared to a deflocculated system [27,29–31], which is demonstrated in Fig. 4. In addition to the ϕ_m, the difference between ϕ_m and ϕ_y (or ϕ_{dif}) is less than the deflocculated mix; that

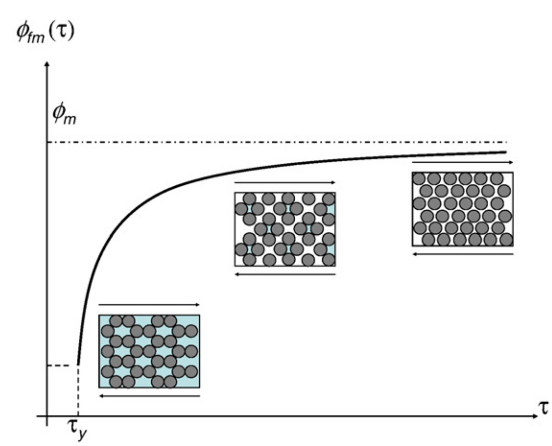

Fig. 1. Evolution of maximum packing density of flocs as a function of stress.