

Time dependent rheological behavior of modified bentonite suspensions

J.S. Yoon¹ and C.S. El Mohtar²

¹Department of Civil, Architectural and Environmental Engineering, The University of Texas at Austin, Austin, TX 78712-0280; PH (512) 970-5143; FAX (512) 471-6548; email: koyapple@mail.utexas.edu

²Department of Civil, Architectural and Environmental Engineering, The University of Texas at Austin, Austin, TX 78712-0280; PH (512) 471-3695; FAX (512) 471-6548; email: ElMohtar@mail.utexas.edu

ABSTRACT

Time dependent rheological behavior of modified bentonite suspensions was measured to investigate their applicability in permeation grouting. Permeation grouting of bentonite suspensions has been investigated as an effective way to deliver fine particles into soils for ground improvement. The ideal grout for this application needs to have low enough initial flow properties, such as yield stress and apparent viscosity for permeation, followed by rapid buildup of stiffness to obtain the desirable post grouting performance and durability. In order to achieve these properties, concentrated bentonite suspensions were modified with an ionic additive, Sodium Pyrophosphate (SPP). The addition of SPP improves the penetrability of the concentrated bentonite suspensions through soils while maintaining the thixotropic nature of the bentonite suspensions resulting in a gel-like structure in pores with time.

In this study, stress ramp tests were conducted, immediately after mixing, to examine the initial reduction in yield stress and apparent viscosity of the modified suspensions at 7.5, 10 and 12% bentonite suspensions with 1 to 4% SPP (by dry weight of bentonite). In addition, oscillatory shear tests (strain sweep) were performed to investigate the time dependent variation in stiffness (critical storage modulus) at the 7.5 and 12% bentonite suspensions with 1 and 4% SPP and resting times (0 to 120 hours). The results showed that both flow parameters and storage modulus of the modified suspensions was significantly reduced immediately after mixing (liquid state), but storage modulus rapidly increased by two (2) to three (3) orders of magnitude within short resting times (gel state). The proposed modification of bentonite suspensions would be an effective method of enhancing permeation of concentrated bentonite suspensions through sands by improving the mobility of the suspensions, and then forming gel-like structures with time after being placed in pore space to resist washing out.

INTRODUCTION

The delivery of plastic fines by permeation grouting is an effective way to mitigate liquefaction phenomenon. The presence of plastic fines such as bentonite reduces the generation of excess pore water pressures, resulting in an increase in the cyclic resistance of sands (Polito 1999, Haldavnekar et al. 2003, and El Mohtar et al. 2008). Moreover, El Mohtar et al. (2008) and Rugg et al. (2011) observed that the generation of excess pore water pressures in sand was reduced with the increase in stiffness of pore fluids. In addition, Hwang et al. (2011) showed that the permeation grouting using bentonite grouts can be an effective method to control seepage problems in granular deposits by significantly reducing their hydraulic conductivity. However, the application of the concentrated bentonite suspensions (exceeding 5% by weight) in permeation grouting has been limited due to their low penetrability through soils and rock fractures. Therefore, there is a need to enhance the mobility of the concentrated suspensions to increase the penetration depth of the grouts. In addition, this effect needs to be temporary, and the suspensions should start gelling rapidly over time to achieve the resistance to dynamic loading after permeation.

The rheological behavior of bentonite suspensions is related to the structural association (3-D network) of bentonite particles, which depend on pH conditions, cations and types of ionic additives due to their effect on the diffuse double layers surrounding bentonite particles (Abend and Lagaly 2000 and Kelissidiss et al. 2007). Previous researchers have studied the effect of the various ionic additives on bentonite suspensions and reported that the ionic additives such as sodium hydroxide, sodium silicate and sodium polyphosphate tended to reduce flow properties of bentonite suspensions by disrupting their structural association (Tchillingarian 1952, Jessen and Turan 1961, Gonzales and Martin-Vivaldi 1963, and Abend and Lagaly 2000). However, the time dependent behavior of the treated suspensions varies with the type of ionic additives because of their complex reactions with bentonite particles. Bentonite suspensions treated with sodium hydroxide produced substantially low yield stress and apparent viscosity compared to the untreated suspensions after 24 hours (Gonzales and Martin-Vivaldi 1963), implying lower degree of structural recovery; no flocculation was observed in these tests. On the other hand, Tchillingarian (1952) observed complete flocculation in clay suspensions treated with sodium hexametaphosphate after 3 days. This implies that the stiffness of clay suspensions may be increased with time by a delayed formation of the 3-D network when a polyphosphate is used as an additive, since the stiffness of suspensions is also controlled by the network formed in the clay suspensions.

The objective of this study is to investigate the rheological behavior of the bentonite suspensions modified with sodium pyrophosphate (SPP), focusing on their time dependent behavior. The SPP was selected to control the mobility of the concentrated bentonite suspensions because, contrasting to sodium hydroxide and sodium silicate, it displays pronounced dispersing capability (Tchillingarian 1952 and Penner and Lagaly 2001) while allowing gradual increase in stiffness with time; both of which are desirable properties for the proposed application. The flow behavior of the bentonite suspensions are described with apparent viscosity and yield stress. Especially, critical storage modulus is utilized to investigate the time dependent

behavior of the modified bentonite suspensions since it provides information on the stiffness of the flocculated 3-D network structures at low strain ranges.

EXPERIMENTAL PROGRAM

Materials and Sample preparation

Commercially available sodium-bentonite was used to prepare the suspensions. The clay minerals consist of a 2:1 structure formed with an octahedral layer sandwiched between two tetrahedral layers. The shape of particle is platy and the size of particle is usually less than 1 or 2 μm (Mitchell and Soga 1976). The raw bentonite was screened through a No.200 sieve to minimize the impurities and large particles (Abend and Lagaly 2000 and Clarke 2008). The main component of the bentonite includes SiO_2 of 61%, AlO_3 of 18%, CaO of 1%, Na_2O of 2%, Fe_2O_3 of 4%, and 12% of organic materials. The Na/Ca ratio, which strongly affects rheological properties of bentonite suspensions, is 2. The weight fraction of bentonite suspension was calculated as the ratio of bentonite weight to the total weight of suspension. In the calculation, the initial water content of bentonite (8.3%) was considered. The average pH of the suspensions (measured using JENCO 60 pH meter) is 9.3. Commercially available Sodium Pyrophosphate (SPP) decahydrate ($\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$) has a specific gravity of 1.8, Molecular weight of 446.06, and the pH of a 5% SPP solution is 9.5.

Bentonite powder was mixed for 15 min with de-ionized water and SPP. The de-ionized water was utilized for controlling ionic strength and consistency. The mixing process of bentonite suspensions includes three steps; each step consisted of 5 minutes of high shear mixing of the suspension followed by manual scraping of the sides and base of the mixing cup to remove bentonite flocs attached to the cup. For samples rested for extended periods of time, the specimens were poured into the measuring cups and tightly sealed after mineral oil was added at the top of the bentonite suspensions to prevent any evaporation from the samples. The physical properties of bentonite are summarized in Table 1.

Table 1. Properties of bentonite

Plastic Limit	38%	Cation Exchange Capacity	91 meq/100g
Liquid Limit	440%	Specific area	712 m^2/g
Specific Gravity, Gs	2.7	pH	9.3
Initial water content	8.3%	Swelling capacity	8 ml/g

Test equipment

The rheological properties of bentonite suspensions were measured using an Anton Paar MCR301 rheometer. Figure 1 shows a schematic of the rheometer and measuring system used in this study. Vane and cup geometry was selected to estimate storage modulus at a specific resting time in order to avoid severe

disturbance and risk of wall slip in samples when using the traditional cone and plate setup (Walls et al. 2003). The vane used was six-bladed, with each blade having a 1 mm thickness and a length of 16 mm. The vane radius was 11 mm and the cup has an internal diameter of 29 mm, resulting in a 3.5 mm measuring gap. Additional cups were manufactured for this research for long term testing; the manufactured cups are 80 mm in length and 29 mm in internal diameter. Sample volume was maintained at 37 ml, which allowed the vane to penetrate approximately twice the length of its blades. No surface treatment such as sand blasting on the surface of cup or vane was applied. End effect of vane was small enough so that it can be ignored for practical purpose (Barnes and Carnali 1990). All tests were performed at a controlled room temperature of 22 ° (±0.03 °).

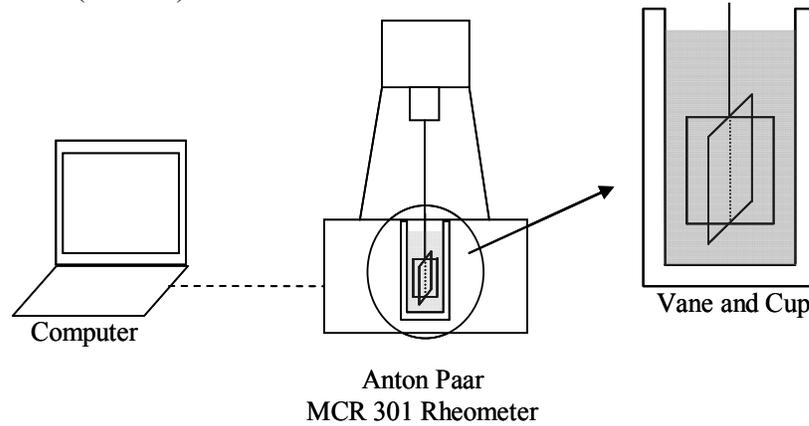


Figure1. Schematic of rheological test setup

Testing Methods

Stress ramp test

In stress ramp technique, the applied shear stress is increased in a stepwise function at a constant rate (3 Pa/step in this study), resulting in a flow curve. The stress level maintained for 12 sec and data was recorded at the end of the interval. In addition, the tests were programmed such that samples rested for 2 min after inserting the vane to provide a consistent initial condition. Preshearing was not applied prior to starting the stress ramp since all the tests were performed immediately after mixing. Rheological properties in this technique are typically determined by fitting the experimental data to constitutive models such as Bingham and Herschel-Bulkely model. In this study, Herschel-Bulkely model (Eq. 1) was utilized since it has been widely adopted for bentonite suspensions (Bekkour et al. 2005 and Kelessidis et al. 2007). As shown in Figure 2, the model was fitted to experimental data, producing an R^2 of at least 0.99.

$$\tau = \tau_y + K \left(\dot{\gamma} \right)^n \quad (1)$$

Where τ is the shear stress, τ_y is the yield stress, K is the flow consistency, n is the flow behavior indices, and $\dot{\gamma}$ is the shear rate. Since it is difficult to capture the effect of SPP from the Herschel-Bulkley model which has 3 variables (yield stress, flow consistency and flow behavior indices), the apparent viscosity, which is the ratio between the applied shear stress and shear rate, was monitored (Kelessidis et al. 2007). The accurate measurement of the apparent viscosity with the stress ramp technique is challenging because two parameters (shear rate and time) change simultaneously during testing. However, the effect diminishes at high shear rates. For the proposed application of bentonite suspensions, the apparent viscosity at high shear rates is more important than that at low shear rates since the injection process in permeation grouting is typically performed at high flow velocities. In this study, the shear rate of 100 s^{-1} was considered as the high shear rate.

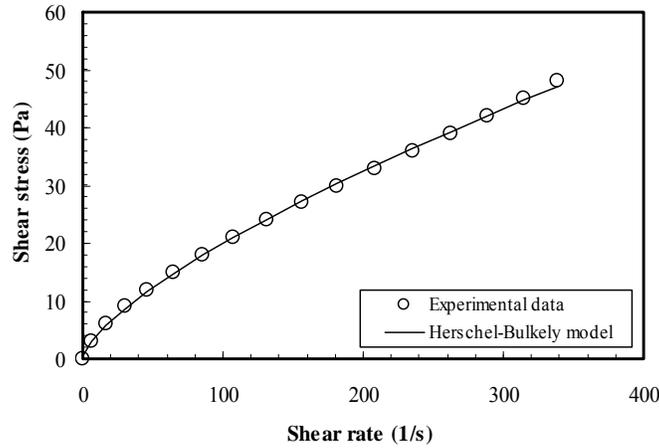


Figure 2. An example of determination of yield stress: 10% suspension modified with 2% SPP

Oscillatory shear test

This test applies oscillatory strains (Eq. 2) by increasing amplitudes at a constant level of frequency. The shear stress is shifted by a phase angle δ with respect to the applied strain so that it can be expressed as the sum of an elastic component (in-phase, G') and a viscous component (out-of-phase, G'') with the applied strain (Eq. 3). These two components are often referred to as storage and loss moduli, respectively.

$$\gamma = \gamma_o \cdot \sin(\omega t) \quad (2)$$

$$\tau = \gamma_o \cdot [G' \sin(\omega t) + G'' \cos(\omega t)] \quad (3)$$

Where γ is the shear strain, γ_o is the maximum applied shear strain, ω is the frequency, t is the time, and G' and G'' are the storage and loss modulus, respectively. A series of oscillatory shear tests were conducted at a constant oscillation rate of 1Hz over the range of strains (strain sweep). This method was slightly modified to obtain

relatively constant value of critical storage modulus (G') by reducing the disturbance effect which occurs during inserting vane. The oscillatory shear stress at the strain of 0.01% was applied for 2min before testing, followed by increasing strain in stepwise recording 6 points per log-cycle. This modification was found to provide consistent initial state in the sample prior to the measurement. As shown in Figure 3, storage modulus (G') and strain were not significantly changed by the method compared to the unmodified method. The critical storage modulus is determined as small strain plateau where G' is constant.

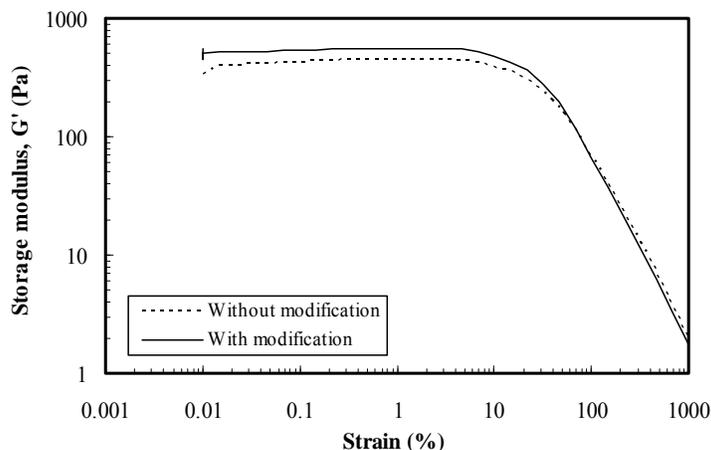


Figure 3. Modified strain sweep result of 10% bentonite suspensions at zero resting time

RESULTS AND ANALYSIS

Yield stress and apparent viscosity

Figure 4 shows the change in yield stress with SPP concentrations. The yield stress decreased significantly from 25, 137 and 467 Pa to 0.2, 0.3 and 0.9 Pa for 7.5%, 10% and 12% bentonite suspensions, when mixed with 2, 3 and 4% of SPP, respectively. The result implies that SPP disrupts the formation of the condensed 3-D network, leading to more liquid state. This is attributed to the adsorption of phosphates ions on the edge of bentonite particles (either by the attachment of phosphate ions to the edges or their adsorption at the edges by exchanging structural OH^- groups of bentonite particles) leading to an increase in the negative edge charge and repulsion between particles, thus retarding the formation of a 3-D network. In addition, the results showed that the yield stress of the suspensions could significantly be reduced with a very small amount of SPP (2 to 4% by dry weight of bentonite).

Figure 5 shows the variation of apparent viscosity at the shear rate of 100 s^{-1} . Similar to yield stress, the apparent viscosity decreased with the addition of SPP. These results imply that the modification of bentonite suspensions with SPP increases the mobility of the suspensions so that the penetration of the bentonite suspensions will be improved. The yield stress and apparent viscosity started to converge at a certain percentage of SPP (1, 3 and 4% for 7.5, 10 and 12% suspensions), which indicates a limit of dosage of SPP that can be added, effectively. Beyond these percentages of SPP, the effect of additional SPP diminishes since all network structure buildup in bentonite suspensions is halted.

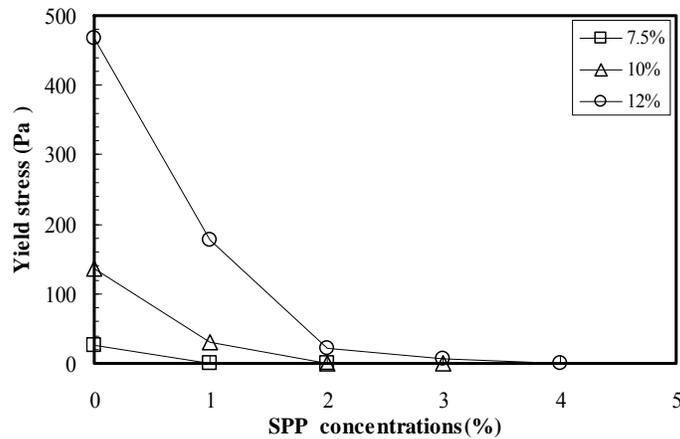


Figure 4. Variation of yield stress with SPP concentrations (0-4%) at the bentonite fractions of 7.5, 10 and 12%

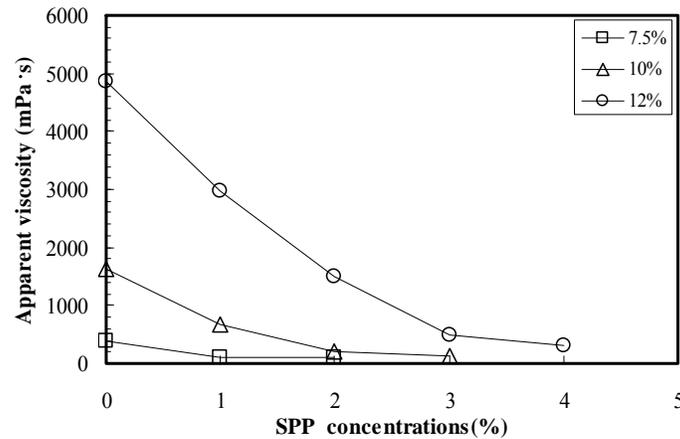


Figure 5. Variation of apparent viscosity with SPP concentrations (0-4%) at the bentonite fractions of 7.5, 10 and 12%: shear rate of 100 s^{-1}

Critical storage modulus

Figure 6 shows storage and loss modulus of 12% bentonite suspensions with 0 and 4% SPP. The critical storage modulus was reduced from 1915 Pa to 2.3 Pa with the addition of SPP. In addition, the storage and loss modulus became similar after the SPP addition, indicating that the suspensions were transformed to more liquid like state. However, the degree of reduction depends on the bentonite fractions as shown in Figure 7. This may attribute to the fact that the suspensions having higher bentonite fractions include more 3-D networks than the diluted suspensions and thus, require more SPP to lower the stiffness.

The reduced critical storage modulus gradually increases with time. As particles assume their positions of minimum free energy under Brownian motion, 3-D networks consisting of face (-) to face (-) (FF) association are formed (Luckham and Rossi, 1999). Figure 8 displays the time dependent evolution of the critical storage modulus

for 7.5 and 12% bentonite suspensions without SPP and with 1 and 4% SPP, respectively, up to 120 hours. The initially reduced stiffness of the modified suspensions was gradually recovered with time and approached those of the unmodified suspensions. The relative buildup between the modified and unmodified suspension was faster in 7.5% than 12% suspension possibly due to high degree of Brownian motion of particles in the diluted suspension and the hydrolysis of SPP (Michaels 1958), which increases the amount of cations in bentonite suspensions. The increased cations may promote the particle associations by exerting attractive forces between particles and the effect becomes more pronounced at the suspensions having low bentonite fractions. In addition, the consistent increase in stiffness with time implies that sedimentation was not significant during the resting time (this was confirmed through visual inspection of the cups after the conclusion of the tests).

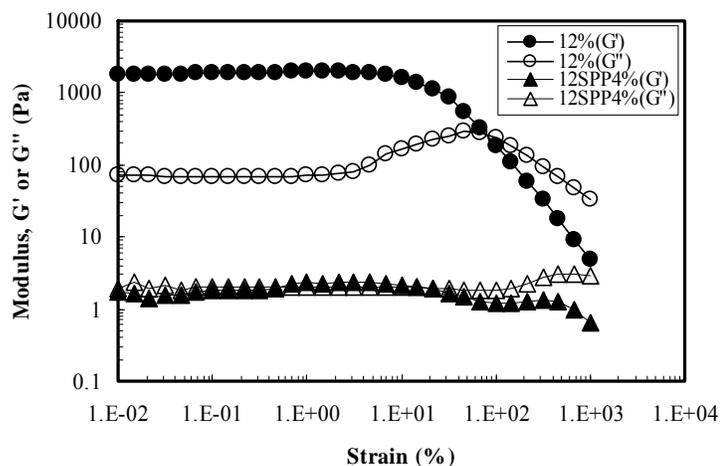


Figure 6. Storage (G') and loss modulus (G'') of 12% bentonite suspensions with 0 and 4% SPP

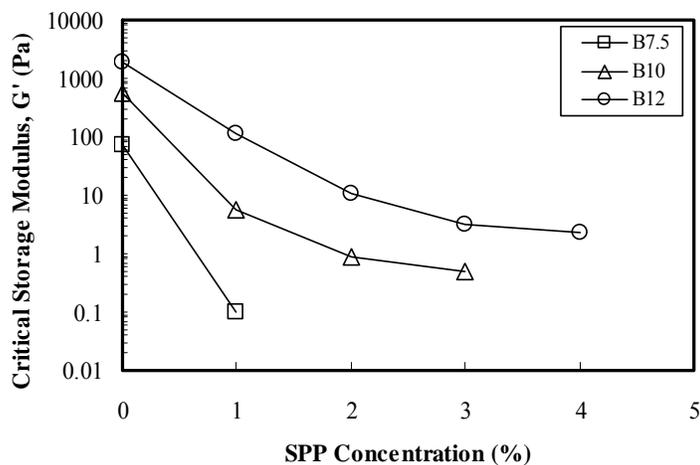


Figure 7. Variation of critical storage modulus with SPP concentrations at the bentonite fractions of 7.5, 10 and 12%

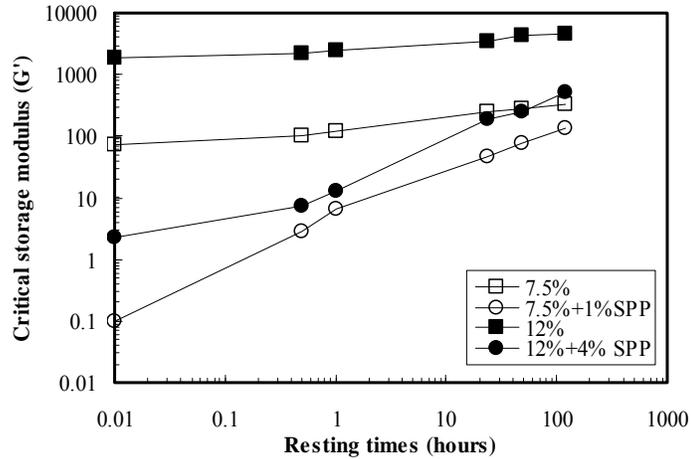


Figure 8. Critical storage modulus of the modified and unmodified 7.5 and 12% suspensions at various resting times (0 to 120 hours)

CONCLUSIONS

In this study, the rheological properties of the SPP modified bentonite suspensions were measured to investigate a possible application of the concentrated suspensions in permeation grouting for ground improvement such as liquefaction mitigation and seepage control. The addition of sodium pyrophosphate reduced the initial apparent viscosity and yield stress, indicating an increase in mobility of the bentonite suspensions. The critical storage modulus was also reduced significantly similar to yield stress and apparent viscosity, but it gradually increased with time by the reformation of 3-D networks in the suspensions. These observations support a possible application of the modified bentonite suspensions for permeation grouting by (1) increasing penetration depth due to initial reduction in apparent viscosity and yield stress, (2) recovering the stiffness of the suspension once it is permeated, which is necessary for the grout stability within the pores and its ability to resist dynamic loading.

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