

## 동적전단유동하에서 측정된 시멘트 페이스트의 히스테리시스곡선

민병현<sup>†</sup> · L. Erwin\* · H.M. Jennings\*\*

<sup>†</sup>고등기술연구원 생산기술연구소, \*노스웨스턴대학 기계공학과  
\*\*노스웨스턴대학 재료공학과  
(1993년 6월 1일 접수)

### Hysteresis Loops of Cement Paste Measured by Oscillatory Shear Experiments

Byeong-Hyeon Min<sup>†</sup>, Lewis Erwin\* and Hamlin M. Jennings\*\*

<sup>†</sup>Institute for Advanced Engineering,  
Manufacturing Technology Lab., C.P.O. Box 2810 Seoul, Korea

\*Department of Mechanical Engineering

\*\*Department of Material Science and Engineering and Civil Engineering  
Robert R. McCormick School of Engineering and Applied Science,  
Northwestern University, Evanston, Illinois 60208, U.S.A.

(Received June 1, 1993)

#### 요 약

시멘트 페이스트의 비선형적 점탄성 거동을 연구하기 위해 동적인 전단유동 시험이 수행되었다. 전단응력과 전단변형 또는 전단변형률간의 관계를 보여주는 히스테리시스 곡선을 얻기 위하여 전단응력이 연속적으로 측정되었다. 이는 기존의 주파수 혹은 변형의 증가에 의한 실험(frequency or strain sweep experiment)과는 달리, 저자에 의해 수정된 점성계(HAAKE Model RV20/RC20/CV20N)의 조정프로그램을 이용하여 수행되었다. 동적 전단유동시험에서 얻어진 히스테리시스 곡선은 시멘트 페이스트가 전단변형을 받는 동안 선형탄성, 입자간 연결 고리의 파괴 및 점성유체 거동을 보여준다. 측정된 항복전단응력은 전단변형률의 증가에 따라 파워어함수(Power law equation)에 의해 증가함을 보여준다.

**Abstract**—Oscillatory shear test was performed to study the nonlinear viscoelastic behavior of cement paste. Shear stress was continuously measured during the cycle to represent the hysteresis loop between stress and strain or strain rate. This measurement technique is different from the conventional frequency or strain sweep experiments. Time varying quasi-linear viscoelasticity was considered to calculate viscoelastic properties of cement paste such as phase angle, dynamic modulus, and dynamic viscosity during the cycles. Hysteresis loop from oscillatory shear test was divided into linear elastic, structure breakdown and viscous fluid regions. Yield shear stress increased by Power law equation with increasing the amplitude of shear rate.

**Keywords:** Rheology, cement paste, viscoelastic properties, viscometer, oscillatory shear test, hysteresis loop, yield stress

<sup>†</sup>To whom any correspondence should be addressed

## 1. Introduction

In recent years rheologists have been an increasing interest in the technique of oscillatory testing as applied to material analysis. By measuring the response of a material subjected to sinusoidal excitation it is possible to measure the elastic component and the viscous component of the response measured as a function of the frequency of oscillation [1]. The effect of particle migration can be minimized by performing the experiments in an oscillatory manner rather than in steady shear [2]. Viscoelastic properties such as dynamic modulus ( $G'$ ) and dynamic viscosity ( $\eta'$ ) are very sensitive to structural changes of the particle network in the matrix. The presence and breakdown of agglomerates, therefore, is indicated by an unexpected change in the viscoelastic properties as a function of amplitude and frequency of oscillation.

Cussen and Harris [3] have conducted oscillatory shear experiment using a cone/plate viscometer and showed cement pastes exhibited a nonlinear response. They found the total stress response was composed of both fundamental and third harmonic stresses. However, the method for the computation of the dynamic viscosity was different from the present method (see Eqs. (13a) and (13b) in the following section) and detailed procedure to get viscoelastic properties was not mentioned even though they concluded cement pastes exhibited a nonlinear viscoelastic response. Jones *et al.* [4] showed that from a sinusoidal input a sinusoidal output is obtained with no evidence of a harmonic test, and concluded that cement paste was elastic, and possessed a degree of structure intermediate between a clay suspension and polymer. The technique was used to study the strength and rate of degradation of flocs in artificially flocculated sediments [5] and should be capable of giving the same information for cement paste. Chow *et al.* [6] have also studied cement slurry structure during early setting using oscillatory testing technique that was carried out with a plate/plate sensor. The testing consisted of frequency sweep (measurement of shear stress

with increasing of frequency under constant amplitude of strain) and strain sweep (measurement of shear stress with increasing of amplitude of strain under constant frequency) experiments. The relative values of  $G'$  and  $\eta'$  can indicate whether the material is more solid-like (elastic) or fluid-like (viscous). Saasen *et al.* [7] have evaluated viscoelastic properties of cement slurries, which have their application in the oilfields industry, using an oscillating rheometer. Linear viscoelastic properties were obtained through frequency sweep experimental methods, and analyzed for various types of cement slurries. Viscoelasticity was not restricted to gelled slurries but observed after the gel structure has been broken.

Previous papers did not show sufficient proofs of nonlinear viscoelastic behavior of cement paste under oscillatory shear motion, and did not explain a detailed method to calculate complex modulus or viscosity in spite of nonlinear viscoelastic behavior of cement paste. There were not literatures to show the linear viscoelastic characteristic of cement paste at very small strain region using conventional strain and frequency sweep experiments; that is, the constant region of dynamic modulus ( $G'$ ) through a very small amplitude oscillation. In this paper linear viscoelastic characteristic of cement paste is shown by the presentation of hysteresis loop between stress and strain, but can not be obtained using strain and frequency sweep experiments because of the limit of the viscometer used even though the results are not shown.

In case of other materials such as clay [8] and polymer melts [9, 10], hysteresis loops between stress and strain or strain rate were represented during the cycle, and nonlinear viscoelastic characteristic was graphically analyzed. Astbury and Moore [8] showed that plastic clay when subjected to symmetrical cyclic torsional strain behaves in a nonlinear manner and produces a stress-strain hysteresis loop of characteristic shape. Tee and Dealy [9] defined three material functions for the characterization of nonlinearity of material: the stress amplitude divided by the strain rate amplitude, a measure of elasticity defined as the stress occurring when the strain rate passes th-

rough zero divided by maximum stress, and a measure of nonlinearity defined in such a way as to be sensitive to asymmetry in the loop.

An obvious way of interpreting nonlinear test results is to compute the material constants of an assumed constitutive equation. All of the models which have been proposed for isotropic fluids are examples of simple fluids. Yanas and Haske [11] employed the simple assumption, that the stress can be represented as some functional of the history of the deformation gradient, to analyze weakly nonlinear behavior of solid polymers in relaxation. A more promising possibility is the use of explicit empirical constitutive equations containing a reasonable number of material constants like Bird-Carreau model [12]. A method of analyzing the stress response which does not rely on any specific model is the use of harmonic analysis. Dodge and Kriger [13] have successfully employed harmonic analysis in their technique for characterizing inelastic fluids by use of oscillatory shear. However in general, harmonic analysis does not appear to provide a useful basis for the characterization of rheologically complex materials.

This paper represents hysteresis loop between stress and strain or strain rate for the qualitative analysis before the theoretical study of nonlinear viscoelastic behavior of cement paste. In order to figure out hysteresis loop, shear stress was continuously measured during the cycles that was operated under constant frequency and amplitude of oscillation. Nonlinear viscoelastic behavior of cement paste was clearly shown from the hysteresis loop since the amplitude of shear stress decreased during the cycles. Time varying quasi-linear behavior is proposed for the computation of viscoelastic properties of cement paste as nonlinear viscoelastic material.

## 2. Time Varying Quasi-Linear Viscoelasticity

Under a sinusoidal oscillatory shear motion shear strain and shear rate can be represented as a complex function of time as shown in Eqs. (1) and (2), respectively.

$$\gamma(t) = \gamma_0 e^{j\omega t} \quad (1)$$

$$\dot{\gamma}(t) = \dot{\gamma}_0 e^{j\omega t} \quad (2)$$

where  $\gamma_0$  and  $\dot{\gamma}_0$  are the amplitude of shear strain and shear rate, respectively and  $\omega$  is the angular velocity of oscillation. In case of linear viscoelastic materials [14], the response of shear stress ( $\tau$ ) has also a sinusoidal function as expressed by Eq. (3), and then the amplitude ( $\tau_0$ ) and the phase angle ( $\phi$ ) are constants.

$$\tau(t) = \tau_0 e^{j(\omega t + \phi)} \quad (3)$$

As the basic characteristic of the harmonic regime of deformation, the ratio  $\tau(t)/\gamma(t)$ , will be defined; and it will be termed the complex modulus  $G^*$ , so that:

$$G^* = \tau(t)/\gamma(t) = \tau_0/\gamma_0 e^{j\phi} \quad (4)$$

$$G^* = \frac{\tau_0}{\gamma_0} \cos\phi + j \frac{\tau_0}{\gamma_0} \sin\phi \quad (5)$$

$$G' = \frac{\tau_0}{\gamma_0} \cos\phi \quad \text{and} \quad G'' = \frac{\tau_0}{\gamma_0} \sin\phi \quad (6)$$

The components of the complex modulus,  $G'$  and  $G''$ , are called the storage modulus (or dynamic modulus) and the loss modulus, respectively. Phase angle,  $\phi$ , represents the relationship between storage modulus and loss modulus. A material with high  $G'$  and low  $G''$  approximates a Hookean solid, while one with high  $G''$  and low  $G'$  approximates a Newtonian liquid.

In this experiment, amplitude ( $\gamma_0$ ) and the frequency ( $f$ ) of oscillation are given as input variables for oscillatory shear motion:

$$\gamma(t) = \gamma_0 \sin(2\pi f t) = \gamma_0 \sin\omega t \quad (7)$$

Then, the shear rate of oscillation is:

$$\dot{\gamma}(t) = \gamma_0 \omega \cos\omega t = \dot{\gamma}_0 \cos\omega t \quad (8)$$

The viscoelastic properties of cement paste are not well analyzed by linear viscoelasticity because the amplitude of stress and the phase angle are not constants but a function of time or strain as shown in Fig. 1. Then, the shear stress can be expressed by the harmonic function with phase:

$$\tau(t) = \tau_0(t) \sin(\omega t + \phi(t)) \quad (9)$$

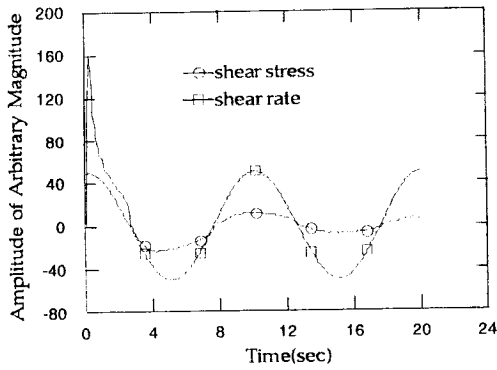


Fig. 1. Shear stress and shear rate vs. time for cement paste as a non-linear viscoelastic material.

Here, we consider the quasi-steady state of the material so that the amplitude of shear stress and the phase angle can be assumed as a constant at each time and then, Eq. (9) can be expressed:

$$\tau = \tau_0 \sin(\omega t + \phi) \tag{10}$$

If we take the first derivative of Eq. (10) to time:

$$d\tau/dt = \dot{\tau} = \tau_0 \omega \cos(\omega t + \phi) \tag{11}$$

From Eqs. (10) and (11), if we eliminate  $\tau_0$  the phase angle is expressed:

$$\phi = \text{Tan}^{-1} \left[ \frac{\tau_0 \omega \cos \omega t - \dot{\tau} \sin \omega t}{\dot{\tau} \cos \omega t + \tau_0 \omega \sin \omega t} \right] \tag{12}$$

where  $\dot{\tau}(t)$  was computed from the measured shear stress using the numerical differentiation method. If the amplitude of shear stress and the phase angle are restored to a function of time, the components of complex modulus,  $G'$  and  $G''$ , can be obtained as a function of time using the computed phase angle:

$$\begin{aligned} G'(t) &= \frac{\tau_0(t)}{\gamma_0} \cos \phi(t) \\ G''(t) &= \frac{\tau_0(t)}{\gamma_0} \sin \phi(t) \end{aligned} \tag{13a}$$

The components of complex viscosity ( $\eta^*$ ) as the ratio ( $\tau/\dot{\gamma}$ ),  $\eta'$  and  $\eta''$ , can be obtained by using  $G'$  and  $G''$ :

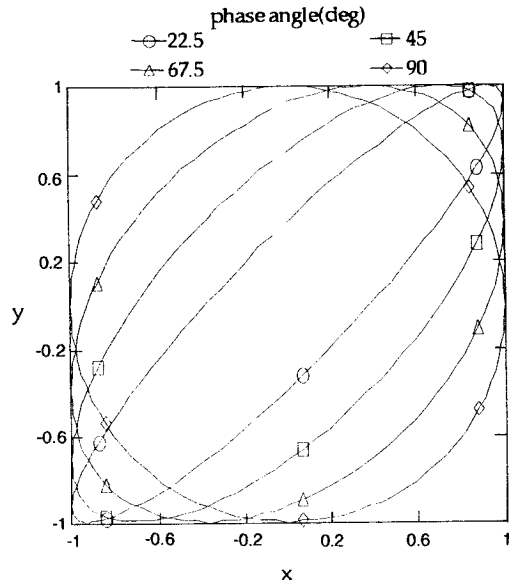


Fig. 2. Effect of phase angle on hysteresis loop of linear viscoelastic material.

$$\eta'(t) = G'(t)/\omega \text{ and } \eta''(t) = G''(t)/\omega \tag{13b}$$

The representation of the  $\tau(t)$  and  $\dot{\gamma}(t)$  curves in the form of harmonic function allows a useful graphical interpretation of the function  $f(\tau, \dot{\gamma}) = 0$  specified in parametric form. Eliminating "t" from Eqs. (7) and (10), we obtain:

$$\left(\frac{\tau}{\tau_0}\right)^2 + \left(\frac{\dot{\gamma}}{\gamma_0}\right)^2 = \sin^2 \phi + 2 \left(\frac{\tau}{\tau_0}\right) \left(\frac{\dot{\gamma}}{\gamma_0}\right) \cos \phi \tag{14}$$

Designating the quantity  $(\dot{\gamma}/\gamma_0)$  as x and  $(\tau/\tau_0)$  as y:

$$x^2 + y^2 = 2xy \cos \phi + \sin^2 \phi \tag{15}$$

This equation can be analyzed to investigate the effect of phase angle on the shape between shear stress and strain as shown in Fig. 2. If  $\phi = 0$ , the material is pure solid, the equation generates a straight line with a slope of  $45^\circ$  to the x-axis, and if  $\phi = \pi/2$ , the material is pure liquid, the equation generates a circle. On the other hand if  $0 < \phi < \pi/2$ , the material is viscoelastic, the equation creates an ellipsoidal shape with a center axis slanted to x-axis.

### 3. Experimental Design

#### 3.1. Sample Preparation

A typical Type I Portland cement was used, and cement paste was prepared by mixing cement and water in Bosch food mixer. Mixing intensity and time was 30 rpm and 5 minutes, respectively. The water: cement ratio by weight was 0.35.

#### 3.2. Experimental System

Experimental system (manufactured by HAAKE) is composed of three parts that include the display function of shear rate and shear stress (RV20), the control function of rotational or oscillational speed of sensor by internal or external program (RC20), and a measuring unit (CV20N) that can use the plate/plate, cone/plate, and coaxial cylinder sensors. The plate/plate sensor used had an upper plate diameter of 19.57 mm and a lower plate diameter of 45 mm as shown in Fig. 3. The gap size was fixed at 2 mm. Under a given internal experiment program of HAAKE system, constant shear motion (steady shear rate) and oscillatory shear motion (unsteady shear rate) experiments are available. Since there is a limit to vary the kinematic condition of sensors, the measurement system will be controlled by an external program that was programmed by the author. By using this external experiment program, the effects of many kinds of shear rate history may be observed. Another interesting characteristic is the relationship between shear stress and shear rate or strain during the cycles contrary to the general oscillatory shear experiment using strain sweep

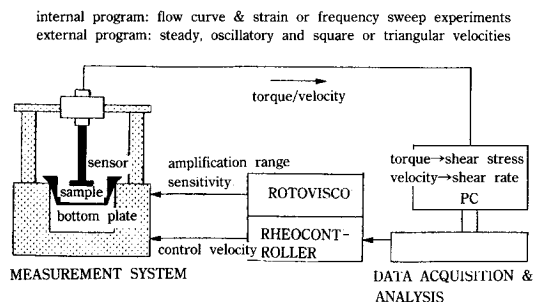


Fig. 3. Schematic diagram of experimental system.

or frequency sweep experiments. There is a difference in the method of data acquisition between internal and external experiment programs. Under frequency sweep experiments, shear stress will be measured discretely by increasing a frequency according to time at constant amplitude of oscillation. Under strain sweep experiments, shear stress will be measured discretely by increasing the amplitude of oscillation according to time at constant frequency of oscillation. Measured points are not continuous but discrete by given step. On the other hand, under external programs shear stress will be measured continuously during a cycle; and it is possible to represent a hysteresis loop. Experimental conditions are shown in Table 1.

### 4. Results and Discussion

#### 4.1. Shear Stress vs. Time

Fig. 4 shows a plot of one cycle of shear stress vs. time under constant frequency ( $f=0.1$ ) for various amplitudes of oscillation. Yield stresses appear in the small strain region similar to the result of steady experiment [15], and depend on the amplitude and frequency of oscillation. Shear stress has a sinusoidal function of time, but the first quarter cycle shows a little different behavior from a normal sinusoidal function. It seems to be the characteristic behavior of a cement paste that shear stress displays an abrupt drop passing a yield point with increasing of a strain. From

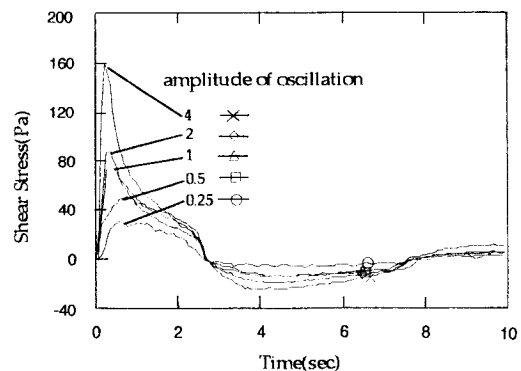


Fig. 4. Shear stress vs. time under one cycle of oscillatory shear motion ( $f=0.1$  Hz).

this behavior we can infer that the microstructure of an early age cement paste is very weak to deformation. Since the amplitude of shear stress and the phase angle depend on time as well as the amplitude and frequency of oscillation, the decreasing behavior of shear stress can be modelled by the following equation:

$$\tau_m(\gamma_o, f, t) = \tau_o(\gamma_o, f, t) \sin(\omega t + \phi(\gamma_o, f, t)) \quad (16)$$

where,  $\tau_m$  is a modelled shear stress,  $\tau_o$  is the amplitude of shear stress,  $\phi$  is a phase angle, and  $\gamma_o$ ,  $f$ , and  $t$  are the amplitude and frequency of oscillation, and time, respectively. The amplitude and the phase angle are assumed as the following equations:

$$\tau_o(\gamma_o, f, t) = a(\gamma_o, f) e^{-b(\gamma_o, f)t} \quad (17)$$

$$\phi_o(\gamma_o, f, t) = 90(1 - e^{-c(\gamma_o, f)t}) \quad (18)$$

The coefficients  $a$ ,  $b$  and  $c$  are functions of amplitude and frequency of oscillation and obtained from a curve-fitted method as expressed by Eqs. (19), (20) and (21):

$$a(\gamma_o, f) = \frac{c_1}{f^{1.127}} + \frac{c_2}{f^{0.758}} \gamma_o \quad (19)$$

$$b(\gamma_o, f) = \frac{c_3}{f^{0.32}} + \frac{c_4}{f^{0.5}} \ln(\gamma_o) \quad (20)$$

$$c(\gamma_o, f) = (d_1 + d_2 \ln(f)) - (d_3 + d_4 \ln(f)) \gamma_o \quad (21)$$

The values of  $c_1$ ,  $c_2$ ,  $c_3$  and  $C_4$  are 1.287, 3.172,

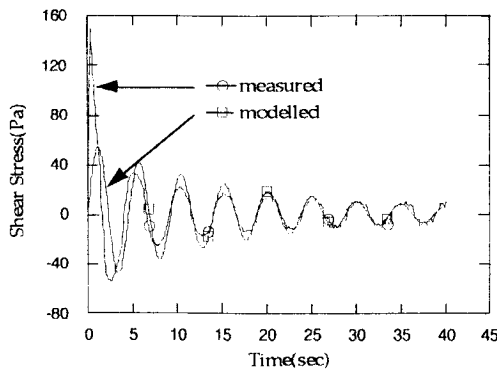


Fig. 5. Comparison of measured and modelled shear stresses ( $f=0.2$  Hz,  $\gamma_o=4$ ).

0.03 and 0.0047, respectively. The values of  $d_1$ ,  $d_2$ ,  $d_3$  and  $d_4$  are 0.1785, 0.025, 0.0066 and 0.00165, respectively.

Fig. 5 shows the comparison of measured and modelled shear stresses. Except for an initial period of experiment, the modelled shear stress shows good agreement. The deviation at an initial period was accredited to both the small amplitude of stress and the retarded increase of phase angle of modelled equation, and the deviation degree during initial period was reduced with decreasing of shear rate.

#### 4.2. Hysteresis Loop between Shear Stress and Strain

Fig. 6 shows the general relationship between shear stress and strain during a typical cycle. The behavior of an early age cement paste can be divided into three zones. Zone I, the region below a yield point, is concerned with the elastic solid behavior of an early age cement paste. The existence of an elastic linear region of an early age cement paste may be explained by connection with the microstructural points of view. Powers [16] described that fresh cement pastes made at the usual w/c ratio were composed of floccula which particles in a cement suspension or sol are mutually attracted by a combination of van der Waals and electrostatic forces, stick together to form agglomerate. The mixing of cement particle and water produces the hydraulic forces which

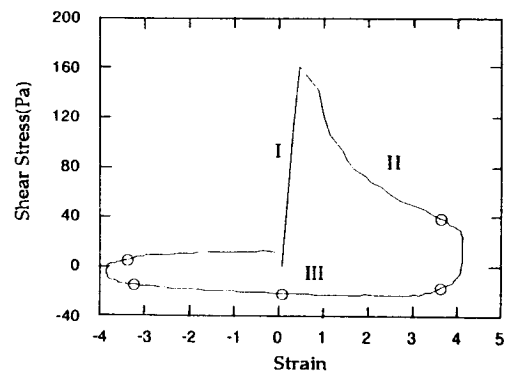


Fig. 6. Typical hysteresis loop of cement paste under oscillatory shear motion ( $f=0.1$  Hz,  $\gamma_o=4$ ).

tend to separate the individual particles and to create an uniform dispersion state. When the mixing action ceases, a continuous structure forms. Under these circumstances shear motion is given to a cement paste. Then the existence of elastic linear region means that the structure of cement paste at small strain only deforms without breakdown of structure whatever structure cement paste has. According to Goodwin [17], a stable, small particle-size dispersion may show linear behavior for strains  $<0.05$ , however, if large, weakly flocculated systems are used, linearity is unlikely to be found for strains in excess of 0.01. For coagulated systems, linearity is unlikely to be found if the strain is larger than 0.001. In case of cement paste, the yield strain approximately has the large values, between 0.1 and 0.9, obtained from the numerical integration of shear rate. Fig. 7 shows the relationship between shear stress and strain for various amplitudes of oscillation under constant frequency during 4 cycles. A linear elastic region increases with increase of shear rate like the result of steady shear motion experiment [15]. After several cycles, a cement paste has nearly a constant shear stress in spite of various experimental conditions. This means that cement paste has a constant structure after breakdown (at large strain) even though it is affected very much by experimental conditions before structure breakdown (at small strain). Zone II represents the structure breakdown of cement paste that is

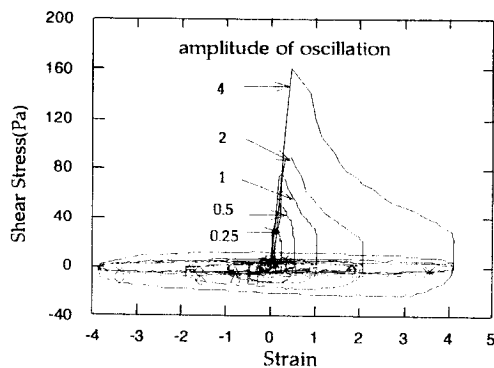


Fig. 7. Effect of amplitudes of oscillation on hysteresis loop under constant frequency of oscillation ( $f=0.1$  Hz).

induced by the deformation passing a yield point. When the deformation of sine function is given to a sample, the shear stress has a in-phase (sine function) if a sample is a pure solid and a out-of-phase (cosine function) if a sample is a pure liquid. From these points of view, Zone II is closer to out-of-phase state, but the shape is a little different from a sinusoidal function; that is, the degree of dropping of shear stress is large just after a yield point although it is reduced little by little at large deformation (Zone III). The degree of deviation of shear stress from the shape of sinusoidal function means that the quantity of dissipated energy increases with increasing of the amplitude of oscillation at constant frequency. At zone III, the material loses strength and resiliency continuously with the proceeding of cycle, and then its shape looks like an ellipsoidal body with a central axis parallel to strain axis compared with the graphical interpretation as shown in Fig. 2. The structure breakdown of Zone III does not occur largely in spite of a continuous deformation compared with Zone II. Although cement paste shows a liquid property passing through Zone II and the breakdown of floccules forming separate clusters of particles, the flocculate structure has still a weak viscoelastic characteristic with a slight slope to the strain axis.

#### 4.3. Shear Stress vs. Shear Rate

Fig. 8 shows the relationship between shear stress and shear rate during 4 cycles. The flow cu-

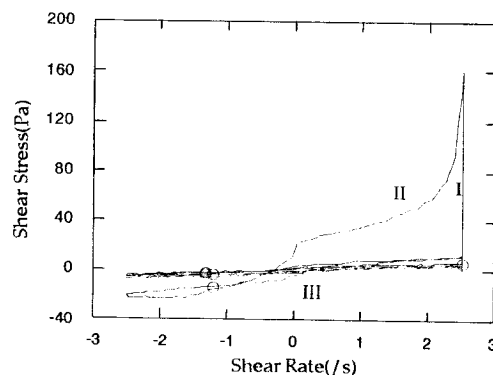


Fig. 8. Shear stress vs. shear rate under oscillatory shear motion ( $f=0.1$  Hz,  $\gamma_0=4$ ).

rive can be divided into the same three zones as explained in the section of shear stress and strain. Zone I occurred instantaneously as soon as the shear rate was given, and the gradient of the curve between shear stress and shear rate becomes infinity. Zone II divided the apparent viscosity into three regions such as the first fast decrease, the moderate decrease, and the second fast decrease. At zero shear rate cement paste has still some shear stress considered as characteristic shear stress under a given cycle. As the cycle proceeds, this value decreases more and more. Banfill and Saunder [18] show that the structural breakdown due to shear is outweighed by the effects of continuing hydration when they take the use of hysteresis of long duration with a higher shear rate. In this experiment of short experimental time (40 seconds) and low shear rate, the structure breakdown is showed, but we may expect a stronger hydration effect than the structure breakdown if the experimental time increases. At Zone III, there are thixotropic and anti-thixotropic behavior during cycles; these show that the structure of cement paste forms or breaks down continuously under the application of shear rate, and can be explained by the results of Tattersall and Banfill [19]. They proposed that during the initial reaction the aggregates of particles already contact were coated with a continuous membrane of all gel which, if destroyed by shearing, was replaced by separate coatings around each particle, which were less effective in bonding the particles together. The behavior of cement paste has a straight line across the shear stress coordinate with increasing the number of cycle, and the gradient of straight line reduced more and more. This means that cement paste has a low viscosity at the region of large deformation and shows non-Newtonian liquid behavior. Liquid of simple and stable molecular structure generally obeys the Newtonian law, and suspensions show Newtonian behavior only if there is no long-range structure. From this point of view, we can consider that a cement paste has a long-range or flocculate structure before the application of shear, and the structure is broken continuously by shear motion.

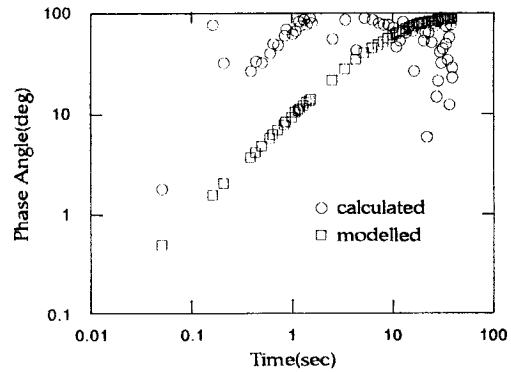


Fig. 9. Comparison of calculated and modelled phase angles ( $f=0.1$  Hz,  $\gamma_0=4$ ).

Table 1. Experimental conditions of oscillatory shear test (amplitude of shear rate  $s^{-1}$ )

$f$ (Hz)	0.025	0.05	0.1	0.2
$\gamma_0$				
0.25	0.039	0.079	0.157	0.314
0.5	0.079	0.157	0.314	0.628
1	0.157	0.314	0.628	1.257
2	0.314	0.628	1.257	2.513
4	0.628	1.257	2.513	5.027

#### 4.4. Complex Modulus and Viscosity under Oscillatory Shear Flow

Fig. 9 shows a phase angle as a function of time. The symbol of a circle shows the results calculated from the experimental data using Eq. (12); but the symbol of square shows the modelled result using the exponentially increasing function expressed by Eq. (18). The former represents the real phenomena of the phase angle of a cement paste under the assumption of time varying quasi-linear viscoelasticity. Passing through a yield point (from Zone I to Zone II), the phase angle changed abruptly from 0 to 80 degrees approximately. At zone II, it decreases slightly for a very short time (0.2 sec) and increases slowly. At zone III, phase angle keeps the constant value even though there is much scattering of data; thus, a cement paste sustains the structure closer to a viscous liquid material under large deformation. The latter based on a curve-fitted equation shows different be-



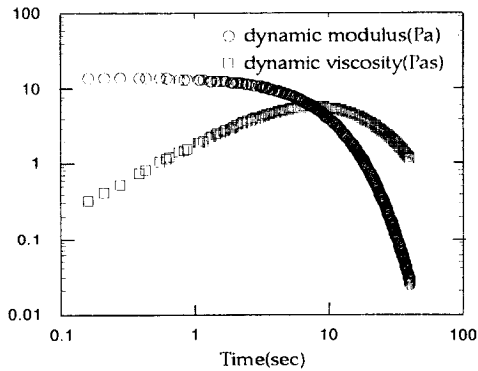


Fig. 10. Dynamic modulus and viscosity as a function of time based on modelled phase angle and amplitude of shear stress ( $f=0.1$  Hz,  $\gamma_0=4$ ).

havior, that is, it doesn't follow the abrupt change of a phase angle at the region of small deformation. At the region of large deformation, it increases slowly even though the real phase angle arrives at about  $90^\circ$  after a very short time. The effects of amplitude and frequency of oscillation on the dynamic modulus and viscosity are analyzed by the curve-fitted result due to its analytical simplicity. Fig. 10 shows the dynamic modulus and viscosity obtained from the curve-fitted equation. Compared with the result based on the real phase angle, the starting time, that the values of  $G'$  and  $\eta'$  decreased, was delayed from  $t=0.2$  sec to  $t=8$  sec due to the retardation of the increase of phase angle. At Zone III, the value of  $G'$  decreased very much compared with that of  $\eta'$ . In other words, there is much energy dissipation due to the flow behavior of cement paste. The curve-fitted equation can be used for the analysis of the viscoelastic properties of cement paste at large deformation.

## 5. Conclusion

Nonlinear viscoelastic behavior of cement paste was confirmed by the representation of hysteresis loops between stress and strain or strain rate through oscillatory shear tests. Time varying quasi-linear viscoelasticity was tried to calculate viscoelastic properties of nonlinear viscoelastic material

such as phase angle, dynamic modulus, and dynamic viscosity. This method shows good agreement at later stage although there was much difference from real behavior, that was shown by the plots of stress and strain vs. time, due to the retarded prediction of phase angle at initial stage. From the hysteresis loop obtained from oscillatory shear test cement paste shows linear elastic, structure breakdown, and viscous fluid regions. Nonlinear viscoelastic characteristic is well graphically analyzed by the representation of hysteresis loop, and this information may be helpful for the theoretical study of nonlinear viscoelastic behavior of cement paste in the future.

## Acknowledgement

The authors would like to express their appreciation to Concrete Technology of Santa Barbara, CA for instrumentation and financial support of this work, and the National Science Foundation Center for Advanced Cement Based Materials, Grant DMR-8808432. Professor Lewis Erwin died during the final stages of this research.

## Nomenclature

- a : coefficient of modelled equation
- b : index of modelled equation
- f : frequency
- $G^*$  : complex modulus
- $G'$  : dynamic modulus
- $G''$  : loss modulus
- t : time
- $\phi$  : phase angle
- $\gamma$  : shear strain
- $\gamma_0$  : amplitude of shear strain
- $\dot{\gamma}$  : shear rate
- $\dot{\gamma}_0$  : amplitude of shear rate
- $\eta^*$  : complex viscosity
- $\eta'$  : dynamic viscosity
- $\eta''$  : loss viscosity
- $\tau$  : shear stress
- $\tau_0$  : amplitude of shear stress
- $\tau_m$  : modelled shear stress

## References

1. T.E.R. Jones and G. Brindley, Proc. of 7th Int'l. Cong. on Rheology, 329-331 (1976).
2. B.C. Mutsuddy, *Langmuir*, **6**, 24-27 (1990).
3. A.R. Cusen and J. Harris, Proceedings of a RI-LEM Seminar, **1**, 2.8.1-2.8.34 (1973).
4. T.E.R. Jones, G. Brindly, and B.C. Patel, Conference Proceedings, University of Sheffield, Slough, Cem. and Conc. Asso., 135-149 (1976).
5. R.J. Akers and G.P. Machin, Proceedings and 2nd World Filtration Congress, Croydon, The Filtration Society, 363-375 (1979).
6. T.M. Chow, L.V. McIntire, K.R. Kunze, and C.E. Cooke, SPE Production Eng., 543-550 (1988).
7. A. Saasen, C. Marken, J. Dawson, and M. Rogers, *Cem. and Conc. Res.*, **21**, 109-119 (1991).
8. N.F. Astbury and F. Moore, *Rheol. Acta*, **9**, 124-129 (1970).
9. T.T. Tee, and J.M. Dealy, *J. Rheol.*, **19**, 595-615 (1975).
10. J.M. Dealy, J.F. Petersen, and T.-T. Tee, *Rheol. Acta*, **12**, 550-558 (1973).
11. I.V. Yanas and V.C. Haskel, *J. of Applied Physics*, **42**, 610-613 (1971).
12. R.B. Bird and P.J. Carreau, *Chem. Eng. Sci.*, **23**, 427-434 (1968).
13. J.S. Dodge and I.M. Kriger, *J. Rheol.*, **15**, 589-601 (1971).
14. G.V. Vinogradon and A. Ya. Malkin, "Rheology of Polymers," Mir Publishers Moscow, Springer Verlag Berlin Heidelberg, New York (1980).
15. B.-H. Min, L. Erwin, and H.M. Jennings, *Ceramic Trans.*, **16**, 337-346 (1990).
16. T.C. Powers, "The Properties of Fresh Concrete," John Wiley & Sons (1968).
17. J.W. Goodwin, *Ceramic Bulletin*, **69**, 1694-1698 (1990).
18. P.F.G. Banfill and D.C. Saunders, *Cem. and Conc. Res.*, **11**, 363-370 (1981).
19. G.H. Tattersall, and P.F.G. Banfill, "The Rheology of Fresh Concrete," Pitman Advanced Publishing Program (1983).