VISCOELASTIC SHEAR RESPONSE OF A KAOLINITE

by

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ABSTRACT

RECOGNITION of the fact that clays exhibit both viscous and elastic response characteristics has led to the use of the theory of viscoelasticity for describing their mechanical behavior. This paper presents a brief outline of pertinent concepts from this theory to establish a framework for the presentation and interpretation of the experimental results. The experimental program was conducted on a water-washed Georgia kaolin at nominal moisture contents of 50%, 75%, and 100%, and included a series of oscillatory shear tests over a frequency range of two decades. These tests were performed on a Weissenberg Rheogoniometer with a cone-and-plate sample holder; this arrangement produces essentially homogeneous shear strains throughout the specimen.

The experimental results show that the stress–strain response of the clay is frequency-dependent and is definitely nonlinear, even at small strains. The greatest frequency dependence, as manifested in the complex shear modulus and phase angle, occurs in a region characteristic of many polymer systems. The logarithm of the complex shear modulus is found to vary approximately as the water content or consistency of the clay–water mixture.

INTRODUCTION

THE mechanical properties of clay are very important in many stages of industrial processes. Efficiency can be achieved in the planning of the process, the design of appropriate equipment, and the suitable preparation of the clay only by obtaining control of the phenomena governing response. The initial step in obtaining this control involves the use of precise methods for measuring all components of clay response under various types of mechanical action; then, these data must be correlated by an appropriate theory in order that subsequent behavior of the clay in other types of apparatus and under other conditions can be predicted.

The mechanical properties of a material are generally defined as parameters relating stresses, strains, and the various time derivatives of each. Since these parameters may be functions of a multitude of other variables, such as particle size, size distribution, particle shape, mineralogy, exchangeable ions, degree of flocculation, degree of crystallinity, water content, temperature, history, etc., the overwhelming task of formulating such behavior into any general expression can be easily appreciated. As a consequence, most studies,

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including this one, have necessarily restricted the scope of the investigation to one or two parameters and maintained the others constant, or as nearly so as possible. Although this study is directed toward investigating the mechanical behavior of an aqueous clay suspension under very restricted conditions, it is not the intention to imply that the many other parameters which were maintained constant are unimportant.

Advances in the technology of aqueous clay suspensions will come from the fields of mineralogy, geology, crystallography, and physical chemistry, as well as soil rheology, and progress can be maximized by coordinating the efforts of all of these disciplines into a coherent formulation and explanation of observed phenomena. The work reported herein will contribute toward the advancement of clay technology from a rheological point of view.

One of the very difficult problems associated with testing a material such as clay is the fact that it is virtually impossible to test an invariant material; by its very nature, the material changes during the test. For example, an originally flocculated structure at the start of a test may become a very dispersed structure as the test progresses. Such shear thinning, as well as shear thickening, phenomena are well known. This work adopts the viewpoint that if a material is tested under a homogeneous state of stress (or strain), its response, including any change in structure which may occur, is the quantity to be measured. The fact that the clay may exhibit structural changes during a test is regarded as a manifestation of its behavior and a basic property or characteristic of the clay.

THEORETICAL CONSIDERATIONS

Recognition of the fact that clays exhibit both viscous and elastic response characteristics has led to the use of viscoelastic theory for describing the mechanical behavior of such materials. In summing up the state-of-the-art, Schmid and Kitago (1965) state that: "There appears to be general agreement, however, that saturated clay soils do behave like viscoelastic or viscoplastic materials." The theory of viscoelasticity, as used herein, is a phenomenological one; it is concerned with the observed macroscopic behavior of a material, which is regarded as a continuum, and is not concerned with the microscopic mechanisms responsible for that behavior. Rather, it supposes that the material can be characterized by a number of specific macroscopically measurable parameters which describe its mechanical behavior.

Viscoelastic Theory

The following brief summary of linear viscoelastic theory is presented to establish the framework within which the experimental data are interpreted, and it is not intended to be comprehensive. More detailed treatments of such theory may be found in the works of Gross (1953), Ferry (1961), and others.

Stress–strain–time relations.—The theory of viscoelasticity is a generalization of the classical theories of elasticity and viscosity; it supposes that the deformation of a material under stress includes energy storage components which are elastically reversible and viscous components which are irreversible and dissipate energy. In linear viscoelasticity, it is assumed that there is a unique relationship between increments of stress and strain at any point in time, and that this relationship is independent of stress level. The constitutive relation for a linear viscoelastic material can be written in the general form

$$a_0\sigma + a_1\dot{\sigma} + a_2\ddot{\sigma} + \ldots = b_0\epsilon + b_1\dot{\epsilon} + b_2\ddot{\epsilon} + \ldots \tag{1}$$

where a_n and b_n are parameters which are independent of stress, strain, and their time derivatives, but may be functions of other physical variables, such as temperature or moisture content. The symbols σ and ϵ in equation (1) represent either dilatational (bulk, or volume change) or deviatoric (shear, or shape change) components of stress and strain; although the two kinds of behavior can be considered separately, superposition of their effects is subject to question.

Response spectrum.—The formulation of a stress–strain–time relationship for any given engineering material must by its very nature be comprehensive enough to include the entire time response spectrum of interest. Transient experiments (creep and relaxation tests) are most advantageous for measuring material behavior in the region of large time, and steady-state experiments (oscillatory tests) are most useful for short time response measurements. Thus, the two types of experiments are mutually complementary and may be synthesized to describe phenomenologically, response characteristics over many decades of time. The resulting formulation may then be used to calculate material response under other types of conditions, such as constant strain rate applications.

Creep and relaxation functions.—Using the principle of superposition, linear viscoelastic shear behavior can be expressed by the hereditary integrals

$$\gamma(t) = \int_{-\infty}^{t} J(t-s)\,\frac{\mathrm{d}\tau(s)}{\mathrm{d}s}\,\mathrm{d}s \tag{2}$$

and

$$\tau(t) = \int_{-\infty}^{t} G(t-s)\,\frac{\mathrm{d}\gamma(s)}{\mathrm{d}s}\,\mathrm{d}s \tag{3}$$

where $J(t-s)$ is the creep compliance function, $G(t-s)$ is the relaxation modulus function, s is a parameter of integration, and γ, τ, and t are shear strain, shear stress, and time, respectively. These integral equations are not independent, and it can be shown that the inversion of one yields the other. Alternatively, treating the two equations as separate expressions will produce a set of compatibility conditions resulting from their intrinsic dependence.

Considering the shear stress relaxation test with constant strain γ_0 applied at $t=0$ and neglecting hereditary effects, equation (3) can be integrated by parts to give

$$\tau(t)=\gamma_0 G(0)+\gamma_0 \int_0^t \frac{\mathrm{d}[G(t-s)]}{\mathrm{d}(t-s)}\,\mathrm{d}s. \tag{4}$$

Dividing equation (4) by γ_0 and defining the right side as the relaxation modulus $G(t)$ gives

$$G(t)=\frac{\tau(t)}{\gamma_0}. \tag{5}$$

A material exhibiting linear response will have a unique relation independent of strain level between relaxation modulus and time. However, any single relaxation response curve, even for a nonlinear material, can be represented in such a form.

The creep compliance of a material is studied by imposing a constant stress τ_0 on a specimen and measuring the strain $\gamma(t)$ as a function of time. In a manner similar to that described above, the creep compliance $J(t)$ may be defined from equation (2) as

$$J(t)=\frac{\gamma(t)}{\tau_0}. \tag{6}$$

Complex viscoelastic parameters.—If a linear viscoelastic material is subjected to a sinusoidally varying strain of amplitude γ_D at a given frequency of oscillation ω, its steady-state response will be a sinusoidally varying stress of amplitude τ_D at the same frequency but out of phase with the strain by a phase angle δ, as shown in Fig. 1. The existence of a phase angle leads to the consideration of the stress components in phase and out of phase with the

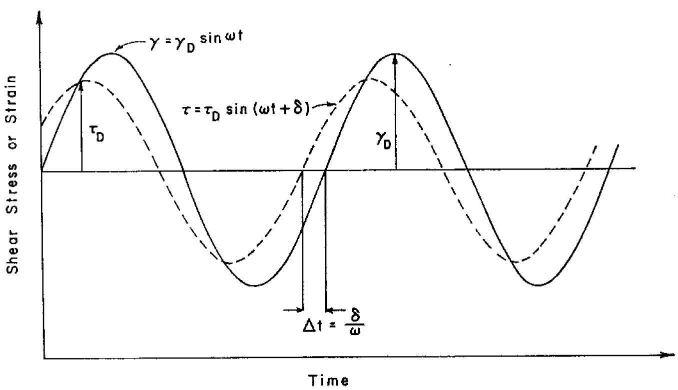

FIG. 1. Oscillatory stress–strain–time response.

applied strain. The component of stress in phase with the strain divided by the strain is called the storage modulus G' and can be written

$$G' = \frac{\tau_D \cos \delta}{\gamma_D}. \tag{7}$$

The storage modulus is related to the energy stored and completely recovered for a single cycle of deformation. The component of stress in quadrature with the strain divided by the strain is called the loss modulus G'' and can be expressed

$$G'' = \frac{\tau_D \sin \delta}{\gamma_D}. \tag{8}$$

The loss modulus is associated with the energy dissipated for a single cycle of deformation. The storage and loss moduli can be combined vectorially in the complex plane to give a complex modulus G^* written as

$$G^* = G' + iG''. \tag{9}$$

The absolute value of the complex modulus $|G^*|$ may be expressed as

$$|G^*| = \sqrt{[(G')^2 + (G'')^2]} = \frac{\tau_D}{\gamma_D}. \tag{10}$$

In terms of the components of the complex modulus, the loss tangent (or $\tan \delta$) can be written

$$\tan \delta = \frac{G''}{G'}. \tag{11}$$

In similar manner, material response may be expressed alternatively in terms of storage, loss and complex compliances, given as

$$J' = \frac{\gamma_D \cos \delta}{\tau_D}, \tag{12}$$

$$J'' = \frac{\gamma_D \sin \delta}{\tau_D}, \tag{13}$$

and

$$J^* = J' - iJ'', \tag{14}$$

respectively. The magnitude of the complex compliance $|J^*|$ may be written

$$|J^*| = \frac{1}{|G^*|} = \frac{\gamma_D}{\tau_D} \tag{15}$$

while the loss tangent is given as

$$\tan \delta = \frac{J''}{J'}. \tag{16}$$

Transformations.—There are two distinct methods of obtaining the complex modulus of a material. The first is based on a series of dynamic tests to investigate the steady-state response under sinusoidal strains of various frequencies. In this case, discrete pairs of values for $|G^*|$ and δ are obtained. These may then be approximated by representative functions and utilized with equations (7) through (9) to yield an analytic expression for G^*.

The second method is based on applying a known strain $\gamma(t)$ to a material and measuring the resulting stress $\tau(t)$ which consists of both transient and steady-state components. The applied strain $\gamma(t)$ and resulting stress $\tau(t)$ may then be approximated by appropriate equations and transformed into the frequency domain by means of one-sided Fourier transforms. The ratio of the transformed stress to the transformed strain yields directly the complex modulus G^* in analytical form.

A similar technique may be used to determine the complex compliance J^*. Hence, a single transient test conducted in the proper range of the time spectrum can produce all the information contained in an extensive series of variable frequency tests. The one-sided Fourier transform expressions for strain and stress may be given as

$$\gamma^*(\omega) = \int_0^\infty \tau(t)\, \mathrm{e}^{-i\omega t}\, \mathrm{d}t \tag{17}$$

and

$$\tau^*(\omega) = \int_0^\infty \gamma(t)\, \mathrm{e}^{-i\omega t}\, \mathrm{d}t \tag{18}$$

where ω is expressed in radian frequency. An application of this latter transformation method to a clay soil has been presented by Krizek (1964).

In an analogous manner, frequency-dependent response may be transformed into the time domain. This feature gives added significance to the oscillatory type tests conducted in this experimental program.

Limitation of linear viscoelasticity.—The principle of superposition was proposed by Boltzmann (1874) as a starting-point to reduce the complex manifestations of primary creep to some simple scheme. At the time of its initial presentation, Boltzmann adopted the viewpoint of relaxation of stress in a body subjected to a given strain history and gave no theoretical basis for his rule. Thus, the original formulation was purely an empirical law and was suggested only as a first approximation to actual creep behavior.

While the principle of superposition provides the backbone for the structure of a mathematical theory of linear viscoelasticity, it is this very principle which so severely limits the direct extension of such a comprehensive theory into the field of clay rheology. In general, most clays do not exhibit linear stress–strain–time behavior; hence, the superposition principle is not strictly valid. Nevertheless, linear viscoelastic theory can provide an insight into the analysis of experimental data and the development of new test procedures designed to obtain more fundamental clay properties, and these techniques are being pursued with some degree of success.

Stress and Strain Distribution

One of the prime requirements for testing materials is that the applied external forces or deformations should result in the development of a homogeneous stress or strain distribution in the sample. In view of the non-linearities generally associated with clays, the need for stress and strain homogeneity is most essential. Furthermore, due to the difficulty of preparing satisfactorily homogeneous samples, it is preferable that sample geometry remain simple, as well as small.

The geometry of a cone-plate viscometer satisfies to a large degree the requirements mentioned above. The principles of cone-plate viscometer operation and other details have been described by Markovitz *et al.* (1955), McKennell (1956, 1960), Slattery (1961, 1964), and others and will not be repeated herein. For this discussion it will suffice to study briefly the cone-plate geometry shown in Fig. 2, and to examine the argument for the development of a homogeneous shear strain throughout the sample.

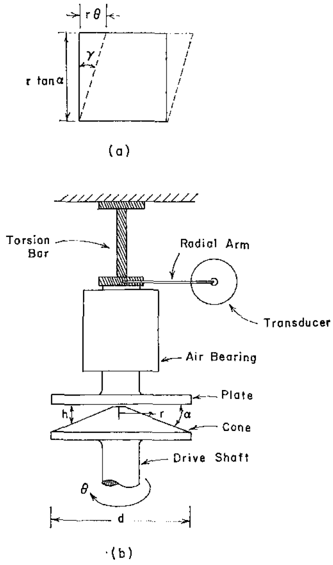

FIG. 2. Schematic diagram of cone-plate assembly.

In the theory of continuum mechanics, shear strain γ is defined as the angle change of an original right angle in an infinitesimal element of the material. Referring to the geometry shown in Fig. 2, consider a typical element located at some distance r from the central axis of the cone-plate assembly; if the cone angle is α, the height of this element is $r \tan \alpha$. Now, if the cone is rotated

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through an angle θ relative to the plate, the distortional displacement of the top of this element is $r\theta$. For small strains γ is approximately equal to tan γ, and we have

$$\gamma=\frac{r\theta}{r\tan\alpha}=\frac{\theta}{\tan\alpha}. \tag{19}$$

Hence, the shear strain γ, given by equation (19), is independent of the location of the element, and is constant or homogeneous throughout the sample. In dilatant materials hydrostatic stresses would be developed, and these would not necessarily be homogeneous.

CLAY TESTED

The clay used in this investigation was a water-washed Georgia kaolinite of a grain size distribution commonly used in paper-coating applications; it was supplied through the courtesy of the Georgia Kaolin Company of New Jersey. Powdered clay was mixed manually with a predetermined amount of distilled water to obtain aqueous clay mixtures with nominal water contents of 50%, 75%, and 100% (water content is defined as weight of water divided by weight of solids and converted to per cent). After being mixed as thoroughly as possible by hand, the mixtures were sealed in air-tight containers and stored in a high-humidity room for a period of approximately two months before they were tested.

EXPERIMENTAL INVESTIGATION

The experimental phase of this study includes oscillatory shear tests at frequencies ranging from 0.0095 to 3.0 cps in order to examine the frequency dependence of the clay response. The effect of water content or consistency variations is investigated by testing the clay at three nominal water contents. Several different stress and strain amplitudes are applied at a constant frequency to each sample to study the nonlinearity of the clay.

Test Apparatus

The tests described herein were performed on a Weissenberg Rheogoniometer, which is a unique instrument highly regarded by experimentalists investigating the rheological properties of materials. As employed in this study, the device utilized a 2.5-cm diameter cone-plate assembly, as shown in Fig. 2, and imposed on the specimen a homogeneous state of shear strain. A truncated cone with a clearance of approximately 0.03 cm was used to avoid the effects of clay particles wedging at the apex of the cone-plate; Markovitz *et al.* (1955) have shown that such truncation does not seriously affect experimental results.

Experimental Procedure

Particular attention was given to the problem of water evaporation during placing and testing of the sample. An excess of the clay–water mixture was placed on the cone, and the plate was immediately lowered into operating position so that the exposed surface was minimal. At the same time a specimen of clay was taken from the container to determine the moisture content; these moisture contents varied from their average values by approximately $\pm 1.5\%$. After the excess clay was trimmed, the cone-plate assembly and sample, together with a small pan of distilled water, were enclosed in a chamber to minimize water content losses. All tests were conducted in a temperature-controlled room at a temperature of $72.5 \pm 0.5°F$; the sample containers were placed in the room several days before testing to insure that they attained room temperature.

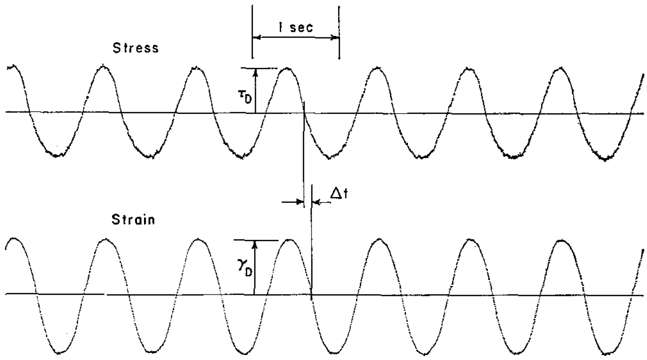

FIG. 3. Typical experimental response curves.

All specimens were subjected to a periodic torsional shear deformation by oscillating the cone platen at a constant frequency by means of the drive mechanism. The upper plate was fixed to a calibrated torsion bar; the angle of twist of the torsion bar was measured by a transducer located at the tip of a radial arm fastened to the torsion bar. Since the actual angular deformation in the sample is given by the relative displacements of the two platens, appropriate correction procedures, as explained by Weissenberg (1963), were applied to account for rotation of the torsion bar, as well as inertial and damping effects in the torsion head assembly.

Each test consisted of several stages of constant-frequency oscillatory shear stresses and strains with monotonically increasing amplitudes. Each strain amplitude was applied for at least 1 min in order that a steady-state condition be used for all measurements. The imposed deformation and stress response were recorded on a two-channel oscillograph to produce a record like that shown in Fig. 3. Stress and strain amplitudes, as well as phase angles, were scaled from these records; several readings were averaged for each stage of the test, and these values were corrected as indicated above.

Interpretation of Results

A typical response curve for stress amplitude τ_D versus strain amplitude γ_D for a constant frequency ω is shown in Fig. 4. As can be seen, the relationship between these two parameters is definitely nonlinear, even for very small values of strain. This response may be likened to that for a nonlinear "soft" spring, that is, one in which the modulus decreases with increasing deformation. The effect of this nonlinearity can be observed in the shape of the wave forms at higher strain amplitudes; although the imposed strain wave is sinusoidal, the resulting stress wave has a flattened peak. While such

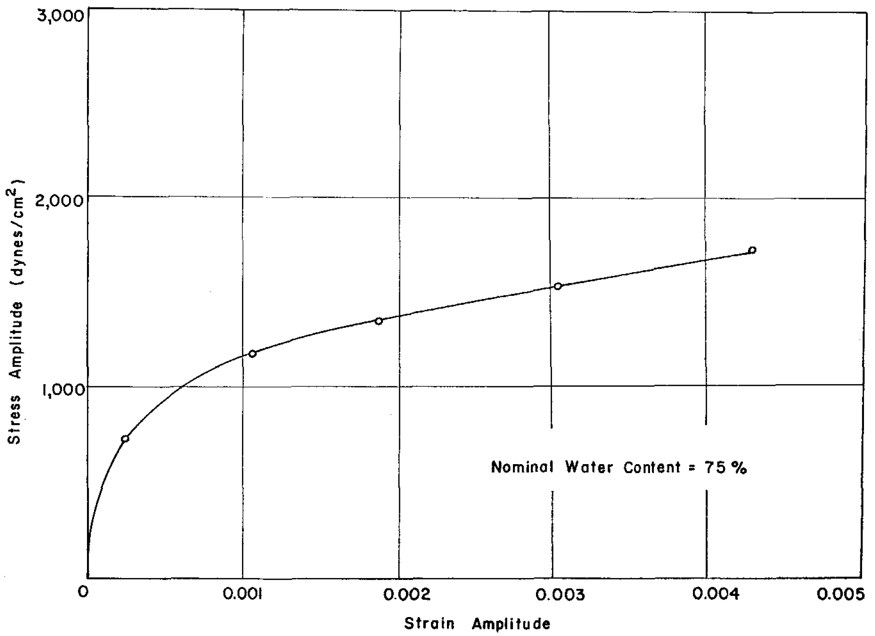

FIG. 4. Typical response curve for constant frequency.

mechanical behavior invalidates the rigorous application of linear viscoelastic theory, it is felt that the interpretation of experimental results within this framework offers the hope of a more comprehensive explanation of clay behavior than is available from the even more limited theories of Hookean elasticity or Newtonian viscosity.

Since the response was found to be frequency-dependent, a further study of this effect was made by plotting the magnitude of the complex shear modulus $|G^*|$ versus frequency. The curve shown in Fig. 5 was obtained by calculating the secant modulus associated with a strain amplitude of 0.001. If different values of strain amplitude were selected, a family of similar curves would result, each curve corresponding to a particular value of γ_D. This family of curves is indicative of nonlinear behavior, since a linear material would exhibit a unique frequency-dependence curve. Although the level of this curve in the high-frequency range cannot be determined from the data available, the characteristic S-shaped pattern is similar to that reported by Krizek (1964) and Krizek and Kondner (1966) for a different clay tested in uniaxial compression. Also, such behavior is similar to that manifested by many polymers. The modulus plateaus are associated with the high and low relaxation time mechanisms within the clay structure.

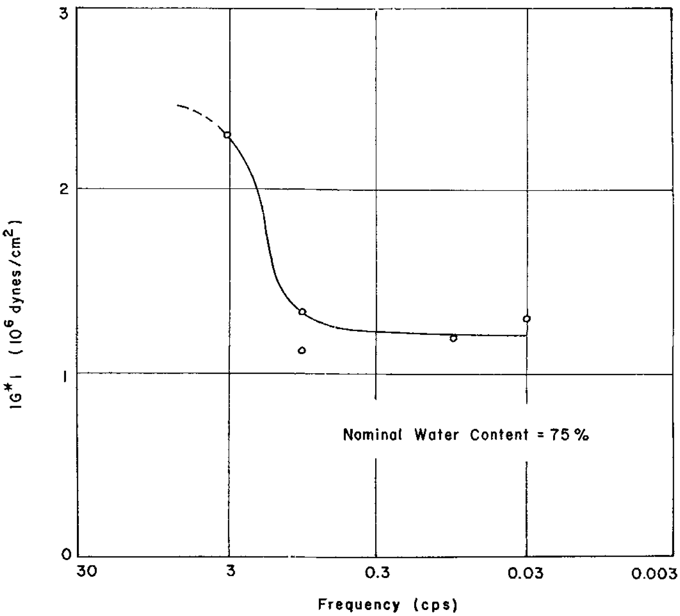

FIG. 5. Modulus versus frequency for constant water content.

Figure 6 shows a plot of phase angle δ versus frequency for a strain amplitude level of 0.001. Since, in general, experimental data were not obtained at this particular value of strain amplitude, the phase angle value was obtained by linear interpolation between the two values measured on either side of 0.001. The bell-shaped curve is characteristic of those reported by Krizek (1964) and Kondner and Ho (1965) for another clay tested under different conditions and for a large variety of polymer systems. As is the case for the modulus function, selection of a different strain amplitude value would result in a family of similar curves. The so-called dispersion region in the neighborhood of where the phase angle curve reaches a maximum corresponds to the region of maximum slope of the modulus–frequency curve shown in Fig. 5 and is associated with the conditions under which maximum energy dissipation will occur in the clay.

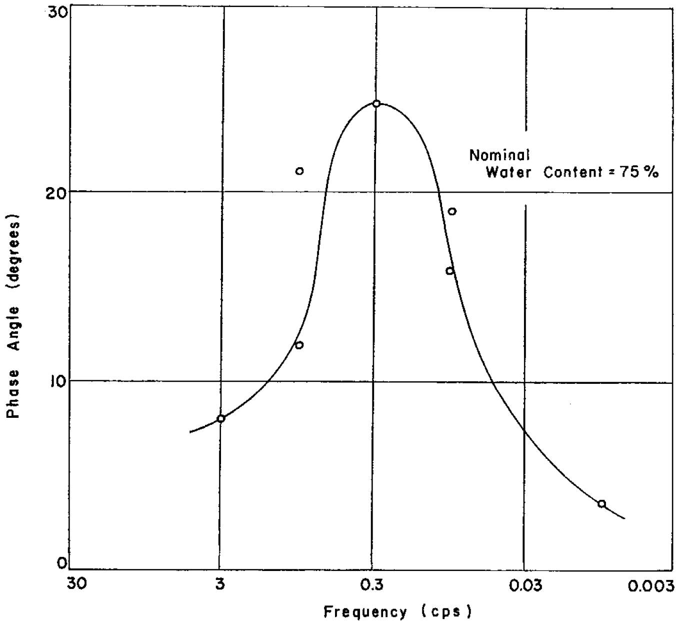

FIG. 6. Phase angle versus frequency for constant water content.

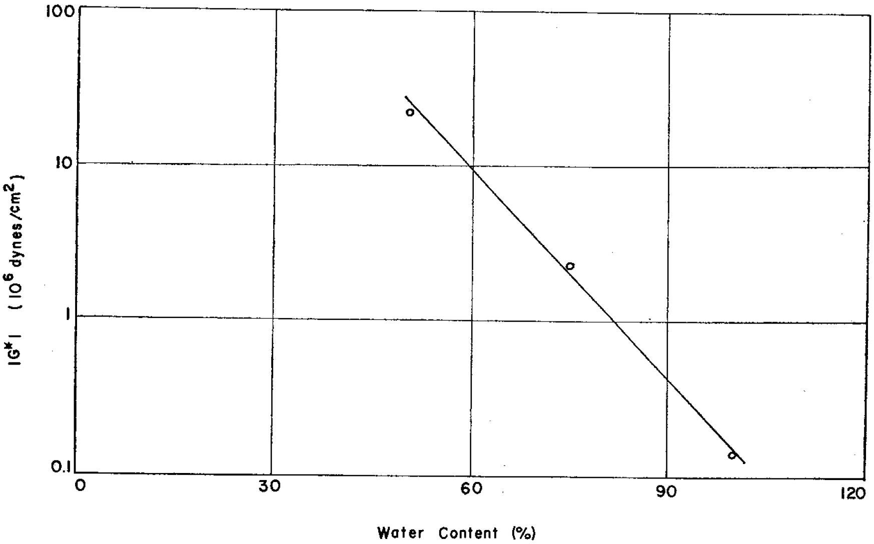

FIG. 7. Modulus versus water content for constant frequency.

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The effect of water content on consistency variations can be seen from the graph shown in Fig. 7; the magnitude of the complex shear modulus at a constant frequency of oscillation is plotted versus the water content for tests conducted at each of three nominal water contents. The logarithmic dependence of $|G^*|$ on w indicates that water content plays a major role in governing the mechanical response of clay–water suspensions and must be controlled or measured as precisely as possible if accurate experimental data are to be recorded. Krizek and Kondner (1964) have reported a similar relationship between the unconfined compressive strength and water content of a different soil. Although not necessarily explaining the entire variation in the magnitude of the complex modulus, changing the water content of a clay changes the relaxation times which govern the mechanical response. Similar behavior is observed when changing the temperature of a polymer.

CONCLUSIONS

Based on this exploratory study of the mechanical response characteristics of a water-washed kaolinite subjected to oscillatory shear strains by means of a Weissenberg Rheogoniometer with a cone-plate assembly, the following conclusions can be drawn for the ranges of variables tested:

1. The stress–strain behavior of the clay is definitely nonlinear, even for small values of strain.
2. The magnitude of the complex shear modulus is frequency-dependent and exhibits a dispersion region characteristic of many polymer systems.
3. The phase angle, which is a measure of energy dissipation characteristics of the clay, is frequency-dependent; a plot of phase angle versus frequency produces a bell-shaped curve which reaches a maximum in the neighborhood of where the complex shear modulus manifests its greatest frequency dependence.
4. The logarithm of the complex shear modulus varies approximately as the water content of the clay suspension; this indicates that water content is a very critical clay property and must be precisely controlled if accurate experimental results are to be obtained.

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