

The Temperature Dependence of Viscoelasticity of Allophane Colloid

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Synopsis

The study has been done to investigate the temperature dependence of the mechanical behaviour of allophane clay. The allophane colloid, dispersed in water by HCl and urea, was very thixotropic and showed a Bingham body at the concentration of suspension about more than 0.5 %. The yield value and the dynamic visco-elasticity of the suspension increased with the temperature rise, probably because the cluster of the strings of allophane particles were expanded to make a tighter structure. When greater stress than yield point was given, the behaviour of suspension followed a pattern similar to that of a plastic flow under the influence of a considerable amount of water released from the broken structure.

Introduction

The allophane mineral confines a greater amount of water in its microstructure under natural condition. However, it was considered that this clay mineral has a gel state so far as the structure is kept unbroken and it becomes a sol only when some forces from the outside facilitate to release the water by breaking the structure. If once broken, it is not expected that the mineral regain its original structure in a short time. The fact suggests that the fall of strength is produced by the loose packing of particle in amorphous structure and also by the slow regaining of the original structure for which electrostatic and hydrogen bond are responsible.

The behaviour of clay mineral colloid has been generally thought to be independent of the temperature change except that owing to solvent viscosity.¹⁾ But the consistency of the allophane suspension is very sensitive to the temperature change. The hardening of consistency of suspension is observed at a higher concentration. The study of hardening process of allophane suspension with the temperature rise is important to see the formation and behaviour of entropy elasticity.

Experimental

1. Sample of colloidal suspension of allophane

The allophane mineral was supplied by Kanto Loam in the field of Ibaraki Univ. and Utsunomiya Univ. The allophane clay was dispersed in water and its suspension was added by NaCl for the standardization of cation on the mineral, and urea for breaking down hydrogen bond between the particles,²⁾ and centrifuged to get colloidal particles which diameters are under 100 nm by high speed centrifuge (50,000G), then the suspension of colloidal particles were dialysed against dilute HCl for preparing the sample of colloidal suspension at a given pH's. The temperature dependence of viscoelastic properties and yield value of the suspension were measured by a coaxial cylindrical viscometer and a quartz crystal resonator. The deferrated sample treated after an ordinary method by dithionite-citrate system deferrated with sodium bicarbonate was taken as a control to the results of no-deferrated one.

2. Co-axial cylindrical viscometer

This viscometer is generally used for the measuring the consistency of the suspension under a stationary shearing forces. The sample of the colloidal suspension was put in a gap between internal and external cylinder to which drive force was applied. The internal cylinder (Ri) responses to the torque of external cylinder (Re) through the sample. The rate of shear V and shearing force P acting on the surface of internal cylinder are calculated as next.

$$V = \frac{2 \Omega_e}{1 - (R_i/R_e)^2} , \quad P = \frac{M}{2\pi R_i^2 \ell} \quad \dots \dots \dots (1)$$

where Ω_e : angular velocity of external cylinder, M: torque, ℓ : length of cylinder in the sample, η : viscosity is defined by the ratio of P/V. The gradual increase of external cylindrical angular velocity ($d\Omega_e/dt$) was adjusted to within the no-effect range ($\leq 3.3 \times 10^{-3}$ rpm/s) to get stationary values of P and V. Yield value θ was obtained by the extrapolation of final consistency curve (a coordinates of P and V) as shown in Fig. 1. The measurement by this apparatus will be valied to extend until the range of nonlinear behaviour.

3. Forced oscillation rheometer

The coaxial cylindrical viscometer was converted to a oscillation rheometer with the same cylinders by switching gears. When the forced sin-

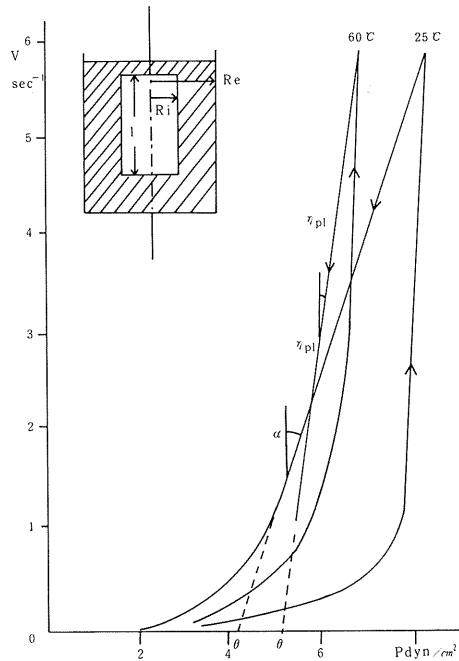


Fig. 1 Consistency curves of Allophane colloid suspension (deferrated, pH 1.3, $\phi = 8.16$ cc/g)
 θ : yield value by extrapolation of down curve
 η_{pl} : plastic viscosity ($\cot\alpha$)

uous oscillation is applied to the sample, through which a response of the sinuous oscillation with a smaller amplitude and a retarded phase are given. From these difference between applied oscillation and its response the dynamic elasticity and viscosity are calculated. The analysis by this apparatus is based on the assumption that the sample behaves as a Kelvin body.

$$I\ddot{x} + R\dot{x} + Kx = K(X - x) \quad \dots\dots\dots (2)$$

- Where I : inertia of internal cylinder
- x : response displacement by internal cylinder
- X : forced displacement by external cylinder
- R : coefficient of rigidity, K : coefficient of viscosity
- k : rigidity of torsion wire

Dynamic viscosity η and rigidity r given by the oscillation equation reads as next.

$$\eta = \frac{R}{4\pi\ell} (1/Ri^2 - 1/Re^2) \quad \dots\dots\dots (3)$$

$$r = \frac{K}{4\pi\ell} (1/Ri^2 - 1/Re^2) \quad \dots\dots\dots (4)$$

4. Torsional crystal resonator

The measurement of viscoelastic properties of the suspension was carried out by the torsional quartz crystal resonator method as experimented by Nakamura and Amari.³⁾ The principle of the measurement is the same to the oscillation rheometer except the range of oscillation frequency. That is, the sample behaves as a Kelvin body to which a small deformation generated by the Piezo effect was applied. Dynamic viscosity η' and dynamic rigidity and component of complex (γ' and γ'') are given by the next formulae.

$$\eta' = 2 R_M X_M / \rho w \quad \dots \dots \dots (5)$$

$$\gamma' = (R_M^2 - K_M^2) \rho \quad \dots \dots \dots (6)$$

$$\gamma'' = 2 R_M X_M / \rho \quad \dots \dots \dots (7)$$

$$R_M = (\pi f \rho \eta_S)^{1/2} + [(R_\rho - R_S) / K_1] \quad \dots \dots \dots (8)$$

$$X_M = (\pi f \rho \eta_S)^{1/2} + [(f_S - f_\rho) / K_2] \quad \dots \dots \dots (9)$$

Where f = frequency of applied shear stress (78 KHZ, ρ : density of solution, η_S : viscosity of solvent, R_S and R_ρ : electrical resistance of crystal in solvent and suspension. K_1 and K_2 : electromechanical constant calculated from the dimensions and piezoelectric constant of the crystal. f_S , f_ρ : resonant frequency of crystal in solvent and suspension, w : angular frequency of shear stress.

5. Temperature control

The temperature control for the apparatus mentioned above was given by the water circulation with heat regulator. The measurement was done at the interval of 10 °C from 20 °C to 70 °C. The evaporation of water from the suspension at the high temperature is corrected by getting average the difference between the initial and final concentration of the sample during the measurement. This difference was, in many cases, negligible.

Results

The results obtained by the three different types of measurement, which are mentioned above, showed a same tendency of visco-elastical change with temperature. Though the measurement by the coaxial cylindrical viscometer is statical method and that by the other two are dynamic ones.

The consistency curves of the deferrated samples show less thixotropic and smaller viscosity than that of no-deferrated ones at the same concentration of the suspension. The sample of low concentration less than about 0.5 % in volume concentration has low yield value and shows a Newtonian flow, but that of high concentration more than about 1 % does the typical Bingham flow. As shown in Fig. 2-1 yield value and plastic viscosity decrease with temperature rise at lower concentration of the sample. The higher the concentration becomes, the more yield value increases while plastic viscosity decreases (Fig. 2-2). The change of temperature from 30 °C to 60 °C gave rise to yield value from 20 to 35 dyn/cm² and on the other hand, plastic viscosity goes down from 50 to 30 poise respectively. The yield value and plastic viscosity of both the deferrated and no-deferrated sample at pH 5.6 and concentration of 1.63 decreased with temperature rise. Here thixotropic sensitivity was measured by the area of hysteresis loop in consistency curve.

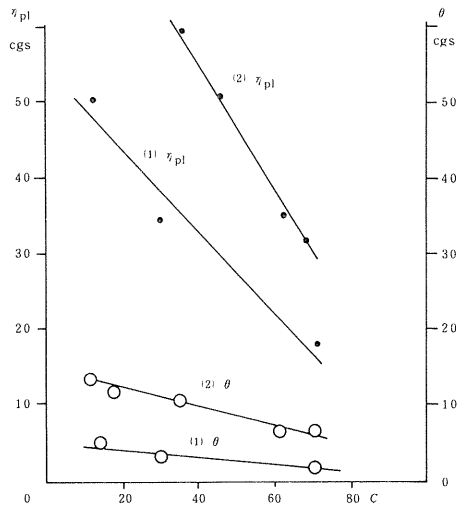


Fig. 2-1 Simultaneous decrease of plastic viscosity (η_{pl}) and yield value (θ) with temperature rise

- (1) Allophane (no deferrated), pH 7.5 , $\phi = 0.78$
- (2) Allophane (no deferrated), pH 3.5 , $\phi = 0.71$

The dynamic viscosity and rigidity by the forced oscillation method are given in Fig. 3. The viscosity and rigidity value increase with temperature up to at least 70°C. The period of oscillation T was varied between T = 1.3 sec to 146 sec. The viscosity change at low concentration with temperature is negligible but at high concentration, viscosity also rigidity decreased up

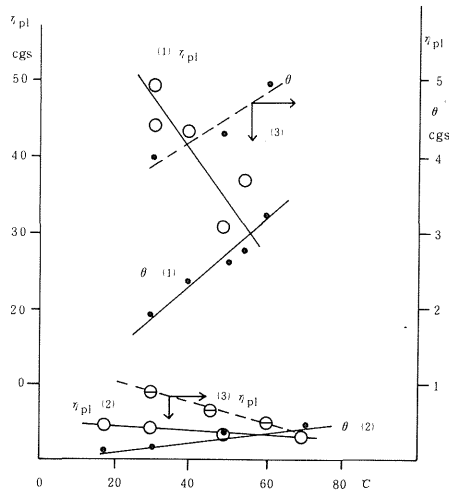


Fig. 2-2 Decrease of plastic η_{pl} and increase of yield value θ with temperature
 (1) Allophane (no deferrated), pH 3.9, $\phi = 2.49$
 (2) Allophane (no deferrated), pH 3.1, $\phi = 1.43$
 (3) Allophane (deferrated), pH 1.3 $\phi = 8.16$

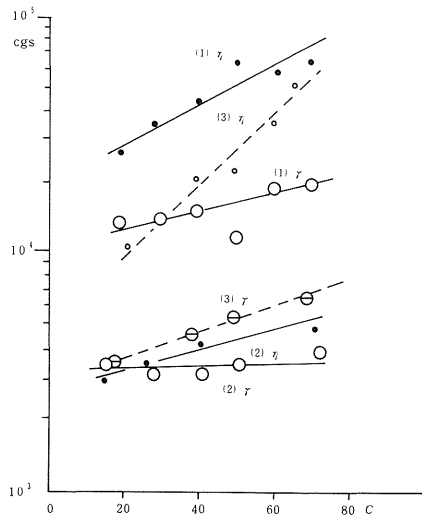


Fig. 3 Dynamic visco-elasticity by forced oscillation method
 γ : rigidity modulus (dyn/cm^2) at $T = 13$ sec
 η : viscosity (poise) at $T = 13$ sec
 (1) Allophane(no deferrated) pH 3.7, $\phi = 2.55$
 (2) Allophane(no deferrated) pH 3.9, $\phi = 2.50$
 (3) Allophane (deferrated), pH 5.6, $\phi = 1.8$

to 20 % when it increases from 30 °C to 60 °C.

The viscosity and rigidity obtained by the torsional quartz crystal rhe-

ometer are given in Fig. 4. This measurement takes advantage of getting the dynamic viscosity and rigidity in a small distortion of material without any destruction. As is shown in Fig. 4, the viscosity of the sample increased while rigidity decreased as well as the deferrated one.

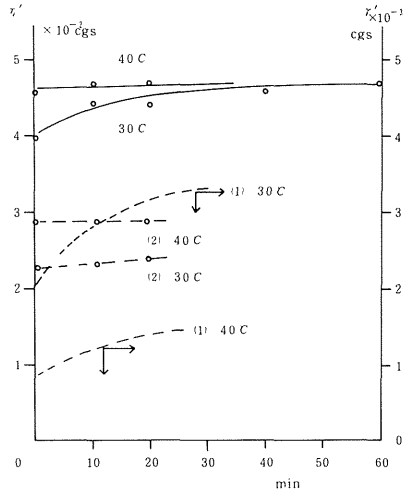


Fig. 4 First prime of viscosity (η') and rigidity (γ') by quartz resonator
 (1) No deferrated sample (pH 3.9, 2.5 %)
 (2) Deferrated sample (pH 5.6, 1.8 %)

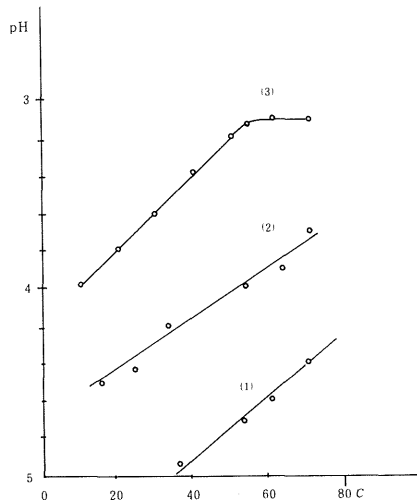


Fig. 5 pH change of allophane suspension with temperature (no - deferrated)
 (1) $\phi = 0.95$, (2) $\phi = 1.28$, (3) $\phi = 2.49$

Discussion

1. Increase of visco elasticity and plastic yield with temperature rise and

H ion concentration rise

In some of allophane colloid suspension, the increase of dynamic viscosity and rigidity and yield value can be observed with the temperature rise, while true solution often shows the decrease of viscosity. The results obtained by the cylindrical viscometer using the colloid deferrated and the no-deferrated sample in which the particles had an radius of less than 100 nm, at pH 3-3.3 show that the yield value increase with temperature, though the deferrated sample of allophane colloidal suspension has a less sensitivity than the no-deferrated one. No marked increase of viscosity and yield value can be seen at pH more than 6. Yield value and the results obtained by the forced oscillation method corresponds with the increasing tendency of visco-elastic properties. These results suggest that the colloidal particles are not single ones but they make clusters or ribbons. The EM photograph may also show this structure (Photo 1, 2). A cluster consisting of the allophane particles has its domain, which is activated by the temperature rise. However, the clusters will make a sterical hindrance to increase the freedom of their movement by the overlapping of domains.

The relation between temperature and pH of allophane colloid suspension is presenting itself that the temperature rise builds a more resilient structure of the particles as well as H ion does. The structural building in the suspension has a close relationship with the interaction forces, the repulsive force of electrical double layers where the concentration of H ion has a big influence on the increase of visco-elasticity with the temperature rise.

2. The change of pH by temperature

As shown in Fig. 5, the decrease of pH value with the temperature rise will give the higher electrostatic repulsive pressure that predominates the van der Waals attractive force at distance more than several nm. Temperature change will produce the same effect to pH change on the cluster of the strings of particles in colloidal solution.

3. Yield value and dynamic visco-elasticity

Yield value obtained by cylindrical viscometer is a transition point between solid and liquid, above which a plastic flow occurs. Therefore, when applied force is small enough to fall within visco-elastic region, that is, deformation given by the forced oscillation method is so small, the structure will be kept unbroken. A good coincidence of increase between yield value and dynamic viscosity and rigidity can be seen with temperature rise, though plastic viscosity is not the case. The phenomena that the plas-

tic viscosity decreases while yield value increases at high concentration could be explained as the water confined in the structure is freed to behave like a lubricant around the kinetic units under shearing force.

4. Difference between no-deferrated and deferrated sample in rheological behaviour

A contrast was made between the results of no-deferrated sample and that of deferrated one because Fe and Al ion-complex in allophane are supposed to play a role to build the structure of the suspension. Viscosity, yield value and dynamic properties of deferrated allophane colloid are smaller than that of no-deferrated. Temperature dependency, which is discernible from consistency curve, make fundamentally no marked difference from no-deferrated one except the deferrated sample is less thixotropic with the temperature and H ion rise.

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Summary

The allophane colloid suspension is supposed to build the cluster made of the strings of allophane particles. This structure is developed with the temperature and H ion increase. The development of solid structure in suspension can be seen by the increase of yield value and dynamic viscosity and rigidity. When the concentration of the colloid is less than about 1%, the marked structural building could not be expected, because of less chance of overlap with the clusters. The behaviour of allophane colloid in water solvent is supposed to have something like that of carbohydrate solution sensitive to temperature³, and shows entropy elasticity.

References

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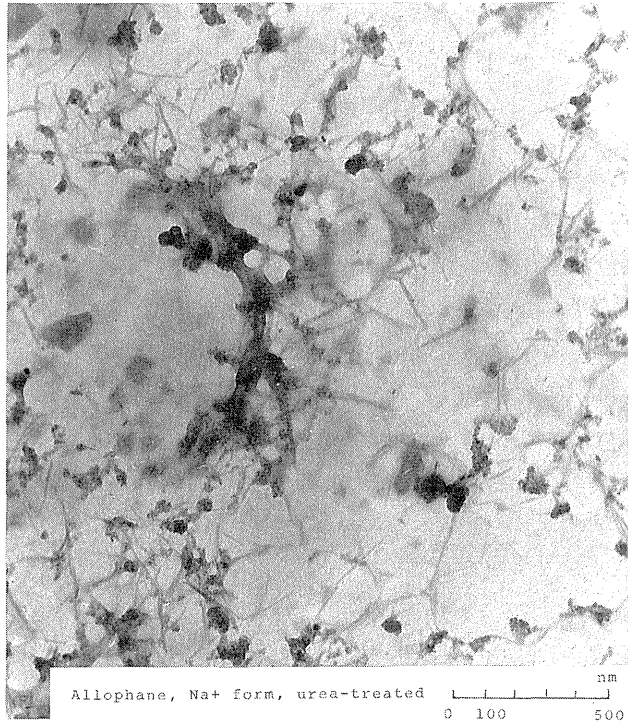


Photo 1

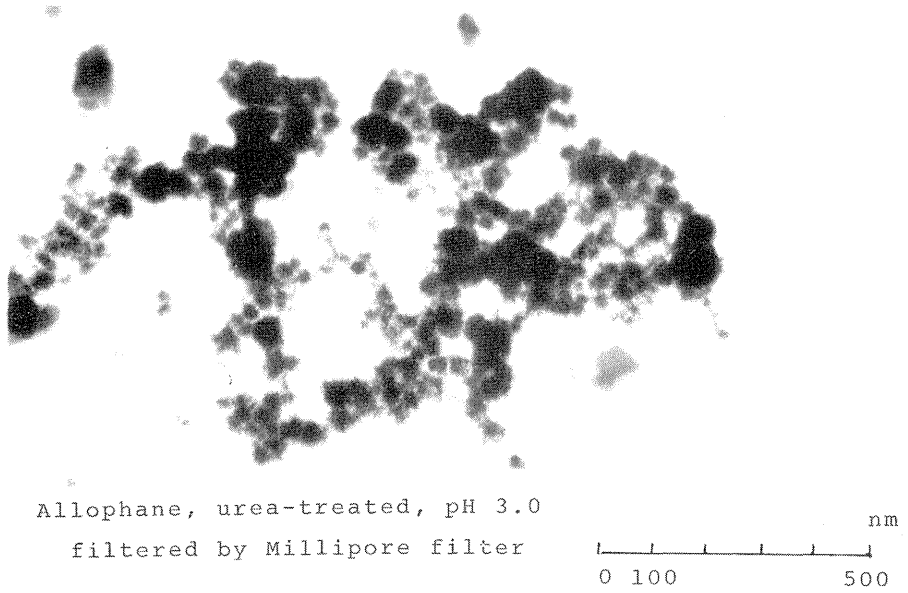


Photo 2

アロフェンコロイドにおける粘弾性の温度依存性

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粘弾性挙動およびコンシステンシー特性からアロフェンサスペンションには発達した網目構造があることがわかった。この構造形成はサスペンションのpHが低いほど、また濃度が高いほど著しい。したがって粘弾性挙動は網目構造の発達したものほど固体的性質が強いビンガム体と考えられる。

一方アロフェン・コロイド・サスペンションは温度上昇によってpHの低下を示す。この結果、温度上昇によってサスペンションの構造は発達する。脱鉄処理したものと脱鉄処理しないアロフェンのサスペンションには温度変化によるそれらのレオロジー特性には基本的な差は見られなかった。サスペンション濃度が1%以下の低濃度では20℃から70℃までの温度上昇によって粘弾性、

降伏値の上昇は見られず、むしろ低下するが、1%以上では粘弾性および降伏値の上昇を示す。但し塑性粘性はいずれの場合も低下する。これらの現象は温度上昇によってアロフェン粒子のクラスター構造が発達し、からみあいが増加し、網目構造が強固になるが、降伏値を越えると構造は破壊され、構造内に拘束されていた水の自由化によってサスペンションの流動化が容易となり塑性粘性も低下すると理解される。

このようなアロフェン・コロイド・サスペンションはエントロピー的粘弾性を示し、そのレオロジー特性は炭水化物高分子と同じような鎖状分子の模型によって説明できる。

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