Modeling the Time-Dependent Rheological Behavior of Clays Used in Fabrication of Ceramic

L. Hammadi, N. Boudjenane, R. Houdjedje, R. Reffis, M. Belhadri

Abstract—In this study, we investigated the thixotropic behavior of two clays used in fabrication of ceramic. The structural kinetic model (SKM) was used to characterize the thixotropic behavior of two different kinds of clays used in fabrication of ceramic. The SKM postulates that the change in the rheological behavior is associated with shear-induced breakdown of the internal structure of the clays. This model for the structure decay with time at constant shear rate assumes nth order kinetics for the decay of the material structure with a rate constant.

Keywords—Ceramic, clays, structural kinetic model, thixotropy, viscosity.

I. INTRODUCTION

THE clays are commonly used in many industrial applications, especially in the manufacture of ceramics, drug manufacturing, the treatment of polluted water, such as the adsorption of toxicorganic compounds [1], [2], paper, cement, pharmaceuticals [3] and stabilization of emulsions of oil-water [4]. The study of the rheological properties of clays is important in industrial applications such as in a ceramics factory building in the determined purpose of the good operating conditions of the pumps during the realization of ceramics operation. The rheological properties of clays depend on different factors, including the type and concentration of clays [5], the size of the solid particles, the temperature [6] and pH of the clay [7]. Many clays exhibit the thixotropic behavior, in which, the apparent viscosity of material decreases with time of shearing at constant shear rate. Although many researchers have investigated the time-dependent rheological behavior of materials, in general, the thixotropic characteristics of many types of clay are not so carefully studied.

The objective of the present study is to investigate the effect of mass concentration and shear rate on thixotropic behavior of two different clays used in fabrication of ceramic.

II. THEORETICAL BACKGROUND

The thixotropic behavior of clays can be modeled using the structural kinetic model (SKM), which has been successfully employed for concentrated suspensions of minerals [8], [9]. The kinetic structural approach assumes that the change in the rheological behavior is associated with shear-induced breakdown of the internal structure in the clays. The analogy with chemical reactions can be used to express the structural breakdown process in the following form:

$$\text{Structured state} \rightarrow \text{Non} - \text{structured state} \qquad (1)$$

The rate of breakdown of the clays structure during the shearing process depends on the kinetics of the above reaction. The model assumes that the structure of food products breaks down irreversibly under the effect of shear without significant buildup. The structured state of the thixotropic structure at any time t and under an applied shear rate, $\dot{\gamma}$, can be represented by a dimensional structural parameter:

$$\lambda = \lambda(t, \dot{\gamma}) \qquad (2)$$

which $\lambda(t, \dot{\gamma})$ is defined as:

$$\lambda(t, \dot{\gamma}) = \frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} \qquad (3)$$

where η_0 is the initial apparent viscosity at t=0 (structured state), and η_∞ is the equilibrium apparent viscosity as $t \rightarrow \infty$ (non-structured state). Note that, both η_0 and η_∞ are functions of the applied shear rate only. The dimensionless structural parameter, λ, is subjected to the following conditions: initially, at the fully structured state, $t = 0$; $\lambda = \lambda_0$, and at non-structured state, $t \rightarrow \infty$; $\lambda = \lambda_\infty$. The rate of structural breakdown can be expressed as:

$$-\frac{d\lambda}{dt} = k(\lambda - \lambda_\infty)^n \qquad (4)$$

where $k = k(\dot{\gamma})$ is the rate constant and n is the order of the structure breakdown reaction. At a constant applied shear rate, integration of (4) from t=0 to t yields:

$$(\lambda - \lambda_\infty)^{1-n} = (n-1)kt + (\lambda_0 - \lambda_\infty)^{1-n} \qquad (5)$$

Substituting (3) into (5) yields for a constant shear rate:

$$\left(\frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty}\right)^{1-n} = (n-1)kt + 1 \qquad (6)$$

The form of (6) is valid only under the constant shear rate conditions.

III. MATERIALS AND METHODS

A. Materials

A clay (Clay of Nedroma) and a slip of ceramic were recovered from the new ceramic tiles Company Remich,

L. Hammadi, N.Boudjenane, R. Houdjedje, R. Reffis, and M. Belhadri are with the Laboratory of Rheology, Transport and Treatment of the Complex Fluids, University of Science and Technology, Mohamed Boudiaf, B.P. 1505, El M'Naour, Oran 31000, Algeria (e-mail: hammadi7280@yahoo.f).

World Academy of Science, Engineering and Technology
International Journal of Physical and Mathematical Sciences
Vol:9, No:7, 2015

Algeria a form of powder. The clay of Nedroma in powder form is heated in an oven for 24 hours at 40 ° C to dehydrate, then crushed and passed to the 80μm sieve. Follows the clay powder is mixed at the desired consultation (30% and 60%), in distilled water. To ensure homogenization of clays; the resulting suspensions were stirred magnetically continuously for a minimum of 24 hours. Note the slurry is mixed in distilled water without sieving

B. Experimental Set Up

The rheological measurements were performed by using a torque controlled rheometer (RS600 from Thermo-Fischer), equipped with a cone-plate geometry (diameter: 60 mm; angle: 2 degrees; gap: 105 μm). It has a Peltier temperature control system that allows having a very quick response to any change in temperature. In order to prevent changes in composition during measurements due to water evaporation, a solvent trap was placed around the measuring device.

C. Experimental Methods

After a rest time of 180s, the samples were sheared during 180s at constant shear rates (250s^{-1} and 100s^{-1}) at a constant temperature of 20°C. In order to prevent any irreversible evolution of the clays, a new fresh sample was used for each concentration.

IV. RESULTS AND DISCUSSION

These samples were sheared at constant shear rate of 250 s^{-1} and 100 s^{-1} for 180 s. Figs. 1 and 2 shows the apparent viscosity of slip and clays of Nedroma as a function of shearing time fitted with the SKM. At a constant shear rate, the apparent viscosity of both samples decreases rapidly with time within the first 60 s of shearing and reaches a constant value corresponding to an equilibrium state after approximately 80 s. As can be shown in Figs. 1 and 2, the rate and extent of viscosity reduction of clays samples depend on solid content. This dependence can be quantified by determining the parameters k, η_0 and η_∞.
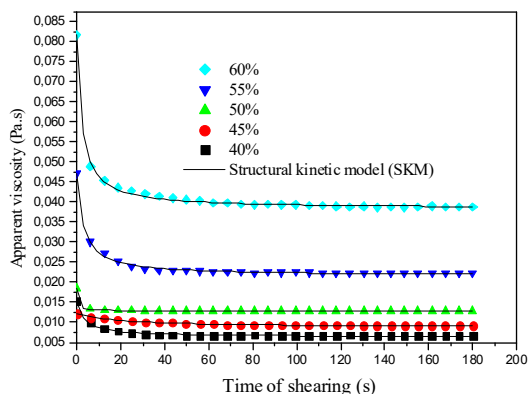

Fig. 1 Effect of mass concentration on the thixotropic behavior of slip at constant shear rate $\dot{\gamma} = 250 \ s^{-1}$

Figs. 3 and 4 show the initial apparent viscosity and equilibrium apparent viscosity as a function of mass concentration of clays. Fig. 5 shows the degree of thixotropy k as a function of mass concentration. This result suggests that the rate and the extent of breakdown of the network structure in clays under shearing increased with increasing the solid content. A stronger and much denser structure can be expected as a result of more clay–clay interactions at higher concentration levels.
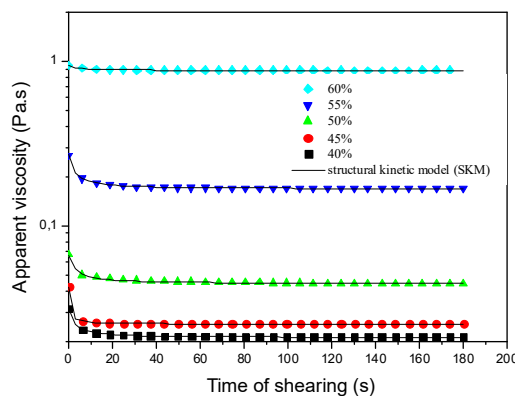

Fig. 2 Effect of mass concentration on the thixotropic behavior of clay of Nedroma at constant shear rate $\dot{\gamma} = 100 \ s^{-1}$
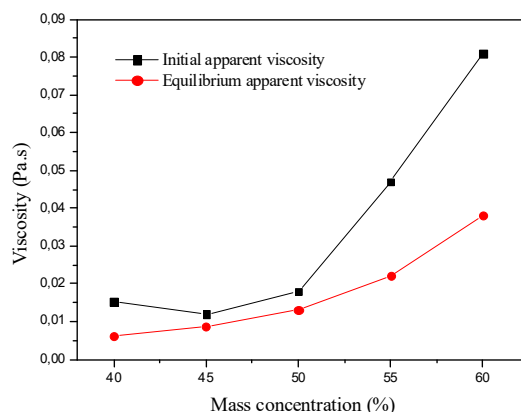

Fig. 3 Effect of mass concentration on initial apparent viscosity and equilibrium apparent viscosity of slip at constant shear rate $\dot{\gamma} = 250 \ s^{-1}$
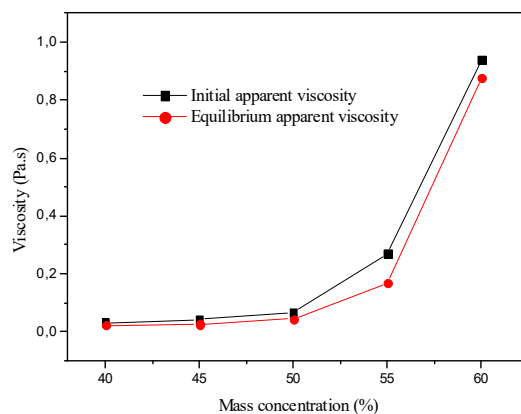

Fig. 4 Effect of mass concentration on initial apparent viscosity and equilibrium apparent viscosity of clay of Nedroma at constant shear rate $\dot{\gamma} = 100 \ s^{-1}$

World Academy of Science, Engineering and Technology
International Journal of Physical and Mathematical Sciences
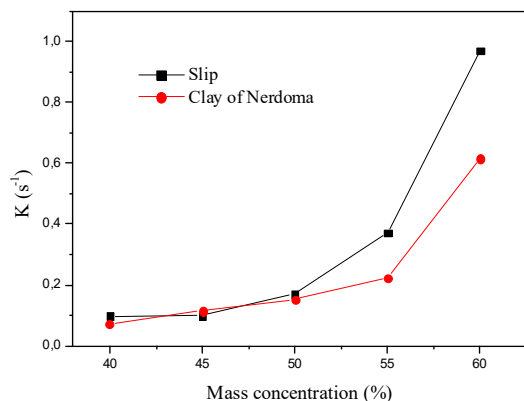Vol:9, No:7, 2015

Fig. 5 Effect of mass concentration on the degree of thixotropy of slip and clay of Nedroma at constant shear rate

Fig. 6 shows structural parameter as a function of mass concentration of slip. The structural parameter of both samples decreases rapidly with time within the first 60 s of shearing and reaches a constant value corresponding to an equilibrium state after approximately 80 s. At high concentration of slip (55% and 60), the applied shear rate of 250s⁻¹ is not sufficient to break weak particle-to-particle bonds, and the suspensions is fully developed network or structure.
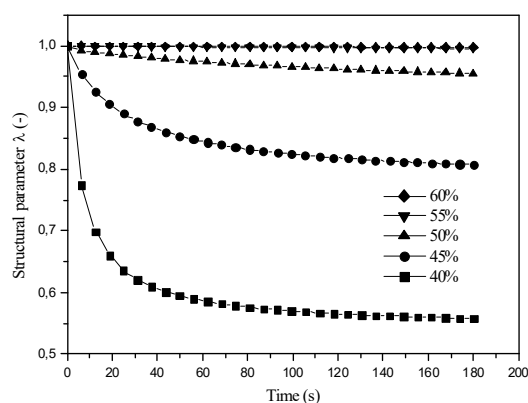

Fig. 6 Effect of mass concentration on structural parameter of slip

Fig. 7 shows the apparent viscosity of based slip (60%wt) evolution as a function of time for different steady shear rate varying from 100 to 300 s⁻¹fitted with the structural kinetic model (SKM). At a constant shear rate, the apparent viscosity decreases rapidly with time in the initial stage which was then followed by a constant at plateau region. On average after a shearing period of 100 s, no significant changes in viscosity can be observed. This indicates that the slip is at an equilibrium state. The results clearly demonstrate that the apparent viscosity can be drastically reduced from the initial unperturbed (structured) state to an equilibrium (de-structured) state with the application of shear. This indicates that the slip samples are highly sheared thinning in nature.

Figs. 8 shows the equilibrium structural parameter $\lambda_\infty = \frac{\eta_\infty}{\eta_0}$ of slip (60%) and clay of Nedroma (45%) as a function of shear rate. This result suggests that the rate and the extent of

breakdown of the network structure in clays under shearing increased with increasing the shear rate. A stronger and much denser gel structure can be expected as a result of more particles –particles interactions at higher shear rate levels.
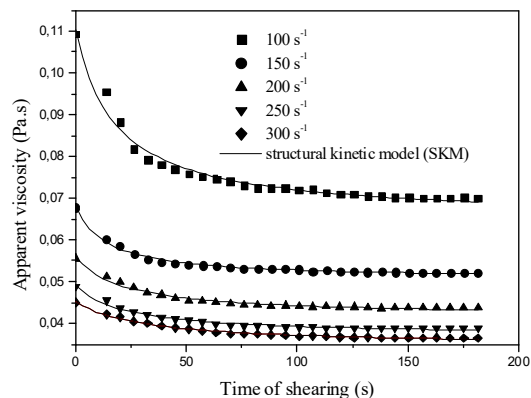

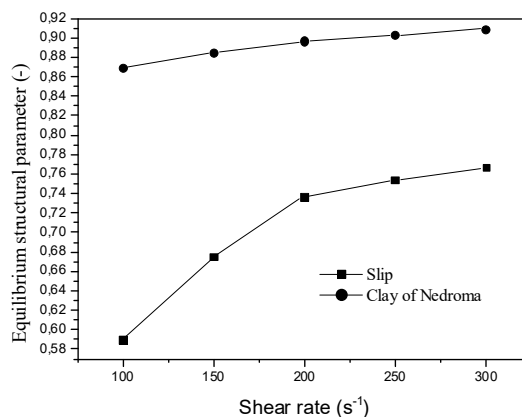Fig. 7 Effect of shear rate on the thixotropic behavior of slip (mass concentration 60%)

Fig. 8 Effect of shear rate on equilibrium structural parameter $\lambda_\infty = \frac{\eta_\infty}{\eta_0}$ of slip (60%) and clay of Nedroma (45%)

TABLE I
UNITS FOR RHEOLOGICAL PROPERTIES

Symbol	Quantity	Conversion from Gaussian and CGS EMU to SI [a]
η_0	Initial	Pa.s
η_∞	Equilibrium apparent viscosity	Pa.s
η	apparent viscosity	Pa.s
$\dot{\gamma}$	shear rate	s⁻¹
λ	Dimensional structural parameter	-
t	Time	s
k	The degree of thixotropy	s⁻¹

V. CONCLUSION

The time-dependent flow behavior of two clays used in fabrication of ceramic possessing thixotropic characteristics were analyzed and modeled using the SKM. The SKM postulates that the change in the rheological behavior is associated with shear-induced breakdown of the internal structure of the clays. The rate of structure breakdown (degree

World Academy of Science, Engineering and Technology
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of thixotropy) increases with increasing both mass concentrations. On the other hand, the amount of structure breakdown (extent of thixotropy) and equilibrium structural parameter increases with increasing mass concentration and shear rate.

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