

*Dedicated to the memory of
Professor Ecaterina Ciorănescu-Nenitzescu (1909–2000)*

RHEOLOGICAL BEHAVIOR OF SMECTITE AQUEOUS DISPERSIONS

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The rheological properties of two smectite - Laponite RD and Gelwhite H - aqueous dispersions with the concentration of 2.5% were studied at 20°C. The viscoelastic moduli showed that Laponite RD dispersion has the solid-like properties and Gelwhite H dispersion is in liquid state at the concentration of 2.5%. The flow tests revealed that Laponite RD dispersion presents a pseudoplastic flow with yield stress whereas Gelwhite H dispersion has a pseudoplastic behavior without yield stress. The presence of a typical hysteresis loop demonstrated the anti-thixotropic nature of Laponite RD dispersion. The apparent viscosity of Laponite RD dispersion higher than the one of Gelwhite H dispersion may be attributed to the high organization degree of Laponite RD particles in water.

INTRODUCTION

Clay minerals are used as additives which improve the performances of a wide range of industrial and consumer products making them more valuable to their users. They are used mainly as rheology modifiers and may be added to the formulation of many waterborne products such as surface coatings, household cleaners and personal care products (toothpaste, cosmetics, depilatory creams, exfoliant cleaners, antiperspirants, shampoos, etc.).¹ The smectite clays belong to the structural family known as the 2:1 phyllosilicates and they have a crystal structure consisting of nanometer thick layers of aluminum octahedron sheet between two silicon tetrahedron sheets.²⁻⁴ The unique characteristic of smectite is its ability to swell in water and it is generally accepted that most clay particles are platelets with a negative face charge and a positive edge charge as a function of pH conditions. The smectite dispersions can exhibit different physical states: sol, liquid, repulsive or attractive glasses, stable gel and flocculation state (unstable gel).⁵⁻⁸ Colloidal gels and glasses are solid states of condensed matter with static elasticity. The

process of liquid-glass transition is called “aging” and that of sol-gel transition is called “gelation”. The transitions between states can be induced by changing the concentration of clay, pH and/or the temperature or inducing the interparticle interactions by adding the salts or polymers.⁹⁻¹³

Rheological measurements of clay dispersion can provide useful information concerning the interactions between clay particles and the physical state of the studied sample. The knowledge of the rheological parameters of clay dispersions is very important for development of flow models for engineering applications, formulation of commercial production, design and process evaluation, quality control and storage stability.

The aim of this study was to investigate the flow behavior of two smectites (Laponite RD and Gelwhite H) aqueous dispersions at 20°C.

RESULTS AND DISCUSSION

For the present study, two aqueous dispersions of Laponite RD and Gelwhite H having the con-

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centration of 2.5% were prepared. Laponite RD is a synthetic hectorite type clay and Gelwhite H is a highly purified white bentonite in powder form. The platelets of Laponite RD and Gelwhite H have a well-defined thickness of 1 nm and a diameter of 25 nm and approx. 300 nm, respectively.

The rheological behavior of the clay dispersions was analyzed by oscillatory and shear measurements at 20°C. The oscillatory experiments were performed in the linear viscoelastic regime, where

the storage and loss modulus are independent of the applied stress. In Figure 1 are shown the evolutions of the viscoelastic moduli (G' and G'') as a function of frequency (ω) for Laponite RD and Gelwhite H aqueous dispersions at 20°C (shear stress was 1 Pa). G' (storage or elastic modulus) and G'' (loss or viscous modulus) give information on energy storage and energy dissipation during the flow, respectively.

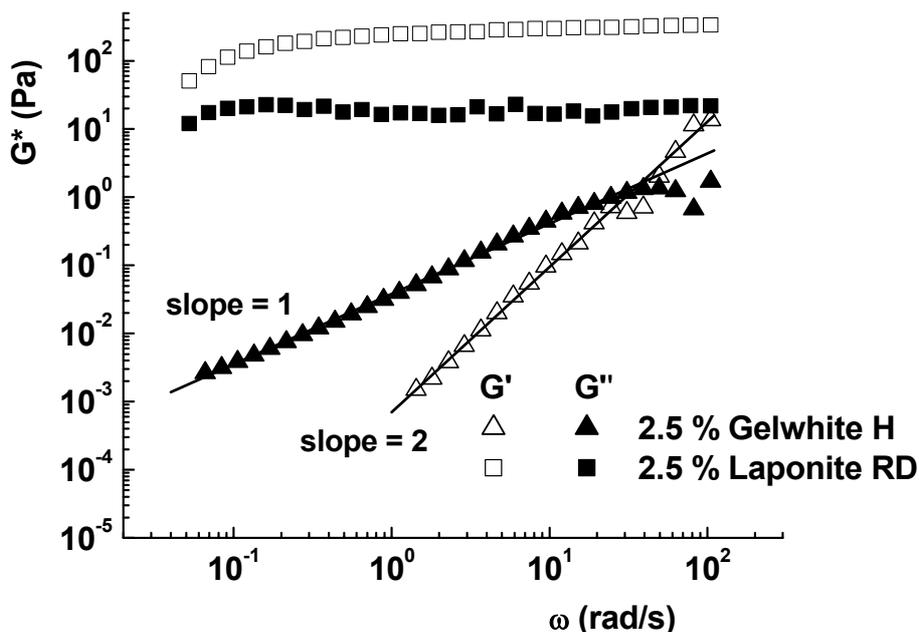


Fig. 1 – Evolution of viscoelastic moduli as a function of frequency for studied clay dispersions.

The moduli variation with the frequency for Gelwhite H dispersion is typically for viscoelastic Maxwellian fluids, that is, G'' scales with ω^1 and G' with ω^2 . Laponite RD dispersion has the solid-like properties (G' higher than G'') by comparison with Gelwhite H dispersion that shows more viscous than elastic response. The viscoelastic parameters of sample with Gelwhite H are lower than those corresponding to sample containing Laponite RD in the investigated frequency range. According to the phase diagram,^{9,10} the 2.5% Laponite RD aqueous dispersion at low ionic strength and room temperature forms a repulsive glass. In this state the long-range electrostatic repulsions between Laponite RD particles dominate.

The flow behavior of any system is described in terms of the relationship between the shear stress and the shear rate. The shear rate is defined as the change of shear strain per unit time, and the shear stress as the tangential force applied per unit area. The ratio of shear stress to shear rate is called ap-

parent viscosity that is a measure of the resistance to flow of the fluid (eq. (1)).

$$\eta = \frac{\tau}{\dot{\gamma}} \quad (1)$$

where τ is the shear stress and $\dot{\gamma}$ represents the shear rate.

The investigated clay dispersions exhibit an apparent viscosity (η) that decreases with increasing shear rate up to 500 s^{-1} due to the destruction of the dispersion microstructure at high shear (Figure 2). The higher viscosity of Laponite RD dispersion is as a consequence of more stronger electrostatic interactions between clay particles.

The flow curves for the studied dispersions are shown in Figure 3. Laponite RD aqueous dispersion shows pseudoplastic (shear thinning) flow behavior having a yield stress defined as the stress above which the material flows like a viscous fluid.

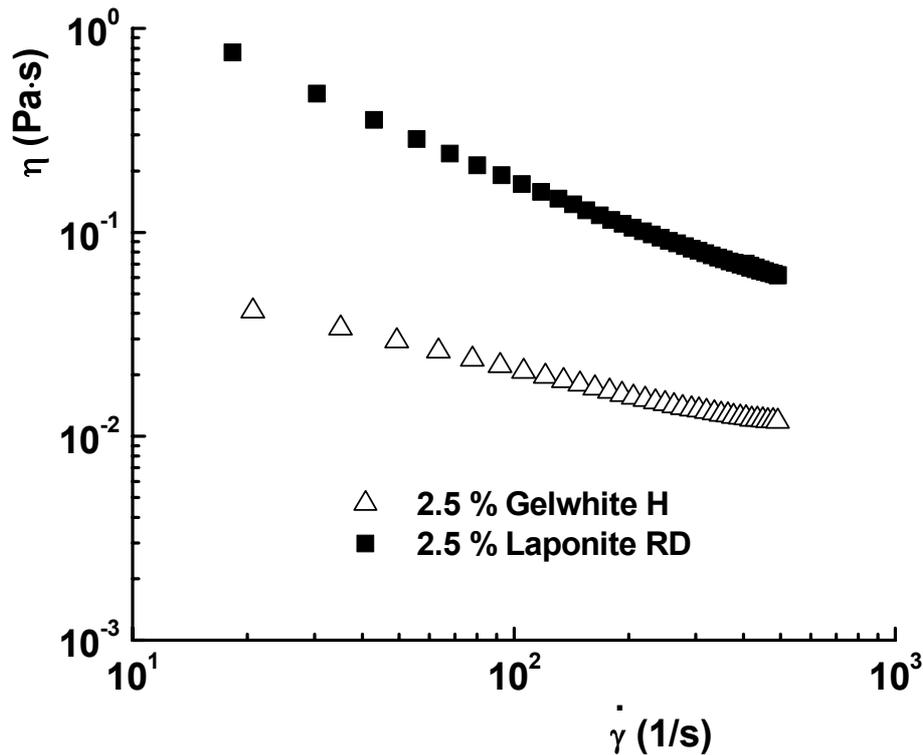


Fig. 2 – Steady shear viscosity versus shear rate for the clay dispersions at 20°C.

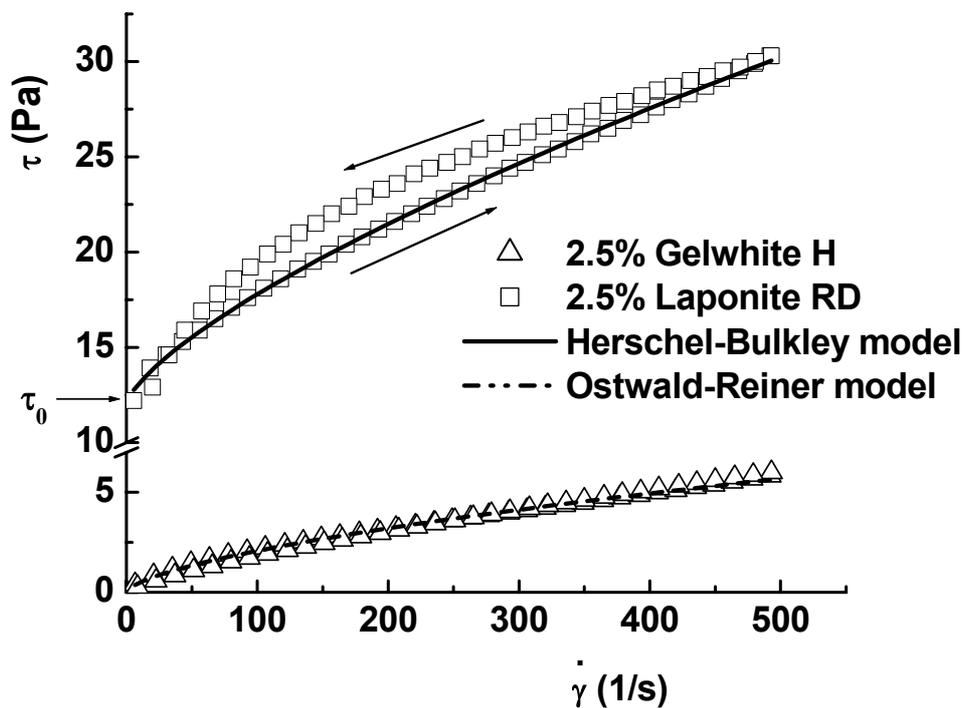


Fig. 3 – Upward and downward flow curves for of clay aqueous dispersions.

The flow curve of Laponite RD dispersion can be described very well using the Herschel-Bulkley equation:¹⁴

$$\tau = \tau_0 + K \cdot \dot{\gamma}^n \quad (2)$$

where τ_0 is the yield stress, K represents the consistency factor and n is a parameter that characterizes the pseudoplasticity of the system.

Generally, the yield stress is determined as the intercept of the flow curve at zero shear rate (Figure

3). The value obtained using this method can be strongly influenced by the shear rates range used and by the rheological model selected to do the extrapolation. The knowledge of the yield stress of this dispersion is very important for its use in industrial applications.

$$\tau = (12.027 \pm 0.133) + (0.213 \pm 0.016) \cdot \dot{\gamma}^{0.716 \pm 0.011} \quad (3)$$

Gelwhite H dispersion exhibits pseudoplastic flow behavior without yield stress (Figure 3). The flow curve of this dispersion can be described by Ostwald-Reiner power law equation:¹⁵

$$\tau = K \cdot \dot{\gamma}^n \quad (4)$$

where K is a measure of consistency of the system and n is the degree of non-Newtonian behavior. Based on the experimental data, the following power law was obtained:

$$\tau = (0.108 \pm 0.003) \cdot \dot{\gamma}^{0.634 \pm 0.007} \quad (5)$$

According to eq. (3), Laponite RD dispersion starts to flow above 12.027±0.133 Pa. Both clay dispersions have shear thinning characteristics ($n < 1$) more accentuated for Laponite RD dispersion. In addition, Laponite RD dispersion shows a higher consistency which would indicate the more stronger association between clay particles.

The thixotropy is defined as the continuous decrease of viscosity with time when flow is applied to a sample that has been previously at rest and the subsequent recovery of viscosity in time when the flow is discontinued.¹⁶ The shearing determines a gradual break-down in structure over time.

Anti-thixotropy or negative-thixotropy is the opposite phenomenon from thixotropy. In this case the flow causes an increase in viscosity under constant shear stress or shear rate followed by a gradual recovery when the stress or shear rate is removed. In some dispersions, the viscosity increases with time at low shear rates after shearing at high shear rates.¹⁷ Although many authors often name this phenomenon as anti-thixotropy, this is not the real “opposite of thixotropy” and this behavior was called rheopexy.

Thixotropic and anti-thixotropic behaviors are indicated by a hysteresis loop between the flow curves at increasing and decreasing rates.¹⁸ In or-

The Herschel-Bulkley model applied to the experimental data obtained for Laponite RD dispersion gives the following relation:

der to study the hysteresis of the flow curves, cyclic tests were performed by increasing the shear rate up to a maximum value (500 s⁻¹) followed by its decrease. The anti-thixotropic behavior of Laponite RD dispersion was confirmed by a pronounced hysteresis loop. The flow behavior of Gelwhite H dispersion is not with yield stress and its anti-thixotropy is very weakly.

The hysteresis area between the ramps up and down for an anti-thixotropic system represents the energy per volume required to build-up the structure. The hysteresis loop areas for Laponite RD and Gelwhite H dispersions are 568.36 Pa·s⁻¹ and 24.58 Pa·s⁻¹, respectively. These values indicate that Laponite RD dispersion requires a higher energy to build-up the dispersion structure due to the high interactions between the clay particles.

Figure 4 shows the variation of the apparent viscosity of the studied clay aqueous dispersions as a function of time when a stepwise sequence of 2.25 s⁻¹ - 100 s⁻¹ - 2.25 s⁻¹ was applied for an overall time of 1200 s. In the steps (first and third)

where is applied a low shear rate ($\dot{\gamma} = 2.25$ s⁻¹), the studied clay dispersions have different behaviors.

Laponite RD dispersion shows a more accentuated increase of the apparent viscosity with the time than Gelwhite H dispersion. This phenomenon observed for the studied dispersions is typical for the anti-thixotropic materials and often indicates an aggregation or gelation of the sample. As

the shear rate was increased at $\dot{\gamma} = 100$ s⁻¹, the apparent viscosity values of both dispersions decreased, indicating a pseudoplastic (shear thinning) behavior. It can be observed from Figures 3 and 4 that the initial structure of Gelwhite H dispersion is faster rebuilt and it is less influenced by the shear rate.

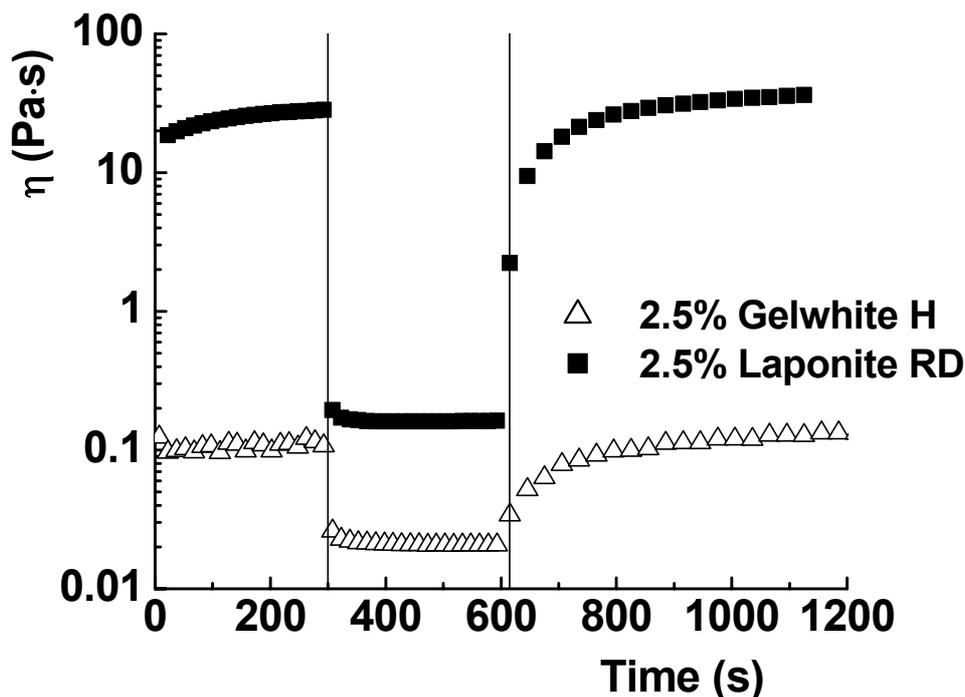


Fig. 4 – Apparent viscosity as a function of time obtained using a shear rate stepwise procedure (2.25 s^{-1} - 100 s^{-1} - 2.25 s^{-1}) for the studied samples.

EXPERIMENTAL PART

The clays used in the present investigation are Laponite RD and Gelwhite H procured from Rockwood Additives Limited U.K. The chemical formula of Laponite RD is: $\text{Si}_8(\text{Mg}_{5.45}\text{Li}_{0.4})\text{H}_4\text{O}_{24}\text{Na}_{0.75}$. The typical characteristics of Laponite RD are: the bulk density $1 \text{ g}\cdot\text{cm}^{-3}$ and pH for 2% aqueous dispersion 9.8.¹⁹ Gelwhite H is a Na-montmorillonite (bentonite) with chemical formula $\text{Na}_{0.33}[(\text{Al}_{1.67}\text{Mg}_{0.33})(\text{O}(\text{OH}))_2(\text{SiO}_2)_4]$ having the bulk density of $2.6 \text{ g}\cdot\text{cm}^{-3}$ and pH for 2% aqueous dispersion 10.¹⁹

Clay aqueous dispersions with the concentration of 2.5% were obtained by adding Laponite RD or Gelwhite H in deionized water followed by high speed stirring for a few minutes. The clay dispersions were then ultrasonicated for 15 min. The static and dynamic investigations were realized after one day from the preparation of samples which were ultrasonicated for 5 min before the measurements.

The rheological measurements were performed at 20°C using a controlled stress CVO Rheometer with parallel plate geometry (60 mm diameter and 500 μm gap) and thermal control by Peltier effect. The oscillatory shear measurements were performed in the frequencies range $0.03 \text{ rad}\cdot\text{s}^{-1}$ - $100 \text{ rad}\cdot\text{s}^{-1}$ within the linear viscoelastic regime, where the storage and loss moduli are independent of the shear stress. Also, steady flow measurements were carried out in the range of shear rates from 10 s^{-1} to 500 s^{-1} in order to determine the apparent viscosity.

CONCLUSIONS

In this paper, two smectites (Laponite RD and Gelwhite H) aqueous dispersions were prepared and their rheological properties at 20°C were in-

vestigated. The variation of viscoelastic moduli with the frequency is different for the studied samples. Laponite RD dispersion has the solid-like properties and Gelwhite H dispersion shows liquid-like behavior. Also, the studied dispersions exhibit different flow behaviors: Laponite RD dispersion presents a pseudoplastic flow with yield stress whereas Gelwhite H dispersion has a pseudoplastic behavior without yield stress. For the same clay concentration in the dispersion, the apparent viscosity of Laponite RD dispersion is higher than one of Gelwhite H dispersion, which can be related to the higher degree of organization of the clay particles in water.

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