ACADEMIA ROMÂNĂ

Revue Roumaine de Chimie

http://web.icf.ro/rrch/

Rev. Roum. Chim.,
2013, *58*(2-3), 145-152

*Dedicated to Professor Bogdan C. Simionescu
on the occasion of his 65th anniversary*

THIXOTROPY AND YIELD STRESS EVALUATION FOR CLAY AQUEOUS DISPERSIONS

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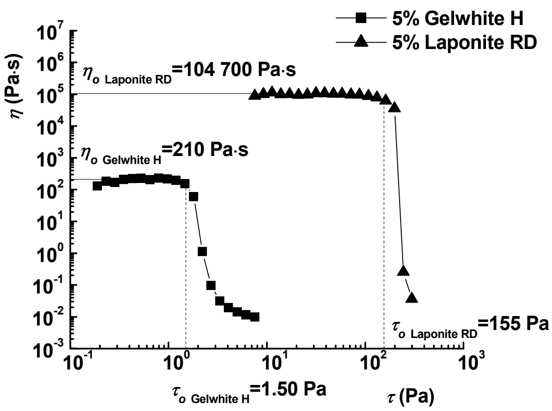
Received September 28, 2012

The thixotropy and the yield stress of two aqueous dispersions of Laponite RD and Gelwhite H with the concentration of 5% were determined at 20 °C. The samples are shear thinning and the strong interactions between Laponite RD platelets in water explain the higher viscosity for this dispersion as compared with Gelwhite H one. In addition, the presence of a typical hysteresis loop demonstrated the thixotropic nature of the Laponite RD dispersion. Two classical models (Bingham, Herschel-Bulkley) were applied to calculate the yield stress of the clay dispersions and the obtained values were discussed. The Laponite RD dispersion has shown a minimum stress in its flow curve which makes difficult to fit this behavior by using the traditional methods. A critical stress value in the flow curve of the Laponite RD dispersion was determined by using a recent model proposed by Moller, Mewis and Bonn. The competition between the aging phenomena and the shear rejuvenation is considered to be responsible for the unusual rheological behavior of the Laponite RD aqueous dispersion.



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.).[1-5] The incorporation of a small amount of clay into a polymer matrix affords the possibility to obtain polymer-clay nanocomposites with improved thermal, mechanical and barrier properties expanding the application area of the polymer.[6,7] Polymer/clay nanocomposites present an increasing interest due to their specific physical and mechanical properties. Over the past decade, numerous experimental investigations have shown that the dispersion of exfoliated nanoparticles in the polymer matrix leads to a remarkable increase in elastic stiffness, beginning at a very low nanoparticle volume fraction.[3,8,9] The reinforcing effect of clay is attributed to several factors, such as matrix properties, nature of the clay, particle

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volume fraction, particle aspect ratio, particle size, particle orientation, particle distribution, particle structural parameters (*i.e.* number of silicate layers in the particle and interlayer spacing) and strength of the interactions. Thus the reinforcement mechanism in nanocomposites may be considered similar to that in microcomposites except for the fact that both particle size effects and clay structural parameters are expected to play a major role in the mechanical behavior of polymer/clay nanocomposites. Recently, the evaluation of the reinforcing effect of clay was discussed on the basis of the elastic stiffness and yield stress simultaneously.[10]

Rheological measurements of clay dispersions can provide useful information concerning the interactions between clay particles and the physical state of the samples.[11,12] 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. This paper presents some experimental data concerning the thixotropy and the yield stress of two aqueous dispersions of Laponite RD and Gelwhite H.

RESULTS AND DISCUSSION

Two smectite clays, Laponite RD and Gelwhite H (sodium montmorillonite), belonging to the structural family known as the 2:1 phyllosilicates were used in the present study. These clays have a crystal structure consisting of an octahedral sheet of hydrous metal oxide (aluminum, sodium, magnesium, lithium or calcium) between two silicon tetrahedron sheets (Fig. 1).[13-15]

The chemical formula of Laponite RD and Gelwhite H are $Si_8(Mg_{5.45}Li_{0.4})H_4O_{24}Na_{0.75}$ and $Na_{0.33}[(Al_{1.67}Mg_{0.33})(O(OH))_2(SiO_2)_4]$, respectively. The platelets of Laponite RD and Gelwhite H have a well-defined thickness of 1 nm and a diameter of 25 nm and aprox. 300 nm, respectively. The characteristic of smectite clays is their ability to swell in water to form dispersions in which the clay particles have a strongly negative charge on the faces due to the release of Na^+ ions and a weakly positive charge on the edges due to the protonation of the OH groups.

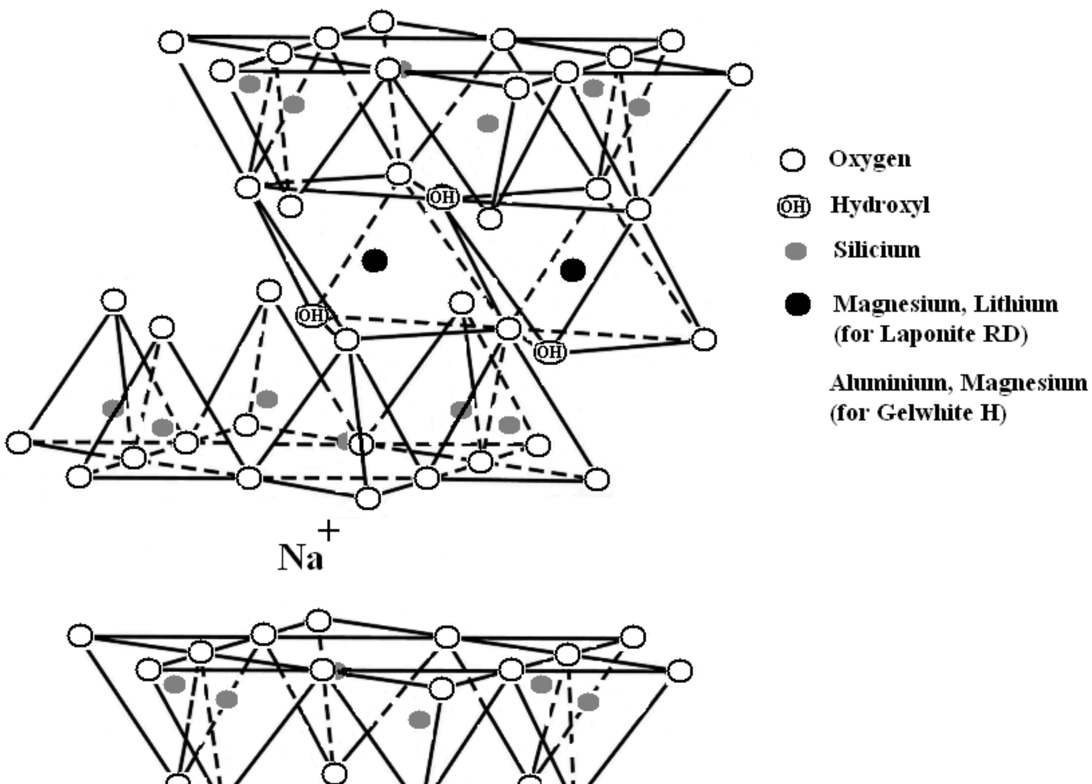

Fig. 1 – Structure of Laponite RD and Gelwhite H.

Generally, according to the phase diagram the smectite aqueous dispersions at low ionic strength and room temperature formed a repulsive glass.[16,17] In this state, the long-range electrostatic repulsions between clay particles dominated. For the present study, two aqueous dispersions of Laponite RD and Gelwhite H, with the concentration of 5%, were prepared and their rheological behavior was analyzed by shear measurements at 20 °C.

The flow behavior of any system is described in terms of the relationship between shear stress (τ) and shear rate ($\dot{\gamma}$). 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 apparent viscosity (η); it is a measure of the resistance to flow of the fluid (eq. (1)).

$$\eta = \frac{\tau}{\dot{\gamma}} \tag{1}$$

The investigated clay dispersions exhibited an apparent viscosity that decreased with increasing shear rate up to 500 s^{-1} due to the destruction of the dispersion microstructure at high shear (Fig. 2), showing a pseudoplastic (shear thinning) flow. The smaller particle size, and consequently the greater number of particles dispersed in water, explains the higher viscosity of Laponite RD dispersion as compared with Gelwhite H one (Laponite RD has a larger surface area per gram at the same concentration).

Thixotropy can simply be defined as the time dependence of viscosity on the preceding state of movement. Various experimental methods can be considered in order to quantify this behavior. A continuous decrease of the viscosity with time can be observed under constant shear stress or shear rate, when flow is applied to a sample assumed to be at rest for a sufficiently long time and the subsequent recovery of viscosity in time when the flow is discontinued.[18-20] Thixotropic behavior is indicated by a hysteresis loop between the flow curves at increasing and decreasing shear rates.[21] The magnitude of the loop indicates the degree of time dependency.

In our study, cyclic tests were performed by increasing the shear rate up to a maximum value (500 s^{-1}) followed by decreasing it. The thixotropic behavior of the studied samples was observed, with the hysteresis loop of Laponite RD dispersion being more pronounced (Fig. 3).

The hysteresis area between ramps up and down for a thixotropic system represents the energy per time and volume consumed in structure breakdown. The hysteresis loop areas for Laponite RD and Gelwhite H dispersions were 11 255 Pa·s^{-1} and 309 Pa·s^{-1}, respectively. These values indicate that the Laponite RD dispersion required a higher energy to build-up the dispersion structure due to the higher interactions between the clay particles.

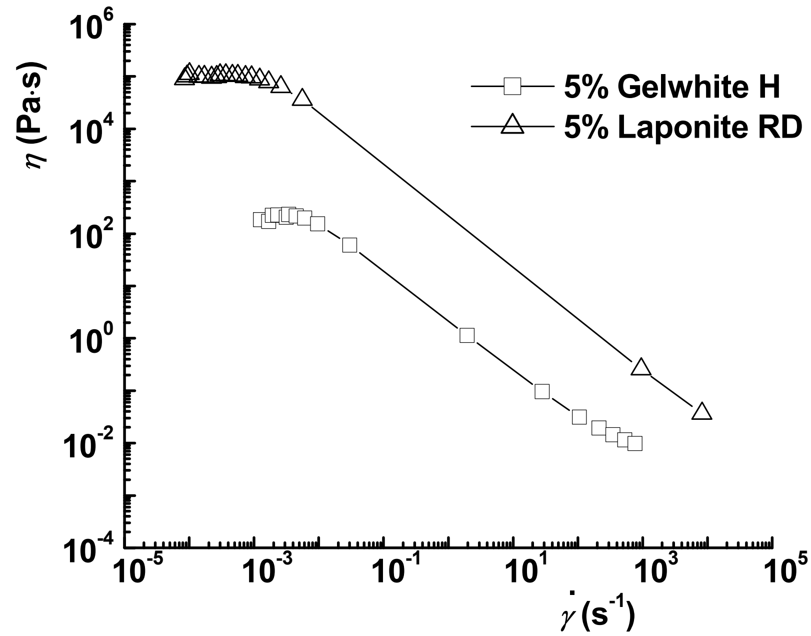

Fig. 2 – Steady shear viscosity *versus* shear rate for the clay dispersions at 20 °C.

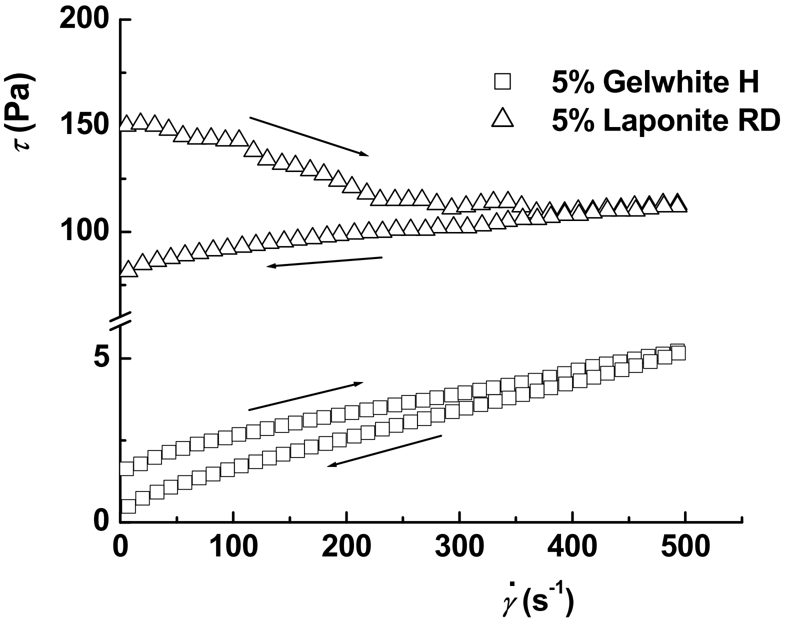

Fig. 3 – Flow curves of clay aqueous dispersions obtained at increasing and decreasing shear rate.

Some concentrated clay dispersions revealed a maximum on upward curve at very low shear rate[22-24] explained by Burgentzle *et al.*[25] as a consequence of the fact that a large shear stress must be applied to break the strongly network between clay particles and to orient the nanoplatelets in the flow direction. The clay aqueous dispersions exhibit peculiar properties, namely, they stop to flow abruptly below a critical stress and start to flow at a high velocity beyond a critical stress.[26] The rheological behavior of concentrated Laponite RD dispersions is the result of the competition between the two processes which occur in these systems: i) "aging phenomena" which consists of a viscosity increase at rest due to the buil-up of the microstructure and ii) "shear rejuvenation" process associated with the decrease of the viscosity in time under shear due to the destruction of the microstructure. For stress lower than a critical stress, the viscosity of the samples increases in time until the flow is halted completely. At a stress above the critical value, the viscosity decreases with the time towards a low steady state value, η_∞ (the limiting viscosity at high shear rates).[27]

The Laponite RD aqueous dispersion has a continuous network structure as a result of the attractive interaction between the clay platelets which are supposed to be elastic. When a stress is applied, the network is broken resulting smaller agglomerates and when the external stress is released some interactions may be restored. During reversible deformations of the aggregates, the elastic energy is stored. The elastic effect results from the attractive interparticle forces and the effect of the flow arises due to the network ruptures. In the upward flow curve of the Laponite RD dispersion (Fig. 3) a minim was observed at about 370 s^{-1}. The shear stress decreases at low shear rates as a result of the decrease of the stored elastic energy and it increases at high shear rates when viscous dissipation becomes significant.[28]

Generally, the yield stress which is defined as "the stress above which the material flows like a viscous fluid"[29] is determined as the intercept of the flow curve at zero shear rate. The value obtained using this method can be strongly influenced by the used shear rates range and by the selected rheological model in order to do the extrapolation. The yield stress value for concentrated Laponite RD aqueous dispersion is difficult to be determined by using the extrapolation method due to its elastic behavior on the first part of the flow curve (at startup). For this reason, a first evaluation of the yield stress was realized by following the variation of the apparent viscosity as a function of the shear stress (Fig. 4). Both samples exhibit constant apparent viscosity values up to the yield stress at which the apparent viscosity decreases abruptly. The yield stress values determined for Laponite RD and Gelwhite H dispersions were 155 Pa and 1.50 Pa, respectively. One can observe that the viscosity of the Laponite RD dispersion at zero shear rates, η_o, is with three orders of magnitude higher than that corresponding to the Gelwhite H dispersion (Fig. 4 and Table 1).

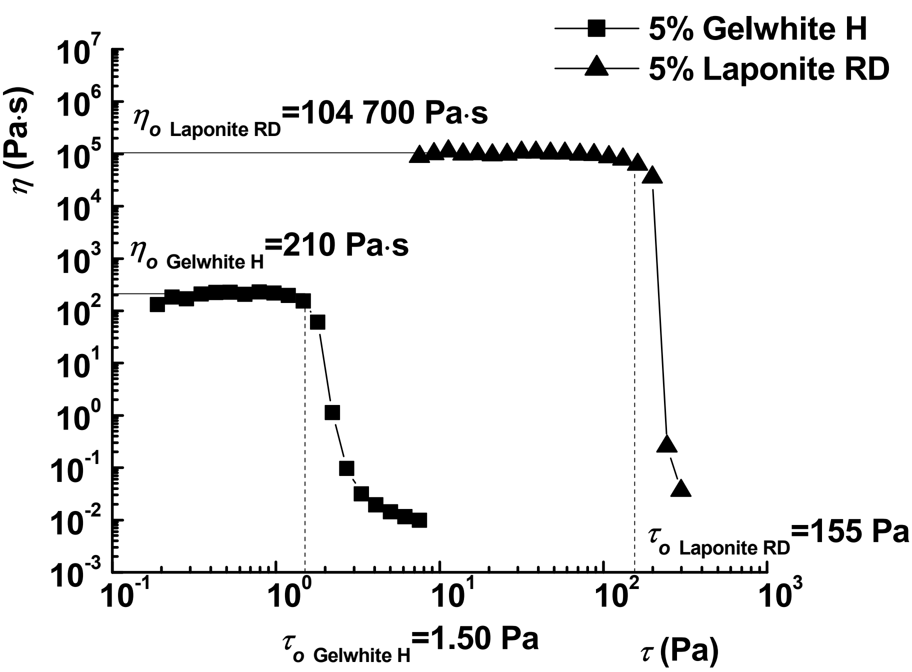

Fig. 4 – Variation of apparent viscosity as a function of shear stress for both samples.

Table 1

The parameters obtained by application of the different models to the experimental data

Sample		Bingham model		Herschel-Bulkley model			From $\eta = f(\tau)$	
		τ_o (Pa)	η_p (Pa s)	τ_o (Pa)	η_p (Pa s^n)	n	τ_o (Pa)	η_o (Pa s)
Gelwhite H	upward	1.87 (±0.02)	0.007 (±0.9 x 10^{-4})	1.64 (±0.03)	0.02 (±0.2 x 10^{-2})	0.82 (±0.01)	1.50	210
	downward	0.702 (±0.02)	0.009 (±0.8 x 10^{-4})	0.475 (±0.02)	0.02 (±0.1 x 10^{-2})	0.87 (±0.01)		
Laponite RD	upward (plastic zone)	94.12 (±1.10)	0.039 (±0.2 x 10^{-2})	94.62 (±28.50)	0.03 (±0.41)	1.03 (±1.83)	155	104700
	downward	86.17 (±0.42)	0.055 (±0.1 x 10^{-2})	79.82 (±0.76)	0.80 (±0.15)	0.59 (±0.02)		

The most popular models which are able to describe with accuracy the rheological behavior of different systems, being easy to use, are the Bingham and Herschel-Bulkley models:

– the Bingham model[29]

$$\tau = \tau_O + \eta_p \cdot \dot{\gamma} \qquad \tau > \tau_o \qquad (2)$$

– the Herschel-Bulkley model[30]

$$\tau = \tau_O + \eta_p \cdot \dot{\gamma}^n \qquad \tau > \tau_o \qquad (3)$$

If n <1 the fluid is shear-thinning, while n >1 is characteristic for a shear-thickening fluid.

For the Laponite RD dispersion, the two methods, Bingham and Herschel-Bulkley, can not be applied on the whole upward flow curve due to the elastic response revealed in its first part (Fig. 3). Therefore, the Bingham and the Herschel-Bulkley models were applied only on experimental data corresponding to the plastic zone at the shear rates higher than 370 s^{-1}. In Table 1 are shown the parameters of the two models applied on upward and downward curves for the investigated clay dispersions.

As we can see from Table 1, both models provide for the Gelwhite H dispersion the yield stress values higher than the value determined from the test which follows the variation of the apparent viscosity as a function of the shear stress. The flow behavior index from Herschel-Bulkley relationship, n, was less than 1 for Gelwhite H dispersion for both upward or downward curves, indicating the pseudoplastic behavior (shear thinning) (Table 1).

The parameters obtained for the Laponite dispersion by using the Bingham and Herschel-Bulkley methods are very different. However, the yield stress values, τ_o, calculated by using the theoretical methods applied to the downwards curves are not the true values. We consider that the true parameters of Gelwhite H dispersion are those established by using the experimental data from upward curve. Thus, the Bingham and Herschel-Bulkley models are not able to describe the rheological behavior of Laponite RD dispersion. For the Laponite RD dispersion, the value of the flow behavior index from Herschel-Bulkley relationship applied to the plastic zone of the upward curve is higher than unity. This abnormal value suggests that the Laponite RD dispersion is a shear-thickening fluid contrary to the observations derived from Fig. 2. In addition, the application of the rheological models to downward curves could be considered only to compare the rheological properties of the two clay dispersions. The parameters obtained from the downward curves are not the true values for the Gelwhite H and Laponite RD dispersions because of the samples were already sheared in order to obtain the upward curve. The Laponite RD dispersion which is a structured fluid with thixotropy and yield stress does not correspond to the classical description due to that fails to take stress-dependent structure into account.

For predicting the flow behavior of thixotropic fluids with yield stress, Moller, Mewis and Bonn[27] proposed a method that takes into account three parameters which characterize the material in an experiment at any given time: the stress (τ), the shear rate ($\dot{\gamma}$) and a structural parameter, λ, that gives the local degree of interconnection of the microstructure (and, through it, the viscosity, η). For a thixotropic system at low or zero shear rate, λ increases when the flow breaks down the structure, while at sufficiently high shear rates λ decreases and reaches a steady state value. Based on the following equation:

$$\frac{d\lambda}{dt} = \frac{1}{\tau} - \alpha\lambda\dot{\gamma} \qquad (4)$$

combined with the relationships (5) or (6) that give the viscosity:

$$\eta = \eta_\infty e^{\beta\lambda} \qquad (5)$$

$$\eta = \eta_\infty (1 + \beta\lambda^m) \qquad (6)$$

the following equation can be written under steady state conditions:

$$\tau = \dot{\gamma}\eta_\infty (1 + \beta(\alpha\, t\dot{\gamma})^{-m}) \qquad (7)$$

where α, β, m are material specific parameters, η_∞ is the limiting viscosity at high shear rates and t is the characteristic time of the build-up of the microstructure at rest.

When $0 < m < 1$ a simple shear thinning fluid without a yield stress is produced and when $m > 1$ a yield stress appears according to model. For 5% Laponite RD dispersion m was calculated as being 1.19. The flow curve described by equation (7) shows that for low shear rates the stress decreases with increasing shear rate, whereas for high shear rates it increases. Thus, the flow curve shows a minimum that defines a critical stress and a critical shear rate (Fig. 5). For shear rate lower than the critical value the flow is unstable. The limiting viscosity at high shear rates required by the Moller, Mewis and Bonn model was determined by using the Carreau-Yasuda relationship:[31,32]

$$\eta = ((\eta_o - \eta_\infty)\cdot((1 + (a\dot{\gamma})^a)^{\frac{n-1}{a}})) + \eta_\infty \qquad (8)$$

where η_o and η_∞ refer to the asymptotic values of viscosity at very low and very high shear rates, respectively, a is a constant parameter with the dimension of time and n is the power law index.

The values of η_∞ for the studied Gelwhite H and Laponite RD dispersions determined by Carreau-Yasuda method were 0.008 Pa·s and 0.05 Pa·s, respectively.

According to Moller-Mewis-Bonn method, the critical shear stress and the critical shear rate for the Laponite RD dispersion was determined as being 115.25 Pa and 370 s^{-1}, respectively (Fig. 5). In the region $\dot{\gamma} < \dot{\gamma}_{cr}$ the flow is unstable because the shear stress-shear rate curve decreases due to aging. One can observe that the critical stress from which the flow is homogenous and the shear rejuvenation becomes predominantly is lower than the yield stress with 39.75 Pa. The critical stress depends on the flow history of the material.

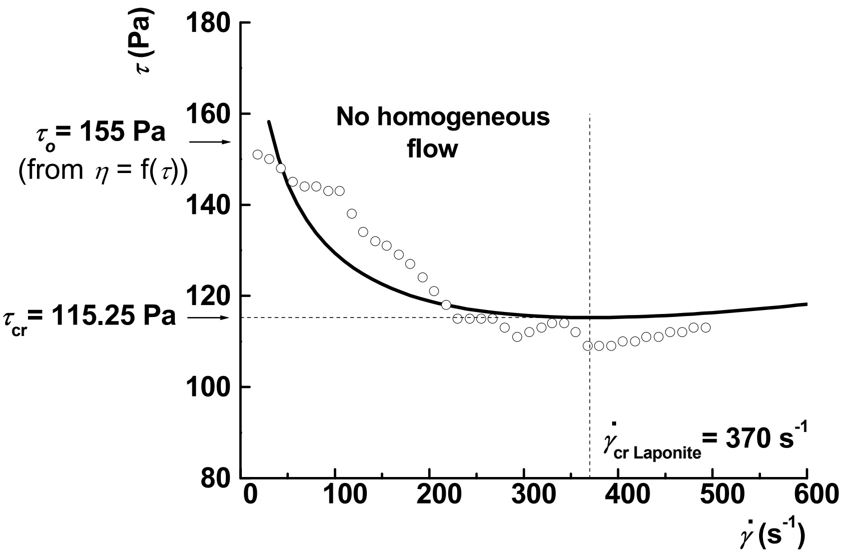

Fig. 5 – The steady state flow curves for the Laponite RD dispersion:
(○) experimental data (upward curve) and (▬) curve obtained according to Moller-Mewis-Bonn model.[27]

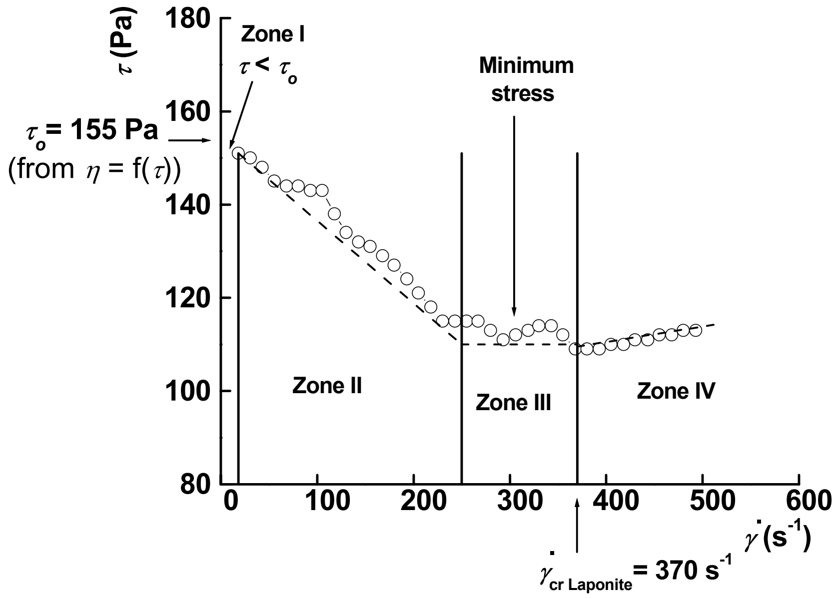

Fig. 6 – Illustration of the flow regimes of 5% Laponite RD aqueous dispersion: (○) experimental data; continuous line represents the Pignon *et al.*[33] approximation; the value of $\dot{\gamma}_{cr}$ represents the critical stress according to Moller-Mewis-Bonn model[27]. The dotted line is guide for the eye only.

For such curves with minimum, in the case of Laponite XLG aqueous dispersions, Pignon *et al.*[33] identified four regions: 1) at small deformation, the gel has an elastic behavior corresponding to a homogeneous strain field (regime I), 2) at low shear rates, shear is located within a fine layer of the sample (regime II), 3) at intermediate shear rates, shear remains within a layer whose thickness depends on the shear rate and the clay concentration (regime III, in this regime the shear stress is independent of shear rate), 4) at high shear rates, a homogeneous shear is obtained throughout the bulk of the sample (regime IV). On the upward flow curve of 5% Laponite RD aqueous dispersion, the regimes mentioned above were identified and the minimum value of shear stress was localized in regime III (Fig. 6).

The regime I is localized at very low shear rates up to the first experimental point corresponding to shear rate and shear stress of 18.10 s^{-1} and 151 Pa, respectively. The shear stress starts to decrease when the flow occurs within a low layer of the dispersion at shear rates up to about 250 s^{-1} (regime II). The shear stress could be considered constant between 250 s^{-1} and 370 s^{-1} (regime III) and it starts slightly to increase at higher shear rates (regime

IV). The $\dot{\gamma}_{cr}$ value established by using Moller-Mewis-Bonn method represents the shear rate value which separates the zones III and IV.

The shaping of the flow curves which display a minimum stress remains a subject still debated.

EXPERIMENTAL

The clays used in the present investigation were Laponite RD and Gelwhite H procured from Rockwood Additives Ltd., U.K. Clay dispersions with the concentration of 5% were obtained by adding Laponite RD or Gelwhite H to deionized water followed by high speed stirring for a few minutes. The clay dispersions were then ultrasonicated for 15 min. The dynamic investigations were conducted within a day from the preparation of samples which were ultrasonicated again for 5 min before the measurements.

The rheological measurements were performed at 20 °C using a controlled stress Bohlin CVO Rheometer (Malvern Instruments UK) with parallel plate geometry (60 mm diameter and 500 μm gap) and thermal control by Peltier effect. The shear sweeps tests were carried out in controlled stress mode from 10^{-4} s^{-1} to 10^{4} s^{-1} in order to determine the apparent viscosity, the viscosity at zero shear rate and the yield stress. The hysteresis of the flow curves for the studied samples was established by increasing the shear rate up to a maximum value (500 s^{-1}) followed by decreasing it.

CONCLUSIONS

Two aqueous dispersions with 5% smectite clay (Laponite RD and Gelwhite H) were investigated by rheology at 20 °C. The studied systems exhibited a pseudoplastic flow with the yield stress. The yield stress values for both Gelwhite H and Laponite RD dispersions were determined by following the evolution of the apparent viscosity as a function of the applied stress.

The flow behavior of the studied samples was modeled by using the Bingham and Herschel-Bulkley relationships. These classical models can not be applied to 5% Laponite RD aqueous dispersion due to its unusual rheological properties that arise from the competition between the aging phenomenon and shear rejuvenation effect. A critical stress of the Laponite RD dispersion was determined by using a new method that take into account traditional shear thinning and yield behavior and adds a component that models structural connectivity in the fluid.

Acknowledgments: This work was supported by a grant of the Roumanian National Authority for Scientific Research, CNCS-UEFISCDI, project number PN-II-ID-PCE-2011-3-0199 (contract 300/2011).

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