

FLOW BEHAVIOUR AND RHEOLOGICAL ASSESMENT OF KAOLINITE/PDMS PASTES VIA CAPILLARY RHEOMETER

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ABSTRACT

An improved understanding of the influence of some parameters such as solid:liquid ratio, particle size and temperature on the rheology of kaolinite/silicone oil AK 60 000 pastes is needed so that new application areas of this clay can be brought into existence. Kaolinite/PDMS paste forms were used to measure the rheological properties with high pressure capillary rheometer. All pastes were exhibited non-Newtonian, pseudoplastic shear-thinning behaviour under experimental conditions. The viscosity decreased with an increase in temperature and particle size and with a decrease in solid:liquid ratio. Herschel-Bulkley model is capable of predicting the extrusion behaviour of the whole pastes.

KEYWORDS:

Kaolinite/PDMS paste, non-Newtonian, Herschel-Bulkley model, High Pressure Capillary Rheometer.

INTRODUCTION

A suspension consists of solid particles dispersed in a solution. The addition of particles affects the flow field and rheological properties of the fluid. Characterization of concentrated suspension has been conducted extensively [1]. Suspensions of solid particles in viscous fluids are often encountered in various applications such as paints, polymer, ceramics, pharmaceutical products, drilling muds and food products.

Rheology is a science dealing with the mechanical behaviour of fluids and plastic bodies when subjected to external stresses. However, its technical application has been more conventional in chemical industry, e. g. food science, polymer research, but uncommon in soil mechanics, yet [2]. The term “paste” is not precisely defined and there are many definitions in common use most of which focus upon the perceived mechanical response. For example, one of the definitions is ‘any composition and mixture containing just enough moisture to render itself soft and plastic’[3]. Pastes, or highly filled suspensions, are important intermediates in

the manufacture of a wide range of products, including catalysts, agrochemicals and ceramics [4]. The ceramic paste flow is different from molten polymers or metals because the flow behaviour is dependent on the properties of solid and liquid components. Theoretical analysis and prediction of paste rheology have been studied by many workers. The origins of theoretical analysis of paste rheology can be found from Benbow [5] who used a capillary attached to a ram extruder [6]. Rheological studies of pastes are required to develop novel extrusion applications, and to improve product quality and process optimization [7]. The rheological properties of suspension of solid particles in polymeric matrices (pastes) are important in analyzing the processing of such materials, which are encountered in several industries. The flow behaviour of these composite systems depends on the particle shape, size and size distribution, volume fraction of particles, particle-particle and particle-matrix interactions, matrix rheology, and measurement conditions such as temperature and shear rate [8].

Clay minerals are extensively used in a wide range of applications. They are a key component in the formulation of ceramic products, cement, drilling fluids, moulding sands, paints and paper, among others [9]. An important characteristic that clay minerals are able to provide in such applications is adequate particle dispersion, which is necessary to obtain a uniform and stable system. Under certain conditions the clay particles may become aggregated, which leads to the variation of important properties required for a particular function. In drilling fluids, for example, the flow behaviour of the system is of utmost importance due to its circulation around the wellbore [10]. The aggregation of the clay particles under varying conditions of temperature and electrolytes leads to strong variations of the flow properties. It becomes necessary therefore to add certain additives, or polymers, to stabilise the clay particles and prevent this behaviour.

As indicated in literature [1], a suspension consists of solid particles dispersed in a solution and its characterization has been performed widely. However, it remains a challenge as the flow behaviour of concentrated suspension is complicated by the microstructural change with the

occurrence of particle migration and wall slip, as well as yield stress. There is a wide range of studies on rheological properties of kaolinite dispersions, however, few of which involve kaolinite pastes. Kaolinite mineral is an environmentally safe material with no adverse health problems as long as the fine particle dust is controlled. Paste is an intimate mixture of particulate solids and liquids. The rheological behaviour of pastes is not nearly so well defined as that of pure fluids, be they Newtonian fluids or macromolecular-based, non-Newtonian fluids [11]. Numerous empirical and theoretical models have been proposed to describe the rheological behaviour of pastes [12]. Establishing the optimal amount of fluid is particularly important for ceramic pastes. Not only are pastes important in agriculture, food, cosmetics, construction, pharmacy, and ceramics, but their behaviours can be extremely complex due to the relative movement of the liquid phase within the solid matrix [13]. Theoretical rheological flow models applied to pastes are currently not adequate to predict the material flow properties under extrusion process conditions. Therefore, these properties usually must be measured experimentally [14]. Capillary extrusion flow has been very often utilised for a wide variety of paste-like materials in an attempt to characterize their bulk intrinsic rheology as well as their wall interface boundary conditions. The wall slip phenomenon is basically the occurrence of apparent relative velocity between the wall and the fluid at the wall. However, since the fluid is continuum, even in concentrated suspensions there is no 'true slip'. It is in reality an 'apparent slip' created by a region of high velocity gradient close to the wall compared to the bulk. This appears as an apparent slippage of the suspension through a thin liquid-rich layer (slip layer) of thickness δ at the wall [15]. The flow of paste-like materials invariably involves interactions at the interface between the material and the processing engine wall [16]. This wall influence, which generally reduces shear strength of the particle network, extends from the wall to a distance of approximately a few particle diameters. At sufficiently high shear loadings the particle structure collapses in the layer of paste near the wall, causing formation of a thin film, which allows the paste to flow via slip along the wall [12]. The relative slip velocity changes with increase in temperature. In general, the behaviour of the particulate pastes during extrusion depends on: 1. the amount and rheological properties of liquid phase, 2. the interference between particles, 3. the extrusion conditions, and 4. the time scale of the experiments [17]. Lin et al. designed a study to measure the yield stress, thixotropy, and viscosity at different shear rates of commercially available screen-printing pastes and self-prepared pastes by using a rheometer. Their results showed that

commercial pastes are not totally suitable for application in screen-printing process [18].

Previously, work in this field has been confined to capillary rheometry of chemical additives/silicone oil pastes and no consideration of has been given to the rheological behaviour of kaolinite/ PDMS (silicone oil AK 60 000) pastes. The aim is to investigate flow behaviour and rheological characteristics of kaolinite/silicone oil AK 60 000 pastes via capillary rheometry. This paper is a part of a research project focused on rheological characteristics of kaolinite/silicone oil pastes. Doğan et al. [11] reported the flow behaviour of kaolinite/silicone oil AK 1 000 000 paste as a non-Newtonian and time-dependent material.

EXPERIMENTAL

Materials. Kaolinite paste consists of a combination of kaolinite powders having a particle size less than 25 μm (obtained from Kalemaden, a local mining corporation) and commercial silicone oil. Kaolinite, a natural geological sample and one of the most versatile industrial clay mineral, have a chemical formula $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ and its specific gravity is 2.62. As received, the kaolinite was in powder form and light cream in colour. The particle size distribution of the kaolinite was determined using fine sieves having diameter size between 0 and 25, 25 and 50, and 50 and 75 μm , corresponding to upper- and lower-size fractions. Silicone oil used as binder material is polydimethylsiloxane (PDMS) which is known for low weight, good thermal stability, inert, nontoxic and a water-repellent surface. The surface hydrophobicity of PDMS prevents the formation of a continuous water band on the surface. This leads to improved insulator performance, even in extreme environments [11]. Silicone oil (trademark name: silicone oil AK 60 000) supplied generously by Wacker-Chemie GmbH was utilized as continuous phase.

Paste Preparation. Processed kaolinite powders were mixed thoroughly in the dry state prior to adding the silicone oil in a kneader (IKA HKD-T0,6 kneader) and then the liquid phase, silicone oil, was added to solid phase. Aforementioned ingredients were mixed thoroughly batchwise for 4 h to ensure favorable homogenization. All of pastes were prepared in accordance with same procedure. The IKA high-efficiency laboratory kneader is suitable for processing nonflowable, highly viscous media. The uniform mixing is based on intensive processing by means of wide-bladed kneading elements. The kneading medium is moved within the trough both horizontally and vertically. Additional media

TABLE 1
Paste parameters prepared for the rheological measurements (solid:kaolinite, liquid:silicone oil).

solid:liquid ratio (g:g)	particle size (µm)	temperature (°C)
75:25:00	0-25	25
77:23:00		
80:20:00		
77:23:00	0-25	25
	25-50	
	50-75	
77:23:00	0-25	25
		50
		75

quantities may be added during the kneading operation. The double-walled kneading chamber allows cooling or heating of the product. The product temperature was measured directly behind the kneading blades. In the experiments, kaolinite-silicone oil pastes were prepared in different silicone oil content in the range of 0-25, 25-50, and 50-75 µm [19]. Table 1 shows the compositions and particle sizes of six pastes prepared for these experiments with the dies of various L/D ratios, respectively [11].

Apparatus and Methodology. Capillary rheometry is a pressure-driven technique which mimics flow through an extruder die or injection moulding nozzle, capable of providing shear and extensional rheological properties of the melt at rates experienced during processing [20]. Besides this, capillary rheometry is a standard experimental technique for paste characterization and used to determine rheological characteristics of the pastes as a function of shear rate. [11]. Also it is the simplest and most popular system to measure the viscosity of fluids at high shear rates and, because of this, it is normally used to simulate industrial processes in the polymer processing industry. Thus, traditionally the rheometers have been equipped with high pressure transducers, which means that they present some limitations in the characterization for low viscosity (lower than 0 (10¹) Pa s) fluids [21].

The shear rheology of all pastes prepared with four different silicone oils was studied employing twin bore (RH10) precision advanced capillary rheometer (Malvern Instruments, UK) using Flowmaster version 8.3.10 control software. Figure 1 shows a cross-section of such a rheometer with barrel diameter D_0 , die land diameter D , and die

land length L . A common crosshead is used to drive twin pistons at a range of speeds causing paste to flow at known flow rate through capillary dies. Pressure drop at the entrance of each capillary die was monitored by the control software. The inner diameter and length of the barrel used were 15 and 240 mm, respectively. One barrel of the rheometer was fitted with a capillary die of L/D ratio 16 and the other bore was fitted with an orifice die. The bore diameter of both capillary dies was 1 mm, with die entry angle of 180°, whilst the lengths were 16 and less than 0.25 mm for long and orifice dies, respectively. Twin bore capillary rheometers allow two geometries of die to be examined simultaneously, thus corrected shear viscosity can be measured during a single test. In addition to measuring viscosity, capillary rheometry can, through the use of specialist test equipment, provide information relating to time dependent behaviour, die swell (a measure of elasticity), melt fibre strength, wall slip velocity and P-V-T data. Capillary dies, made from tungsten carbide-cobalt alloy in order to maintain tight geometrical integrity, were fitted into the bottom of the barrels and pressure transducers located directly above the dies [20].

The barrel could be fitted with different orifice and capillaries (or dies) of different diameters; an orifice is a capillary of negligible length. The arrangement used consisted of orifice and capillary of diameter was 1.0 mm, and the length of the capillary was 16 mm. The paste compounded in the kneader was fed into both bore of the barrel and manually compressed before the test was started. All pastes were extruded from capillary rheometer at a wide shear rate range. The shear viscosity and shear stress of pastes were measured as a function of shear rate. [11]

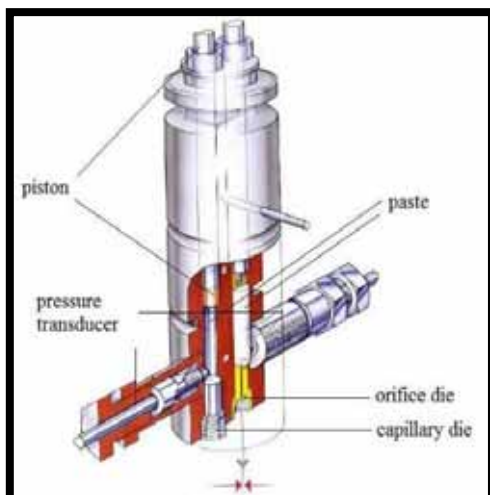


FIGURE 1
Outlines of a twin bore capillary rheometer.

RESULTS AND DISCUSSION

Structural and Morphological Characterization. XRD diffractogram obtained for the kaolinite/silicone oil paste is reported in Fig. 2. Patterns of the kaolinite and silicone oil are also represented to determine whether adding silicone oil affected the interlayer spacing. Characteristic maxima of the kaolinite were observed located at $2\theta=12.42^\circ$, 20.89° , 24.93° and 26.68° (very intense, sharp and narrow peaks), which referred to the basal spacing of the kaolinite (Table 2). After dispersion in silicone oil, considerable changes occurred in the XRD diffractogram compared to kaolinite. The peaks at $2\theta=20.89^\circ$, 24.93° and 26.68° in the original kaolinite greatly shifted in the intercalates to small reflection angles ($2\theta=22.37^\circ$,

26.38° and 28.12°) originated by presence of silicone oil. As seen in Figure 2c significant difference occurred at the $2\theta=12.42^\circ$ peak of kaolinite. This peak disappeared completely due to kaolinite-silicone oil intercalating. The diffraction pattern presented in Figure 2c illustrated that some kaolinite layers were delaminated, whereas certain layers retained their basal spacing. It can be concluded from these results that kaolinite-silicone oil composite material was obtained because of the dispersing of kaolinite into the polymer matrix of silicone oil.

The DTA peak temperatures are characteristic for each mineral, and DTA curves are applicable for the identification and determination of many types of clay. As seen from Figure 3, the DTA pattern of the crude clay exhibits characteristic endothermic and exothermic peaks of kaolinite at 523 and 1008°C , respectively. [22,23] In the first step of transformation in the range of 400 - 620°C , kaolinite, due to dehydroxylation and predehydration, was transformed to metakaolinite phase with loss of structural hydroxyl groups. In the second step, metakaolinite decomposes and forms Al-Si spinel phase generally during heating around the exothermic peak temperature [24].

Scanning electron microscopy (SEM) was also used in order to more closely observe the dispersion of the kaolinite in the silicone oil and to provide further confirmation of morphology. SEM micrographs of kaolinite and kaolinite/silicone oil paste presenting the microstructure are shown in Figs. 4,5. The formation of dispersion of kaolinite clay layers in the matrix can be said with the aid of these SEM micrographs.

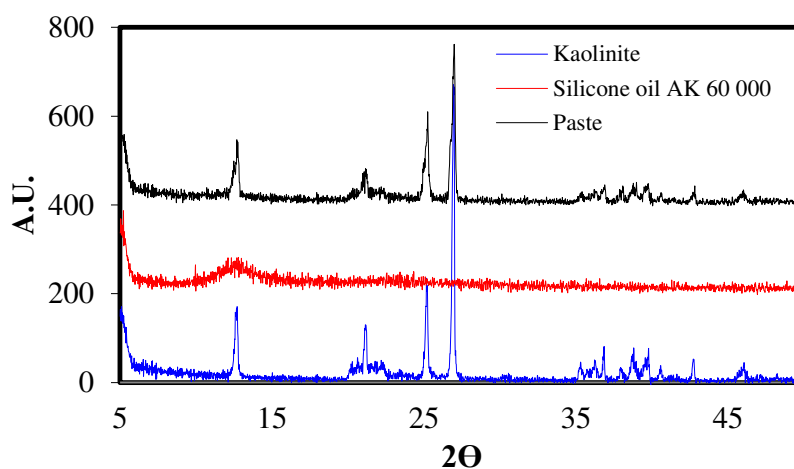


FIGURE 2
X-ray diffraction results of kaolinite, silicone oil AK 60 000 and the paste.

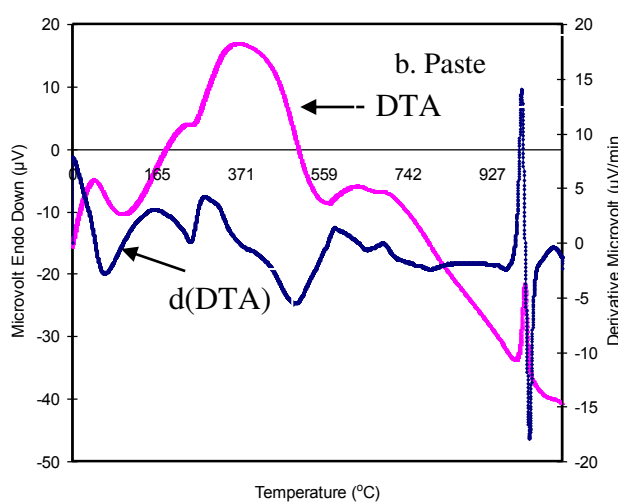
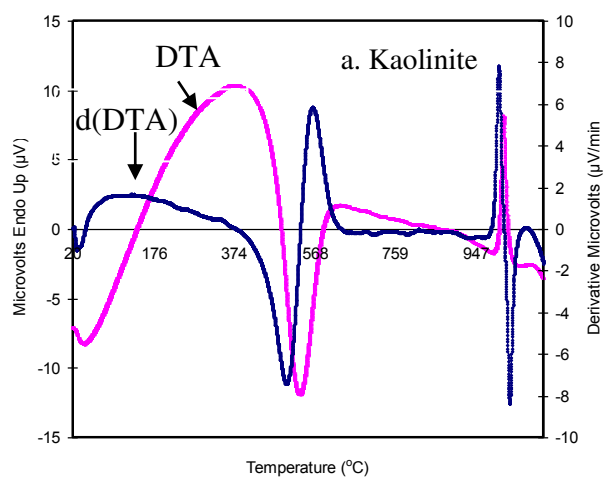


FIGURE 3
DTA spectra of kaolinite and paste.

TABLE 2
XRD data of kaolinite, silicone oil AK 60 000 and the paste.

Sample	2θ	d (Å)	% relative intensity
Kaolinite	12,678	6,977	21,75
	21,210	4,185	15,41
	25,209	3,529	28,75
	26,982	3,302	100,00
Silicone oil AK 60 000	5,206	16,960	100,00
Paste	12,787	6,917	24,64
	21,219	4,184	14,60
	25,264	3,522	49,26
	26,734	3,312	36,77
	27,012	3,298	100,00

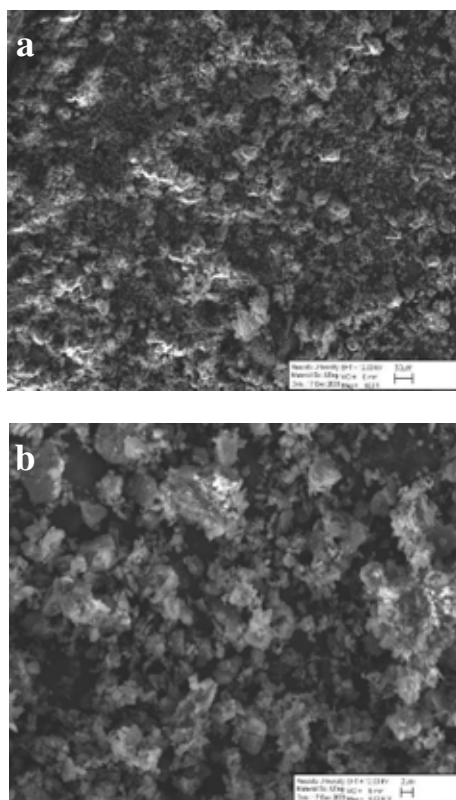


FIGURE 4
SEM image of kaolinite: a) 500 and b) 5000.

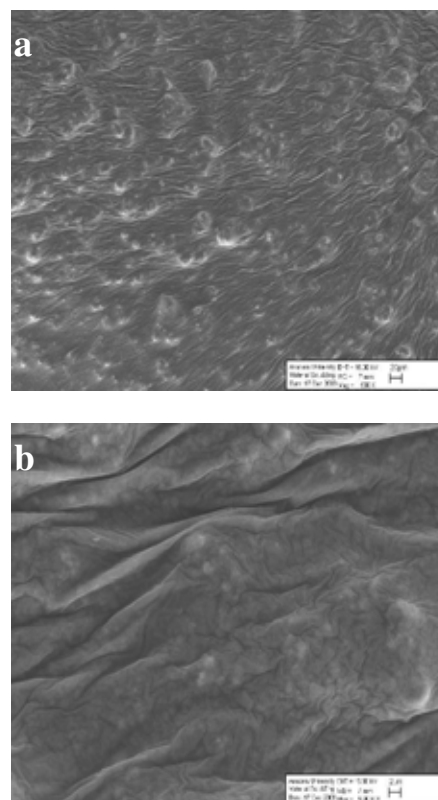


FIGURE 5
SEM image of kaolinite/silicone oil AK 60 000
paste: a) 500 and b) 5000.

Rheological Characterization of Pastes.
Flow Behaviour of Pastes. The flow processes that occur during extrusion are very complex. Many effects are apparent, some of which are difficult to separate, e.g. shear flow with yield point, wall slippage with slippage limit, elastic and time effects such as thixotropy. These effects should be identifiable in measuring processes. The capillary rheometer can be used to determine such effects [25]. Fluids and pastes may be studied by subjecting them to continuous shearing at a constant shear rate. One of the fundamental parameters that characterizes flow behaviour of liquid and semiliquid materials is viscosity, which is an intrinsic parameter and a measure of a fluid's resistance to flow when a shearing stress is applied. The flow behaviour of these materials under applied stresses classifies them as Newtonian or non-Newtonian, a classification that is based on their stress-strain relationship [26]. The majority of the pastes do not show Newtonian behaviour. For non-Newtonian liquid, the viscosity or shear stress is a function of the shear rate, meaning that for an applied shear rate the corresponding shear stress

remains constant provided the shear rate has not changed. [27,28]. A non-Newtonian fluid is any fluid that doesn't obey the Newtonian relationship (shear stress is linearly proportional to shear strain rate) between the shear stress and shear rate, as seen from Figs. 6-8,a [29]. Flow plots of shear stress versus shear rate do not exhibit a linear relationship. In this case, it can be said that the paste is a non-Newtonian material. When the material exhibits a diminish in viscosity as shear rate increases, it is called shear thinning or pseudoplastic [27,28]. Flow plots of shear viscosity versus shear rate point out that paste in the studied shear rate ranges displays a non-Newtonian and pseudoplastic behaviour [30]. A pseudoplastic material is one in which viscosity decreases with increasing shear rate. Pseudoplastic or shear thinning fluids have a lower shear viscosity at higher shear rates. It is generally supposed that the large molecular chains tumble at random and affect large volumes of fluid under low shear but that they gradually align themselves in the direction of increasing shear and produce less resistance [31].

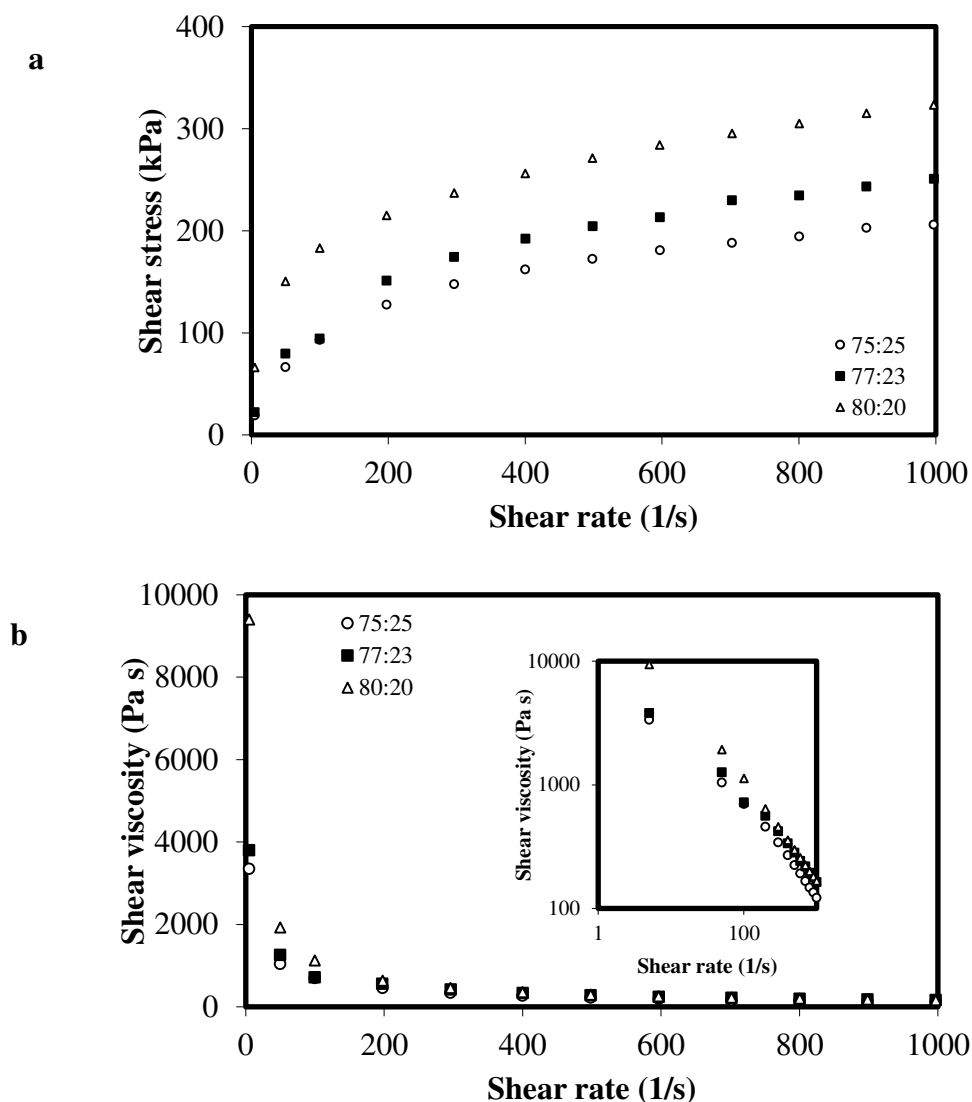


FIGURE 6

The plots of shear stress (a) and shear viscosity (b) versus shear rate for pastes with different solid:liquid ratios. (L/D=16 mm/1 mm).

Effect of Rheological Parameters. Various factors affect the flow behaviour of clay suspensions. Naturally, the clay concentration will bring about an increase of all rheological properties. Additionally, a rise of the temperature increases the interparticle attractive forces, which in turn, leads to enhanced particle-particle interactions affecting yield stress and suspension viscosity. The suspension viscosity also depends to a great extent on the viscosity of the medium, which is also a function of temperature [32]. The effects of rheological parameters such as solid:liquid ratio, particle size and temperature on the flow of kaolinite/silicone oil AK 60 000 pastes through the capillary dies as function of shear rate will be presented in this section.

Figure 6 presents the comparison of kaolinite/silicone oil AK 60 000 pastes with three

different solid:liquid ratios for the die dimension of L/D=16mm/1mm. Curve plotted shear stress versus shear rate for the paste changes systematically which proceed below that of lower solid:liquid ratios and above that of higher solid:liquid ratios. The pattern and magnitude of the flow curves of the pastes based on silicone oil are strongly dependent on the solid concentration. A higher solids fraction tends to cause a paste to display more plastic characteristics [33].

Figure 7 reports experimental findings of the influence of shear rate and particle size on shear stress and shear viscosity. One of the parameters affects the flow behaviour is particle size of kaolinite powder used for the pastes. Three different groups of particle size were employed and incorporated with silicone oil in the kneader for the capillary rheometric measurements. Maintaining a

constant mass of particles in a suspension while reducing the particle size of the solid phase leads to an increase in the number of particles in the system. In general, a higher number of smaller particles results in more particle-particle interactions and an increased resistance to flow. Clearly as shear rate increases, this effect becomes less marked, suggesting that any particle-particle interactions are relatively weak and broken down at high shear rates. As particle size increases, shear stress values decrease regularly. Besides viscosity decreased with increasing shear rates, showing only a marginal decrease thereafter. The same scenario was found in the temperature change of the pastes. As shown in Fig. 8, the shear stress decreased by increasing temperature. The viscosity of a fluid is affected by the binding between molecules that make up the solution or the relationship between the solvent and the solute, both factors which are affected by solution concentration or temperature [11]. Besides, Rha noted that the decrease in

viscosity with increasing shear rate is related to the increasing alignment of constituent molecules [34].

Wall Slip Analysis. For determining the wall slip behaviour of extrusion pastes, the high-pressure capillary rheometry equipped with a computer for data acquisition is particularly well-suited. Figs. 9-11 show the plots of wall slip velocity versus shear stress as a function of solid:liquid ratio, particle size and temperature, respectively. The shear stress values for all pastes during capillary flow changes systematically when the amounts of liquid or solid are altered. The corrected shear stress has decreased with an increase in the amount of solid. As seen from Figs. 9-11, V_{slip} for all paste samples have increased at high shear stress values. The change in slip velocity indicates that the surface layer properties rely on the amount of solid or liquid. All pastes depending on the solid:liquid ratio show low wall slip velocity in the shear stress range of 0-100 kPa, but wall slip velocity has significantly increased at above 100 kPa (Fig. 9).

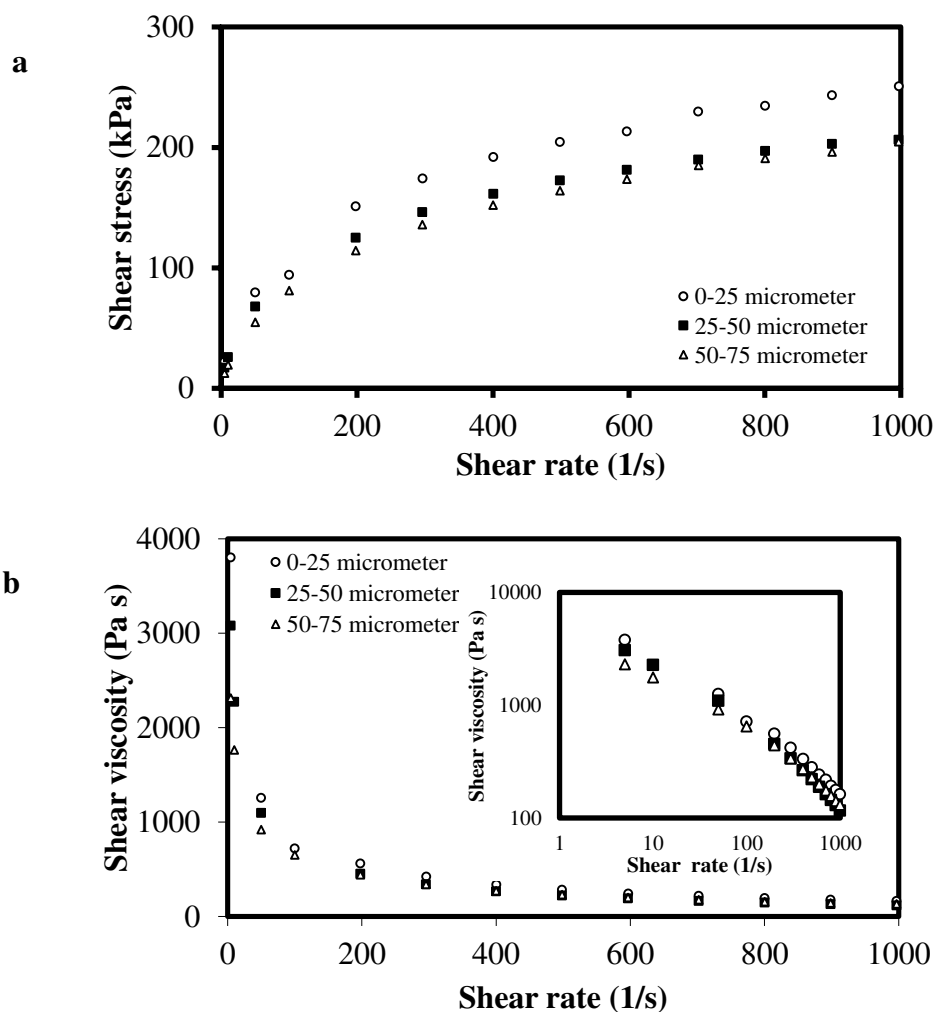


FIGURE 7

The plots of shear stress (a) and shear viscosity (b) versus shear rate for pastes with different particle sizes. ($L/D=16 \text{ mm}/1 \text{ mm}$).

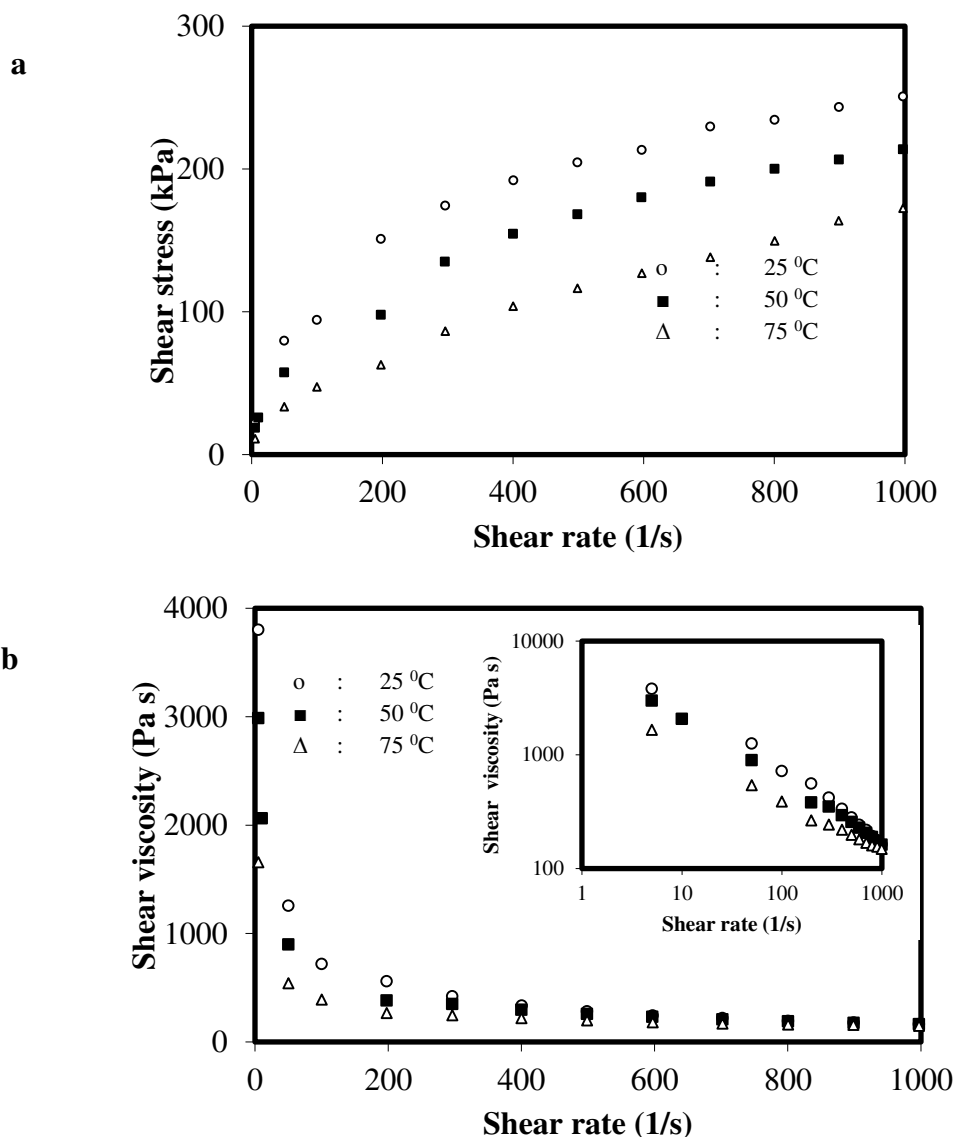


FIGURE 8

The plots of shear stress (a) and shear viscosity (b) versus shear rate for pastes with different temperatures. (L/D=16 mm/1 mm).

This may be a result of phase separation for pastes. Some degree of phase separation is essential for paste flow as wall slip is often caused by the presence of a liquid rich-layer of material at the wall which deforms preferentially to the bulk material (sometimes called *apparent slip*: the layer is thin as evidenced by imaging) [35,36]. To examine the effect of particle size on wall slip velocity, the volume fraction was preserved constant at 77:23 of the maximum volume fraction during the experiments. As seen from Fig.10, as particle size increases, the wall slip velocity values are low and the wall slip velocity has not significantly changed until a shear stress value is

100 kPa. But at high shear stress values above 100 kPa (Fig.10) the wall slip velocity increases markedly for all particle sizes. This indicates that the shear stress values of process conditions of pastes are lower than 100 kPa. Since the kinetic energy of molecules increases with temperature, the interaction between the kaolinite and silicone oil reduces and phase migration can occur more easily. The relationship between shear stress and V_{slip} with increasing temperature is shown in Fig. 11, indicating that wall slip has a significant contribution to the flow of the paste through the capillary die. Besides, it represents that the wall slip velocity of pastes increases with increasing temperature.

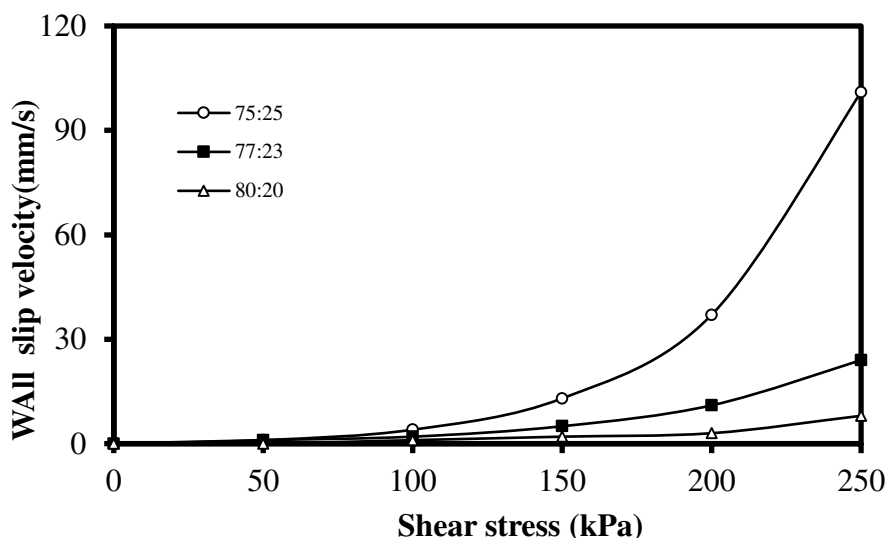


FIGURE 9

Wall slip velocity versus shear stress for different solid:liquid ratios.

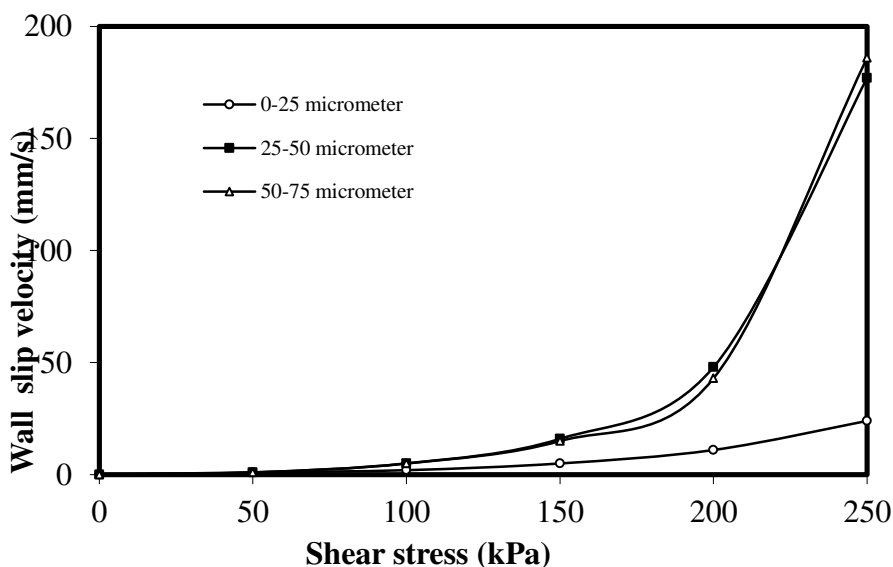


FIGURE 10

Wall slip velocity versus shear stress for different particle sizes.

Rheological Models. Aqueous clay suspensions that possess a relatively high particle concentration have been described traditionally in accordance to the Bingham theory of plastic flow [37]. The Bingham model postulates that a finite stress must be applied to initiate flow and at greater stresses the flow will be Newtonian. The resistance of the suspension to flow can therefore be considered as consisting of two parts: a Newtonian part in which the shear stress is proportional to the shear rate and a non-Newtonian part in which the shear stress is constant irrespective of the shear rate. The equation for the Bingham model is:

$$\tau = \tau_0 + \mu_{\infty} \dot{\gamma} \quad (1)$$

Where μ_{∞} is the plastic viscosity, defined as the slope of the curve, and τ_0 is the bingham yield stress normally taken as the intercept of the flow curve at high shear rates. Very dilute clay suspensions or drilling fluids that contain polymers behave as pseudoplastic fluids, which may be described by the power-law equation [38]:

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

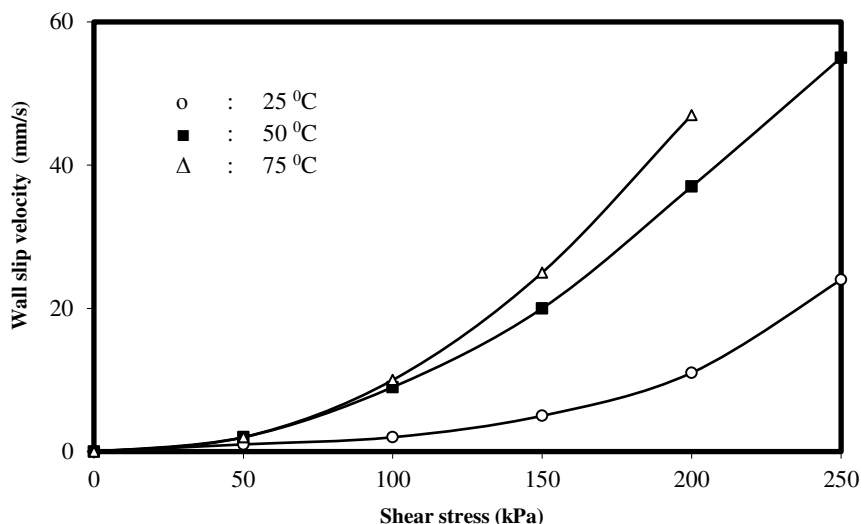


FIGURE 11
Wall slip velocity versus shear stress for different temperature values.

$$\tau^{1/2} = \tau_0^{1/2} + \mu_\infty^{1/2} \dot{\gamma}^{1/2} \quad (3)$$

and the Herschel-Bulkley equation [40]

$$\tau = \tau_0 + K(\dot{\gamma})^n \quad (4)$$

Both Eqs. (3) and (4) have been used to describe the consistency curves of drilling fluids, with the Herschel-Bulkley equation being the most suitable. In both cases, the suspension has an initial yield stress at low shear rates, and afterwards presents pseudoplastic or 'shear-thinning' type behaviour at higher shear rates. In the last case, the viscosity decreases with shear rate.

The model parameters obtained by fitting the experimental shear stress-shear rate data of kaolinite-silicone oil pastes to the Power Law, Casson, Bingham and Herschel-Bulkley (HB) models as a function of particle size, solid/liquid ratio, and temperature are given in Table 3. The coefficients of determination (R^2) obtained were high, which confirms the HB model to be adequately suitable for describing the flow behaviour of the pastes within the range studied. In all cases, R^2 values were higher than 0.994. The results showed that the shear stress-shear rate relationship at all experimental conditionals are nonlinear, indicating that these pastes behave as a non-Newtonian fluid. From the values of the HB model parameters, reported in Table 3, it can be seen that the consistency coefficient and the yield stress of kaolinite pastes increased with an increase in solid concentration and particle size and decrease in temperature. Similarly, Rao and Tattiyakul⁴¹ showed that an increase in the starch concentration would increase the volume fraction of solids in starch dispersion and this led to an increase in yield

stress. The yield stress, which represents a finite stress required to achieve flow, is an important factor that plays a vital role during mechanisation of paste preparation. Below the yield stress a material exhibits solid-like characteristics. This characteristic is highly crucial in process design and quality assessment for materials. Furthermore, the fact that (n) values were less than unity indicates that these products are pseudoplastic materials. The smaller the (n) values, the greater the departure from Newtonian behaviour. All pastes exhibited a shear thinning behaviour because the values of flow behaviour index (n) were less 1 for all pastes.

CONCLUSIONS

The shear viscosity of the suspension decreased with increased loading of silicone oil.

At a certain particle size distribution the shear viscosity of paste increases with the increase of solid concentration.

It was found that the pastes behaved as a non-Newtonian, shear-thinning fluid in the temperature range of 25-75 °C.

The extrusion behaviour of concentrated pastes was found to be strongly affected by slip at the wall at a

high shear stress.

All pastes were successfully described by the Herschel-Bulkley model.

The consistency coefficient of pastes increases greatly upon increasing the solid level and decreasing temperature.

TABLE 3
Model parameters calculated for the kaolinite/silicone oil AK 60 000 pastes.

Parameters			Rheological models												
Die dimension (L/D) (mm/mm)	Variable factors		Power Law			Casson			Bingham			Herschel-Bulkley			
			n	K (kPas ⁿ)	R ²	τ_0 (kPa)	μ_∞ (kPa s)	R ²	μ_∞ (kPa s)	τ_0 (kPa)	R ²	τ_0 (kPa)	K _H (kPas ⁿ)	n _H	R ²
16/1	Solid:liquid ratio (g::g)	75:25	0,4	10,9	0,98	35,1	0,09	0,89	0,16	73,5	0,83	13	21,1	0,3	0,994
		77:23	0,5	12	0,99	37,9	0,12	0,91	0,2	82,4	0,85	15	22,7	0,4	0,994
		80:20	0,3	44,8	0,99	94,9	0,08	0,9	0,21	147	0,83	16	55,7	0,3	0,998
16/1	Particle size (µm)	0-25	0,5	12	0,99	37,9	0,12	0,91	0,2	82,4	0,85	11	22,7	0,4	0,994
		25-50	0,5	9,1	0,99	25,6	0,11	0,91	0,18	60,3	0,84	16	23,7	0,3	0,999
		50-75	0,5	6,2	0,99	20,4	0,12	0,92	0,18	52,8	0,87	19	24,5	0,4	0,999
16/1	Temperature (°C)	25	0,5	12	0,99	37,9	0,12	0,91	0,2	82,4	0,85	11	22,7	0,4	0,994
		50	0,5	8,9	1	21,2	0,12	0,96	0,19	50,2	0,91	9	14,8	0,4	0,996
		75	4,4	0,5	1	11,4	0,1	0,99	30,35	0,2	0,97	7	4,9	0,5	0,995

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REFERENCES

- [1] Lam, Y.C., Wang, Z.Y., Chen, X., Joshi, S.C., Wall slip of concentrated suspension melts in capillary flows, *Powder Technology* 177 (2007) 162-169.
- [2] Markgraf, W., Horn, R., Peth, S., "An approach to rheometry in soil mechanics-Structural changes in bentonite, clayey and silty soils", *Soil&Tillage Research*, (2006) 91, 1.
- [3] Khan, A. U., Briscoe B.J., Luckham P.F., "Evaluation of slip in capillary extrusion of ceramic pastes", *Journal of the European Ceramic Society*, (2001) 21, 483.
- [4] Amarasinghe A. D. U. S. and Wilson, D. I., "Interpretation of paste extrusion data, *Trans IChemE*, Vol 76, Part A, January 1998.
- [5] Benbow, J. J. "The dependence of output rate on die shape during catalyst extrusion", *Chemical Engineering Science* (1971) 26, 1467-1473.
- [6] Li, Y.Y. and Bridgwater, J., "Prediction of extrusion pressure using an artificial neural network", *Powder Technology* (2000) 108, 65-7
- [7] Martin, P. J. and Wilson, D. I., Bonnett, P. E., "Rheological study of a talc-based paste for extrusion-granulation", *Journal of the European Ceramic Society*, (2004) 24, 3155.
- [8] Gülmüş, S. A., Yılmaz, Ü., "Effect of volume fraction and particle size on wall slip in flow of polymeric suspensions", *Journal of Applied Polymer Science*, (2005) 98, 439.
- [9] Grim, R.E., *Clay Minerology*, 2nd ed., McGraw-Hill, NY, 1968, pp.596.
- [10] Darley, H.C.H., Gray, G.R., *Composition and Properties of Drilling and Completion Fluids*, 5th edn., Gulf Publ. Co., TX, USA, 1988.
- [11] Doğan, M., Yılmaz, Z., Alkan, M., "Characterization and Rheological Properties of Kaolinite-Silicon Oil Pastes", *Ind. Eng. Chem. Res.*, (2008) 47, 8218.
- [12] Graczyk, J., Buggisch, H., Güner, S., "Wall Slip Behavior of Alumina-Silicon Oil Pastes During Extrusion", *Chem. Eng. Technol.* (2001), 24 (5), 489-491.
- [13] Chandler, H. W.; George, S. D.; Liddle, J. "Deformation and Flow of Stiff Pastes: Review of Rheology of Some Soft Solids", *Br. Ceram. Trans.*,(2002), 101 (2), 47.
- [14] Buggisch, H.; Graczyk, J. *Rheometrical Methods for Studying Flow Behavior of Pastes*. International Congress for Particle Technology; Nuremberg, Germany, March 2001.
- [15] Vand, V., 1948. Viscosity of solutions and suspensions I. Theory. *J. Phys. Colloid Chem.* 52, 277-299.
- [16] Khan, A. U., Briscoe B.J., Luckham P.F., "Evaluation of slip in capillary extrusion of ceramic pastes", *Journal of the European Ceramic Society*, (2001) 21, 483.
- [17] Benbow, J. J., Blackburn, S., Mills, H., "The effects of liquid-phase rheology on the extrusion behaviour of paste", *Journal of Materials Science*, (1998) 33, 5827.
- [18] Lin, H.W., Chang, C.P., Hwu, W.H., Ger, M.D., "The Rheological Behaviours of

- Screen-Printing Pastes” *Journal of Materials Processing Technology*, (2008) 197, 284-291.
- [19] Doğan, M., Graczyk, J., Buggisch, H., “Kapillarrheometrische Charakterisierung der Extrusionseigenschaften Von Pasten”. *Wissenschaftliche Abschlussberichte 38; Internationales Seminar, Universität Karlsruhe, Karlsruhe-Germany*, (2003).
- [20] Paradkar, A., Kelly, A., Coates, P., York, P., “Shear and Extensional Rheology of Hydroxypropyl cellulose Melt using Capillary Rheometry” *Journal of Pharmaceutical and Biomedical Analysis* (2009) 49, 304-310.
- [21] Barroso, E.G., Duarte, F.M., Couto, M., Maia, J.M., “High Strain Rate Rheological Characterization of Low Viscosity Fluids”, *Polymer Testing* (2010) 29, 419-424.
- [22] Alkan, M., Kalay, B., Doğan, M., Demirbaş, O., “Removal of copper ions from aqueous solutions by kaolinite and batch design”, *J. Hazard. Mater.*, (2008) 153, 867.
- [23] Kakali, G., Perraki, T., Tsivilis, S., Badogiannis, E., “Thermal treatment of kaolin: The effect of mineralogy on the pozzolanic activity”, *Appl. Clay Sci.*, (2001) 20(12), 73.
- [24] Alkan, M., Yılmaz, Z., Hopa, Ç., Güler, H., “The effect of reaction temperature and time on the zeolitisation of natural kaolinite”, *Fresen Environ Bullet*, (2009) 18(3), 240-248.
- [25] Händle F. (Ed.), *Extrusion in Ceramics*, Springer, 2007, pp.175.
- [26] Bhattacharya, S.N., *Rheology: Fundamentals and Measurements*; Royal Melbourne Institute of Technology: Melbourne, Australia, 1997.
- [27] Daubert, C.R.; Foegeding, E.A. *Rheological Principles for Food Analysis*. In *Food Analysis*, 3rd ed.; Nielsen, S. S., Ed.; Kluwer Academic/ Plenum Publishers, nc.; New York, 2003, pp.507-508.
- [28] Tabilo-Munizaga, G., Barbosa-Canovas, G.V. *Rheology for the Food Industry*.
- [29] Skelland AHP, *Non-Newtonian Flow and Heat Transfer*, New York: John Wiley and Sons Inc; 1967.
- [30] Razavi, S. M. A., Najafi, M. B. H., Alae, Z., “The time independent rheological properties of low fat sesame paste/date syrup blends as a function of fat substitutes and temperature”, *Food Hydrocolloids*, (2007) 21, 198.
- [31] Mezger, T. G., *The Rheology Handbook*, Vincentz Network: Hannover, (2006).
- [32] Luckham, P.F., Rossi, S., “The colloidal and Rheological Properties of Bentonite Suspensions”, *Advances in Colloid and Interface Science* 1999, 82, 43-92.
- [33] Benbow, J. J., Bridgewater J., *Paste Flow and Extrusion*, Clarendon Press, Oxford, (1993), s. 28.
- [34] Rha, C., *Theories and Principles of Viscosity Theory in Determination and Control of Physical Properties of Food Materials*, Ed. Reidel, Inc. Dordrecht, The Netherlands, , s. 7-249, 1975.
- [35] Götz, J., Kreibich, W. and Peciar, M., “Extrusion of pastes with a piston extruder for the determination of the local solid and fluid concentration, the local porosity and saturation and displacement profiles by means of NMR imaging”, *Rheol. Acta*, 2002, 41(1-2), 134-143.
- [36] Barnes, E.C., Wilson, D.I. and Johns, M.L., “Velocity profiling inside a ram extruder using magnetic resonance (MR) techniques”, *Chem. Eng. Sci.*, 2006, 61(5), 1357-1367.
- [37] Bingham, E.C., *Fluidity and Plasticity*, McGraw-Hill, 1922.
- [38] Metzner, A.B., *Non-Newtonian Technology: Fluid Mechanics and Transfers*, Adv. Chem. Eng., Acad. Pres, 1956.
- [39] Casson, N., in: C.C. Mills (Ed.), *Rheology of Disperse Systems*, Pergam, 1959, p.84.
- [40] Herschel, W., Bulkley, J., *Test of Materials*, Proc. Am. Soc., 26 (1926) 621.
- [41] Rao, M.A., Tattiyakul, J., “Granul Size and Rheological Behaviour of Heated Tapioca Starch Dispersions”, *Carbohydr. Polym.*, 1999, 38, 123.

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THE INFLUENCE OF THE EM-A PREPARATION ON THE PROPERTIES OF STRUCTURE IN ARABLE MINERAL SOILS

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ABSTRACT

The paper presents results of the research which tested the influence of two doses of activated form of microbial inoculants known as “Effective microorganisms” (EM-A) on the properties of epipedones of two lessive soils (Luvisols). “The soil primary aggregates models” (in the further text they are called “aggregates”) in the form of intact soil cores of 1 cm³ volume was taken (cut) from experimental fields in two consecutive years: 2008 and 2009. Apart from basic soil physical properties such as: texture, and porosity other soil traits as its static and dynamic water-resistance, secondary aggregation after static and dynamic water action, the compression strength of aggregates, maximal and minimal capillary water capacity, swelling of the aggregates and the speed of maximal and minimal capillary rise were also determined. The addition of EM-A into the soil had a visible, yet minor influence on parameters of the aggregate structure. The positive influence of EM-A addition on secondary aggregation, both after static and dynamic water action was noticed. In the case of other soil structure parameters, application of the EM-A preparation seems groundless.

KEYWORDS:

EM-A preparation, water resistance, secondary aggregation

INTRODUCTION

Microbial communities can be considered as architects of soils [1]. Other authors noticed that the soil matrix as well as chemical and physical properties of soils, like quality and amount of soil organic matter have an influence on the microbial communities [2]. What is emphasized in the literature, is the influence of microorganisms on the

soil structure properties [3]. Schluz *et al.* [4] noticed a loss of soils quality. The authors underline a need to develop a strategies for sustainable protection of soils. Application of bio-fertilizers are frequently recommend for improving biological, and physical properties of soil as well as for sustainable agriculture. [5,6]. One of the world’s most commonly used biofertilizers are effective microorganisms [7]. The author claims that EM is a specially selected composition of naturally occurring microorganisms. Among others, the inoculums consists of lactic acid bacteria, photosynthetic bacteria, actinobacteria and a filamentous fungus. The aim of the study was the assessment of the effects of EM-A preparation on the physical features of structure of two arable mineral soils under field conditions.

MATERIAL AND METHODS

The object of the research was an individual farm in Poland, in Małachowo (Wielkopolskie voivodeship, gnieźniński district, 52°26’56”N, 17°44’51”E, Witkowo commune – 52°26’20”N, 17°46’27”E). The field experiment, was conducted in this farm, within its natural production cycle, in 2008 - and 2009 years. Two arable fields were used (field A and field B) which were located on broad areas of Luvisols. Texture of the arable-humus horizon of field A was characteristic to sandy loam (SL), whereas that of the corresponding level of field B – to loamy sand (LS) [8] (Table 1). In both experimental fields, (300m long and 60m wide), three stripes were marked: A0, A0+EM1, A0+EM2 and B0, B0+EM1, B0+EM2. Soil aggregates were collected from two depths: 7 and 20 cm.

A0 and B0 were the control areas – without EM-A addition. Two other stripes were sprayed with various doses of the preparation (EM-A = 1 dm³ of EM1 concentrate + 1 dm³ of treacle + 20 dm³ of water). EM1 was produced by *Greenland*