

# Characterization and Rheological Properties of Kaolinite–Silicon Oil Pastes

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A description of experiments carried out to determine the effect of some parameters on the extrusion behavior of particulate pastes is given. The effects of particle size, solid/liquid ratio, temperature, shear rate, and die dimensions on rheological behavior of kaolinite–silicon oil pastes were investigated. These pastes were prepared by mixing kaolinite powder with chosen amounts of silicon oil. Capillary rheometry was used to determine the extrusion properties of the pastes. All pastes were found to exhibit non-Newtonian, pseudoplastic behavior under all experimental conditions. The viscosity decreased with an increase in temperature and particle size and with a decrease in solid/liquid ratio. The whole paste was properly described by the Herschel–Bulkley model and exhibited a shear thinning behavior. The yield stress increased with an increase in particle size and kaolinite amount and a decrease in temperature, reflecting the increase in paste viscosity. The flow behavior index,  $n$ , varied in the range of 0.077–0.534. The Arrhenius model gave a good description of the temperature effect on the shear viscosity of paste, and the  $E_a$  value appeared in the range of 7.4–32.6 kJ/mol.

## 1. Introduction

Concentrated suspensions occur in numerous particle-forming applications in ceramic, food, and pharmaceutical processing.<sup>1</sup> A paste can be described as a very dense suspension of solid particles in a viscous liquid phase with sufficiently high solids volume fraction to render the material stiff but readily deformable.<sup>2</sup> Pastes are often intermediate products but are also produced by the chemical industry as end products.<sup>3</sup> The rheological characteristic of a paste changes depending upon the composition, concentration, particle size, temperature, and formulation. For example, a paste made from wheat flour and water will naturally have somewhat different rheological character from a ceramic paste made of a ceramic powder and other ingredients. Similarly, different ceramic pastes are likely to show different rheological behavior, depending upon the composition of the paste. A typical ceramic paste comprises ceramic particles, dispersing agents, binders, plasticizers, and liquid phases. The need to include these ingredients arises from the fact that ceramic powders cannot always be effectively extruded in their dry powder form, as they offer a very high friction at the interface of the bulk material and the processing engine. Also, the submicron powders usually form agglomerates of a nonhomogeneous nature and do not produce a coherent dispersed mass that is suitable for useful processing. Therefore, a liquid, which functions as a continuous medium, is a necessary component and provides both a vehicle to homogenize the particles and also the medium to incorporate the necessary processing aids, such as the binders and dispersants.<sup>4</sup> Paste flow and the material properties are crucial factors for product quality at late technological progress.<sup>5</sup> Extrusion is commonly utilized to achieve the desired shape, and finds application in the production of a range of goods, including catalyst supports, ceramic items, foods, and electronic components. Rheological studies of pastes are required to develop novel extrusion applications and to improve product quality and process optimization.<sup>2</sup>

The extrusion process has been well recognized for engineering objects having extended length with uniform cross section.

The conventional extrusion process requires the use of organic vehicle as binders to impart fluidity for assembling of ceramic powder into a shape.<sup>6</sup> Particle–particle interactions play an important role in paste flow behavior.<sup>3</sup> Since the flow of dry particles is a frictional process, a liquid phase is invariably added to form an extrusion paste.<sup>7</sup> The addition of a lubricating fluid phase helps to overcome the interparticle frictional interactions that would otherwise require prohibitively high tooling and energy costs. This liquid phase is commonly an aqueous solution of a rheology modifier such as clay or methyl cellulose, although in the case of some ceramic injection molding processes molten polymers are used.<sup>3</sup>

In modern ceramic industry, reducing the cost of raw materials and use of alternative raw materials in order to obtain energy economy have gained great importance. Kaolinite is a mineral that has a wide variety of applications in industry, particularly in ceramics, in medicine, on coated paper, as a food additive, in toothpaste, as a light diffusing material in white incandescent light bulbs, and in cosmetics. It is also used in most paints and inks. Kaolinite is an inexpensive clay that can improve the properties of the material in which it is dispersed, provided that a stable dispersion is formed. It may be added to bulk out a material, to modify its flow properties, or to modify the final product properties.<sup>8</sup> Understanding the relationships between paste formulation, processing conditions, and the final product properties would enable better quality control and product design.

A complete knowledge of the material's rheology would allow one to describe the extrusion behavior and also, by considering the appropriate boundary conditions, predict a material's behavior during a given extrusion process. Pastes are an intimate mixture of particulate solids and liquids. The rheological behavior of pastes is not nearly so well defined as that of pure fluids, be they Newtonian fluids or macromolecular-based, non-Newtonian fluids. Numerous empirical and theoretical models have been proposed to describe the rheological behavior of pastes.<sup>9</sup> 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 behaviors can be extremely complex due to the relative movement of the liquid phase within the solid matrix.<sup>10</sup>

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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.<sup>3</sup> A capillary rheometer is generally used to characterize the rheological properties of a wide variety of fluids. Capillary extrusion flow has been very often utilized for a wide variety of pastelike materials in an attempt to characterize their bulk intrinsic rheology as well as their wall interface boundary conditions.<sup>4</sup> The technique has proved particularly advantageous in characterizing high-viscosity materials such as polymer melts and suspensions.<sup>3</sup>

Rheological properties give important information about physical and chemical properties of materials. Most ceramic pastes behave as a partly viscous, elastic, and plastic fluid because they consisted of a liquid phase, ceramic particles, and polymer additives. Although, ceramic pastes are difficult to analyze rheologically, it is important to investigate the rheological performance to determine the optimum condition for extrusion.<sup>11</sup> The ceramic paste flow is different from molten polymers or metals, because the flow behavior is dependent on the properties of solid and liquid components. The shear stresses in the pastes during capillary flow change systematically when the amounts of liquid phases are altered. In general, the behavior of the particulate pastes during extrusion depends on (1) the amount of liquid present in excess of that needed to fill the interparticle voids, (2) the rheological properties of their liquid phases, (3) the interference between particles, (4) the extrusion condition, and (5) the time scale of the experiments.<sup>12</sup> For a variety of application fields and as its industrial importance increases, the determination of the rheological properties of kaolinite is necessary. As mentioned above, there are a lot of application fields of kaolinite, and day-by-day the variety of its application field increases. The fact that kaolinite determines the rheological properties will cause new application areas of this clay. The purpose of this work was to investigate (1) the time-dependent rheological behavior of kaolinite–silicon oil pastes and (2) the influences of die dimensions, particle size, solid/liquid ratio, temperature, shear time, and shear rate on flow properties. A silicon oil that is well-known as a dielectric liquid was used as the suspending liquid medium.<sup>13</sup> Polydimethylsiloxane (PDMS) is a commercially available physically and chemically stable silicone rubber. Polydimethylsiloxane is the most widely used silicon-based organic polymer and is particularly known for its unusual rheological (or flow) properties. Its applications range from contact lenses and medical devices to elastomers. PDMS is optically clear and is generally considered to be inert, nontoxic, and nonflammable. The advantages of PDMS include low weight, good thermal stability, good weatherability, and, most of all, 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. A detailed examination of the rheology under shear conditions was also carried out. The suitability of the rheological models employed to fit the shear rate and shear stress data has also been evaluated. The resulting ceramic composites were also characterized by thermogravimetry (TG), differential thermal analysis (DTA), and X-ray diffraction (XRD).

## 2. Material and Methods

**2.1. Materials.** Silicon oil was supplied by Wacker-Chemie GmbH (trade name silicon oil AK 1 000 000). Kaolinite was obtained from Kale Maden (Balikesir, Turkey). Kaolinite samples were first dried, crushed in a ball mill, and sieved to

**Table 1. Some Properties of Silicon Oil AK 1 000 000 Used in This Study**

property	inspection method	value
density at 25 °C	DIN51757	ca. 0.97 g/cm <sup>3</sup>
flash point	ISO 2592	>320 °C
ignition temperature (liquids)	DIN51794	ca. 450 °C
surface tension at 25 °C		0.022 N/m
viscosity, kinematic at 25 °C	DIN53018	ca. 1 000 000 mm <sup>2</sup> /s

**Table 2. Parameters Investigated in the Experiments for Different Kaolinite–Silicon Oil Pastes<sup>a</sup>**

particle sizes (μm)	solid/liquid ratios	temperature (°C)
0–25 <sup>b</sup>	70	25
25–50 <sup>b</sup>		
50–75 <sup>b</sup>		
0–25	60 <sup>b</sup>	
	70	
	75 <sup>b</sup>	
	80 <sup>b</sup>	
0–25	70	25
		50
		75

<sup>a</sup> Die dimensions [ $L$  (mm)]/ $D$  (mm)] were 8/0.5, 16/1, or 32/2.

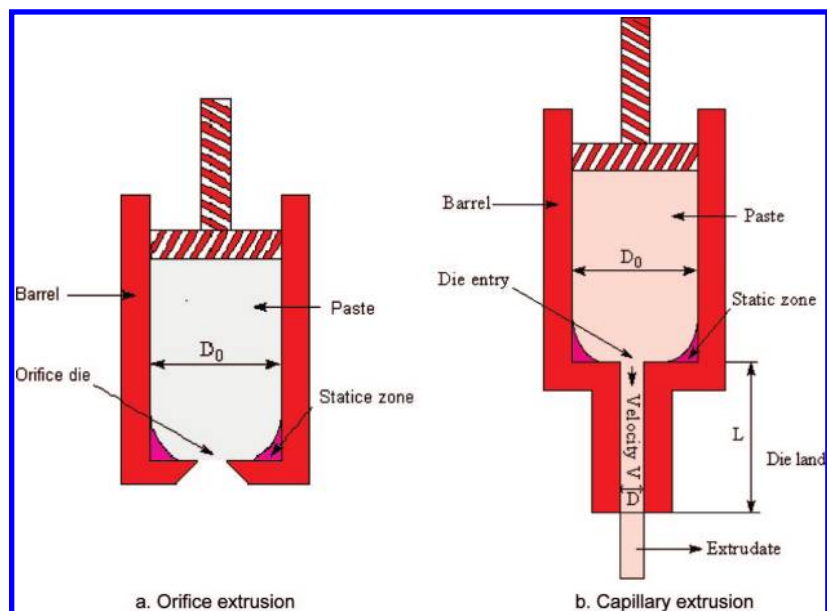
<sup>b</sup> Pastes prepared in the experiments.

obtain a particle size between 0 and 25, 25 and 50, and 50 and 75 μm, corresponding to upper- and lower-size fractions. The model pastes consisted of kaolinite particles with a particle size 0–25 μm, except the experiments in which the effect of particle size was investigated, and silicon oil with a molecular weight MW 200 000 and limiting viscosity at zero shear rate  $\eta_0 = 1170$  Pa s was used. Some properties of silicon oil are given in Table 1.<sup>14</sup>

**2.2. Preparation of the Pastes.** Kaolinite powders were mixed in a kneader (IKA HKD-T0,6 kneader) and then the liquid phase was added. The silicon oil based pastes were mixed batchwise in the kneader for 4 h to achieve better homogenization. All the pastes were prepared by the 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 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–silicon oil pastes were prepared in different silicon oil content in the range of 20–40 wt % and in different particle sizes in the range of 0–25, 25–50, and 50–75 μm.<sup>15</sup> Table 2 shows the compositions and particle sizes of the six pastes prepared for these experiments with the dies of various  $L/D$  ratios, respectively.

**2.3. Characterization of Pastes.** X-ray diffraction measurements of kaolinite, silicon oil, and paste were performed using an Analytical Philips X'Pert-Pro X-ray diffractometer equipped with a back monochromator operating at 40 kV and a copper cathode as the X-ray source ( $\lambda = 1.54$  Å). A simultaneous thermogravimetric and differential thermal analysis (TG/DTA) system was applied in order to observe the reactions taking place during the thermal treatment of the samples. A Perkin-Elmer Diamond DTA/TG instrument was used. Powdered samples were heated from ambient to 1100 °C at a rate of 20 °C/min under nitrogen atmosphere.

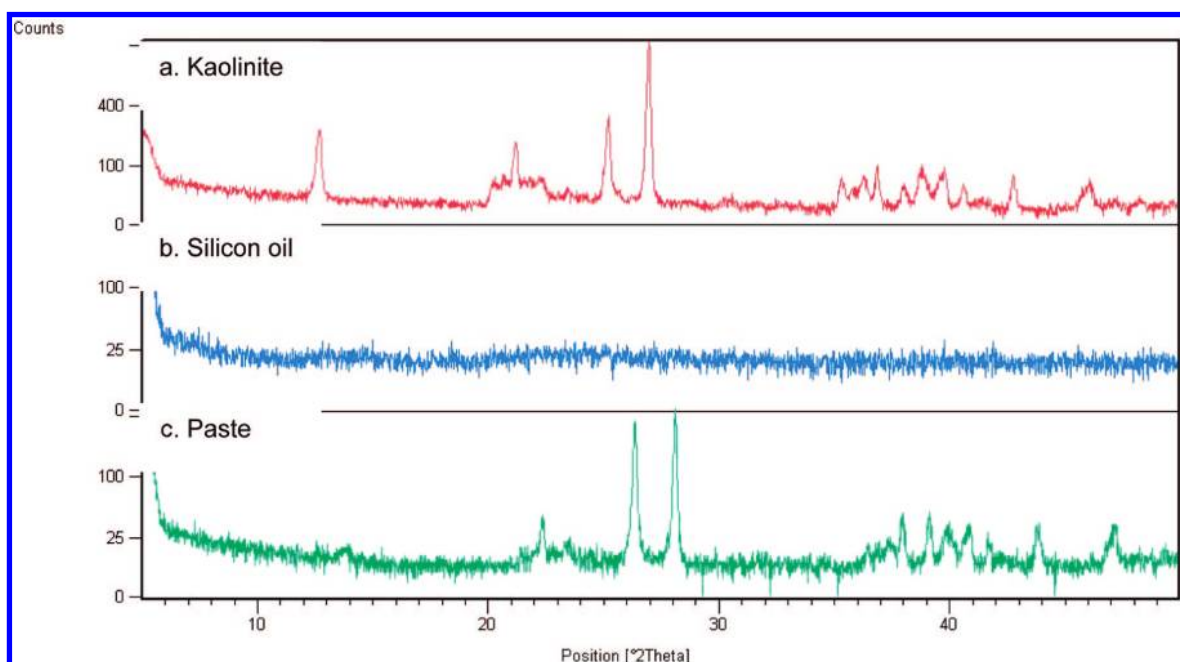
**2.4. Rheological Measurements.** The most important point for extrusion systems was a characterization technique based



**Figure 1.** Schematic representation of the cross section of the basic elements of a capillary rheometer apparatus.

on extrusional flow. Capillary rheometry is a standard experimental technique for paste characterization. In this study, measurements were conducted using a high-pressure capillary rheometer (Rosand RH10). Figure 1 shows a cross-section of such a rheometer with barrel diameter  $D_0$ , die land diameter  $D$ , and die land length  $L$ . The region upstream of the constriction, where bulk deformation and extensional flow occurs, is known as the die entry region, and sometimes a static zone of paste forms in the corner of this region. The die entry region may extend slightly into the die land, but usually only to a negligible extent. The flow within the die land is usually pure shear and laminar, with mean velocity  $V$ ; it may be considered as capillary flow. The force required to extrude the material through the die is expressed as an average extrusion pressure,  $P$ .<sup>2,15</sup>

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 orifices and capillaries of diameters ranging from 0.5 to 2.0 mm. The lengths of the capillaries were 8, 16, and 32 mm. The barrel of the extruder was completely filled with the paste before every experiment. The ram forces paste to flow with a volumetric rate from the barrel into the die land. Capillaries of different size were attached to the bottom of the barrel and the ram was moved downward by moving the top cross head of machine. All pastes were extruded from capillary rheometer at a wide shear rate range. The shear viscosity and shear stress of pastes as a function of shear rate were measured.<sup>15</sup> Each measurement was repeated three times using the same die and paste; hence, the reported



**Figure 2.** XRD diffractograms of kaolinite, silicon oil, and kaolinite–silicon oil paste.

value is the average of three measurements. Error bars for statistical evaluation are given in the figures.

### 3. Results and Discussion

#### 3.1. Characterization of Pastes. 3.1.1. XRD Analysis.

XRD analysis can provide important information about the pure clay minerals and their composite or paste samples. The XRD spectra of kaolinite (Figure 2a), silicon oil (Figure 2b), and paste (Figure 2c) are illustrated in Figure 2. Characteristic maxima of raw kaolinite were observed at  $2\theta = 12.42^\circ$ ,  $20.89^\circ$ ,  $24.93^\circ$ , and  $26.68^\circ$  (very intense, sharp, and narrow), which corresponded to the basal spacing of kaolinite. After silicon oil intercalation, we observed that the XRD pattern of the original kaolinite was dramatically modified. The peaks at  $2\theta = 20.89^\circ$ ,  $24.93^\circ$ , and  $26.68^\circ$  in the original kaolinite greatly shifted in the intercalates to small reflection angles ( $2\theta = 22.37^\circ$ ,  $26.38^\circ$ , and  $28.12^\circ$ ) produced by the presence of silicon 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–silicon oil intercalating. The diffraction pattern shown in Figure 2c showed that most kaolinite layers were delaminated, whereas some layers retained their basal spacing. These results show that the kaolinite–silicon oil composite was obtained because of the dispersing of kaolinite into the polymer matrix of silicon oil.

**3.1.2. DTA/TG Analysis.** We investigated the thermal properties of the kaolinite and kaolinite–silicon oil paste using TGA and DTA methods. Simultaneous DTA/TG can differentiate between peaks associated with mass loss and those associated with phase transition. DTA has been used very widely in the study of thermal reactions of clay minerals. 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.<sup>8,16,17</sup> In the first step of transformation in the range of 400–620 °C, kaolinite, due to dehydroxylation and predehydratation, was transformed to metakaolinite phase with loss of structural hydroxyl groups. When the kaolinite is heated, the adsorbed water is liberated at above 100 °C and the weakest part of the chemical bond is broken or perturbed and then dehydroxylation takes place at 400–600 °C range. In the second step, metakaolinite decomposes and forms spinel phase generally during heating around the exothermic peak temperature. The exotherm peak in the range of 980–1020 °C is related to crystallization of Al–Si spinel phase at the medium scale of temperature. DTA spectrum of paste, different from that of natural kaolinite, has shown an endotherm peak about 220 °C. This peak may be due to the carbonization or the combustion of organic compounds due to the loss of carbon, hydrogen, and oxygen.<sup>18</sup>

TGA data indicated the sample started to lose weight near 50 °C and reached a constant weight at around 800 °C. As seen from TG and d(TG) curves of kaolinite in Figure 4, dehydroxylation of kaolinite results in a mass loss of 11.6%. In the case of paste, there are three weight loss stages, viz., initial gradual weight loss below 100 °C, comparatively sharper weight loss between 100 and 400 °C, and a sharp loss of weight between 400 and 800 °C. Below 100 °C, the weight loss is due to the evaporation of water. The weight loss of about 28.5% in the temperature region 50 and 400 °C is the most predominant one and is due to the dehydroxylation of kaolinite and carbonization or combustion of organic compounds. There is 5.7% mass loss in the temperature range of 400–800 °C. The total mass loss

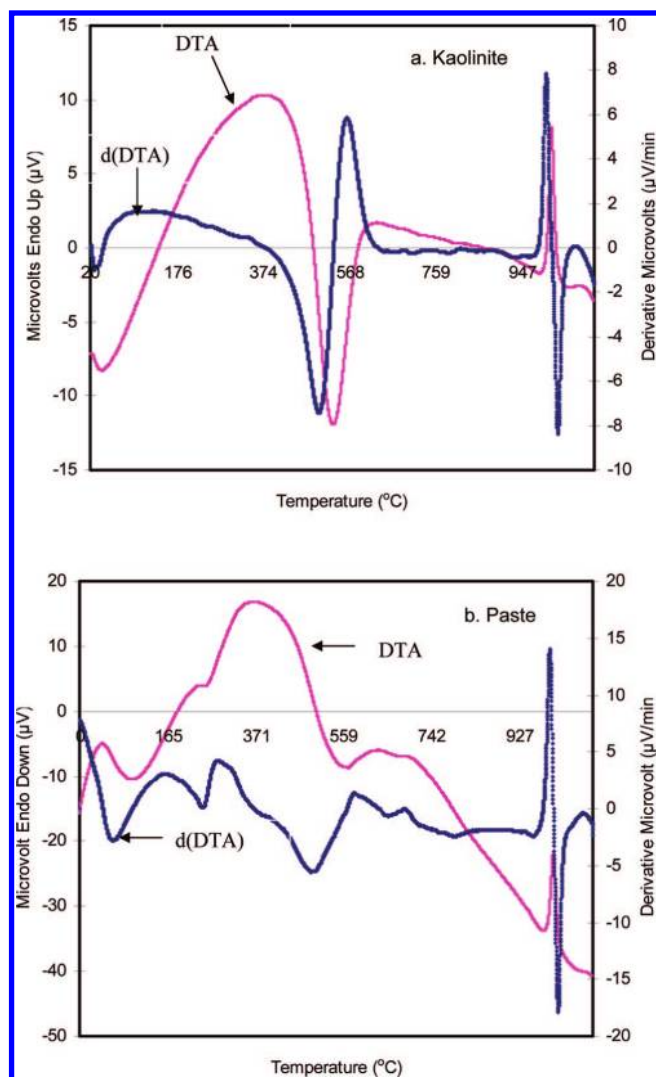


Figure 3. DTA spectra of kaolinite and paste.

for paste is 34.2%. It may be noted here that there is no sharp loss of weight at the high-temperature region.

#### 3.2. Rheological Characterization of Pastes. 3.2.1. Time-Independent Behavior.

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 behavior 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 behavior of these materials under applied stresses classifies them as Newtonian or non-Newtonian, a classification that is based on their stress–strain relationship. The flow behavior of a material during processing may vary significantly, because the consistency and composition of the material could be drastically altered due to mixing, heating, cooling, compounding, aeration, homogenization, crystallization, etc.<sup>19</sup> The majority of the pastes do not show Newtonian flow behavior. 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. In such a case, the fluid flow is time-independent. Time-independent deviation from ideal Newtonian behavior will cause the relationship between shear stress and shear rate to be nonlinear. The time-independent shear stress of kaolinite–silicon oil paste was determined at constant shear rates of 20, 50, and 100 s<sup>-1</sup> for two dies. Data obtained for the paste at 25 °C are

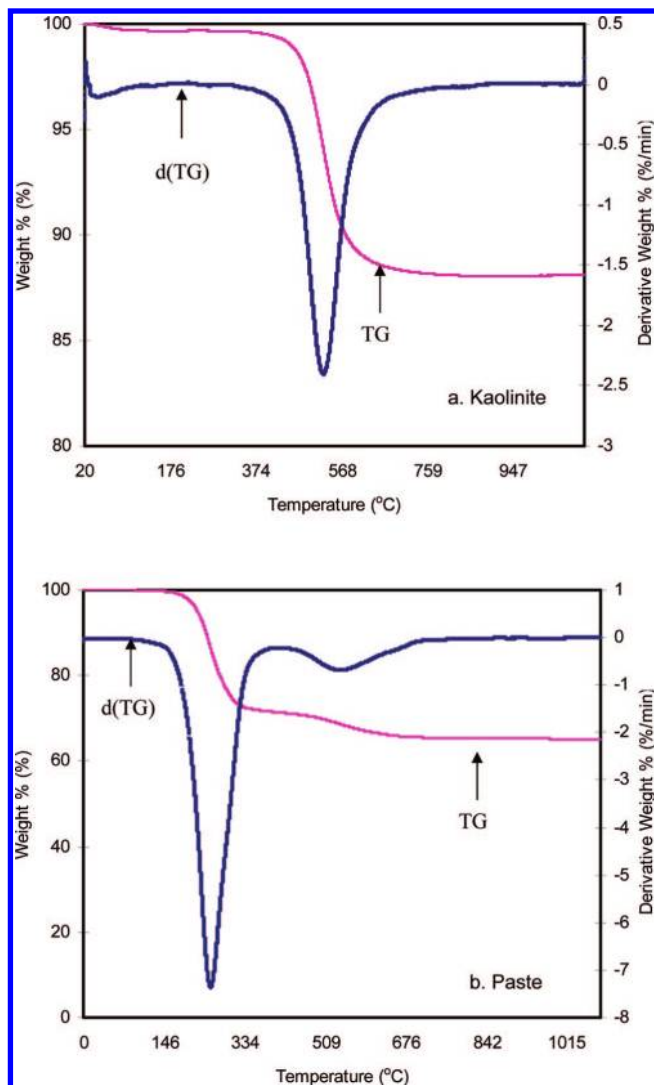


Figure 4. TG spectra of kaolinite and paste.

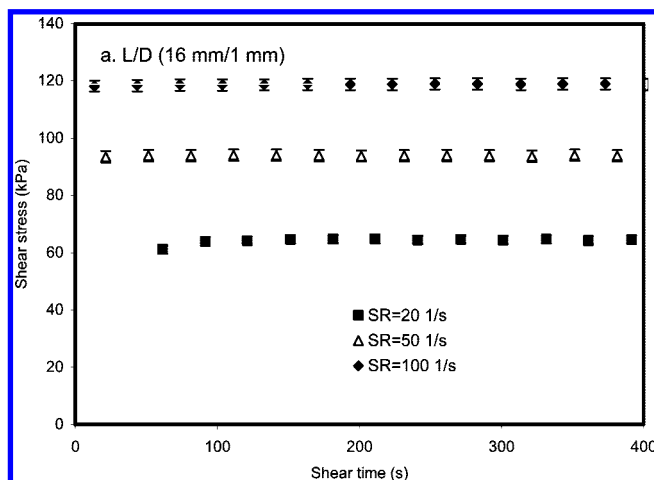


Figure 5. Time-independent flow behavior of kaolinite-silicon oil paste.

shown in Figure 5. At a constant shear rate, the shear stress remains constant with increasing shearing time. This has shown that paste flow is time-independent. When the material exhibits a diminish in viscosity as shear rate increases, it is called shear thinning or pseudoplastic. Pseudoplasticity is a time-independent properties.<sup>20,21</sup>

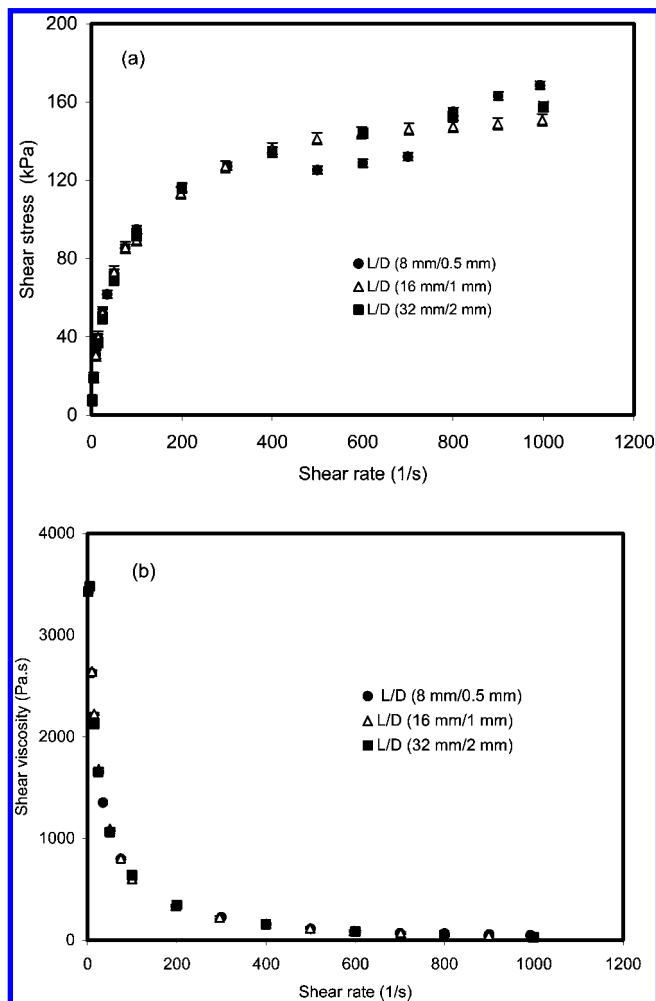


Figure 6. The plots of shear stress (a) and shear viscosity (b) versus shear rate for paste with a solid/liquid ratio of 70 and 0–25  $\mu\text{m}$  particle size.

**3.2.2. Flow Behavior of Paste.** The behavior of shear stress of pastes as a function of shear rate is shown in Figure 6a. Newtonian fluids have a straight line relationship between shear stress and shear rate with a zero intercept. All fluids that do not exhibit this behavior may be called non-Newtonian.<sup>22</sup> As seen from Figure 6a, flow plots of shear stress versus shear rate do not exhibit a linear relationship. In this case, it can be said that paste exhibits non-Newtonian behavior. A non-Newtonian fluid is a fluid in which the viscosity changes with the applied strain rate, as seen from Figure 6b. It is evident from the figure that the shear viscosity of paste decreased with increasing shear rate. This figure also confirmed that paste in the studied shear rate ranges show a non-Newtonian and pseudoplastic behavior.<sup>23</sup> The shear thinning fluid displays decreasing viscosity with increasing shear rate. The viscosity of shear thinning material is dependent on the degree of shear stress or shear rate. The terms, shear thinning and pseudoplastic, are identical in their meaning. 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.<sup>24</sup>

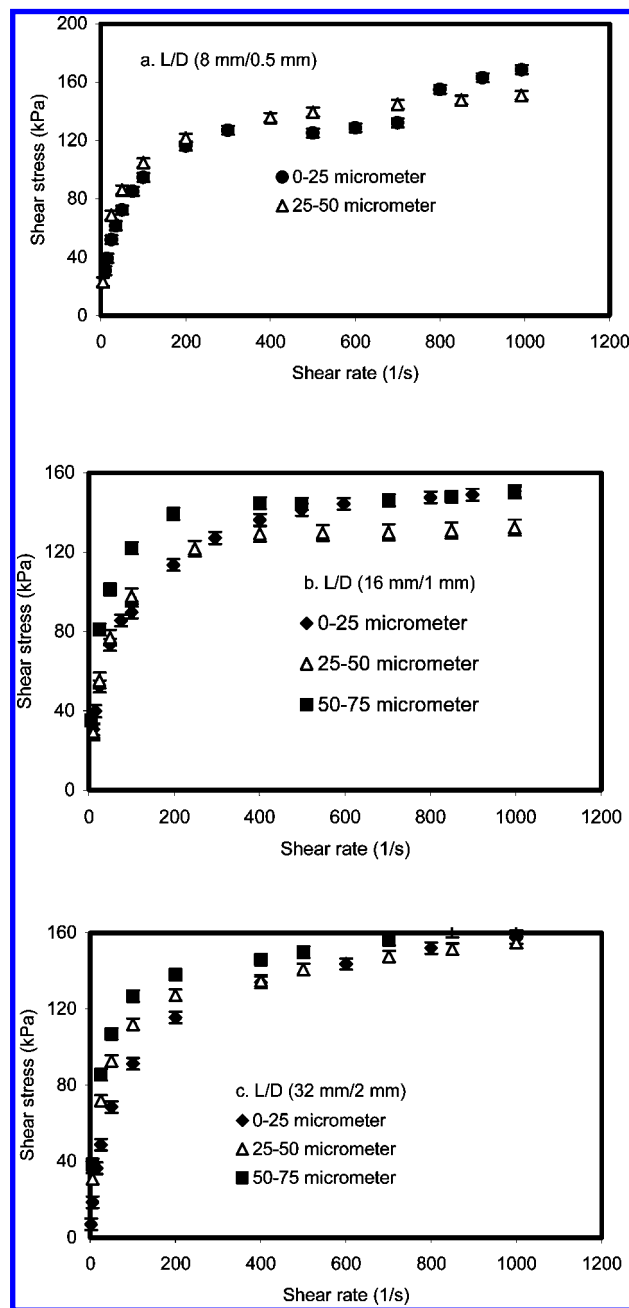
**3.3. Effect of Rheological Parameters.** Rheology is very useful for characterizing the morphology of suspensions. The die dimensions, particle size, concentration, temperature, speed, and particle-particle interactions can be studied by rheology.

We discuss the effect of some parameters on the rheological properties of kaolinite–silicon oil pastes in below.

**3.3.1. Die Dimensions.** As seen from Figure 6a, the values of shear stress are plotted as a function of shear rate for various capillary tube lengths and diameters, but for all of them,  $L/D$  ratios are the same. In order to model and/or optimize paste extrusion, one must have knowledge of the material's flow properties. The flow properties of the pastes, particularly the flow behavior of the wall-adjacent layers, i.e., the wall slip properties, are very significant in extrusion processes. Understanding the material's wall slip behavior inside a capillary or an extrusion die is particularly important, both for modeling the process and attaining good practical results. As seen from Figure 6, the capillary dies having the same length to diameter ( $L/D$ ) ratios have similar flow curves. This result shows that the wall slip behavior does not have any important effect on flow properties of the kaolinite–silicone oil paste.

**3.3.2. Particle Size Effect.** A number of factors influence the rheology of a suspension, including particle size, concentration, and the volume fraction of solids present. Here, we examine the relationship between rheology and particle size. Particle size and viscosity would also play an important role in the physical quality of paste and similar products.<sup>25</sup> To understand the role played by particle size in the rheology of kaolinite–silicon oil pastes, the solid particles were separated from the original kaolinite into three main groups, 0–25, 25–50, and 50–75  $\mu\text{m}$ . Suspensions of kaolinite–silicon oil pastes for each size group were prepared for rheological testing. 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. The effect of this change on the shear stress of the system across a range of shear rates is shown in Figure 7 as depending on die dimensions. 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 seen from Figure 7, it appears that particle size has negligible influence on the shear stress. This result probably indicates that particle interactions do not strengthen with increase in particle size. Viscosity decreased with increasing shear rates, showing only a marginal decrease thereafter. If viscosity remains constant as shear rate increases, a fluid is described as being Newtonian. Non-Newtonian fluids, which fail to exhibit this behavior, fall into one of two categories, shear thinning or shear thickening. With shear thinning materials, viscosity decreases as shear rate increases: application of shear leads to a breakdown of the material's structure so that it flows more readily. Most fluids and semisolids fall into this group. All the pastes showed shear thinning behavior and were pseudoplastic in nature.

**3.3.3. Solid/Liquid Ratio.** Figure 8 shows the flow functions for four kaolinite–silicon oil pastes as a function of solid concentration. The flow curve of the paste with 80% solids lies above that of the paste with 60% solids. The shape and magnitude of the flow curves of the pastes based on silicon oil are strongly dependent on the solid concentration. There is a slight increase in the shear stress while the solid/liquid ratio changes from 70 to 75 and from 65 to 70, whereas shear stress sharply increases when solid/liquid ratio increased from 75 to 80. This may be due to decreasing silicon oil amount. In the process, silicon oil behaves as dispersing agent, binder, and liquid phase. In the low-solid case, paste behaves as a semisolid material. In the high-solid situation,



**Figure 7.** Plots of shear stress versus shear rate for pastes with different particle sizes.

paste cannot be effectively extruded due to its increasing dry powder form, since this form has a very high friction between particles. Therefore, it can be said that shear stress will sharply increase with high solid amounts. The phenomenon of shear thickening was not observed in our systems. It can be seen that paste is a shear thinning fluid; the shear viscosity has shown an evident tendency to increase with the increase of the solid concentration in paste at each value of shear rate. This can be explained by the fact that the increase of kaolinite concentration results in an increase of the volumetric fraction of the solid particle phase and a decrease of the volumetric fraction of the effective flow phase.<sup>26</sup>

**3.3.4. Temperature.** Figure 9 shows the effect of temperature on the rheological properties of kaolinite–silicon oil pastes. At higher temperature, shear stress was lower than those values obtained at lower temperatures, as seen from Figure 9. The viscosity of a fluid is affected by the binding

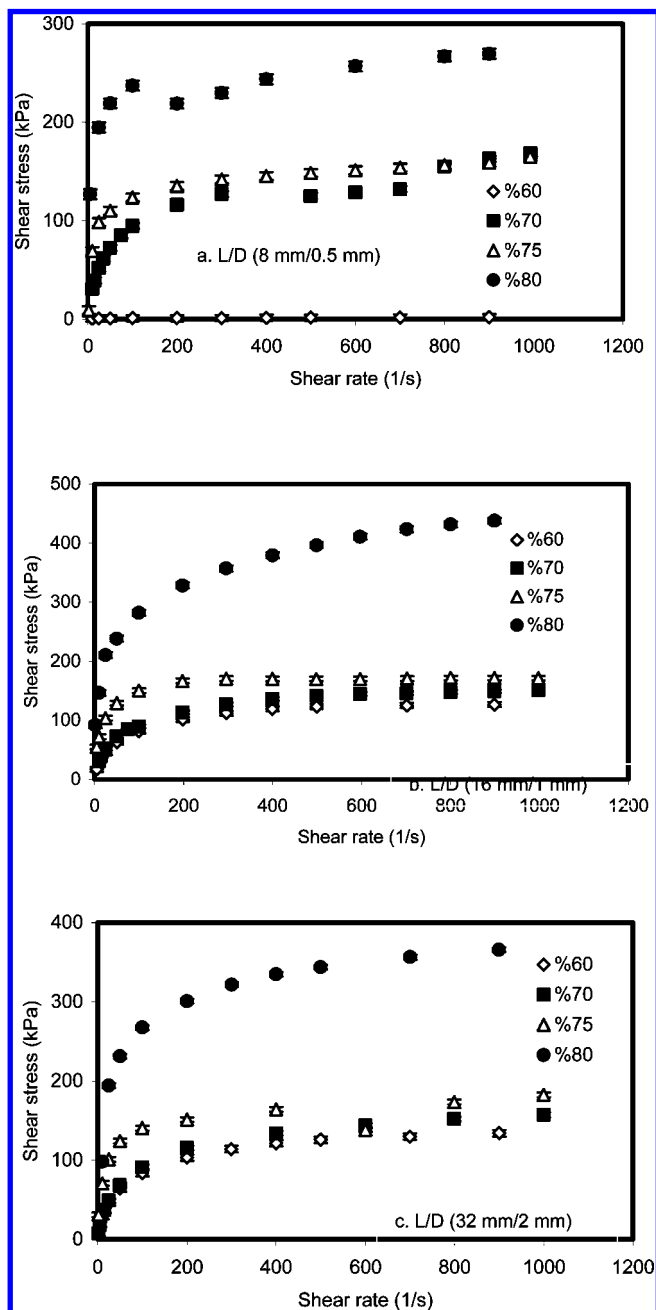


Figure 8. The plots of shear stress versus shear rate for pastes with different solid/liquid ratios.

between molecules that make up the solution or the relationship between the solvent and solute, both factors which are affected by solution concentration or temperature. In general, all curves exhibit pseudoplastic type behavior, with a linear section at moderate and high shear rates and a nonlinear section at low shear rates. When external energy is supplied by heating to increase temperature, it increases the energy of the molecules. The decrease in viscosity can be attributed to the increase in intermolecular distances, because of the thermal expansion caused by the increase in temperature.<sup>27</sup> Moreover, an increase in temperature softened the granules, and the stresses imposed on them were large enough for deformation and flow.

**3.4. Activation Energy.** The temperature effect on shear viscosity of pastes at a constant shear rate can be described by the Arrhenius equation,<sup>28</sup> in which the shear viscosity decreases as an exponential function with temperature

$$\eta = \eta_{\infty} \exp\left(\frac{E_a}{RT}\right) \quad (1)$$

where  $\eta$  is viscosity (Pa s),  $\eta_{\infty}$  is a material constant (Pa s),  $E_a$  is flow activation energy (J/mol),  $R$  is the gas constant (J/mol K), and  $T$  is the absolute temperature (K).<sup>29,30</sup>

The parameters of the Arrhenius equation describing the viscosity–temperature relationship were determined by linear regression. A linear relationship of  $\ln(\eta)$  versus  $(1/T)$  was observed. The high  $R^2$  values showed that the shear viscosities of pastes with temperature obey the Arrhenius-type equation. The Arrhenius model gave a good description of the temperature effect on shear viscosity at a different constant shear rates, as seen in Figures 10 and 11. From Figure 11, it was found that the flow activation energy values determined different constant shear rates such as 10, 50, 100, 200, and

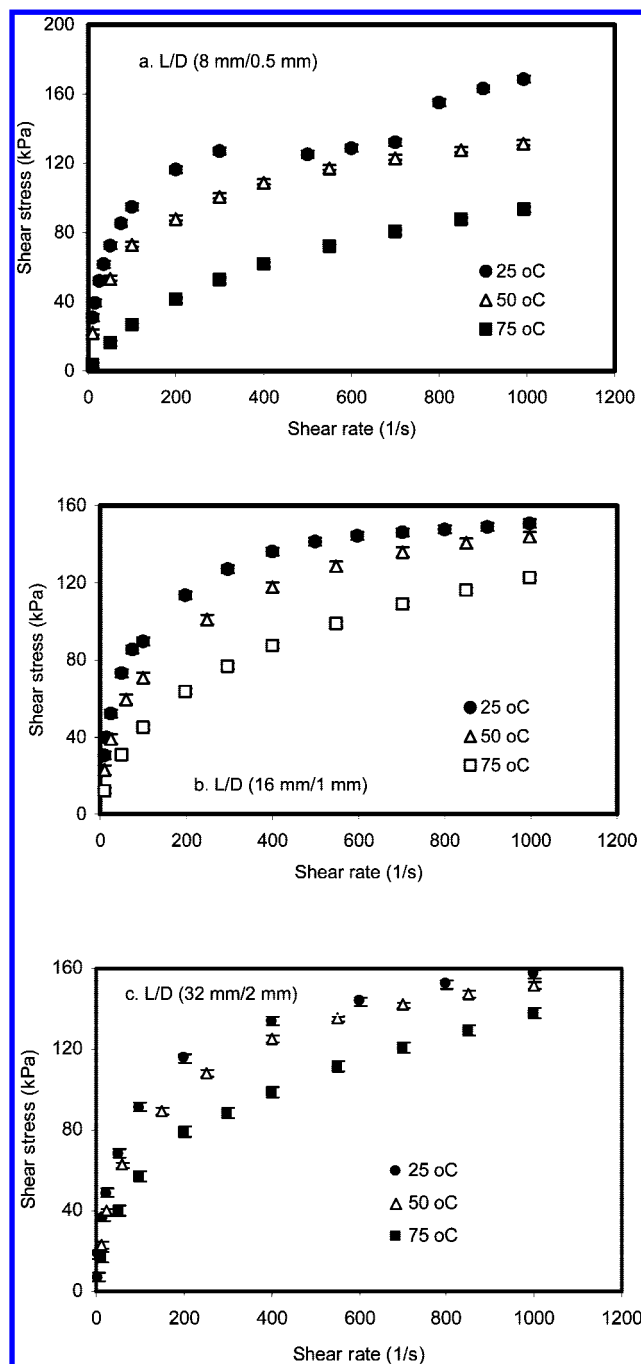


Figure 9. The plots of shear stress versus shear rate for paste at different temperatures.

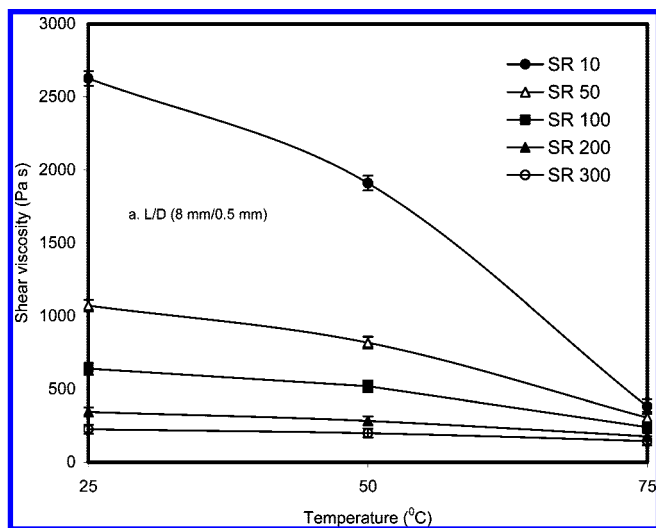


Figure 10. The plots of shear viscosity versus temperature for paste with 70 solid/liquid ratio.

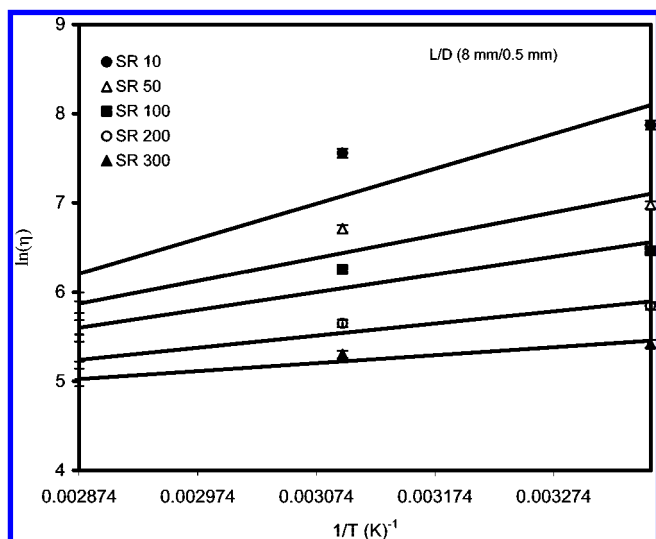


Figure 11. Arrhenius plots for different shear rates.

300  $s^{-1}$  using capillary die with 8 mm/0.5 mm  $L/D$  ratio were 32.6, 21.3, 16.6, 11.3, and 7.4 kJ/mol, respectively. According to Steffe,<sup>22</sup> in a system, higher  $E_a$  values indicate a more rapid change in viscosity with temperature. Activation energy is necessary for movement of a molecule, and as the temperature increases, the liquid flows more easily due to higher activation energy in high temperatures.<sup>31</sup> Besides, Rha<sup>32</sup> noted that the decrease in viscosity with increasing shear rate is related to the increasing alignment of constituent molecules.

**3.5. Rheological Models.** Numerous factors influence the selection of the rheological model used to describe flow behavior of a particulate fluid. Numerous empirical and theoretical models have been proposed to describe the rheological behavior of pastes. However, the most widely used equations are those of power law, Casson, Bingham, and Herschel–Bulkley. These models are also known as time-independent flow models.<sup>22</sup>

**3.5.1. Power Law Model.** Flow behavior was described by the fitting of the experimental data (shear stress–shear rate) with the power law model

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

where  $\tau$  is the shear stress (Pa),  $\dot{\gamma}$  is the shear rate ( $s^{-1}$ ),  $K$  is the consistency coefficient ( $Pa s^n$ ), and  $n$  is the flow behavior index (dimensionless).<sup>33</sup> The plot of  $\ln(\tau)$  against  $\ln(\dot{\gamma})$  for eq 2 should give a linear relationship, from which  $n$  and  $K$  can be determined from the slope and the intercept, respectively.

**3.5.2. Bingham Model.** Bingham plastic equation has been one of the simplest approaches used to compute  $\eta_B$  and  $\tau_0$  values. This equation is written as

$$\tau = \tau_0 + \eta_B \dot{\gamma} \quad (3)$$

where  $\tau$  is shear stress (Pa),  $\dot{\gamma}$  is shear rate ( $s^{-1}$ ),  $\tau_0$  is yield point (Pa), and  $\eta_B$  is characteristic viscosity for viscoplastic flow behavior ( $Pa s$ ).<sup>34</sup>

**3.5.3. Casson Model.** The Casson equation is given as

$$\tau^{0.5} = \tau_y^{0.5} + \eta_C^{0.5} \dot{\gamma}^{0.5} \quad (4)$$

where  $\tau$  and  $\tau_y$  are the shear stress (Pa s) and yield stress/shear stress (Pa s) at zero shear rate, respectively,  $\dot{\gamma}$  is the shear rate ( $s^{-1}$ ), and  $\eta_C$  is the viscosity at infinite shear rate (Pa s). This equation suggests that, if the square root of shear stress is plotted against the square root of the shear rate, a straight line will be obtained with intercept equal to the square root of yield stress and the slope gives the value of plastic viscosity. Most viscosity–shear rate data can be fitted successfully by the Casson equation. The two parameters  $\eta_C$  and  $\tau_y$  can be related to the product performance and composition variations.<sup>34</sup>

**3.5.4. Herschel–Bulkley Model.** The Herschel–Bulkley model is based on the combination of the Bingham and power law models. Thus, Herschel–Bulkley fluids exhibit a yield stress,  $\tau_{yp}$ , which is the minimum stress required for the material to deform. The existence of yield stress in semisolid materials is due to bonding and dry friction between particles. Once the yield stress is exceeded, the material behaves either as a shear-thickening or as shear-thinning fluid with a nonlinear stress strain relationship

$$\tau = \tau_{yp} + K\dot{\gamma}^n \quad (5)$$

where  $\tau_{yp}$  is the yield point (Pa),  $K$  is the flow consistency ( $Pa s^n$ ), and  $n$  is the flow exponent.<sup>15,22</sup>

**3.6. Model Analysis.** The model parameters obtained by fitting the experimental shear stress–shear rate data of kaolinite–silicon oil pastes to the power law, Casson, Bingham, and Herschel–Bulkley models as a function of particle size, solid/liquid ratio, and temperature are given in Tables 3, 4, and 5, respectively. The coefficients of determination ( $R^2$ ) obtained were high, which confirms the Herschel–Bulkley model to be adequately suitable for describing the flow behavior of the pastes within the range studied. In all cases,  $R^2$  values were higher than 0.92. 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 Herschel–Bulkley model parameters, reported in Tables 3–5, it can be seen that the consistency coefficient and the yield stress of kaolinite pastes increased with an increase in the solid concentration and particle size and decrease in temperature. Similarly, Rao and Tattiyakul<sup>28</sup> 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 mechanization of paste preparation. Below the yield stress, a material



**Table 3. Model Parameters Calculated for the Effect of Particle Size on Rheological Properties of Kaolinite–Silicon Oil Pastes**

parameters				rheological models										
				power law			Casson			Bingham		Herschel–Bulkley		
particle size ( $\mu\text{m}$ )	temperature ( $^{\circ}\text{C}$ )	solid/liquid ratio	die dimensions [L (mm)]/D (mm)]	$n$	$K$ (kPa s $^n$ )	$R^2$	$\tau_y$ (kPa)	$\mu_c$ (kPa s)	$R^2$	$R^2$	$\tau_{yp}$ (kPa)	$K$ (kPa s $^n$ )	$n$	$R^2$
			0–25	25	70	8/0.5	0.32	18.25	0.9509	42.39	0.045	0.8791	0.8360	6.0
16/1	0.33	17.85				0.9558	43.48	0.045	0.8549	0.7572	3.0	42.64	0.18	0.9948
32/2	0.46	8.76				0.9331	24.88	0.081	0.8254	0.7593	2.0	28.91	0.25	0.9917
25–50	25	70	8/0.5	0.31	20.51	0.8871	50.64	0.037	0.7446	0.6681	9.0	49.70	0.15	0.9800
			16/1	0.27	26.08	0.8863	56.55	0.028	0.7133	0.6066	4.0	72.06	0.08	0.9698
			32/2	0.27	26.71	0.9067	57.58	0.032	0.7539	0.6677	8.0	47.03	0.17	0.9762
50–75	25	70	8/0.5	0.19	57.43	0.7871	93.41	0.024	0.7211	0.6609				
			16/1	0.24	193.65	0.8577	67.62	0.024	0.6542	0.5305	8.0	75.06	0.10	0.9542
			32/2	0.24	35.02	0.8858	69.68	0.027	0.7163	0.6246	10.0	67.91	0.12	0.9716

**Table 4. Model Parameters Calculated for the Effect of Solid/Liquid Ratio on Rheological Properties of Kaolinite–Silicon Oil Pastes**

parameters				rheological models									
				power law			Casson			Bingham		Herschel–Bulkley	
temperature ( $^{\circ}\text{C}$ )	solid/liquid ratio	die dimensions [L (mm)]/D (mm)]	$n$	$K$ (kPa s $^n$ )	$R^2$	$\tau_y$ (kPa)	$\mu_c$ (kPa s)	$R^2$	$R^2$	$\tau_{yp}$ (kPa)	$K$ (kPa s $^n$ )	$n$	$R^2$
			25	60	8/0.5	0.27	0.31	0.9293	0.57	0.0001	0.9371	0.9294	0.50
16/1	0.38	12.25			0.9391	33.60	0.051	0.7941	0.669	0.50	48.7	0.14	0.9876
32/2	0.34	15.81			0.9617	38.49	0.046	0.8499	0.7301	0.50	41.7	0.17	0.9900
25	70	8/0.5	0.32	18.25	0.9509	42.39	0.046	0.8791	0.836	4.00	29.3	0.24	0.9664
		16/1	0.33	17.85	0.9391	43.48	0.045	0.8549	0.7572	4.00	38.7	0.20	0.9940
		32/2	0.46	8.75	0.9331	24.88	0.081	0.8254	0.7593	4.00	31.7	0.23	0.9933
25	75	8/0.5	0.34	19.42	0.7358	58.23	0.037	0.6013	0.5735	5.00	59.3	0.14	0.9504
		16/1	0.20	50.26	0.878	87.47	0.022	0.6668	0.5031	10.00	94.7	0.08	0.9574
		32/2	0.24	37.59	0.8589	71.13	0.033	0.6452	0.5533	10.00	63.7	0.13	0.9430
25	80	8/0.5	0.12	121.06	0.8549	168.01	0.016	0.684	0.5923	10.00	109.2	0.13	0.9261
		16/1	0.25	84.83	0.9875	144.65	0.115	0.8792	0.7897	15.00	94.7	0.22	
		32/2	0.25	74.38	0.8786	152.27	0.073	0.7557	0.6513	15.00	133.7	0.14	0.9707

**Table 5. Model Parameters Calculated for the Effect of Temperature on Rheological Properties of Kaolinite–Silicon Oil Pastes**

parameters				rheological models										
				power law			Casson			Bingham		Herschel–Bulkley		
particle size ( $\mu\text{m}$ )	temperature ( $^{\circ}\text{C}$ )	solid/liquid ratio	die dimensions [L (mm)]/D (mm)]	$n$	$K$ (kPa s $^n$ )	$R^2$	$\tau_y$ (kPa)	$\mu_c$ (kPa s)	$R^2$	$R^2$	$\tau_{yp}$ (kPa)	$K$ (kPa s $^n$ )	$n$	$R^2$
			0–25	25	70	8/0.5	0.32	18.25	0.9509	42.39	0.046	0.8791	0.8360	4.0
16/1	0.33	17.85				0.9558	43.48	0.045	0.8549	0.7572	2.5	32.3	0.22	0.9925
32/2	0.46	8.76				0.9331	24.88	0.081	0.8254	0.7593	4.0	29.3	0.24	0.9920
0–25	50	70	8/0.5	0.37	11.19	0.9629	32.65	0.043	0.8631	0.7846	2.0	20.2	0.27	0.9912
			16/1	0.39	10.93	0.9813	50.04	0.033	0.8499	0.8447	1.0	20.3	0.29	0.9954
			32/2	0.40	10.92	0.9761	30.74	0.059	0.8974	0.8185	2.0	23.3	0.27	0.9945
0–25	75	70	8/0.5	0.68	1.02	0.9822	5.08	0.066	0.9501	0.9265	0.5	2.3	0.54	0.9973
			16/1	0.50	4.25	0.9929	14.73	0.063	0.9445	0.8999	0.1	9.3	0.37	0.9992
			32/2	0.50	6.56	0.9897	21.00	0.060	0.933	0.8857	0.6	14.3	0.32	0.9994

exhibits solidlike characteristics. It stores energy at small strains and does not level out under the influence of gravity to form a flat surface. This characteristic is very important in process design and quality assessment for metaterials. 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 behavior. As shown in Tables 3–5, the all pastes exhibited a shear thinning behavior because the values of flow behavior index ( $n$ ) were less than 1 for all pastes.

### 3.7. Conclusions

The effects of particle size, solid/liquid ratio, temperature, shear rate, shear time, and die dimensions on the rheological properties of kaolinite–silicon oil pastes have been presented. The kaolinite–silicon oil paste exhibited a time-independent

rheological behavior. The shear viscosity of the suspension decreased with increased loading of silicon oil. At a certain particle size distribution the shear viscosity of paste increases with the increase of solid concentration. The presence of solid particles up to a relatively high level of 80% simply increased the viscosity of the suspensions. It was found that the pastes behave as a non-Newtonian, shear thinning fluid in the temperature range of 25–75  $^{\circ}\text{C}$  and is successfully described by the Herschel–Bulkley model. The consistency coefficient of pastes increases greatly upon increasing the solid level and decreasing temperature. The Arrhenius equation represented well the temperature effect on shear viscosity of the paste. The flow activation energy values determined at different constant shear rates such as 10, 50, 100, 200, and 300  $\text{s}^{-1}$  using capillary die with 8 mm/0.5 mm  $L/D$  ratio were 32.6, 21.3, 16.6, 11.3, and 7.4 kJ/mol, respectively. The

results show that the pastes behave as non-Newtonian Herschel–Bulkley fluids in the experimental ranges.

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