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Contributed Paper

The Rheological Behavior of Kaolin Suspensions

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ABSTRACT

The rheological behavior of three kaolins (Narathiwat, Lampang and Ranong) having different chemical and mineral compositions were studied. The viscosity and thixotropy of kaolin suspensions were measured as a function of solid content, pH and electrolyte concentrations. From rheological measurements, it was found that the viscosity and thixotropy increased with the increasing of the solid content. The highest viscosity of Narathiwat, Lampang and Ranong kaolins showed at pH 2, 6 and 4, respectively. However, thixotropy of three kaolins tends to increase with decreased pH. Plots of Binghan yield stress against pH at different ionic strengths intersect at about pH 7.1, 6.8 and 4.0, for Narathiwat, Lampang and Ranong kaolins, respectively. These values are identified with the isoelectric point of the particle edge surface. The rheological behavior of kaolins may be explained in terms of the influence of solid content, particle size, morphology, and pH and electrolyte concentrations on particle interaction.

Keywords: bingham yield stress, isoelectric point, kaolin, rheological behavior, thixotropy, viscosity.

1. INTRODUCTION

The structure of the kaolin minerals is based on the combination of two layer structures. One layer, known as the silica layer, is composed of silicon and oxygen atoms, and the second layer, known as the gibbsite layer, is composed of aluminium atoms and hydroxyl groups. The kaolin crystal consists of a large number of two-layer units held together with hydrogen bonds [1-4]. Kaolin platelets have negative charges on basal surfaces, due to substitution, and positive and negative charges on edge surfaces, due to broken bond at the edge [3-5]. It is generally accepted that most clay particles are platelets with a negative face charge and a positive edge charge under the proper pH conditions. A well-known electron micrograph first published by Thiessen in 1942 clearly shows negatively charged gold sol particles attached to the edge of kaolinite platelets which are routinely found to have a net negative charge [4]. Clays are therefore thought to set up a gel or thixotropy where the positively charged particle edges are attracted to the negative faces in a "house of cards" conformation.

The kaolin group of minerals with example of ideal formulas for kaolinite $Al_2(OH)_4.Si_2O_5$ and halloysite $Al_2(OH)_4.Si_2O_5.2H_2O$ [1,3,4]. The two species also differ in particle shape. Kaolinite occurs almost invariably as hexagonal platelets while halloysite can assume a tubular and spheroidal morphology. Particle shape or morphology is an important factor in influencing the rheological behavior of suspensions [6-9].

The rheological behavior of kaolin suspensions and their sensitivity to pH and ionic strength have been interpreted in terms of heteropolar nature of the particles. Diz and Rand [10,11], and Diz et al. [12] showed that a common intersection in the curves of extrapolated yield stress against pH, at different sodium chloride concentrations, could be interpreted as being the pH of the isoelectric point of the edge surface. This common intersection point is not the same for all kaolinite samples and Diz and Rand [10] also suggested that isoelectric point was determined by the alumina:silica ratio at this surface which, as a result of differential leaching, could vary according to the aqueous environment to which the clay mineral had been exposed. Besides, Theng and Wells [6] found intersection point at pH 6.0 for Matauri Bay halloysite and at pH 7.1 for Te Akatea halloysite. These values are identified with the point of zero charge of the particle edge surface. The flow characteristic of halloysite may be explained in terms of the influence of pH, electrolyte concentrations, and layer composition on particle interactions.

The aim of this study is to examine the rheological behavior of kaolin suspensions. The rheological behavior of kaolin suspensions may be explained in terms of the influence of solid content, particle size and morphology, pH and electrolyte concentrations on particle interactions.

2. MATERIALS AND METHODS

2.1 Materials

Kaolin powders were used in the experiments. Kaolins were obtained from Narathiwat, Lampang and Ranong (Thailand). The three kaolins samples were sieved through 325 mesh screen in a wet state, allowing it to settle, and discarding the supernatant. The washed samples were dried at 80 ^{o}C for over 48 h and all samples were grounded in a rod mill.

2.2 Particle Size Analysis

Particle sizes of the three kaolins (Narathiwat, Lampang and Ranong) have been determined by a laser light diffraction instrument (Mastersizers, Malvern). Distilled water was used as a dispersive medium.

2.3 Chemical Analysis by X-ray Fluorescence (XRF)

The chemical composition of the three kaolin powders were determined by Bruker D8/plus XRF spectrometer. The powders, fused in a pellet, were irradiated with x-rays. The elements in sample absorbed part of that radiation and emitted their own characteristic x-ray fluorescence spectra, which allow their identification and quantification to be performed.

2.4 Mineralogical Analysis by X-ray Diffraction (XRD)

Panalytical model X'pert Pro MPD X-ray diffractometer was used to determine the phases present in the three kaolins powders. Powders were placed in a flat glass holder and scanning was taken, using CuK radiation, over the 2θ range 5° to 95° at scan speeds 0.003 s^{-1} and 0.008 s^{-1}.

2.5 Transmission Electron Microscopy (TEM)

Particle morphology of three kaolins (size and shape) was assessed by transmission electron microscopy (JEOL JEM-2010), operating at 200 keV and fitted with an ultra thin window energy dispersive X-ray (EDX) detector was used. To prepare the sample for transmission electron microscopy, a powder was dispersed in acetone with the aid of ultrasonic vibration. A drop of dilute suspension was placed on a carbon coated 400 mesh copper grid, and allowed to dry at room temperature.

2.6 Rheological Measurements

2.6.1 Effect of Solid Content and pH

Brookfield rheometer DVIII+ was used to determine the rheological behavior of the three kaolins samples. The kaolin samples were prepared in the range of 30-40% (w/w) solid content in distilled water, and mixed by electric mixer for 10 minutes. 40% (w/w) suspension was found to be the most suitable to observe viscosity and thixotropy, for comparing of the effects of pH. The suspensions were adjusted to pH 2-10 with 12 M HCl and 12 M NaOH. Viscosity and thixotropy were measured by Brookfield rheometer DV-III+ at 15 rpm and spindle number Sc 29.

2.6.2 Isoelectric Point Determinations

At 40% (w/w) kaolin suspensions in sodium chloride solutions (0.02, 0.04, 0.06 and 0.08 M) were adjusted to pH 2-10 with 12 M HCl and 12 M NaOH, and mixed by an electric mixer for 10 minutes. Bingham yield stress was determined by Brookfield rheometer DV-III+ at 15 rpm and spindle number Sc 29. The isoelectric point was estimated from the common intersection points of Bingham yield stress-pH curves at different ionic strengths.

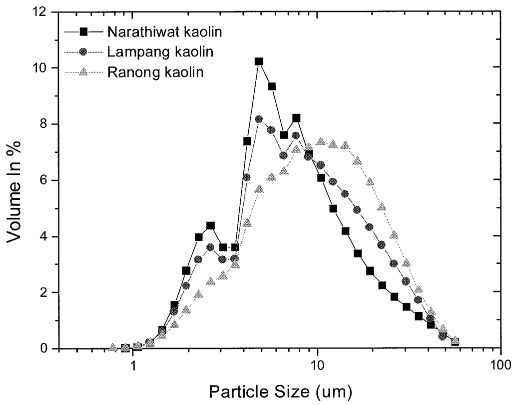

Figure 1. The particle size distribution of Narathiwat, Lampang and Ranong kaolins.

3. RESULTS AND DISCUSSION

3.1 Particle Size Analysis

Figure 1 illustrates particle size of the three kaolins samples. It was found that Narathiwat kaolin was smaller particle size than those of the Lampang and Ranong kaolins, respectively. The particle size analysis of Narathiwat, Lampang and Ranong kaolins gave an average median particle size D[4,3] of 9.82, 11.42 and 13.47 μm, respectively.

3.2 Chemical Analysis

Chemical constituents of the three kaolins analyzed by XRF are shown in Table 1. It was found that the main components of the three kaolins are Al_2O_3 and SiO_2 with minor components Fe_2O_3, TiO_2, Na_2O, K_2O, CaO, MgO, MnO and P_2O_5.

Table 1. Chemical composition of the three kaolins.

Compounds,%	N	L	R
Al_2O_3	36.18	31.06	35.87
SiO_2	44.76	53.05	46.25
Fe_2O_3	0.83	1.33	1.71
TiO_2	0.84	0.07	0.08
Na_2O	3.12	1.93	1.27
K_2O	1.15	4.19	2.06
CaO	0.13	0.21	0.40
MgO	0.11	0.24	0.25
MnO	0.01	0.06	0.05
P_2O_5	0.06	0.01	0.03
LOI	12.82	17.86	12.04
SiO_2/Al_2O_3	1.24	1.71	1.29

N: Narathiwat kaolin L: Lampang kaolin
R: Ranong kaolin LOI: Loss on ignition

3.3 Mineral Analysis

From the diffractograms as shown in Figures 2-4 and SiO_2/Al_2O_3 ratio, the Narathiwat kaolin consists of kaolinite, illite and quartz. The major compositions of the Lampang kaolin are mostly kaolinite, illite, quartz and albite. The Ranong kaolin is composed of mostly halloysite, kaolinite, illite, quartz and microcline.

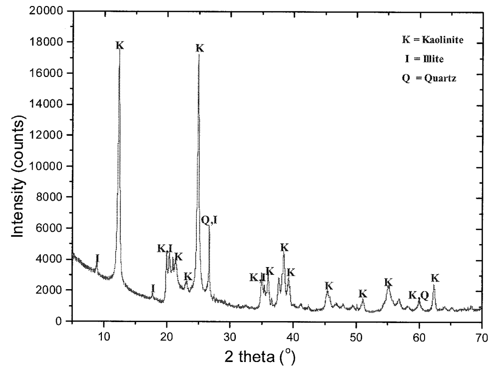

Figure 2. XRD diffractogram of the Narathiwat kaolin.

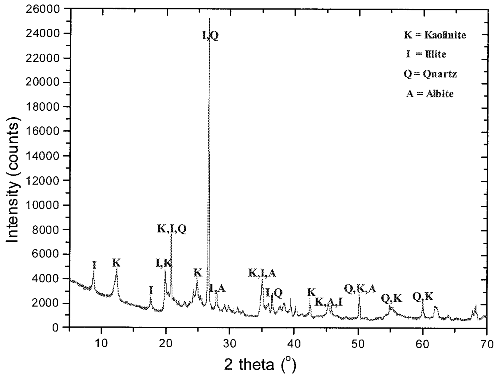

Figure 3. XRD diffractogram of the Lampang kaolin.

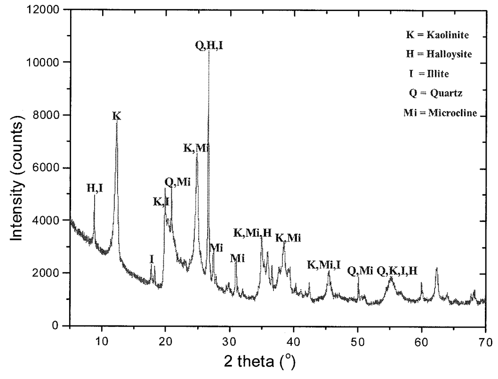

Figure 4. XRD diffractogram of the Ranong kaolin.

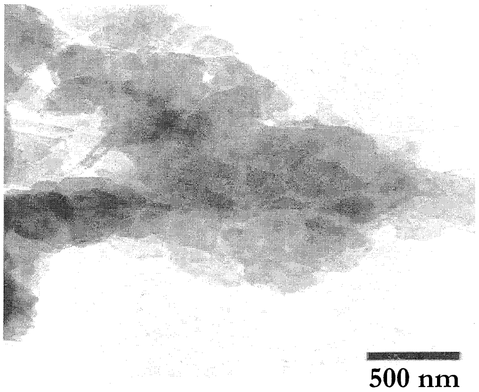

Figure 5. TEM micrograph of Narathiwat kaolin.

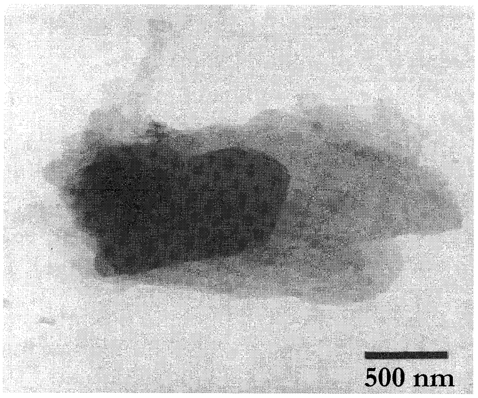

Figure 6. TEM micrograph of Lampang kaolin.

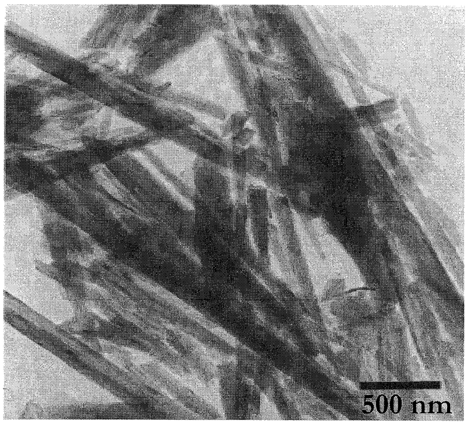

Figure 7. TEM micrograph of Ranong kaolin.

3.4 Transmission Electron Microscopy (TEM)

Figures 5-7 show TEM images of Narathiwat, Lampang and Ranong kaolins, respectively. From the literature reviews of Franco et al., and Xu and Van Deventer, it was found that the well-ordered kaolinite displays the large crystals of clear hexagonal shape [13,14]. Surprisingly, disordered kaolinite [13] and halloysite [15,16] show the irregular shape and tubular morphology, respectively. From experimental results, it was found that the TEM image of Ranong kaolin had tubular morphology which corresponded to the structure of halloysite and was strongly supported by X-ray diffractogram. However, the electron micrograph of Narathiwat kaolin had hexagonal shape matching the main peaks of well-ordered kaolinite. On the other hand, the particles of Lampang kaolin have irregular shape and its diffractogram corresponds to the disordered kaolinite.

3.5 Rheological Measurements

3.5.1 Effect of Solid Content

Figure 8 shows the plastic viscosity for all three kaolins suspensions as a function of solid content within the range investigated (30-40% w/w). From the experimental results, it was found that increasing the solid content of suspensions resulted in increasing the plastic viscosity of the three kaolins [6,9,17,18]. It can be explained that the small water inaccessible to the void resulted in high close-pack of particles. Nevertheless, in the suspensions, the Narathiwat kaolin had a higher plastic viscosity than those of Ranong and Lampang kaolins at the same solid content. It can be explained that the Narathiwat kaolin was well-defined hexagonal plate and smaller particle size than those of Lampang and Ranong kaolins, respectively. Therefore, it gives the highest compaction. By comparison of the particle size between Ranong and Lampang kaolins, it can be seen that Ranong kaolin has larger particle size than that of Lampang kaolin. But the Ranong kaolin showed higher plastic viscosity than that of Lampang kaolin due to the morphology of Ranong kaolin shows

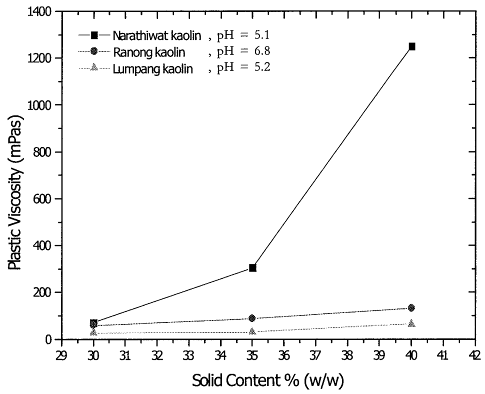

Figure 8. Plot of solid content vs. plastic viscosity for Narathiwat, Lampang and Ranong kaolin suspensions.

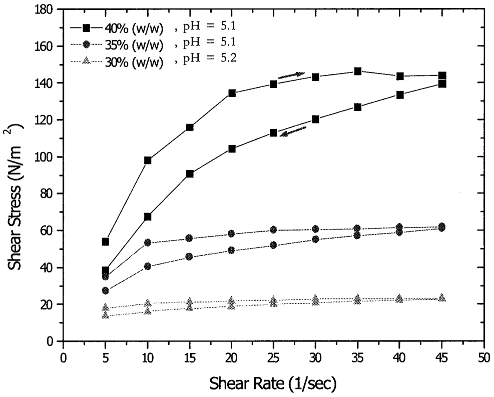

Figure 9. Plot of shear rate vs. shear stress for Narathiwat kaolin suspensions.

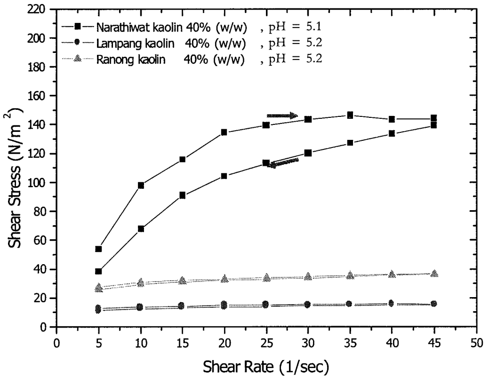

Figure 10. Plot of shear rate vs. shear stress for Narathiwat, Lampang and Ranong kaolin suspensions.

tubular halloysite. Therefore, it gives the highest particle packing resulting in an increase in the plastic viscosity.

The relation between shear rate and shear stress for known flow curves is illustrated in Figure 9 for the suspensions of Narathiwat kaolin at 30-40% w/w solid content. By increasing the solid content of suspensions, the thixotropy (the area of the hysteresis loop of the flow curves) increases [8,17,18] due to the small water inaccessible to the void resulted in closely packed particles and while van der Waals attraction between particles. For the Lampang and Ranong kaolins, the effect of thixotropy is similar to that found in the Narathiwat kaolin (not shown). From the comparison of thixotropy of three kaolins as shown in Figure 10, it can be seen that the Narathiwat kaolin provides the highest thixotropy, higher than those of Lampang and Ranong kaolins because it has the smaller particle size and the highest compaction.

The results clearly demonstrated the importance of solid content, particle size and morphology as controlling factors of kaolin rheology. Previous studies have indicated that the rheological behavior of kaolin suspension is governed by the fundamental properties of kaolin particles: their solid content, particle size and morphology. It was reported by Staneva et al. [17] measured the rheological of porcelain mixture. It was found that the yield stress, viscosity and thixotropy increase by increasing the solid concentration due to the increased number of particle-particle interaction. Theng and Wells [6] determined the flow characteristics of halloysite suspensions. The three halloysite from New Zealand used were: a thick long tubules from Matauri Bay, a short thin lath from Te Akatea, and a spherules from Opotiki. It was observed that the increase of solid content of halloysites resulted in an increase in the plastic viscosity due to the increased number of particle-particle interaction. Besides, the short thin lath halloysite had a higher plastic viscosity than those of the thick long tubules and spherules halloysite because of good particle packing. According to Yuan and Murray [7], the effects of particle morphology on the rheological behavior of high-solids kaolin suspensions were investigated using Hercules viscometer. It was found that the spherical halloysite showed the lowest viscosity, followed by the platy kaolinite and tubular halloysite. The trends can be best explained by the change of particle packing which is ultimately controlled by particle geometry. According to Yildiz et al. [18], it was found that by increasing the kaolinite content of suspensions, the area of the hysteresis loop of the flow curve and yield stress increase. The comparison of plastic viscosity and thixotropy as a function of solid content of kaolins determined by Staneva et al., Theng et al., Yuan and Murray, and Yildiz et al., were similar to the three kaolins from Thailand used in this study.

3.5.2 Effect of pH

The plastic viscosity of 40% w/w kaolin suspensions were measured at various pH levels as shown in Figures 11-13. From the experimental results, it was found that the decrease of the suspension pH resulted in an increase in the plastic viscosity [6,9,19-21] of Narathiwat kaolin as shown in Figure 11. This can be ascribed to either the lower the pH of the larger the amount of positive charges on the edges of kaolin. Therefore, the edge-to-face attraction between the positively charged edges and negatively charged basal surfaces in a "house of cards" conformation. On the other hand, the higher the pH, the larger amount of negative charges on the edges of kaolin. Therefore, the repulsion between the same negatively charged particles increases [6,19-21]. The result also indicates that the highest plastic viscosity of Narathiwat kaolin occurred at pH 2. According to Michaels and Bolger [20] who studied the particle interactions in aqueous kaolinite dispersions, a change in parameters was found in the structural of flocculated kaolinite suspensions, as deduced from pH and viscosity data. The high viscosity and pseudoplasticity of acidic kaolinite suspensions are a consequence of strong electrostatic interaction between particles due to the coexistence of negatively and positively charged basal surfaces. Elevation of pH by addition of sodium hydroxide causes gradual weakening of interparticle attractions via neutralization of positive edge charges resulting in a decrease of the viscosity. Theng and Wells [6] measured the flow characteristics of halloysite suspensions. It can be seen that the plastic viscosity for halloysites increases with decreasing suspensions pH due to the magnitude of the positive charge on particle edges increases, therefore, edge-to-face association, and vice versa. It was reported by Tombácz and Szerkeres [21], the lower the pH, the larger the amount of positive charges on the edges of montmorillonite. Therefore, the edge-to-face attraction between the positively charged edges and negatively charged basal surfaces results in an increase of the viscosity, and vice versa. The plastic viscosity of kaoin and montmorillonite as a function of pH found by Michaels and Bolger, Theng and Wells, Tombácz and Szerkeres are similar to that of Narathiwat kaolin suspensions used in this study.

Furthermore, the plastic viscosity of Lampang and Ranong kaolins were measured at 40% w/w solid content at various pH levels as shown in Figures 12-13. On the basic side (pH 7-10), the plastic viscosity decreases with pH, reaching a minimum at pH 10 due to the positive charge on edges kaolins reversed negatively charged, therefore, particles get good dispersion due to repulsion between negatively charged on both edge and surface of particles [6,19-21]. On the acidic, the plastic viscosity increases with pH, reaching a maximum at pH 6 and 4 of Lampang and Ranong kaolins, respectively. As discussed earlier, the kaolin suspensions tend to form a house of cards structure due to the edge-to-face interaction between the negatively charged edges and positively charged basal surfaces [19-21]. Besides, the decreases in the plastic viscosity at lower pH suggest that the ionic strength will be raised. The ionic species strength may first interfere with the negative electrical double layer of the faces reducing the edge-to-face interactions resulting in a decrease of the system plastic viscosity. The result also indicates that the highest of plastic viscosity of Lampang and Ranong kaolins showed at pH 6 and 4, respectively, suggests that these points are isoelectric and the particle of these points will be associated with van der Waals forces[10]. Similar trends with low and high pH are shown in the data of Chang et al. [19], and Williams and Williams [22]. Chang et al. studied effect of pH and ionic strength on the rheology and stability of aqueous clay suspensions. It was found that on the basic side, the viscosity first decreases with pH, reaching a minimum near pH 11 due to the positive charges of the edges which may be reversed at high pH. This will disrupt the house of cards structure and result in a lowering of the viscosity of system. On the acidic side, as pH decreases (i.e., addition of more HCl) the ionic strength will be raised. The ionic species strength may first interfere with the negative electrical double layer of the faces reducing the edge-to-face interactions resulting in a decrease of the system plastic viscosity. This is in agreeable with Williams and Williams [22] who reported that viscosity decreases at low pH due to the effects of reduced number of interparticle links.

Figure 14 also shows the hysteresis loop

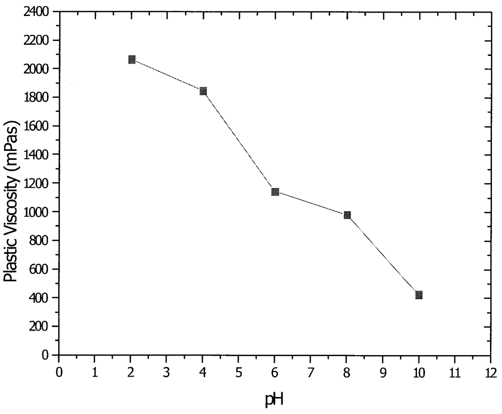

Figure 11. Plot of pH vs. plastic viscosity for Narathiwat, kaolin suspensions at 40 %w/w.

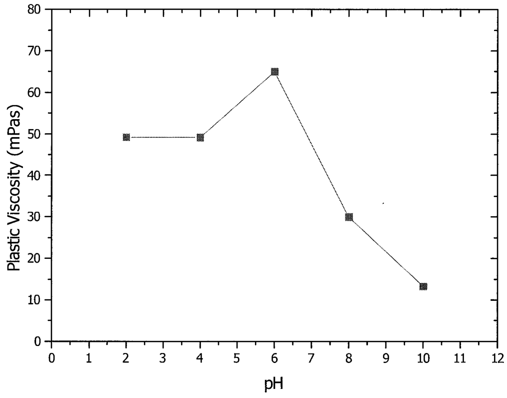

Figure 12. Plot of pH vs. plastic viscosity for Lampang kaolin suspensions at 40 %w/w.

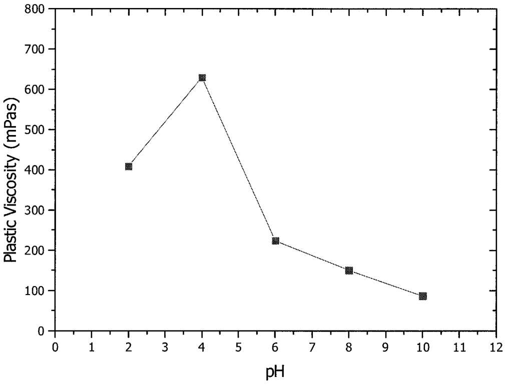

Figure 13. Plot of pH vs. plastic viscosity for Ranong kaolin suspensions at 40 %w/w.

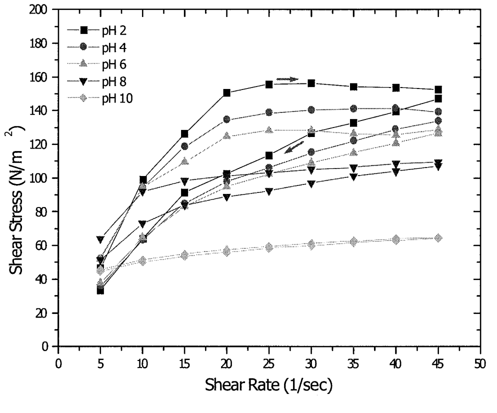

Figure 14. Plot of shear rate vs. shear stress for Narathiwat kaolin suspensions at various pH at 40 %w/w.

enclosed by the acceleration ('up') and deceleration ('down') branches of the flow curves of Narathiwat kaolin (40% w/w) at various pH levels. It was found that the decrease of the suspensions pH resulted in an increase in the thixotropy. Here the edge-to-face heterocoagulated network can form because of the attraction oppositely charged edges and surface of kaolin-platelets [6,21], and vice versa. For the Lampang and Ranong kaolins, the effect of pH on the thixotropy is similar to that found in Narathiwat kaolin (not shown). The thixotropy show a trend similar to that found by Theng and Wells [6], and Tombácz and Szerkeres [21] at all pH who report increasing value of thixotropy with an increase of the suspension pH due to the edge-to-face association, and vice versa.

3.5.3 Isoelectric Point Determinations

The Bingham yield stress measurements were made as a function of pH and sodium chloride concentration of three kaolin suspensions (40% w/w) as shown in Figures 15-17. The results are interpreted in terms of the heteropolar model of kaolin and edge surface isoelectric points are estimated from the common intersection of Bingham yield stress-pH curves at different ionic strengths [6,10-12]. From the experimental results, it can be seen that the isoelectric points of Narathiwat, Lampang and Ranong kaolins showed at about pH 7.1, 6.8 and 4.0, respectively.

According to the heteropolar model, at pH value below the edge surface isoelectric point the particles are flocculated in an edge-to-face co-ordination as a result of electrostatic attraction between the positive edges and negatively charged basal surfaces. The effect of increasing the concentration of counter ions (sodium chloride) in this pH regime is the compression of the electrical double layer on both surfaces so as to reduce the electrostatic attraction (i.e. it reduces the depth of the primary medium in the total potential energy of the interaction curve). Consequently, all those properties that depend on the strength of this interaction are changed. Specifically, the Bingham yield stress is reduced. At pH values above the edge surface isoelectric point, both surfaces of the kaolin particle have the same sign and the system may be deflocculated. Compression of the electrical double layers by increasing the ionic strength (sodium chloride) in this region has the effect of increasing the depth of primary minimum and increasing the attractive forces due to the van der Waals effect, so increasing the Bingham yield stress. It is this different behavior above and below the edge surface isoelectric point that gives rise to the point of intersection in the Bingham yield stress-pH curves. This point of intersection essentially locates the pH at which the predominant influence of the yield stress changes from electrostatic attraction to van der Waals attraction [6,10-12].

According to Diz and Rand [10], the rheological measurements have been made as a function of pH and sodium chloride concentration for kaolinite, without washing and washing three times with acidic 1 mol/dm-3 sodium chloride solution. The results are interpreted in terms of the heteropolar model of kaolinite and edge surface isoelectric points in the extrapolate yield stress-pH curves, at different ionic strengths. The isoelectric point of kaolinite at without washed and washed three times showed at about pH 5.6 and 6.8, respectively. This is in agreement with Rand et al. [12] which reported that kaolinite has an isoelectric point at about pH 6.2. Theng and Wells [6] found that Bingham yield value is sensitive to variation in ambient electrolyte concentration. For Matauri Bay halloysite and Te Akatea halloysite the plots of pH vs. Bingham yield value at different concentration of sodium chloride intersect at about pH 6.0 and 7.1, respectively. When this is compared with the isoelectric point of kaolin group determined by Diz and Rand, and Rand et al., it is found to be similar to the Narathiwat and Lampang kaolin from Thailand used in this study. On the other hand, Ranong kaolin composed of tubular halloysite showed isoelectric point at about pH 4.0 which was different from that observed by Theng and Wells [6].

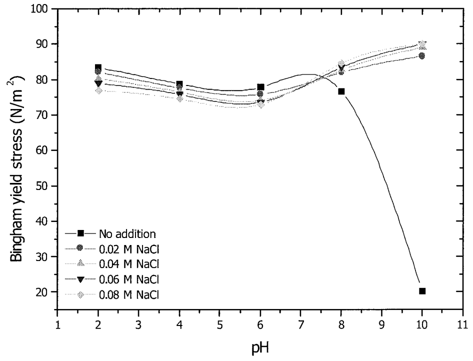

Figure 15. Plot of pH vs. Bingham yield stress at different electrolyte concentrations for Narathiwat kaolin suspensions.

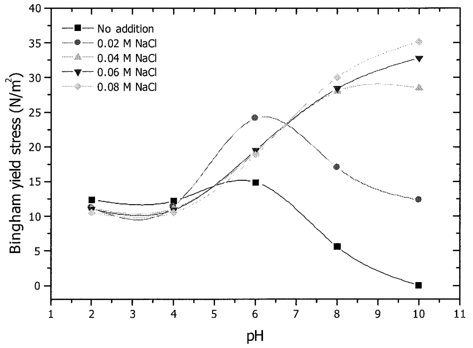

Figure 16. Plot of pH vs. Bingham yield stress at different electrolyte concentrations for Lampang kaolin suspensions.

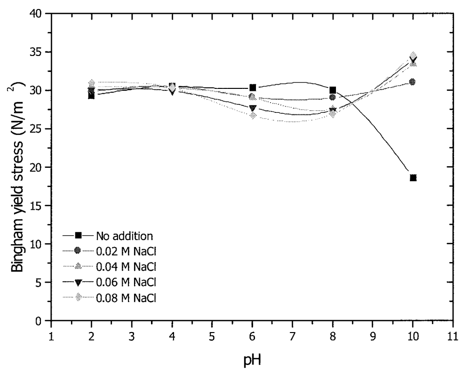

Figure 17. Plot of pH vs. Bingham yield stress at different electrolyte concentrations for Ranong kaolin suspensions.

4. CONCLUSIONS

From the performed investigation, the following conclusions can be derived:

1. Increased solid content causes the plastic viscosity and thixotropy of Narathiwat, Lampang and Ranong kaolin suspensions to increase because the small water inaccessible to the void results in closely packed particles. Besides, the plastic viscosity and thixotropy are dependent on particle size and morphology of kaolins.

2. The high viscosity of acidic kaolin suspensions are a consequence of strong electrostatic interaction between particles due to the coexistence of positively charged edges and negatively charged basal surfaces. Elevation of pH by addition of sodium hydroxide causes gradual weakening of interparticle attractions via neutralization of positive edge charges, therefore, the repulsion between the same negatively charged particles results in a decrease of the system plastic viscosity. Besides, the decreases in the plastic viscosity at lower pH due to the ionic species strength may first interfere with the negative electrical double layer of the faces reducing the edge-to-face interactions resulting in a decrease of the system plastic viscosity.

3. The decrease of the suspensions pH results in an increase in the thixotropy. The edge-to-face heterocoagulated network can form because of the attraction of oppositely charged edges and surface of kaolin-platelets.

4. From the experimental results, it was found that the isoelectric points of Narathiwat, Lampang and Ranong kaolins existed at pH 7.1, 6.8 and 4.0, respectively.

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