The Properties of Kaolin from Different Locations and Their Impact on Casting Rate

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Abstract

It has been well known that mineral samples from different locations and origins can exhibit a significant shift in their properties and behavior. The present study of three samples of kaolin from a wide set of origin of deposits, composition, and ceramic properties, provided an important and perhaps a unique opportunity for investigating the interdependence of mineralogy, chemical composition, particle morphology, and surface property with their rheological behavior in ceramic applications such as casting rate. The X-ray diffraction patterns of kaolin samples #2 and #3 suggested low crystallinity with Hinckley Index (HI) ranging between 0.78 and 0.8. On the other hand, kaolin sample #1 was highly ordered with HI of about 1.21, and it had higher quartz content. This free quartz could enhance the permeability and hence increase the casting rate. The abundance of divalent ions (Ca 2+ and Mg 2+) in samples #2 & #3 could result in the collapse of the electrical double layer and reduction of zeta potential, consequently, coagulation of the particles leading to an increase of viscosity and dispersant demands. The morphology study suggested the platelet particles in sample #2 & #3 would lead to slower dewatering, thus, lower casting rate than that of blocky (lower aspect ratio and narrower size distribution) particles in sample #1.

Keywords: kaolinite, kaolin, clay, powder, particles, casting

1. Introduction

Kaolin has a global market with an estimated value of 5.42 billion USD in 2018 (Kumar S., 2019). The market size is expected to grow continuously due to the increasing demand of ceramic products in a wide variety of applications (Dondi M. et al., 2008), such as whiteware (Sanz A. et al., 2018), paper (Frías M. et al., 2015), construction (Heah C. et al., 2011), paint (Ahmed N.M., 2013), drilling fluid (Au P.-I. and Leong Y.-K., 2013), etc. Furthermore, kaolin has great potential to be tailored for more innovative products including rapid-casting clays, engineered paper with kaolin coating, and nanocomposites (Dondi M. et al., 2003; Murray H.H., 2000). These advanced applications require more in-depth knowledge of the structure-property-behavior relationship of kaolin, which is not fully understood. In fact, it is difficult to comprehend the complexity because kaolin samples exhibit different particle size, size distribution, shape, chemical composition, surface chemistry and charge due to their diverse geological conditions and processing parameters.

The main scope of the present study is to investigate the kaolin properties that either directly or indirectly impact the rheological behavior. The key characteristics of the kaolin samples include mineralogy, the degree of kaolin crystallinity, chemistry, morphology, particle size distribution, shape and shape distribution, surface chemistry, interfacial properties, and the interaction with various deflocculants or dispersants.

2. Materials and methods

2.1 Materials

Three kaolin samples #1, #2, and #3 were carefully selected. Sample #1 was coarse-grained kaolin that had been engineered to achieve improved casting rate. This kaolin is currently commercialized by an American kaolin producer. The original geological source of the primary kaolin was from Georgia (USA). Sample #2 was wet processed kaolin from Colombia, South America. The
The raw material for this sample was primary kaolin. Wet processing of this raw material resulted in a kaolin slurry which, in turn, was filter pressed to obtain the kaolin represented by Sample #2. Sample #3 was a result of mechanical processing of Sample #2.

2.2 Methods

X-ray diffraction (XRD). The phase of each kaolin sample, as well as the crystallinity, was characterized using Panalytical Xpert Powder with 1400W Cu X-ray tube.

Thermal gravimetric analysis (TGA). The weight loss due to dehydroxylation, phase transition, or thermal decomposition of each kaolin sample was measured and analyzed using TGA/SDTA851e.

Scanning electron microscopy (SEM). The texture, particle morphology of the kaolin sample was analyzed using the micrographs obtained by Hitachi S3000 SEM.

The zeta potential of kaolin particles was measured using Zeta Reader Mark 21.

The casting rate was measured following the protocol described by Eygi et al. (Eygi M.S. and Ateşok G., 2008)

3. Results and discussion

3.1 Mineralogical composition

The X-ray diffraction patterns of the three kaolin samples are illustrated in Fig. 1. Samples #2 and #3 were observed to be disordered and poorly crystalline and contained traces of quartz and very sparse mica (illite). Their Hinckley Index (HI)—a measure of crystallinity of kaolin ranged between 0.78 and 0.8. Kaolin was indicated by its characteristic reflection peaks at 7.14 Å (001), and 3.56 Å (002), quartz (SiO$_2$) at 3.33 Å and illite appears at 10 Å.

Sample #1 was highly ordered with HI of almost 1.21 and characteristic peaks at 7.14 Å (001) and 3.56 Å (002), which suggested higher quartz content compared with samples #2 and #3.

The measurement of HI (degree of crystallinity of kaolin) is shown in Fig. 2 using the range of 2θ 19–22° of kaolin samples. The calculated I (020)/I (110) ratios of studied kaolin samples were 0.63, 1.09 and 1.10 for sample #1, #2, and #3, respectively. The smaller the value, the higher the crystallographic order of kaolin (Qiu X. et al., 2014). The average flake thickness of kaolin along the c-axis was calculated using the Debye-Scherrer equation,

$$L = \frac{K\lambda}{\beta\cos\theta}$$

where L is the crystallite size; K is the Scherrer constant that depends on the shape and size distribution of the crystal; λ is the wavelength of incident X-ray; β is the full width at half maximum (FWHM); θ is the Bragg angle. The estimation of crystal size using FWHM of (001) peak is shown in Fig. 3. Table 1 summarizes the calculated results of kaolin samples from XRD patterns. According to the FWHM (001) data of the three kaolin samples, the average flake thickness along the c-axis of sample #1, #2, and #3 were 517 Å, 160 Å, and 152 Å, respectively (as shown in Table 1). It was evident that sample #1 had thicker flakes than sample #2 and #3, and it was consistent with the results of SEM images.

From the XRD patterns of kaolin samples, it was clear that sample #1 was highly ordered kaolinite with HI 1.21 and average flake thickness along the c-axis of 517 Å; while kaolin sample #2 and #3 had HI of 0.8–0.76 and an average flake thickness along the c-axis of 152–160 Å, re-
spectively. Moreover, the narrow and sharp (001) diffraction peak with an FWHM of 0.15° was characteristic of sample #1. Whereas the FWHM (001) of sample #2 and #3 was about 0.33°. Poor crystallinity of sample #2 and #3 kaolin resulted in irregular morphology and subsequently in poor rheological behavior.

3.2 Thermal gravimetric analysis (TGA)

3.2.1 Low-temperate endothermic region

The peak observed in TGA curves of sample #2 and #3 at 53 °C could be due to dehydration of poorly crystallized kaolin (#2 and #3) or due to the loss of adsorbed water (Δm = 2.211%). It could also be due to the trace of hydrated halloysite (its characteristic peak at 10 Å overlapped with illite peak). However, low-temperature endothermic peak at 252 °C in DTA curves of sample #2 and #3 could be attributed to amorphous materials—goethite FeO(OH) or gibbsite Al(OH)_3 (Δm = 0.941%). Samples #2 and #3 seemed to be stained with iron. Also Fe₂O₃ content of these samples was higher than in sample #1. Generally, highly crystalline goethite is known to produce a maximum at 280 °C. However, low crystalline goethite is known to produce a peak at 250 °C in TGA curves (Fig. 4 and 5).

### Table 1: Calculated results of kaolin samples.

| Sample | HI | I(020)/I(110) | FWHM (001) | Crystallite Size | Number of Unit Layer |
|--------|----|---------------|------------|------------------|----------------------|
| #1     | 1.21 | 0.63 | 0.151° | 517 Å | 76 |
| #2     | 0.80 | 1.09 | 0.334° | 160 Å | 28 |
| #3     | 0.76 | 1.10 | 0.32°  | 152 Å | 32 |

![Fig. 3](image1.png) The FWHM measurement of the (001) XRD peak revealed the crystallite size of kaolin particles.

![Fig. 4](image2.png) Differential thermal analysis of kaolin samples.

![Fig. 5](image3.png) Derivative thermos-gravimetric curves of the samples.

Additionally, sample #1 had shallow losses below 200 °C (Δm = 0.585%) as compared to samples #2 and #3. This could be the result of a reasonable degree of crystallinity, in the case of sample#1, whereas the weight losses observed in case of the other samples could be attributed to the presence of less ordered kaolinite, halloysite and/or amorphous materials.
3.2.2 Medium-temperature—endothermic region

The DTA curve for kaolinite showed an endothermic peak in the range 400–600 °C due to dehydroxylation of sample #2 and #3. These peaks were associated with a weight loss of 11 % contaminated kaolinite (Fig. 6). In the case of sample #1 kaolin, the dehydroxylation peak temperature ranged between 440–700 and a 9.6 % weight loss. The dehydroxylation of sample #1 compared with that of sample #2 and #3 could be attributed to the difference in the degree of crystallinity as well as the degree of substitution of Al in the octahedral sheet by Fe in various samples. Low degree of crystallinity and the relatively higher degree of structurally substituted -Fe caused a low dehydroxylation temperature of samples #2 and #3. Sample #1 was distinguished mainly by the decrease in peak intensity around 530 °C indicating lower kaolinite content. Also, the peak was broader and more curved to the right for samples #2 and #3. These characteristics could be attributed to the higher thickness of the crystals and/or the higher degree of crystallinity.

3.2.3 High-temperature-exothermic region

The main difference was observed at the exothermic peak around 1000 °C (Fig. 4). This peak was wider and less pronounced in samples #2 and #3 than that for Sample #1. Besides, it developed at a temperature 10–15 °C lower than for Sample #1. One possible explanation for this difference in DTA behavior would be a higher degree of crystallinity and, eventually, a larger crystallite thickness for Sample #1 in comparison to samples #2 and #3. The dehydroxylation of kaolinite occurred between 600–700 °C along with the formation of metakaolin. The phase was further transformed into either γ-alumina or aluminum-silicon spinel with the presence of amorphous silica.

The major loss in mass was observed in the temperature range from 400 to 900 °C indicated by an endothermic peak in Fig. 4. The total mass loss observed on the TG curve was 11.035 % for sample #1 (Fig. 6). DTG and DTA curves of sample #1 showed that the temperature at the maximum mass loss was 533 °C. On the other hand, the mass loss of sample #2 and #3 was 12.3455 % that occurred at 520 °C. The mass loss for sample #2 and #3 was higher compared with that of sample #1 and could be correlated to the higher percent of kaolin in sample #2 and #3 (90.18 %) as compared to 80.5 % for sample #1. The metakaolin was a disordered layer structure with some hydroxyls present (1/8) and probably had the same Al/Si as kaolinite plus the vapor phase which was considered to be pure H2O (Roy R. et al., 1955). Metakaolin eventually becomes amorphous with additional heating (Brindley G. and Nakahira M., 1959).

The conversion of quartz during the calcination of kaolin was masked by the big and very broad dehydroxylation peak of clay minerals generally within the same temperature range. So, calculation of quartz and illite associated with kaolin of studied samples should be based on XRD patterns.

3.3 Phase and chemical analysis

The chemical analysis of the investigated samples given in Table 2 & 3 agreed with the mineralogical composition of the samples determined by the X-ray diffraction (Figs. 1–3) and DTA-TG (Figs. 4–6) analysis, as well as confirmed by the SEM micrographs (Figs. 9–11). Based on the normal weight loss at 400–700 °C corresponding to dehydroxylation of kaolinite the kaolin/halloysite content ranged between 78–80 % for sample #1 as compared with 87–89 % for samples# 2 and # 3. The higher quartz and illite content in sample #1 may explain the lower content of kaolin in sample #1.

On the other hands, sample #2 and #3 had higher Fe2O3, TiO2, CaO, MgO compared with sample#1. Generally, Fe could be located in two forms: 1) Fe- substitution in octahedral and tetrahedral sheets of kaolin, or 2) as amorphous
iron (staining iron). Also, the Fe had a significant influence on the rheological properties of kaolin. High K₂O% in sample #1 compared with the other two samples revealed the presence of mica mineral. Illite impurity was indicated in XRD patterns of kaolin.

The presence of divalent ion in terms of Mg followed by Ca in abundance in sample #2 and #3 kaolin could result in the compression of the electrical double layer resulting in the lower zeta potential of these samples. Low zeta potential would result in higher interaction between clay particles and an increase of viscosity and finally the flocculation of clay particles.

3.4 Zeta potential

The zeta potential of the three kaolin samples was measured at specific pH to obtain the isoelectric point (IEP) as plotted in Fig. 7. The IEP of all three samples were interpolated to be 3–4 which agreed with the literature values (Au P. and Leong Y., 2016). Sample #1 exhibited slightly higher isoelectric point as compared to samples #2 & #3. This could affect the interaction between clay particles in aqueous suspension thereby influencing their flocculation properties.

3.5 Physical properties

3.5.1 Particle sizes and size distribution

The particle size distribution of the three samples is summarized in Table 4, which did not reveal any significant differences.

3.5.2 Specific surface area (SSA) and cation exchange capacity (CEC)

The higher SSA and CEC (MBI) in case of samples #2 and #3 could be attributed to the imperfectly stacked poorly crystallized kaolin with a lot of curly, rough and eroded edges compared to sample #1 (well-crystallized books of kaolin). High CEC of samples #2 and #3 using MBI could be attributed to the exposure of more charged sites for the exchange to occur. The SSA and CEC of kaolin appeared to increase with a lower degree of crystallinity as refer to Table 4.

![Zeta potential of the Kaolin samples.](image-url)
3.5.3 Morphological Analysis

SEM micrographs (Figs. 8–10) revealed the morphological characteristic of kaolin samples.

Kaolin sample #1 had revealed more regular pseudo-hexagonal edge, smooth surface, thicker flakes and smaller diameter to thickness ratio (Fig. 8). During the grinding process, these particles tended to become more rounded resulting in better packing. This blocky morphology could have enhanced the dewatering and casting rate of sample #1.

The morphology of sample #2 and #3 (Figs. 9–10) was different from that of sample #1. This morphology revealed the poorly crystalline structure of these samples. The platelets had curly, rough, highly eroded edges with high aspect ratios. The eroded edges revealed the partial dissolution of this kaolin and explained the presence of amorphous materials that covered the platelets. These surface defects were strongly associated with the adsorption characteristic of this kaolin. The packing of plate-like particles (samples #2 & #3) could result in lower casting rate of the samples than that of the sample with blocky particles (lower aspect ratio). The densely-packed platelets of samples #2 and #3 would lie flat in the casting mold thereby slowing down the dewatering process.

3.6 Slip casting performance

The present investigation offered a good opportunity to study the property-performance relationship of kaolin. It was observed that the slip casting rate of kaolin sample #1 was significantly higher as compared to sample #2 & #3 (Fig. 11) in which the particles were more platy (higher aspect ratio) and exhibit lower crystallinity. The low casting rate of kaolin sample #2 & #3 also could be attributed to the high slip viscosity and the abundant divalent cations. For these reasons, kaolin sample #2 & #3 were less suitable for most of the traditional applications unless they are further treated or modified specifically.

4. Conclusions

Three kaolin samples from different geological origins were characterized and the relationship between their properties and slip casting performance were studied. Overall, it was found that kaolin sample #1 exhibited significantly higher slip casting rate than the other two samples. Characterization showed that kaolin sample #1 had
the highest crystallinity among the three samples studied, and its particles exhibited the most globular shape as compared to the other samples. The globular shape of the particles could be one of the key elements that were beneficial to the dewatering process leading to faster slip casting. The thermal gravimetric analysis confirmed that kaolin sample #1 experienced less weight loss, in low to medium temperature endothermic regions than the other two samples. This could possibly be due to less moisture content of sample #1 and thus less dehydroxylation due to a higher degree of crystallinity. Nevertheless, further investigation is needed to fully understand the complex nature of different kaolins and their rheological behavior.

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