Variation in textural properties of aplitic kaolin from Kinta Valley

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Abstract: Textural properties are among one of the fundamental characteristics especially important to be understood before suitable application(s) of a kaolin can be determined as they have direct influence on the other properties such as plasticity, brightness, firing and rheological behavior. This paper presents an investigation on the textural properties of aplitic kaolin from Kinta Valley. Two degritted kaolin samples from different location of Kinta Valley were measured for their particle size distribution by laser diffraction method. The samples were then classified into different size fractions followed by examination of their morphological property by various techniques which X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and field emission scanning electron microscope (FESEM). Generally, the kaolin can be classified into two different types based on the fine fraction content which may be consists of; i) delaminated platy kaolinite, or ii) tubular shaped halloysite. These fine fractions however constitute only to minor amount or not more than 12 % of the clays, as both clay consist predominantly of coarse book like kaolinite stacks. The degree of crystallinity of kaolinite samples shows a positive correlation to its particle size during examination by XRD, but FTIR spectrum shows a high degree of crystallinity for all kaolinite samples regardless of their particle size. Slight presence of halloysite is sufficient to give an adverse effect on the clay crystallinity index measured from XRD pattern. Sorting of the clay into different size and morphological fraction creates a product with less variation in properties between individual particles, and with more potential for tailoring or engineering of their properties.

Keywords: Kaolin, soft kaolin, kaolinite, halloysite, texture, textural properties, crystallinity index

INTRODUCTION

Kaolin minerals are hydrous phyllosilicate mineral form with the formula of $Al_2Si_2O_5(OH)_4$ (Newman & Brown, 1987). A single unit structure of kaolin mineral is formed by stacking of one silica tetrahedral sheet onto one aluminum hydroxide octahedral sheet (Al-Shameri & Rong, 2009). Kaolin has a wide range of industrial applications due to the unique characteristics it possesses (Murray, 2000). The major consumers of kaolin included the paper, paint, rubber, plastic, ceramic, refractory and glass fibre industry (Siddiqui *et al*., 2005; Sengupta *et al*., 2008). Kaolin also find its applications in production of Portland cement, pesticides, and pharmaceutical products (Aras *et al*., 2007). The applicability of kaolin into these fields however depends largely on the physio-chemical properties of kaolin which can vary significantly according to their origin and parent material (Wilson & Jiranek, 1995; Varajao *et al*., 2001; Sayin 2007; Masoud *et al*., 2013; Yuan *et al*., 2014; Gina *et al.,* 2020). Textural properties are among one the fundamental properties especially important to be understood as they have direct influence on the other properties related to the applications of kaolin such as plasticity, brightness, firing behavior and rheological properties of kaolin. The texture of a clay material refers to the particle size distribution of the constituents, the particle shape which is related to the morphology, the orientation of the particles with respect to each other, and the forces which bind the particles together (Murray, 2007). In this paper, two of the important physical aspects (particle size and morphology) which define the texture of clay will be examined. The importance of particle size distribution and the particle shape to the properties of clay with kaolinite as its major components had been emphasized by Murray (2000). Systematic and proper characterization of the particle size and morphology of kaolin is necessary to enable better understanding on the behavior of the clay.

Morphology and shape of kaolin

In nature, kaolin may be encountered in different morphological form other than kaolinite such as halloysite, nacrite and dickite (Senoussi *et al*., 2016). Kaolinite, nacrite and dickite has very similar crystal structure and differs from each other by the ordering pattern of vacant octahedral site in subsequent layers (Bailey, 1980). Halloysite on the other hand is formed by rolling of a planar 1:1 layer (Bailey, 1990). The layer curls with the tetrahedral sheet on the outside of the curve to minimize the

misfit of the larger tetrahedral and smaller octahedral sheets (Singh & Mackinnon, 1996). The crystal morphologies of kaolin particles should be accurately identified as it has a large effect on the possible application of kaolin. Plasticity of clay is related to the morphology of the plate-like clay mineral particles that slide over the others when water is added (Ryan & Radford, 1987). Tube like halloysite particles are unsuitable for coating application due to the adverse effect on rheological properties they provide to kaolin even if they presence only in minor amount, but can be utilized for more advanced application as catalyst, adsorbent and carrier at molecular level (Yuan *et al.*, 2015). However, uses of kaolin are very limited if kaolinite and halloysite are found to co-exist. The only known application of halloysite-kaolinite mixture are utilized for ceramic and porcelain production (Churchman *et al.*, 2016). Degree of crystallinity is an alternative method to explain the morphology of clay minerals, although they cannot provide direct information on the texture of the clay. Higher degree of crystallinity signifies a clay with coarser particle sizes and is commonly associated to soft kaolin where the composition is dominated by book like kaolinite stacks (Kogel *et al.*, 2006). Poor crystallinity index indicates the presence of fine kaolinite or halloysite (Brindley, 1980).

Particle size distribution

The particle size distribution also influences the physical and optical properties of the clay. Particle size distribution is a major factor controlling the ceramic behavior of a clay which included the plasticity, shrinkage and strength after drying and firing (Ryan & Radford, 1987). The brightness, opacity or hiding power which is affected by the degree of light scattering in the clay is a function of the particle size distribution. In term of ceramic properties, body formed by coarser particles usually has a lower shrinkage after firing or drying but is associated with a lower flexural strength due to the higher porosity of the ceramic body (Wilson, 2004). Fine and platy kaolinites with size finer than 2 μm are the major material responsible for the plastic behaviour (Andrade *et al.*, 2011).

PROBLEM STATEMENT AND OBJECTIVE

The most well-known and established kaolin producing region in Malaysia is located at the Bidor-Tapah area of Perak state. Kaolin from the area have a long history of being examined by various researchers (Aw, 1983; Liew *et al.*, 1985; Aw, 1986; Baioumy, 2012; Cheang *et al.*, 2013). The kaolin from Kinta Valley however had not received as much attention as the above kaolinitic occurrence. Although it had been studied by few researchers (Arrifin *et al.*, 2008; Baioumy, 2012; Chin *et al.*, 2017), no in-depth investigation on the textural properties of the kaolin from Kinta Valley had been provided. This paper is aimed to

report and discuss the textural variation of aplite derived kaolin from East Kinta Valley.

METHODOLOGY

Two degritted kaolin originated from different location from East Kinta Valley labelled as SA and SC are selected for this study. Particle size analysis by laser diffraction method with the instrument Malvern Mastersizer 2000 is first adapted to determine the quantity of fine fraction in each material. The next step involve extraction of < 2 μm fraction through decantation technique. The clay is first mixed in distilled water in the ratio 1:5, followed by dispersion using ultrasonic bath for 5 minutes. Calgon is added into the suspension in an amount of 0.1 % to the weight of clay to assist the deflocculation of the clay particles. The < 2 μm fraction is then extracted as the suspension located above 5 cm from the bottom of the clay suspension container after allowing the coarser particles to settle for 24 hours. The given settling time is computed according to Stokes' law. The collected suspension containing the fine and coarse fraction after separation are then dried at 105 ºC and pulverized into powder form for subsequent analyses. It must be emphasized that the clay should be pulverized gently to prevent any alteration or destruction of original clay morphology from excess grinding (Sánchez-Soto *et al.*, 2000; Ding *et al.*, 2012). The morphological variation between the raw material, fine fraction and coarse fraction are then observed under scanning electron microscope (ZEISS Gemini 500). Identification of clay and determination of crystallinity of different size fraction are also performed using Fourier transform infrared spectroscopy (FTIR) (Perkin-Elmer) at the scan range of 4000 cm^{-1} – 400 cm^{-1} and X-ray diffraction scanning (XRD) (Bruker D8 Advanced) is performed at the scan range of 5 º2θ – 70 º2θ. The crystallinity index is computed from the XRD pattern according to the method proposed by Hinckley (Kogel *et al.*, 2006).

RESULT AND DISCUSSION
Particle size distribution (PSD)

The result of PSD analysis is tabulated into Figure 1. Clay SA and SC has an average particle diameter of 20 μm and 11 μm respectively. The < 2 μm fraction of both clay constitutes to only 9 %vol and 12 %vol composition in SA and SC respectively. The clays are exceptionally coarse, thus failed to meet the specification of commercial kaolin for coating and filler applications which require 15 % – 92 % of < 2 μm fraction (Siddiqui *et al.*, 2005). Locally, the clay has particle size coarser than the kaolin from Bidor-Tapah area with an average content of 42.5 % of < 2 μm fraction (Cheang *et al.*, 2013).

Scanning electron microscope (SEM)

SEM images supported by the particle size analysis reveal that for both materials are principally the soft
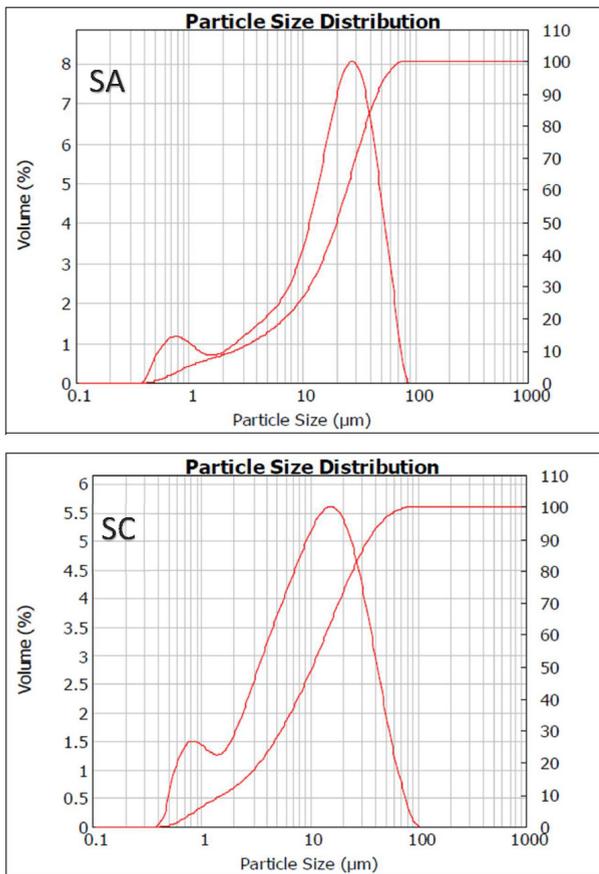
Figure 1: Particle size distribution of processed clay from samples SA and SC.

kaolin type dominated by coarse book like kaolinite stacks (Pruett, 2016). SA consists of mixture of halloysite and book like kaolinite as in Figure 2(a), while SC is the typical soft kaolin type made up of fine platy kaolinite and coarse kaolinite stacks as shown in Figure 2(b). Decantation had efficiently classified the clay into two fractions based on their size. Clay SA had it finer tube like halloysite particles separated from the book like stacks of kaolinite as shown in Figure 2(c). Sample SC on the other hand had the finer delaminated platy kaolinites separated from the coarse kaolinite stacks as shown in Figure 2(d).

X-ray diffraction (XRD) pattern

The 7.0Å basal peak of kaolin minerals are observable from all samples in Figure 3 (Masoud *et al.*, 2013). Poorer resolution for the pair of triplets perceived at the scan range from 34 º2θ - 40 º2θ is observed following the increases of fine fraction in for both sample SA and SC. Removal of -2 µm fraction from SC increased the Hinckley crystallinity index from 0.52 to 0.74 where the clay is promoted from the category of poorly crystallized to well crystallized kaolinite. Halloysite containing clay displays a broad asymmetrical peak with more weight at the lower angle covering 20 º2θ – 23 º2θ, rendering the computation of crystallinity index impossible. Halloysite presence in slight amount is sufficient to cause the -50 µm fraction from SA to displayed a poorly resolved diffraction pattern similar to the solely halloysite containing -2 µm
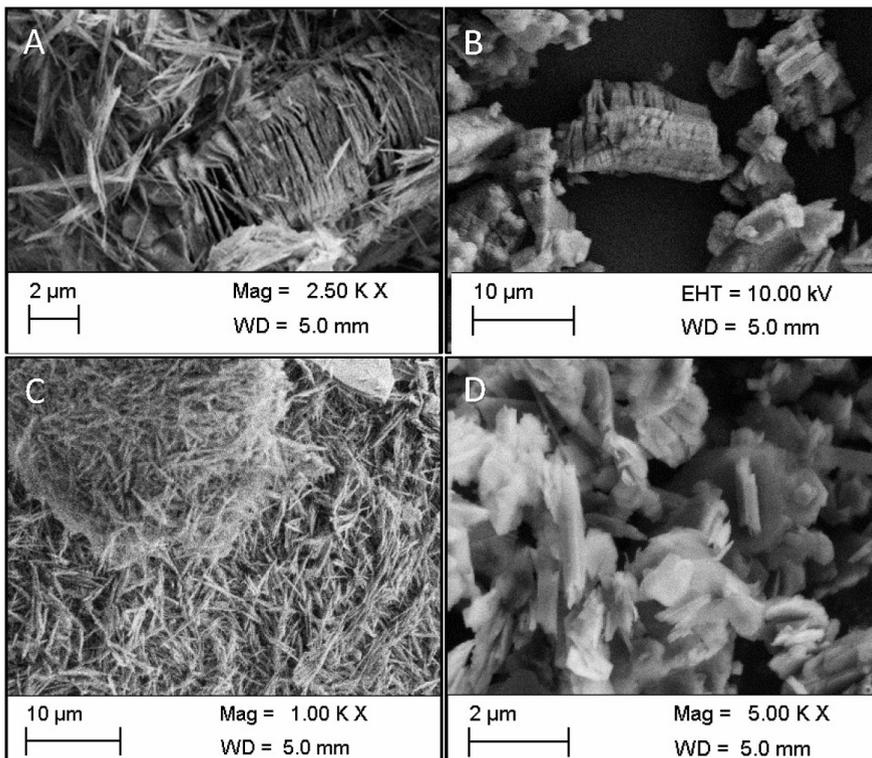
Figure 2: SEM images of processed aplitic kaolin. (A) Halloysite-kaolinite mixture from SA. (B) Platy and stacked kaolinite from SC. (C) Tubular halloysite separated from SA by decantation. (D) platy fine size kaolinite separated from SC by decantation.

fraction from SA. Halloysite shows a more deteriorate effect to the crystallinity displayed on the diffractogram of kaolinite compare to platy kaolinite as demonstrated by comparing XRD pattern of -50 μm fraction of SA to SC, although both are expected to exist as highly disordered crystallites (Brindley, 1980). The +20-50 μm fraction from SA shows a crystallinity index of 0.86 which is categorized as well crystallized kaolinite after the interference of halloysite is eliminated.

Fourier transform infrared spectroscopy (FTIR)

Degritted clay samples displayed the typical kaolinite hydroxyl stretching absorption bands at the position of 3696 cm^{-1}, 3672 cm^{-1}, 3650 cm^{-1} and 3622 cm^{-1} (Figure 4). These four sharp and well resolved peaks indicate a high degree of structural order for all these kaolinite samples (Brindley *et al.*, 1986). After the classification by size, all kaolinites samples still displayed four highly resolved absorption peaks at the range of 3700 cm^{-1} – 3620 cm^{-1}. On the other hand, the solely halloysite containing sample
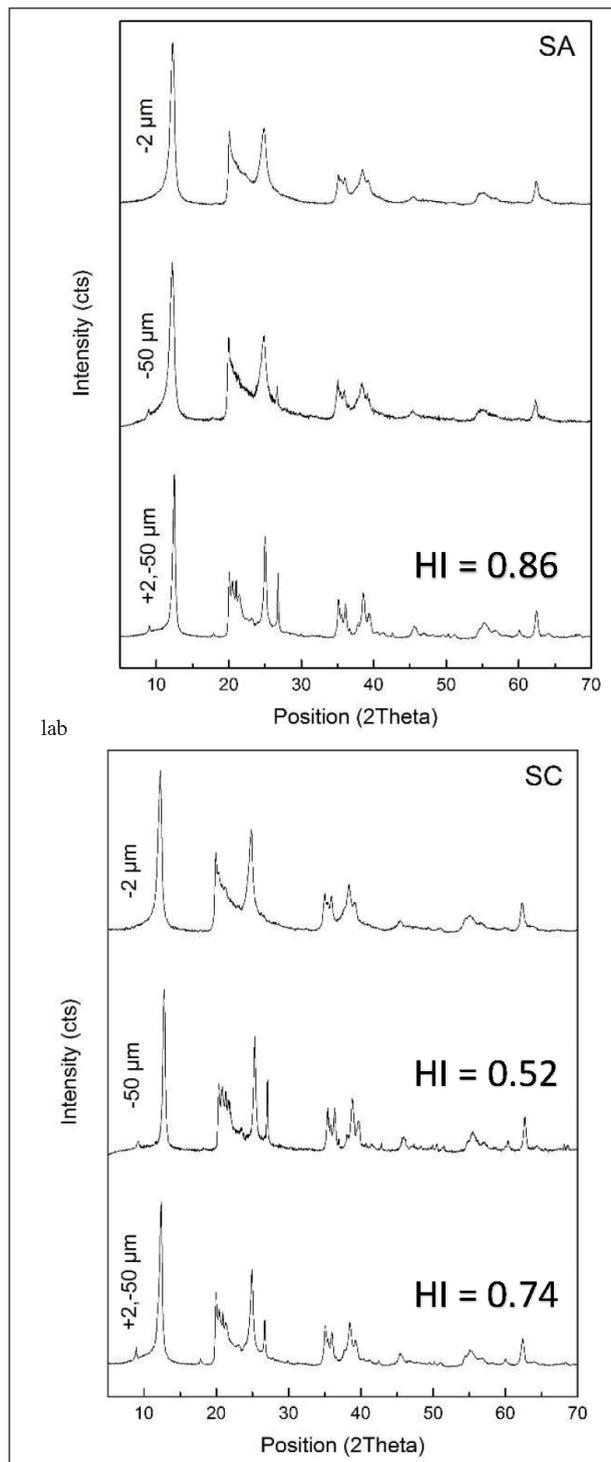
Figure 3: X-ray diffraction pattern of different sized fraction clay from SA and SC. -50 μm = original degritted clay, -2 μm = clay fraction obtained from decantation, -2 +50 μm = coarse settled fraction from decantation. HI = Hinckley crystallinity index.
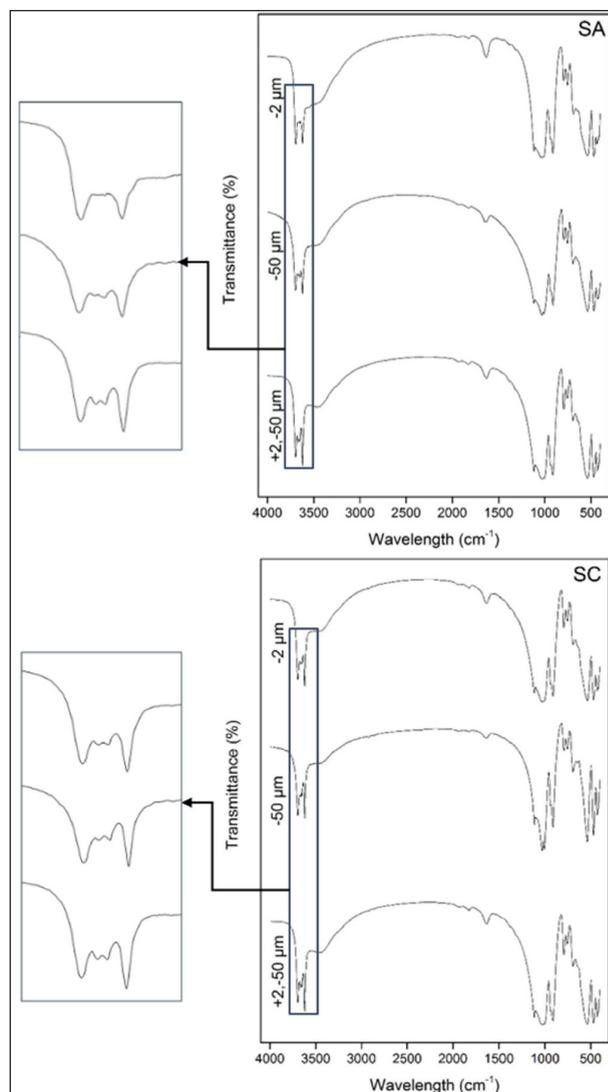
Figure 4: Infrared transmittance spectrum of different sized fraction clay from SA and SC. -50 μm = original degritted clay, -2 μm = clay fraction obtained from decantation, -2 +50 μm = coarse settled fraction from decantation.

shows a poorly resolved pattern at this scan range that is similar to the absorption spectrum of highly disordered kaolin. The OH-bending absorption bands which kaolin clay exhibits at 938 cm^{-1} and 915 cm^{-1} (Ekosse, 2005) are visible for all samples, except the halloysite containing samples which included the -50 μm and +2, -50 μm fraction from SA which displayed an inflexion point instead of a peak at 938 cm^{-1}. The weak doublets with about equal transmittance at 795 cm^{-1} and 758 cm^{-1} is another feature to distinguish well crystallized kaolinite from halloysite (Vaculíková *et al.*, 2011). Unlike the diffractogram by XRD method, the high crystallinity kaolinite stacks are observed to play a major role in the affecting the FTIR spectra. Sample SA which consists of kaolinite and halloysite mixture shows four well resolved peak at the range between 3700 cm^{-1} – 3620 cm^{-1}.

CONCLUSION

The textural and morphological properties of aplitic kaolin had been successfully investigated and characterized using PSD and SEM techniques. The kaolins are principally the soft type where coarse kaolinite stacks contribute to the major composition. The kaolin however can be classified into two types based on the morphology of finer particles which may be consists of: i) delaminated platy kaolinite, or ii) tubular shaped halloysite. These fine fractions however constitute only to minor amount or not more than 12 % of the clays. Both clay consist predominantly of coarse book like kaolinite stacks. The degree of crystallinity of kaolinite samples shows a positive correlation to its particle size when examined by XRD, but the FTIR spectrum shows a high degree of crystallinity for all kaolinite samples regardless of their particle size. Slight presence of halloysite gives an adverse effect on the crystallinity determined from XRD. Sorting of the clay into different size and morphological fraction creates a product with less variation in properties between individual particles, and with more potential for tailoring or engineering of their properties.

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