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Mineralogy and geochemistry of clays from Malaysia and its industrial application

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Abstract. In Malaysia, kaolinitic clays are still viable as an important industrial minerals. Tepoh, Nitar and Lenggor clays represent the deposit found within Johor and Trengganu, considered to be one of the major deposit for local demand. This paper outlines an assessment of the basic characterisation and calcination behaviour of thus clays. Tepoh clay is of kaolinitic clay, Nitar clay is mica rich kaolinitic clay while Lenggor clay is kaolin. To the naked eyes, Tepoh clays seem to be darker with 72% brightness value, high plasticity, LOI (10.56-12.87), CEC (6.73-8.41 meq/100g), BET surface area (16.6 m²/g), zeta potential (-24.1 mV), poor rheological properties, very slow sedimentation rate and composed mainly kaolinite, illite and muscovite. The chemical composition of Tepoh clay was dominantly consists of SiO₂ and Al₂O₃, yet insignificantly contains carbonate. The calcinations from 500°C to 1100°C remarkably transformed Tepoh clays into brighter metaclays. Nitar clay consists of kaolinite (22.01%), illite/mica (38.95%) and quartz (33.77%). High brightness value (94.36%-98.39%) due to low contaminants such as TiO₂ (0.75% to 0.99%) and Fe₂O₃ (0.77% to 1.35%). The plasticity of Nitar clay is equal to kaolinite and contain low proportion of particle < 2 µm fraction (10.2%). Cation exchange capacity (CEC) ranging from 4.37 meq/100g to 5.13 meq/100g which comply to the CEC value of kaolin. Low specific surface area (5.2 m²/g) corresponds to the amount of coarse particles, and zeta potential (-50.9 mV to -54.7 mV) show the colloidal stability. Transformation to metakaolin happened at 510°C and formation of mullite at 900°C. Calcination (up to 1100°C) seems decreased the brightness value of the metakaolin at 0.72%. Lenggor clay is identified as kaolin which essentially comprised of kaolinite (53.60%), mica (10.87%) and quartz (28.66%). Low contaminants such as TiO₂ (0.79% to 0.82%) and Fe₂O₃ (0.61% to 0.62%) increased the brightness value which ranging from 94.50% to 95.5%. Plasticity is low due to low proportion of < 2 µm fraction (30.9%). CEC value (5.24 meq/100g to 6.89 meq/100g) falls between kaolin range. Low specific surface area (23.7 m²/g dan 7.3 m²/g) due to lower amounts of finer particles. Zeta potential (-0.89 mV to -3.76 mV) reflects the instability of the colloid. Formation of metakaolin is interpreted at 520°C. Calcination increased the brightness at 0.25%. Nitar clay is less viscous but higher sedimentation rate than Lenggor clay. Both clays show good crystallization of pseudohexagonal to hexagonal kaolinite particles. Beneficiations such as sizing and classification are essential to increase the clays quality and therefore comply to the industrial requirement.

1. Introduction
Clay properties are important in determining the type, stability and also their usage either as the basic material in the construction, ceramics or pharmaceutical industries. Clay minerals generally consist of
aluminosilicate minerals such as kaolinite, montmorillonite, illite, halloysite and nacrite. The crystallinity of clay minerals will affect the cation exchange capacity values, dispersibility and rheology. Dispersibility is better for well crystallized kaolin.

Rheological property is important for the particle segregation and lost of water. Kaolin also has low viscosity and used as coating materials. Brightness and whiteness character is controlled by the contaminants such as iron and titania. Kaolin was chemically stable in a wide pH range, white in colour, high brightness, good opacity, fine size and flaky texture which made it suitable for use as pigments or extenders, fillers and coatings. The other kaolin characters such as less abrasive, low thermal and electrical conductivity and low viscosity also important in determining the use for coating and filler, but each uses has different specification [36]. In addition for use as coating materials, kaolin also contributes to the suspension stability, rheological properties, strength, smoothness and resistance to weathering while calcined kaolin will improve scrubbing resistance for paper products [16]. The rubber industry uses kaolin as a filler or extender to increase strength and resistance to abrasion.

Calcination will change their optical properties; it will increase the brightness, opacity and oil absorption. Calcined kaolin is used as coating materials where as the difference of dispersion index between air and mullite minerals produced light scattering which increases the opacity of the product [24]. In the paper industry, calcined kaolin is used as filler and coating that give the nature of smooth, shiny, increase brightness and opacity and the ability to print more clearly. The plastic industry uses kaolin as a filler to improve the surface smoothness, stability and resistance to chemical reaction and not easily broken. Calcined kaolin can accelerate hydration of cement and replace 5-10% of the mass of Portland cement in concrete mixtures. It acts as an agent improving the sulfate reaction resistance, ASR, strength, reduces pores and permeability [16].

The kaolinite minerals calcined at the temperature range of 600°C-900°C show the pozzolanic reactivity ([4]; [14]; [25]; [49]). The mullite crystals will partially formed when the clay is calcined at the temperature over 900°C, with higher brightness properties, hidrofobicity, abrasion resistance and dielectric properties ([10]; [37]; [12]; [15]; [18]).

Calcination period is important and influence the mineralogical changes of kaolin. Metakaolin transformed to mullite at the temperature of 1170°C when heated for five minutes while their mineralogy changes at the temperature of 930°C after heating for five hours and the changes to the mullite mineral occurs at 900°C when calcined in 14 days [19]. The higher quantity of clay minerals compare with quartz contribute to finer granulometry relatively and higher LOI when calcined at temperatures between 850°C to 1200°C [34].

Illitic clay is started sintering at 900°C and dominantly transformed to sericite at 1000°C. At 1100°C it begins to melt and form mullite crystals ([43]; [50]; [39]). Low percentage of quartz in clay content will deform it to amorphous at lower temperatures compared with the higher quartz content [3]. Type of clay minerals will also affecting the exothermic and endothermic temperatures of the sample studied [33]. Finer particle size will decrease the thermal insulation due to the increases of sintering rate during the calcination process [23].

2. Materials and Methods
In Malaysia, mostly the clays were extracted mainly for construction industry and only several resources such as in Bidor and Mersing being utilized for better use. After considering lack of scientific research has been done on the clay properties deposited in the area, induced a study on the samples of clay deposited in Tepoh, Terengganu, Nitar and Lenggor in Johor (Figure 1). The objective of the study is to identify the basic clay characteristics and also the effect on calcination process at the temperature of 500°C, 700°C, 900°C, 1100°C.

The samples are firstly dried at room temperature and then were crushed using ceramic mortar grinder and finally being sieved. Only the particles passed the <63μm sieve size will be used for analysis. The calcined samples are soaked for 4 hours to make sure the process is fully completed. The expected output of the research are the variation of mineralogical changes from kaolinite to mullite, phases transition from normal to amorphous and later to spinel phase and the geochemical
composition of the clays. Basic characterization analysis of the uncalcined clay will be identified by screening the samples, mineralogical composition by X-Ray Diffraction (XRD), geochemical composition by X-Ray Fluorescence (XRF), brightness by Chromameter, weight loss by Differential Thermal Gravimetry (DTG-TGA), structure by Field Emission Scanning Electron Microscope (FESEM-EDX + mapping analysis), plasticity, cation exchange capacity (CEC), surface area (BET), zeta potential, rheology, pozzolanic characteristic and sedimentation rate. The calcined clay samples will be analysed for their brightness, structure and mineralogical changes.

3. Results and Discussion
3.1 Basic Characteristic
Fourteen basic characteristics of Tepoh, Nitar and Lenggor clays were analysed and discussed below (Table 1). The results of the brightness test show that the value of the Tepoh, Nitar and Lenggor clays ranges from 70.52% - 71.77%, 94.36% - 98.39% and 94.50% - 95.50% respectively. These indicate that the Nitar clay has a higher brightness than Tepoh and Lenggor clays. Contaminants such as iron oxide, titania, organic matter and carbon content reduce the optical properties of clay, illite minerals reduced the level of white kaolinite, while the brightness decreases with increasing of K₂O [15]. K₂O and MgO content is closely related to mica. The sample is white in color when the white pigment content, Al₂O₃ increased [21].

The brightness of Nitar clay is higher than Lenggor eventhough the K₂O, TiO₂ and Fe₂O₃ content in Nitar clay is higher. It is caused by the lower carbonaceous materials in Nitar Clay (1.49%) compared with Lenggor (4.95%). This brightness value is required to meet the criteria required for use as coating and filling materials that is 90%-92% [24].

Figure 1. Location map of Tepoh, Nitar and Lenggor clays
The liquid limit (LL) of Tepoh, Nitar and Lenggor clays range from 52%-60%, 48%-63%, 8%-14%, plastic limit (PL) ranging from 22%-43%, 1%, 36%-50% and plasticity index (PI) range from 17-30%, 5% -26%, 7% -13% respectively. According to Scott [44], the PI <10% indicates that the samples are less cohesive because they contain well and coarse crystalline kaolinite. Plot PL-PI compared with Atterberg limits chart for brick clay and pottery resulted only two samples of Nitar clay located outside the boundaries of the clay plasticity for moulding while Lenggor clay is only suitable for the brick purposes. Tepoh clay samples showed that the samples T3, T5 dan T9 are suitable for pottery purposes. T1 samples still can be considered for pottery but has a relatively high plastic limit and T7 samples were not suitable due to very high plastic limit (Figure 2). Plasticity will increase with the increasing of kaolinite minerals [34]. Higher silica content will also reducing the plasticity [40]. Plasticity is inversely proportional to the grain size where as the specific surface area (coarse grain) will reduce the amount of water absorbed ([40] and [6]). Nitar and Lenggor clays contain high percentage of coarse grain size about 70% (Lenggor) and 90% (Nitar) particle size of more than 2μm.

LOI analysis show the Lenggor clay has the highest value which ranges from 12.23%-13.43%, followed by Tepoh clay (10.56%-12.87%) and Nitar clay is the lowest (5.60%-7.07%). LOI indicates the purity of raw materials where as pure kaolin clay will give LOI value of 13.9%, caused by weight loss of water when the samples heated. If the LOI value is lower, this is due to the contaminants especially the quartz content is higher.

| Basic Characteristic | Tepoh | Nitar | Lenggor |
|---------------------|-------|-------|---------|
| Plasticity Index (%)| 17-30 | 5-26  | 7-13    |
| Zeta Potential (mV) | -24.133 | -50.9- (-54.7) | -0.89- (-3.76) |
| Cation Exchange Capacity (meq/100g) | 6.73-8.41 | 4.73-5.13 | 5.24-6.89 |
| Sedimentation Rate | slow | slow | slow |
| Rheology | weak | weak | weak |
| Brightness (%) | 70.52-70.82 | 94.36 | 95.50 |
| Surface Area (m²/g) | 16.63 | 5.18, 5.22 | 23.66, 7.32 |
| Pozzolanic Reactivity | good | good | good |
| Particle Size | 0.48-120.26 | 0.38-130 | 0.7-130 |
| XRD | Quartz, kaolinite, mica, hematite | Quartz, kaolinite, mica | Quartz, kaolinite, mica, albite |
| XRF | Kaolinitic clay | Kaolinitic clay | Kaolin |
| FESEM-EDX | Hexagonal kaolinite | Hexagonal kaolinite | Hexagonal kaolinite |
| DTG-TGA | Weight loss at 120°C, 270°C, 490°C | Weight loss at 120°C, 510°C, 730°C | Weight loss at 120°C, 520°C |
| LOI | 10.56-12.87 | 5.60-7.07 | 12.23-13.43 |
Figure 2. Atterberg limit for brick clay and pottery, Tepoh, Nitar and Lenggor samples

The results of chemical analysis of major elements present in the Tepoh clay show that the SiO$_2$ is the most abundance with the percentage ranging between 59.14-60.49% followed by Al$_2$O$_3$ (19.70-20.62%), Fe$_2$O$_3$ (4.73%-5.15%), K$_2$O (1.65%-1.04%) and MgO (0.82%-0.9%) as presented in Table 2. Other elements such as Na$_2$O and CaO contains <0.3%, while the content of P$_2$O$_5$ and MnO <0.1%. For minor elements, the chromite content is in the range of 69-74 ppm, cobalt (11-12 ppm), vanadium (195-208 ppm), strontium (77-81 ppm), rubidium (109-117 ppm) and zircon (315-406 ppm). These minor elements, even exist in small amounts will affect the color of the clay due to their durability of heating at high temperature [31]. The zircon and chromite minerals are more refractories which has a melting point >1100 °C. Percentage of K$_2$O and TiO$_2$ depend on illite/mica and anatase content. MgO content is explained by the presence of montmorillonite minerals ([18]; [20]). The XRF result used to estimate the major minerals percentage in the Tepoh clay show that the average of kaolinite is 45%, illite/mica (12%), quartz (31%) and organic matter (5%). The Tepoh clay is of kaolinitic clay as the total percentage of kaolinite is less than 50%. Chemical composition of clay is important because they influenced the properties of ceramic materials during calcination, Al$_2$O$_3$ content >30% would increase the refractory properties and mechanical strength [9]. Major element analysis on Nitar clay shows the SiO$_2$ is most abundant (57.26%-64.98%) followed by Al$_2$O$_3$ (22.38%-27.62%), K$_2$O content is quite high (4.32%-5.34%). The value of the TiO$_2$, P$_2$O$_5$, MgO, MnO, CaO and Na$_2$O <1%, Fe$_2$O$_3$ is relatively low (0.77%-1.35%) and MnO is below detection limit. Lenggor clay showed the SiO$_2$ content is most abundant (58.37%-59.87%), followed by Al$_2$O$_3$ (25.16%-25.96%). The value of TiO$_2$, P$_2$O$_5$, MgO, MnO, CaO, Na$_2$O and Fe$_2$O$_3$ <1%, and MnO is below detection limit. K$_2$O values of Lenggor clay (1.27%-1.29%) was lower than K$_2$O content in Nitar clay (4.32%-5.34%) showed the illite/mica mineral is more abundance in the Nitar clay than Lenggor clay. This is also proven by the lower contents of Fe$_2$O$_3$, MgO, Rb and Zn in Lenggor clay. Based on calculations using the Mica Convention, Nitar clay consists of quartz (33%), mica (39%) and kaolinite (23%), while the water trapped within the lattices (4.9%) and carbonaceous material (1.5%). Lenggor clay consists of quartz (28%), mica (11%) and kaolinite (66%), while the water trapped within the lattices (9.8%) and
carbonaceous material (3.1%). Both clays contain a similar percentage of quartz, but mica and kaolinite content are different. The Nitar clay is classified as kaolinitic mica clay and Lenggor clay as kaolin. According to Dombrowski (2000) kaolin is a material which the kaolinite content exceeds 50%.

Pozzolanic property is a special feature of the clay where it reacts with cement to form the insoluble materials to improve the mechanical strength and durability of concrete structures. ASTM standard C618 (1980), determines that the criteria of the pozzolanic activities of calcined clay should contain the total amount of SiO₂, Al₂O₃ and Fe₂O₃ more than 70%, and SO₃ <4% with LOI <10%. In addition, Indian standards specify that to the nature of good pozzolan, CaO content must be <10% and the amount of SiO₂ and Al₂O₃ > 50% [14].

Table 2. Major elements of Tepoh, Nitar and Lenggor clays

| Element (%) | Sample |
|-------------|--------|
|            | T₁     | T₃     | T₅     | T₇     | T₉     | NA    | NB    | NC    | NSP   | LB    | LC    | LD    | LE    |
| SiO₂        | 59.14  | 60.49  | 59.21  | 60.91  | 59.8   | 62.96 | 57.66 | 64.98 | 63.20 | 58.47 | 59.04 | 58.37 | 59.87 |
| TiO₂        | 0.99   | 0.97   | 1.03   | 0.96   | 1.04   | 0.75  | 0.99  | 0.87  | 0.85  | 0.81  | 0.81  | 0.82  | 0.79  |
| Al₂O₃       | 20.62  | 19.84  | 19.97  | 19.7   | 20.14  | 24.11 | 27.62 | 22.38 | 22.41 | 25.96 | 25.72 | 25.96 | 25.16 |
| Fe₂O₃       | 5.15   | 5.13   | 4.73   | 4.78   | 4.95   | 0.77  | 1.01  | 0.98  | 1.35  | 0.62  | 0.61  | 0.64  | 0.61  |
| MgO         | 0.87   | 0.9    | 0.82   | 0.85   | 0.85   | 0.81  | 0.77  | 0.44  | 0.87  | 0.40  | 0.39  | 0.39  | 0.39  |
| CaO         | 0.24   | 0.25   | 0.25   | 0.23   | 0.24   | 0.02  | 0.02  | 0.04  | 0.01  | 0.02  | 0.02  | 0.02  | 0.02  |
| Na₂O        | 0.22   | 0.23   | 0.05   | 0.26   | 0.22   | 0.07  | 0.14  | 0.10  | 0.07  | 0.08  | 0.07  | 0.07  | 0.07  |
| K₂O         | 1.81   | 1.79   | 1.64   | 1.8    | 1.65   | 3.27  | 5.34  | 4.37  | 4.39  | 1.29  | 1.29  | 1.29  | 1.27  |
| P₂O₅        | 0.05   | 0.06   | 0.06   | 0.06   | 0.06   | 0.01  | 0.02  | 0.02  | 0.04  | 0.04  | 0.04  | 0.04  | 0.04  |
| LOI         | 10.8   | 10.66  | 12.87  | 11.5   | 10.56  | 6.15  | 7.07  | 5.60  | 6.71  | 13.43 | 13.16 | 12.23 | 13.03 |
| Total       | 99.89  | 100.35 | 100.66 | 101.07 | 99.54  | 99.97 | 100.64| 99.78 | 99.87 | 101.12| 101.15| 99.83 | 101.25|

Note: BDL-below detection limit, T-Tepoh samples, N-Nitar Samples, L-Lenggor samples

Comparing data obtained from the XRF results of Tepoh, Nitar and Lenggor clays, the total amount of silica, alumina and iron the three clays are more than 85% and CaO content is <1% confirmed that it has good pozzolan properties. To obtain the pozzolanic reactivity more precise, the sample must be calcined at 700°C and comparison with standard samples compressive strength should be taken into account ([14]; [49]).

CEC values of Tepoh clay ranges between 6.73-8.41 meq/100g, Nitar clay (4.37 to 5.13 meq/100g) and Lenggor clay (5.24-6.89 meq/100g). Typical CEC values for kaolinite is 3-15 meq/100g, montmorillonite (80-150 meq/100g), and illite (10-40 meq/100g) [44]. The CEC values of the three clays was located in the range of typical kaolinite. CEC value increases with increasing specific surface area or a reduction in particle size [48]. CEC value of Lenggor clay is higher than Nitar clay because Lenggor clay is of finer size.

Specific surface area of Tepoh clay is 16.6318 m²/g, Nitar (5.2167 m²/g), Lenggor B (23.6652 m²/g) and Lenggor C (7.3155 m²/g). Specific surface area of kaolinite is ranged between 15 m²/g-20 m²/g (Uehara & Gillman 1981). Tepoh clay is of kaolinitic clay but Nitar and Lenggor C clay samples are lower while the Lenggor B is higher. Total specific surface area is influenced by particle size in which the finer particle size will increase the specific surface area and cation exchange capacity value ([13], [47]). This is probably due to Nitar clay finer grain size (<2um) is lower (<31%) and contain higher percentage of quartz. Tepoh, Lenggor and Nitar clays are not suitable for paper industry because they need the calcined kaolin with the specific surface area from 18m²-19m² [24].

Zeta potential values for the Tepoh clay is -24.133 mV, Nitar (-50.9mV to -54.7mV) and Lenggor (-0.89mV to -3.76). Tepoh and Lenggor clays values are in the range between +30 mV and -30 mV.
which are located in unstable dispersion while Nitar clay located in stable location. Stability properties of colloidal particles are influenced by the surface charges and this is a function of pH and ionic strength. Colloids are not stable when the distance between the particles is closer compared with stable colloidal [2]. The flow properties and stability of such suspensions depend critically on the characteristics of the colloidal fraction, particularly on the zeta potential of the particles [26]. The study by Hussain et.al [29] found that kaolinite zeta potential is ranges between -24.0 mV to -49.5 mV while illite between 0.0mV to -42.0 mV. The value obtained in Nitar clay is higher than the zeta potential of kaolinite. Lenggor and Tepoh clays found to have the zeta potential equal to illite. Rheological properties of clay suspensions depend on the clay concentration, the size and shape of the clay particles, and the level of interaction between them [46]. High zeta potential of Nitar Clay (of the order of 50 mV) shows good rheological characteristic where the particles (in suspension) tend to deflocculate. Progressive replacement of the calcium with a deflocculating cation (generally sodium) will decrease the degree of the flocculation and therefore the viscosity of a suspension will decrease until the point is reached at which the attractive forces are neutralized. A partially deflocculated suspension is usually thixotropic, meaning that, if it is left undisturbed, its viscosity will increase. This thixotropic condition is readily destroyed by agitation. Deflocculation thus makes it possible to form suspensions of high solids content and low viscosity [26]. Kaolin used for paper coating requires a solid content of 70% kaolin in the suspension and it is needed for clay to flow even at high concentrations [27].

The increase in the size of the solid particles will cause the apparent viscosity increase in clay dispersion [5]. The presence of kaolinite with a high Hinckley index show good rheological properties and low drying shrinkage while low crystallinity content and the presence of illite showed weak rheological properties and higher dry shrinkage [9]. Hinckley index is a dimensionless number which normally varies between ~ 0.2 and 1.5; the larger the value, the greater the “crystallinity” [42]. Calculation of Hinckley index on 110 and 111 peaks obtained from XRD analysis showed the index for the Tepoh, Nitar and Lenggor clays are <0.5, 0.98, 0.86 respectively. Low values of Hinckley index showed that the kaolinite in the Tepoh, Nitar and Lenggor clays are poorly crystallized and have weak rheological properties.

Clay suspensions typically exhibit either shear thinning behaviour (thixorophic) or near-Newtonian behavior. Shear thinning behavior is associated with deflocculation in that the number of interparticle bonds in a flocculated suspension decreases with increasing shear rate [28]. All the tested samples show the typical behaviour of shear-thinning fluids which is decreasing in shear stress with increasing of shear rate. The Nitar clay has a lower dynamic viscosity and therefore is viscous flow as compared to Lenggor and Tepoh clay. This show that the rheological characteristics of Nitar clay is better. This is also in line with high zeta potential value of Nitar clay.

The structures for kaolinite sediments formed from suspensions exhibiting flocculation and dispersed settling behaviors [41] and the sedimentation (settling) rate of suspension with this mixed mode settling behaviours varies from slow to rapid [38]. Nitar clay sedimentation rate is higher than the Lenggor clay and Tepoh clay. The sedimentation rate is influenced by grain size, density and inter grains reactions. Interaction between the solid and liquid substances play an important role in determining the details of the distribution or dispersion, especially for fine particles [1].

Grain-size analysis results obtained indicated that Tepoh, Lenggor and Nitar clays containing a total of 9.37%, 10.2% and 30.9% grain size <2μm respectively. Nitar clay contains 94.9% grain size <45μm, Tepoh clay (76.5%) and Lenggor clay (83.9%). Grain size <2μm is very important to determine the use of clay in ceramic products [32]. Clay used as coating and filling materials need at least 60-90% grain size <2 μm calcined kaolin [36]. Thus the purification processes such as classification and sizing is necessary to obtain the desired size range.

Two analyses conducted to determine the clay mineralogy and basic mineralogical behaviour, x-ray diffraction (XRD) and also the effect of temperature on the sample weight loss (DTG-TGA). The XRD results indicated Nitar clay contains kaolinite, illite/mica and quartz while Lenggor clay containing kaolinite, illite/mica and quartz with some albite. Kaolinite and illite are the main clay
minerals and quartz is a non-clay minerals. Major minerals content in Tepoh clay are quartz, kaolinite, illit/mica and hematite with trace amount of montmorillonite minerals.

DTG-TGA analysis performed on the Tepoh clay shows a reduction in weight that occurs with a temperature increase at 120°C, 270°C and 490°C while the weight loss on Nitar clay occurs at 120°C, 510°C and 730°C and Lenggor clay at 120°C and 520°C (Figure 3). At 120°C a slight reduction in weight occurs which at this temperature the water evaporated, while at the temperature of 270°C loss of water are higher and might also caused by the burning of organic materials ([35]; [33]). At the temperature of 490°C, 510°C and 520°C, dehydroxilation of kaolin minerals to amorphous form occurs.

Weight loss at 730°C on Nitar clay shows the dehydroxilation process of illite. Muscovite experience progressive dehydroxilation process of for a wide temperature range of 800°C to 1100°C and experience a long endothermic reaction [22]. At temperatures above 800°C, the TG curve shows a visible uniform weight loss or no weight change of the horizontal graph. It is likely dehydroxilation process of muscovite occur. At around 920°C possible changes to the spinel phase.

Theoritically metakaolin will change to mullite at 900°C [19] which can be indicated by exothermic reaction. Without DTA curve which can show the occurrence of exothermic or endothermic reaction, it is uncertain for the Tepoh, Nitar and Lenggor clays transformed from metakaolinite to mullite.

![Figure 3. Graph showing the result of DTG-TGA analysis of Tepoh, Nitar and Lenggor samples](image)

FESEM analysis showed that the flaky texture clay minerals (Figure 4). Kaolinite mineral is characterized by pseudo-hexagonal shape. Poorly crystallized kaolinite indicated by small particles with a broken edge will increase the surface charge and also an increase of contaminants absorption. Kaolinite may poorly crystallized due to the presence of contaminants which will also reduce the kaolinite brightness. Crystallinity and morphological properties can be used to determine the usage of clay [33]. High content of contaminants (iron and montmorillonite) makes the clay only suitable for industrial ceramic and poorly crystallized clays can be used as a pottery basic materials and building materials such as bricks. Fine grain particle size refers to the better adhesive properties [33]. Weight percentage value of the main elements is shown in Figure 4-6. Fe element in Tepoh clay is disseminated in the clay lattices and is likely to replace Al atoms in the kaolinite structure [8]. EDX
mapping on chemical composition on selected area show the element content, equivalent with the percentage of oxide obtained by XRF. K element content also showed a high proportion as K₂O obtained by XRF. EDX mapping on Lenggor clay showed a pattern consistent with the results of XRF. O, Al and Si content in Lenggor clay is in the same range with Nitar clay. The significant difference is in the K content is <2%, while Nitar clay containing K> 4%.

Figure 4. FESEM analysis of raw Tepoh (T), Nitar (N) and Lenggor (L) samples

Figure 5. EDX+‘mapping’ analysis of raw sample, Tepoh clay

Figure 6. EDX+‘mapping’ analysis of raw sample, Nitar clay
3.2 Calcination
The selected samples were calcined at four different temperatures, at 500°C, 700°C, 900°C and 1100°C which is the brightness, mineralogical and structural changes were recorded and presented in Table 3. Analysis was done by calcining a representative Tepoh, Nitar and Lenggor clay samples.

The brightness value, L of the Tepoh clay increases when the sample was calcined at different temperatures from 70.82% (raw clay) to 74.495 (500°C), 78.39% (700°C), 79.82% (900°C) but decreased drastically to 69.76% when being calcined at 1100°C. The presence of iron and titanium will result in the decrease of brightness [15]. The absence of carbonate minerals, will facilitate the formation of Fe₂O₃ which will give the red pigmentation of brick when calcined at 1100°C because the presence of carbonate will cause the Fe element present in the matrix trapped in the calcium silicate structure [17].

Brightness of Nitar clay calcined at 1100°C was found to decrease slightly from the raw sample 94.36% to 93.64%. Lenggor clay has a higher brightness after calcined up to 1100°C from 95.50% (raw) to 95.75%. In comparison Lenggor clay have a higher brightness than Nitar clay mainly due to illite/mica content is higher in Nitar clay. Brightness is an important factor to determine the content of contaminants existed in the clay. ‘L’ is the rate of brightness/darkness, and ranged from 100 (white) to 0 (black). Fe₂O₃ content which is relatively high (≈ 5%) will generally produced the red colour end product due to crystallization of hematite with the increase of temperature [7]. Significant correlation between the colour range and trace element contents also can be found in clay samples [21].

Basic mineral content present in the Tepoh clay are quartz, kaolinite, mica/illite, hematite and montmorillonite. When the sample was calcined at 500°C, the montmorillonite mineral detected at 2Ѳ = 5.8° has been disappeared and the intensity shown by the kaolinite mineral also dissappeared. The intensity of quartz minerals, illite/mica and hematite remained unchanged (Figure 8).

Mineralogy of Tepoh clay calcined at 700°C remained unchanged in intensity of illite/mica, quartz and hematite minerals. At 900°C, the intensity of illite/mica is lower while the intensity values of quartz and hematite remained unchanged. Formation of mullite initially detected at this temperature. At 1100°C, the intensity values of hematite are steadily increasing and quartz minerals remained unchanged. The formation of mullite mineral can be clearly detected at 1100°C. No illite/mica and kaolinite minerals detected at this stage. At 700°C, only illite/mica minerals existed and the amount decreases with the increase of temperature and completely disappeared at 1100°C comparable to the study by Buchwald et al. [11].

XRD pattern of Nitar clay shows the decomposition of kaolinite to metakaolin starts after 500°C at which the intensity of kaolinite was dissappeared at 700°C. Mullite peak was first detected at 900°C. Illite/mica and quartz are detected up to 1100°C. Lenggor clay shows the decomposition of kaolinite to metakaolin starts after 500°C and the peak of kaolinite dissappeared at 700°C. Albite peaks disappeared completely at 700°. No mullite peak detected even at 1100°C. Illite/mica and quartz are detected up to 1100°C.
Table 3. The characteristic of the calcined Tepoh, Nitar and Lenggor clay samples

| Sample | Analysis | 500°C | 700°C | 900°C | 1100°C |
|--------|----------|-------|-------|-------|--------|
| Tepoh  | Brightness, L (%) | 74.49 | 78.39 | 79.82 | 69.76 |
| XRD    | Q,M,H    | Q,M,H | Q,M,H | Q,M,H |
| FESEM-EDX | Melting phase | |
| Nitar  | Brightness, L (%) | 86.64 | 90.24 | 92.99 | 93.64 |
| XRD    | Q,M,K    | Q,M   | Q,M   | Q,M   |
| FESEM-EDX | Melting phase | |
| Lenggor| Brightness, L (%) | 90.41 | 94.87 | 94.53 | 95.75 |
| XRD    | Q,M,K,A  | Q,M   | Q,M   | Q,M   |
| FESEM-EDX | |

Q-Quartz, M-Mica, K-Kaolinite, H-Hematite, Mu-Mullite, A-Albite

Figure 8. XRD analysis of raw and calcined samples from Tepoh, Nitar and Lenggor

FESEM analysis shows the Tepoh clay sample calcined at 500°C remains unchanged. At 700°C, there was no evidence of fusion or vitrification process. Vitrification process can be clearly seen in samples calcined at 1100°C. At the temperature of 900°C, pores existed still have no specific shape and angular, but phyllosilicate minerals shape began to change and start to form aggregates (Figure 8).
At 1100°C, the surface of phyllosilicate mineral in Tepoh clay is smoother and the pores are spherical shape with a smooth edge (Figure 9). Vitrification process is more extensive occurs in the clay samples tested because of their high phyllosilicate minerals content [17]. As the temperature increased particles flocculation will cause a reduction in porosity. At 1100°C, there is extensive vitrification process in the sample analysed causing the pores coalesce and transform into spherical shape due to melting of clay particles in the matrix and gas emission. FESEM photomicrograph on the samples calcined at 1100°C clearly show the formation of mullite minerals with bladed textures but the quartz mineral is remained unchanged.

FESEM image showing kaolinite minerals in Nitar and Lenggor clays are well crystallized consisting of piles and books of kaolinite flakes. This feature is typical for kaolinite resulting from the weathering process [30]. Kaolinite sheet size range from 0.5μm to 6μm and quartz grain can achieve 11μm. No mullite mineral images found and although XRD results showed that they presence at 700°C and 900°C. However, partially melting kaolinite can be seen at 1100°C.

Conclusions

- Tepoh clay is of kaolinitic clay, Nitar clay is of mica-rich kaolinitic clay while Lenggor clay is kaolin. Mineral content are mainly consist of quartz, kaolinite, mica / illite. Nitar clay containing 39% mica.
- Nitar and Lenggor clays contains low material or mineral contaminants such as iron oxide (<1.35%), titania (<0.99%) and low organic matter (<1.5%) causes both clays have the brightness 94% suites the minimum criteria for paper and ceramic industry. The Tepoh clay contain higher contaminants resulted the brightness is only about 70.8% and only suitable for bricks and pottery industry.
- The grain size <2μm of Tepoh, Nitar and Lenggor clays are around 9%, 10% and 30% respectively which is considered very low and not suitable for use in paper industry, simple beneficiation is required.
- Kaolinite crystals in both Nitar and Lenggor clays are well crystallized with pseudohexagonal to hexagonal shape but Tepoh clay is poorly crystallized. Poorly crystallized of Tepoh clay can be determined it has good pozzolanic reactivity properties. It can also be used to determine the
The rheological properties of Tepoh clay in which the rheological properties are weak indicated by the low index value.

- Zeta potential value of Nitar Clay shows that the colloids stability while Lenggor clay is unstable. Nitar clay also found to have better rheology. Nitar and Lenggor clays have low specific surface area compared to the value for kaolinite. Tepoh clay zeta potential is unstable with a large specific surface area. Specific surface area is useful to conclude that the size of the Tepoh clay is of fine-sized.
- Calcination to 1100°C increased the brightness of Lenggor clay about 0.25%, the brightness of Nitar clay decreased about 0.72% but the the brightness of Tepoh clay dropped about 0.3% after increased about 13% at 900°C due to the crystallization of Fe₂O₃. Tepoh samples calcined at 1100°C show the melting of clay minerals occurs with the formation of aggregates and reduction of pore size and changes of inter particles pore shape.
- Calcination produces the refractory mineral, mullite from 900°C in the Nitar and Tepoh clays but cannot be detected in the Lenggor clay.

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