International Journal of Current Science, Engineering & Technology
ISSN : 2581-4311
Original Research Article | Open Access | AMCT 2017 Malaysia | *Special Issue*

Rheological Behaviour and Fired Properties of Malaysia Clay from Mersing(Johor) In Application to Manufacturing of Ceramic Tile

Chee Lung CHIN[1,2,a*], Zainal Arifin AHMAD[1,b], Sew Seng SOW[2,c]

[1]Structural Materials Niche Area, School of Materials and Mineral Resources Engineering, Engineering Campus, UniversitiSains Malaysia, 14300 NibongTebal, Penang, Malaysia.

[2]Ceramic Research Company SdnBhd, Lot 7110 (Guocera – Hong Leong Group), JalanKapar, 42100 Klang, Selangor, Malaysia.

[a]clchin@guoceratile.com.my, [b]srzainal@usm.my, [c]sssow@guoceratile.com.my

ABSTRACT. The aim of this research work was to evaluate the rheological behaviour and firing properties of Mersing clay from the state of Johor, Malaysia. The knowledge of this study is crucial to evaluate the potential of the clay as a raw material in application to ceramic tiles. Rheological behaviour was identified by deflocculant demand, thixotropy, zeta potential and cation exchange capacity (CEC). Fired properties were determined by linear fired shrinkage, water absorption, bulk density, apparent porosity and fired colour. It is found that the clay is suitable to be used for wet milling process in manufacturing of tiles with low in CEC value (16 meq/100g) and high in zeta potential between -40 to -45 mV from pH of 6 to 12. The fired properties of the clay are greatly influenced by its mineralogical and chemical composition, especially fluxing oxides of K_2O from illite, which promotes formation of liquid phase. Therefore, the Mersing clay demonstrates that it is most appropriate to be used as a raw material for the production of ceramic tiles.

Keywords: *Clay, Deflocculant demand, Zeta potential, Thixotropy, CEC;*

Received: 15.10.2017, Revised: 15.12.2017, Accepted: 30.02.2018, and Online: 20.03.2018;

DOI: *10.30967/ijcrset.1.S1.2018.160-165*

Selection and/or Peer-review under responsibility of Advanced Materials Characterization Techniques (AMCT 2017), Malaysia.

1. INTRODUCTION

Clay is widely used as the main raw materials in the manufacturer of ceramic tiles. In Malaysia, clay can be easily found in the state of Johor especially in the Mersing District [1]. The land in Johor is mostly utilized for agriculture, mainly oil palm and rubber plantations [2]. For geological survey, Johor has six main geological formations underlying the soil, namely Quaternary, Tertiary, Cretaceous-Jurassic, Triassic, Permian, Intermediate Intrusive, Acid Intrusive and Devonian. The soils of Johor can be classified into three groups, namely sedimentary, alluvial and miscellaneous soils where these soils have been differentiated into soil series and associations. The distribution pattern of these soil series and associations reveals a close relation with those of different geological lithologies within the state [2]. However, very little research works were conducted on the clay in Mersing as most researchers is focusing on research work related to advanced ceramic materials.

Rheological properties of slurries during wet milling process and fired properties are important measurement to ceramic tile manufacturer. The dispersion of clay by wet milling process is a fundamental step to obtain homogeneous and stable system, which is characterized by rheological properties [3]. The viscosity of clay suspension can be reduced by introducing suitable deflocculant with minimum concentration, where it can be measured bydeflocculant demand. Furthermore, clay undergoes changes during firing process as a result of physical, chemical and mineralogical modification [4]. In terms of clay mineral, kaolinite-illite mixture is widely used in ceramic tile industry, where alkaline fluxes (such as K_2O and Na_2O) in reaction with silica and alumina promote liquid phase formations that facilitate densification [4]. Rheological and fired properties of clay will depend on the composition and the homogeneity of the mixture mainly on the clay minerals [5]. Therefore, the aim of this research work is to evaluate the rheological behaviour of Mersing clay together with their fired properties viz. linear fired shrinkage, water absorption, bulk density, apparent porosity and fired colour. The knowledge derived from this study is crucial for evaluating the potential applications of Mersing clay in designing the ceramic tiles body formulation.

2. MATERIALS AND METHODS

2.1 Sample Preparation. Raw clay from Mersing (Johor) supplied by KBB Minerals Industries SdnBhd was collected for this research work. For sample preparation, the clay was dried at 110 °C for 24 hours and grounded to fine particles by using agate mortar. Later, the clay was homogenised by coning and quartering technique to collect representative samples. The sample was wet milled according to common industrial ceramic tiles procedures and dried at 110 °C for 24 hours. Milled powder was moisturized to moisture content of about 6% [6] and follow by crushing and sieving operations through 500 µm sieve to ensure break down of agglomerates. Later, the sample was aged for 2 hours in enclosed environment to ensure homogeneity of moisture across the powder particles. The humid samples were pressed to button of 50 mm in diameter (powder of 24 g) with pressing pressure of 27 MPa and dried at 110 °C for 24 hours. Dried buttons were fired using Nabertherm N60/14 furnace with firing temperature of 1000 to 1250 °C with holding time of 30 min.

2.2 Characterization. The thermal behaviour, mineralogical and chemical composition (Table 1) of the studied clays were described elsewhere [7], where Mersing clay has reported containing high illite and quartz. The studied clay was characterized by deflocculant demand, thixotropy, zeta potential and Cation Exchange Capacity (CEC). Deflocculant demand and thixotropy were obtained by using Torsion Viscometer(Gallenkamp type)with fluidity and over swing as measurement for rheological behaviour. Three types of deflocculant were used, namely sodium tripolyphosphate(STPP), sodium hexametaphosphate (SHMP) and sodium metasilicate (SMS). Zeta potential was measured by using Brookhaven Zeta plus zeta meter[8]. CEC was measured and by using ammonium acetate method and expressed as mili-equivalents(meq) of cation adsorbed per 100g of clay [9]. For fired properties,linear fired shrinkage was measured from the variation of the length between the dried and fired samples. The water absorption was determined from weights differences between the as-fired and water saturated (immersed in boiling water for 2 hours and follow by cooled water for 4 hours) samples. Bulk density and apparent porosity of fired samples were determined by Archimedes principle by using distilled water.The fired colour of fired samples were analysed in terms of L^*, a^* and b^* values by using Hunter Lab Mini Scan EZ.

Table 1 Chemical analysis of Mersing clay

	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	Na_2O	K_2O	CaO	MgO	LOI *
Raw form	68.14	20.58	1.11	0.93	0.06	3.63	0.00	0.66	5.03

* Loss on Ignition

3. RESULTS AND DISCUSSION

3.1 Deflocculant Demand and Thixotropy. Fig. 1 shows the rheological behaviour of Mersing clay with various deflocculantwith concentration of 10% of solid content of deflocculant. Deflocculant is used during wet milling process to disperse slip. Fig. 1a shows that both STPP and SHMP shows low in deflocculant demand with Mersing clay of about 0.06% of deflocculant added as compare with SMS of 0.18%deflocculant added to achieved maximum fluidity, which indicates that SMS is not the preferable options to be used in processing of Mersing clay through wet milling process. Similar observation was observed for thixotropy of Mersing clay after 1 min at rest (Fig. 1b).

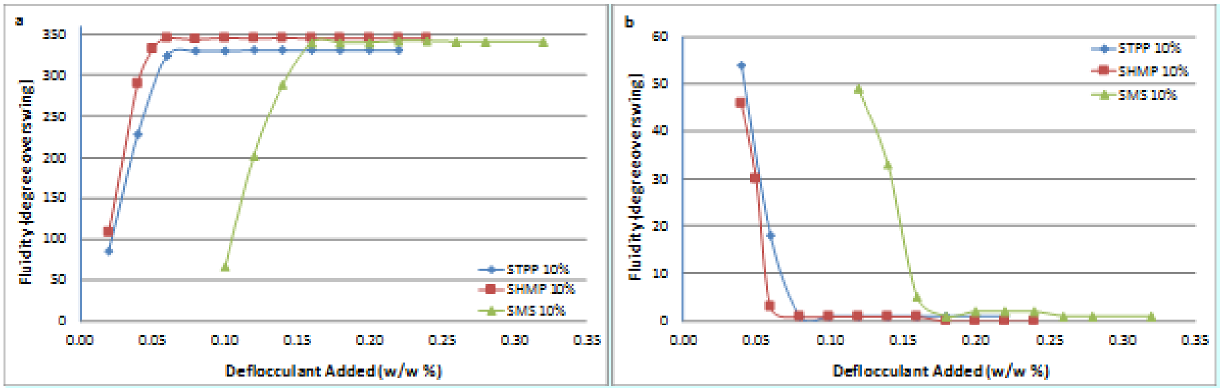

Fig. 1 Rheological behaviour of Mersing clay of various deflocculantby (a) Deflocculant Demand and (b) Thixotropy at 1 min

3.2 Zeta Potential and CEC. Fig. 2 shows the zeta potential of Mersing clay. For pH range of 2 - 12, the zeta potential of Mersing clay is negative and indicate that the clay particles consists of net negatively charge over the whole range of pH [8,14,15]. An increase in the pH of clay suspension is resulted in drastic increase of the negatively charge until pH of 6 (acidic region). The zeta potential of Mersing clay was saturated between -40 to -45 mV from pH of 6 to 12 (alkaline region). The main contribution to the negatively potential is the structural or permanent negative charges located on the basal face of the clay particles formed by isomorphic substitution of Al and Si ions in the crystal lattice with lower valence metal ions. Therefore, the basal face is permanently net negatively even with very low pH [16-18]. At low pH (acidic region), it was observed that the negative zeta potential becomes smaller in magnitude, which was due to the permanent surface charges formed isomorphic substitution of lower valency metal ions in the clay crystal structure being progressively neutralised by the pH - dependent positive edge charges that become more important with decreasing pH. These positive charges are not sufficient to completely neutralise all the permanent negative charges even at low pH [15-17].

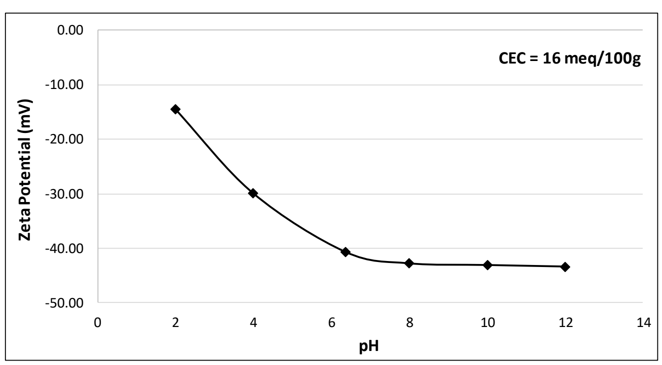

Fig. 2 CEC and Zeta Potential of Mersing clay

CEC value of Mersingclay is 16 meq/100 g. The extent of clay's ability to adsorb cations indicates the extent of disorder in its structure by CEC measurement. Typical CEC value of well - ordered kaolinite, disordered kaolinite and illite are 3 - 6 meq/100g, 15 - 40 meq/100g and 10 - 40 meq/100g, respectively [10-13]. Generally, the CEC reading of Mersing clay is considered low and coincided within the range of CEC value mentioned above. It gives guide to likely physical characteristics and indication of amount of electrolyte required to be added to achieve flocculation or deflocculation [12]. For tile manufacturer with wet milling process, it is always desired to select clay with low CEC value, which will promote low in viscosity of ceramic body suspension (such as clay) after milling process.

Both CEC and zeta potential characterised the surface property of Mersing clay's particles in suspension, where the magnitude of these parameters is often used to measure the strength of the repulsive interaction between particles [15]. Stable colloidal suspension can be achieved by increasing the negatively charged of clay particles [19]. If zeta potential of ceramic suspension has not achieved sufficient negatively charged of clay particles to counter positive ions in medium, low repulsion force between particles occurred and particles will approach each other by attractive Van der Waal's force and hence agglomeration will occur, which is not desired by tile manufacturer by wet milling process. It is always desired to select clay with low CEC and higher zeta potential in negative values in processing of tile body formulation by wet milling operation.

3.3 Fired Properties. Fig. 3 (a) shows the linear fired shrinkage and water absorption of Mersing clay. Fired linear shrinkage increased (from about 1% to 11%) and water absorption (from 18% to 0%) decreased from firing temperature of 1000 to 1200 °C. Water absorption was saturated above firing temperature of 1200 °C, while fired linear shrinkage shows small reduction trend which is due to forced expulsion of the entrapped gases resulting in blisters and bloating at firing temperature of 1250 °C [20]. Fig. 3 (b) shows the bulk density and apparent porosity of Mersing clay, which provide information of densification behaviour. Bulk density increased and apparent porosity decreased from firing temperature of 1000 to 1200 °C.Water absorption is closely related to porosity and densification of clay after firing operation, where increasing firing temperature leads to liquid phase formation due to present of fluxing oxides especially K_2O [7] from illites [7]. The liquid phase formation will penetrate the pores, decreases the porosity and water absorption and increase the bulk density, where it has greatly contributed to densification processes after firing operation [21]. The liquid surface tension and capillarity of liquid phase will help to bring pores close together and reduce porosity [4,21,22].

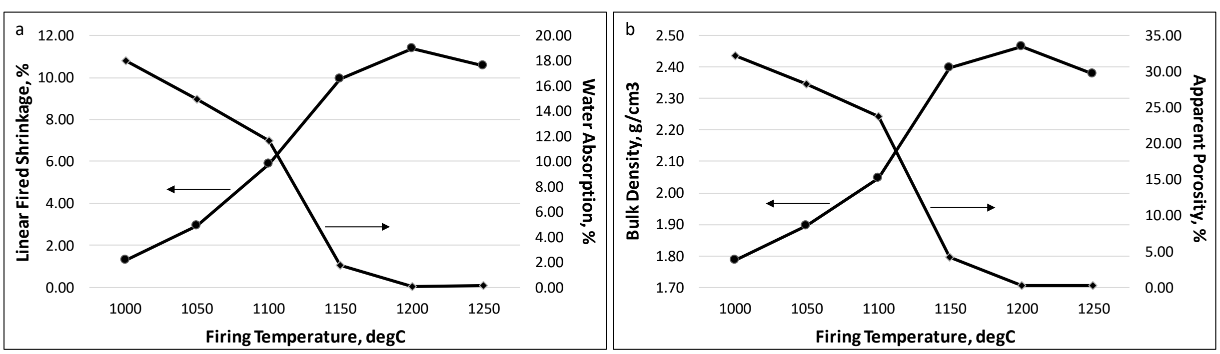

Fig. 3 Fired properties of Mersing clay by (a) Linear fired shrinkage and water absorption (b) Bulk density and apparent porosity

Water absorption is determining parameters to define the category of ceramic tiles. According to ISO 13006 (1998) [23], ceramic tile has divided into four categories on the basis of water absorption: ≤ 0.5% (Group BI_a), 0.5 - 3.0% (Group BI_b), 3 - 6% (Group BII_a), 6 - 10% (Group BII_b) and >10% (Group BIII). Mersing clay is considered suitable to be used by tile manufacturer for wide ranges of application.

Table 2 shows the fired colour of Mersing clay in $L*$, $a*$ and $b*$ values. $L*$ value indicates the lightness scale with 0 is black and 100 is white. The $L*$value decreased with increasing firing temperature from 1000 to 1200 °C, which later maintain at $L*$ value of 62 to 63 from firing temperature of 1200 to 1250 °C. The $a*$ value shows saturated trend from firing temperature of 1000 to 1150 °C and reducing trend after firing temperature of 1150 °C. The $b*$ values shows overall increasing trend from firing temperatureof 1000 to 1150 °C and decreasing trend from firing temperature of 1150 to 1250 °C, where increasing $b*$ values will increase the intensity of yellowish colour. The fired colour of Mersing clay is affected by the present of TiO_2 and Fe_2O_3. Fig. 4 shows Physical appearance of fired buttons.

Table 2 Fired colour of Mersing clay

Firing Temperature, °C	Fired colour, $L*$ value	Fired colour, $a*$ value	Fired colour, $b*$ value
1000	83.88	5.03	10.33
1050	84.17	4.43	9.64
1100	80.48	4.68	11.77
1150	71.31	5.05	14.44
1200	62.33	3.01	11.28
1250	63.61	2.29	10.65

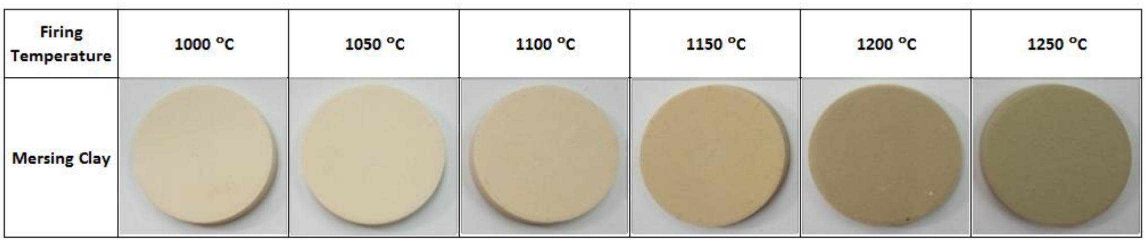

Fig. 4 Physical appearance of fired buttons of Mersing clay

4. SUMMARY

Mersing clay from Johor, Malaysia was investigated and characterised by rheological and fired properties. For rheological properties, Mersing clay shows low in CEC and high in zeta potential in negative value without flocculation and thixotropy issue. Mersing clay is considered suitable to be used in wet milling process for manufacturing of ceramic tiles. The fired properties of Mersing clay is greatly influenced by its mineralogical and chemical composition. The densification, water absorption and fired colour of Mersing clay is influenced by fluxing oxides of K_2O from illite, which promotes formation of liquid phase. At low firing temperature, Mersing clay is considered suitable for production of wall tiles with good in fired colour. At high firing temperature, Mersing clay is suitable for production of floor and porcelain tiles with darker tone in fired colour. In general, Mersing clay is suitable to be used for all ranges of ceramic tiles. It is expected that the present investigation work will also help to expand the application of Mersing clay to other ceramic industries such as bricks, sanitary wares, refractories, decorative wares and etc.

ACKNOWLEDGEMENT

The authors would like to acknowledge the School of Materials and Mineral Resources Engineering (SMMRE) and Ceramic Research Company SdnBhd (Guocera) for funding the research under company sponsorship (REF: 2309/LD/Gen/CRC/15).

REFERENCES

[1] S. Ismail, Z.C. Kasim, H.C. Harun,Malaysia Minerals Year Book 2010, Minerals and Geoscience Department of Malaysia, Ministry of Natural Resources and Environment Malaysia (2010) 74 – 87.

[2] M.A. Saleh, A.T. Ramli, K. Hamzah, Y. Alajerami, M. Moharib, I. Saeed, Prediction of terrestrial gamma dose rate based on geological formations and soil types in the Johor State, Malaysia,J. Environ. Radioact.,148 (2015) 111 - 122.

[3] A.J. Ayadi, J. Soro, A. Kamoun, S. Baklouti, Study of clays mineralogy effect on rheological behaviour of ceramic suspensions using an experimental design, IJRRAS 14 (2013)374 - 384.

[4] H. Baccour, M. Medhioub, F. Jamoussi, T. Mhiri, Influence of firing temperature on the ceramic properties of Triassic clays from Tunisia, J. Mater. Process. Technol.,209 (2009) 2812 - 2817.

[5] A. Aras, The change of phase composition in kaolinite- and illiterich clay-based ceramic bodies, Appl. Clay Sci., 24 (2004) 257- 269.

[6] S. Ferrari, A.F. Gualtieri, The use of illiticclays in the production of stoneware tile ceramics,Appl. Clay Sci., 32 (2006) 73 - 81.

[7] C.L. Chin, Z.A. Ahmad, S.S. Sow, Relationship between the thermal behavior of the clays and their mineralogical and chemical composition: Example of Ipoh, Kuala Rompin and Mersing (Malaysia), Appl. Clay Sci., 115 (2017) 327 - 335.

[8] I. Ibrahim, M.M Alimon,Effect of diesel on adsorption of coco amine in muscovite and quartz, Asian American Min. Mineral Process. Res. J., 1 (2015) 1 - 6.

[9] C.J. Schollenberger, R.H. Simon,Determination of exchange capacity and exchangeable basses in soil: Ammonium acetate method, Soil Sci.,59 (1945) 13 - 24.

[10] F. Bergaya, B.K.G. Theng, G. Lagaly, Handbook of clay science,department in clay science, Vol. 1, Elsevier Ltd, 2006.

[11] H.H. Murray,Applied clay mineralogy: occurrence, processing and application of kaolins, bentonite, palygorskite -sepiolite and common clays, Developments in Clay Science 2, Elsevier, 2007.

[12] W. Ryan, C. Radford,Whitewaresproduction, testing and quality control (including materials, body formulation and manufacturing pocesses),Pergamon Press, 1987.

[13] W.E. Worrall,Clays and ceramic raw materials, 2nd Edition, Elsevier Applied Science Publishers London and New York, 1986.

[14] W.M. Carty, U. Senapati, Porcelain – raw materials, processing, phase evolution and mechanical behaviour,J. Am. Ceram. Soc., 81 (1998) 3 - 20.

[15] P.I. Au, Y.K. Leong, Rheological and zeta potential of kaolin and bentonitecomposite slurries, Colloid and Surface A: Physiochemical and Engineering Aspects 436 (2013) 530 - 541.

[16] A. Nosrati, J.A. Mensah, W. Skinner, Rheological behaviour of muscovite clay slurries: effect of water quality and solution speciation,Int. J. Miner. Process., 102 (2012) 89 - 98.

[17] A. Nosrati, J.A. Mensah, W. Skinner, Muscovite clay mineral particle interactions in aqueous media, Powder Technol.,219 (2012) 228 - 238.

[18] P.I. Au, S.Y. Siow, L. Avadiar, E.M. Lee, Y.K. Leong, Muscovite mica and kaolin slurries: yield stress-volume fraction and deflocculationpoint zeta potential comparison, Powder Technol., 262 (2014) 124 - 130.

[19] W. Ryan,Properties of ceramic raw materials, 2nd Edition,Pergamon Press, 1978.

[20] J. Martín – Márquez, J.M. Rincón, M. Romero,Effect of firing temperature on sintering of porcelain stoneware tiles, Ceram. Int., 34 (2008) 1867 - 1873.

[21] İ.Özkan, Densification behaviour of red firing Menemen clay,J Aust. Ceram. Soc.,51 [2] (2015) 36 - 39.

[22] B.K. Ngun, H. Mohamad, S.K. Sulaiman, K. Okada, Z.A. Ahmad, Some ceramic properties of clays from central Cambodia, Appl. Clay Sci., 53 (2011) 33 - 41.

[23] ISO 13006, Ceramic tiles–definitions, classification, characteristics and marking, International Standard, First Edition, 1998.