Interrelationship of Kaolin, Alkaline Liquid Ratio and Strength of Kaolin Geopolymer

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Abstract. Geopolymer is an incredible alternative green cementitious material which has ceramic-like properties, but does not require calcining that leads to reduction in processing energy usage. The purpose of this research is to study the correlation between kaolin: liquid ratio with the performance of kaolin geopolymer. Kaolin, a prominent raw geopolymer material was used to prepare enhanced geopolymer paste by mixing with alkaline activator solution. Interrelationship of kaolin to alkaline liquid ratio with hardness and flexural strength was the focus of this work. Therefore kaolin geopolymer paste with varying solid to liquid ratio ranging from 0.7 to 1.1 was prepared. Geopolymer paste was coated on low grade wood substrate prior to Vickers hardness and flexural strength. X-ray diffraction was conducted on geopolymer paste itself after 7 days to analyze the change in phase identification at early age. Kaolin geopolymer coating on wood with solid/liquid(S/L) ratio of 0.7 shows the most promising hardness and flexural strength of 15.3 Hv and 94.73MPa. X-ray diffraction test showed high existence of kaolinite on higher S/L ratio whereas sodalite was observed in S/L ratio of 0.7. Microstructural studies also compliments our finding which further proves the positive dependency of S/L ratio and kaolin geopolymer strength.

1. Introduction
The Geopolymer was first introduced by Joseph Davidovits in 1978 were it was rarely known to many [1-4]. However ever since various research development took place, geopolymers is now prevalent materials that is being rapidly developed world wide. This is mainly because of its environmental friendly nature, specific performances of high temperature resistance, high compressive strength, low density and low permeability [5]. Geopolymer source materials are materials rich in aluminosilicate such as kaolin, fly ash, metakaolin, and slag [6-9]. Geopolymers are class of largely X-ray amorphous
aluminosilicate materials that is produced when solid source material powders are mixed with concentrated alkali metal silicate or hydroxide solution [10]. Geopolymers are inorganic binder that exhibits promising mechanical properties. Few works has attempted to use many materials that are rich in silica and alumina to synthesize geopolymers and succeeded [11-15]. Usage of kaolinite clays and sintered kaolin has also gained interest of multiple researchers worldwide [5, 8, 16-18]. Generally Kaolin consists of alumina octahedral sheets and silica tetrahedral sheets stacked alternately and has the theoretical formula (OH)₈Si₄Al₄O₁₀ and the theoretical composition 46.54% SiO₂, 39.5% Al₂O₃, 13.96% H₂O[15].

Wood regardless of hard wood or low grade (LG) wood consist of mainly lignin, cellulose and hemicelluloses [19]. The structural and non-structural grade woods contains different grain orientation and texture, therefore their strength will also differ [20-23]. Apart from that, processing and multiple types of inherent defects also contributes to the strength of wood products. Low grade wood are natural polymeric material with lower mechanical properties [24]. LG woods are also cost competitive, architecturally attractive, natural resource and a recyclable material [25]. LW wood was used in this work to analyse if there are any improvements in terms of its mechanical properties upon being coated with kaolin geopolymer paste.

Kaolin has been used for various application but never as a coating geopolymer paste. To best of our knowledge, apart from our research group, CEGeoGtech, there are no active research on kaolin based geopolymer coating. This is an area of study that are still not studied in detailed. Focus of this work is to find kaolin based geopolymer coating paste with optimum kaolin to alkaline activator liquid ratio that exhibits enhanced mechanical properties. Thus, for mechanical testing, kaolin geopolymer paste was coated on low grade wood substrate to observe the change in properties.

2. Materials and Methods
Kaolin, raw material for this work was obtained from Associated Kaolin Industries Sdn. Bhd, Malaysia. Kaolin was the sieved using desired mesh size and stored in an air tight container at our laboratory. Sodium chloride flakes were purchased from Formosa Plastic Corporation, Taiwan. Technical grade liquid sodium silicate was supplied by South Pacific Chemicals Industries Sdn. Bhd. (SPCI) Malaysia. Sodium chloride flakes were then used to prepare stock solutions of NaOH solution with 8 M.

Liquid Na₂SiO₃ and NaOH solution are needed for preparation step. The alkaline activator solution was prepared by adding NaOH solution into liquid Na₂SiO₃ and continuously stirring until a clear solution was obtained. However the alkaline activator mixture must be prepared and kept aside minimum 24 hours prior to use to achieve equilibration and a homogenous solution. The ratios of Na₂SiO₃/NaOH used in this work is 0.45 which is the optimum range based on our findings and previous literature [26].

Sieved kaolin was mixed with alkaline activator solution at desired various solid/liquid ratio ranging from 0.7 to 1.10. The mixture was then stirred via mechanical stirrer manufactured by TPG Motors & Drives Corporation type ML712-4 at a speed of 20 rpm for 5 minutes until homogenous slurry was obtained.

Upon mixing, kaolin based geopolymer paste is obtained. For the Vickers hardness and flexural strength test, geopolymer paste was brushed evenly onto low grade wood substrates with a stabilo painting brush. After the first coating layer, the wood substrates were allowed to dry for 60
seconds. Next, subsequent layers were brushed onto the low grade wood until desired thickness is obtained. For the X-ray diffraction test, kaolin geopolymer paste was analysed.

After coating process, the coated LG wood and geopolymer paste were placed into hot air Table Top Oven by KCG for drying and curing process. The curing time was maintained at 72 hours. Upon curing in oven, samples were removed, allowed to cool to room temperature and sealed in thin plastic bags to prevent dust and impurity in surrounding prior to testing.

2.1. Vickers Hardness
Vicker hardness test is performed to obtain the resistance of sample towards plastic deformation. Kaolin geopolymer coated LG wood samples were cured at 60°C for 3 days for complete geopolymerisation to occur. This test will measure the geopolymer coating resistance to a localised load that leads to plastic deformation. Vickers hardness test was conducted under the test procedure of ASTM E-384 which specifies a light load range with a diamond indenter that causes the indentation to be measured in hardness value. Benchmarking previous studies and ASTM standard, for kaolin geopolymer coating, load of 1.0 kg (9.807 N) was used to provide a reasonable indent for geopolymer coating hardness determination. Vickers hardness number, \( H_v \), is a number representing hardness value related to the applied force (\( P \)) and the area of an indent is given by a square-based pyramidal diamond indenter having included face angle of 136° as shows in Figure 1. Vickers hardness value, \( H_v \) can also be calculated in MPA by the equation 1 shown as per below. For this test, five samples were tested and average value was obtained.

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H_v = \frac{P}{A_s} = 2P \frac{\sin (\alpha/2)}{d^2} = 1.8544 \frac{P}{d^2}
\]

(Eq 1)

Where by, \( P \) = load (N),
\( A_s \) = Surface area of indentation (mm²),
\( d \) = mean diagonal of indentation(mm)
\( \alpha \) = face angle of indenter (136°)

2.2 Flexural Strength
Flexural strength test is performed to analyse the behavioural change of material subjected to a simple beam loading Kaolin geopolymer coated low grade wood was prepared as per the standard testing size of 150mm*15mm*3mm rectangular shape. The flexural test of these coated samples were conducted.
under the ASTM D709 using Automatic Max (Instron, 5569 USA). This test also determines the properties of control and reinforced materials, which allows the comparison of control and coated low grade substrates.

2.3 X-Ray Diffraction (XRD) Test
X-Ray Diffraction (XRD) measurements were performed for phase analysis of the starting materials and to investigate the degree of crystallinity of the resulting geopolymer coat. The sampling for this analysis was made by grinding the sample with pestle and mortar to obtain very fine powder before the sample spread on the surface of the sample holder using pieces of glass to minimize the effect of preferred orientation on the XRD pattern. Random powder samples of kaolin were prepared by lightly pressing powder samples into aluminium holders. XRD powder diffractograms of geopolymer specimens are collected on a XRD-6000 Shimadzu X-Ray Diffractometer with CuKα radiation generated at 30 mA and 40 kV. Step scans are performed from 10 - 70° 2θ at 0.02° 2θ steps, integrated at a rate of 1.2 second per step.

3. Results and discussions
Vickers hardness is conducted to measure the resistance to permanent deformation or damage layer of kaolin geopolymer coating on wood substrate. The applied load used for geopolymer is in range of 0.1 – 1.5 kg appropriate to the hardness of cementitious materials in geopolymer coating [27]. Benchmarking previous studies, for kaolin geopolymer coating, load of 1.0 kg (9.807 N) was used to provide a reasonable indent for geopolymer coating hardness determination. Table 1 shares the hardness values of various kaolin to alkaline liquid ratio of kaolin geopolymer coating on LG wood substrates. As per shown in Table 1 and Figure 2, hardness value of kaolin geopolymer coated wood substrate with S/L of 0.7 has the highest value. This is due to its good workability that enhances the dissolution of aluminosilicates in kaolin. As the S/L ratio is increased, the hardness value drops gradually. When geopolymer paste with S/L ratio below 0.6 was prepared, the geopolymer paste failed at curing stage as severe crack were observed. Thus, it can be concluded that kaolin geopolymer with S/L ratio of 0.7 is the most suitable ratio in terms of the hardness value.

Table 1. Parameters of kaolin geopolymer coating at different solid/liquid ratio tested for Vickers hardness

| Sample                  | Solid/Liquid | Na2SiO3/NaOH | Vickers Hardness (Hv) | Hv (MPa) | Hv (GPa) |
|-------------------------|--------------|--------------|-----------------------|----------|----------|
| Control                 | -            | 4.5          | 44.13                 | 0.04     |          |
| 0.7                     | 0.45         | 15.3         | 150.05                | 0.15     |          |
| 0.8                     | 0.45         | 13.6         | 133.38                | 0.13     |          |
| 0.9                     | 0.45         | 10.3         | 101.02                | 0.10     |          |
| 1.0                     | 0.45         | 8.8          | 86.31                 | 0.09     |          |
| 1.1                     | 0.45         | 6.3          | 61.79                 | 0.06     |          |
The relationship between hardness results with flexural strength is displayed in Figure 3. The line graph exhibit similar features which has enhanced result at S/L ratio of 0.7 for kaolin geopolymer coated wood substrates. These results may lead to the successful optimization of the mix design of kaolin geopolymer coating thus obtaining good performance in term of mechanical strength.

X-Ray diffraction (XRD) analysis were performed to classify phase indentification, degree of crystallinity and monitor the transformation in amorphous peak from raw kaolin materials into geopolymer paste. Selected XRD patterns of kaolin geopolymer with S/L of 0.7, 0.9 and 1.1(Figure 4) was compared and analysed. As per illustrated by Figure 4, major mineral contribution in geopolymer
paste is kaolinite peaks (K) at 20 values of 12.5°, 20.0°, 24.51°, 32.1° and 35.03° in XRD patterns of kaolin geopolymers tested after 7 days. Lower intensity of kaolinite in XRD pattern of kaolin geopolymer with S/L of 0.7 shows the higher dissolution of kaolin as compared to the rest. Kaolinite peaks shows the unreacted kaolin that remained in geopolymer paste [30-31]. Another major mineral quartz (Q) at 2θ values of 26.76°, 43.4°, 46.1°, 53.09°, 55.28°, 59.23°, 62.7° and 79.97°, is the mineral compound that is not involved in the geopolymerisation process[32]. New peak of sodalite that was narrow at 20 value of 17.70°, 21.59°, 28.1° and 33.39°. The patterns show the existence of sodalite peak indicates the geopolymerization reaction between Na, SiO₂ and Al₂O₃. The low counts in XRD pattern of geopolymer products between 25° and 35° (2θ) attributed the geopolymer products have amorphous structure [33-34].

![Figure 4: X-Ray Diffraction pattern of solid/liquid ratio of 0.7, 0.9 and 1.1.](image)

4. Conclusions
Kaolin geopolymer paste showed promising enhancement which makes it a very reliable repair or coating material. Mechanical properties such as Hardness and flexural strength of these kaolin geopolymer that was coated on LG wood substrates gave the best results at kaolin/ alkaline activator liquid ratio of 0.7. This finding was further supported by the X-Ray diffraction results also gave positive results for the solid/liquid ratio of 0.7 Thus, our findings can be summarize that with the optimum kaolin to alkaline liquid ratio, strength of kaolin geopolymer can be further enhanced.

Acknowledgments

References
[1] A.M. Mustafa Al Bakri, H. Kamarudin, M. Bnhussain, I. Khairul Nizar, Y.Zarina and A.R. Rafiza.(2012). Fly Ash Based Geopolymer Lightweight Concrete Using Foaming Agent. International Journal of Molecular Science 13, p.7186-7196.
[2] Zhang Yunsheng, Sun Wei, and Li Zongjin. (2010). Composition design and microstructural characterization of calcined kaolin-based geopolymer cement, Applied Clay Science, 47, p.271–275.

[3] Zhang, Wei and Li. (2009). Preparation and microstructure of K-PSDS geopolymeric binder. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 302, 473-482.

[4] Heller-Kallai L and Lapides I. (2007). Reactions of kaolinites and metakaolinites with NaOH comparison of different samples (Part 1), Appl Clay Sci 35, p.99–107

[5] Alonso and Palomo. (2001). Alkaline activation of metakaolin and calcium hydroxide mixtures: Influence of temperature, activator concentration and solids ratio, Materials Letters, 47(1-2), 55-62.

[6] Fernandez-Jimenez and Palomo. (2007). Factor affecting early compressive strength of alkali activated fly ash (OPC-free) concrete. Materials de Construction, 57, 7-22.

[7] Chindapasrit, Charerat and Sirivivatnanon. (2007). Workability and strength of coarse high calcium fly ash geopolymer. Cement and concrete composites, 29(3), 224-229.

[8] Wang, Li and Yan. (2005). Synthesis and mechanical properties of metakaolinite-based geopolymer. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 268(1-3), 1-6

[9] Y.M. Liew, H. Kamarudin, A.M. Mustafa Al Bakri, M. Binhussain, M. Luqman, I. Khairul Nizar, C.M. Ruzaiddi, and C.Y. Heah. (2011). Influence of Solids-to-liquid and Activator Ratios on Calcined Kaolin Cement Powder, Physics Procedia, 22, p.312 – 317.

[10] M.M.A. Abdullah, H. Kamarudin, H.Mohammed, I. Khairul Nizar, A.R. Rafiza, and Y.Zarina. (2011). The relationship of NaOH Molarity, Na2SiO3/NaOH Ratio, Fly Ash/Alkaline Activator, and Curing Temperature to the strength of Fly Ash –Based Geopolymer, Advanced Materials Research 328-330, p 1475-1482.

[11] A.M. Mustafa Al Bakri, H. Kamarudin, M. Binhussain, I. Khairul Nizar, A.R. Rafiza, and Y.Zarina. (2012). The Processing, Characterization, and Properties of Fly Ash Based Geopolymer Concrete, Rev.Adv.Mater. Sci 30, p90-97

[12] Duxson, Lukey and Van Deventer. (2007). Physical evolution of Na-geopolymer derived from metakaolin up to 1000°C. Journal of Materials Science, 42,3044-3054.

[13] Tempest, Sanusi, Gergely, Ogunro and Weggel. (2009). Compressive strength and embodied energy optimization of fly ash based geopolymer concrete. Paper presented at the 2009 World of Coal Ash (WOCA).

[14] Hardjito and Rangan. (2005). Development and properties of low-calcium fly ash based geopolymer concrete. Research report GCI. Faculty of Engineering Curtin University of Technology, Perth, Australia.

[15] Y.Zarina, A.M. Mustafa Al Bakri, H. Kamarudin, Khairul Nizar, and A.R. Rafiza. (2013). Review on The Various Ash From Palm Oil Waste As Geopolymer Material, Rev.Adv. Mater. Sci 34, p37-43.

[16] Yip, Lukey and Van Deventer. (2005). The coexistence of geopolymeric gel and calcium silicate hydrate at the early stage of alkaline activation. Cement and concrete research, 35(9), 1688-1697.

[17] C.Y. Heah, H. Kamarudin, A.M. Mustafa Al Bakri, M. Bnhussain, M. Luqman, I. Khairul Nizar, C.M. Ruzaiddi, Y.M. Liew. (2012). Study on solids-to-liquid and alkaline activator ratios on kaolin-based geopolymers, Construction and Building Materials 35, p.912–922.

[18] A.M. Mustafa Al Bakri, J.Liyaana, H. Kamarudin, M. Bnhussain, C.M. Ruzaiddi, and M.A. Izzat. (2012). Fly Ash Porous Material using Geopolymerization Process for High Temperature Exposure. International Journal of Molecular Science 13, p.4388-4395.

[19] Łukasz Czajkowski, Wiesław Olek, Jerzy Weres, and Ryszard Guzenda. (2016) Thermal properties of wood-based panels: specific heat determination, Wood Science and Technology, 21,1-9.

[20] Ataollah Haddadi, Brigitte Leblon, Zarin Pirouz, Joseph Nader, and Kevin Groves (2016)
Prediction of wood properties for thawed and frozen logs of quaking aspen, balsam poplar, and black spruce from near-infrared hyperspectral images, Wood Science and Technology, 50(2), p 221-243.

[21] J. Fernández-Moya, A. Alvarado, W. Forsythe, L. Ramírez, N. Algeet-Abarquero, and M. Marchamalo-Sacristán. (2014). Soil erosion under teak (Tectona grandis L.f.) plantations: General patterns, assumptions and controversies, Catena 123, p. 236–242.

[22] Stephen Adu-Bredu, Alphonse Foua Tape Bi, Jean-Pierre Bouillet, Martial Kouame’ Me’, Samuel Yamoah Kyei, and Laurent Saint-Andre. (2008). An explicit stem profile model for forked and un-forked teak (Tectona grandis) trees in West Africa, Forest Ecology and Management 255, p.2189–2203.

[23] Narong Koonkhunthod, Katsutoshi Sakurai, and Sota Tanaka. (2007) Composition and diversity of woody regeneration in a 37-year-old teak (Tectona grandis L.) plantation in Northern Thailand, Forest Ecology and Management 247, p. 246–254.

[24] William D. Greason, (2013). Triboelectrification of wood with PTFE, Journal of Electrostatics, 71, 140–144.

[25] Magnus Wiman, Benny Palmqvist, Eva Tornberg, and Gunnar Lidén (2011). Rheological characterization of dilute acid pretreated softwood, Biotechnology and Bioengineering, 108(5), 1031-1041.

[26] Rovnanik (2010). Effect of curing temperature on the development of hard structure of metakaolin-based geopolymer. Construction and Building Materials, 24, 1176-1183.

[27] Rattanasak and Chindaprasirt (2009). Influence of NaOH solution on the synthesis of fly ash geopolymer. Minerals Engineering, 22(12), 1073-1078.

[28] Tempest, Sanusi, Gergely, Ogunro and Weggel (2009). Compressive strength and embodied energy optimization of fly ash based geopolymer concrete. Paper presented at the 2009 World of Coal Ash (WOCA).

[29] Sami Ullah, Faiz Ahmad, A.M Shariff and M.A. Bustam (2014). Synergistic effects of kaolin clay on intumescent fire retardant coating composition for fire protection of structural steel substrate.

[30] Y.M. Liew, H. Kamarudin, A.M. Mustafa Al Bakri, M. Bnhusain, M. Luqman, I. Khairul Nizar, C.M. Ruzaidi, and C.Y. Heah.(2012).Optimization of solids-to-liquid and alkali activator ratios of calcined kaolin geopolymeric powder, Construction and Building Materials 37, p. 440-451.

[31] Prasad, M.S., Reid, K.J., and Murray, H.H. (1991).Kaolin: processing, properties and applications, Applied Clay Science, 6, p 87-119.

[32] Provis, Yong, Duxson and Van Deventer (2009). Correlating mechanical and thermal properties of sodium silicate-fly ash geopolymers. Colloids and surfaces A: Physicochemical and Engineering Aspects, 336(1-3), 57-63.

[33] Zuhua, Xiao, Huajun and Yue (2009).Role of water in the synthesis of calcined kaolin based geopolymer. Applied Clay Science, 43, 218-223.