

Studies On Mechanical Activation Of Kaolin In Synthesis Of Geopolymers

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Abstract: The effect of mechanical activation of kaolin on properties of geopolymers was investigated. The analysis on mechanical-activated kaolin showed that kaolin's particle size decreased accompanied with increase in surface area along with activation time. XRD diffraction peaks of kaolinite decreased as well. FTIR analysis demonstrated the distortion of the tetrahedral and octahedral layers after the activation process. The compressive strength of geopolymers produced using mechanical-activated kaolin rose with activation time from 1 to 28 days. Thus, mechanical activation was deduced to have altered the particle size and surface area as well as the reactivity of kaolin towards geopolymerization reaction.

Key words: kaolin, mechanical activation, grinding, geopolymers

INTRODUCTION

Kaolin is an aluminosilicate material with low reactivity due to its plate-like structure and close-to-zero layer charge (Murray, 2007; Theng, 2012). The reactivity of kaolin is closely related to structure and composition of particular mineral as well as on the particle size, surface area, porosity and crystal morphology (Kumar *et al.*, 2008). Generally, reactivity of kaolin can be improved by thermal, mechanical or chemical treatment (San Cristobal *et al.*, 2009). Thermal treatment of kaolin involves heating of kaolin above 550 °C, forming metakaolin as the result of the loss of structural OH groups. Besides, chemical treatment with acid or alkali is rather difficult because of high passivity. On the other hand, mechanical activation of kaolin entails grinding process on solid particles. Mechanical activation breaks down kaolinite structure and OH bonds which lead to changes in fineness of solid particles, surface area and number of active sites of the materials (Pacheco-Torgal *et al.*, 2011; San Cristobal *et al.*, 2009). San Cristobal *et al.* (2009) obtained spherical particle shape of kaolin after the grinding process. Mechanical activation for improving bulk and surface reactivity is well accepted where this method offers the possibility to alter the reactivity of solids through changes in bulk and surface without altering overall chemistry of the material (Kumar & Kumar, 2011).

In the study, the effect of mechanical activation of kaolin on the properties of geopolymers was studied. The influence of mechanical activation on the particle size and surface area of kaolin was studied. In addition, compressive strength of mechanical-activated kaolin geopolymers was accessed and the geopolymers were analyzed using X-ray diffraction (XRD) and fourier transform infrared spectroscopy (FTIR) analyses.

Experimental:

Materials:

Sodium Hydroxide (NaOH) powder used was classified as caustic soda micropearls, 99% purity with brand name of Formosoda-P, made in Taiwan. A technical grade sodium silicate solution (Na₂SiO₃) was supplied by South Pacific Chemicals Industries Sdn. Bhd. (SPCI), Malaysia. The chemical composition was comprised of 30.1% SiO₂, 9.4% Na₂O and 60.5% H₂O with modulus SiO₂/Na₂O of 3.2, specific gravity at 20°C = 1.4 and viscosity at 20°C = 0.4 Pa·s. Kaolin was supplied by Associated Kaolin Industries Sdn. Bhd., Malaysia. The general chemical composition is tabulated in **Table 1**, which was obtained from XRF analysis. The physical form of kaolin used was of powder type, and has minimum 40% of particle size less than 2 µm and maximum 2% of moisture content. It was used as Si-Al cementitious materials. Distilled water was used throughout.

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Table 1: Chemical composition of kaolin

Chemical composition	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	K ₂ O	ZrO ₂	MnO ₂	LOI
Wt (%)	54.0	31.7	4.89	1.41	6.05	0.10	0.11	1.74

Sample Preparation:

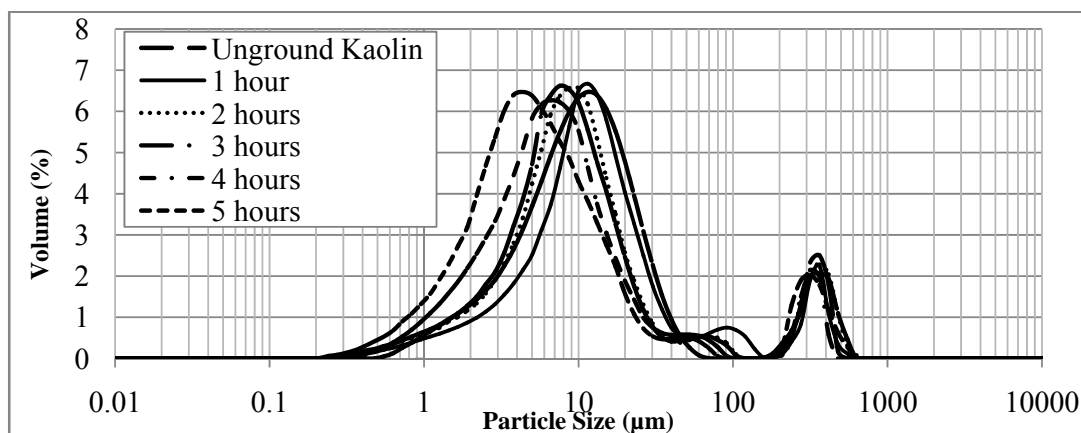
Kaolin was ground for 1, 2, 3, 4 and 5 hours using Fritsch pulverisette 6, type laboratory planetary mills. Each grinding process was carried out with 40g of powder in an 80 cm³ capacity stainless steel pot using 48 stainless steel balls (10mm diameter); the applied rotation speed was 370 rpm in order to produce mechanically-activated kaolin. In order to produce mechanically-activated kaolin geopolymer, NaOH pellets and water were first prepared and mixed in a volumetric flask to obtain a concentration of 8M and then allowed to cool down to room temperature. NaOH solution was mixed with Na₂SiO₃ with Na₂SiO₃/ NaOH ratio of 0.32 to prepare a liquid alkali activator, 24 h prior to use. Mechanically-activated kaolin powder and alkali activator were mixed with the solids-to-liquid (S/L) ratio of 1.0, and stirred well for a few minutes by using mechanical mixer. The fresh paste was then rapidly poured into a 50 x 50 x 50 mm steel mould and the samples were compacted to approximately one half of the depth (about 1 in. or [25 mm]) of the mould in the entire cube compartment, and the paste was tamped in each cube compartment at each layer as described in ASTM C109 (*ASTM C109/C109-05. Standard test method for compressive strength of hydraulic cement mortars (Using 2-in. or [50mm] cube specimens)*, 2008). The sample was cured at temperature 60°C in oven up to 3 days. The water evaporation was prevented by sealing the top of the moulds with a thin plastic layer during the curing process.

Testing and Analysis Methods:

Particle size distribution of kaolin was measured using Malvern Mastersizer 2000 with measuring range between 0.02 µm to 2000 µm. BET surface area of kaolin was determined by using nitrogen adsorption in Micromeritics TriStar 3000. Compressive strength tests of all specimens were evaluated according to ASTM C109/C109M-08 by using the Instron machine series 5569 Mechanical Tester. All specimens were taken out after curing; and put in room temperature until the day of testing. The compressive test was carried out to evaluate the strength development for the specimens. The samples were compressed at 1, 3, 7, and 28 days. Specimens were prepared in powder form and undergone XRD examination. XRD – 6000, Shimadzu x-ray diffractometer equipped with auto-search / match software as standard to aid qualitative analysis was used. Perkin Elmer FTIR Spectrum RX1 Spectrometer was used to evaluate the sample. The specimen for FTIR analysis was prepared by using KBr pellet technique.

RESULTS AND DISCUSSION**Particle Size Distribution:**

Fig. 1 presents the particle size distribution of raw kaolin ground at various grinding times. Mean particle sizes (X_{50}) for unground kaolin, ground kaolin for 1 hour, 2 hours, 3 hours, 4 hours and 5 hours were 14.517 µm, 13.986 µm, 12.486 µm, 11.517 µm, 9.734 µm and 8.001 µm, respectively. The mean particle size decreased when the mechanical activation time was increased (San Cristobal *et al.*, 2010). The proportion of larger particles decreased while the proportion of smaller particles increased. This meant that mechanical activation broke the kaolin particles into smaller size (Kumar *et al.*, 2008).

**Fig. 1:** Particle size distribution of raw kaolin mechanically-activated at various activation times.

BET Surface Area:

Fig. 2 demonstrates the BET surface area of raw kaolin ground at various mechanical activation times. It can be observed that the surface areas increased with increasing grinding time (Blanco *et al.*, 2005; San Cristobal *et al.*, 2010). Grinding for 1 hour did not show great difference in surface area compared to unground kaolin. The surface area improved marginally after 2 hours. This suggested that mechanical activation broke down the kaolin particles into smaller size which tended to enhance the surface area for geopolymerization reaction.

Compressive Strength:

Fig. 3 presents the compressive strength of kaolin geopolymers. In all cases, the mechanical-activated kaolin geopolymers exhibited higher compressive strength, compared to unground kaolin geopolymers. Geopolymer produced from ground kaolin for 4 to 5 hours showed greater gain in initial strength. By performing mechanical activation, a wide particle size distribution of the predominantly spherical particles produced. This promoted a high packaging density in the sample which resulted in higher strength (Kumar & Kumar, 2011; Temuujin *et al.*, 2009). Mechanical activation of kaolin increased the reactivity of the kaolin, causing faster dissolution of kaolin and thus improved the polymerization and hardening of gel phase.

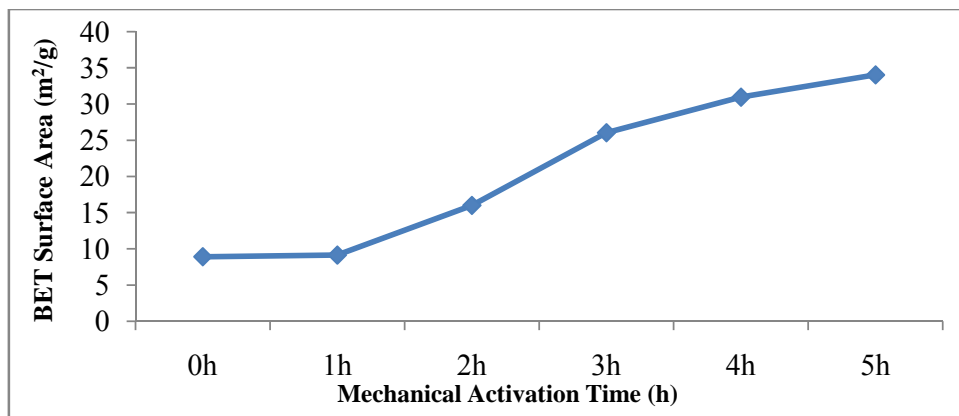


Fig. 2: BET surface area of raw kaolin at various mechanical activation times (0h – unground kaolin).

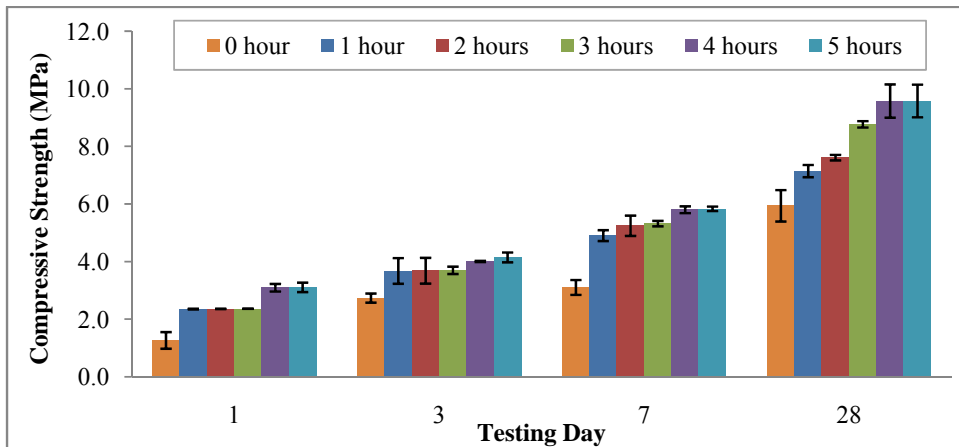


Fig. 3: Compressive strength of mechanical-activated kaolin geopolymers over ages at various grinding times.

XRD Analysis:

Fig. 4a displays the XRD diffractograms of raw kaolin mechanically-modified at various grinding times. **Fig. 4b** and **Fig. 4c** show the XRD diffractograms of kaolin geopolymers using mechanically-activated kaolin at various mechanical activation times on 7 days and 28 days, respectively. Kaolin showed intense kaolinite peaks at 2θ values of 12.5° and 25.5° . Less intense kaolinite peaks could be found at 2θ values of 45.5° , 49.5° , 50.9° and 59.9° . Small diffuse humps at 2θ values = $19.8^\circ - 21.9^\circ$, $35.0^\circ - 36.0^\circ$ and $37.8^\circ - 39.2^\circ$. Quartz diffraction peaks were observed at 2θ values of 20.8° , 26.5° , 55.2° and 62.3° . Besides, alunite and dickite were found at 2θ values of 17.8° and 22.4° , respectively. As compared to unground kaolin, ground kaolin was becoming more

amorphous with the grinding time (Vizcayno *et al.*, 2010). The intensity of kaolinite peak at 12.5° and 25.2° 2θ decreased with grinding time. This inferred that the bonds between the kaolinite layers were broken down (Vizcayno *et al.*, 2010). The crystalline network of kaolin was destroyed (San Cristobal *et al.*, 2009). According to Vizcayno *et al.* (2010), the amorphization of kaolin depended on the types of kaolin ground. Some less intense quartz peaks vanished during the grinding process. However, intense quartz peaks at 26.5° remained almost unchanged (San Cristobal *et al.*, 2009). Kumar & Kumar (2011) characterized ground fly ash for use in synthesis of geopolymers, observed the decrease in peak density and the broadening of quartz peaks due to the destroy of crystalline structure during the grinding process.

Referring to the XRD diffractogram of kaolin geopolymers in **Fig. 4b** and **Fig. 4c**, diffuse halo at 2θ values between 20° and 40° was observed. This was the amorphous characteristic of geopolymers (Davidovits, 1994). Kaolinite diffraction peaks decreased in intensity when compared to unground raw kaolin. Quartz diffraction peaks remained in the geopolymers even after the alkali-activation which might be due to quartz did not take part in geopolymerization reaction (Lecomte *et al.*, 2003). New crystalline peaks found in the XRD diffractogram corresponded to the zeolites diffraction peaks. On 28 days, the kaolinite peaks further decreased in intensity. The observation was accompanied by the increased in the compressive strength (Fig. 3). This inferred that the decreased of crystallinity favored the geopolymerization reaction. Similarly, quartz peaks remained almost unchanged. From XRD diffractogram of kaolin geopolymers on 7 days to 28 days, the XRD patterns showed the broadening of peaks and diffuse halos, suggesting the increase of amorphous content in kaolin geopolymers. On 28 days, kaolin geopolymers also displayed the growth of few new zeolite peaks.

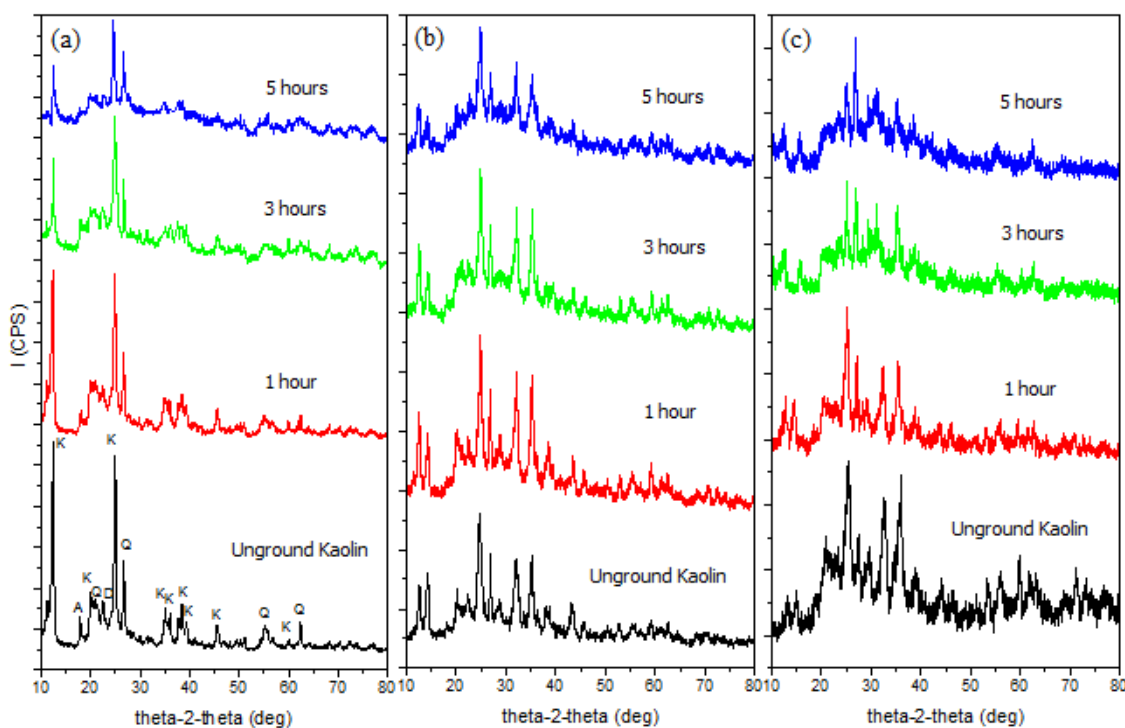


Fig. 4: XRD diffractogram of (a) unground and ground kaolin and the corresponding geopolymers on (b) 7 days and (c) 28 days. (K – kaolinite; Q – quartz; A – alunite; and D – dickite)

FTIR Analysis:

Fig. 5a shows the FTIR spectra of raw kaolin subjected to mechanical activation at various mechanical activation times. On the other hand, **Figs. 5b** and **5c** separately, illustrate the FTIR spectra of mechanically-activated kaolin geopolymers on 7 and 28 days. Mechanical activation of kaolin caused the reduction in the bands near 3600 cm^{-1} and 1640 cm^{-1} . These bands were attributed to the OH stretching and bending of water molecules. The same observation has been reported by San Cristobal *et al.* (2010). Besides, the band at 1113 cm^{-1} , 994 cm^{-1} , 907 cm^{-1} , 790 cm^{-1} and 741 cm^{-1} , 641 cm^{-1} and 530 cm^{-1} decreased after mechanical activation. In the ground kaolin for 3 and 5 hours, the peaks of 1113 cm^{-1} became invisible. The reduction in the absorption bands deduced the distortion of tetrahedral and octahedral layers of kaolinite. These bands became broad after grinding, suggested the amorphization of kaolin.

Kaolin geopolymers showed absorption bands at: 3300 cm^{-1} (OH stretching); 1650 cm^{-1} (OH bending); 1390 cm^{-1} (Si-O-Si/Si-O-Al); 950 cm^{-1} (Si-O-Si/Si-O-Al); 740 cm^{-1} (Si-O-Si/Si-O-Al); and 660 cm^{-1} (zeolites). Bands at 1390 cm^{-1} , 950 cm^{-1} and 740 cm^{-1} denote the geopolymer bonding formed after geopolymerization reaction. The band at 950 cm^{-1} shifted from lower wavenumber on 7 days to higher wavenumber (960 cm^{-1}) on 28 days. This was due to the polycondensation of the alternating Si-O and Al-O bonds. Besides, new absorption bands at 740 cm^{-1} only showed out on 28 days' kaolin geopolymers. The observation confirmed the formation of more geopolymer bonding in the samples and hence contributed to the strength development. According to Alonso & Palomo (2001), the formation of new peak at 740 cm^{-1} was a proof of geopolymerization.

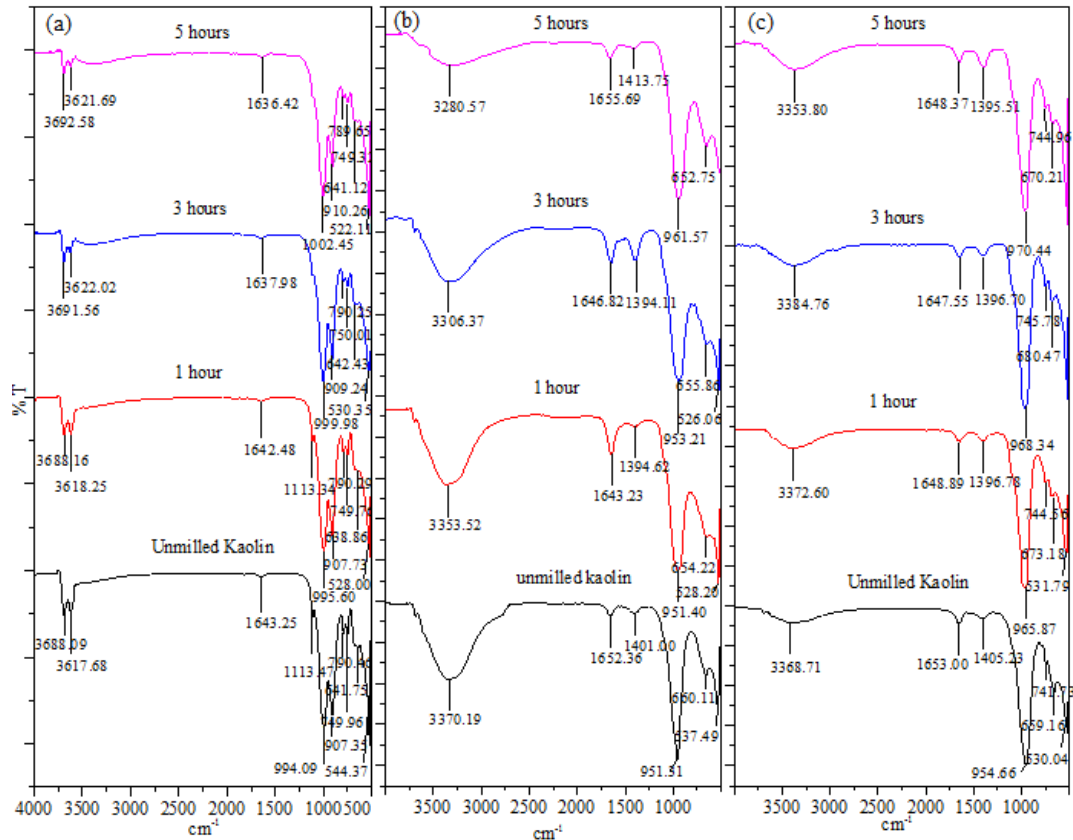


Fig. 5: FTIR spectra of (a) unground kaolin and ground kaolin for 1, 3 and 5 hours; and kaolin geopolymers produced from mechanical-activated kaolin on (b) 7 days and (c) 28 days.

Conclusion:

The study on the effect of mechanical activation of kaolin on the properties of geopolymer has drawn conclusions as the following:

1. Mechanical activation reduced the particle size from 13 μm to 8 μm when activation time increased from 1 hour to 5 hours and consequently affected the surface area and activity of raw materials.
2. Mechanical activation of kaolin increased the surface area of kaolin as well as the reactivity of kaolin towards alkali-activation.
3. Mechanical activation changed the particle size and surface area of kaolin which improved the geopolymerization reaction and hence the compressive strength.

ACKNOWLEDGEMENTS

The authors of the present work wish to acknowledge the KACST for funding this study through collaboration between KACST – UniMAP.

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