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# The Properties of Nano $TiO_2$-Geopolymer Composite as a Material for Functional Surface Application

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**Abstract.** The aim of this study is to examine the properties of Nano $TiO_2$-geopolymer as a material for functional surface applications such as walls, floors, bench top, arts and decoration materials. Class-C fly ash and metakaolin were used as raw materials to produce geopolymers pastes (binder). Geopolymers were synthesized through alkali activation method cured at 50°C for 2 hours using molar oxide ratios of $SiO_2/Al_2O_3$ = 3.0, $Na_2O/SiO_2$ = 0.2, and $H_2O/Na_2O$ = 10. Nano $TiO_2$ was added into geopolymers paste at different concentration namely 0 wt%, 5wt%, 10wt% and 15wt % relative the weight of fly ash or metakaolin). The measurements were commenced after the samples aged 7 days. The samples made from fly ash were immersed in 1 M $H_2SO_4$ solution for 3 days for acid resistance examination. The self-cleaning properties of the composites were observed by immersing the sample into red clays solution. The X-Ray Diffraction (XRD) was performed to examine the structure and phase of the samples before and after acid resistance measurement. Scanning Electron Microscopy (SEM) was performed to examine the surface morphology of the resulting composites. The measurements results showed that Nano $TiO_2$–geopolymers composite can be applied as functionally surface materials.

## 1 Introduction

The quality of building materials can be valued not only by their mechanical, but also durability and structural performance. Structural application refers to application that requires mechanical performance (e.g. strength, stiffness and vibration damping ability) in material [1]. The essential requirements consist of low density, corrosion resistance, and ability to resist high temperature. Functional or hybrid composite based on geopolymer are currently investigated due to its excellent properties such as durability, mechanical, and thermal properties [2].

Geopolymer, is a green and eco-friendly material, developed as a promising material because of its high mechanical strength, heat and fire resistance, good surface and

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resistance to acid attack [3,4]. In addition, geopolymers have been recognized as excellent binder material and with an addition of certain aggregate such as organic or inorganic fibres or particles will form high performance composites. The advantages of producing composite are to prevent the presence and development of cracks and to enhance the mechanical strength, particularly flexural strength, of geopolymer matrix [4]. Recently, composites based on geopolymer have been studied for producing high performance and functionally surface materials such as walls and floors, bench top, and other applications [3-5,6].

Nanomaterial is one of the promising material because of its size (1-100 nanometres) produced for wide range applications. Metal oxide such as $TiO_2$ is a semiconductor material which has photo-catalyst properties [7-10] and it is one of the most practical nanoparticles which offer a promising platform for different applications, e.g. high performance catalysis, photo-catalysis, self-cleaning and electro-catalysis systems [8-9, 11-13]. Titanium dioxide ($TiO_2$) is one of the most used materials to realize self-cleaning and its general use is attributed to high catalysis efficiency and chemical stability [14-17].

This study used Class-C fly ash and metakaolin as raw materials for producing geopolymers pastes and nano $TiO_2$ as filler. The study was carried out to determine the properties of the resulting composite such as mechanical strength, self-cleaning ability, and resistance to acid attack.

## 2 Experimental

This research is aimed at developing geopolymer composites made from fly ash and metakaolin added with $TiO_2$ nanoparticles as filler for functional surface. Fly ash is derived from Bosowa Power Plant Jeneponto, South Sulawesi and it is categorized as class-C. The molar oxide ratios of the starting materials were $SiO_2/Al_2O_3$ = 3.0, $Na_2O/SiO_2$ = 0.2 and $H_2O/Na_2O$ = 10.0. This composition will result in geopolymer type poly (sialate-siloxo) according to Davidovits's terminology. The concentration of $TiO_2$ (Anatase phase) was varied relative to the weight of fly ash or metakaolin, namely 0%, 5%, 10% and 15%. $TiO_2$ nanoparticle was prepared through ball milling process for 10 hours. The mixture between geopolymer paste and $TiO_2$ was stirred manually, poured in various moulds and cured at $50^oC$ for 2 hours. The resulting materials were stored in open air for 7 days before commencing any measurements. The compressive strength was measured by using Tokyo Testing Machine (TTM). X-ray diffraction (XRD) measurements were conducted to study the structure and phase of the starting and the resulting composites. The acid resistance of the material was measured by immersing the samples into 1M $H_2SO_4$ solutions for 3 days. The self-cleaning ability of the samples was observed by immersing the samples into red clay solution for several minutes. The surface morphology of the samples was examined by using scanning electron microscopy (SEM).

## 3 Results and discussion

The chemical compositions of fly ash and metakaolin used in this study were examined by using Energy Dispersive Spectroscopy (EDS) as shown in table 1.

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**Table 1.** Chemical composition (wt%) of fly ash and metakaolin (EDS result).

| | $Al_2O_3$ | CaO | FeO | $K_2O$ | MgO | $Na_2O$ | $SiO_2$ | $SO_3$ | $TiO_2$ |
|---|---|---|---|---|---|---|---|---|---|
| Fly ash | 22.25 | 13.95 | 23.41 | 1.39 | 6.20 | 0.99 | 30.10 | 0.51 | 1.20 |
| Metakaolin | 50.88 | - | 1.14 | 0.89 | 0.29 | 0.18 | 46.46 | - | 0.16 |

Table 1 shows that the content of CaO is more than 10wt% and this make the time setting of geopolymer paste is much less than 30 minutes and made difficult to produce in large volume. In contrast, the time setting of geopolymer paste made from metakaolin exceeded 2 hours and therefore much easier to produce in large scale.

Figure 1 show photographs of the example of the composites produced in this study. It can be seen that the surface of the composite is smooth and shiny, free from apparent pores or air bubbles. The densities of the composite with $TiO_2$ addition of 0 wt%, 5wt%, 10wt%, and 15wt% relative to the weight of fly ash were 2.10 g/cm$^3$, 2.16 g/cm$^3$, 2.18 g/cm$^3$ and 2.20 g/cm$^3$, respectively.

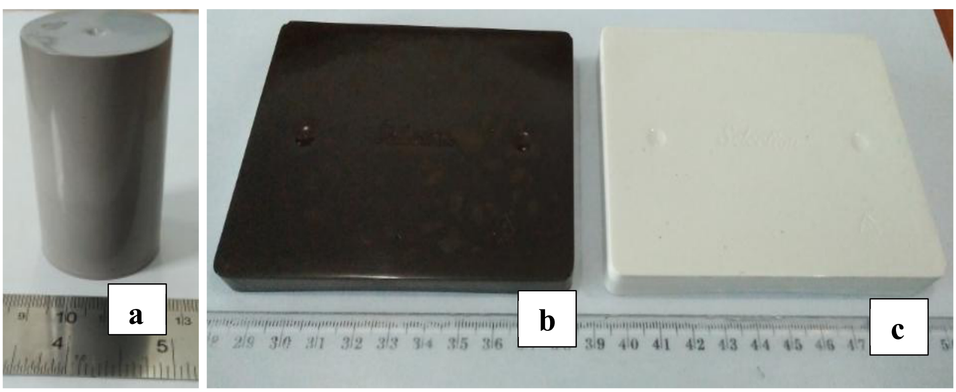


**Fig. 1.** Photographs of geopolymers; (a) & (b) Fly Ash + TiO2 nanoparticle, (c) Metakaolin + $TiO_2$ nanoparticle.

The compressive strength of the composites were measured for samples having cylindrical in shape with a length of 4.00 cm and 2.00 cm in diameter. Table 2 shows the compressive strength of the samples contain different concentration of $TiO_2$. It can be seen that the magnitude of the compressive strength increases as the weight of $TiO_2$ increase up to 10% and start to decrease at the addition of 15wt% $TiO_2$. Data for mechanical characterisations of nano $TiO_2$-geopolymers composite made from metakaolin unfortunately did not available at the time of writing this paper.

**Table 2.** The average of 7 days compressive strength of Composite $TiO_2$-Geopolymers made from fly ash.

| Sample ID | Compressive Strength (MPa) |
|---|---|
| HDS 0% $TiO_2$ | 25.79 |
| HDS 5% $TiO_2$ | 28.98 |
| HDS 10% $TiO_2$ | 39.65 |
| HDS 15% $TiO_2$ | 37.56 |

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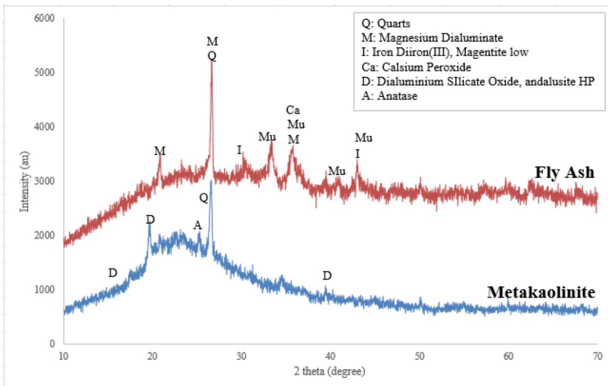
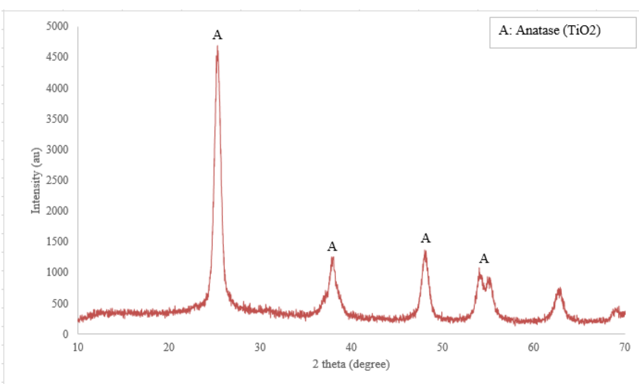
Figure 2(a) shows typical diffractogram of fly ash and metakaolin. The crystallinity level and chemical compositions of fly ash and metakaolin are very much different. Metakaolin is x-ray amorphous and considered as pure aluminosilicate although contain some minor phases such as Quartz and Anatase. Figure 2(b) shows diffractogram of $TiO_2$ nanoparticle used in this study.




**(a)**




**(b)**

**Fig. 2.** Diffractogram of (a) Metakaolin and Fly Ash (b) $TiO_2$ nanoparticle.

The average size of $TiO_2$ nanoparticle was about 62 nm as calculated by using Debye-Scherer equation. Previous research which utilizes vanadium-doped $TiO_2$ nanoparticles has identical anatase phase with an average crystal size of 10-20 nm [16].

Diffractogram of as-prepared composite $TiO_2$-geopolimer based on fly ash and metakolin is shown in Figure 3. The peak of $TiO_2$ increase as the concentration of $TiO_2$ increase in the network of geopolymers. Figure 3 also shows that there was no new phase formed in the structure of geopolymer due to the addition of nano $TiO_2$ indicating that $TiO_2$ did not react with other fly ash or metakaolin constituents.

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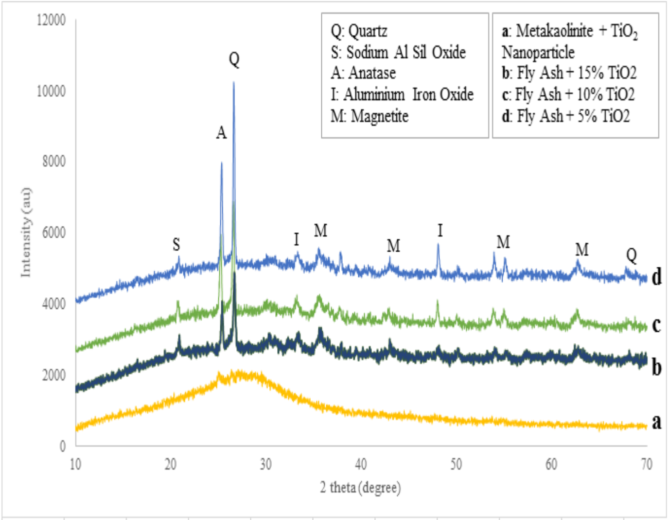


**Fig. 3.** Diffractogram of $TiO_2$-geopolymers composite made from fly ash containing 5 wt%, 10wt%, 15wt% of $TiO_2$ along with $TiO_2$-geopolymer made from metakaolin.

Figure 4 shows SEM micrographs of composite nano $TiO_2$-geopolymer produced from fly ash and metakaolin. Substantial cracks on the surface of composites made from fly ash occurred due to polishing and water loss during evacuation in coating and SEM chambers. This kind of cracks is known as secondary cracks [17]. Cracks development in composite made from metakaolin did not as extensive as those of fly ash. The micrographs also show good mechanical bonds between geopolymer matrix and $TiO_2$ nanoparticles.

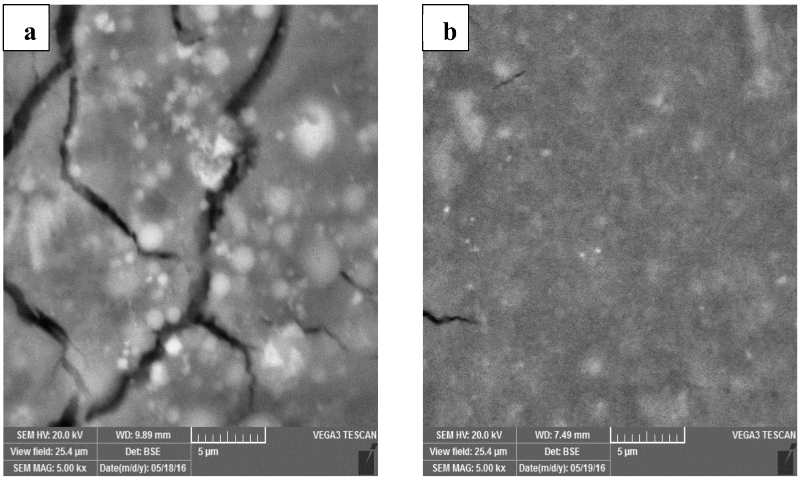


**Fig. 4.** SEM micrographs of composite $TiO_2$-geopolymers made from (a) fly ash and (b) metakaolin. The composites contain 10% of $TiO_2$.

The composites made from fly ash which contains 0%, 5% and 15% of $TiO_2$ were subjected to acid resistance measurement by using 1M $H_2SO_4$ solution for 3 days. Figure 4 shows the diffractogram of the sample after 3 days in $H_2SO_4$ solution. The diffractogram revealed that $H_2SO_4$ react strongly with CaO in fly ash forming gypsum ($CaSO_4.2H_2O$)

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crystal. The sample containing 5wt% TiO2 showed the highest formation of gypsum. The presence of excess gypsum in the interior of geopolymers will reduce its mechanical strength [18].

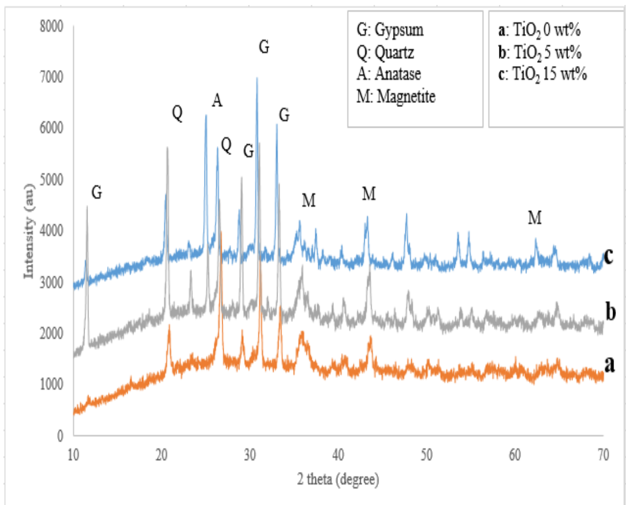


**Fig. 5.** Diffractogram of samples with 0%, 5% and 15% $TiO_2$ after 3 days acid attack.

SEM results on the composite samples made from fly ash after 3 days immersed in $H_2SO_4$ solutions is shown in Figure 6. The micrographs confirmed the formation of gypsum crystals in geopolymer network as observed in the diffractogram figure 5. Samples contain 5% $TiO_2$ showed the largest formation of gypsum crystal. This result suggests that geopolymers produced from fly ash containing high CaO will form gypsum crystals when in contact with $H_2SO_4$ solution and hence deteriorating the mechanical strength of geopolymers.

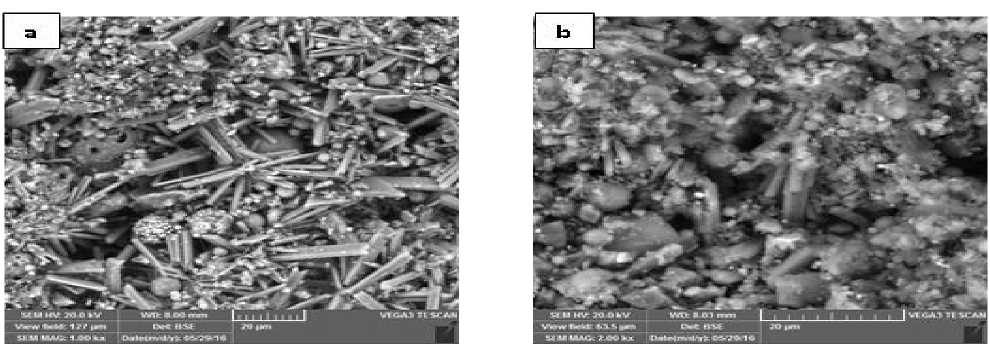


**Fig. 6.** SEM micrographs of composites made from fly ash after 3 days in $H_2SO_4$ solution showing the growth of gypsum crystals (a) 5% $TiO_2$, (b) 10% $TiO_2$.

The addition of $TiO_2$ nanoparticles in the network of geopolymers result in functional composite which have a self-cleaning ability. It is well known that $TiO_2$ nanoparticle is an excellent photocatalyst material particularly when it size below 100 nm. The self-cleaning ability of the composites made from fly ash and metakaolin were examined by immersing the sample into red clay solution for several minutes as in Figure 7. The sample was then taken out and it was found that the surface of the composite remains clean and no dirt or clay particulates remain on its surface.

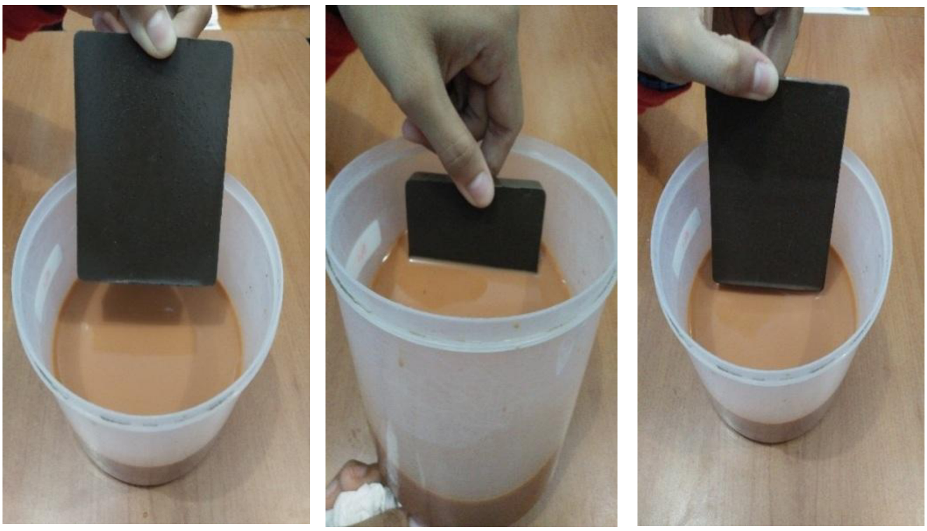

**Fig. 7.** Functional composite $TiO_2$-geopolymer made of fly ash exhibited self-cleaning ability.

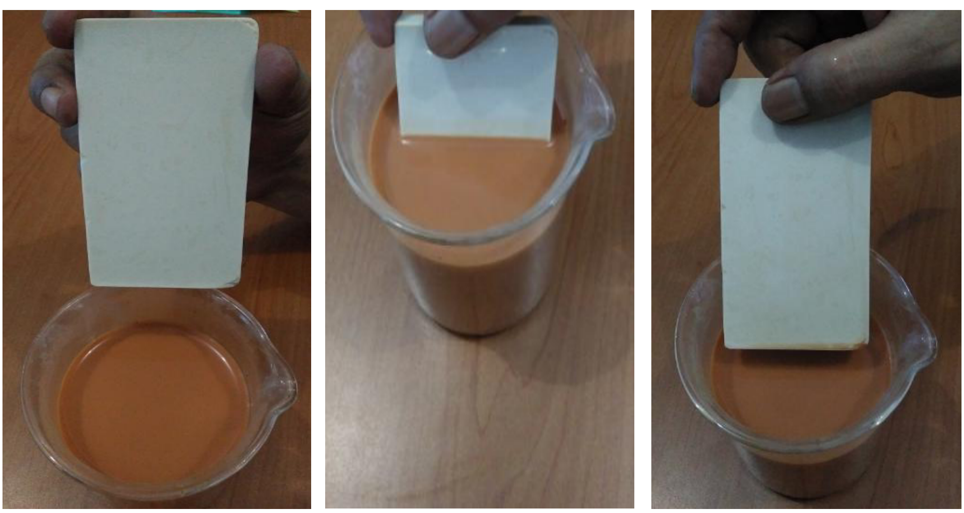

**Fig. 8.** Functional composite $TiO_2$-geopolymer made of fly ash exhibited self-cleaning ability.

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# 4 Conclusions

Nano $TiO_2$-geopolymer composites based on fly ash and metakaolin have been successfully produced through alkali activation method. The mechanical strength of the composites (made from fly ash) increase with the increase of $TiO_2$ concentration up to 10wt%. The composite made from high CaO fly ash suffer from the formation of substantial gypsum crystal when in contact with $H_2SO_4$ solution. The nano TiO2-geopolymers composite has a potential to be applied as functionally surface material and exhibit self-cleaning properties.

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