Influence of TiO$_2$ nanoparticles (wt%) onto the physical and mechanical properties of the TiO$_2$-geopolymer paste

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Abstract. The TiO$_2$-geopolymer paste had been prepared by dry-mixing of the fly ash with various concentration (wt%) of TiO$_2$ nanoparticles (2.5%, 5.0%, 10.0% and 15.0%). Those powder mixtures were then mixed with the alkali activator with the ratio of 2.5 and were cured at room temperature for 28 and 640 days. The phase and chemical bonding analysis revealed that the incorporation of TiO$_2$ nanoparticles did not create any additional phase or functional group, but only physical interaction might have occurred in between the TiO$_2$ and geopolymer matrix. However, the physical properties were depending on the TiO$_2$ nanoparticles content where setting time of the geopolymer can be shortened by the addition of certain amount of TiO$_2$ nanoparticles (up to 5.0 wt%). The water absorption also increased as a function of TiO$_2$ content, due to the formation of the micro cracks as a result from the agglomeration of TiO$_2$ nanoparticles. The compressive strength reaches its maximum value, 85.9 MPa with 5.0 wt% of TiO$_2$ nanoparticles. Beyond 5wt%, the strength decreased almost half of the maximum value, where agglomeration becomes a main factor. While for 640 days of ageing, sample with 15.0 wt% shows triple increment from 30.6 MPa to 95.3 MPa.

1. Introduction
Geopolymer is an innovative green construction material that was developed for Ordinary Portland Cement (OPC) substitution. It was invented by Davidovits and belong to the family of inorganic polymers [1]. Geopolymer is produced by combining the compound of pozzolanic or aluminosilicate source materials with alkaline activator solution [2]. It can be applied as a paste, mortar or concrete in construction materials. Other than that, it can also be applied commonly in our living surroundings i.e. paving blocks, lightweight concrete, etc [3-6]. Till this date, geopolymers have been reported to exhibit an excellent physical and mechanical properties, environmentally friendly, long term durability, etc. Due to their performances and high demand of application, many research has been conducted for developing their properties.

Research has been conducted in incorporating the nanoparticles into the geopolymer matrix or concrete in order to enhance the physical and mechanical properties. For example, zinc oxide (ZnO) nanoparticles, copper oxide (CuO) nanoparticles, nano-silica (SiO$_2$), iron oxide, alumina (Al$_2$O$_3$), nanoclays, etc. For example, Zidi et al. [7] studied the influence of zinc oxide nanoparticles onto the mechanical and thermal properties of the geopolymer. Results showed that the addition of ZnO nanoparticles can increase the compressive strength to its maximum value depending on the ZnO content. For CuO nanoparticles-based mortar sample, a better strength performance also has been
reported [8]. Assaedi et al. [9] indicated that the addition of nano-SiO\(_2\) into the geopolymer matrix can improve their strength, structural and morphology of the concrete. Research work also has been focused on titanium dioxide (TiO\(_2\)) nanoparticles due to their advantages in the mechanical properties. For example, the compressive strength of self-compacting concrete containing 4 wt% of TiO\(_2\) nanoparticles are much higher than the mixtures that only containing the fly ash [10]. From those studies, it can be concluded that influence of nanoparticles admixtures onto the properties of the geopolymer depending on the nanoparticles content in the geopolymer matrix, the distribution of the particles, particles size and shape, etc.

So far, very little work has been done on study of TiO\(_2\) nanoparticles onto the strength of the concrete, especially on the geopolymer paste. Thus, this paper focused on the influence of different content (weight percentage, wt%) of TiO\(_2\) nanoparticles onto the performance of the fly ash based geopolymer paste. The physical properties were measured through the setting time and water absorption test, while the mechanical strength of the prepared geopolymer paste was analyzed by compressive strength test.

2. Experimental

The materials and chemicals that were used during the research consist of fly ash (FA, CIMA Perlis, 6.7% of calcium oxide content), sodium silicate (Na\(_2\)SiO\(_3\), South Pacific Chemical Industries Sdn. Bhd. Malaysia), sodium hydroxide (NaOH, Formosa plastic corp. Taiwan), titanium dioxide powder 99.9% (TiO\(_2\), 30-50nm, Hongwu Nanometer) and deionized water.

For the preparation of TiO\(_2\)-geopolymer paste, the fly ash (FA) was sieved about ± 150 μm in size. The alkali activator (combination of NaOH and Na\(_2\)SiO\(_3\)) was prepared separately. During the process, about 480.0 gram of NaOH pellets were dissolved in 1L of deionized water in a volumetric flask to obtain 12M of concentrations. Then, about 178.6 gram of water glass (Na\(_2\)SiO\(_3\)) was added. The ratio of Na\(_2\)SiO\(_3\): NaOH was 2.5:1. This solution was prepared a day before mixing with TiO\(_2\)-fly powder in order to ensure the solution will be mixed evenly. The mixing process was carried out accordance to ASTM 109/C standard test method. About 487.5 gram of FA was dry-mixed with 2.5 wt% of TiO\(_2\) nanoparticles by using a ball mill for 30 minutes at 25 rpm. Then, the powder mixture was transferred into a mechanical mixer. About 250 ml of the as-prepared alkali activator was added slowly (190 rpm). The solid-to-activator ratio (S/L ratio) was 2.0. Then, the speed was increased to 2096 rpm for 15 minutes to ensure the homogeneity of the slurry.

Table 1. Mix design of TiO\(_2\)-geopolymer paste.

| Samples | Mix Design | Mass Ratio |
|---------|------------|------------|
|         | TiO\(_2\) (wt%) | Fly Ash (g) | S/L | Na\(_2\)SiO\(_3\)/NaOH |
| T\(_0.0\) | 0.0 | 500.0 | 2.0 | 2.5 |
| T\(_1.5\) | 1.5 | 492.5 |          |          |
| T\(_2.5\) | 2.5 | 487.5 |          |          |
| T\(_5.0\) | 5.0 | 475.0 |          |          |
| T\(_10.0\) | 10.0 | 450.0 |          |          |
| T\(_15.0\) | 15.0 | 425.0 |          |          |
2.1 Samples
The phase of the prepared TiO$_2$-geopolymer phase was analyzed by using the X-ray diffraction (XRD D8-Advance, Bruker, Germany) over a 2Ɵ range 10 to 70° using CuK$_\alpha$ ($\lambda=1.5046$). The analysis of the XRD pattern was carried out by using an X’pert HighScore plus software incorporating ICCD PDF-4 files. The chemical bonding of the prepared geopolymer samples were identified by using Fourier-transform infrared spectroscopy (FTIR Spectrum RX 1, Perkin Elmer, Japan). The analysis was performed in a transmittance mode, which has frequency range from 4000 to 650 cm$^{-1}$.

The setting time test was conducted by following the ASTM C 191-99. The water absorption test was conducted by following the ASTM C642-06. The mechanical property (compressive strength) of the prepared geopolymer paste was investigated by using a universal testing machine (UTM N950602, Shimadzu, Japan) followed the ASTM C109/C.

3. Results and Discussion
Figure 1 shows the XRD patterns of the TiO$_2$-geopolymer paste. By adding 2.5wt% of TiO$_2$ nanoparticles, the anatase peak started to appear at 25°(20 degree). This peak became more intense as higher wt% of TiO$_2$ were added, with the additional peaks of anatase at 35°, 40°, 48°, 54° and 62° (PDF#00-021-1272). The typical peaks of geopolymer products (mullite, quartz and hematite) also were observed. When compared with TiO$_2$-free geopolymer paste of XRD pattern, there were no significant peak changed except the additional peaks of anatase. Thus, the addition of TiO$_2$ nanoparticle might not change the geopolymer phase.

The FTIR analysis was conducted to study the influence of TiO$_2$ photocatayst onto the chemical bonding of the geopolymer. Fig. 2 shows the FTIR spectra of different wt% of TiO$_2$-geopolymer paste. For TiO$_2$-free paste, the spectrum shows a sharp and intense (Si, Al)–O–Si asymmetric stretching vibration band at 979 cm$^{-1}$. By adding different wt% of TiO$_2$, the intensity of the (Si, Al)–O–Si band increased and slightly shifted in between 978-961cm$^{-1}$ showing there was interaction between the geopolymer and photocatalyst. Nevertheless, based on the spectrum, there were no additional functional group appeared after the addition of the TiO$_2$. Thus, it was proved that only physical interaction occurred between the TiO$_2$ photocatalyst and the geopolymer matrix that is in agreement with the XRD result.

![Figure 1. XRD patterns of TiO$_2$-geopolymer paste.](image-url)
Figure 3 shows the initial and final setting time of geopolymer paste with different wt% of TiO$_2$ nanoparticles content. Without the photocatalyst (sample T$_{0.0}$), the geopolymer paste took about 30 hours before the paste started to harden at ambient temperature (21 to 23°C). The longer initial time (more than 24 hours) was due to the slow chemical reaction of the paste, caused by the low content of CaO (6.70%). Calcium plays an important role in supplying the heat during geopolymerization process, which aiding the aluminosilicate dissolution and therefore the geopolymer paste take longer time to be hardened, since the lower CaO content of the fly ash was used [11,12]. The final setting time was recorded to be 36 hours. Thus, it took about 6 hours for the paste to fully hardened. When 2.5 wt% (T$_{2.5}$) of TiO$_2$ photocatalyst was added, the initial setting time of the paste decreased to 24 hours, while the final setting time decreased to 30 hours. Although the setting time were decreased, it still took about 6 hours for the sample to be fully hardened. However, as the amount of the ZnO photocatalyst was increased to 5.0 wt% (Z$_{5.0}$), 10.0 wt% (Z$_{10.0}$) and 15.0 wt% (Z$_{15.0}$), the initial setting time keep increasing to 29, 32 and 34 hours, respectively. Same goes to the final setting time, which increased to 34, 40 and 41 hours. It is known that the TiO$_2$ nanoparticles itself can act as activator to promote the hydration process of the paste [13]. Thus, the setting time was shortened when 2.5 wt% of the TiO$_2$ added. In most cases, higher TiO$_2$ content in paste/cement can shorten the initial and final setting time that attributed to the acceleration rate. However, in this case the setting time increase after the addition of 5.0 wt% of TiO$_2$ nanoparticles onward. This situation can be explained as follows. Apart from promoting the hydration process, the addition of TiO$_2$ nanoparticles on the geopolymer matrix might also reduce the precipitation of calcium hydroxide (Ca(OH)$_2$), which led to the decrement in the hydration degree. In addition, the effect of TiO$_2$ nanoparticles onto the physical properties of the paste also depending on the cement/geopolymer matrix, water to cement ratio, TiO$_2$ content, TiO$_2$ size and type and also the dispersion degree [14].

Figure 4 shows the water absorption (%) of the TiO$_2$-geopolymer paste as a function of the wt% of the TiO$_2$ content. The water absorption increased up to 17% when 2.5, 5.0 and 10.0 wt% of TiO$_2$ nanoparticles were added. This absorption behavior showed that the samples are full with pores, which might due to the agglomeration of the TiO$_2$ particles in the matrix that caused the micro cracks as observed from the SEM images (not shown). The water absorption drops to about 3% when 15.0 wt%
of the TiO$_2$ added. This small decrement still indicated that the dispersion of the nanoparticles in the geopolymer matrix might not be homogenous.

The mechanical property of the prepared TiO$_2$-geopolymer paste was investigated through a compressive strength test. Figure 5 shows the compressive strength of the TiO$_2$-geopolymer paste for 28 and 640 days of ageing. For 28 days of ageing, the strength of the geopolymer paste increased with the addition of TiO$_2$ photocatalyst up to 5.0 wt% (T$_{5.0}$), with the strength value of 85.9 MPa. As the amount of TiO$_2$ photocatalyst was increased to 10.0 wt% (T$_{10.0}$) and 15.0 wt% (T$_{15.0}$), the strength of the geopolymer paste decreased to 32.7 and 30.6 MPa, respectively. The strength decreased might due to the agglomeration of the TiO$_2$ nanoparticles, which not uniformly dispersed in the geopolymer matrix. This agglomeration or poor dispersion of the nanoparticles might had created weak zones in the geopolymer system, thus reduced the strength [15]. For 640 days of ageing, the geopolymer paste with 15 wt% of TiO$_2$ photocatalyst (T$_{15.0}$) shows the highest compressive strength which is 95.3 MPa. Sample T$_{15.0}$ shows a major strength difference between 28 and 640 days of ageing, which is from 30.6 MPa increased up to 95.3 MPa. This showed that the geopolymerization process keep ongoing although the samples had been aged for 640 days. The geopolymer paste sample T$_{3.0}$ shows 92.5 MPa of strength and followed by sample T$_{2.5}$ and T$_{10.0}$ which is 78.0 MPa and 65.5 MPa, respectively.

Figure 3. Setting time of TiO$_2$-geopolymer paste

Figure 4. Water absorption (%) of the TiO$_2$-geopolymer paste

Figure 5. Compressive strength of TiO$_2$-geopolymer paste
4. Conclusion
The TiO$_2$-geopolymer pastes were successfully been prepared by varying the TiO$_2$ content (wt%) in the geopolymer matrix. The addition of the TiO$_2$ nanoparticles did not chemically changed the geopolymer matrix as proved by the phase and chemical bonding analysis where no additional peaks or functional groups can be observed. For the physical properties, the addition of TiO$_2$ nanoparticles can promote the acceleration of hydration process, thus shortened the setting time. However, excess amount of TiO$_2$ can cause the slow hydration rate might due to the precipitation of calcium hydroxide. The water absorption also increased as a function of the TiO$_2$ nanoparticles content, due to the agglomeration of the particles. From the compressive strength, maximum strength can be obtained for sample with 5.0 wt% of TiO$_2$ content (85.9 MPa), that was aged for 28 days. Sample with 15.0 wt% of TiO$_2$ nanoparticles shows triple increment from 30.6 to 95.3 MPa after ageing for 640 days.

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