Development of Nano TiO₂–Geopolymer Functional Composite as Antifouling Bricks

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Abstract. The purpose of study is to examine the ability of nano TiO₂ – geopolymer functional composite as antifouling bricks. The samples were synthesized through alkali-activation method at 70°C for 1 hour by mixing metaclay with TiO₂ nanoparticles and activated with sodium silicate solution. There were two series of samples produced, namely, GT_A with addition of 2% nanoTiO₂ and GT_B with addition of 4% nano TiO₂ relative to the mass of metaclay. The samples were immersed in water and in 1M H₂SO₄ solution for 4 days to examine the resistance of composites in hars environment. The x-ray diffraction (XRD) was performed to examine the chemical compositions of the samples before and after environmental test. The morphology of the samples surfaces was examined by using Scanning Electron Microscopy (SEM) coupled with energy dispersive spectroscopy (EDS). Based on this study, sample GT_A shows its excellent properties as antifouling bricks. The addition of nano TiO₂ was found to improve the quality of geopolymers as a high performance bricks.

1 Introduction

Brick is one of construction materials that have been known by people around the world, both in rural and urban areas. Conventionally, manufacture of bricks need to be burned and dried (traditional bricks) and it may cause air pollution in the surrounding environment [1-2,19]. Traditional bricks as a raw material in the building are vulnerable to weathering both chemically and mechanically, brittle and sensitive to the salting reaction, and directly related to the presence of micro-organisms deposit on the building [3-5, 20-21]. Biofouling can be defined as the accumulation of micro-organisms, plants, and animals which are attached to either temporary or permanent on building facades [6]. One of the promising material which has abundant precursor and easy to produce is geopolymer bricks.

Geopolymer was developed by Davidovits in the late 1978, synthesized through polycondensation of aluminosilicate minerals (e.g., metakaolin, clay, fly ash) with a solution of alkali (e.g., sodium hydroxide and sodium silicate) [7- 9]. Many researchers use clay as raw material for manufacturing geopolymer for bricks application [10-11]. The most important advantages of geopolymer bricks are resistance to acid attack, high early strength, long-term durability, good fire resistance, low manufacturing energy consumption, and low CO₂ emission, which make these novel material to be categorized as “green material”

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[11-14]. Recently, the latest innovation that provides added value to the geopolymer bricks is to incorporate anti-fungal or anti biofouling material.

Nanomaterials are increasingly developed due to its size (1-100 nanometers) in at least one dimension. Their physical and chemical properties differ from those of bulk materials (controlling matter at atomic level). It can be used as prevention of building materials from organic contamination. Titanium dioxide (TiO_2) is one of the most used material to realize self-cleaning and its general use is attributed to its main features: high catalysis efficiency and chemical stability, inexpensiveness, compatibility with traditional construction [15]. The advantage of using TiO_2 as follows: (i) protective or anti corrosion coating mechanism; (ii) thermal control; (iii) easy to clean; (iv) anti bacterial coating for work surfaces; (v) anti graffiti coating for building and structure, (vi) low-cost [16, 17]. Furthermore, the most importance of nano- TiO_2 is its inert properties, corrosion resistance due to light or chemicals and non-toxic [18].

This study utilizes clay-based geopolymer as the raw material forming the matrix of geopolymer and nano TiO_2 as antifouling agent. This study was carried out to determine the quality and capability of functional composite nano TiO_2 - geopolymer as antifouling bricks.

2 Experimental

This study is a development research that lead to the development of Nano TiO_2 – geopolymer as antifouling bricks through alkaline-activation method. Metaclay was produced from calcined clay at 750°C for 6 hours as a source of aluminosilicate and TiO_2 (anatase) as antifouling agent (filler). The alkaline solution for geopolymerization was a mixture of sodium hydroxide (NaOH), sodium silicate ($\text{Na}_2\text{O} \cdot 3\text{SiO}_2$) and distilled water (H_2O) with a certain concentration. Geopolymer bricks was produced by mixing the basic ingredients of the metaclay with nano TiO_2 and activated with an alkaline solution to obtain a homogeneous paste.

Geopolymer paste was poured into the block-shaped glass mold with size 20 cm x 8 cm x 4 cm and then cured in an oven at 70°C for 1 hour. After the age of 24 hours, the samples were removed from the mold and tested after 3 days. After the age of 7 days, the samples were immersed in water solution and sulfuric acid (H_2SO_4 1 M). The physical properties (pH levels, bulk density, mass, and colour change) were monitored daily. Durability test have been performed to the geopolymer bricks containing Nano TiO_2 , which consist of acid attack and environment test. Samples which have been tested were characterized by XRD to examine the structure of the samples. SEM characterization was used to study the structure and morphology of the sample before and after testing.

3 Results and discussions

After the age of 7 days, Nano TiO_2 -Geopolymer samples were tested. Each sample was immersed in solutions of sulfuric acid (H_2SO_4 1 M) and water for 4 days. Table 1 below shows the value of bulk density of each sample before and after testing. Sample geopolymer without nano- TiO_2 was produced by Riska [22] with an average composite strength 58.44 MPa. This research focused on the mechanical strength.

Table 1. The Apparent Porosity and Bulk Density before and After Testing

Sample ID	Bulk density (gr/cm ³)			
	Acid Attack Test		Environmental Test	
	Before	After	Before	After
Sample GT_A	1.68	1.24	1.65	1.58
Sample GT_B	1.64	0.76	1.68	1.18

Figure 1 shows the appearance of (a) GT_A (b) GT_B before acid attack and environment test of each sample.

Fig. 1. (i) The appearance of : (a) MC + 2% NanoTiO₂; (b) MC + 4% NanoTiO₂ before acid attack, (ii) The appearance of (c) MC + 2% NanoTiO₂; (d) MC + 4% NanoTiO₂ before environmental test

The appearances of each sample before and after testing in strong acid solution 1 M H₂SO₄ and water for 4 days were shown clearly in Figure 2. It can be explained that there are physical change and densification after immersing in acid solution.

Fig. 2. The appearance of: a) MC + 2% Nano TiO₂; (b) MC + 4% Nano TiO₂ after acid attack, (ii) The appearance of: (c) MC + 2% Nano TiO₂; (b) MC + 4% Nano TiO₂ after environment test

In this study, clay is used as raw material due to its abundant availability in South Sulawesi, Sidrap Regency, Indonesia. Table 2 shows the composition of clay raw material. Based on XRF analysis, it can be shown that the main oxide composition of clay were SiO₂, Al₂O₃, and Fe₂O₃ followed by TiO₂ and K₂O.

Table 2. Composition of Clay as Raw Material Based on XRF Result

Compound	wt (%)	Element	wt (%)
SiO ₂	66.140	Si	30.920
Al ₂ O ₃	16.310	Al	8.630
Fe ₂ O ₃	14.780	Fe	10.330
TiO ₂	1.310	Ti	0.780
K ₂ O	0.860	K	0.718
CaO	0.240	Ca	0.172
MnO	0.151	Mn	0.117
ZrO ₂	0.018	Zr	0.063
BaO	0.032	Ba	0.028
SrO	0.023	Sr	0.019
Nb ₂ O ₅	0.018	Nb	0.013
MoO ₃	0.012	Mo	0.008
ZnO	0.010	Zn	0.008
Y ₂ O ₃	0.007	Y	0.006
In ₂ O ₃	0.005	In	0.004

Figure 3a shows the XRD pattern of meta-clay that has a certain crystalline structure with the highest peak lies between 25⁰– 27⁰ (2θ). The XRD analysis shows that the main compositions of meta-clay were SiO₂ in the form of *quartz*, magnetite and hematite. Figure 3b shows the characterization results of the Nano TiO₂ and all the peaks can be indexed as anatase form of TiO₂ (the average particle size is 12 nm).

Fig. 3. Phase characterization of (a) metaclay; (b) nano TiO₂

Figure 4 is the result of phase characterization of sample namely GT_A with addition of 2% nano TiO₂ relatively to its precursor mass and GT_B with addition of 4% nano TiO₂. The diffraction pattern shows the sample maintain its level of crystallinity.

Fig. 4. Phase characterization of (a) GT_A (b) GT_B as prepared samples

Phase characterization shows that the most dominant peaks both of GT_A and GT_B lies between 20⁰-30⁰ (2θ) which consist of quartz, almandite, magnetite, hematite, rutile, sodium calcium-cyclo hexasilicate joining with anatase. Overall, there is no significant change due to the addition of nano TiO₂ in geopolymer structure. Table 2 shows the chemical composition of the phase of nano TiO₂-geopolymer (in wt%).

Table 3. Chemical composition of the sample in Figure 4 based on XRD measurement

Phase	Sample	
	(GT_A) wt (%)	(GT_B) wt (%)
Quartz	72	75
Anatase	8.2	10.6
Rutile	7.2	7
Magnetite	3.4	3.1
Hematite	5.2	5.1
Sodium calcium cyclo-hexasilicate	4	-
Almandine	0.3	-

Figure 5a shows the diffraction pattern of the sample after acid attack and Fig.5b shows the diffraction pattern of the sample after environmental test.

Fig. 5. Phase Characterization of sampel (a) GT_A (b) GT_B after acid attack and XRD pattern of sampel (a) GT_A (b) GT_B after environmental test.

Phase characterization shows that the most dominant peaks both of GT_A and GT_B after acid attack lies between 27⁰-30⁰ (2θ) which consist of quartz, almandine, magnetite, hematite, rutile, sodium calcium-cyclo hexasilicate and anatase. Figure 5b shows that all

samples consist of quartz, anatase, rutile, hematite, with addition of sodium dialuminium-phylo decaoxodihydroxo allumotrisilicate and favalite. Similarly, its diffractogram shows that the most dominant peaks after environment test lies between 27° - 30° (2 θ).

Fig. 6. SEM images of (a) GT_A; (b) GT_B after acid attack; (c) GT after environment testing

Fig.6 clearly shows the SEM image of geopolymers surface displaying the presence of nano TiO₂ represented with white spots. The microstructure of samples, (i) before testing is shown in Fig. 6a and 6b; (ii) after acid attack is shown in Fig. 6c and 6d; (iii) and after environmental test is shown in Fig.6e. It is well known that nano TiO₂ with particle size below 500 nm, can strongly bonded in geopolymer although it was attacked by strong acid solution and harsh environmental [20]. In addition, the most commonly used oxide is the anatase form of TiO₂, which for practical reason of safety and easily for handling and encapsulated in an inorganic matrix [16-19]. The chemical composition of each sample before and after acid attack testing is presented in Table 3.

Table 4. Chemical composition of Nano-TiO₂ – Geopolymer before and after acid attack test based on EDS result

Element	Compound norm.	Comp. C (wt%)		
		Before	After Acid Attack Test	After Environment Test
Sodium	Na ₂ O	12.10	12.17	11.81
Magnesium	MgO	0.93	1.15	1.31
Aluminium	Al ₂ O ₃	21.78	22.31	24.50
Silicon	SiO ₂	53.40	52.15	52.13
Potassium	K ₂ O	0.38	0.38	0.81
Titanium	TiO ₂	4.90	4.70	3.36
Iron	FeO	6.52	6.58	6.26

4 Summary

Functional composite of nano TiO₂ - geopolymers have been successfully synthesized from a mixture of meta-clay with nano TiO₂ through alkali-activation method at 70 °C for 1 hour. The addition of nano TiO₂ improved the quality of geopolymer to resist acid attack and harsh environment. Based on this research, sample containing 2% nano TiO₂ shows excellent properties as antifouling bricks.

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