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Effect of Na_2SiO_3/NaOH on Mechanical Properties and Microstructure of Geopolymer Mortar Using Fly Ash and Rice Husk Ash as Precursor

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Abstract. Geopolymer concrete is an eco-friendly concrete that can reduce carbon emissions on the earth surface because it used industrial waste material such as fly ash, rice husk ash, bagasse ash, and palm oil fuel. Geopolymer is semi-crystalline amorphous materials which has irregular chemical bonds structure. The material is produced by geosynthesis of aluminosilicates and alkali-silicates which produce the Si-O-Al polymer structure. This research used the ratio of fly ash and rice husk ash as precursors e.g. 100:0, 75:25, 50:50, and 25:75. NaOH solutions of 14 M and Na_2SiO_3 solutions with the variation e.g. 2.5, 2.75, 3.00, and 3.25 were used as activators on mortar geopolymer mixture. The tests of fresh mortar were slump flow and setting time. The optimum compressive strength is 68.36 MPa for 28 days resulted from mixture using 100% fly ash and Na_2SiO_3 and NaOH with ratio 2.75. The largest value of slump flow test resulted from mixture using Na_2SiO_3 and NaOH with ratio 2.50 is 17.25 cm. Based on SEM test results, mortar geopolymer microstructure with mixture RHA 0% has less pores and denser CSH structure.

INTRODUCTION

Concrete is a most common material used in Geopolymer was first applied by Professor Joseph Davidovits in 1978. According to Davidovits, pyramid of Giza in Egypt are not limestone. From the result of the research, Davidovits found that chemical bond structure and the microstructure of pyramid stone are similar with geopolymer concrete in the laboratory.

Geopolymer term was obtained from the process of forming geopolymer material. Geopolymer could be described as a material which produced from geosynthetis process of polymeric alumina-silicate and alkali-silicate that result in a tetrahedral polymer silica and alumina bonds [1]. Geopolymer was produced from shyntesis of organic and inorganic material through polymerization. Geopolymer could be formed by using recycle material which had rich silica content. During synthesification process, a combination of silica and aluminium produced chemical bond structures that can be compared with nature stone bond.

Geopolymer is used as an effort to replace some or a whole parts of ordinary Portland cement in the process of making concrete to reduce the CO_2 emissions from the cement industry. In order to produce geopolymer, fly ash must be activated by alkali silicate solution to produce Si – O – Al polymeric bonds [2].

Geologycal origin material or by-product material such as fly ash, rice husk ash, palm oil fuel ash, metakaolin, and sugarcane bagasse ash had high silica content that can be used as a precursor in geopolymer concrete manufacture. The materials were not able to be a binder as well as ordinary Portland cement, so the activator solution like Na_2SiO_3 and NaOH is very required to react the precursor in polymerization process.

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Geopolymer material has an amorphous microstructure and resemble with high performance zeolite, such as very good fire and acid resistance and also can produce high compressive strength. Some earlier research showed that adding some minerals to the geopolymer can improve the performance [3]. The first geopolymer applications were building product developed in 1973 – 1976 [4]. Geopolymer applicated in many aspects such as fire resistance fiber composite, coating, mortar, concrete, ceramic, etc., depend on the chemical composition of the precursor and activator [5].

Fly ash is the finely devided that result from coal combustion and transported from the combustion chamber. The perfection of the combustion process could be affecting the performance of fly ash. Fly ash is a pozzolanic material and mostly consist of SiO_2, Al_2O_3, Fe_2O_3, and CaO, and also magnesium, potassium, sodium, titanium, and sulfur in fewer content. According to [7], geopolymer concrete using class C type fly ash produced higher compressive strength than class F type fly ash, either in room temperature or oven curing.

Rice husk ash is produced from the combustion of rice husk which is a by-product of rice milling. Before the combustion process, rice husk consisted of 75% – 80% organic substance and 15% – 20% inorganic substance. The burning is an efficient way to remove the organic substance while generating energy, leaving behind an inorganic ash consisting mostly silica [8]. Based on the study that conducted by [9], showed that the pozzolanic activity in rice husk ash depends on the amorphous silica content, specific surface area, and particle size distribution. According to [10], rice husk combustion at 500°C - 700°C produced optimal silica content. Rice husk ash has higher pozzolanic activity than silica fume [11]. The higher pozzolanic activity in rice husk ash can lead to enhanced hydration reactions, increased later-age strength, reduced porosity, and improved durability [12, 13]. There various factor affected geopolymer mortar characteristic are NaOH molar concentrations, sodium silicate and sodium hidroxyde ratio, activator and precursor ratio, and fine aggregate and precursor ratio.

Alkaline activator is required in polymerization. Alkali solution used to the activating the precursor by dissoluting their into $Si(OH)_4$ and $Al(OH)_4^-$ monomer. The most common used alkaline activator in geopolymerization are a combination of sodium silicate and sodium hydroxide or a combination of sodium silicate and sodium hydroxide. Silicate solution such sodium silicate generate faster reaction than hydroxide solution. Sodium hydroxide (NaOH) is used to reacting the aluminium and silicate by adding Na^+ ion. Na^+ ion only used during the polymerization.

Based on the study that conducted by [14, 15] concerning the effect of rice husk ash substitution on fly ash based geopolymer concrete, produced a product with 28 days compressive strength as high as 59 MPa. The result showed that the use of rice husk ash in large amount can cause the decrease of compressive strength.

MATERIALS AND METHODS

In this research, the ratio of fly ash and rice husk ash are 100:0, 75:25, 50:50, and 25:75 and Na_2SiO_3 to NaOH ratio are 2.5, 2.75, 3.0, and 3.25. Sodium hydroxide concentration used was 14 M. Activator to precursor ratio was 0.45. The superplasticizer's dosage used in this study is 3% of precursor content. The test of fresh mortar were slump flow test and setting time. The geopolymer mortar was placed in a 50 mm x 50 mm x 50 mm cube mold and cured in an oven at 90°C for 24 hours. Their compressive strength tested after 3, 7, 14, and 28 days.

Materials used in this research are fly ash, rice husk ash, sodium silicate, sodium hydroxide, water, fine aggregate, and superplasticizer. Fly ash that used in this research was Class F type fly ash from PT Bukit Asam. This type of fly ash is produced from combustion of coal bitument. The result of fly ash chemical composition is shown in Table 1 and fly ash SEM microstructure is shown in Fig. 1. The test of fly ash chemical composition is done at PT Semen Baturaja Chemistry Laboratory and fly ash SEM test is done at Geologic Survey Center Laboratory, Bandung.

TABLE 1. Chemical composition of fly ash

Composition	Weight (%)
Silicon Dioxide (SiO_2)	51,40
Aluminum Oxide (Al_2O_3)	33,20
Iron (III) Oxide (Fe_2O_3)	5,20
Calsium Oxide (CaO)	6,63
Magnesium Oxide (MgO)	4,09
Sulfur Trioxide (SO_3)	0.96
LOI	-

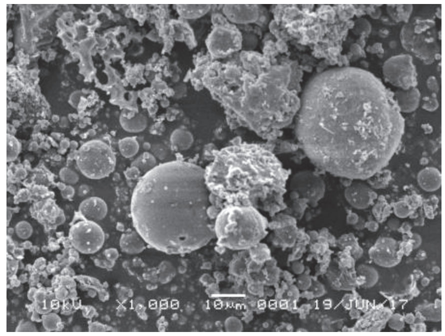


FIGURE 1. SEM microstructure of fly ash

Rice husk ash that used in this research was from PT Buyung Putra Sembada. Rice husk ash is produced from rice husk combustion. The result of RHA chemical composition is shown in Table 2 and RHA SEM microstructure is shown in Fig. 2. The test of RHA chemical composition is done at PT Semen Baturaja Chemistry Laboratory and RHA SEM test is done at Pusat Survey Geologi Laboratory, Bandung. Sodium silicate (Na_2SiO_3) or *waterglass* is used to accelerate the polymerization. The mass of sodium hydroxide pallets in a solution varied according to molar strength. The water that used as a solvent must be clean, no oil, and no impurities which can damage the specimen. Fine aggregate used natural sand from Tanjung Raja. The particle sizes that used in this research are 0,125 – 4 mm.

TABLE 2. Chemical composition of RHA

Composition	Weight (%)
Silicon Dioxide (SiO_2)	93,26
Aluminum Oxide (Al_2O_3)	0,44
Iron (III) Oxide (Fe_2O_3)	0,16
Calsium Oxide (CaO)	4,20
Magnesium Oxide (MgO)	0,48
Sulfur Trioxide (SO_3)	0.70
LOI	-

TABLE 3. Mix proportion of 6 pieces geopolymer mortar

Mix	Fly ash (gram)	RHA (gram)	Fine Agg. (gram)	Na_2SiO_3 (gram)	NaOH (gram)	SP (gram)
MG1-2.5	500	0	1,000	160.6	64.4	15
MG1-2.75	500	0	1,000	164.9	60.1	15
MG1-3.0	500	0	1,000	168.7	56.3	15
MG1-3.25	500	0	1,000	172.1	52.9	15
MG2-2.5	375	125	1,000	160.6	64.4	15
MG2-2.75	375	125	1,000	164.9	60.1	15
MG2-3.0	375	125	1,000	168.7	56.3	15
MG2-3.25	375	125	1,000	172.1	52.9	15
MG3-2.5	250	250	1,000	160.6	64.4	15
MG3-2.75	250	250	1,000	164.9	60.1	15
MG3-3.0	250	250	1,000	168.7	56.3	15
MG3-3.25	250	250	1,000	172.1	52.9	15
MG4-2.5	125	375	1,000	160.6	64.4	15
MG4-2.75	125	375	1,000	164.9	60.1	15
MG4-3.0	125	375	1,000	168.7	56.3	15
MG4-3.25	125	375	1,000	172.1	52.9	15

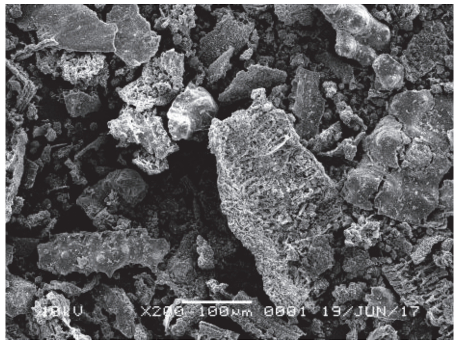


FIGURE 2. SEM microstructure of RHA

RESULT AND DISCUSSION

The Result of Fresh Mortar Test

The test of fresh mortar in this research are slump flow test and setting time. Fresh mortar test can only done on MG1 (FA 100: ASP 0) and MG2 (FA 75: ASP 25), because of mixture MG3 (FA 50: ASP 50) and MG4 (FA 25: ASP 75) are not able to flow.

Slump flow

The result of slump flow test are shown in Fig. 3 and Fig. 4. Slump flow value is obtained from the average measurement of the fresh mortar flow in four perpendicular directions. Figure 3 show that the maximum slump diameter is 17.25 cm in Na_2SiO_3 and NaOH ratio 2.5 and the minimum slump diameter is 10.63 cm in Na_2SiO_3 and NaOH ratio 3.25. The variation of Na_2SiO_3 and NaOH ratio affect slump flow diameter, the lower usage of Na_2SiO_3 and NaOH ratio caused the bigger slump flow diameter. Fig. 3 show that the decreasement of slump flow along with the increasement of rice husk ash content. This is due to the rice husk ash high water absorption. The maximum slump diameter is 17.25 cm in the mixture FA 100: RHA 0 and the minimum slump diameter is 10.63 cm in the mixture FA 75: RHA 25.

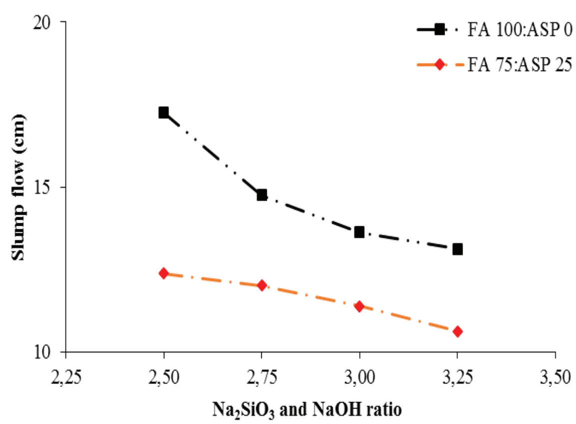


FIGURE 3. The effect of Na_2SiO_3 and NaOH ratio on slump flow test result

Setting time

Fig. 5 and Fig. 6 show that the variation of Na_2SiO_3 and NaOH ratio are not gave significant affect in setting time, the lower usage of Na_2SiO_3 and NaOH ratio caused the faster setting time. The fastest initial time happened in MG1-2.50 (FA 100: RHA 0) with 155 minutes and the final time 245 minutes. Meanwhile, the longest initial time happened in MG2-3.25 (FA 75: RHA 25) with 200 minutes and 290 minutes final time.

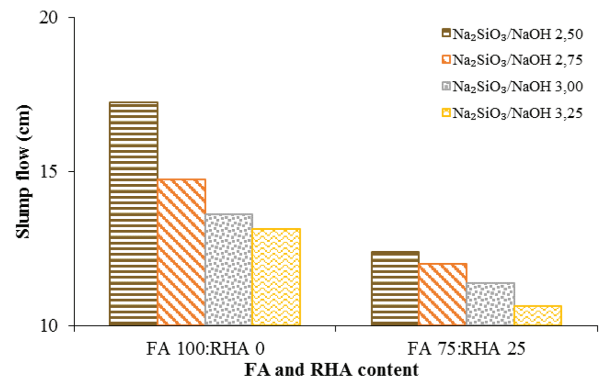


FIGURE 4. The effect of fly ash and RHA content on slump flow test result

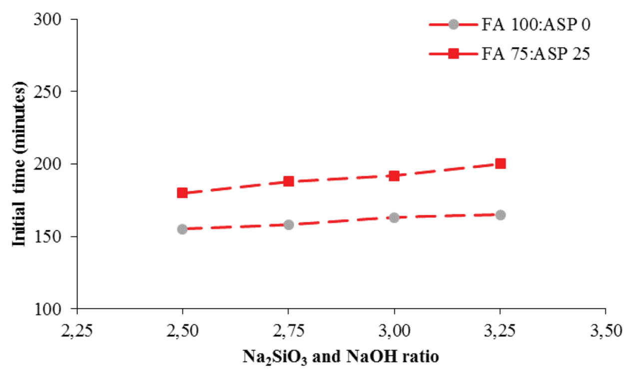


FIGURE 5. The effect of Na_2SiO_3 and NaOH ratio on initial setting time test result

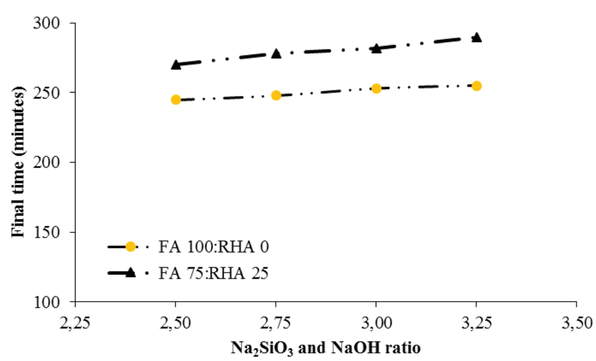


FIGURE 6. The effect of Na_2SiO_3 and NaOH ratio on final setting time test result

The Result of Compressive Strength

The result of compressive strength for age 3, 7, 14, and 28 days shown in Fig. 7 for FA 100: RHA 0, Fig. 8 for FA 75: RHA 25, Fig. 9 for FA 50: RHA 50, Fig. 10 for FA 25: RHA 75. The correlation of 28 days compressive strength and Na_2SiO_3 and NaOH ratio shown in Fig.11, and then Fig. 12 for the correlation of 28 days compressive strength and FA and RHA content. The result of FA 100: RHA 0 with 3.0 Na_2SiO_3 and NaOH ratio compressive strength showed a unsignificant increase at age 3, 7, 14, and 28 days, and also happened in Na_2SiO_3 and NaOH ratio 2.75 at age 7 days until 14 days. The result of 2.5, 2.75, and 3.0 showed a low increasement. 3.25 Na_2SiO_3 and NaOH ratio compressive strength showed significant increase from age 3, 7, 14, and 28 days. Based on Figure 8, 3 days compressive strength result of geopolymer mortar with 2.5 and 3.0 Na_2SiO_3 and NaOH ratio showed similar result. The result of mixture with 2.5 and 3.25 Na_2SiO_3 and NaOH ratio compressive strength showed any significant increase at age 3, 7, 14, and 28 days.

Fig. 9 showed that the increasement of compressive strength result for all Na_2SiO_3 and NaOH ratio variation were insignificant. The compressive strength result of geopolymer mortar with 2.5 and 3.25 Na_2SiO_3 and NaOH ratio showed similar value at age 14 and 28 days.

Based on Fig. 10, the increasement of mixture with 2.5 and 3.25 Na_2SiO_3 and NaOH ratio are only significant at age 3 days until 7 days. The increasement of Na_2SiO_3 and NaOH ratio 3.0 compressive strength began significant at age 14 days. Whie with 2.75 Na_2SiO_3 and NaOH ratio showed the compressive strength were only significant at age 3 days until 14 days.

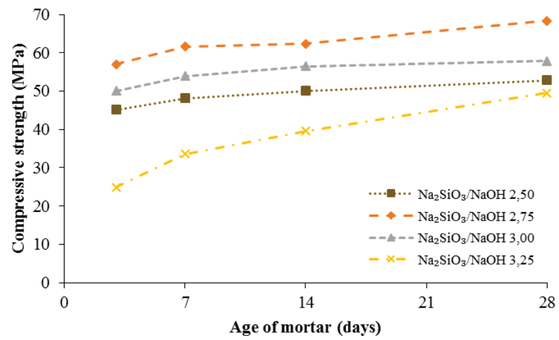


FIGURE 7. The effect of age of mortar on mixture FA 100: RHA 0 compressive strength

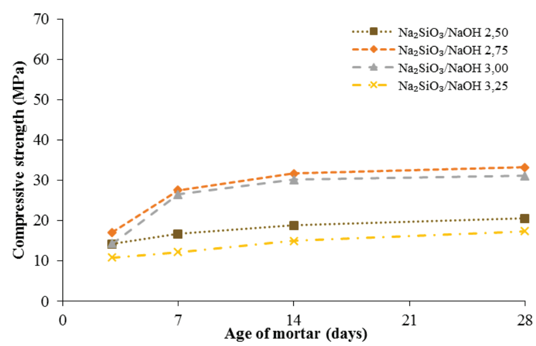


FIGURE 8. The effect of age of mortar on mixture FA 75: RHA 25 compressive strength

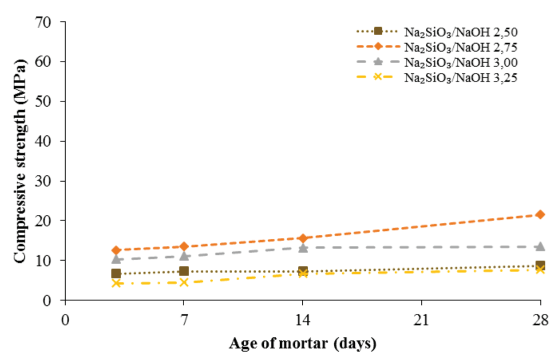


FIGURE 9. The effect of age of mortar on mixture FA 50: RHA 50 compressive strength

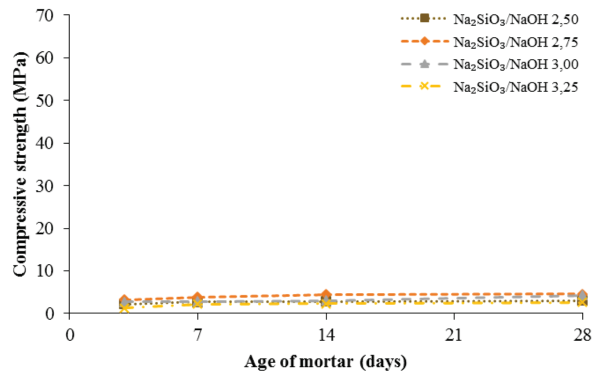


FIGURE 10. The effect of age of mortar on mixture FA 25: RHA 75 compressive strength

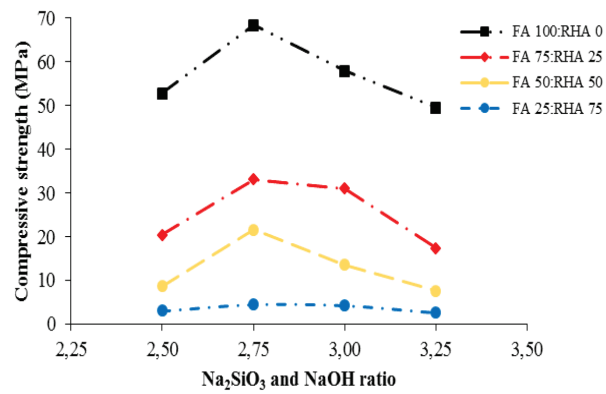


FIGURE 11. The effect of Na_2SiO_3 and NaOH ratio on compressive strength result of 28 days

Fig. 11 showed that the optimum compressive strength is 68.360 MPa in 2.75 Na_2SiO_3 and NaOH ratio and the minimum is 2.662 MPa in 3.25 Na_2SiO_3 and NaOH ratio. The optimum value is in the mixture with 2.75 Na_2SiO_3 and NaOH ratio for all FA and RHA content and the minimum value is in the mixture with 3.25 Na_2SiO_3 and NaOH ratio for all FA and RHA content.

Fig. 12 showed that the decreasement of compressive strength along with the increasement of rice husk ash content. The maximum compressive strength is 68.360 MPa in FA 100: RHA 0 and the minimum is 2.662 MPa in FA 25: RHA 75.

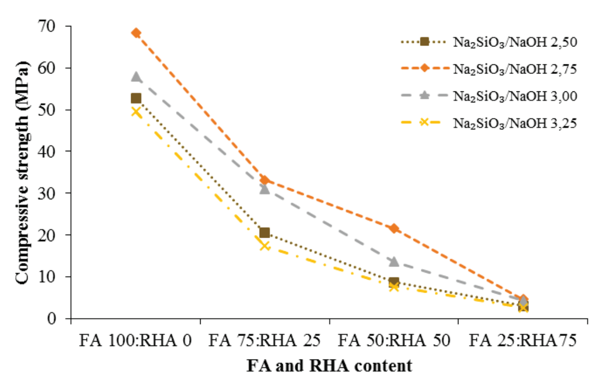
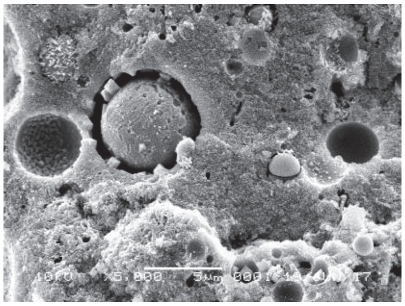


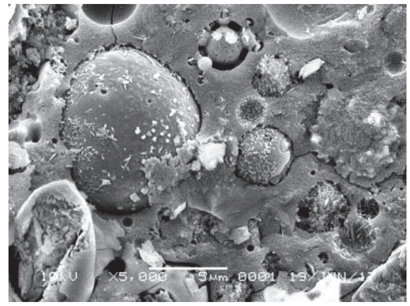
FIGURE 12. The effect of FA and RHA content on compressive strength result of 28 days

The Results of Microstructure Test

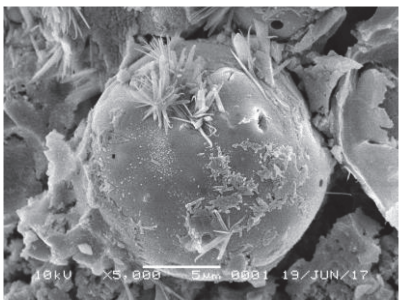
Microstructure geopolymer mortar data test was taken from highest compressive strength sample result at the age of 28 days. The result of SEM test can be seen on Fig. 13 to 16.



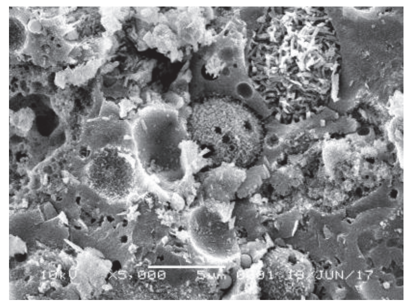
(a) Na_2SiO_3/NaOH 2.50



(b) Na_2SiO_3/NaOH 2.75

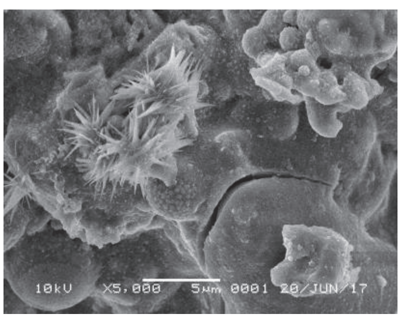


(c) Na_2SiO_3/NaOH 3.00

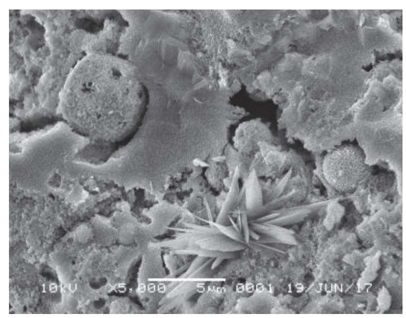


(d) Na_2SiO_3/NaOH 3.25

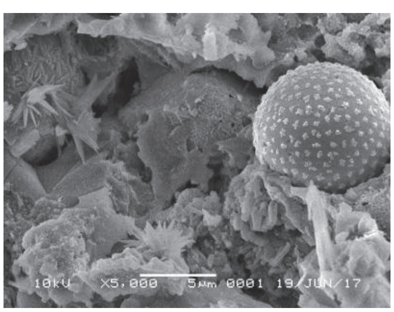
FIGURE 13. The result of SEM FA 100: RHA 0



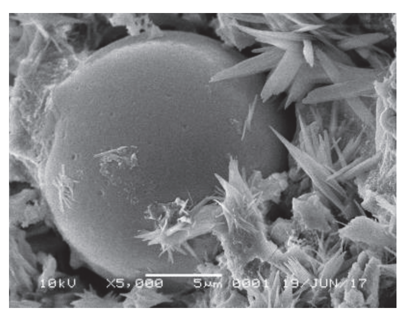
(a) Na2SiO3/NaOH 2.50



(b) Na2SiO3/NaOH 2.75



(c) Na_2SiO_3/NaOH 3.00



(d) Na_2SiO_3/NaOH 3.25

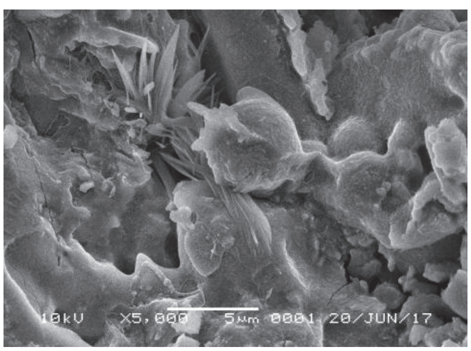
FIGURE 14. The result of SEM FA 75: RHA 25

Based on the Fig. 13, it shows that there are pores formation with the size of 5 μm and below. CSH reaction that is produced by the mixture of FA 100: RHA 0 with Na_2SiO_3 and NaOH ratio 2.75. Fig. 13(b), it shows, sems more solid than the other mixed, this reaction was produced because of hydration residue between fly ash and Na_2SiO_3 and NaOH ratio, hydration residue is reacting with active silica which is contained on fly ash so that CSH reaction from seconder result is filling the pore. Etringite which produced by the age of 28 days gives bad impact on mortar because a lot of etringite content will make the compressive strength low. Fig. 13(c) and 13(d) is the mixture FA 100 : RHA 0 with Na_2SiO_3 and NaOH ratio 3.00 and FA 100:RHA 0 with Na_2SiO_3 and NaOH ratio 3.25, shows more pores formation, so it makes the compressive strength of mortar geopolymer decrease.

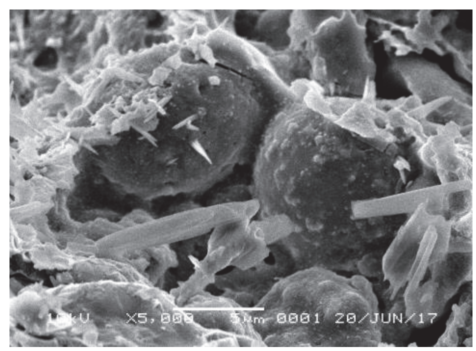
Based on the Fig. 14, produced ettringite are more compared to Fig. 13. Ettringite that are produced from FA 75: RHA 25 with Na_2SiO_3 and NaOH ratio 3.25 had a lower compressive strength than a mortar in FA 75: RHA 25 mixture. There is micro crack at the Fig. 14(a) it is caused by a chemical reaction that found on mortar mixture, chemical reaction causing hydration that generate crack on the mortar pasta. Ramficated pores from FA 75: RHA 25 mixture are more compared to FA 100: RHA 0 however the size of pores are no more than 5 μm, it happen because weakness of bond on geopolymer mortar structure.

CSH reaction on the result of SEM test in FA 50: RHA 50 mixtures are rarely found, CSH reaction only available in FA 50: RHA 50 with Na_2SiO_3 and NaOH ratio 2.75 mixture on Fig. 15(b). Pores that are produced in the 50% RHA mixture has a larger pore size shows a weak connection on a geopolimer mortar, so it causing a decrease in compressive strength. Ettringite produced more than other mixture and has a varying size. Pores on fig. 15(b) have a larger pore size than the pores on other FA 50: RHA 50, however the mixture has quite a lot CSH reaction so the bond in the mortar are stronger than the bond in other mortar.

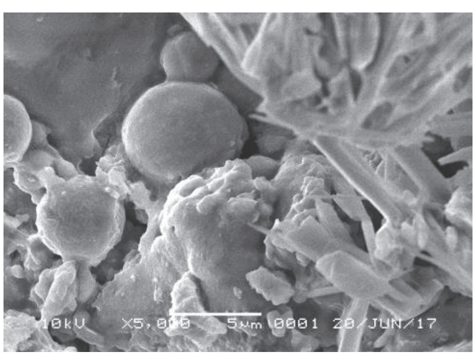
Figure 16 shows that produced pores from FA 25: RHA 75 mixture are more than the other mixtures and the pores are big sized and no more than 5 um CSH only found in FA 25: RHA 75 at figure 16(b). Ettringite in RHA 75% mixture are larger than in any other mixture. It caused an expansion on concrete volume that increase an internal tension that can generate the microcrack. Fly ash that reacts well on the geopolimer mortar mixture can be seen at picture 16(b), it can be seen from linked fly ash with geopolimer mortar pasta without detached from the bounding compound.



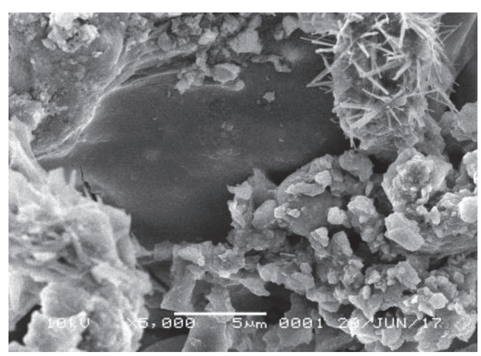
(a) Na_2SiO_3/NaOH 2.50



(b) Na_2SiO_3/NaOH 2.75

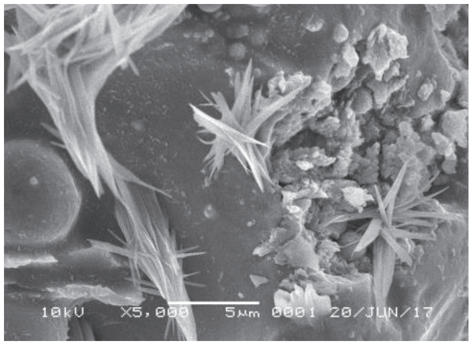


(c) Na_2SiO_3/NaOH 3.00

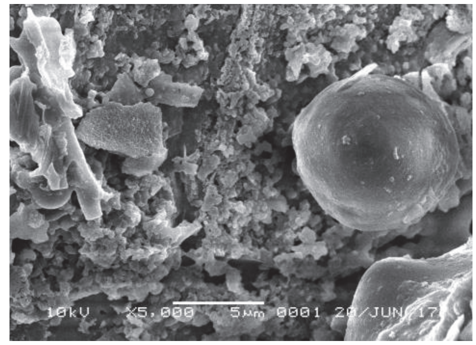


(d) Na_2SiO_3/NaOH 3.25

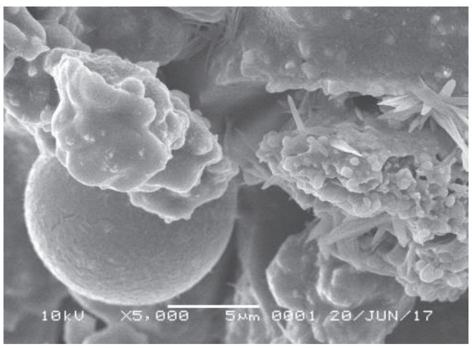
FIGURE 15. The result of SEM FA 50: RHA 50



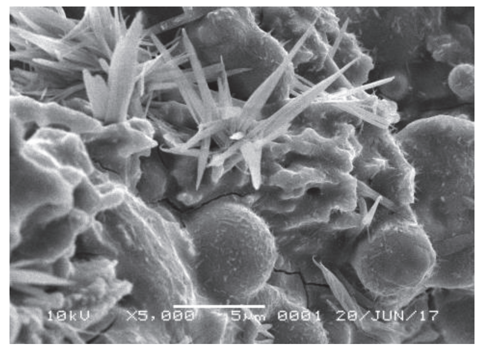
(a) Na_2SiO_3/NaOH 2.50



(b) Na_2SiO_3/NaOH 2.75



(c) Na_2SiO_3/NaOH 3.00



(d) Na_2SiO_3/NaOH 3.25

FIGURE 16. The result of SEM FA 25: RHA 75

CONCLUSIONS

The conclusions of the research that has been done are:

1. The optimum composition geopolymer mortar mixture is 100% fly ash and 0% RHA as precursor. This gave the maximum compressive strength, which is 68.36 MPa, has a less pore and the densest microstructure.
2. Effect of Na_2SiO_3 and NaOH ratio on compressive strength at 28 days, and geopolymer mortar microstructure are:
   - The results of slump flow test on fresh concrete show the largest diameter at mixture MG1-2.5 which is 17.25 cm and the smallest diameter at mixture MG2-3.25 with RHA 25% which is 10.63 cm.
   - The result of setting time test geopolymer mortar shows the fastest on FA 100: RHA 0 with Na_2SiO_3 and NaOH ratio 2.50 mixture has a initial time and final time is 155 minutes and 245 minutes. While at FA 75: RHA 25 with Na_2SiO_3 and NaOH ratio 3.25 has a 200 minutes and 290 minutes for initial time and final time. The research shows the decrease Na_2SiO_3 and NaOH ratio along with the increase of setting time.
   - The results of compressive strength test at 28 days geopolymer mortar with Na_2SiO_3 and NaOH ratio 2.75 gave the optimum compressive strength is 68.36 MPa, after using Na_2SiO_3 and NaOH with ratio below 2.75 it makes the compressive strength of mortar decrease.
3. The effect of using fly ash and rice husk ash as precursor on workability, compressive strength at 28 days, and geopolymer mortar microstructure are:
   - The result of slump flow test on fresh geopolymer mortar shows the decrease in the flow diameter along with the increasing of RHA content.
   - The result of setting time geopolymer mortar with FA 100 : RHA 0 mixture has a initial time and final time is 155 minutes and 245 minutes , however with FA 75:RHA 25 needs 200 minutes and 290 minutes for initial time and final time. The research shows the increase using RHA comparable with the increase of setting time.

- The result of compressive strength at 28 days with using FA 100: RHA 0 show the optimum compressive strength is 68.36 MPa.
- Geopolymer mortar microstructure with using FA 100: RHA 0 show has less pores and denser CSH structure.

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