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INVESTIGATION OF SETTING TIME AND FLOWABILITY OF GEOPOLYMER MORTAR USING LOCAL INDUSTRY AND AGRICULTURE WASTE AS PRECURSOR IN INDONESIA

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ABSTRACT: Geopolymer is a renewable construction material that reduces dependence on ordinary portland cement (OPC), where OPC manufacturing impacts carbon dioxide (CO_2) emissions. The main aspect of geopolymers being studied is the precursor of pozzolanic material, used as a cement substitute because it contains aluminosilicate (Si-Al). Polymerization occurs between the precursors, reacted by alkaline activator solution (AAS). Sodium hydroxide (NaOH) and sodium silicate (Na_2SiO_3) were used as AAS. In this study, local precursors from industrial waste and biomass were utilized. Fly ash was employed as a reference in the precursor by 5% - 10% substitution of glass powder, rice husk ash, bagasse ash, and palm shell ash. Moreover, 2% superplasticizer and 5% extra water were used to increase the flowability of fresh geopolymer. Tests were carried out on the setting time of paste, flow table, and compressive strength of geopolymer mortar. The tests were on the initial setting time of 25-75 minutes and the final setting time of 40-115 minutes. The setting time results revealed that the time of each substitution accelerated geopolymerization due to the substitution of precursors containing higher CaO and SiO_2. Setting time and flowability/workability had a linear regression correlation (R^2) of 0.95, with the flow table ranging from 180-250 mm. The compressive strength ranged from 25.88 – 36.36 MPa through a curing temperature of 70^{o}C for 24 hours, followed by curing at ambient temperature for up to 28 days.

Keywords: Geopolymer, Precursor, Setting time, Flowability, Compressive strength

1. INTRODUCTION

Geopolymer is an innovation of concrete development, in which geopolymer concrete is designed without hydraulic cement as a binder. The binder of geopolymer uses powdered material as a precursor containing activated aluminosilicate with an alkali activator; thus, it becomes a geopolymer synthesis bond [1-3]. The geopolymer aims to reduce the impact of carbon dioxide (CO_2) emissions by up to 80%, as well as dependence on the use of conventional cement [4]. Ordinary portland cement (OPC) is the dominant hydraulic binder in the material construction industry to date [5,6]. Chatam House [7] reported that there are 4 billion tons of global cement production annually, producing an estimated 8% of global CO_2 emissions. The geopolymer material is necessary used to be a patch repair material of deteriorated reinforced concrete structures protected by cathodic protection due to its lower electrical resistivity than ordinary normal concrete [8,9,10]

Researchers have looked for alternative precursors from various sources such as waste from mining, industrial, agricultural, and others. In Indonesia, the potential of pozzolanic materials as geopolymer precursors is obtained through industrial and biomass waste. Coal fly ash is the potential primary precursor existing in Indonesia. It is due to the dependence of electricity production in Indonesia, which is still dependent on coal energy sources [11]. In 2020, the utilization of fly ash in Indonesia was only 0.9% of the total production of 7.8 million tons [12]. The latest regulations for the issuance of fly ash from hazardous and poisonous waste are expected to increase fly ash utilization in Indonesia [13]. Another industrial waste with the potential to be a substitute for precursors is glass powder as it contains high silica [14]. Additionally, as one of the world's agricultural countries, Indonesia has a lot of biomass waste of rice husks, palm shells, and bagasse, with a total of 15 million tons of waste annually [15].

The effect of the geopolymer can be determined by the constituent material and curing. The study of the chemical content of precursors in geopolymers affects the quality of geopolymers. The ratio of silicon dioxide (SiO_2)/aluminum oxide (Al_2O_3) and calcium oxide (CaO) will affect the geopolymer setting time. ratio SiO_2/Al_2O_3 accelerates initial and final setting time [16,17]. Furthermore, the alkaline activator solution (AAS) influences flowability, setting time, and strength. The dominant ASS used in geopolymer research is sodium hydroxide (NaOH) and sodium silicate (Na_2SiO_3). Malkawi et al. [18] have tested the effect of concentration of NaOH (8, 10, and 12 molarity), with variations in the ratio of Na_2SiO_3/NaOH from

1 to 2.5. Increasing the NaOH concentration and Na_2SiO_3/NaOH ratio decreased the flow diameter but was effective for the geopolymer strength. To achieve optimal strength, the geopolymerization formation process requires a temperature higher than room temperature. Zhang et al. [19] stated that curing geopolymer should be carried out at a temperature of 60-100 ºC for 24-28 hours. Panigrahi et al. [20] have studied the effect of curing temperature at 50, 60, 70, and 80 ºC and discovered that curing at 70 ºC for 24 hours had provided the optimum geopolymerization to achieve higher mechanical properties.

This experiment is intended to explore the feasibility of the geopolymer made with locally available precursors in Indonesia. In addition, superplasticizers and extra water were used to obtain high workability. This research aims to provide information on the setting time of paste, the flowability of fresh mortar, and the compressive strength of hardened mortar. The information would be useful and provide the groundwork for future investigation of waste precursors for geopolymers.

2. RESEARCH SIGNIFICANCE

Geopolymer is a novel construction material for future. Unfortunately, there is no official standard in the field of geopolymer research. Therefore, previous studies on geopolymer can be used as a reference regarding material selection and curing. The precursor variations were based primarily on fly ash and secondarily on the substitution of glass powder, rice hush ash, palm shell ash, and bagasse ash. Use of high alkali activator, superplasticizer, and extra water were kept constant. This investigation unveils optimal results of compressive strength and linear correlation between setting time and flowability. Hence, it could be a reference for further research on self-compacting/consolidating geopolymer.

3. METHOD

2.1 Material Preparation

The precursors used were local waste materials in Indonesia. These materials were obtained from industrial waste and biomass, comprising fly ash (FA), glass powder (GP), rice husk ash (RHA), palm shell ash (PSA), and bagasse ash (BA). Fly ash was obtained from the waste of PT. Tjiwi Kimia Indonesia, while the glass powder was from the processing of glass into powder. In addition, agricultural waste/biomass through the combustion process at a temperature of 600-900 ^{O}C was held for 2 hours, 600 ^{O}C for bagasse, 800 ^{O}C for rice husk, and 900 ^{O}C for palm shell. All precursors passed through a sieve mesh 200, and the physical and chemical properties of the different precursors are displayed in Table 1. In addition, Fig. 1 presents the x-ray diffraction (XRD) pattern of precursors, where the peak is 20 - 30 º2θ of amorphous quartz (Q).

The ratio of NaOH/Na_2SiO_3 was 2.5, and the concentration of NaOH was 12 molarity. It has been studied that NaOH/Na_2SiO_3 was 2.5, and 12M NaOH was the most optimal mixture of AAS to produce the most optimal compressive strength [20]. Moreover, 12M NaOH was produced by mixing 480 grams of NaOH pellets dissolved with aqua dest/distilled water to reach one liter of solution. NaOH was prepared at least one day before the mixture. High NaOH/Na2SiO3 caused the viscosity of the liquid to become stiff, needing the use of superplasticizer (SP) and extra water to improve workability. The fine aggregate used was local sand sourced from the Progo River, Yogyakarta. Locally available river sand of 2.4 specific gravity, 2.27% fineness modulus, and 3,31% moisture content were applied as fine aggregate

Table 1 Chemical and physical content of precursors

Content	FA	GP	RHA	PSA	BA
SiO_2 (%)	32	42.6	88.2	11	47.3
Al_2O_3 (%)	13	-	-	-	-
Fe_2O_3 (%)	27	1.2	0.9	19.1	14.7
CaO (%)	19.5	8.34	1.3	38.3	18.6
MnO (%)	0.28	0.08	0.31	0.27	0.54
K_2O (%)	2.02	5,16	4.25	5.65	8.66
Particle size (µm)	≤74	≤74	≤74	≤74	≤74
Spefic gravity	2.53	2.34	2.14	2.0	1.94
Color	gray	white	black	black	black

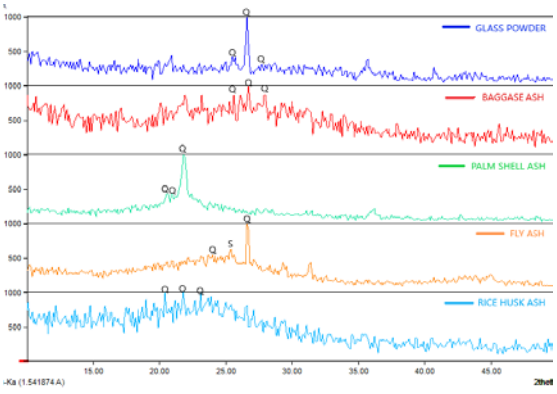

Fig. 1 XRD pattern of precursors

2.2 Mix Proportion

The primary precursor in this experiment was fly ash (containing aluminosilicate). Rice husk ash, palm shell ash, and powder glass were fixed at 10%, while bagasse ash was fixed at 5% as fly ash replacement. In addition, superplasticizer was 2%

and extra water was 5% by weight's precursor. The fine aggregate content was 60% of the volume mortar. The details of mixture proportions are depicted in Table 2

Table 2 Mixture proportions (kg/m^3)

Mixture Variation	Precursor		ASS		Fine aggregate	SP	Extra water
	Primary	Subs	Na_2SiO_3	NaOH			
FA100% (F)	750	0	214.29	85.71	1200	15	37.5
FA95%+GP10% (FG)	675	75	214.29	85.71	1200	15	37.5
FA90%+PSA10% (FP)	675	75	214.29	85.71	1200	15	37.5
FA90%+RHA10% (FR)	675	75	214.29	85.71	1200	15	37.5
FA90%+BA5% (FB)	712.5	37.5	214.29	85.71	1200	15	37.5

2.3 Mixing, Casting, and Curing

The mortar mixing process was carried out in several steps for 6 minutes using a planetary mixer. Initially, precursor and ASS were mixed for 2 minutes, then SP and extra water were added for a minute. Finally, the fine aggregate was added for 3 minutes.The fresh mortar mixture was then assessed for flowability. After performing the flowability test, the fresh mortar was placed in 5 cm x 5 cm x 5 cm of cube molds according to ASTM C109 [21]. After casting, each variation of the test samples was removed from the molds following the final setting time in Fig. 2. After that, the samples were cured in an oven at 70 ^{O}C for 24 hours. The samples were then wrapped in plastic and cured at ambient temperature for 28 days.

2.4 Testing of Paste and Mortar Geopolymer

2.4.1 Setting time of paste

The setting time test aimed to determine initial and final setting time as a determinant of the mold's release from the specimens according to ASTM C191 using Vicat at room temperature [22]. The variation of precursors in the setting time test is the same as that in Table 2. However, the constituent materials were only paste (precursors and ASS). Each variation consisted of 300 grams of precursor and 120 grams of ASS (ratio of NaOH/ Na_2SiO_3 was 2.5 and 12M of NaOH).

2.4.2 Flowability of fresh mortar

The flowability test aimed to determine the percentage distribution of the fresh mortar used to achieve optimal conditions, as shown in Table 3, using the flow table test according to ASTM C1437-20 [23].

Table 3 Workability criteria [24]

No	Flow Diamter (mm)	Workability
1	>250	Very High
2	180-250	High
3	150-180	Moderate
4	120-150	Stiff
5	<120	Very stiff

2.4.3 Compressive strength of hardened mortar

A compressive strength test was performed using the universal testing machine (UTM). Each variation mixture was tested after a curing period of mortar at the age of 28 days.

4. RESULTS AND DISCUSSION

4.1 Setting Time

The initial and final setting time was known at penetration 25 mm and 0 mm by the Vicat apparatus. The final setting is the condition of fresh mixture that has hardened. Fig. 2 demonstrates the setting time results; the initial setting ranges from 25 – 75 minutes, while the final setting ranges from 40 – 115 minutes. The influence of the precursor's physical and chemical properties on the setting time could be considerable [25]. FA100% was selected as the major precursor in this study, classified as high calcium (CaO>10%) based on BS EN 450-1:2012 [26]. FA100% with CaO 19.5% had a final time of 115 minutes. These results are consistent with the study of setting time by Malkawi et al. [18], using fly ash (CaO 20.9%) and ASS (NaOH/ Na_2SiO_3 was 2.5 and 12M of NaOH), with the final setting time of 115 minutes. In addition, Chen et al. [27] stated that the effect of higher SiO_2/Al_2O_3 and CaO could accelerate the setting time. It has been proven by each substitution precursor that has accelerated setting time in this investigation.

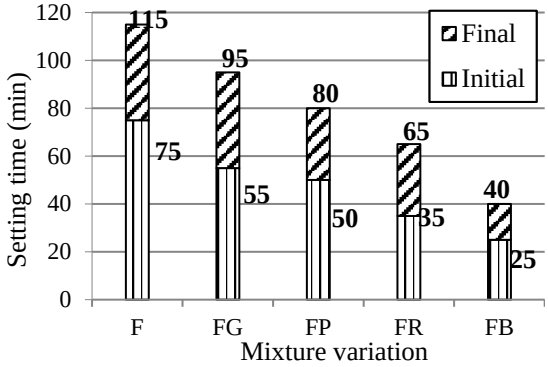

Fig. 2 Setting time of geopolymer paste

It was discovered that 88% of SiO_2 of RHA substitution influenced geopolymerization acceleration, whereas PSA and GP substitutions had inversely proportional SiO_2 and CaO percentages, which were able to accelerate based on remarkably similar initial and final results. The fastest setting time was found in the BA substitution because both SiO_2 and CaO were relatively high.

4.2 Flowability

Flow table test was used to measure flowability by flow diameter as an indicator of workability. Fig. 3 exhibits the effect of SP and extra water on diameter flow to reach high workability according to Table 3, and the flow diameter ranging 180 – 250 mm. Each substitution of GP and agricultural ash (RHA, PSA, and BA) experienced a decrease in flow diameter. Agriculture ash had the lowest flow diameter due to the effect of water absorption. Saleh et al. [28] have tested RHA, PSA, and BA as cementitious materials and reported using more replacement agricultural waste that reduced flow diameter.

The aligned specific gravity for each substitution was a parameter that could only be considered a reference regarding flow reduction in the diameter of this study. Moreover, 1.94 – 2.53 ranged in the specific gravity's precursors. However, further research is required on the flowability of geopolymer effect indicators of the precursors' physical and chemical characteristics.

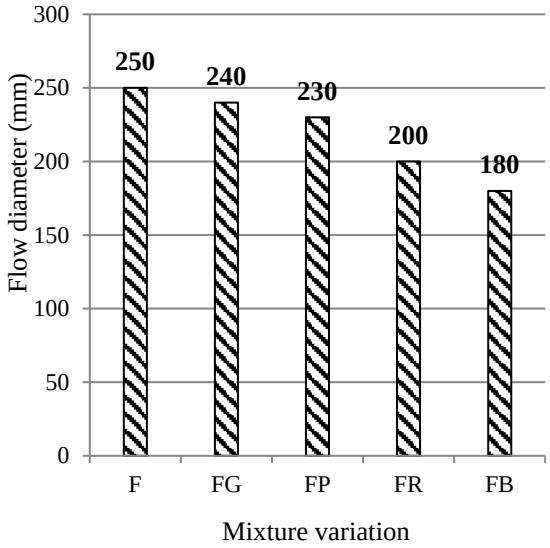

Fig. 3 Flowability of fresh geopolymer mortar

4.3 Correlation of Setting Time and Flowability

The setting time of geopolymer is related to its flowability/workability in geopolymer experiments. Longer setting time is associated with higher flow/slump in the geopolymer case [29-31]. Fig. 4 displays the correlation graph between setting time and flowability, revealing a regression equation (R^2) of 0.95

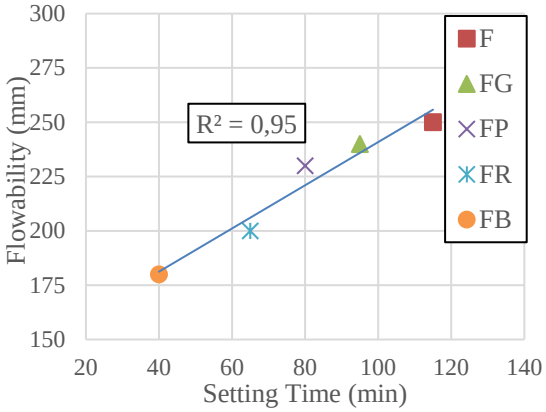

Fig. 4 The correlation of setting time-flowability

3.2 Compressive Strength

Fig. 5 presents the compressive strength of geopolymer mortar based on industrial and agricultural waste, ranging from 25.88 – 36.36 MPa. The primary reference mixture variation was 31.35 MPa of FA100%. Based on Fig. 4, two results increase and decrease compressive strength. The highest compressive strength in this investigation was 36.36 MPa by FA90%+RHA10%. The known parameter of increasing the compressive strength was by 88% of SiO_2. FA90%+PSA10% was the lowest compressive strength of 25.88 MPa due to 11% of SiO_2 of the PSA. Further research is required to achieve optimal compressive strength's performance of replacement of GP and PSA in a more specific range of 1% - 9%.

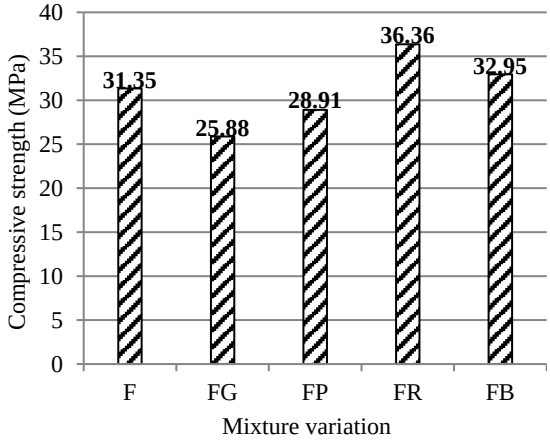

Fig. 5 Compressive strength of geopolymer mortar

5. CONCLUSIONS

Investigation on the utilization of industrial (fly ash and glass powder) and agricultural waste (rice husk, palm shell, and bagasse) has been carried out. Processing of agriculture waste into ash required 2 hours of combustion at 600 – 900 °C. This

experiment emphasizes fresh and hardened geopolymer. The use of 12M NaOH and 2.5 of $NaOH/Na_2SiO_3$ affected the stiffness of the fresh geopolymer. It is necessary to add a superplasticizer and extra water to increase flowability, although the impact of water in geopolymer will decrease the compressive strength. The following summarizes the results of five mixture variations in the study of setting time, flowability, and compressive strength in this paste and mortar geopolymer experiment.

1) Higher SiO_2/Al_2O_3 and CaO of substitution precursors accelerated the geopolymerization of the paste based on the results of the initial and final setting time.
2) Using 2% superplasticizer and 5% extra water by weight of the precursor increased the flowability of fresh mortar in the flow diameter range of 180-250 mm. It was classified as high workability.
3) Longer setting time was related to higher flow diameter. The R^2 of the correlation between setting time and flowability was 0.95.
4) The compressive strength of hardened mortar geopolymer ranged from 25.88 – 36.36 MPa, whereas the optimum was influenced by 10% rice husk ash due to its high SiO_2 content.

The results of this investigation could be a reference for further research on self-compacting/consolidating geopolymer concrete due to high workability.

6. ACKNOWLEDGMENTS

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