STUDY OF POLY (ETHYLENE-CO-VINYL ACETATE) AS A SELF HEALING AGENT IN GEOPOLYMER WITH EXPOSURE TO VARIOUS CURING TEMPERATURE

YAP SIN WEE

Thesis submitted in fulfillment of the requirements
for the award of the degree of
Bachelor of Civil Engineering

Faculty of Civil Engineering and Earth Resources

UNIVERSITI MALAYSIA PAHANG

JULY 2015

ABSTRACT

Different studies have been done on the characteristics of fly ash based geopolymer concrete and yet there is quite less studies on the addition of self-healing agent to reduce the shrinkage phenomenon during heat curing. Reduction of pores percentage in the fly ash based geopolymer concrete was achieved via the addition of PVA (poly ethylene vinyl acetate) to fill up the pores during heat curing process. Fly ash based geopolymer in this research was the combination of fly ash (350kg/m^3), fine aggregates (645kg/m^3), NaOH solution (41kg/m^3) and Na_2SiO_3 solution (103kg/m^3). PVA was included at 1% of fly ash weight and subjected to heat curing of 60ºC, 70ºC and 90ºC for 24 h without any post-cast detainment period. This research has shown that PVA started to melt when temperature reach the melting point of PVA and filled the voids in fly ash based geopolymer concrete. The batch that undergoes 90 ºC heat curing showed lower void percentage and higher compressive strength than the other specimens cured with different temperatures. Conclusively, the results has revealed a new finding that addition of PVA with 90 ºC as the activation temperature could increase the compressive strength and decrease the void percentage in fly ash based geopolymer concrete.

ABSTRAK

Kajian yang berlainan telah dilakukan pada ciri-ciri Geopolimer konkrit berdasarkan abu namun terdapat kurang kajian mengenai penambahan agen pemulihan diri untuk mengurangkan fenomena pengecutan semasa pengawetan haba. Pengurangan liang peratusan dalam Geopolimer konkrit boleh dicapai melalui penambahan PVA (etilena vinil asetat poli) untuk mengisi liang semasa proses pengawetan haba. Geopolimer konkrit berasaskan abu dalam kajian ini adalah gabungan abu (350kg/m^3), agregat halus (645kg/m^3), NaOH penyelesaian (41kg/m^3), dan Na2SiO3 (103kg/m^3). PVA telah dimasukkan pada 1% daripada berat badan abu dan tertakluk kepada pengawetan haba 60ºC, 70ºC dan 90ºC selama 24 jam tanpa apa-apa tempoh penahanan. Kajian ini telah menunjukkan bahawa PVA mula cair apabila suhu mencapai takat lebur PVA dan memenuhi lompang dalam Geopolimer konkrit. Kumpulan yang mengalami pengawetan pada suhu 90ºC haba menunjukkan peratusan yang lebih rendah dalam kekosongan dan kekuatan mampatan yang lebih tinggi daripada spesimen lain yang mengalami pengawetan pada suhu 70ºC dan 80ºC. Oleh itu, penemuan baru yang boleh didedahkan ialah penambahan PVA pada suhu 90 ºC dan ini boleh meningkatkan kekuatan mampatan dan mengurangkan peratusan kekosongan di Geopolimer konkrit berasaskan abu terbang.

TABLE CONTENT

	Page
SUPERVISOR'S DECLARATION	ii
STUDENT'S DECLARATION	iii
ACKNOWLEDGENMENTS	iv
ABSTRACT	v
ABSTRAK	vi
TABLE OF CONTENTS	vii
LIST OF TABLES	x
LIST OF FIGURES	xi
LIST OF SYMBOLS	xiii
LIST OF ABBREVIATONS	xiii

CHAPTER 1 INTRODUCTION

1.1	Background	1
1.2	Problem Statement	2
1.3	Objectives	2
1.4	Scope of Study	2
1.5	Significance of Research	3
1.6	Layout of Thesis	3

CHAPTER 2 LITERATURE REVIEW

2.1	Introduction	5
2.2	Geopolymer Concrete	
	2.2.1 History of Geopolymer Concrete	5
	2.2.2 Durability of Geopolymer Concrete	8
	2.2.3 Compressive Strength	10
	2.2.4 Factors Influence the Compressive Strength	
	2.2.4.1 Compressive Strength at Different Age	11
	2.2.4.2 Effect of Curing Time	12

2.2.4.3 Effect of Superplasticizer 13
2.2.4.4 Effect of Water Content 14
2.2.5 Creep and Drying Shrinkage 15
2.2.6 Types of Curing 17
2.2.7 Mixing Ingredient 18
2.3 Self-Healing Mechanisms 19
2.3.1 Intrinsic Self-Healing (Autogenuos Healing) 20
2.3.2 Capsule Based Self-Healing 20
2.3.3 Vascular Based Self-Healing 21
2.4 Types of Self-Healing Agent 22

CHAPTER 3 METHODOLOGY

3.1 Introduction 24
3.2 Material Preparation 25
3.2.1 Fly Ash 26
3.2.2 Fine Aggregates 26
3.2.3 Na_2SiO_3 Solution 27
3.2.4 Poly (Ethylene-Co-Vinyl-Acetate) 27
3.3 Design Mix 27
3.4 Preparation of Specimens 28
3.5 Testing Procedures 29
3.5.1 Compressive Strength Test 29
3.5.2 Porosity Test 30

CHAPTER 4 RESULT AND ANALYSIS

4.1 Introduction 32
4.2 Compressive Strength 32
4.3 Porosity 38
4.4 Correlation Between Compressive Strength and Porosity 39

CHAPTER 5 CONCLUSIONS AND RECOMMENDATIONS

5.1 Introduction 41
5.2 Conclusions 41
5.3 Recommendations 42

REFERENCES 43
APPENDICES
A PARTICLE SIZE DISTRIBUTION 45
B COMPRESSIVE STRENGTH DATA 46
C POROSITY TEST DATA 50

LIST OF TABLES

Table No.	Title	Page
2.1	Applications of Geopolymeric Materials Based on Silica-to Alumina Atomic Ratio	8
2.2	Mixing Proportion For Each Mixture	10
2.3	Mean compressive strength and unit-weight of geopolymer concrete done on the research	10
2.4	Compressive Strength Development of Geopolymer Concrete	18
2.5	Overview of the Self-Healing Agents Reported in the review	22
3.1	Materials used to produce 1 m^3 of geopolymer concrete mixes	27
4.1	Statistical Analysis between Specimen with PVA and without PVA under 90ºC	35
4.2	Statistical Analysis between Specimen with PVA and without PVA under 80ºC	35
4.3	Statistical Analysis between Specimen with PVA and without PVA under 70ºC	36

LIST OF FIGURES

Figure No.	Title	Page
2.1	Compressive Strength at Different Ages	12
2.2	Influence of Curing Time on Compressive Strength	13
2.3	Effect of superplasticizer on compressive strength	14
2.4	Effect of the water-to-geopolymer solids ratio on compressive strength	14
2.5	(A) One Channel, (B) Multiple Channel	
3.1	The flowchart for the whole methodology	25
3.2	Fly Ash	26
3.3	Sieve Analysis of Fine Aggregates-Sand	26
3.4	PVA Self-Healing Agent	27
3.5	Compressive strength test machine	30
4.1a	Casted Specimen	32
4.1b	Demoulded Specimen	32
4.2	Compressive strength of fly ash based geopolymer mortar versus temperature	34
4.3	Compressive strength of fly ash based geopolymer mortar versus temperature at day 28	34
4.4a	Specimen before compress	38
4.4b	Specimen after compress	38
4.5	Pore percentage versus Day with and without PVA under elevated curing temperature	39
4.6	Compressive Strength versus Porosity at Day 1	40
4.7	Compressive Strength versus Porosity at Day 28	40

LIST OF SYMBOLS

P	Maximum load
L	Length of specimen
B	Cross-sectional dimension of specimen
ρ_w	Water density
χ_1	Bulk density
χ_2	Apparent density
A	Mass of oven-dried sample in air
B	Mass of surface-dry sample in air after immersion
C	Mass of surface-dry sample in air after immersion and boiling
D	Apparent mass of sample in water after immersion and boiling

LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Materials
BS	British Standard
PVA	Poly (Ethylene-Co-Vinyl Acetate)
FA	Fly Ash
Al	Aluminum
Si	Silicon
Na_2SiO_3	Sodium Silicate

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

Throughout the whole world, the usage of Portland cement on construction is a very basic needs. Due to high demand of Portland cement, the production of the cement has increased from years to years just to fulfill the demand list. But the production of Portland cement will have the side effect which is the emission greenhouse gasses and cause the rise of surrounding temperature. This problem has been start to tackle by introducing more non cement based concrete and one of the study done is the geopolymer concrete where this concrete doesn't require any usage of cement. Geopolymer concrete become even more environmental friendly due to the usage of the fly ash which is the by-product from the burning of powdered coal in the electric generating power plants. This fly ash is then collected in the dust-collection systems that remove particles from the exhaust gases. The usage of geopolymer concrete not only can reduce the emission of greenhouse gases but it also can achieve early strength compare to using Portland cement.

There is further study related to the behavior of geopolymer concrete to enhance the durability of the concrete so it could use in construction and sustain longer time. Study related to changing the pozzolanic materials, adding admixtures and also shrinkage behavior has been done to improve the durability of geopolymer concrete. Several improvement has been done on the geopolymer concrete throughout the years to make sure the geopolymer concrete can sustain more loads.

1.2 PROBLEM STATEMENT

The introduction of geopolymer concrete start to widely used in industry as a replacement for Portland cement. For an example the University of Queensland's Global Institute (GCI) used the fly ash based geopolymer concrete to construct the concrete floor parts. The use of geopolymer concrete could reduce the green-house effect yet the characteristics of the geopolymer concrete did not have further research on the self-healing mechanism. The production of geopolymer concrete when undergo heat curing will leads to the formation of cracks inside the geopolymer concrete. Therefore this research was proposed to investigate the crack filling mechanism by adopting self-healing method.

1.3 OBJECTIVES OF THE RESEARCH

The objectives of this study are as follows:

i. To investigate the effect of elevated heat curing temperature on compressive strength of fly ash based geopolymer mortar without post-casting detainment period.

ii. To investigate the effect of elevated heat curing temperature on porosity of fly ash based geopolymer mortar without post-casting detainment period.

iii. To determine the optimum activation temperature for PVA in fly ash based geopolymer mortar.

1.4 SCOPE OF STUDY

The aim of this research is to study the effect of elevated curing temperature on compressive strength of the fly ash based geopolymer concrete and also the pores percentage in it. Six batches of mix are prepared which is with self-healing agent and without self-healing agent for future comparison purposes. Then both mixtures will undergoes oven curing for several elevated temperatures (70ºC, 80ºC and 90ºC) for

24hours. After oven curing, the geopolymer concrete will be take out from oven for air dry curing for 1 and 28 days. Compressive strength test and porosity test will be done on the geopolymer concrete.

1.5 SIGNIFICANCE OF RESEARCH

The main purpose of this research is to determine whether the presence of self-healing agent in geopolymer concrete could increase the compressive strength of the geopolymer concrete during elevated temperature oven curing. Oven curing for geopolymer concrete could form cracks due to possibility of shrinkage and the percentage of voids in geopolymer concrete may have lower value so it can achieve maximum compressive strength.

1.6 LAYOUT OF THESIS

Chapter one is the brief introduction on the information for this whole thesis where include the background study, problem statement, objectives, significance of research, scope of study. All the elements is describe in detail that related to this thesis as well in this section.

Chapter two will consist with literature reviews on the shrinkage behavior of the geopolymer concrete, self-healing agent on cementitious materials, and the effect elevated heat curing temperature on shrinkage behavior on the geopolymer concrete. First, the characteristic about the geopolymer concrete will be briefly discussed. The review will further discuss with the characteristic on different type of self-healing agents. Next, discussion on the effect of different elevated heat curing temperature on the shrinkage behavior of the geopolymer concrete.

Chapter three consists of the methodology of this thesis on how to prepare the materials and also the preparation process. Then the procedure for the preparation of the geopolymer concrete mixing will be further elaborate in chapter three. Until the last section of chapter three, testing procedure on the geopolymer concrete to determine the engineering properties of it namely compressive strength test, porosity test, and scanning electron microscope test will be presented.

Chapter four will contain the results from the whole tests. The result will be analysis and further discuss. Graphical analysis will be used to describe the compressive strength of the geopolymer concrete with and without self-healing agent at different heat curing temperature for 24hours. A comparison of result will be discuss between geopolymer concrete with and without self-healing agent under heat curing with zero minutes detention time.

Chapter five will be the conclusion for each objective outlines in this study and further recommendations for future research will be suggested.

CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

Due to production of Portland cement is increasing from years to years, the demand will be increase drastically. The increasing production of Portland cement will also increase the rate of global warming toward the environment around us. This is because the production of Portland cement needs a huge amount of heat energy to burn the cement clinkers to form powder. That will emit the greenhouse gas which consists of carbon dioxide (CO_2). This CO_2 contributes the most percentage to global warming which is 65% (McCaffery, 2002). Mostly this CO_2 comes from cement industry due to this production of one ton of Portland cement emits equals to one ton of CO_2 into the atmosphere (Davidovits, 1994; McCaffery, 2002).

In respect to this global warming issue, geopolymer technology was invented to reduce the emission of CO_2 to the atmosphere produced from the cement industries as shown by the detailed analyses of (Gartner, 2004). The utilization of fly ash from the thermal plant to produce the geopolymer concrete couldn't increase the strength of the geopolymer concrete.

Due to geopolymer concrete also will experience shrinkage same like Portland cement concrete due to high water-cement ratio and the rate of vaporization is high during heat curing which caused cracks in the geopolymer concrete.

To lower down the percentage of cracks found during heat curing, the capsule based self-healing agent is introduced by different researches with different self-healing materials. There are also other type of self-healing method which is intrinsic self-healing and vascular based self-healing method. A review has been done by (KimVan Tittelboom & Nele De Belie, 2013) on the self-healing in cementitious materials.

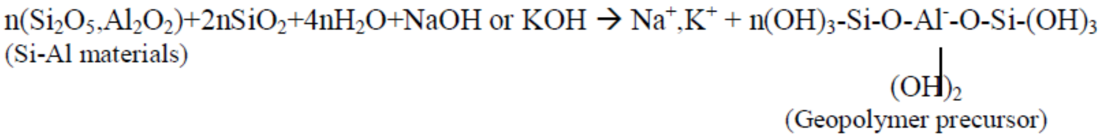
Each of the self- healing agents have its own way to be trigger and heal up the cracks inside the concretes. Different duration and temperature need to be control when need to activate the self-healing agent in the concrete.

When geopolymer concrete undergoes the heat curing, it will experience shrinkage problem which will lead to cracks inside the geopolymer concrete. The cracks appear in the geopolymer concrete means the strength of the geopolymer concrete will be affected when the critical load apply on the geopolymer concrete. This cracks formed need to be solve where the self-healing agent will be introduce into the geopolymer concrete. The shrinkage behavior is greatly affected by the heat curing temperature and caused the moisture in the geopolymer concrete evaporate into the atmosphere and the concrete doesn't have enough moisture to further create the polymeric Si-O-Al bonds.

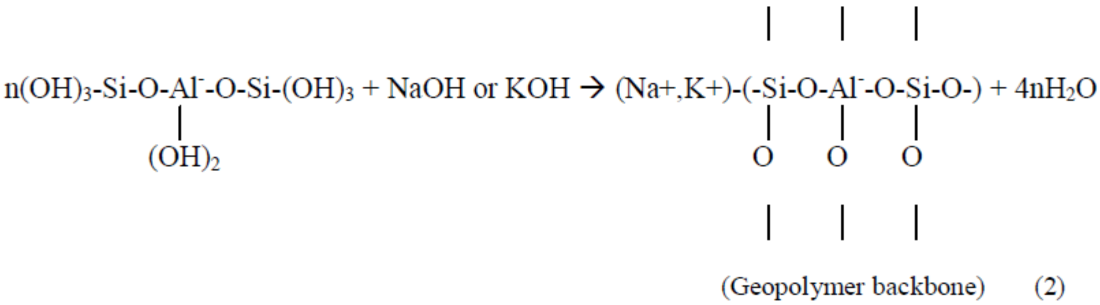
2.2 GEOPOLYMER CONCRETE

2.2.1 History of Geopolymer Concrete

Research conducted by Davidovits (1988; 1994) had proposed that the silicon (Si) and the aluminum (Al) can react with alkaline liquid and fly ash or rice husk ash form in a source material of geological origin or in by-product materials to produce binders. The reaction that creates the geopolymer concrete is a polymerization process and therefore the binders named as "geopolymer". The reaction between alkaline condition on Si-Al minerals that result in a polymeric chain and ring structure consisting of Si-O-Al-O bonds is known as polymerization process (Davidovits, 1994)



(1)



(2)

Above Equations (1) and (2) is the schematic formation of geopolymer material that described by (Davidovits, 1994; van Jaarsveld et al., 1997). In equation 2, the water which formed during the reaction will be evaporated when undergoes curing and further drying periods. This drying process further on will leave behind nano-pores in the matrix which is a benefit to the geopolymer performance. The water plays no role in strengthening the concrete but only increase the workability during casting. Meanwhile the water is important for Portland cement to enable the hydration process to produce the $Ca(OH)_2$ and C-S-H gel where the gel will form a binder for the aggregates.

There are two main types of geopolymers which is the source materials and the alkaline liquids. First, the source materials for geopolymer based on alumina-silicate should be rich in aluminium (Al) and silicon (Si). These could be natural minerals such as clays, kaolinite, etc. Alternatively, by-product materials such as rice-husk ash, silica fume, fly ash, slag, red mud, etc could be used as source materials. The factors which include availability, cost, type of application, and specific demand is the choice of the source materials for making geopolymers depends on. (Prof. B. Vijayan Rangan, 2010)

Prof. B. Vijayan Rangan, 2010 stated that alkaline liquid are usually form from Sodium (NA) or Potassium (K) based which categories as soluble alkali metals. The combination of sodium hydroxide (NaOH) or potassium hydroxide (KOH) and sodium silicate or potassium silicate is called as geopolymerisation process. Geopolymeric materials have a wide range of applications in the field of industries such as in the automobile and aerospace, civil engineering and plastic industries (Davidovits, 1994). The type of application of geopolymeric materials is determined by the chemical structure in terms of the atomic ratio Si: Al in the polysialate. Davidovits (1994) classified the type of application according to the Si:Al in **Table 2.1** shows the application of geopolymer materials based on silica-to-alumina atomic ratio.

Table 2.1: Applications of Geopolymeric Materials Based on Silica-to-Alumina Atomic Ratio

Si:Al ratio	Applications
1	- Bricks - Ceramics - Fire protection
2	- Low CO_2 cements and concretes - Radioactive and toxic waste encapsulation
3	- Fire protection fibre glass composite - Foundry equipments - Heat resistant composites, 200°C to 1000°C - Tooling for aeronautics titanium process
>3	- Sealants for industry, 200°C to 600°C - Tooling for aeronautics SPF aluminium
20 - 35	- Fire resistant and heat resistant fibre composites

Sources: Davidovits (1994)

2.2.2 Durability of Geopolymer Concrete

The main difference between geopolymer concrete and Portland cement concrete is the binder. The binder form in geopolymer concrete is the reaction between the silicon and aluminum oxides in the low-calcium fly ash together with alkaline liquid that binds the coarse and fine aggregates together. While the Portland cement is the combination of cement with water to undergoes hydration process and produce C-S-H gel and $Ca(OH)_2$. The C-S-H gel will act as a binder for the coarse and fine aggregates and form the Portland cement concrete.

The compressive strength and the workability of the geopolymer concrete are affected by the mixing proportions and engineering properties of the constituent materials that make the binder. Below are the results from the experiment done by (Hardjito and Rangan, 2005):

- Compressive strength of geopolymer concrete is affected by the concentration (in terms of molar) of sodium hydroxide solution.
- The ratio of sodium silicate solution-to-sodium hydroxide solution ratio by mass increased, the higher will be the compressive strength of geopolymer concrete.
- The addition of naphthalene sulphonate-based superplasticizer to 4% of fly ash by mass, improves the workability of the fresh geopolymer concrete; however, there is a slight degradation in the compressive strength of hardened concrete when the superplasticizer dosage is greater than 2%.
- When the water content of the mixture increases, slump value of the fresh geopolymer concrete increases.
- The compressive strength of geopolymer concrete decreases same goes to the H_2O-to-Na_2O molar ratio increases

The mass of geopolymer solids is the sum of the mass of fly ash, the mass of sodium hydroxide solids used to make the sodium hydroxide solution, and the mass of solids in the sodium silicate solution (Prof. B. Vijaya Rangan, 2010).

There are two major classes of fly ash that are specified in ASTM C 618 on the basis of their chemical composition resulting from the type of coal burned which is class C and class F fly ash. Class C also known as high calcium fly ash which the CaO content is 10-30% high when produced from burning subbituminous coal or lignite. Class F also known as low-calcium fly ash where the lime (CaO) content is10% less when obtained from the burning of bituminous coal. The class F fly ash possess little no cementing property, but iin a finely divided form and in the presence of water it can react with calcium hydroxide generated during the hydration of cement.

2.2.3 Compressive Strength

Based on research done by Prof. B. Vijaya Rangan, 2010, he tested the compressive strength with different mixture plus different curing on the geopolymer concrete. **Table 2.2 & 2.3** shows the mixing proportion for each mixture and the mean compressive strength and unit-weight of geopolymer concrete done on the research. In this research, it shows that both mixes have the highest mean compressive strength when cure in oven compare to cure it with steam. This results shows that geopolymer concrete could achieve higher strength when cure under heat instead of steam or water due to water curing doesn't work on geopolymer concrete because it doesn't need H_2O compound to start the polymeric reaction between the silicon and aluminum oxides in the low-calcium fly ash together with alkaline liquid.

Table 2.2: Mixing Proportion For Each Mixture

Materials		**Mass (Kg/m^3)**	
		Mixture 1	**Mixture 2**
Coarse aggregates	20 mm	277	277
	14 mm	370	370
	7 mm	647	647
Fine aggregates		554	554
Fly ash (low-calcium ASTM Class F)		408	408
Sodium silicate solution (SiO_2 /Na_2O=2)		103	103
Sodium hydroxide solution		41 (8 Molar)	41 (14 Molar)
Super plasticizer		6	6
Extra water		None	22.5

Table 2.3: Mean compressive strength and unit-weight of geopolymer concrete done on the research

Mixture	**Curing type**	**7th Day compressive strength (heat-curing at 60°C for 24 hours), (MPa)**		**Unit-weight, (kg/m^3)**	
		Mean	**Standard Deviation**	**Mean**	**Standard Deviation**
Mixture 1	Dry curing (oven)	58	6	2379	17
	Steam curing	56	3	2388	15
Mixture 2	Dry curing (oven)	45	7	2302	52
	Steam curing	36	8	2302	49

Sources: B. Vijayan Rangan (2010)

2.2.4 Factors Influence the Compressive Strength

From the research by D. Hardjito et al.,(2004), the research team done test to find out the effects of several factors on the properties of fly ash based geopolymer concrete, mainly on the compressive strength. The test variables which includes the concrete age, curing temperature, curing time, quantity of superplasticizer, the rest period prior to curing and the water content of the mixtures.

2.2.4.1 Compressive Strength at Different Ages

Figure 2.1 shows the effect of a concrete age on the compressive strength. The chemical reaction of the geopolymer gel due to substantially rapid polymerization process, the compressive strength does not differ with the age of concrete. The whole observation is contrast to the Ordinary Portland Cement concrete (OPC), which undergoes hydration process and gains compressive strength over time whereas geopolymer do not need water to undergoes any polymerization process.

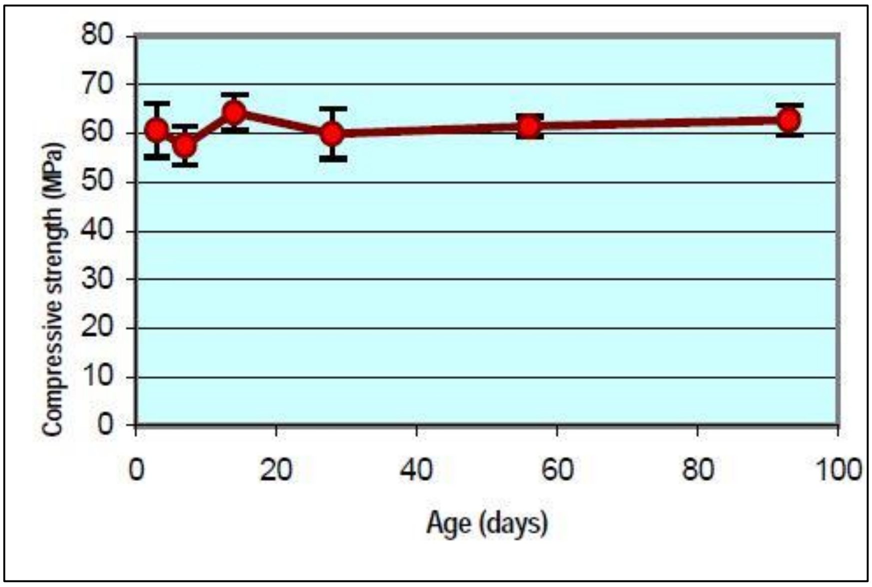


Figure 2.1: Compressive Strength at Different Ages

2.2.4.2 Effect of Curing Time

Figure 2.2 shows the compressive strength influenced by curing time. The graph indicates the longer curing time will improves the polymerization process subsequent increase the compressive strength of the geopolymer concrete. Yet the longer curing time does not produce weaker material as claimed by van Jaarsveld et al. However, the increase in compressive strength after 48 hours curing do not provide significant result.

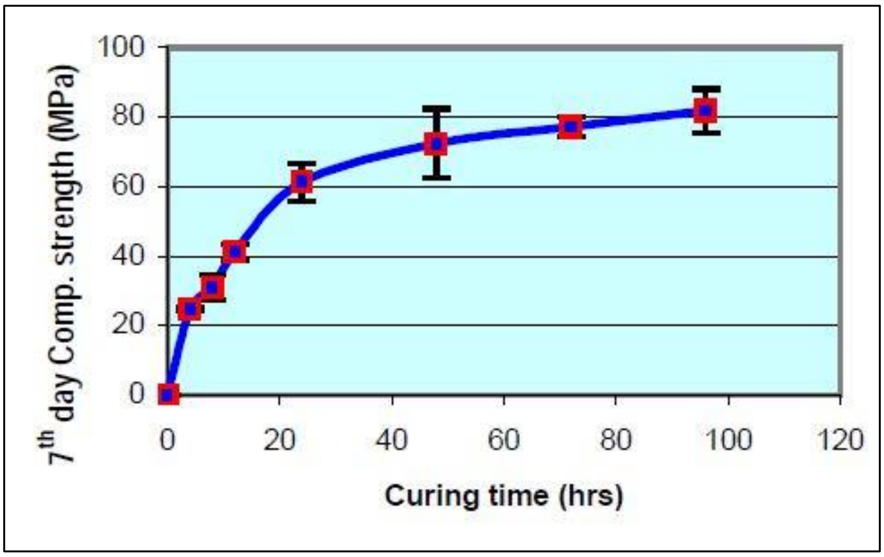


Figure 2.2: Influence of Curing Time on Compressive Strength

2.2.4.3 Effect of Superplasticizer

To test the superplasticizer into fly ash based geopolymer concrete, the mix proportion, curing temperature and curing period is kept constant. The naphthalene-based superplasticizer was added by different proportion into the mixtures by mass. The specimen were tested for its compressive strength at day 7.

Figure 2.3 shows there are two sets of data, one set is undergoes 60 minutes detainment period before went for 60ºC oven curing for 24 hours and another set is 0 minutes detainment period before went for oven curing under the same conditions. The graph shows that there is little significant difference between the compressive strengths of the two sets of specimens. The researcher, D. Hardjito et al.,(2004), found that there is an important outcome when geopolymer concrete is used in precast concrete industry, the results in Figure 2.1 indicate there is enough time between casting of products and direct send the concrete to the curing room.

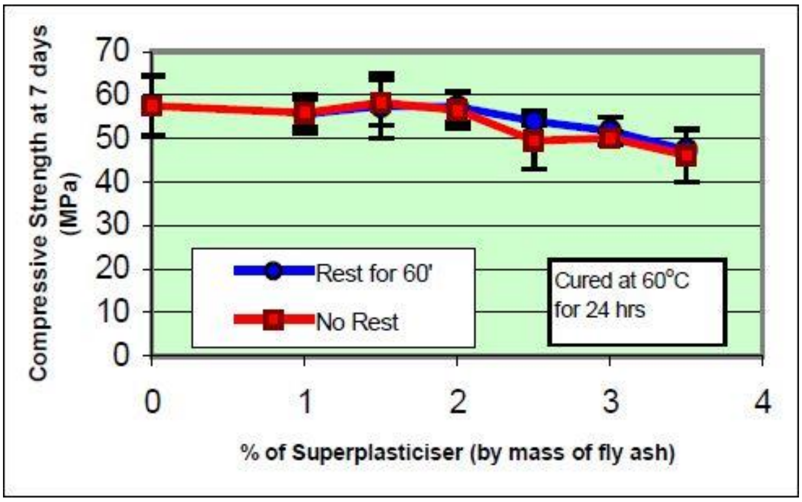


Figure 2.3: Effect of superplasticizer on compressive strength

2.2.4.4 Effect of Water Content

Figure 2.4 shows the effect of water-to-geopolymer solids ratio on compressive strength. The whole observation said the compressive strength is decreasing as the ratio increases. This trend are almost the same to the OPC concrete yet the chemical process inside the geopolymer concrete is different with OPC.

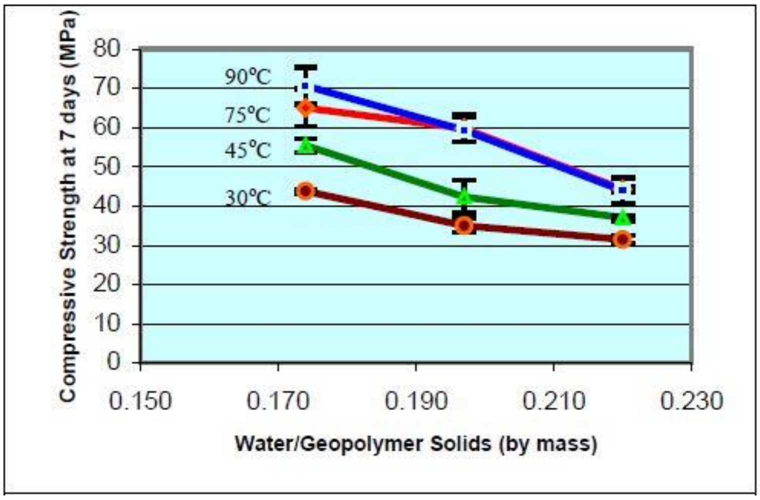


Figure 2.4: Effect of the water-to-geopolymer solids ratio on compressive strength