PHYSICAL PROPERTIES AND WATER ABSORPTION CHARACTERISTICS OF LIGNIN MODIFIED GEOPOLYMER FOR COATING

by

Aizzat Bin Inche Zakuan

14464

Dissertation submitted in partial fulfilment of
the requirements for the
Bachelor of Engineering (Hons)
(Chemical)

Dec 2014

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
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in partial fulfilment of the requirement for the
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(CHEMICAL)

Approved by,

____

(AP Dr. ZAKARIA BIN MAN)

UNIVERSITI TEKNOLOGI PETRONAS
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January 2006

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

AIZZAT BIN INCHE ZAKUAN

ABSTRACT

This paper reviewed with the research that was once initiated by Professor Dr. Joseph Davidovits where the term geopolymer was first applied to alkali aluminosilicate binders formed by the alkali silicate activation of aluminosilicate materials. The application of geopolymer had been one of the biggest founding where this product have been developed and continuously commercialized in during this few years. In this research, the functionality of geopolymer has been brought to another level where the physical properties and water absorption characteristics of geopolymer that is going to be used as a coating substance can be improved. Geopolymer will first be modified by reacting the standard geopolymer made up of fly ash and alkaline activator with lignin; commonly used in the paper pulp industries in the pulping process (pulping is the process which reduces wood to a fibrous mat by separating the cellulose from the lignin). After the preparation of the lignin modifies geopolymer is complete, the paste will then be tested in term of the capability of the prepared paste to sustain water from penetrating the substrate (steel) which it is coating. The finding of this research will help to produce a coat of paste that can resist water thus increasing the durability of the steel.

ACKNOWLEDGEMENT

I would like to express the deepest appreciation to my FYP supervisor AP Dr. Zakaria Bin Man, who has shown the approach and the aptitude of a great motivator where he continually and persuasively conveyed a spirit of adventure in regard to this research, and has supported me throughout my research with his patience and knowledge whilst allowing me the room to work in my own way. Without him this thesis, too, would not have been completed or written. One simply could not wish for a better or friendlier supervisor. I would also want to express my gratitude to the coordinator of FYP I and II for their dedication towards ensuring this course to be completed.

Not to forget, deepest thank to Chemical Engineering Department of Universiti Teknologi PETRONAS who has put a lot of effort towards making the Final Year Project program a great success and a kick start for student to understand deep about related field. This project has given me vast amount of experience and knowledge in engineering and green technology field. Besides, I would like to thank them for their generosity in providing me with all the facilities and technical expertise in making this project successful.

I would also like to deliver my utmost gratefulness to my parents, Inche Zakuan bin Omar and Zaini binti Mohamed whose supportive spirit never faded in inspiring and supporting me to accomplish this course. Without their continuous support and motivation this dissertation would not be complete. Last but not least, a mount thanks to my fellow colleagues and clique, and to anybody who has contributed explicit or implicitly towards accomplishing the objectives

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CHAPTER 1: INTRODUCTION

1.1 Background

The progress of sustainable construction and building resources with lower environmental footprint in both industrial and operational phases of the material lifecycle is drawing an increased attention in the housing and construction industry worldwide(Zhang, Provis, Reid, & Wang, 2014). This explain why the development of the usage of geopolymer in many fields and industries begin to expand globally. The awareness of the people sustaining the environment in this case the mother earth has been in the top spot in the priority list. Besides, the demand for industrial and domestic energy brings upon to the production of a huge volume of fly ash from solid coal fuel, which will intensifies and grow in the world on an unprecedented scale during the coming years(Park & Kang, 2006).

Furthermore, it is known that geopolymer possess good mechanical properties as well as fire and acid resistance (D.M. Roy, P. Arjunan, & M.R. Silsbee, 2001). The application of geopolymer is widely developed nowadays is mainly due to the prevailing and excellence characteristics of the geopolymer itself such as it can withstand a huge amount of heat, survive a high pressure environment and environmentally friendly, durable and primarily it is green. As stated by Sakulich in his journal, the material greenness of cementations systems is a product of three factors which is the virgin resources consumed such as limestone, water, etc.), pollutants produced during processing (primarily gaseous CO2 during the calcination of raw materials), and embodied energy (i.e. energy consumed during production, transportation, and installation of the material)(Sakulich, 2011).

The main factor for the usage of geopolymer is it is make from the reaction between an alkaline solution and an alumina silicate source or feedstock. Alumina silicate or known as fly ash is the finely divided residue resulting from the combustion of ground or powdered coal. Meanwhile, the alkaline activation of materials can be defined as a chemical process that provides a rapid change of some specific structures, partial or totally amorphous, into dense cemented structures(A. M Mustafa Al Bakri et al.). The reaction between the fly ash and the alkaline solution can be described as a physical-chemical process which comprise of the process of mixing a fine powdery solid particle which is the fly ash with a concentrated alkaline solution which in this case is sodium hydroxide under a suitable temperature and curing time to produce a mould of working binding substance. The outcome from combining the two materials can then be used as a coat for a certain substrate or can be used as a replacement of cementing function to replace the usage of Portland cement.

Based on preceding research it has been found out that the final properties of geopolymer can be a product of several factor such as the concentration and type of alkaline solution used; curing method and temperature; rest period; water content; nature of source material; and the solid to liquid ratio used to prepare the geopolymer sample. To acquire good quality sample, these properties can be improved by modifying a certain factor of the geopolymer preparation such as reducing the water content; increasing the binder and aggregate content; using a well-graded aggregate; and using a good curing method and better compaction(Monita Olivia & Nikraz, 2011). This known factor can then be manipulate to give a geopolymer paste that have the most important traits in term of the strength, sturdiness and permeability of liquid into the sample. For example, it has been shown by past research that using low-calcium fly ash and sodium hydroxide activator, a high strength paste with higher compressive strength can be obtained(Park & Kang, 2006).

Regardless of the superior resistance of the low calcium fly ash geopolymer to a huge variety of severe working conditions, fly ash geopolymer paste is known to contain higher proportion of pores in the mesopores sizes. This conditions can lead water to penetrate easily and thus affecting the durability of the materials(M. Olivia, Sarker, & Nikraz, 2008). Water permeability can be defined as the degree to which a material allow the transport of gases, liquids, or ionic species through it. These properties are linked to the performance of porosity, since the harmful ions penetrate into the concrete paste through the pores. Water can be damaging to geopolymer sample because of its ability to: leach calcium hydroxide from the cement paste; carry harmful dissolved species, such as chlorides or acids, into the concrete; form ice in large pores in the paste; cause leaching of compounds from the geopolymer(Monita Olivia & Nikraz, 2011).

1.2 Problem Statement

Based on the background study on the physiognomies of geopolymer shows that considerable research efforts have been directed to this area due to the wide range of potential applications of these materials due to its material greenness and durability.

Even with all the excellence characteristic of geopolymer, there is one setback problem of the geopolymer is it still allow a certain amount of water through the sample. A certain amount of water still can pass through the geopolymer coating. The current permeability of water into the sample causes geopolymer to be unsuitable to be used as a layer of coating. The water that had been absorbs can gradually cause the substance to be eroded after a certain period of time. For example, paint tend to absorb water and cause delamination and corrosion to the steels substrate which it is coating. Penetrability of liquid into the geopolymer consists of permeability through a porous medium, diffusion and absorption. This shows that the geopolymer substance or coating when exposed to severe environments its stability can significantly decline due to deterioration of embedded reinforcement and/or degradation of the geopolymer (D. M. Roy, P. Arjunan, & M. R. Silsbee, 2001).

In response to this problem, this study is done to investigate the effect of modifying the geopolymer with lignin towards the water absorption characteristics of the substance. This study will be done to improve the water absorption characteristic and physical properties of geopolymer coating.

1.3 Objectives

The main objectives of this study is:

- To prepare and study the physical properties of geopolymer coating
- To prepare the lignin modified geopolymer coating
- To analyse the physical properties and water absorption characteristic of lignin modified geopolymer coating

1.4 Scope of Study

The study will involve in experimentation on the effect of modifying geopolymer with lignin and how it will affect the water absorptivity of the geopolymer. At first, geopolymer will be form by the reaction of aluminosilicate and an alkaline solution (sodium hydroxide). The geopolymer will then be modified by mixing it with lignin which allow low absorption of water. The physical properties and the water absorption characteristics will then be analyse. The effectiveness of reacting geopolymer with lignin will then be evaluated by several test to prove that the mixing of lignin and geopolymer can produce a coat of substrate that can resist water.

In order to achieve the above objectives, the scope of the study are categorised as follows:

i. Literature Review/Preliminary work

Theoretical studies on the related topics regarding the geopolymer coating development and application

ii. Geopolymer formulation development

Selection of optimum parameter used to synthesis geopolymer such as percentage of silicate and aluminate, solid to liquid ratio and curing condition in order to obtain improved performance of geopolymer film.

iii. Lignin modified geopolymer composite formulation development

Selection of suitable composition or ratio of geopolymer and lignin in order to obtain the optimum performance of water permeability and physical properties

iv. Characterization & properties analysis for the sample prepared

Several characterization test is carried out on the prepared sample such as scanning electron microscopy test, flexural strength test and water absorption test.

CHAPTER 2: LITERATURE REVIEW

2.1 Geopolymer

Polymer can be categorised under two distinct categories which is the organic polymer and inorganic polymer. The definition of each polymer can be defined as organic polymer is made out carbon based and inorganic polymer is made out of silicon based. Therefore the geopolymer is form from the reaction of a solid materials rich in aluminosilicate with a highly concentrated aqueous alkali hydroxide or silicate solution which will produces a synthetic alkali aluminosilicate material commonly called a ‘geopolymer’ or more widely termed as inorganic polymer(Duxson et al., 2006).

Geopolymer was first patented by a French scientist Joseph Davidovits in 1972. Since it is introduced, the application of these materials had been developed in many fields and industries. The advantages of geopolymer is it is environmentally friendly. Due to its sustainable and nature friendly properties geopolymer had been used primary in the cement and concrete industries. Since the widespread agreement of ‘sustainability’ as a key principle for the assessment of materials by both the engineering community and the general public, the construction materials industry is facing increased pressure as the standard Portland cement production is becoming perceived as unsustainable due to huge amount of contaminant that is gradually being released to the environment(Zhang et al., 2014). By application of alkali activation, geopolymer can be produced by using waste materials or by-products such as fly ash and blast furnace slag (Duxson et al., 2006). Figure 1 shows the alkali activation of fly ash which produce amorphous microstructure geopolymer.

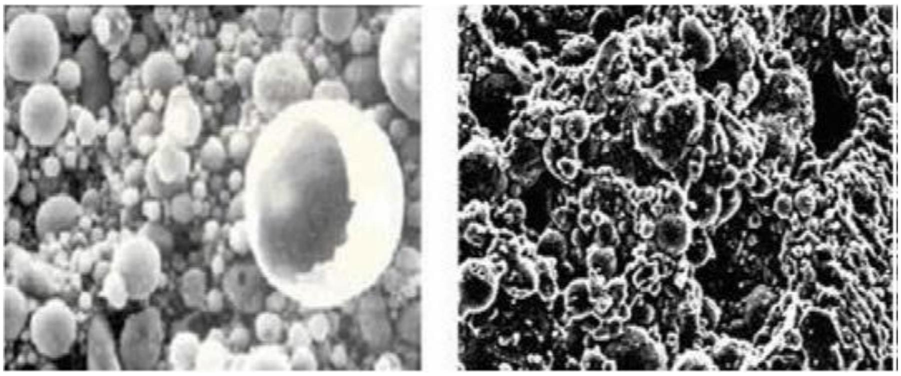


Figure 1: Fly ash before and after reacting with NaOH (Abdullah et. al, 2011)

For the geopolymerisation process, it involves a fast chemical reaction under alkaline conditions, which is provided by the soluble alkali metals such as sodium hydroxide and potassium hydroxide (Nasvi, 2013). The resultant product produced is a three-dimensional polymeric chain and ring that can be shown below.

$$Mn[-(SiO2)z - AlO2]n \bullet wH2O$$

M represents the alkaline element, while n is the degree of polymerisation. Ratio of Si/Al is represented by the value of z in the equation (Nasvi et. al, 2013). From the reaction equation of geopolymerisation, nano-pores formation in the matrix of polymers is able to improve the stability and performance of the geopolymer. The other important factor is that water has no effect in reaction for geopolymer, thus giving it advantage against OPC (Rangan, 2008). Water in geopolymer is only for handling assistant.

Based on these equations, three main mechanisms involved in the setting and hardening of geopolymers are dissolution of aluminate and silicate, positioning of precursor ions into monomers, and polymerisation of monomers into networks.

2.1.1 Fly Ash

Fly ash, also known as powdered fuel ash, is basically a non-combustible mineral portion product of combustion of coal that has been thermally altered. After the consumption of coal in the power plant, it is first ground to powder. Then blown into a power plant’s boiler where the carbon is consumed, leaving behind the molten particles rich in silica, aluminium and calcium. These particles are then solidified as microscopic, glassy spheres that are collected from the power plant’s exhaust(Qazi, 2010).

2.1.2 Properties of Geopolymer

The ability of geopolymer to resist various severe environment has allowed it to be used in many application. Example of the excellence properties of geopolymer are:

1. High strength
    - Geopolymer have a higher strength associated with more desirable internal microstructure and can withstand a high amount of compression
2. Chemical resistance
    - It has a superior resistance towards any chemical attack or any aggressive environment such as acidic solution
3. Porosity
    - Many characteristic will affect the porosity of the prepared geopolymer on either to have a Nano or micro porosity such as the curing time and temperature.
4. Setting time
    - Setting time (time for hardening) is the optimum time that the raw fly ash will fully react with the activator.

2.1.3 Geopolymer Synthesis

The basic requirement of synthesizing geopolymer depends on two main subject which is the raw material and the activator used for this project. This basic requirement need to co-exist as both component is needed to completely synthesized geopolymer that is going to be used as a coating. It is as shown in the figure below:

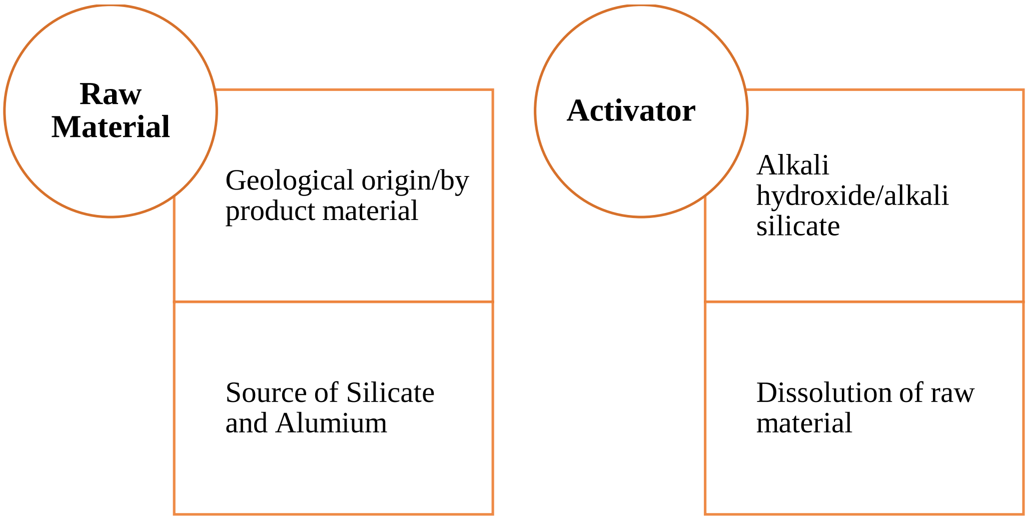


Figure 2: Basic requirement needed to synthesized geopolymer paste

Though geopolymer can exhibit a wide variety of properties and characteristics, including high compressive strength, low shrinkage in fast or slow setting, acid resistance, fire resistance and low thermal conductivity feature however it can adsorb water making it work in a less optimum condition when water is presence. Water permeability of the geopolymer basically is connected to the presence of pores. This pores allows the movement of water in and out from the geopolymer surface. Water permeability is hugely influenced by the connectivity of the pores connectivity in the prepared paste. The presence of these pores is dependent on parameters such as the water content, binder content and the curing method used. Permeability of water can be lowered by preparing a denser geopolymer paste that have smaller pores interconnectivity.

The water presence will then cause the coating to be eroded after prolong exposure to water. This happen as water can be harmful to geopolymer because of its ability to: leach sodium hydroxide from the cement paste and will cause the hardened geopolymer to become unstable and lastly will cause it to crack(Monita Olivia & Nikraz, 2011).. Prolong exposure to water can cause the substance which it is coating to corrode after a certain limit amount of time. Moreover, the presence of water can represent a harmful agent only for the steel reinforcement, accelerating its electrochemical corrosion(Frigione, Aiello, & Naddeo, 2006).

Water presence in the system will reduce the lifespan of the geopolymer coating the steel thus increasing the need of maintenance. This will eventually increase the cost for recoating geopolymer to the steel and also to repair the damage that had been done to the steel. To prevent this problem, a coating that has low permeability of water have to be design. Therefore this study will investigate the effect of reacting geopolymer that adsorb water with lignin which does not permeate water.

Figure 3: Delamination of paint cause by prolong exposure to moisture

Source: *http://www.amteccorrosion.co.uk/coatingbreakdown.html(2014)*

2.1.4 Mechanism of Geopolymerization

Firstly the mechanism of geopolymerization is study on how the new class of synthetic alumina-silicate materials resulting from alkali activation of materials rich in Silica (Si) and Alumina (Al) that could be bring to yielding amorphous to semi-crystalline phase paste. The mechanism of geopolymerization consist of several step which is:

1. Dissolution of the solid aluminosilicate materials in the aqueous solution
2. Formation of Si and/or Si-Al oligomers in the aqueous phase
3. Polycondensation of the oligomeric species or units in the aqueous phase to form an inorganic polymeric material
4. Bonding of undissolved solid particles in the final geopolymeric structure

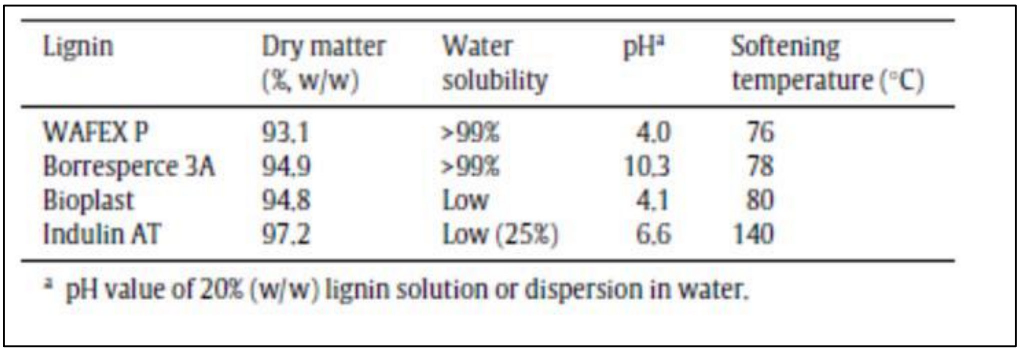
2.2. Lignin

Lignin is a highly abundant bio polymeric material that constitutes with cellulose one of the major components in structural cell walls of higher vascular plants(Laurichesse & Avérous, 2014). Currently, about 70 million tons of lignin are generated annually as a co-product in the paper pulp industry. (Pulping is the process which reduces wood to a fibrous mat by separating the cellulose from the lignin). Lignin are also used in large quantities in the textile industries. Lignin is also often used as a filler or additive, however lignin is rarely exploited as a raw material for chemical production.

However, the main concern here is that only about 2% of the generated lignin is being used for value-added applications while the rest is used as burning fuel in the same generating industries.(Sahoo, Misra, & Mohanty, 2011). Lignin is an amorphous polymer which behave as a thermoplastic material, exhibiting a glass transition temperature T_g which varies widely depending on the method of isolation, sorbed water, molecular weight and thermal history(Laurichesse & Avérous, 2014).

In the Table 2-1 below, four types of commercially available lignin are shown based on their main properties.

Table 1: Properties of lignin(Pe´rez, 2007)



Lignin	Dry matter (%, w/w)	Water solubility	pH^a	Softening temperature (°C)
WAFEX P	93.1	>99%	4.0	76
Borresperce 3A	94.9	>99%	10.3	78
Bioplast	94.8	Low	4.1	80
Indulin AT	97.2	Low (25%)	6.6	140

^{a} pH value of 20% (w/w) lignin solution or dispersion in water.

Referring to the selected properties of lignin above, the water solubility of the lignin is important in determining the water resistance of the lignin. Low in water solubility will indicate that the lignin is more hydrophobic and resistant to water. While for the softening temperature, chemical reactions such as cross linking or any other modifications may occur at this temperature(Mulder & Eastham, 2011). The type of lignin used will be the determining factor on either the geopolymer produce can resist water. In order to overcome this problem, geopolymer has a great potential as the alternative materials that can strengthen the coating composite.

The application of lignin in this study is to be reacted with geopolymer and then be used as a coating agent that can prevent water from penetrating into the geopolymer which eventually will erode the geopolymer. Penetrability of liquid into the geopolymer consists of permeability through a porous medium, diffusion and absorption. Besides, pores in geopolymer have an important role to allow the liquid/fluid move through the geopolymer but the tendency of geopolymer to absorb and transmit water by capillary action not only depends on the porosity but also on its pore diameter, distribution, continuity and tortuosity(M. Olivia et al., 2008).

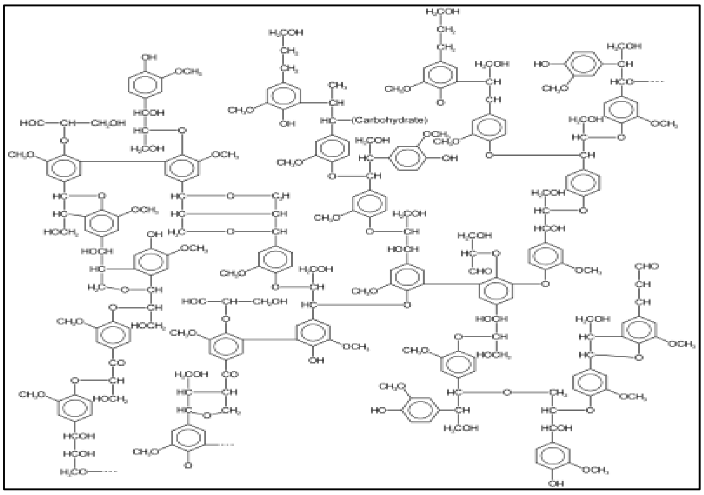


Figure 2: Structure of lignin

Source: *SI Chemical Data Book* (4th ed.), *Gordon Aylward* and *Tristan Findlay*, Jacaranda Wiley

Despite the superior resistance of the low calcium fly ash geopolymer in various severe environments, according to Kong, et al. (2007) and Sindhunata (2006), the fly ash geopolymer paste contains higher proportion of pores in the mesopores size. This condition may lead water to penetrate easily and will affect the durability of the material. Therefore, the usage of the lignin in this project can be manipulated so that the hydrophobic structure of the lignin can prevents any water from diffusing from its surface into the substance that it is coating.

2.3. Fick's Second Law

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} \tag{2.1}$$

Fickian describe the non-steady state diffusion of substance in Cartesian coordinate, x, y, and z.

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2} \tag{2.2}$$

Where c is the concentration in dimensions of [(amount of substances) length^{-3}]. [mol m^{-3}]

T is equal to time[s]

D is the diffusion coefficient in dimensions of [length ^{2} time^{-1}], [m^{2} s^{-1}]

x is the position [length] in m

The analytical solution of equation 2.1 for the concentration profile of a diffusing substance in isotropic plane sheet of finite thickness can be described as a function of time, t and distance, x.

$$\frac{c_{x,t}}{c_\infty} = 1 - \frac{4}{\pi}\sum_{m=0}^{\infty}\frac{1}{(2m+1)} exp\left[\frac{D(2m+1)^2\pi^2 t}{h^2}\right]\sin\left[\frac{(2m+1)\pi x}{h}\right] \tag{2.3}$$

Where $c_\infty$is the saturation of the absorbed substances. Upon solving Equation 2.1 with the following boundary conditions $\mathrm{c} = 0$ when $\mathrm{t} = 0, 0 \leq \mathrm{x} \leq \mathrm{h}, \mathrm{c} = \mathrm{c}_\infty$when t=h, $\partial c/\partial x = 0$, t >0, the relative moisture uptake is expressed as:

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{\infty}\frac{8}{(2n+1)^2\pi^2} \times \exp\left[-\frac{D(2n+1)^2\pi^2 t}{h^2}\right] \tag{2.4}$$

Where $\mathrm{M_t}$ is the mass gain at reduced time and $M_\infty$is the maimum mass gain at the equilibrium state. At the initial satge of diffusion, Equation 2.4 can be approximated by:

$$\frac{M_t}{M_\infty} = 4\left[\frac{Dt}{\pi h^2}\right]^{1/2} \tag{2.5}$$

Therefore the diffusivity, D can be calculated from the initial slope of the moisture gain M_t/M_∞versus time ($t^{1/2}$/h):

$$D = \frac{\pi}{16}\left[\frac{\frac{M_t}{M_\infty}}{\frac{\sqrt{t}}{h}}\right] \qquad (2.6)$$

A relationship has been developed to predict the moisture content that has a form similar to equation 2.4

$$\frac{M_t}{M_\infty} = 1 - \exp\left[-7.3\left(\frac{Dt}{h^2}\right)^{0.75}\right] \qquad (2.7)$$

CHAPTER 3: METHODOLOGY

3.1 Geopolymer formulation development

Based on the previous experimental formulation based on literature review shows that the best properties to formulate a geopolymer is with a solid to liquid mass ratio of alkaline activator-to-fly ash (3:1), optimum concentration of Sodium Hydroxide (12 M) and curing condition of 60^{o}C and 1 days/24 hours of curing temperature and curing time respectively, geopolymer film that is suitable for coating can be developed (A. M Mustafa Al Bakri et al.).

3.1.1 Materials & Equipment

500 mL beaker can be used to mix the prepared sodium hydroxide (NaOH) solution of 12M with the weighted fly-ash based on the optimum solid to liquid ratio of 3:1 by the mass. The dry oven will be used for curing process of the geopolymer film. Figure 4 and 5 below show the main materials used in preparing the geopolymer solution.

Figure 4: Fly ash is weighted in the beaker

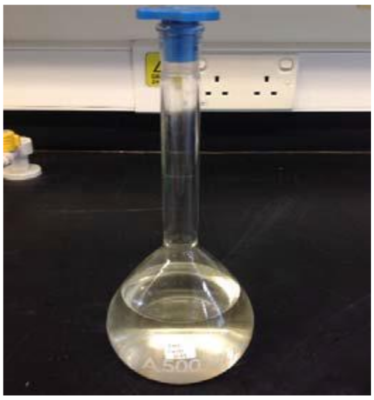


Figure 5:12M sodium hydroxide, NaOH prepared in 1000mL volumetric flask

The sodium hydroxide solution is prepared 24 hours before the geopolymer sample experiment is conducted in order to ensure well mixing of NaOH and distilled water and no vaporization of NaOH occurs during the mixing process.

3.1.2 Experimental Procedure

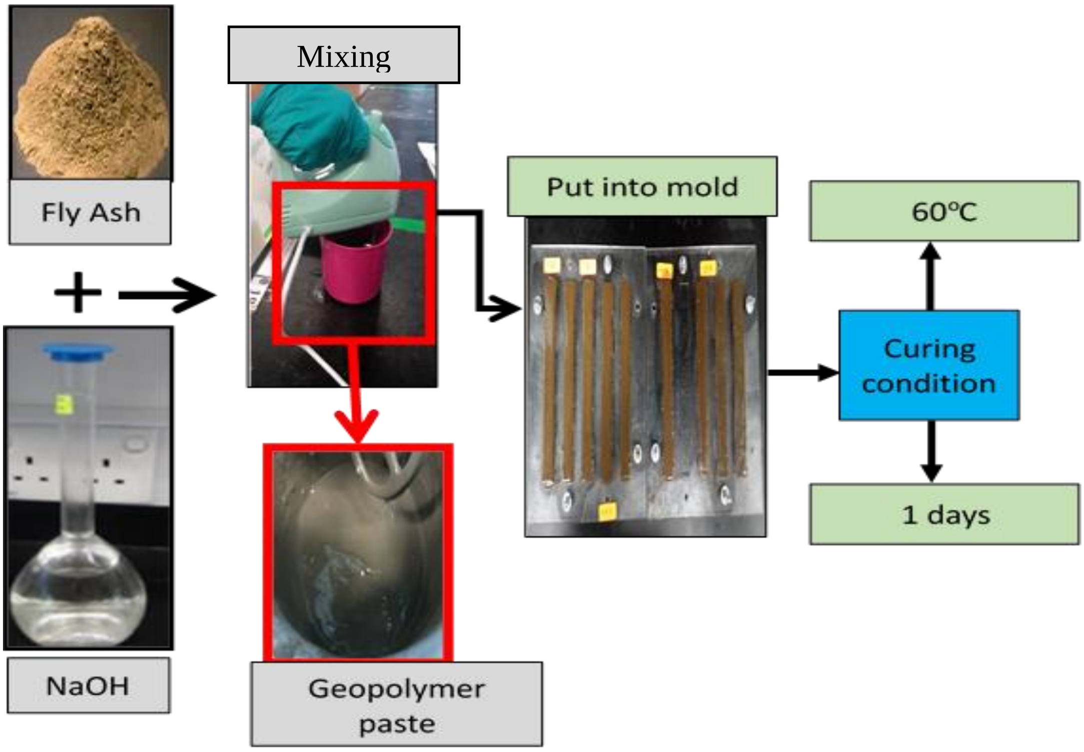


Figure 6: Procedure for preparing the geopolymer paste

1. Fly ash is measured and poured into a beaker

2. Sodium hydroxide solution of 12M concentration is prepared in a 1000mL volumetric flask.

3. Based on the specified mass ratio (3:1 solid to liquid ratio), sodium hydroxide solution and fly ash are weighted and mixed into the beaker. The mixture is stirred for well mixing for about 5 minutes.

4. The mixture is then casted onto the desired mould for specific purposes.

5. The sample films will be cured in a dry oven at 60°C for the specified curing times of 1 days for the required tests on the geopolymer.

3.2 Lignin geopolymer composite formulation development

Development of optimum composition between geopolymer and lignin is required in order to obtain composite film with reliable and applicable hydrophobicity, flexibility, etc. For this study, three different compositions of lignin is selected, which are 1.0 %, 2.5% and 5% of total composition. Figure 7 shows the lignin and fly ash in a 500mL beaker before it is mixed with sodium hydroxide solution for gepolymerisation process to occur.

Figure 7: Lignin and fly ash mix in the beaker ready for mixing

3.2.1 Materials & Equipment

Lignin will be used in this experiment. The prepared geopolymer with optimum ratio will then be used in this part of experiment. The mixing of lignin and geopolymer will be conducted by simple stirring in a 500mL beaker.

3.2.2 Experimental Procedure

1. Based on the total percentages of 1%, 2.5%, and 5% of lignin composition from the total mass of fly ash used, the lignin, fly ash, and sodium hydroxide are weighted in different beakers.

2. The mixture are mixed in a beaker and stirred well.

3. The mixed solution is then put into the mould for the curing condition.

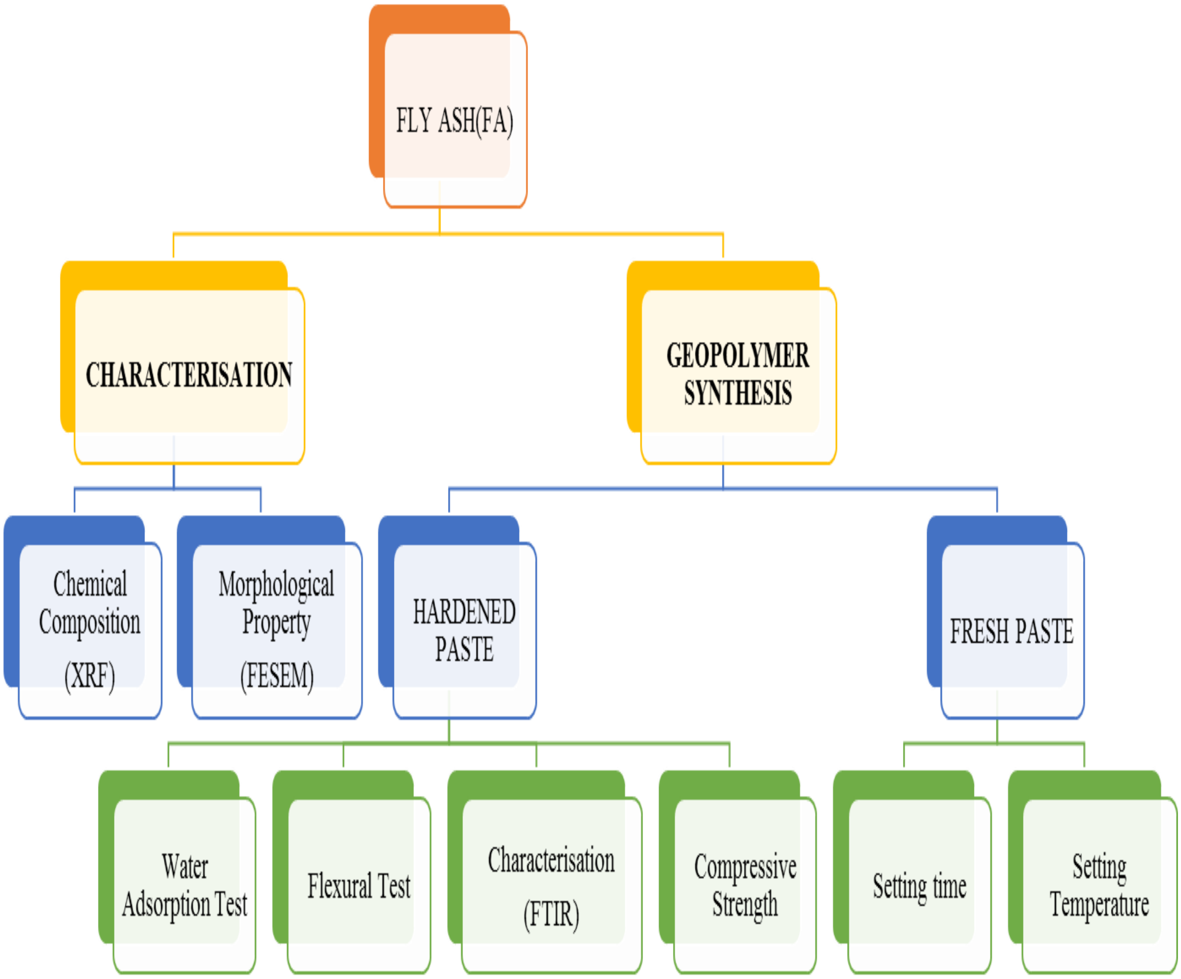


Figure 8: Suggested test for geopolymer paste sample

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3.3 Scanning Electron Microscopy (SEM)

A technique used in materials science to investigate morphological properties which is the molecular surface structures and the geopolymer properties

3.3.1 Materials & Equipment

Geopolymer film, Coating film of lignin geopolymer composite & Hitachi S-3400N SEM equipment.

3.3.2 Operating Procedure

Sample of the film is prepared by using method of sample fracture in order to obtain clean cut of the sample. Sample is placed into the sample holder for gold plating.

Sample is then inserted into the SEM instrument for analysis. Acceleration voltage of

10 kV can be used with secondary electron image as a detector (Perez, et. al, 2007).

3.4 Water Absorption Test

This test is done to determine the susceptibility of geopolymer to the penetration of water. It is done by measuring the increase in the mass of a specimen resulting from absorption of water as a function of time when only one surface of the specimen is exposed to water

3.4.1 Material & Equipment

Oven, airtight container, water

3.4.2 Operating Procedure

1. Sample is heated in the oven at 105^{o}C for half an hour to remove the moisture.

2. The thickness of the sample is measured and recorded.

3. The initial weight of sample is measured and recorded.

4. The sample is immersed in water at room temperature

5. Sample is taken out from water for every 24 hour for weighing until a constant value is obtained. The weight is recorded.

6. Step 1 to 5 is repeated with other sample.

3.5 Flexural test

Flexural test is done to the hardened paste to identify the maximum stain that each specimen can hold. This test is done by bending the specimen to the maximum and the flexibility of each specimen is recorded

3.5.1 Material & Equipment

Simple Beam with Centre-Point Loading

3.5.2 Operating Procedure

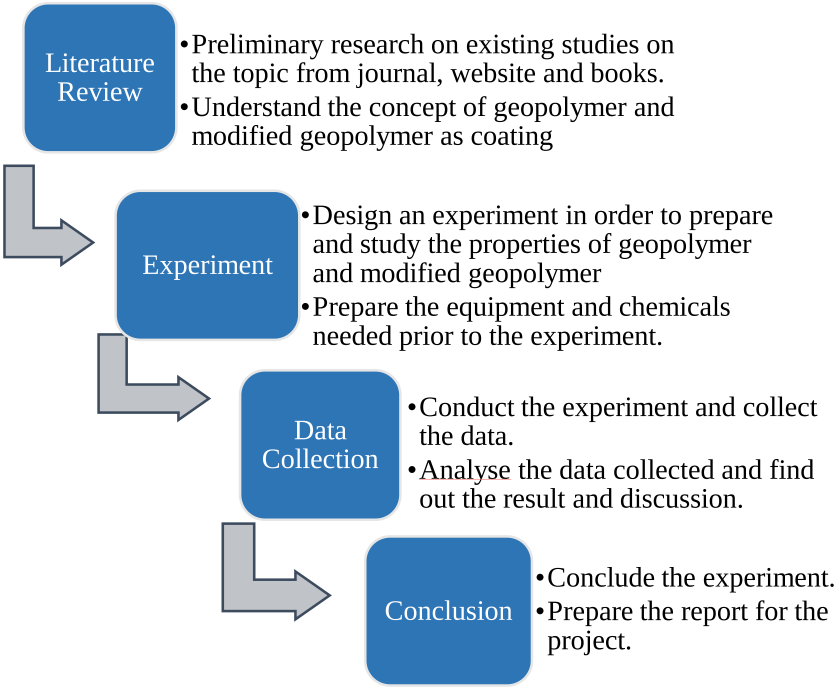
1. Turn the specimen on its side with respect to its position when molded, and center it on the supporting bearing blocks. The load-applying block shall be brought in contact with the upper surface at the center line between the supports.

2. Check to ensure that the beam is in uniform contact with the bearing blocks and the load applying block.

3. Apply load.

3.3 Flow Process of Project Work

According to the time frame, this project is estimated to be finished within approximately 8 months. Stated below is the flow process including research methodology and experimental work suggested for this project:



- Preliminary research on existing studies on the topic from journal, website and books.
- Understand the concept of geopolymer and modified geopolymer as coating

- Design an experiment in order to prepare and study the properties of geopolymer and modified geopolymer
- Prepare the equipment and chemicals needed prior to the experiment.

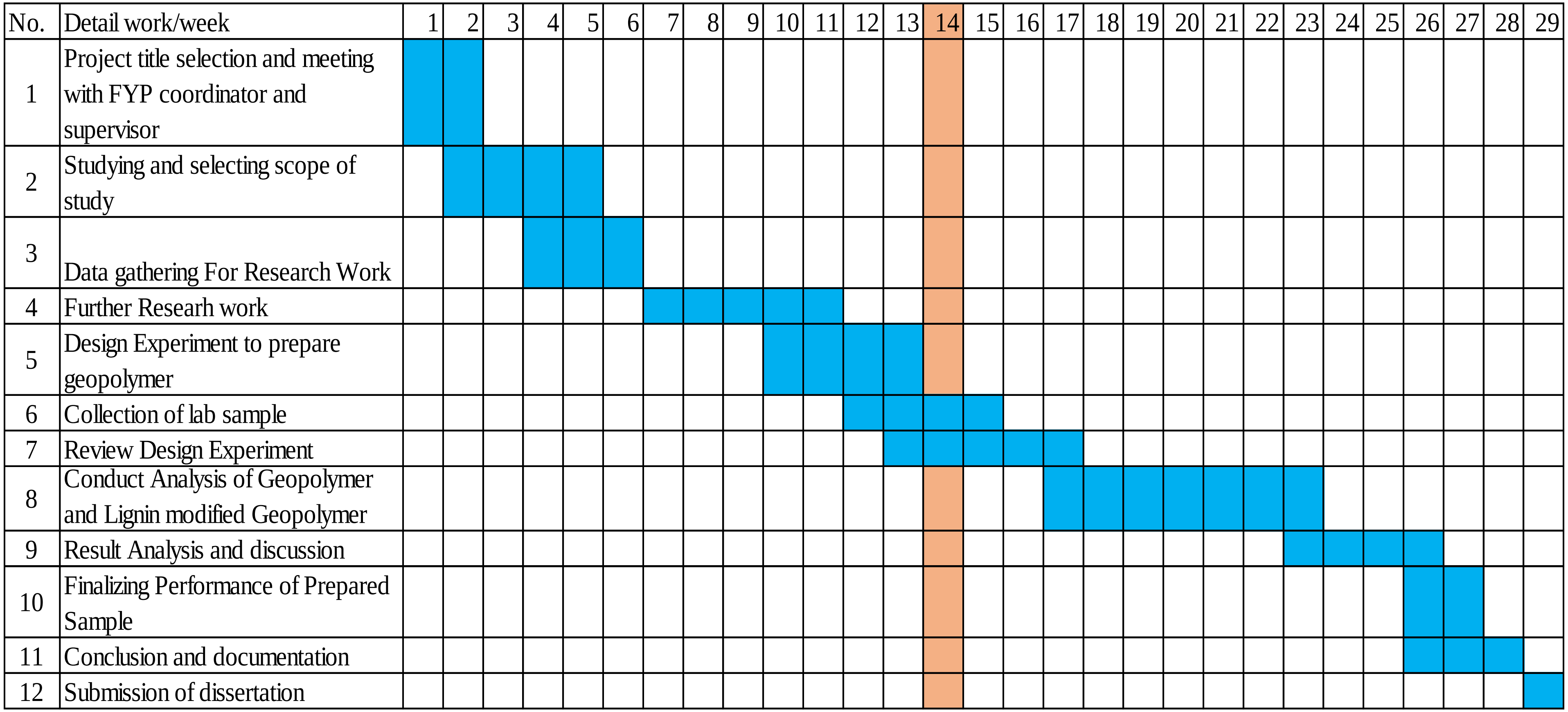
- Conduct the experiment and collect the data.
- Analyse the data collected and find out the result and discussion.

- Conclude the experiment.
- Prepare the report for the project.

Figure 9: Process flow chart of the experiment

3.4 Gantt Chart

To complete the project, an array of steps and procedures are thoroughly identified. These important steps can be used as guidelines to ensure that the project is completed parallel with the timeline given.



No.	Detail work/week	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29
1	Project title selection and meeting with FYP coordinator and supervisor	🟦	🟦												🟧															
2	Studying and selecting scope of study		🟦	🟦	🟦	🟦									🟧															
3	Data gathering For Research Work				🟦	🟦	🟦								🟧															
4	Further Researh work							🟦	🟦	🟦	🟦	🟦			🟧															
5	Design Experiment to prepare geopolymer										🟦	🟦	🟦	🟦	🟧															
6	Collection of lab sample												🟦	🟦	🟦	🟦														
7	Review Design Experiment													🟦	🟦	🟦	🟦	🟦												
8	Conduct Analysis of Geopolymer and Lignin modified Geopolymer														🟧			🟦	🟦	🟦	🟦	🟦	🟦	🟦						
9	Result Analysis and discussion														🟧									🟦	🟦	🟦	🟦			
10	Finalizing Performance of Prepared Sample														🟧												🟦	🟦		
11	Conclusion and documentation														🟧												🟦	🟦	🟦	
12	Submission of dissertation														🟧															🟦

Figure 10: Gantt chart of the Projects

Based on the above figure, author has managed to complete most of the tasks allocated in the chart. The completed tasks are mostly the preliminary work of the project including the selection and confirmation of project title, studying and selecting scope of study and data gathering for research work. Research methodology which involves data gathering is crucial in determining the basic concept of the study. Thus, the experiment will be designed on a strong basic knowledge related to geopolymer. Elements of data gathering, designing the experiment and conducting analysis will take longer period than the other elements.

In designing experiment, author has listed the parameters to be considered and the outcome of the analyses.

3.5 Key Milestone

To monitor the work performance of the project, author has prepared a schedule comprises of tasks that should be completed at specific period. This is important as the schedule helps the author in good deliverability of project by make use of all resources that can be gained. Below is the key milestone for the project which shows the task completed by each week:

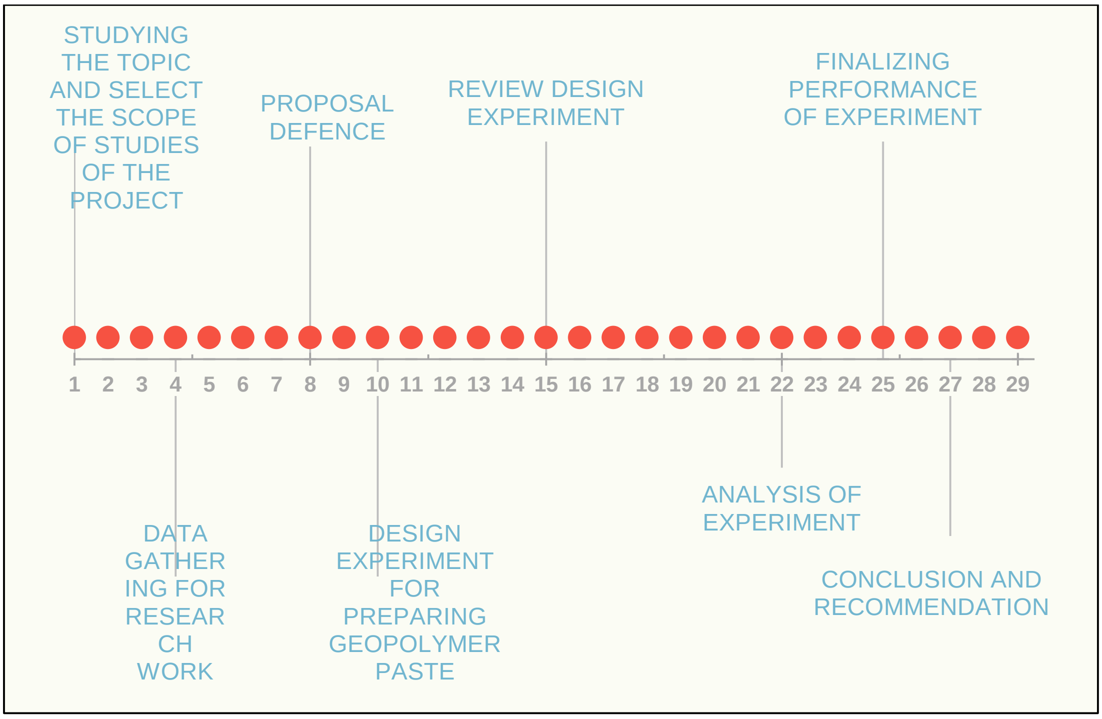


Figure 11: Key Milestone of the project

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Characteristic and Physical Appearance of Sample

The process of mixing the lignin with fly ash and sodium hydroxide is done in a 500ml beaker with well stirring process for about 5 minutes at room temperature. With the introduction of lignin in the geopolymer composite mixing, a significant change can be observed as the viscosity of the mixture increases which caused the mixing process to be more difficult. The maximum percentage of lignin permissible to be mix with geopolymer without changing the other parameter is 5% lignin of the total fly ash mass.

There are two types of sample that had been prepared in this experiment. The first experiment involved the preparation of geopolymer sample without mixing with lignin with different molarity of NaOH and the second experiment involved changing the percentage of lignin in the geopolymer sample. The first experiment is done to test the standard method for preparing the geopolymer sample. From the results of the experiment it is seen that the geopolymer sample of 12M NaOH concentration is the most stable sample as it does not crack during the preparation easily like the other sample.

The purpose of the sample 12M NaOH without lignin is to be compared with the other percentage of the lignin modified geopolymer. From the sample prepared, in figure 12,13,14,15 shows the geopolymer sample without lignin. From the figure, sample with the lower molarity of NaOH have a darker colour compared to sample with higher NaOH molarity.

4.1.1 Geopolymer sample without lignin

Figure 12: Geopolymer sample of 6M concentration of NaOH

Figure 13: Geopolymer sample of 8M concentration of NaOH

Figure 14: Geopolymer sample of 10M concentration of NaOH

Figure 15: Geopolymer sample of 12M concentration of NaOH

4.1.2 Geopolymer sample with lignin

In this experiment the geopolymer sample is prepared using the same molarity of NaOH, same solid to liquid ratio which is 3:1 and the same curing condition. The parameters that is change in this case is the amount of lignin blended into the geopolymer sample. From figure 16, 17, 18 and 19, it shows that the colour of the lignin modified sample is darker as the percentage of lignin is increased in the sample. This is because lignin is brown in colour and this affected the colour of the sample when more lignin is used.

Nonetheless, when the percentage of the lignin is increased more than 5% of the total mass used, the mixing of fly ash, NaOH and lignin shows a significant change as the mixture seems to require additional amount of liquid in order to be mixed well. As seen in figure 20, the sample bend and crack when 7.5% of lignin is used. Therefore, the highest amount of lignin that can be used in this experiment is 5%.

Figure 16: Geopolymer with lignin 0% concentration of lignin in mixture in 12 M NaOH

Figure 17: Geopolymer with lignin 1% concentration of lignin in mixture in 12 M NaOH

Figure 18: Geopolymer with lignin 2.5% concentration of lignin in mixture in 12 M NaOH

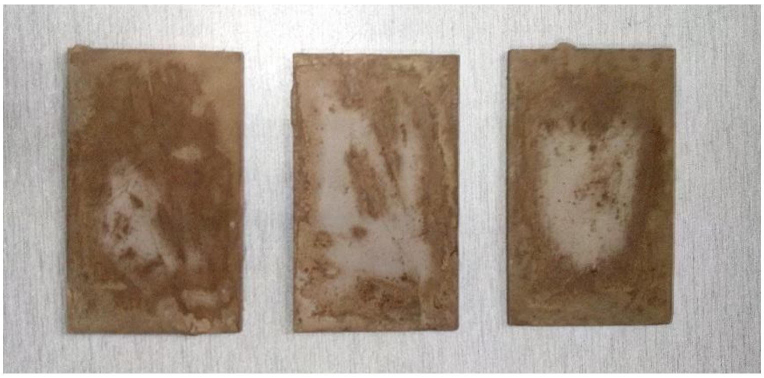


Figure 19: Geopolymer with lignin 5% concentration of lignin in mixture in 12 M NaOH

Figure 20: Geopolymer with lignin 7.5% concentration of lignin in mixture in 12 M NaOH

4.2 Water Absorption Test

The water absorption test had been carried out to study the effect of using different percentage of lignin in the geopolymer sample with the amount of water absorbed by each sample. This test had been done at the room temperature. The rate of water uptake for each lignin modified geopolymer sample were shown in the graph of Percentage of water absorb vs. Time. This test had been carried out by observing the mass changes of each sample. This is done by noting down the mass changes of the sample for each hour starting from the immersion of the sample in water until the mass of the sample is constant.

From the results it is shown that the amount of water uptake of the sample with highest amount of lignin absorb the highest amount of water. The sample of 0% lignin absorb the least amount of water where the percentage of water absorb is 7.6% of the total mass. This is then followed by 1% of lignin where it the percentage of water absorb is 7.8%. The sample with 2.5% lignin absorb the highest amount of water which is 9.1% and lastly lignin modified geopolymer of 5% lignin absorb 9.0% water of the total initial mass. This outcomes contradict with the initial theories where the presence of lignin was supposed to reduce the amount of water permeating into the geopolymer sample. This shows that the presence of lignin does not affect the rate of water uptake. However, the result is considered as insignificant due to the difference of percentage of water uptake between each sample with different percentage of water is very low. Theoretically, sample with higher amount of lignin should absorb the least amount of water. The explanation for this results is explained as the SEM test results is accepted.

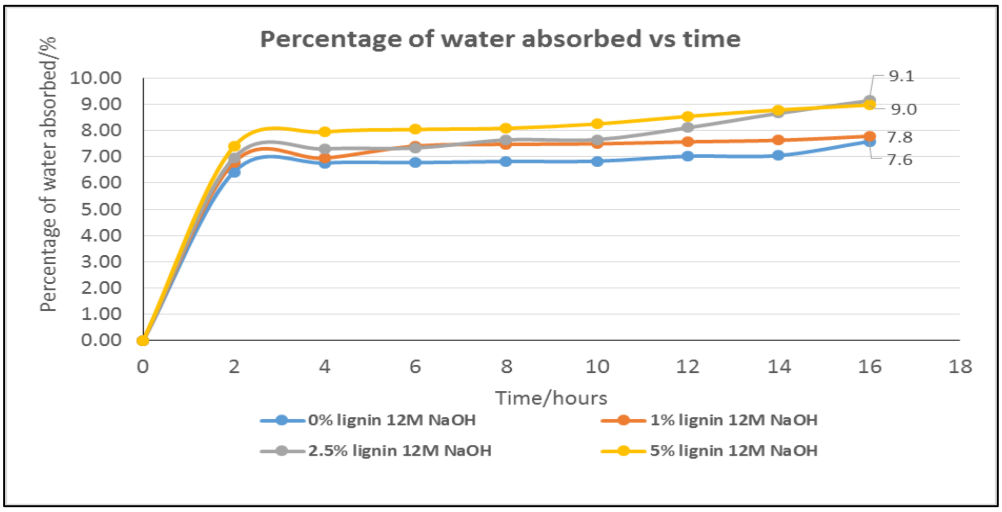


Figure 21: A graph of Water absorption percentage for each composition of lignin

From the data obtained, the diffusion coefficient, D can be found using the Fick's law as stated in "Diffusion in Polymer"(J. Crank, 1968) books that it is possible to deduce an average diffusion coefficient from the initial gradient of the sorption curve when plotted against the square root of time.

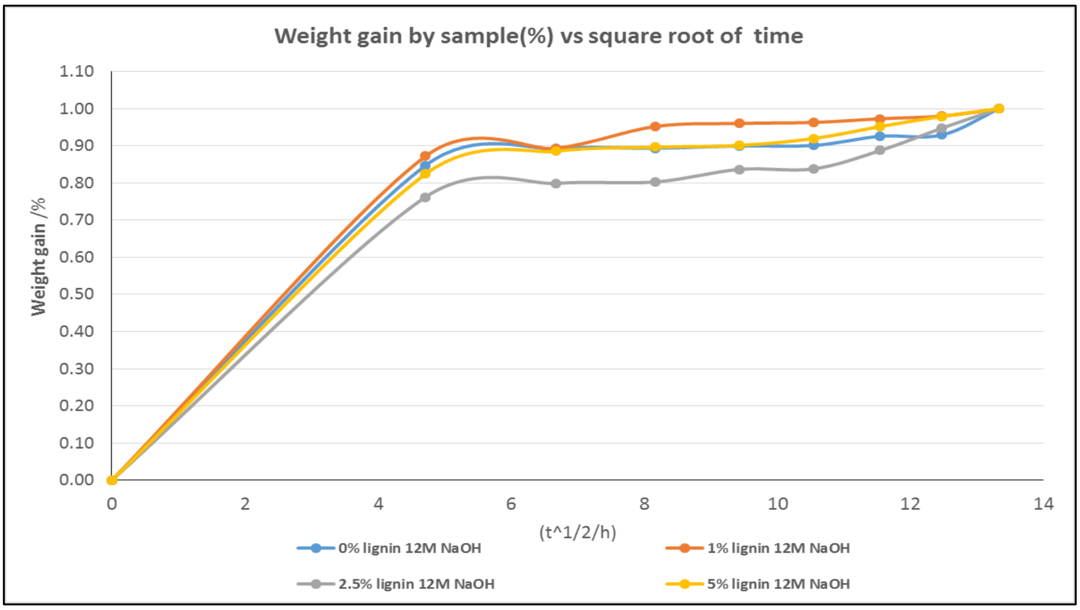


Figure 22: Weight gain (%) vs. square root of time

Therefore the diffusivity, D can be obtained from the initial slope of the moisture gain, M_t/M_∞versus time $(t^{\frac{1}{2}}/h)$(equation 2.5). Based on the plot of the graph, from the initial slope of the graph the value of diffusivity for each sample can be found and is tabulated in the table below:

Table 2: Diffusion coefficient for each sample

Diffusivity, D			
0% lignin 12M NaOH	1% lignin 12M NaOH	2.5% lignin 12M NaOH	5% lignin 12M NaOH
0.0353	0.0363	0.0317	0.0343

Sample calculation (from equation 2.6) for 0% lignin:

$$D = \frac{\pi}{16}\left[\frac{\frac{M_t}{M_\infty}}{\frac{\sqrt{t}}{h}}\right]$$

Where M_t is the mass gain at the reduced time, M_∞ is the maximum mass gain at the equilibrium state. t is the time and h is the thickness of sample.

$$D = \frac{\pi}{16}\left(\frac{6.4261}{7.5855}/\left(\frac{\sqrt{2}}{0.3}\right)\right)$$

$$D = 0.0353$$

From the graph it shows that the water absorption of all specimens was high in the early stages of exposure, after which it slowed down and reached saturation level after prolonged time, following a Fickian's diffusion process. From the diffusion coefficient it can be seen that the diffusivity for the sample of 1% of lignin have the highest value which means the diffusion of water into the geopolymer sample is fastest. And the diffusion of water for sample with the 2.5 % of lignin has the lowest diffusion coefficient of 0.00317 which means water diffuse slower into the sample.

4.3 Flexural test

The flexural test had been done using the 3 point test to determine the flexural strength of each sample that had been prepared. As the data is collected, the strength of sample can then be compared to one another to determine the sample with the highest flexural strength. The test is done using 3 sample. The average results is then calculated.

Based on the result of the flexural test, it shows that the sample with the highest amount of lignin has the lowest flexural strength. This test is also done to the other sample and it shows that as the percentage of lignin is higher in the geopolymer sample, the flexural strength of the sample decreases. The flexural strength of the sample for 0%, 1%, 2.5% and 5% of lignin in geopolymer is 6.08 MPa, 5.301 MPa, 4.253 MPa and 3.514 MPa respectively. The results however contradict with the theories that is used which is the presence of lignin will produce a higher strength sample. The justification of these results is done based on the results of the SEM test that had been produced.

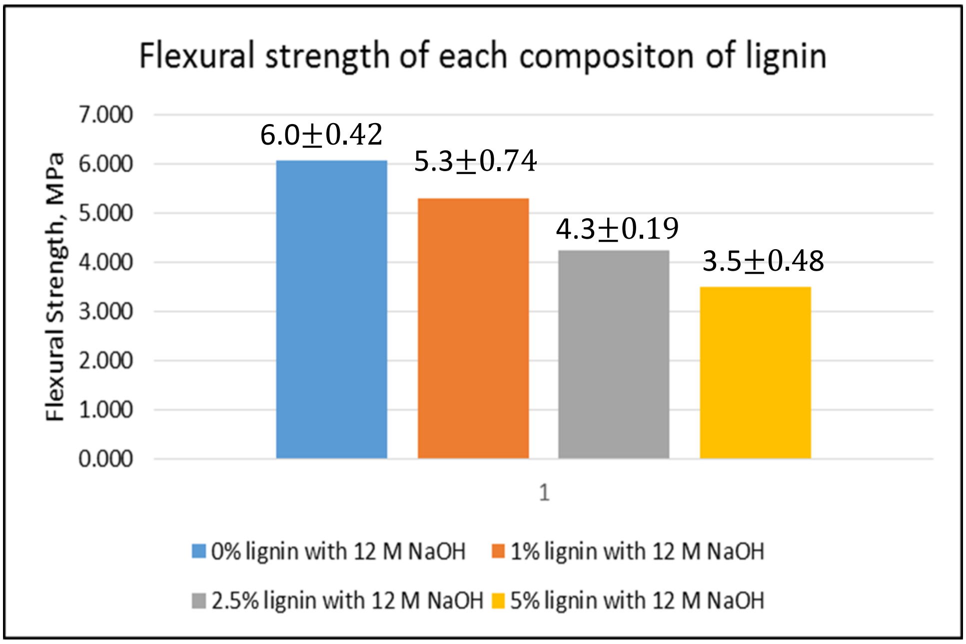


Figure 23: Bar chart of the flexural strength of each composition of sample

4.4 SEM test

SEM test is done to observe the microscopic structure of the samples. The purpose of this test is to observe the surface and fracture surface of the sample.

Based on the Scanning Electron Micrograph (SEM) results, it shows that when the percentage of lignin is increased, the amount and size of unreacted fly ash particle is also higher. The presence of these particle had caused the sample that had been prepared to become unstable. Geopolymer sample with no lignin in this experiment shows that it had a much complete reaction where figure 23 shows that almost all of the fly ash used is reacted with each other.

However, as the amount of lignin increased in the sample, the amount of unreacted fly ash increases. This is because the presence of lignin in the geopolymer system had caused the NaOH used in the mixing had been reacting with the lignin. This caused the sample to have less NaOH to react with the fly ash. Presence of the unreacted fly ash also had caused the sample to have more pores as seen in figure 26. Increased in the percentage of the lignin also brings about the process of mixing for the sample problem.

As explained earlier, the amount of lignin influence the mixing process where the stirred mixture becomes more viscous as the percentage of lignin is higher. This stated problem brings about the formation of air bubble in the geopolymer system. The pores/ air bubble will then allow more water to be absorb into the sample system which is why the percentage of the water absorb in the Water Absorption Test prove that sample with higher amount of lignin absorb a larger quantity of water. Thus, the unreacted fly ash and the presence of pores had decreased the stability of the sample making it to be more fragile.

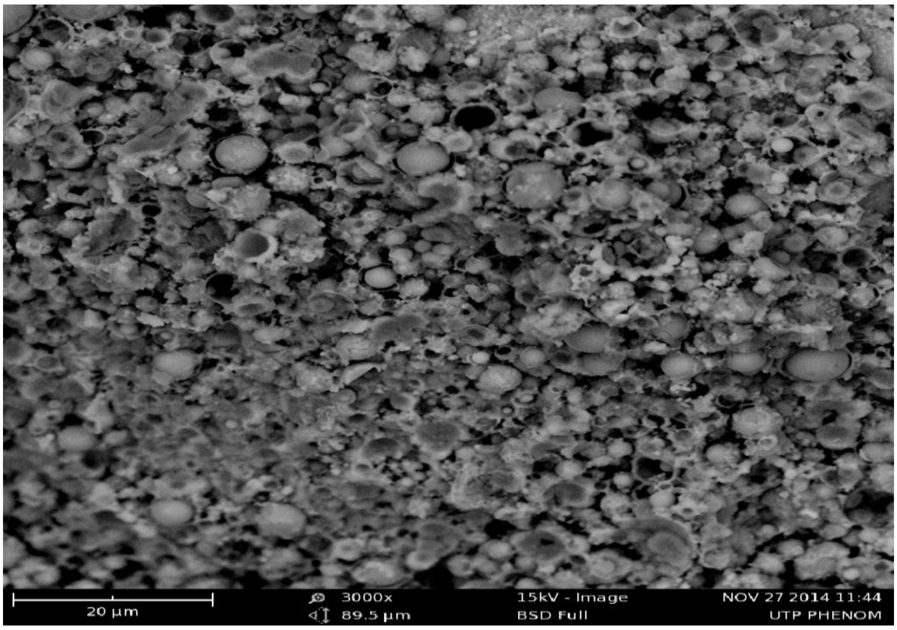


Figure 24: SEM test on 0% lignin of 12M NaOH

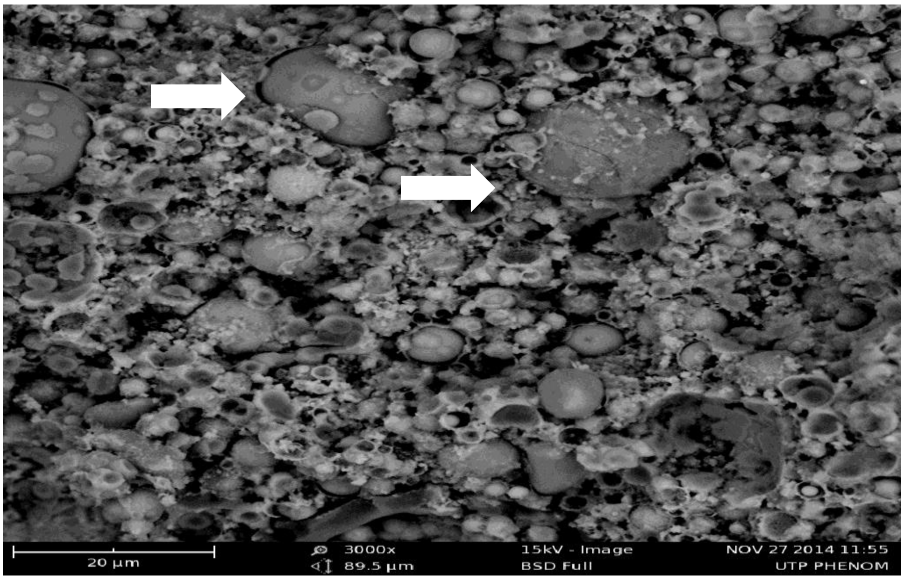


Figure 25: SEM test on 1% lignin of 12M NaOH

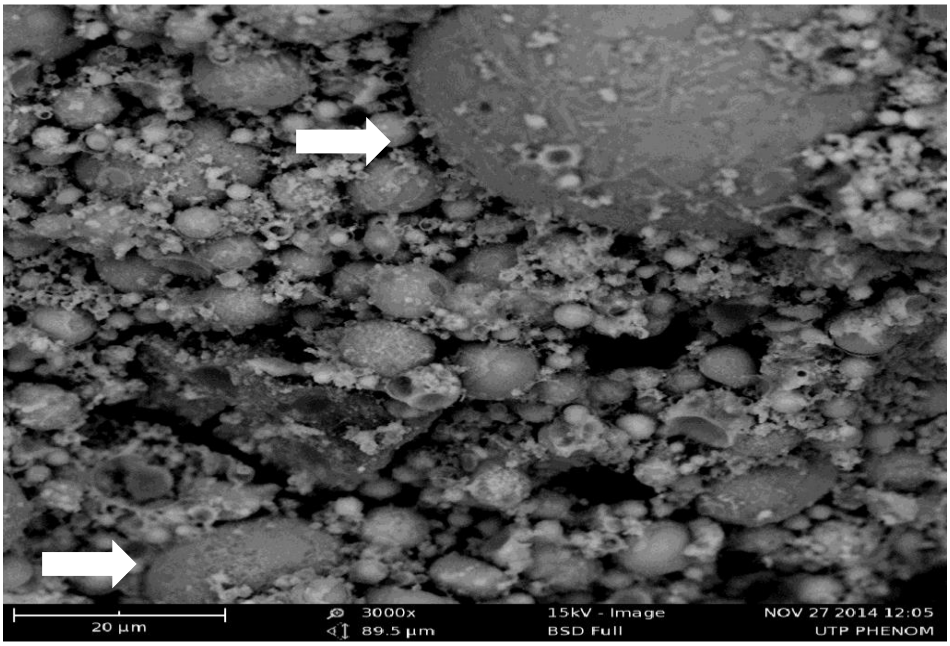


Figure 26: SEM test on 2.5% lignin of 12M NaOH

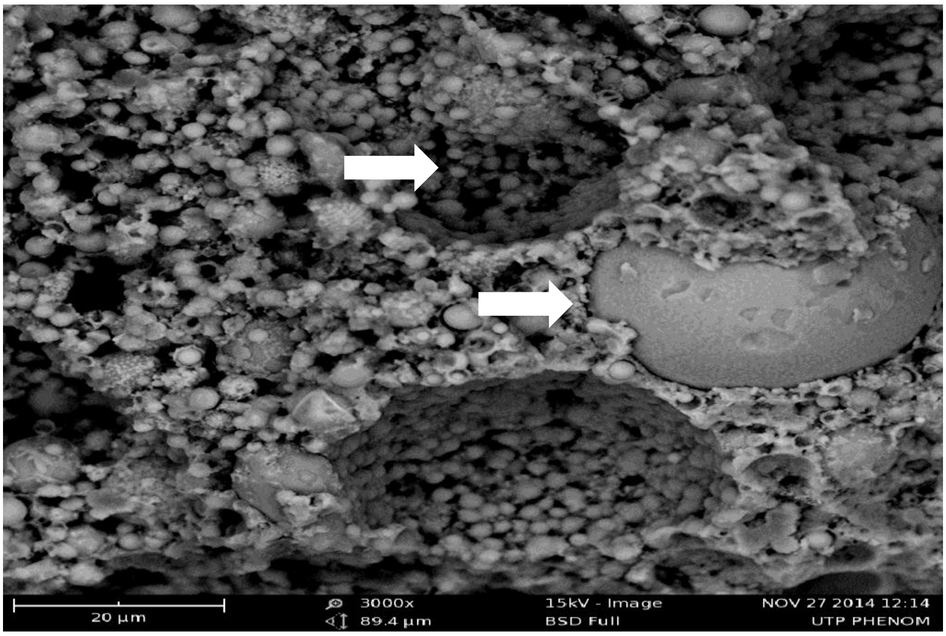


Figure 27: SEM test on 5% lignin of 12M NaOH

CHAPTER 5: CONCLUSION AND RECOMMENDATION

5.1 Conclusion

The aim of this project is to study the effect of implementing the lignin with geopolymer so that the solution to the water absorption criteria of geopolymer can be found. The results of this experiment shows that the application of lignin in the geopolymer sample to have a different results compared to the expected results. The projects shows that the presence of lignin increase the pore size of the sample. Hence, more water is absorbed. The presence of lignin also reduce the flexural strength of the sample.

Nevertheless, as this is a new study on the particular matter, this research can be further carried out by manipulating certain parameters such as the solid to liquid ratio that had been used, the percentage of lignin used and the curing time or temperature of this experimental work. These parameter to synthesize geopolymer can also be further manipulated and modify in a way that the produces product will have a better properties. This research can be modified further to benefit human in long term aspect as we on the verge off acing the issue of depletion of natural resources and the problem of the emission of Green House Gases (GHG). Thus, it is hoped that from the finding of this research can reduce the amount of GHG released beside for it to be applicable in modernizing and to ease human life.

By taking into account all of the performance tests parameters, the preparation of the geopolymer paste and also the lignin modified geopolymer paste, this experiment can be justified and the objectives of the project will be achieved where the physical properties of geopolymer coating had been prepared and analyse, the lignin modified geopolymer coating had been prepared and the physical properties and water absorption characteristic of lignin modified geopolymer coating had been studied.

In addition, this project is feasible by taking into account the time constraint and the capability of final year student with the assist from the supervisor and coordinator. It is a big hope for the accomplishment of this study.

5.2 Recommendation

The recommendation for this project is that the properties of the geopolymer can be further enhance. By enhancing the chemical and mechanical properties of the geopolymer, a product that have a higher resistance towards the severe environment can be produce. A deeper insight into the behaviour of materials and structures exposed to environmental agents would require a proper experimental investigation, in particular under real conditions, in order to properly define the relationships between results obtained under accelerated and long-term exposure tests. The geopolymer can also be further manipulated and modify in a way that the produces product will have a better properties than the existing yields

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APPENDICES

Table 3: Table of changes in mass of geopolymer sample for water absorption test

Time	0% lignin 12M NaOH	Percentage of water absorb/%	1% lignin 12M NaOH	Percentage of water absorb/%	2.5% lignin 12M NaOH	Percentage of water absorb/%	5% lignin 12M NaOH	Percentage of water absorb/%
0	27.1253	0	26.8414	0	21.4389	0	21.0942	0
2	28.8684	6.4261	28.6635	6.7884	22.9319	6.9640	22.6543	7.3959
4	28.9610	6.7675	28.7069	6.9501	23.0040	7.3003	22.7699	7.9439
6	28.9641	6.7789	28.8306	7.4109	23.0117	7.3362	22.7905	8.0415
8	28.9765	6.8246	28.8478	7.4750	23.0776	7.6436	22.7998	8.0856
10	28.9790	6.8338	28.8534	7.4959	23.0803	7.6562	22.8347	8.2511
12	29.0304	7.0233	28.8742	7.5734	23.1772	8.1082	22.8959	8.5412
14	29.0372	7.0484	28.8889	7.6281	23.2949	8.6572	22.9477	8.7868
16	29.1829	7.5855	28.9308	7.7842	23.3977	9.1367	22.9868	8.9721

Table 4: Table for mass gain by geopolymer sample

(t^1/2)/l	M(t)/M(infinity) for sample of 0% lignin	M(t)/M(infinity) for sample of 1% lignin	M(t)/M(infinity) for sample of 2.5% lignin	M(t)/M(infinity) for sample of 5% lignin
0	0	0	0	0
47.14045	0.847152022	0.872068536	0.762201348	0.824315756
66.66667	0.89215591	0.89284005	0.799009598	0.885395752
81.64966	0.893662519	0.952043649	0.802940576	0.896280249
94.2809	0.899688958	0.960275677	0.836583623	0.901194124
105.4093	0.900903966	0.962955872	0.837962018	0.919634365
115.4701	0.925884526	0.972910884	0.88743108	0.951970834
124.7219	0.929189347	0.979946396	0.947518889	0.97934059
133.3333	1	1	1	1

Table 5: Composition of each lignin modified sample and the flexural strength

Test No.	Sample			
	0% lignin with 12 M NaOH(Mpa)	1% lignin with 12 M NaOH(Mpa)	2.5% lignin with 12 M NaOH(Mpa)	5% lignin with 12 M NaOH(Mpa)
1	5.728	4.557	4.173	3.276
2	5.847	6.045	4.519	4.183
3	6.689	-	4.068	3.082
Average	6.088	5.301	4.253	3.514

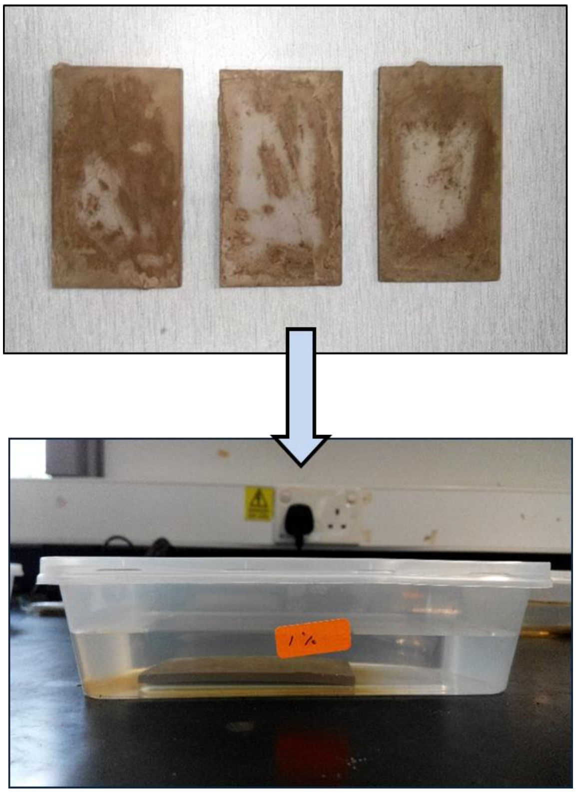

Figure 28: Water absorption test

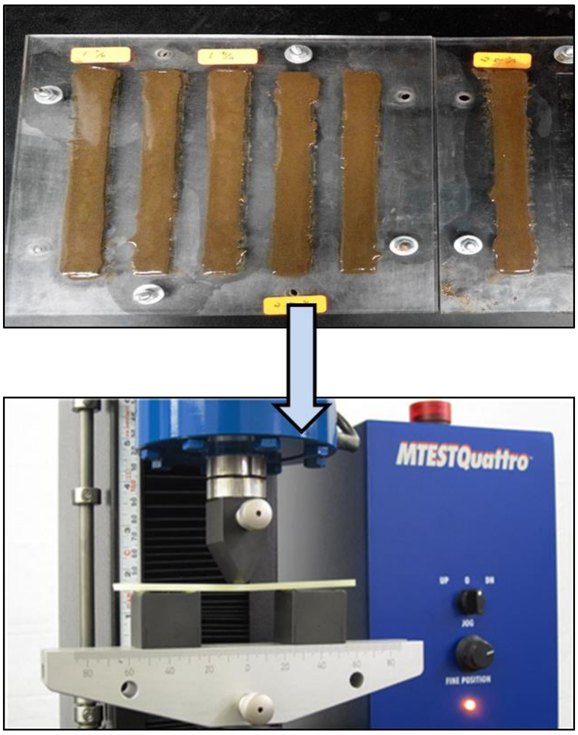

Figure 29: Flexural test

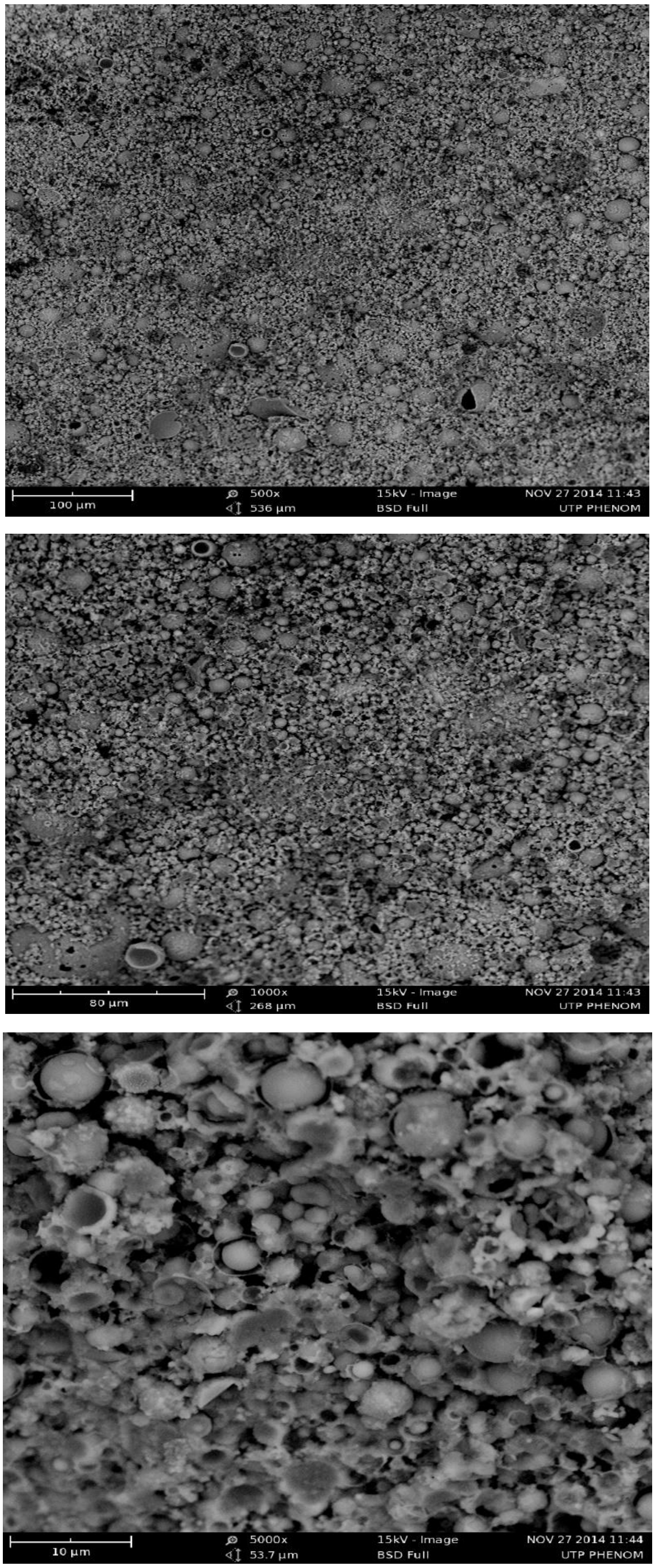

Figure 30: SEM micrograph for 500x, 1000x and 5000x magnifications for 0% lignin

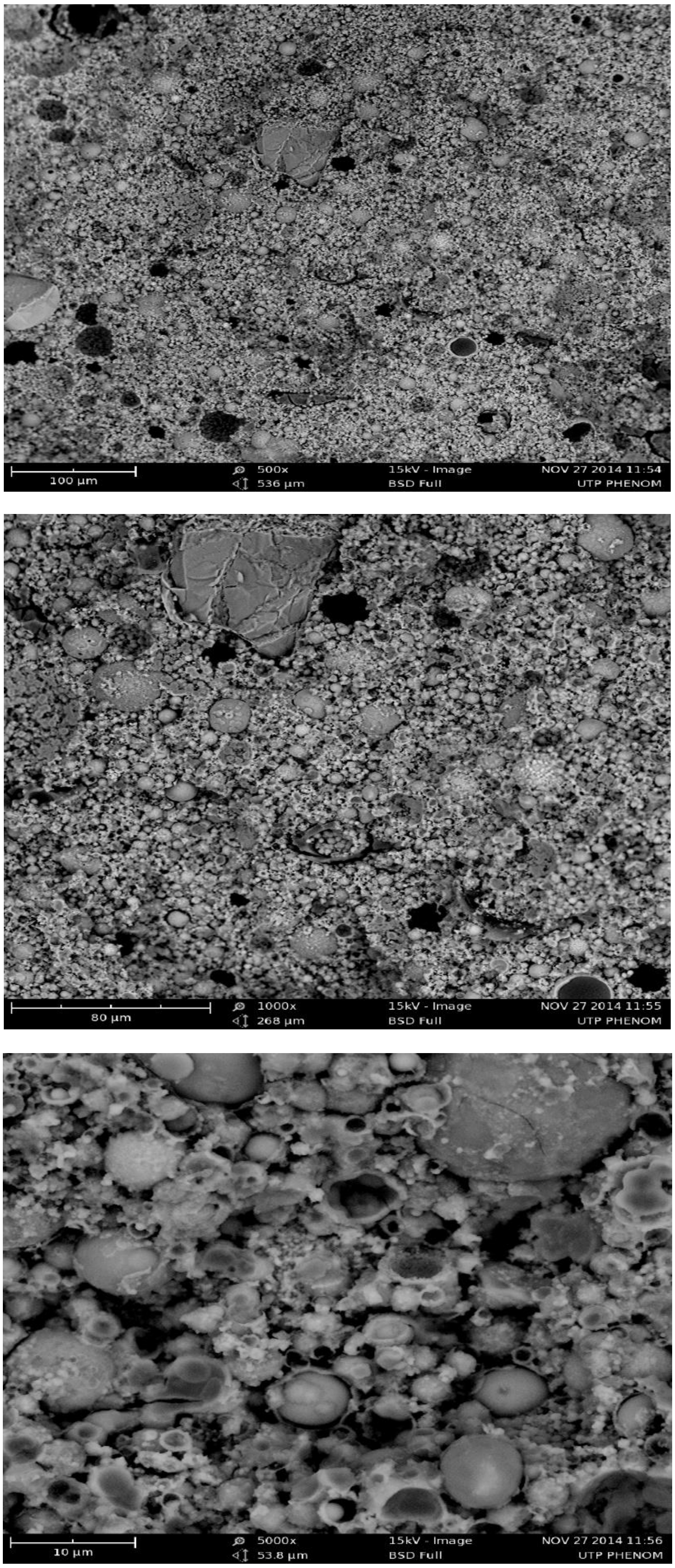

Figure 31: SEM micrograph for 500x, 1000x and 5000x magnifications for 1% lignin

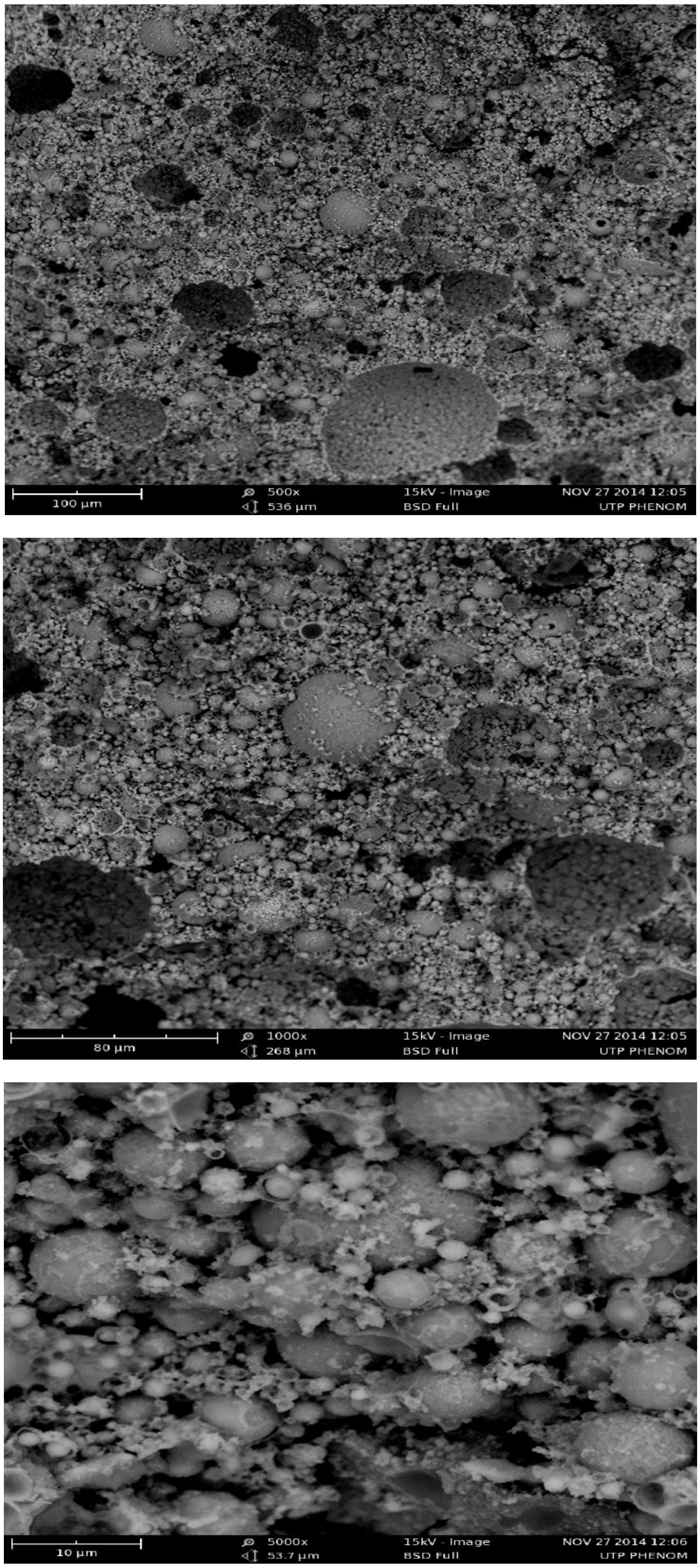

Figure 32: SEM micrograph for 500x, 1000x and 5000x magnifications for 2.5% lignin

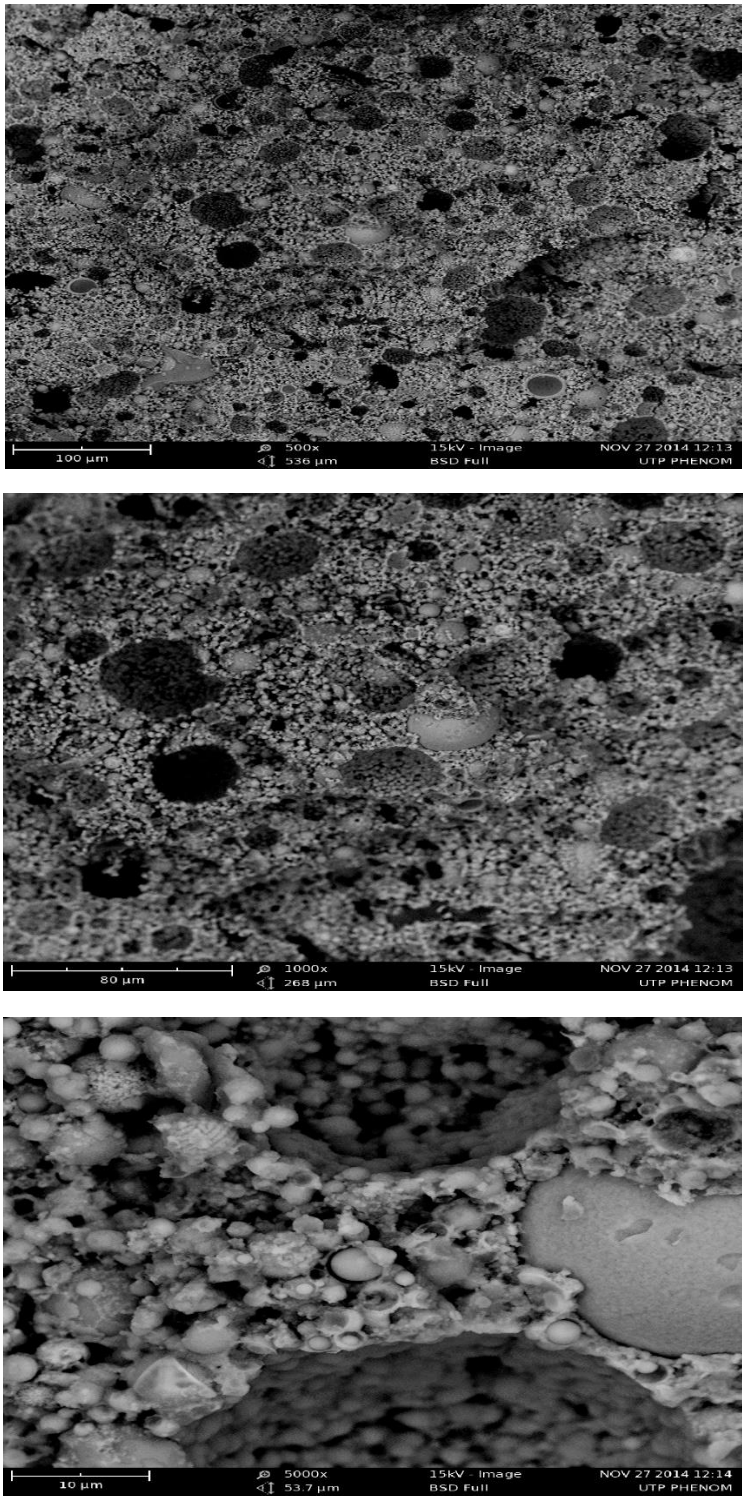

Figure 33: SEM micrograph for 500x, 1000x and 5000x magnifications for 5% lignin