Geopolymer-based Coating Material for Metal Substrate

by

Ho Kit Mun

Dissertation submitted in partial fulfillment of
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CERTIFICATION OF APPROVAL

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Approved by,

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UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

May 2012

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the originality 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.

(HO KIT MUN)

ABSTRACT

Coating is an applied layer on the substrate to enhance properties of the substrate. Geopolymer is produced through geopolymerization between alumina-silicate and alkaline solutions and has a great potential to be utilized as geopolymer-based coating material. The aim of this study is to investigate the properties of the geopolymer and geopolymer coated steel using microwave incinerated rice husk ash (MIRHA) and fly ash as the source of alumina and silica for the geopolymerization process. Characterizations were used to characterize the raw materials and geopolymers such as chemical composition and structure while geopolymerization was done by varying the synthesis parameters such as solid/liquid ratio and SiO_2/Al_2O_3 ratio.

The results showed that the setting time of geopolymer decreased with increasing solid/liquid ratio, while the highest compressive strength of 31.78MPa was obtained when the solid/liquid ratio was 3.0 with 15% MIRHA addition. It was also observed that the change in mass of geopolymer due to water absorption ranged from 0.002% to 0.018% only. The results also showed that the coating thickness increased with increasing solid/liquid ratio while the adhesive strength increased with the reduction in solid/liquid ratio as well as the addition of MIRHA where the highest adhesive strength which was larger than 15MPa, was achieved at solid/liquid ratio and MIRHA addition of 2.0 and 15%, respectively. Moreover, the corrosion level of the geopolymer coated steel decreased with the addition of MIRHA and increasing solid/liquid ratio. From this study, MIRHA could be a potential raw material to enhance the performance of geopolymer as a coating material.

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ABBREVIATIONS AND NOMENCLATURES

ASTM	American Society of Testing and Materials
BET	Brunauer-Emmett-Teller
FESEM	Field Emission Scanning Electron Microscope
FTIR	Fourier Transform Infrared
MIRHA	Microwave Incinerated Rice Husk Ash
OPC	Ordinary Portland Cement
PSA	Particle Size Analyzer
RHA	Rice Husk Ash
RHBA	Rice Husk And Bark Ash
XRD	X-ray Diffraction
XRF	X-ray Fluorescence

CHAPTER 1

INTRODUCTION

1.1 Background of Study

1.1.1 Coating

Coating is a protective layer which can be applied to the surface of metal substrates in order to enhance the properties of the metal substrates in terms of physical, chemical, and mechanical properties. Nevertheless, the current materials used for metal coating such as epoxy resin, cementitious materials and intumescent paints exhibit certain limitations and disadvantages. The disadvantages such as high cost, heavy, poor flexural strength, etc., have been limiting the performance of the coating materials. For instance, epoxy resins possess a relatively short working pot life which increases the cost of coating material in order to protect the metal substrate from corrosion. In order to cope with the limitations of the coating materials, various researches have been conducted to improve the properties of the coating material and there exists a novel class of materials called geopolymer or alkali activated alumina-silicate (Jadambaa et al., 2011) which exhibit favorable properties as coating material.

1.1.2 Geopolymer

Geopolymer, which is also known as inorganic polymer, is similar to the zeolites in chemical composition, but it reveals an amorphous microstructure (Xu H. et al., 2000). The formation of geopolymer may involve the use of byproducts or industrial wastes such as fly ash, slag, and etcetera (Divya et al., 2007). The utilization of byproducts and industrial wastes provide a mature and cost effective solution to many problems where hazardous residue has to be treated and stored under critical environmental conditions.

Geopolymer can be prepared by geopolymerization between alumina-silicate with alkaline solution. It is environmental friendly and need moderate energy to produce. Other than that, its advantages include low cost, reduced greenhouse emissions, high compressive strength, good adhesiveness, acid resistant, fire resistant, low thermal conductivity, durable and etc. (Duxson P. et al., 2007).

1.2 Problem Statement

The purpose of coating is to protect and thus to enhance the properties of the metal substrates. However, the existing coating materials such as epoxy resins, cementitious material and intumescent paint exhibit certain disadvantages include high cost, limited properties performance, harmful to environmental, etc. Geopolymer-based coating materials have high potential to replace the existing coating materials as geopolymer displays properties such as high compressive strength, anti-corrosion, fire resistivity, durability, etc.

More recently, agriculture waste has been researched as a raw material for geopolymerization. In this study, microwave incinerated rice husk ash (MIRHA) has been proposed as the source of raw material in order to enhance the mechanical strength of the geopolymer. As Malaysia is one of the rice producing country in the world, there is a great potential to develop the use of MIRHA which can be achieved by burning the rice husk at high temperature in the production of geopolymer-based coating material. Rice husk contains high SiO_2 content which is one of the necessary raw materials for geopolymerization (Della et al., 2002). The use of MIRHA is expected to improve the performance in properties of geopolymer-based coating materials. Since the source of information available is still limited, this study is considered as an innovative approach in providing better understanding of MIRHA and better parameter control of geopolymerization.

1.3 Objectives of Study

The four main objectives of the study are:

- to characterize the raw materials and geopolymer
- to investigate the effect of solid/liquid ratio and SiO_2/Al_2O_3 ratio on the properties such as setting time, compressive strength and water absorption of the geopolymer
- to investigate the effect of solid/liquid ratio and SiO_2/Al_2O_3 ratio on the coating properties such as coating thickness and adhesive strength of the geopolymer
- to investigate the effect of solid/liquid ratio and SiO_2/Al_2O_3 ratio on the corrosion resistivity of geopolymer coated metal against acid

1.4 Scope of Study

The scope of this study consists of characterizations and synthesis parameters of the geopolymerization process. Firstly, the characteristics of the fly ash and microwave incinerated rice husk ash (MIRHA) were determined and subsequently the geopolymer in order to determine the relationship between the composition of raw materials and the properties of the geopolymer-based coating material. Secondly, the study was continued with the manipulation of the synthesis parameters which are solid/liquid ratio and SiO_2/Al_2O_3 for the purpose of improving the properties of the geopolymer-based coating material. In this study, the solid/liquid ratio was manipulated by changing the ratio of solid fly ash and MIRHA to liquid which consists of sodium silicate and sodium hydroxide whilst the SiO_2/Al_2O_3 ratio was controlled by changing the percentage of MIRHA used to replace fly ash and meanwhile maintaining the ratio of sodium hydroxide to sodium silicate. For the geopolymer in fresh paste form, the setting time was determined whilst the hardened geopolymer was tested to obtain its compressive strength and water absorption. Subsequently, the geopolymer coated metal was tested to determine the thickness coating, adhesive strength and corrosion resistivity of the geopolymer.

CHAPTER 2

LITERATURE REVIEW

2.1 Geopolymerization

Geopolymerization is a geo-synthesis reaction between alumina-silicate and alkaline solution to produce geopolymer (Duxson P. et al., 2006). It is a newly developing field of research which provides a mature and cost effective solution to many problems by utilizing solid wastes and byproducts where hazardous residue has to be treated and stored under critical environmental conditions (Divya et al., 2007). Hence, it is considered environmental friendly and it needs only moderate energy for the process. It has been shown that the raw material selection and processing conditions play crucial role in determining the properties and characteristics, including high compressive strength, low shrinkage, fast or slow setting, acid resistance, fire resistance, and low thermal conductivity of the geopolymers (Duxson P. et al., 2006).

The main sources of geopolymerization can be described in three categories which are raw material, inactive filler, and geopolymer liquor.

2.1.1 Raw Material

Raw material plays vital role as structure forming species during the formation of geopolymer, many studies have been conducted in order to develop various methods to improve the properties and durability of the geopolymer. To achieve this purpose, a wide range of different raw materials have been used. Primarily, Davidovits (1984) used kaolinite and metakaolin as a source of alumina silicate to synthesis geopolymer. Compared to kaolinate, metakaolin which can be derived from kaolinite by a series of treatments include calcination, removal of Fe and bleaching, is a kind of artificial pozzolanic material with higher reaction activation. Thus, it is comparatively used in the industry extensively. Nevertheless, the addition of kaolinite is necessary to produce gel at desired composition as there is insufficient of Al dissolution. Meanwhile, excess addition of kaolinite may cause the cease of reaction since it may not take part in the synthesis process (Van Jaarsveld et al., 2002).

In recent years, the use of natural minerals and industrial wastes such as fly ash, slag, and waste glass was also investigated as the source of raw material for geopolymerization. Fly ash is the main solid waste generated from the coal-fired power stations which can cause significant environmental problems. Currently, the worldwide electric power industry relies on the use of coal as a primary energy source and it is estimated that the amount of fly ash produced can reach as high as 800 MT by the year 2010 (Palomo et al., 2005). Except for use in cement and other construction products, most of the fly ash is disposed-off causing environmental problems such as air, soils, and surface and ground-water pollution (Dimitrios P. et al., 2006). These conditions have led to the use of fly ash as the novel and value-added product in construction materials, recovery of metals, and agriculture (Li L. et al., 2006).

The main component of fly ash is alumino-silicate and hence it is also known as a cheap source of Si and Al for zeolite synthesis. According to Holler and Wirsching (1985), who were the first researchers to synthesize zeolites from fly ash, there were a lot of investigations such as hydrothermal process where the fly ash is mixed with an alkali solution at different conditions of temperature, pressure, and reaction time to convert fly ash to zeolites. Other than that, the hydrothermal conversion of fly ash can also produce alumino-silicate in amorphous form, which can be referred to as geopolymer.

Rice is a primary source of food especially in Asian region and the paddy field covers 1% of the earth's surface. Globally, there is about 600 million tons of rice paddy produced every year. Rice husks are the byproducts from rice paddy field milling industries and there are approximately 22% of husks that can be produced from each ton of dried rice paddy (Della V.P. et al., 2002). Hence, the global production of rice husks can reach 120 million tons annually.

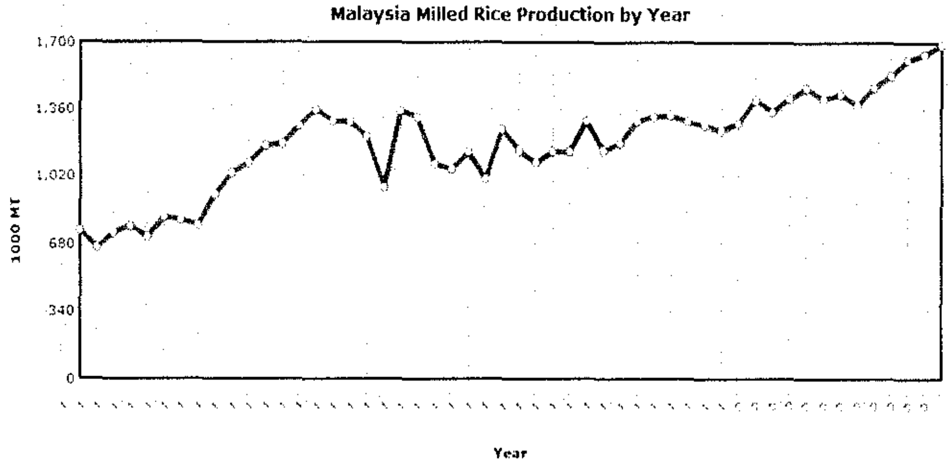


Figure 2.1 Malaysia Milled Rice Production by Year from Index Mundi from 1960 to 2011

Malaysia as one of the worldwide rice growing nations, the generation of waste residue such as rice husk is quite tremendous. According to the Index Mundi as shown in Figure 2.1, the milled rice production of Malaysia reaches 1690,000 MT in 2011, whilst the rice husk produced is as high as 371,800 MT. However, rice husk is highly resistant to natural degradation and this may threaten the environment. This causes a big problem in disposing the rice husk since open heap is not allowable and the only disposal way being used now is going into landfill. In order to cope with this problem, the literature shows that there are varieties potential uses of rice husk when it is burned into ash (Kartini K. at el., 2008). The rice husk ash (RHA) is generated by burning the rice husk from 500 to 1400°C at varying time interval (Della V. P. at el., 2002).

In recent years, microwave incineration has been introduced to produce microwave incinerated rice husk ash (MIRHA) which is proven to be the best method to produce amorphous silica (Nuruddin M. F., et al., 2010). After investigation, it has been shown that RHA from microwave incineration has high content of SiO_2 which assists in enhancing the properties. Thus, the investigations of chemical, mechanical properties and durability are encouraged to develop the use of microwave incinerated rice husk ash besides protecting the environment.

The production of MIRHA is described in Figure 2.2. The controlled burned ash is used as a cement replacement due to its reactivity and the improvement of mechanical strength with the presence of RHA. After burning, the SiO_2 content of microwave incinerated rice husk ash can reach as high as 90% - 95% (Della V. P., 2002). Previous research has shown that the SiO_2 in RHA formed by combustion below 800°C was found to be amorphous with particle average diameter of 20μm, while at the combustion above 900°C, the SiO_2 in RHA consisted of cristobalite and a small amount of tridymite with particle size of 40 – 60μm (Sun L., et al., 2001). The structure and size of RHA may influence the properties of the geopolymer formed. Theoretically, burning the rice husk at higher temperature will increase the SiO_2 content but it is not recommended to burn the rice husk above 800°C longer than 1 hour since it tends to cause sintering effect (coalescing of fine particles) and it is indicated by a dramatic reduction in specific area (Nuruddin M. F., n.d.).

Figure 2.2 The Production of Microwave Incinerated Rice Husk Ash

2.1.2 Inactive Filler

The function of inactive filler in geopolymerization process is to supply Al^{3+} ions and it mainly consists of kaolinite and metakaolin. In the chemistry of geopolymer, the use of inactive filler which is rich in Al^{3+} is to complete the sialate (silicon-oxo-aluminate) network. The mechanism of geopolymer involves the polycondensation reaction of geopolymeric precursor which is alumina-silicate with alkali polysialates. Thus, sufficient Al^{3+} ions are important in the completion of geopolymerization (Divya et al., 2007). However, the utilization of inactive filler in the geopolymer synthesis is optional, which means the utilization of inactive filler is unnecessary when the raw materials contain sufficient Al^{3+} ions to complete the geopolymerization reaction.

2.1.3 **Geopolymer Liquor**

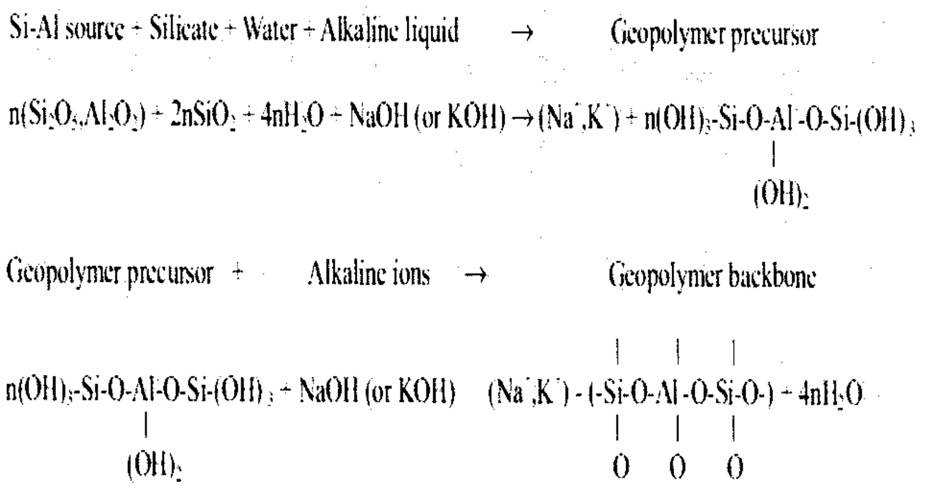
Geopolymer liquor can be divided into two groups which are alkali hydroxide for the dissolution of raw material and sodium (or potassium) silicate solution acting as binder (Phair J. W. at el., 2001). Theoretically, any alkali and alkali earth cation can be used as the alkali element of geopolymerization. Nevertheless, most of the current studies focus on the use and effect of potassium and sodium hydroxide.

According to Divya (2007), the alkali metal salts and/or hydroxide are necessary for the dissolution of silica and alumina as well as for the catalysis of the condensation reaction. It helps to allow the transformation of glassy structure into a very compacted composite partially or totally.

The type of alkali metal cation used for geopolymerization is selected based on many factors where one of the most important factors is the type of source materials as well as the application purpose of the geopolymers (Van Jaarsveld at el., 2002). For instance, the sodium silicate has been used for centuries for the production of commercial products such as special cements, coatings, moulded articles, and catalysts. The addition of alkali metal cations control and influence almost all stages of geopolymerization especially during gel hardening and crystal formation since it contributes more on the structure formation of geopolymer.

2.2 Mechanisms of Reactions

According to Divya (2007), the mechanisms of reactions for geopolymerizations can be described by Figure 2.3 and Figure 2.4.



Si-Al source + Silicate + Water + Alkaline liquid → Geopolymer precursor

$$n(Si_2O_5,Al_2O_2) + 2nSiO_2 + 4nH_2O + NaOH\ (or\ KOH) \rightarrow (Na^+,K^+) + n(OH)_3\text{-}Si\text{-}O\text{-}\underset{\underset{(OH)_2}{|}}{Al^-}\text{-}O\text{-}Si\text{-}(OH)_3$$

Geopolymer precursor + Alkaline ions → Geopolymer backbone

$$n(OH)_3\text{-}Si\text{-}O\text{-}\underset{\underset{(OH)_2}{|}}{Al^-}\text{-}O\text{-}Si\text{-}(OH)_3 + NaOH\ (or\ KOH) \quad (Na^+,K^+)\text{-}(\text{-}\underset{\underset{O}{|}}{\overset{|}{Si}}\text{-}O\text{-}\underset{\underset{O}{|}}{\overset{|}{Al^-}}\text{-}O\text{-}\underset{\underset{O}{|}}{\overset{|}{Si}}\text{-}O\text{-}) + 4nH_2O$$

Figure 2.3 Reactions of Geopolymerization

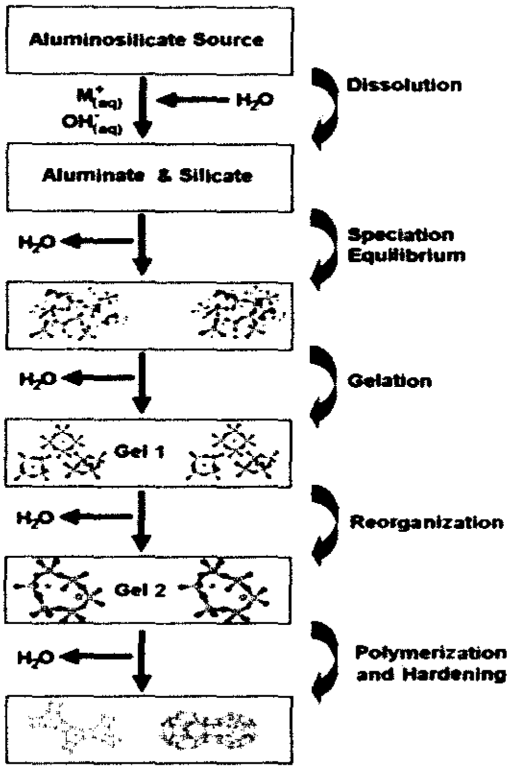


Figure 2.4 Conceptual Model for Geopolymerization

In 1950s, Glukhovsky (1959) had proposed a general mechanism for alkali activation of materials primarily comprising silica and reactive aluminum. According to the Glukhovsky model, there are three stages of geopolymerization which are destruction-coagulation, coagulation-condensation, and condensation-crystallization. Firstly, the dissolution of alumina silicate by alkaline hydrolysis produces aluminate and silicate species. The dissolution of solid particles at the surface causes the liberation of aluminate and silicate into solution. Once the species in the solution released by dissolution are incorporated into the aqueous phase, it may already contain silicate present in the activating solution. Thus, the complex mixture of silicate, aluminate, and alumina-silicate is formed in speciation equilibrium. The dissolution of amorphous alumina-silicate is rapid in high pH, and this result in a supersaturated alumina-silicate solution. Furthermore, the concentrated solution forms gel, as the oligomers in the aqueous phase from large networks by condensation. The gelation process releases water which is nominally consumed during dissolution. The time required for the gel to be formed continuously depends on the raw material processing conditions, solution composition, and synthesis conditions. After gelation, the gels continue to rearrange and reorganize. As the connectivity of the gel network increases, the three-dimensional almina-silicate network which contributes to the geopolymer forms. Finally, the geopolymer forms after polymerization and hardening.

2.3 Synthesis Parameters

The literature show that the raw materials and processing parameters are critical in determining the setting behavior, workability, chemical and physical properties of geopolymeric products. The relevant factors are SiO_2/Al_2O_3 ratio, alkali concentration, curing temperature with curing time, solid/liquid ratio, pH, and etc.

2.3.1 Solid/Liquid Ratio

The water content determines the solid/liquid ratio of the starting materials in the geopolymeric matrices. Refering to Divya et al., (2007), the strength increases as the ratio of geopolymer solid-to-water by mass increases. This trend is analogous to cement-to-water ratio in the compressive strength of Ordinary Portland Cement (OPC) even though their chemical processes involved in the formation of binders are differed. The minimum water-to-cement ratio of OPC approximates to 0.4 by mass while the fresh geopolymeric material is readily workable even at high solid/liquid ratio.

It has been proven that all the stages of geopolymerization process are positively affected by the reducing of water content in the aqueous phase of the synthesis process. However, the continuous decreasing of water content may cause insufficient wetting of the raw materials and influencing negatively the paste workability and hard to be moulded.

Zhang et al. (2009) had studied on the effect of solid/liquid ratio by using calcinated kaolinite as the raw material and he reported that the higher ratio will result in faster setting time due to increase of reaction rate. Since the higher water content will accelerate the rate of polycondensation, it can be concluded that lower liquid/solid ratio has higher polycondensation rate. Nevertheless, the dilution effects of geopolymer might be reduced if too much water is used.

2.3.2 SiO_2/Al_2O_3 Ratio

Generally, the hardening of geopolymer is believed to be due to the polycondensation of hydrolyzed aluminate and silicate species. Condensation can occur between aluminate and silicate species or silicate species themselves, depending on the concentration of Si in the system (De Silva et al., 2007). De Silva at el., (2007) studied the effect of initial Si/Al ratio on the setting based on metakaolin since it is a good source of Al_2O_3 and SiO_2 which is highly reactive with alkaline activators. Typically, a mixture with Al_2O_3/SiO_2 ratios range from 0.26 to 0.29 with a Na_2O/Al_2O_3 ratio of about 1 provides better properties.

From the research of rice husk and bark ash (RHBA) based geopolymerization done by Smith et al., (2010), the compressive strength increased as the SiO_2/Al_2O_3 ratio increased. The addition of RHBA enriched the Si in the matrix, which allowed stronger Si-O-Si bonds to form. When the ratio of SiO_2/Al_2O_3 reached about 10, the rate of compressive strength development became slower and the strength dropped when the ratio exceeded 15.9 for the mixture with SiO_2/Al_2O_3 ratio greater than 15.9, there was expansion of specimens and cracking commenced after a month. As the SiO_2/Al_2O_3 ratio was greater than 8, the mixtures were very sticky and difficult to pour into the mold.

Fletcher et al. (2005) had synthesized the geopolymer from dehydroxylated kaolinite and amorphous silica with SiO_2/Al_2O_3 ratio from 0.5 to 300 and reported that the compressive strength increased as the ratio of SiO_2/Al_2O_3 increased. When the SiO_2/Al_2O_3 ratio is higher than16, the compressive strength dropped and the failure mode changed from crushing to deformation. Through this study, he found that the transformation of geopolymer from brittle to elastic materials at SiO_2/Al_2O_3 of 15.9.

2.4 Types of Coating

Generally, the types of coatings can be divided into different groups which include cementitious materials, intumescent paints, fibrous material, and etc. The common materials for coatings are cementitious materials and intumescent paints (Jadambaa et al., 2009). Besides that, it is well known that there is another type of polymeric coating for metal substrates which is epoxy resins (Ji W. G. et al., 2006).

2.4.1 Epoxy Resins

Epoxy resin can be used as the epoxy coating or paint which protects the material against the corrosive chemicals, heat and ultra-violet light. Besides that, it has convenient drying time, exhibits excellent dimensional stability, extremely tough, and has a strong adhesion to many substrates such as glass, metals, fibers, and others. Hence, it has a wide range of applications which cover building and construction, industrial, electronics, and agriculture. For instance, an epoxy coating can be used as a primer to enhance the adhesion of paints applied as a final coating to hulls and decks as well as protect the internal surface of fiber-reinforced hulls in the marine industry. In the food industry, the epoxy coating may be applied to the metal containers in order to avoid rust and taste degradation.

An epoxy coating, which is also known as polyepoxide coating is a thermosetting copolymer since it is formed from the combination of two different materials which are epoxide resin and polyamide hardened. In the process producing epoxy coating, the hardener is used as a catalyst promoting polymerization where the extensive cross-linking of the two materials contributing to the compound's strength is formed.

Generally, the surfaces of all metals react with oxygen to form a surface oxide layer that can inhibit the attacking substance from reaching the metal surface (Kim H. et al., 1999). The corrosion of the coated metal is strongly dependent on the properties of the coating which means the metals are not susceptible to corrosion as long as the surface oxide film remains intact. However, the lifetime of epoxy coating is relatively short (Grgur B. N. et al., 2006). When the breakdown potential of the coating is reached, the protective oxide layer will dissolve and the onset of surface corrosion commences.

2.4.2 Cementitious Materials

Generally, cementitious materials are inorganic like geopolymer-based coating materials. It is unlikely to combust when exposed to the fire. Due to its low cost, many studies regarding to the improvement of durability and wear resistivity have been done to develop its application for coating.

Basically, the formation of cementitious materials is resulting from the normal mixing of Portland cement. Nowadays, the mixtures contain supplementary cementitious materials which are added as a proportion during mixing while these materials are normally byproduct, industrial wastes and natural materials. These supplementary cementitious materials can be used to enhance the coating performance such as workability, durability, and strength.

Nevertheless, there are some disadvantages since they are made from ordinary Portland cement (OPC). The cementitious materials will lose strength and adversely affected by spalling when exposed to fire. Other than that, the coating made by cementitious material is comparably thick and heavy in order to provide sufficient fire resistance.

2.4.3 Intumescent Paints

Intumescent paints coatings are made from organic materials. When exposed to high temperature, the intumescent paints swell to provide an expanded charred layer of low conductivity foam structure which can reduce the rate of temperature rise in the steel and thus prolong the steel load bearing capacity. Unlike cementitious materials, it exhibits light, aesthetic, and smooth properties, and can be used as thin coatings (Wang G. J. et al., 2010).

Generally, the intumescent paints are used widely for fire resistive coatings such as passive fire protection for steel structure which applied in civil buildings, chemicals, and other facilities. However, there are some limitations for intumescent also. For example, the hydrophilic fire retardant additives in the coatings are very sensitive to corrosive substances such as acid and alkali. This would depress the expected effect of intumescent coatings significantly (Wang G. J. at el., 2010). Other than that, it is comparably expensive, poor water resistance and it may combine with CO_2 to revert back to its original constituents (Jadambaa at el., 2010). Thus, a further development to cope with these limitations is necessary to enhance the coating properties.

2.5 Coating Properties

Coating is an applied layer on the metal substrate in order to expand the durability and enhance the surface properties of the metal. The coating properties that must be considered are adhesiveness, anti-corrosiveness, fire resistivity, and water resistivity.

Steel is one of the most common materials used for engineering applications. Thus, appropriate coating must be applied to protect and enhance the properties of the steel. Geopolymer which is well known as a very promising material for coating of different surfaces can be utilized due to its superior chemical, mechanical and thermal resistance properties (Jadambaa et al., 2010). The main coating properties being investigated are adhesiveness and corrosion resistivity as described below:

2.5.1 Adhesiveness

The adhesion of the geopolymer coatings on the metal substrates is strongly dependent on the composition of the geopolymer produced (Jadambaa et al., 2009). For the fly ash-based geopolymer coated metal substrates, an adhesive strength greater than 3.5MPa was achieved for composition with Si:Al of 3.5 (Jadambaa et al., 2010). In addition, the resultant thickness of the geopolymer coating is affected by the water content in the geopolymer where a greater solid/liquid ratio may lead to a coating with greater thickness.

The terms used to describe the adhesive strength are chemical and physical bonding between the geopolymer and the metal substrates. There was a study conducted by Jadambaa et al. (2010), which showed that the surface roughness was one of the factors influencing the adhesiveness of the coating. There is no evidence regarding to the chemical bonding between the fly ash-based geopolymer and steel. Nevertheless, the adhesiveness of the fly ash-based geopolymer on the stainless steel is much lower than the adhesiveness of fly ash-based geopolymer on the mild steel which is caused by the smoother surface of the stainless steel compared to the mild steel (Jadambaa et al., 2010). In addition, the metakaolin-based geopolymer possess comparatively stronger adhesion strength. Yong et al. (2007) suggested that the growth of geopolymeric gel is more rapid when an iron substrate is used due to chemical bonding while the weak chemical bonding and thus low adhesive strength of the stainless steel was caused by the presence of Cr which prohibited the growth of the geopolymeric gel. Meanwhile, Latella et al. (2006) stated that the bonding of metakaolin-based geopolymer on stainless steel was purely mechanical rather than chemical. These show that there is no clear consensus on either physical or chemical bonding responsible to the adhesion of geopolymeric gel to the metal substrates.

The use of sodium silicate solution helps to enhance the corrosion resistivity of the coating material and its presence may be the reason that contributes to the strong adhesion of the geopolymer to the metal substrates (Jadambaa et al., 2009).

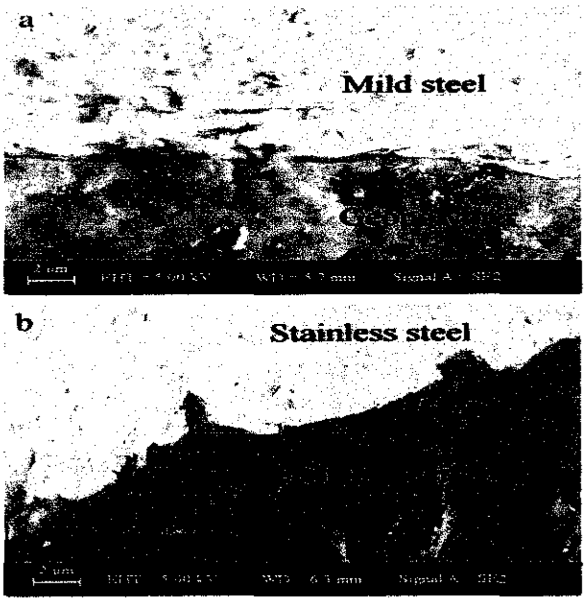


Figure 2.5 SEM Micrograph of Interface Between Geopolymer and (a) Mild Steel, (b) Stainless Steel (Jadambaa et al., 2009)

2.5.2 Corrosion Resistivity

Polymer coating acts as a barrier layer between the metal substrate and the environment to provide corrosion protection on the metal substrate. When the metal substrate is exposed to the environment, the metal substrate may become unstable and it may corrode, releasing metal ions into the environment until equilibrium is reached or until come occurrence impedes the releasing of ions. A passivating film may form to prevent the corrosion of metal substrate through the reaction between the metal surface and oxygen (Hera Kim et al., 1999). This reaction forms an oxide layer on the metal surface to prevent the attacking substance from further reaching the metal surface.

The protection of metal substrates by polymer against corrosion is a complex process and it is dependent on the electrical, chemical and mechanical properties of the polymers, adhesion of the coating to the substrate, sorption characteristics of the coating, ion penetration via the coating and the surface characteristics of the metal substrates (Miskovic-Stankovic et al., 1999).

The metal relies on the passive film formed for corrosion resistance sharing the property that the passive layer has a great potential to be broken down and the metal will no longer be protected consequently. As long as the surface oxide film is still intact, the metal substrates are not susceptible to corrosion. However, the onset of surface corrosion and pitting will begin as the breakdown potential of the surface oxide film is reached (Hera Kim et al., 1999).

The past corrosion studies focus on the observation of the metal surface before and after exposure to the corrosive environment and hence to identify the visible evidence of corrosion such as pitting. Nowadays, the use of salt spray and different cyclic exposure tests are used in the coating industry broadly. But these tests only provide qualitative information regarding to the corrosion resistivity of the coating (F. Galliano et al., 2001).

The adhesion of coatings is crucial for corrosion protection and durability of the coating. This is because the rising in pH from the corrosion cells can deteriorate the adhesion of organic coatings on the metal substrate.

2.6 Geopolymer-based Coating

Geopolymer-based coating is extensively developed due to its superior properties such as fire resistance and capacity to encapsulate hazardous materials (Davidovits J., 2008). However, the studies on this green novel technology are limited and most of the studies focus on the fire resistance and corrosion properties of the geopolymer-based coating.

According to Jadambaa (2011), geopolymer-based coating is investigated due to its great fire resistance properties and its excellent adhesion to the metal. Since the metal such as steel may loss its room temperature yield stress at high temperature (Jadambaa at el., 2011), fire resistance is crucial property for coating in order to protect the metal substrate as well as its adhesiveness to the metal substrate.

There was another study conducted by Zhang et al. (2010) which focused on the application of geopolymer-based coating as a protection for marine concrete where the anti-corrosion property is the main concern of the study. In this study, metakaolin, granulated blast furnace slag, ordinary Portland cement, standard sand, polypropylene fiber, and alkaline activator were used as the raw materials for geopolymerization.

Through this study, the relationship between the microstructure and the anti-corrosion property of the geopolymer was investigated. The results achieved showed that the geopolymer exhibited stable and good anti-corrosion performance when being immersed in the seawater or in the air. This has provided an excellent chemical protection to the marine concrete.

The water content of initial formation also plays a crucial role in determining the geopolymer properties. Duxson el al. (2007) stated that much water is required for synthesizing process of geopolymer from metakaolin to increase the porosity and the geopolymer formed became soft for application as adhesive coatings, and hydro-ceramics. Other than that, Van Jaarsveld et al. (2002) also concluded that the source of materials especially water ratio determine the properties of the geopolymer.

CHAPTER 3

METHODOLOGY/PROJECT WORK

3.1 Research Methodology

The research methodology of this study was divided into four main stages which were preparation of raw materials and alkaline solutions, characterizations of raw materials, geopolymerizations between raw materials and alkaline solutions and properties testing of geopolymer in fresh paste and hardened paste, respectively, and the methodology is presented in Figure 3.1.

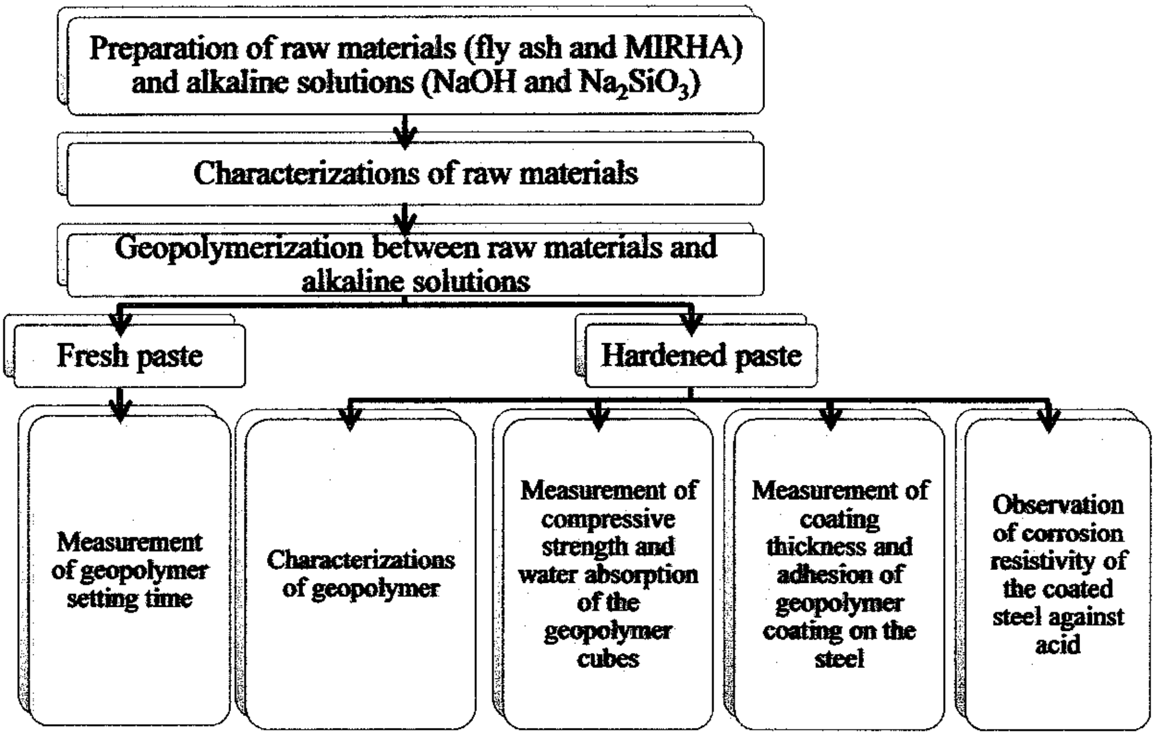


Figure 3.1 Research Methodology of the Study

3.2 Preparation of Raw Materials and Alkaline Solutions

The raw materials used for geopolymerization were fly ash and microwave incinerated rice husk ash (MIRHA), (Refer to Table 3.1):

Table 3.1 Preparation of Raw Materials

Raw Material	Description
Fly ash	• As the raw material to provide alumina-silicate oxides for geopolymetization due to its high Al and Si content. • Can be obtained directly from the industrial waste.
Microwave incinerated rice husk ash (MIRHA)	• As the supplier of SiO_3 of geopolymerization since more Si instead of Al is required for better properties performance. • MIRHA was produced by burning the rice husk using the microwave incinerator (Refer to Appendix 3.1) from room temperature to 600°C for 5 - 6 hours. • The high temperature rice husk ash was cooled inside the microwave incinerator for 24 hours. • The cooled rice husk ash was grinded into finer size using a grinder. • The grinded rice husk ash was ready for use.

The alkaline solutions used for geopolymerization were sodium hydroxide (NaOH) and sodium silicate (Na_2SiO_3), (Refer to Table 3.2):

Table 3.2 Preparation of Alkaline Solutions

Raw Material	Description
Sodium hydroxide (NaOH)	• As the dissolver to liberate Al and Si ions for geopolymerization. • The molarity of NaOH prepared was 8M by dissolving the calculated amount of NaOH pellets in the distilled water.
Sodium silicate (Na_2SiO_3)	• As the binder for geopolymerization. • Pure Na_2SiO_3 was used for geopolymerization.

3.3 Characterizations of Raw Materials and Geopolymer

After preparing the raw materials and alkaline solutions required for geopolymerization, the characteristics of raw materials such as chemical composition, particle properties and component structure were determined where the raw materials were dried before characterization. Besides that, the geopolymers formed after geopolymerization were also characterized as well as raw the materials (Refer to Table 3.3):

Table 3.3 Equipment Used for Characterizations

Equipment	Description
X-ray Fluorescence (XRF) and Fourier Transform Infrared (FTIR) Spectrometer	• To determine the chemical composition of fly ash, microwave incinerated rice husk ash (MIRHA) and geopolymer.
Particle Size Analyzer (PSA)	• To analyze the particle size distribution of fly ash, MIRHA and geopolymer. Theoretically, the finer particle size can achieve properties such as flexural strength.
X-Ray Diffraction (XRF)	• To analyze the crystal structure, chemical composition, and physical properties of the raw materials and geopolymer.
Field Emission Scanning Electron Microscope (FESEM)	• To scan the surface topography, composition and other properties such as electrical conductivity of the raw materials and geopolymer.

3.4 Geopolymerization between Raw Materials and Alkaline Solutions

The geopolymerization process was conducted with the preparation of the corresponding raw materials and alkaline solutions which were MIRHA and fly ash, Na_2SiO_3, and NaOH, respectively according to the experimental setups. Next, the prepared materials were mixed using a mechanical mixer for 2 minutes. The well-mixed mixture was casted in the 50mm x 50mm mould (Refer to Appendix 3.2), where setting time of the fresh paste was measured and the hardened paste was cured for 24 hours at room temperature before further testing. In this study, there were two sets of experimental setups involved in this study namely, the first and second experimental setups focused on the effect of solid/liquid ratio and SiO_2/Al_2O_3 ratio, respectively.

3.4.1 Solid/liquid Ratio

The solid/liquid ratio was controlled by changing the percentage of solid (fly ash and MIRHA) and liquid (NaOH and Al_2SiO_3) in mass (Refer to Table 3.4). The effect of solid/liquid ratio on the setting time and compressive strength of the geopolymer was determined through this experiment.

Table 3.4 Experimental Setup by Varying Solid/liquid Ratio

Series	Solid/Liquid Ratio	Solid by Mass (kg)	Liquid by Mass (kg)		SiO_2/Al_2O_3
		Fly Ash	NaOH	Na_2SiO_3	
1	2.0	1.000	0.142	0.357	4.089
2	2.2	1.000	0.129	0.325	4.023
3	2.4	1.000	0.119	0.298	3.968
4	2.6	1.000	0.110	0.275	3.921
5	2.8	1.000	0.102	0.255	3.881
6	3.0	1.000	0.095	0.238	3.846

3.4.2 SiO_2/Al_2O_3 Ratio

The SiO_2/Al_2O_3 ratio was manipulated through the addition of MIRHA by percentage (Refer to Table 3.5). According to Table 3.5, the SiO_2/Al_2O_3 ratio was manipulated by the addition of MIRHA by mass while the actual ratio of SiO_2/Al_2O_3 was determined after the characterizations of geopolymer formed. The experiment was repeated with different solid/liquid ratio in order to achieve the optimum geopolymerization under different synthesis parameters. Moreover, the testing methods involved for this experimental setup were setting time, compressive strength, adhesiveness, water absorption, and corrosion resistivity.

Table 3.5 Experimental Setup by Varying SiO2/Al2O3 Ratio through Addition of MIRHA by Percentage

Series	Description	Solid/ Liquid Ratio	Solid by Mass (kg)		Liquid by Mass (kg)		SiO_2/ Al_2O_3
			Fly Ash	MIRHA	NaOH	Na_2SiO_3	
1	Control mix (100% fly ash)	2.0	1.800	0.000	0.257	0.643	4.089
		2.4			0.214	0.536	3.967
		3.0			0.171	0.429	3.846
2	95% fly ash + 5% MIRHA	2.0	1.710	0.090	0.257	0.643	4.407
		2.4			0.214	0.536	4.279
		3.0			0.171	0.429	4.151
3	90% fly ash + 10% MIRHA	2.0	1.620	0.180	0.257	0.643	4.760
		2.4			0.214	0.536	4.625
		3.0			0.171	0.429	4.490
4	85% fly ash + 15% MIRHA	2.0	1.530	0.270	0.257	0.643	5.154
		2.4			0.214	0.536	5.012
		3.0			0.171	0.429	4.869
5	80% fly ash + 20% MIRHA	2.0	1.440	0.360	0.257	0.643	5.597
		2.4			0.214	0.536	5.446
		3.0			0.171	0.429	5.295

3.5 Fresh Paste

The fresh paste of geopolymer formed via geopolymerization was used for the measurement of setting time using the Vicat apparatus (Refer to Appendix 3.3).

3.5.1 Setting Time

Setting time is the time required by the fresh paste for hardening. The longer setting time indicated greater water content in the mixture, which reflects the solid/liquid ratio of the geopolymer as well.

Vicat apparatus was used to measure the setting time according to ASTM C191. The fresh paste was placed into the ring immediately once the mixture was well-mixed. Subsequently, the setting time was recorded once the needle of the apparatus didn't penetrate into the mixture anymore.

3.6 Hardened Paste

The two types of hardened geopolymer were geopolymer cube and geopolymer coated steel which was formed by dipping the steel into the fresh paste of geopolymer. The geopolymer cubes formed were used for compressive strength and water absorption testing while the geopolymer coated steel was used for the testing such as coating thickness, adhesive strength of coating and corrosion resistivity.

3.6.1 Compressive Strength

Compressive strength is the capacity of a material or a structure to withstand the force applied on it. When the limit of compressive strength of a material is reached, it will be crushed. Furthermore, this is the basic strength measurement method to determine the flexural strength of a coating material. In this study, the compressive strength shows the ability of the coating material to provide sufficient protection to the metal substrate.

The compressive strength of the geopolymer cube was measured by the compression machine (Refer to Appendix 3.4) according to ASTM C109. The geopolymer cubes were left 3 days before testing. After that, the sample was placed in between of the upper and lower platen and the safety door must be closed for safety purpose. The sample was compressed until the yield stress was reached. Subsequently, the result shown on the indicator was recorded.

3.6.2 Water Absorption

Absorption is a physical or chemical phenomenon or a process in which atoms, molecules, or ions enter some bulk phase (gas, liquid, or solid) material. In this study, the metal substrate being used was steel which is used for engineering purpose. Hence, water absorption into the system should be avoided for safety and efficiency purpose.

In this study, the water absorption of the geopolymer was determined by the measuring change of mass. Firstly, the initial mass of the geopolymer was measured. Next, the geopolymers were immersed into the water for 24 hours and the final mass of the geopolymer was measured. Consequently, the change of mass was calculated as follow:

$$Change\ of\ Mass\ (\%) = \frac{Final\ Mass - Initial\ Mass}{Initial\ Mass} \times 100\% \qquad \textbf{(Equation 3.1)}$$

3.6.3 Coating Thickness

The thickness of the coating was measured by an electronic digital vernier caliper and caliper gauge as shown in Appendix 3.5.

3.6.4 Adhesive Strength

Adhesive strength is the strength of a material to adhere on another material. Since the geopolymer in this study is used as coating material for metal substrate, it is important to ensure that the geopolymer adhesive strength is sufficient for protective purpose.

The adhesion tester (Refer to Appendix 3.6) was used to investigate the adhesive strength of the coating material on the metal substrate according to ASTM D4541. To commence the testing, a small quantity of adhesive was mixed and applied on the surface of the dolly (Refer to Appendix 3.7) and subsequently the dolly was placed on the coated metal substrate (specimen). The specimens prepared were cured under room temperature for not less than 8 hours. After curing, the base around the dolly was cut carefully with the dolly cutter in order to create some space for the pull-off test. The specimen was place into the pull-off adhesion tester and the test was carried out until the dolly was pulled-off from the metal substrate. The strength required to pull-off the dolly was recorded according to the indicator of the pull-off adhesion tester.

3.6.5 Corrosion Resistivity

Corrosion resistivity is the ability of a material to resist the destruction caused by a chemical reaction with its environment. In this study, the corrosion is the oxidation of metal in reaction with an oxidant such as oxygen and it may because of the exposure of metal substrate to an acidic environment. The corrosion resistivity of the coating material is vital since the coated metal substrate may deal with corrosive chemical.

The corrosion chamber (Refer to Appendix 3.8) was used to determine the acid resistivity of the coated steel according to ASTM G85. Sufficient acetic acid with pH

3.1 – 3.3 was prepared and poured into the tank. The acetic acid was sprayed onto the surface of the coated steel regularly through the corrosion chamber. The corrosion resistivity of the coated steel was determined by observing the coating surface condition of the geopolymer coated steel.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Characterizations of Raw Materials

4.1.1 Fly Ash

According to Table 4.1 and Figure 4.1, fly ash used was classified as Class F pozzolanic materials since it satisfies the standard requirement by American Society of Testing and Materials (ASTM) C618 which is the sum of SiO_2, Al_2O_3, and Fe_2O_3 contained must be at least 70%.

Table 4.1 Chemical Composition of Fly Ash (XRF)

Component	Chemical Composition (Mass %)
SiO_2	44.5178
Al_2O_3	22.4785
Fe_2O_3	11.5837
CaO	9.8412
MgO	3.9182
C	2.5365
K_2O	1.7274
SO_3	1.3483
TiO_2	0.6713
Na_2O	0.5038
P_2O_5	0.3330
SrO	0.1462
BaO	0.1014
Cr_2O_3	0.0958
MnO	0.0922

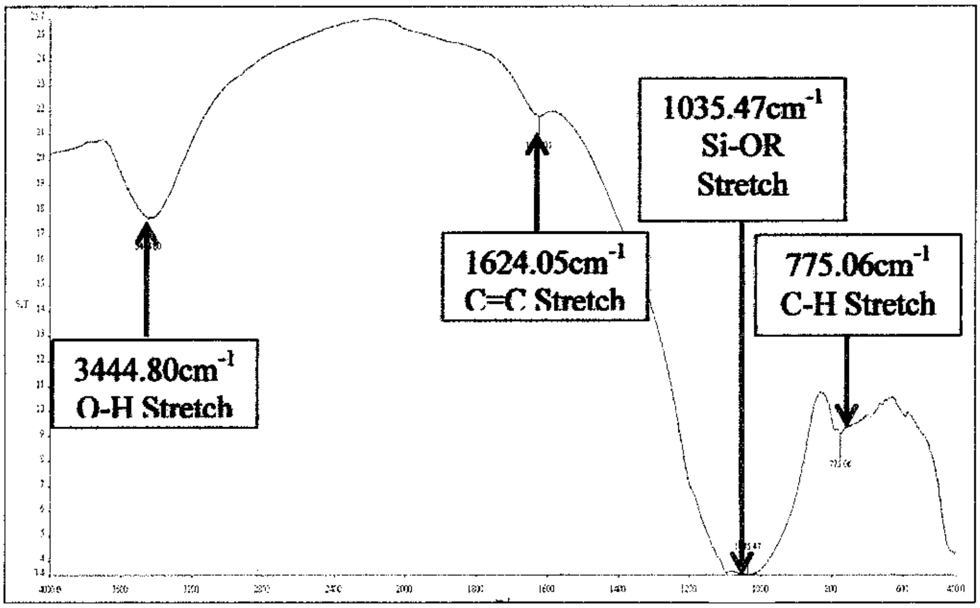


Figure 4.1 FTIR Analysis of Fly Ash

Figure 4.2 dictates that fly ash mainly consisted of amorphous components. Moreover, the particles of fly ash are mostly spherical shape with different size in nature as shown in Figure 4.3. The amorphous structure of fly ash is the readily reactive components which help in a faster development of geopolymer gel as well as the formation of a stronger structure. The morphology of fly ash can be controlled by combustion temperature and cooling rate.

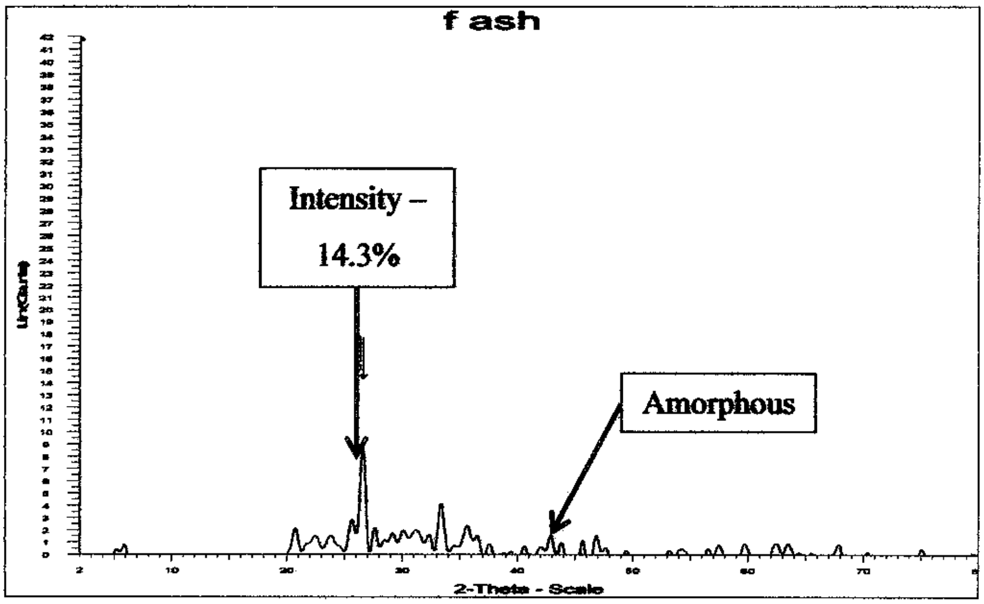


Figure 4.2 XRD Analysis of Fly Ash

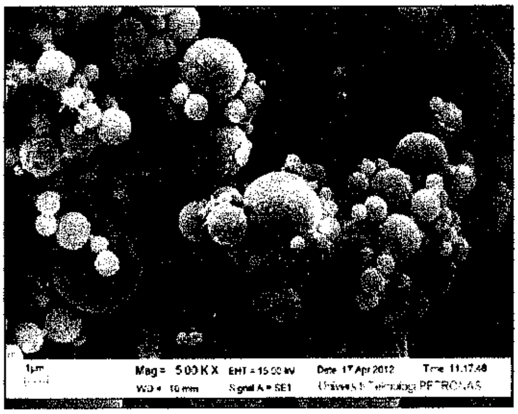


Figure 4.3 SEM Morphology of Fly Ash

The particle size distribution shown in Figure 4.4 dictates that the mean particle size of fly ash is 9µm, which is finer than MIRHA. The lower size of fly ash leads to higher dissolution of raw materials by alkaline solutions as well as greater compressive strength.

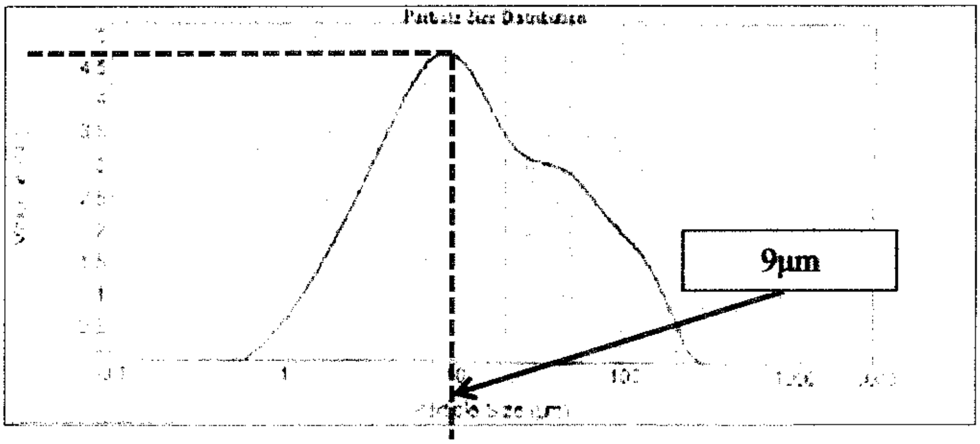


Figure 4.4 Particle Size Analysis of Fly Ash

4.1.2 Microwave Incinerated Rice Husk Ash (MIRHA)

Table 4.2 and Figure 4.5 tell that MIRHA can be classified as Class F pozzolanic material according to ASTM C618 since its sum of SiO_2, Al_2O_3, and Fe_2O_3 is higher than 70%. The high silica content is important in deciding the properties of the geopolymer. Hence, MIRHA is an appropriate material to be used as the source of Si in the process of geopolymerization.

Table 4.2 Chemical Composition of MIRHA

Component	Chemical Composition (Mass %)
SiO_2	70.7665
C	22.9047
K_2O	2.9149
P_2O_5	1.4929
MgO	0.6974
CaO	0.4635
SO_3	0.1964
Cl	0.1587
Fe_2O_3	0.1169
MnO	0.0625
TiO_2	0.0201
Rb_2O	0.0201
Na_2O	0.0122

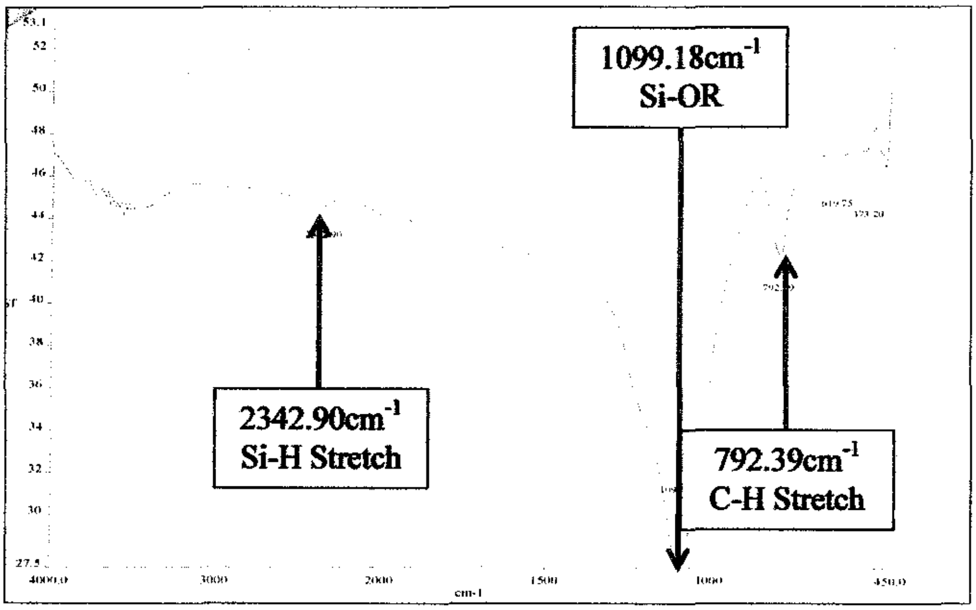


Figure 4.5 FTIR Analysis of MIRHA

Figure 4.6 tells that most of the Si in MIRHA is in amorphous structure. From Figure 4.7, MIRHA has a beehive structure with pores which is different from fly ash. The structure of MIRHA can be controlled by changing the burning temperature of the microwave incinerator, where a smoother beehive structure is formed with a lower burning temperature.

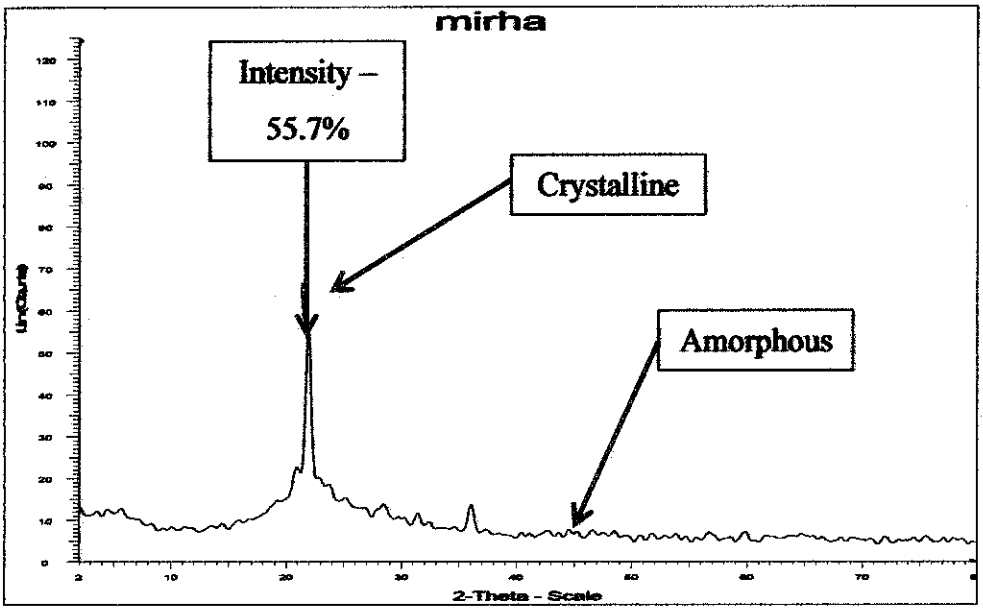


Figure 4.6 XRD Analysis of MIRHA

Figure 4.7 FESEM Morphology of MIRHA

As shown in Figure 4.8, the mean particle size of MIRHA is 43μm, which is higher than fly ash. A higher compressive strength can be achieved with the finer particle size since it allows for optimum dissolution by alkaline solution and geopolymerization process.

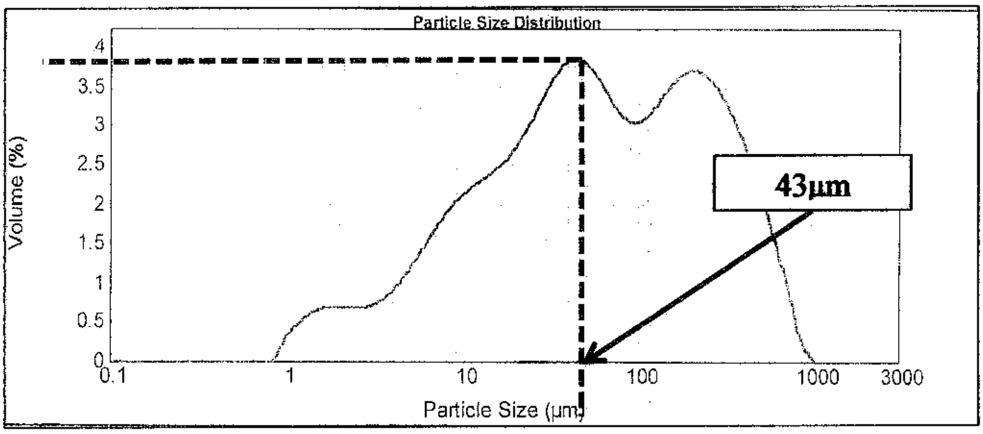


Figure 4.8 Particle Size Analysis of MIRHA

4.2 Solid/liquid Ratio

The first experimental setup was conducted to investigate the effect of solid/liquid ratio on setting time and compressive strength of the geopolymer. According to Figure 4.9, the setting time shows a gradual decrement with increasing in solid/liquid ratio. The setting time is affected by the water content in the fresh mixture, where the higher solid/liquid ratio increases the reaction rate, causing the lesser setting time required for the fresh mixture to be hardened.

Other than that, the compressive strength increases at lower solid/liquid ratio and subsequently decreases since the solid/liquid ratio reaches 2.6. This may due to the increasing of SiO_2/Al_2O_3 ratio where the high reactive silica content contributes to the formation of great amount of alkali alumina-silicate gel and hence increase the compressive strength of the geopolymer. However, the compressive strength may be decreasing after the optimum SiO_2/Al_2O_3 ratio is reached. On another hand, the compressive strength increases with the increasing of solid/liquid ratio since the increasing of solid/liquid ratio causes the faster reaction rate as well as the development of compressive strength until the optimum compressive strength is reached. The highest compressive strength (29.16MPa) is achieved when the solid/liquid ratio is 2.6.

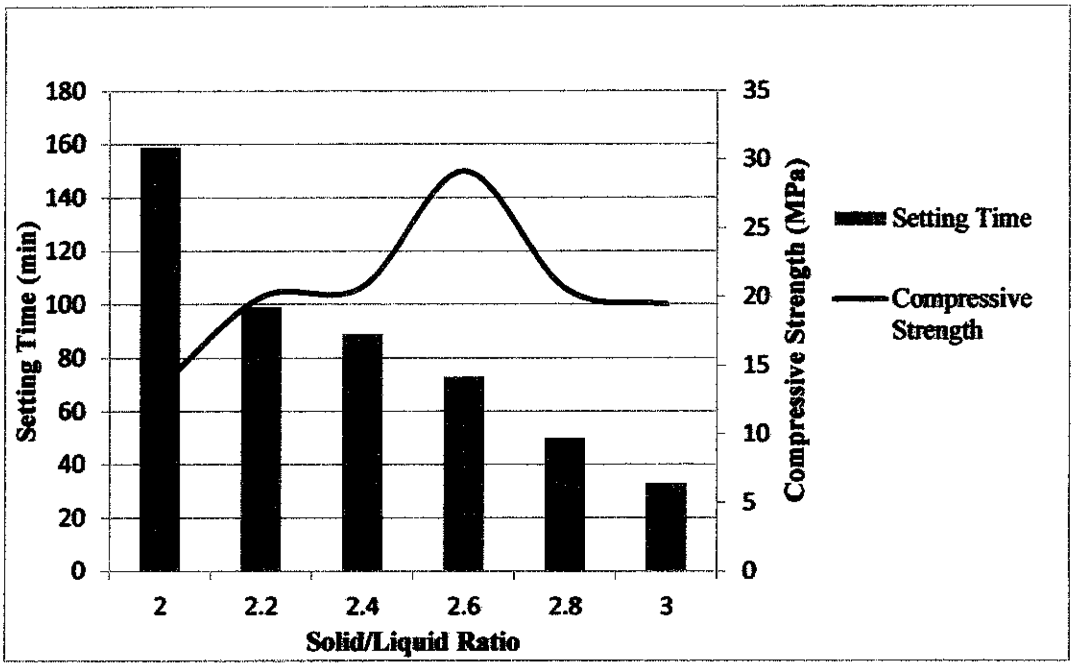


Figure 4.9 The Effect of Solid/Liquid Ratio on Setting Time and Compressive Strength

4.3 SiO_2/Al_2O_3 Ratio

The SiO_2/Al_2O_3 ratio was controlled by the addition of MIRHA for geopolymerization where higher SiO_2/Al_2O_3 ratio was achieved when more MIRHA was added by percentage.

4.3.1 Characterizations of Geopolymer

The geopolymers with 0%, 10% and 20% MIRHA addition had been chosen for characterizations in order to differentiate the effect of MIRHA addition at different quantity on the characteristics of the geopolymers.

(a) XRF and FTIR Analysis

Table 4.3 and Figure 4.10 show the chemical composition of geopolymer where 100% fly ash was used from XRF and FTIR analysis. The SiO_2 and Al_2O_3 contents of the geopolymer after geopolymerization are 45.4581% and 17.3395%, respectively. The SiO_2 is slightly higher than the raw fly ash due to the use of Na_2SiO_3 as the binder of geopolymerization. This helped to increase the reaction rate of geopolymerization as well as the strength of the geopolymer.

Table 4.3 Chemical Composition of Geopolymer (100% Fly Ash)

Component	Chemical Composition (Mass %)
SiO_2	45.4581
Al_2O_3	17.3395
Fe_2O_3	10.4647
CaO	8.6498
Na_2O	6.3335
C	4.7324
MgO	3.0774
SO_3	1.2837
TiO_2	0.5786
P_2O_5	0.2434
SrO	0.1300
BaO	0.0841
MnO	0.0809

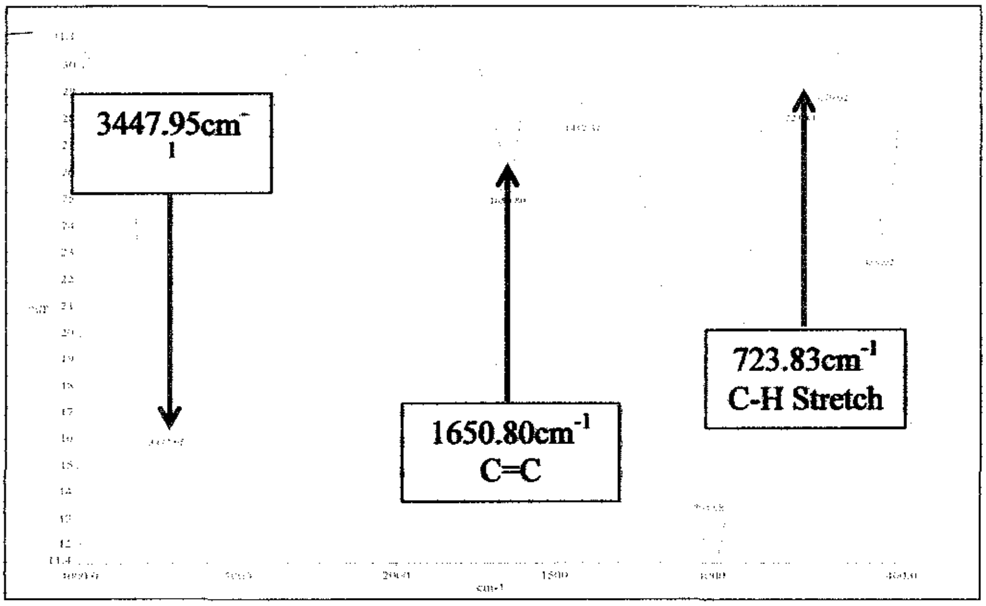


Figure 4.10 FTIR Analysis of Geopolymer (100% Fly Ash)

Table 4.4 and Figure 4.11 show that the SiO_2 and Al_2O_3 (45.1990% and 16.8457%) contents of the geopolymer with 10% MIRHA addition are slightly lower than the geopolymer with 0% MIRHA addition. The difference of these contents may influence the properties especially compressive strength of the geopolymer.

Table 4.4 Chemical Composition of Geopolymer (90% Fly Ash + 10% MIRHA)

Component	Chemical Composition (Mass %)
SiO_2	45.1990
Al_2O_3	16.8457
Fe_2O_3	10.1528
CaO	8.3417
Na_2O	6.8102
C	5.3625
MgO	2.9152
SO_3	1.7191
K_2O	1.3889
TiO_2	0.5566
P_2O_5	0.2546
SrO	0.1269
BaO	0.0958

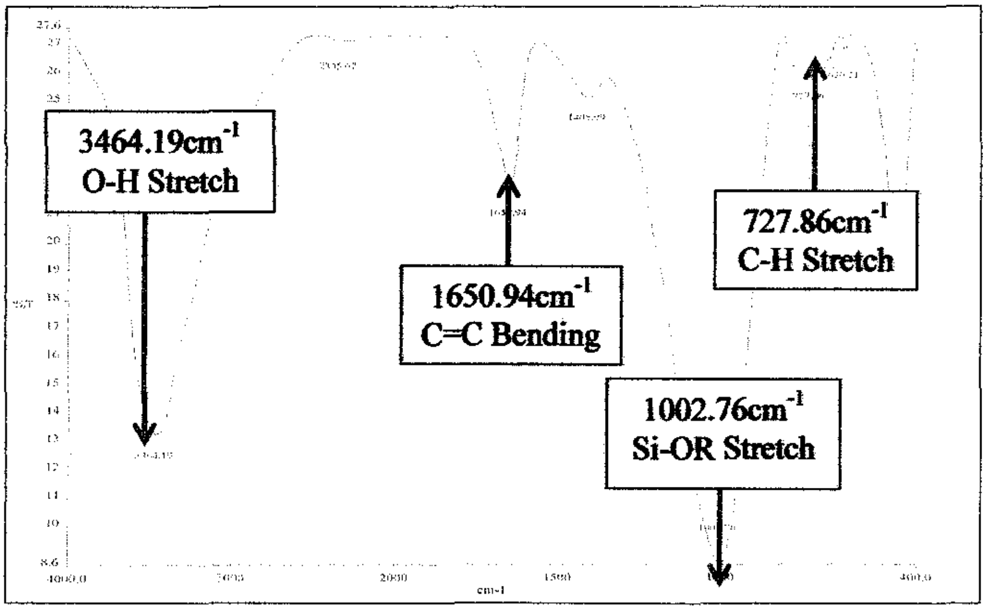


Figure 4.11 FTIR Analysis of Geopolymer (90% Fly Ash + 10% MIRHA)

Table 4.6 and Figure 4.12 tell that the SiO_2 content (46.4595%) increases while the Al_2O_3 content (11.0033%) decreases when 20% MIRHA addition was used. This condition leads to the apparent increasing of SiO_2/Al_2O_3 ratio and hence the increasing of strength of the geopolymer.

Table 4.5 Chemical Composition of Geopolymer (80% Fly Ash + 20% MIRHA)

Component	Chemical Composition (Mass %)
SiO_2	46.4595
C	18.0479
Al_2O_3	11.0033
Fe_2O_3	7.1291
CaO	5.9757
Na_2O	5.4992
MgO	1.9838
K_2O	1.5034
SO_3	1.0523
P_2O_5	0.5415
TiO_2	0.3991
SrO	0.0930
Cl	0.0701

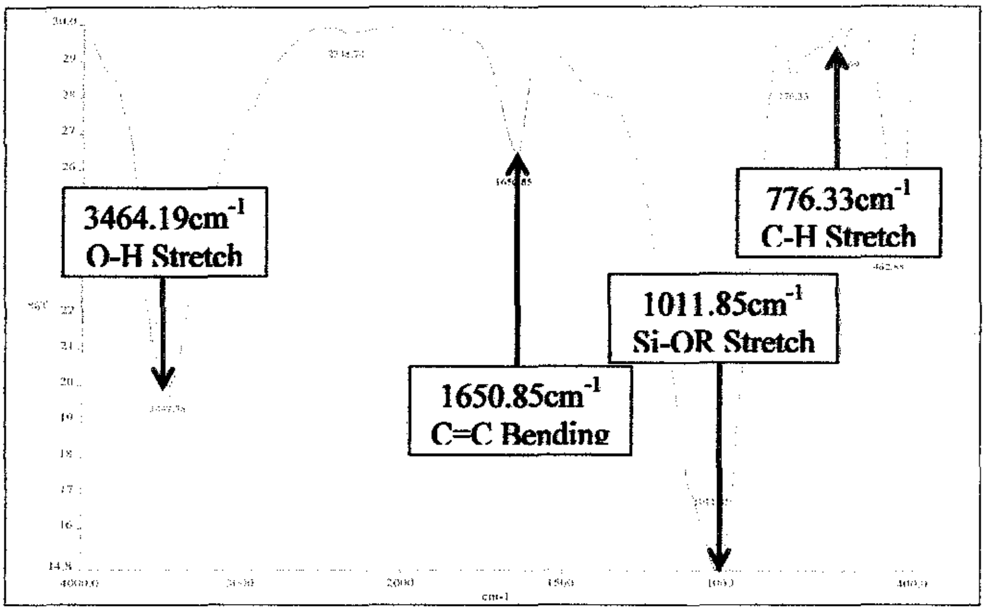


Figure 4.12 FTIR Analysis of Geopolymer (80% Fly Ash + 20% MIRHA)

(b) XRD Analysis

Figure 4.13, Figure 4.14 and Figure 4.15 show the structure of components of the geopolymers with 0%, 10% and 20% MIRHA addition, respectively. Basically, the geopolymers consist of crystalline and amorphous components. However, the quantities of amorphous components of geopolymers increase with increasing in MIRHA addition, which provides reactive raw materials (fly ash and MIRHA) to react with the alkaline solutions (NaOH and Na_2SiO_3).

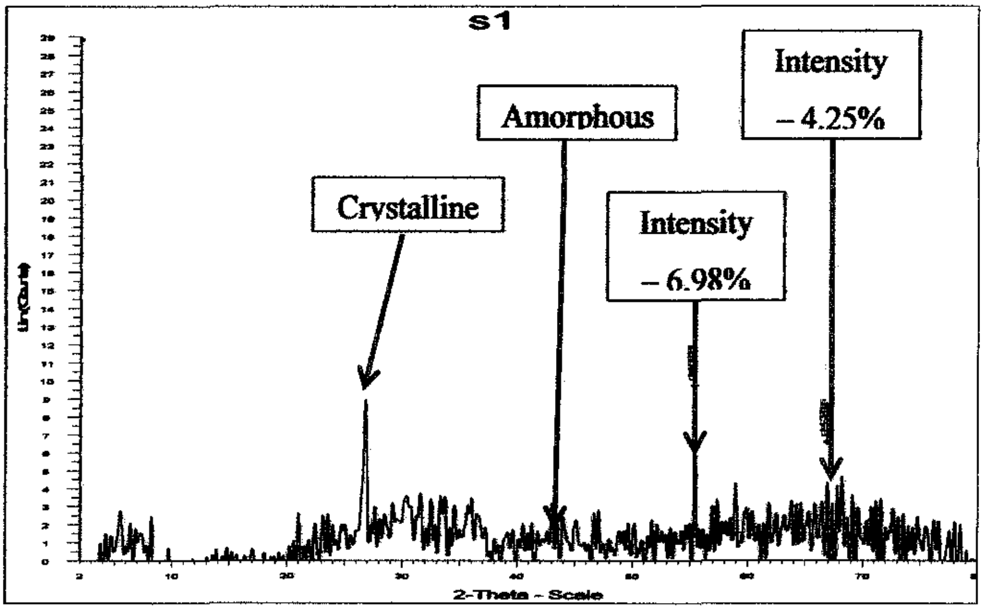


Figure 4.13 XRD Analysis of Geopolymer (100% Fly Ash)

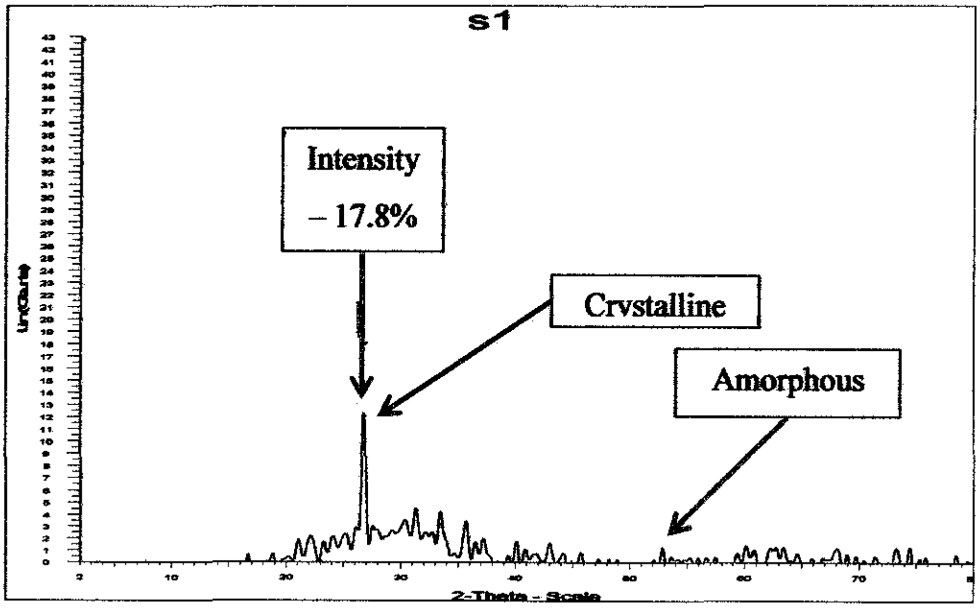


Figure 4.14 XRD Analysis of Geopolymer (90% Fly Ash + 10% MIRHA)

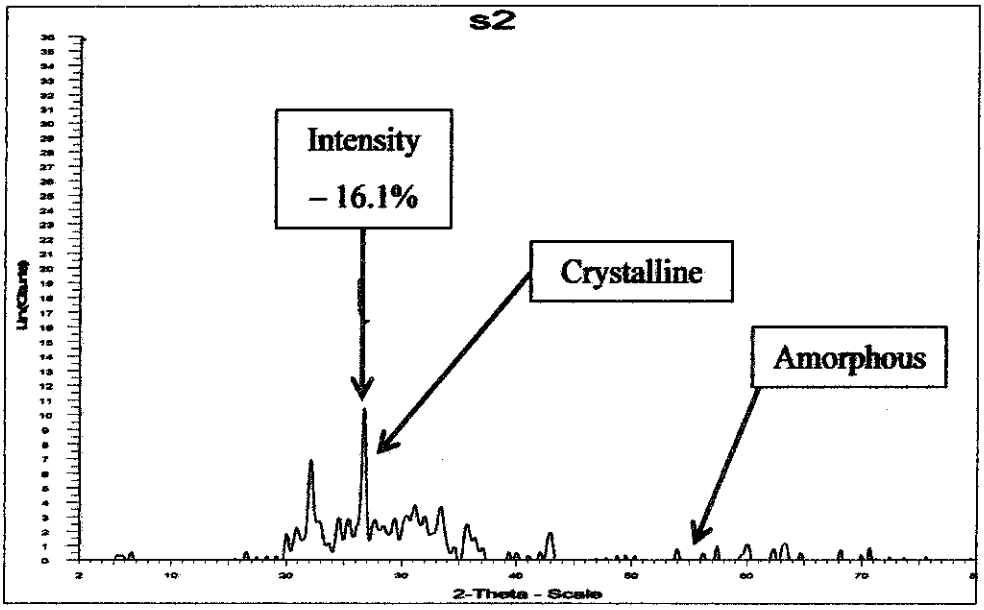


Figure 4.15 XRD Analysis of Geopolymer (80% Fly Ash + 20% MIRHA)

(c) FESEM Analysis

Figure 4.16, Figure 4.17 and Figure 4.18 show the morphology of the geopolymers with 0%, 10% and 20% of MIRHA addition, respectively. Basically, the geopolymers exhibit heterogeneous structure regardless of the percentage of MIRHA addition. The quantities of spheres indicate the presence of fly ash, decreases with the addition of MIRHA for geopolymerization. The geopolymer with lesser spheres (geopolymer with 10% MIRHA addition) has a denser matrix, which contributes to better properties such as compressive strength. Other than that, the beehive structures shown in Figure 4.18 tells that there is some unreacted MIRHA after geopolymerization which means the optimum saturation point of raw materials may be exceeded and meanwhile the compressive strength may decrease.

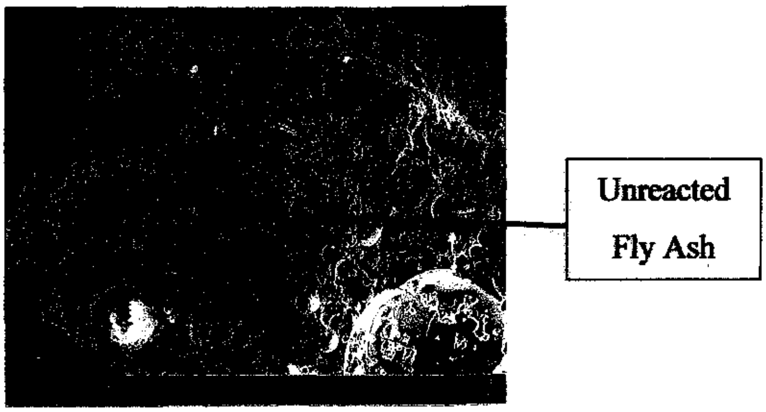


Figure 4.16 Morphology of Geopolymer (100% Fly Ash)

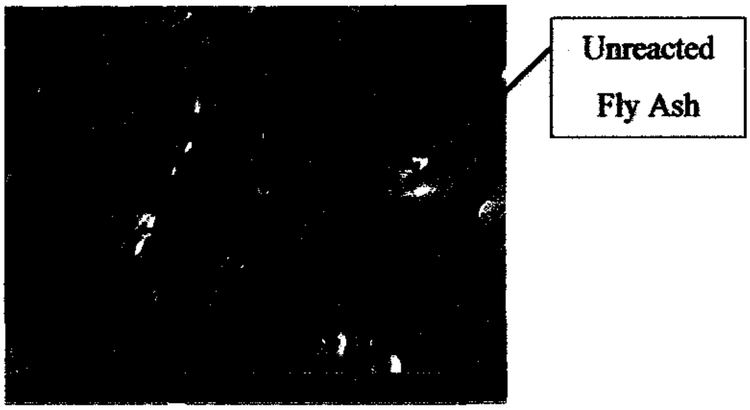


Figure 4.17 Morphology of Geopolymer (90% Fly Ash + 10% MIRHA)

Figure 4.18 Morphology of Geopolymer (80% Fly Ash + 20% MIRHA)

(d) PSA Analysis

From Figure 4.19, Figure 4.20 and Figure 4.21, the mean particle sizes of geopolymers slightly decreases with the addition of MIRHA for geopolymerization. The finer particle sizes of geopolymers cause the increasing of compressive strength due to its higher dissolution of raw materials in the alkaline solutions.

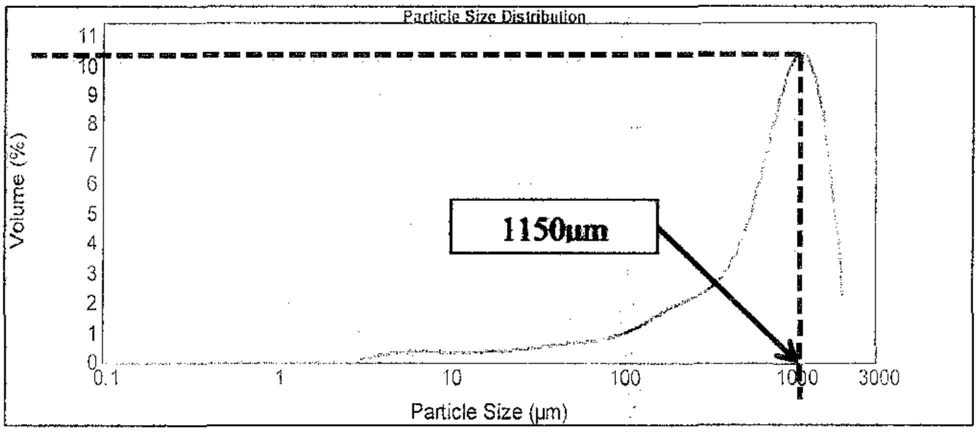


Figure 4.19 Particle Size Analysis of Geopolymer (100% Fly Ash)

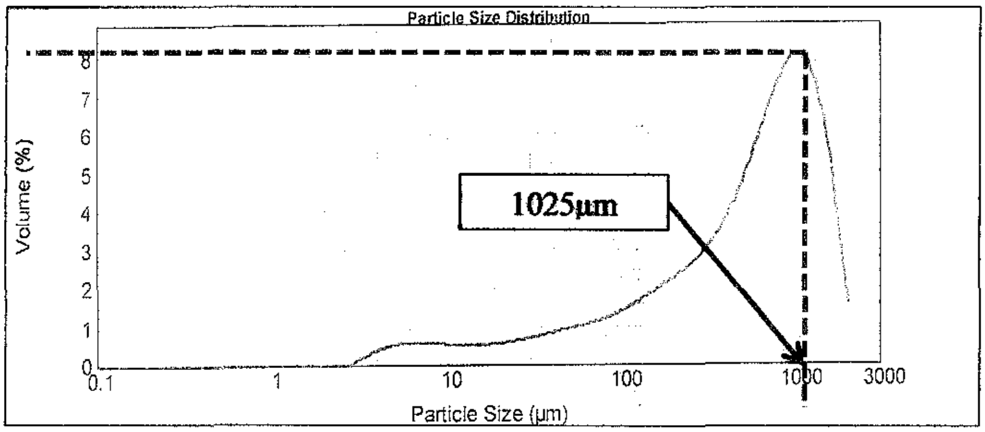


Figure 4.20 Particle Size Analysis of Geopolymer (90% Fly Ash + 10% MIRHA)

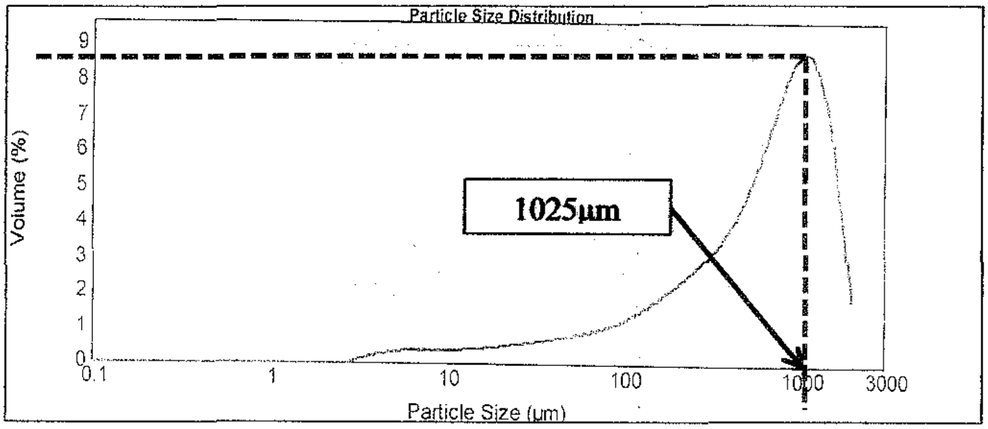


Figure 4.21 Particle Size Analysis of Geopolymer (80% Fly Ash + 20% MIRHA)

4.3.2 Setting Time, Compressive Strength and Water Absorption of Geopolymer

According to Figure 2.24, the setting time of fresh paste decreases with increasing in solid/liquid ratio and MIRHA addition. The low water content and MIRHA addition in the geopolymer lead to faster reaction rate of geopolymerization. However, the graph shows that the setting time was increasing when 5% of MIRHA was added. This may because of the presence of iron component that inhibited the dissolution of raw materials during geopolymerization and thus increased the setting time of the geopolymer mixture.

On another hand, Figure 4.24 also shows that greater compressive strength can be achieved with the increasing in solid/liquid ratio and the addition of MIRHA. This is because the higher solid/liquid ratio increases the reaction rate of geopolymerization while MIRHA provides high reactive silica, contributing to the formation of great amount of alkali alumina-silicate gel and hence the development of compressive strength. However, the compressive strength doesn't increase continuously and this may due to the presence of iron component in the geopolymer. The compressive strength of geopolymer cube may be decreasing after the optimum SiO_2/Al_2O_3 is reached which means further addition of MIRHA may cause the regression of compressive strength. Besides that, the decreasing of compressive strength may be caused by the increasing of particle size of the raw materials (fly ash and MIRHA). The particle sizes of raw materials decide the surface area available for dissolution in the alkaline solutions (NaOH and Na_2SiO_3), where the material with smaller particle sizes is more likely for geopolymerization. From Figure 4.4 and Figure 4.8, it is known that fly ash has lower particle size (9μm) compared to MIRHA (43μm). Thus, it is expected that the addition of MIRHA may lower down the dissolution of raw materials and cause the reduction of compressive strength. The greatest compressive strengths achieved are 22.38MPa, 22.66MPa and 31.78MPa at solid/liquid ratio of 2.0, 2.4 and 3.0, respectively.

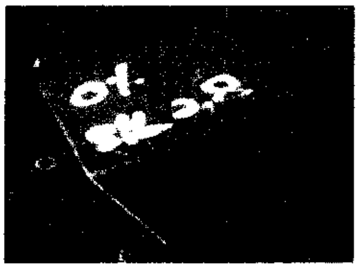


Figure 4.22 Geopolymer Cube before Testing

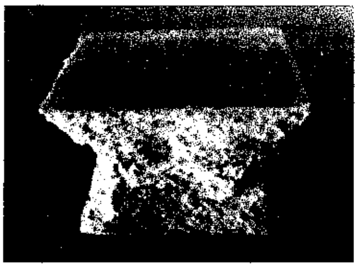


Figure 4.23 Geopolymer Cube after Compressive Strength Testing

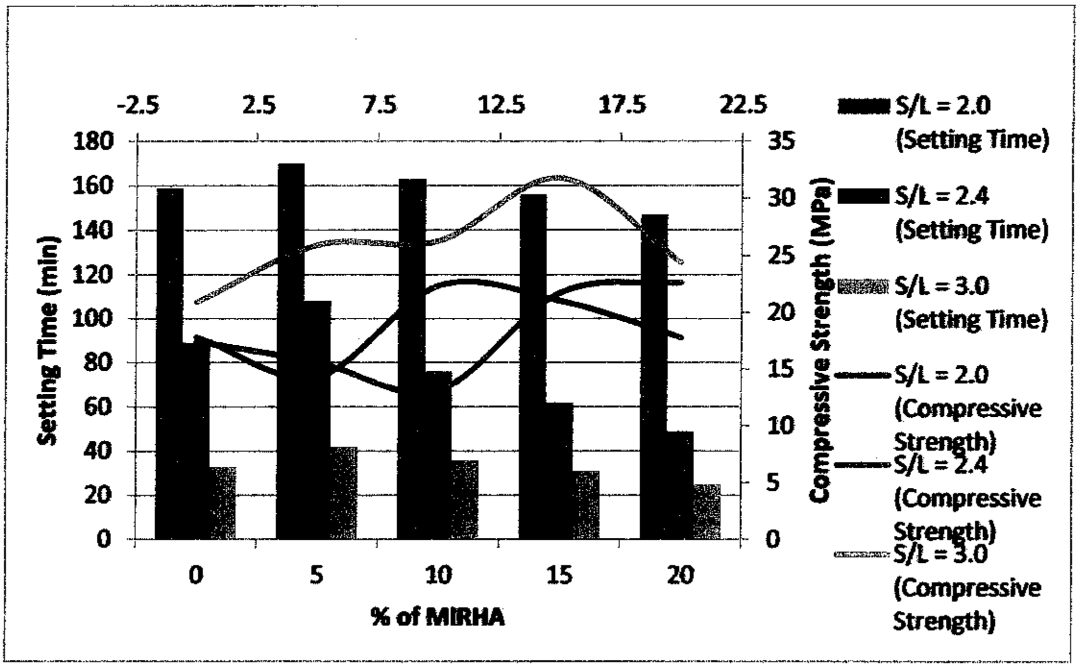


Figure 4.24 The Effect of MIRHA Addition on Setting Time and Compressive Strength

Figure 4.25 shows that the water absorption of geopolymer is low where the change in mass is between 0.002% and 0.018%. This may due to the compactness of structure of the geopolymer formed as shown in Figure 4.16, Figure 4.17 and Figure 4.18. Regardless of the addition of MIRHA and solid/liquid ratio, the variation of water absorption is low (0.016%), which means the water absorption of geopolymer cube is only slightly affected by the SiO_2/Al_2O_3 ratio.

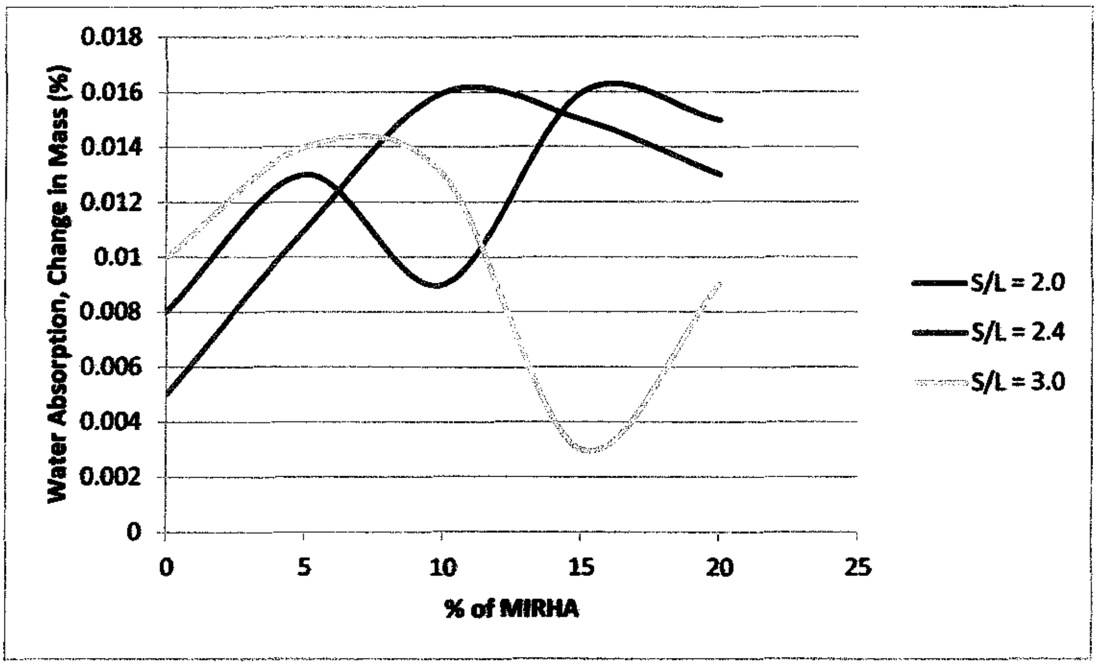


Figure 4.25 The Effect of MIRHA Addition on Water Absorption of Geopolymer

4.3.3 Coating Thickness, Adhesive Strength and Corrosion Resistivity of Geopolymer Coated Steel

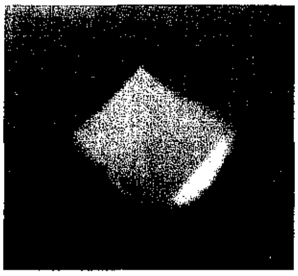


Figure 4.26 Geopolymer Coated Steel before Testing

An ideal coating thickness shouldn't be too high due to economic and energy efficiency reason. Table 4.6 shows that the coating thickness of the geopolymer coated steel increases when solid/liquid ratio and addition of MIRHA are increased. The coating method used was dipping the steel into the well-mixed geopolymer mixture. When solid/liquid ratio and MIRHA addition increase, the setting time of the geopolymer decreases. When the setting time decreases, the geopolymer coating on the steel can be hardened faster and thus forms a thicker coating. Thus, the coating thickness of the geopolymer coated steel reflects the setting time of the geopolymer. More than that, the coating of steel with 20% MIRHA addition at solid/liquid ratio of 3.0 failed due to the fastest setting time and the geopolymer couldn't adhere on the steel immediately when being dipped in the mixture.

As mentioned before, SiO_2 content of the geopolymer increases with the reduction of solid/liquid ratio and addition of MIRHA. Hence, the adhesive strength of the geopolymer coating increases with the reduction of solid/liquid ratio and addition of MIRHA since more alumina-silicate gel is formed with the increasing of SiO_2. However, there is no further proof regarding to the mechanism on the adhesion of geopolymer on the steel substrate and thus more investigations are required as the evidence of chemical bonding between the geopolymer and steel substrate.

Table 4.6 The Effect of MIRHA Addition on Coating Thickness and Adhesive Strength of Geopolymer Coated Steel

Series	Description	Solid/ Liquid Ratio	Coating Thickness (mm)	Adhesive Strength (MPa)
1	Control mix (100% fly ash)	2.0	0.65	1.5
		2.4	0.68	<1
		3.0	1.01	<1
2	95% fly ash + 5% MIRHA	2.0	0.50	2
		2.4	0.75	<1
		3.0	0.80	<1
3	90% fly ash + 10% MIRHA	2.0	0.63	5
		2.4	0.79	1.5
		3.0	2.17	<1
4	85% fly ash + 15% MIRHA	2.0	0.94	15
		2.4	1.24	2
		3.0	4.84	<1
5	80% fly ash + 20% MIRHA	2.0	1.38	>15
		2.4	1.84	2.5
		3.0	-	-

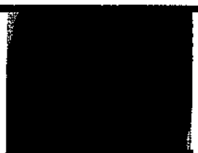
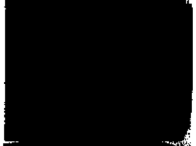
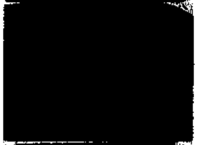
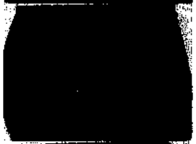
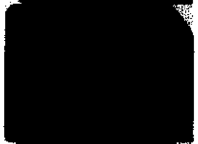
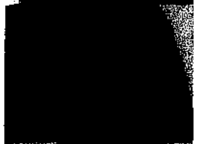
Table 4.7 The Effect of MIRHA Addition on Corrosion Resistivity of Geopolymer Coated Steel

Table 4.7 and Table 4.8 show the corrosion level of the geopolymer coated steel after corrosion testing in the salt spray corrosion chamber for 3 days. The corrosion level of the geopolymer coated steel depends on the coating thickness, solid/liquid ratio and MIRHA addition of the geopolymer. Theoretically, the coating thickness increases with the increasing in solid/liquid ratio as well as the MIRHA addition. As the coating thickness increases, the protection provided by the geopolymer coating on the steel substrate increases and thus lesser crack is formed after being sprayed by acetic acid for 3 days continuously. Other than coating thickness, MIRHA addition also plays important role in determining the SiO_2 content. SiO_2 helps in improving the properties such as compressive strength, fire resistivity, corrosion resistivity and etcetera of the geopolymer. Thus, the addition of MIRHA increases the SiO_2 content and thus enhancing the corrosion resistivity of the geopolymer.

Table 4.8 The Effect of MIRHA Addition on Corrosion Resistivity of Geopolymer Coated Steel (Control Mix)

Series	Description	Solid/ Liquid Ratio	Coating	Surface Condition	Corrosion (Yes/No)
1	Control mix (100% fly ash)	2.0		50% no coating	Yes
		2.4		Crack > 2cm	Yes
		3.0		Crack < 2cm	Yes

Table 4.9 The Effect of MIRHA Addition on Corrosion Resistivity of Geopolymer Coated Steel (with MIRHA)

Series	Description	Solid/ Liquid Ratio	Coating	Surface Condition	Corrosion (Yes/No)
1	95% fly ash + 5% MIRHA	2.0		Crack > 2cm	Yes
		2.4		Crack > 2cm	Yes
		3.0		Crack > 2cm	Yes
2	90% fly ash + 10% MIRHA	2.0		No Cracking	No
		2.4		Crack < 2cm	Yes
		3.0		Crack < 2cm	Yes
3	85% fly ash + 15% MIRHA	2.0		No cracking	No
		2.4		No cracking	No
		3.0		No cracking	No
4	80% fly ash + 20% MIRHA	2.0		No cracking	No
		2.4		Crack < 2cm	Yes
		3.0	-	-	-

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusions

- Fly ash and microwave incinerated rice husk ash (MIRHA) were characterized as Class F pozzolanic materials. The analysis showed that fly ash and MIRHA were consisted of amorphous components in spherical and beehive shapes, respectively. The mean particle size of fly ash was 9μm which was relatively finer than MIRHA with mean particle size of 43μm.
- The SiO_2/Al_2O_3 ratio increased with the addition of MIRHA while the setting time of geopolymer decreased with reduction in water. Additionally, the compressive strength of geopolymer was generally increasing at higher solid/liquid ratio and SiO_2/Al_2O_3 ratio until the optimum SiO_2/Al_2O_3 ratio was reached. The highest compressive strength of 24.41MPa was obtained when 15% of MIRHA was added at solid/liquid ratio of 3.0. Furthermore, the water absorption of geopolymer was slightly affected by the solid/liquid ratio and SiO_2/Al_2O_3 ratio with the change in mass ranging from 0.002% to 0.018%.
- The coating thickness increased with increasing solid/liquid ratio and addition of MIRHA. When the setting time was reduced, the geopolymer adhered on the steel substrate at faster rate and formed thicker coating. In addition, the adhesive strength of the geopolymer coating increased with the addition in SiO_2/Al_2O_3 ratio and the reduction in solid/liquid ratio due to the formation of more alumina-silicate gel during geopolymerization.
- The corrosion resistivity of geopolymer coated steel increased with increase in solid/liquid ratio and SiO_2/Al_2O_3 ratio. Increase in solid/liquid ratio provided

thicker coating protection while increase in SiO_2/Al_2O_3 ratio provided more SiO_2 that contributed to higher strength.

Overall, it could be concluded that the addition of MIRHA enhancing the properties of geopolymer and has the potential in improving corrosion resistivity of geopolymer coated metal.

5.2 Recommendations

- It is recommended to conduct further study regarding the effect of other synthesis parameters such as curing time and temperature. It is expected that the higher curing time and temperature can give better performance in properties to the geopolymer. However, the higher curing time and temperature require more energy consumption. Thus, the optimum curing time and temperature should be further investigated.
- Furthermore, the burning temperature of rice husk should be further studied since higher burning temperature brings more Si content to MIRHA and subsequently influences the properties of the geopolymer. It must be noted that sintering effect may occur if the burning temperature is too high.

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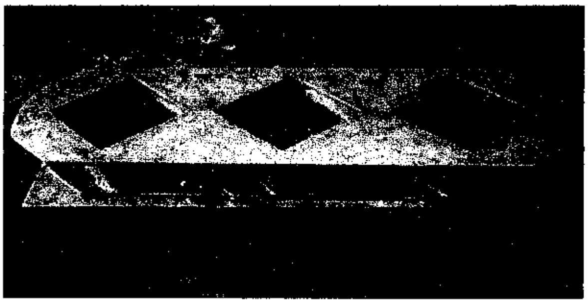
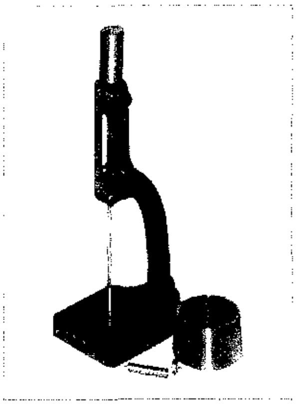
APPENDICES

Appendix 3.1 Microwave Incinerator

Appendix 3.2 50mm x 50mm Cube Mould



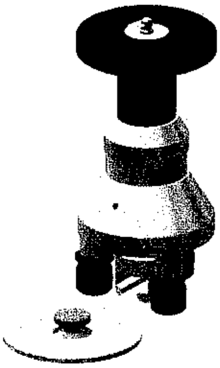
Appendix 3.3 Vicat Apparatus



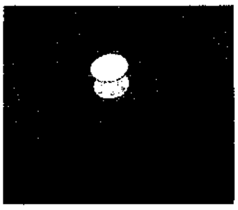
Appendix 3.4 Compression Machine

Appendix 3.5 Electronic Digital Vernier Caliper and Calliper Gauge

Appendix 3.6 Pull-off Adhesion Tester



Appendix 3.7 Dolly



Appendix 3.8 Salt Spray Corrosion Chamber