Study on Geopolymer-type Coating Using Blended Fly Ash and Palm Oil Fuel Ash (POFA)

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Supervised by

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CERTIFICATION OF APPROVAL

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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.

(WAN AMIERUL AZRIF B WAN AZIZI)

ABSTRACT

Inorganic polymer, most commonly known as 'geopolymer', is generically used as a term to describe the amorphous to crystalline reaction products from the reaction of alkali alumina-silicates with alkali hydroxide or alkali silicate solution. Biomass wastes have been lately research as raw materials for geopolymer process in the application of coating. The study was focused on the use of palm oil fuel ash (POFA) as a novel green material with high adhesive strength and slow setting time for application in steel coating. The main variables for the geopolymer produced were solid/liquid ratio and addition of POFA. It has been observed that the setting time and adhesive strength influenced by the water content in the initial mixture and strongly depended on geopolymer composition. Higher solid/liquid ratio will result in shorter setting time. Highest adhesive strength of 12.5MPa is achieved on steel substrates at higher water content mixture with the addition of 25% of POFA. It is believed that the utilization of POFA could be optimized and has a great potential to be developed as geopolymer-based coating materials.

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1. CHAPTER 1

INTRODUCTION

1.1 Background Study

Inorganic polymers, more commonly known as 'geopolymer', are alumina-silicate materials which demonstrate outstanding physical and chemical properties and exhibit a diverse series of potential applications. As it is costly using materials rich in silicon (Si) and Aluminium (Al), geopolymer work has mainly concentrated on the use of by-product or waste materials such as industrial wastes including coal fly ash, steel slag, palm oil fuel ash etc. and natural pozzolons in the geopolymer system. Further studies on these raw materials however are still required due to lack of more detailed scientific understandings and other concerns such as variations in mechanical properties, material characterizations, system parameters etc. (Divya et al., 2007).

Early researches have shown that geopolymers are cheap to produce and cost-effective solution to many problems. Due to the environmental concerns, there is growing demands for replacement of ordinary Portland cement (OPC) by using geopolymers given their numerous advantages including lower carbon dioxide emissions, thermal resistance and combined with enhanced mechanical properties both under normal and extreme exposure conditions (Esther et al., 2011). It has been reported that the wide use of geopolymer is expected to reduce the carbon dioxide (CO_2) emission from the cement industries by almost 80% in comparison with OPC (Kostas et al., 2007). All these contributed to the huge development of research in geopolymerization for different purpose of applications.

Among those potential applications, geopolymer is believed to be utilized as novel coating materials due to its high performance in displaying the strength, fire resistivity, adhesiveness and durability which is comparable or better than that of existing coating materials (Jadambaa et al., 2010). Though this has been an important driving factor for global research, more intensive research efforts are required to position this novel technology within the industrial community.

1.2 Problem Statement

Steel properties can be enhanced by applying layers of coating but the existing coating materials such as cementitious and intumescent have their own limitations and disadvantages. Hence, geopolymer-type coating is introduced due to its potential to substitute those materials. Currently, biomass wastes have been lately researched as raw materials for geopolymer process in the application of coating. Palm oil fuel ash (POFA) is one of those materials that have potential to be developed as the geopolymer-based coating. In fact, Malaysia continually generated millions of tonnes of palm oil waste annually due to its huge productivity. However, there is still limited literature on the characterization of the materials and the parameters involved in the process of geopolymer. Extended studies are therefore needed to investigate the potential of the geopolymer.

1.3 Objectives of Study

The objectives of the study are:

a. To characterize the raw materials i.e. POFA
b. To synthesize and study the effects of setting time profiles of the geopolymer
c. To study the adhesive properties of geopolymer-based coatings

1.4 Scope of Study

The scope of study will be revolving around characterizations and parameters of geopolymerization process. First, to understand the synthesis process and the characteristics of raw materials i.e. POFA. The study will then proceed by conducting experiments to synthesis the geopolymer and determining the effects of time settling profiles in various compositional blends of both raw materials. The study continues with the study on the adhesive properties of the resultant geopolymers. Since there is limited literature on this geopolymer-type coating, this work is an innovative approach in providing better understanding on the synthesis and better control of a novel coating material.

2. CHAPTER 2

LITERATURE REVIEWS

2.1 Introduction

Geopolymer is generically used as a term to describe the amorphous to crystalline reaction products from the synthesis of alkali alumina-silicates from reaction with alkali hydroxide or alkali silicate solution (Davidovits, 1991). The term geopolymer is probably more appropriately referred to as an example of what is more broadly known as 'inorganic polymer' (Van Wazer, 1970). Meanwhile, Rahier H et al. (1996) defined geopolymer as materials that provide comparable performance to traditional cementitious binders in various applications with the added advantage of significantly reduced greenhouse emissions.

In concept of geopolymer, Davidovits (1988) has suggested that some of the major pyramids, rather than being blocks of solid limestone hauled into position, they are composed of geopolymers which is then cast in their final positions in the structure. In fact, it is reported that the Romans extracted volcanic ashes from volcanic craters for use in applications such as buildings, ports, roadways as well as irrigation systems (Barker L, 2000). These historical buildings have their own aesthetic values but yet have also withstood the test of time.

Even though geopolymers have been used in various applications, their widespread use is still restricted due to lack of detailed scientific knowledge and understanding as well as long term durability studies (Perera et al., 2004). Research in this field has historically been applications-focused and the mechanisms and processes underlying geopolymer formation have only relatively recently become the subject of detailed attention. The variation in mechanical and thermal properties is also a source of concern regarding the commercial and industrial maturity of geopolymeric materials.

The main barrier that geopolymerization has to overcome is mainly related with the fixed position of OPC. However, progress is being made in this area and the understandings that have been developed till now indicate the facts that geopolymer technology does have potential for wide scaled utilization specifically in the construction industry.

2.2 Geopolymerization

Geopolymerization is a geo-synthesis where the reaction is chemically integrated minerals that involve naturally occurring silica-aluminates (Hermann et al., 1999). Geopolymers are formed through mixing solid alumina-silicate raw materials with highly concentrated aqueous alkali hydroxide or alkali silicate solutions which result in synthetic alkali alumina-silicate material. Geopolymer synthesis desires three main sources, namely raw materials, inactive filler and geopolymer liquor (Ikeda, 1998). Raw materials could be natural (alumina-silicate) minerals or industrial waste. Inactive filler, such as kaolinite or metakaolinite is used for the supply of Al^{3+} ions. Geopolymer liquor is an alkali hydroxide solution required for the dissolution of raw materials while sodium or potassium silicate solution acts as binder, alkali-activator and dispersant (Phair et al., 2001).

Geopolymerization is based on chemistry of alkali activated inorganic binders, which were accidently discovered by Purdon (Van Jaarsveld JSG et al., 1998). He summarized his study in two steps which are liberation of silica, alumina and lime and formation of hydrated calcium silicates, aluminates as well as regeneration of caustic solution. Similarly, Glukhovsky (1959) proposed a general mechanism for the alkali activation of materials primarily comprising silica and reactive alumina. A highly simplified reaction mechanism for geopolymerization is presented in Figure 2.1. The mechanism highlights the key processes occurring in the transformation of a solid alumina-silicate source into a synthetic alkali alumina-silicate.

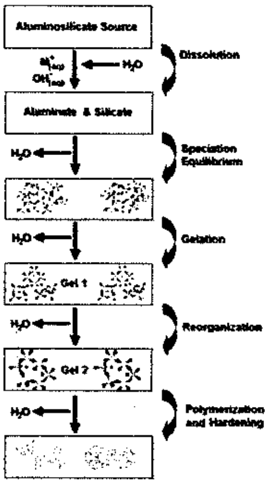
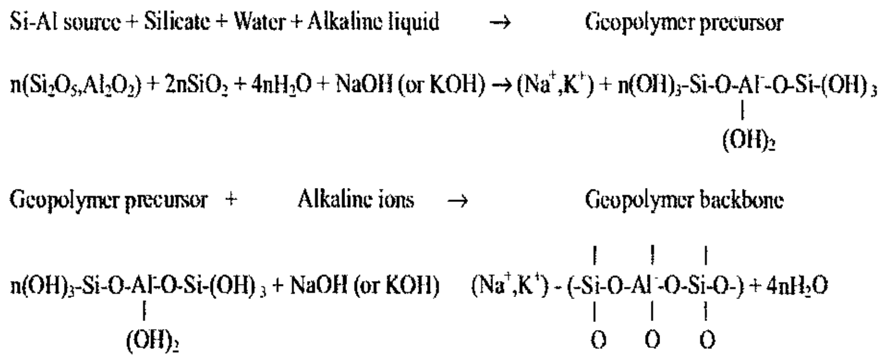


Figure 2.1: Simplified Reaction Mechanism

During geopolymerization, once the alumina-silicate powder is mixed with the alkaline solution a paste forms and quickly transforms into hard geopolymer. Therefore, there is no sufficient time and space for the gel or paste to grow into a well crystallised structure. After shorter setting and hardening time, geopolymers with tightly packed polycrystalline structure are formed exhibiting better mechanical properties which have lower density and cage-like crystalline structure (Xu and Van Deventer, 2000).

The process of geopolymerization involves leaching, diffusion, condensation and hardening steps and usually set at lower temperatures. Factors affecting the synthesis of zeolites include temperature, pH and cations and it is believed that these three factors also affect geopolymerization (Xu, 2001). The geopolymerization reaction that creates a polymeric backbone of aluminium and silicon atoms is described in Figure 2.2 (Davitovits, 1991). Simplistically, geopolymerization engages the dissolution of alumina-silicate from the source material followed by short arrayed polymerization to form a polymeric structure of Al-O-Si which represents the main building blocks of geopolymeric structure.



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

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

Geopolymer precursor + Alkaline ions → Geopolymer backbone

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

Figure 2.2: Geopolymeric Structure (Divya et al., 2007)

2.2.1 Raw Material

Raw material plays an important role in the formation of geopolymer. Many studies have been conducted in order to develop various methods to improve durability of geopolymer including the use of various ranges of raw materials. Any pozzolanic compound or source of silica and alumina that is readily dissolved in the alkaline solution acts as a source of geopolymer precursor species and thus lends itself to geopolymerization (Xu H and Van Deventer JSJ, 2000).

Davidovits (1984) primarily used kaolinite and metakaolin (calcined kaolinite) as source of alumina-silicate oxides in order to synthesis geopolymers. It functioned as structure forming species for overall geopolymerization process. As for insufficient Al dissolution, the addition of kaolinite is necessary to produce a gel of desired composition (Xu and Van Deventer, 2000). However, kaolinite added in excess will not react since it may not take part in the synthesis at all (Van Jaarsveld et al., 2002).

On the other hand, mechanical strength can be improved by using metakaolin due to decrement of water and salt transportation in the final product (Kostas et al., 2007). However, large amount of water may be required to stabilize the increasing porosity and thus it becomes too soft for construction applications but somehow it is suitable for the applications of adhesives, coatings and hydroceramics (Duxson et al., 2007).

In later years, the utilization of natural minerals, by-product and wastes was extensively investigated. Many studies have been done to provide more understanding towards those materials. Xu and Deventer (2002) for example, used fly ash, kaolinite and albite in various combinations for the synthesis of geopolymer. Meanwhile, Astutininsh and Liu (2005) used milled Australian slag with CaO content. In 2007, Yusheng et al. tested the mechanical strength of blast furnace slag-metakaolin based geopolymer. As for binder and coatings applications, many researches are being studied in current years (Smith et al., 2010, Susan et al., 2011, Jadambaa et al., 2009, 2011, Zuhua et al., 2010).

In this work, the use of Palm Oil Fuel Ash (POFA) to control setting time and adhesive properties will be conducted. In Malaysia, this biomass waste are been generated abundantly. As the second largest producer of palm oil industry, it is expected that millions of tonnes of palm oil waste will be produced annually due to its productivity. The usage of the raw materials consequently will be of great interest as well as providing greener option for waste disposals.

Figure 2.3: Palm Oil Fuel Ash

Palm Oil Fuel Ash (POFA)

Palm oil fuel ash is basically a by-product produced as palm oil husks and palm oil shells (as fuels) are burned in the boiler of palm oil mill. Generally, after combustion about 5% palm oil fuel ash by weight of solid wastes is produced (Sata et.al, 2004). The ash produced sometimes varies in terms of colour from whitish grey to darker shade based on the carbon content in it. However, the physical characteristic of POFA is very much influenced by the operating system in palm oil factory.

In practice, POFA produced in Malaysian palm oil mill is dumped as waste without any profitable return (Sumadi and Hussin, 1995). Up until now, POFA is still considered as a pain to the environment and disposed without being put for any other use as compared to other types of palm oil by-products. Since Malaysia continuously increases the production of palm oil, more ashes will be produced and failure to find any solution in making use of this by-product will create severe environmental problems. Figure 2.4 shows the forecasted production of palm oil worldwide.

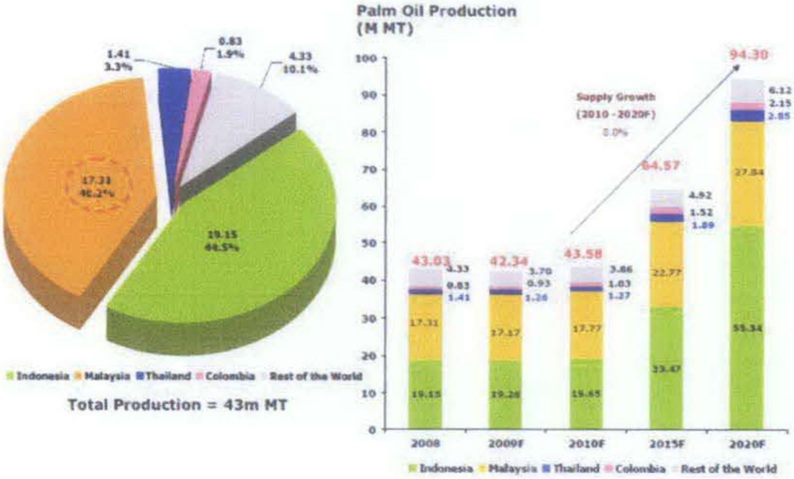


Figure 2.4: Forecasted World Palm Oil Production (LMC, 2009)

The raw palm oil fuel ash collected is greyish in colour due to unburned carbon content in it. However, whitish ash is the best due to absence of unburned carbon. In summary, previous studies in chemical analysis reveal that POFA satisfies the requirement to be pozzolanic as well as may be classified into Class F and are suitable as the raw materials in synthesizing the geopolymer.

2.2.2 Inactive Filler

Inactive filler is used for the purpose of supplying Al^{3+} ions to the geopolymerization process. It mainly consists of kaolinite or metakaolinite. The utilization of these inactive fillers is optional which is wholly dependent on the presence of Al^{3+} ions inside the synthesis process. In other words, raw materials which are enriched in Si^{4+} and Al^{3+} ions do not need the addition of inactive filler to complete the geopolymer process.

In the chemistry of geopolymer, Al^{3+} ions are needed to complete the sialate (silicon-oxo-aluminate) network. The sialate network consists of SiO_4 and AlO_4 tetrahedra linked alternately by sharing all oxygen atoms. Positive ions such as Na^+, K^+ and Ca^{++}, must be present in the framework cavities to balance the negative charge of Al^{3+}. Mechanism of geopolymers involves the polycondensation reaction of geopolymeric precursor which is alumino-silicate oxide with alkali polysiliates yielding polymeric Si–O–Al bond as shown in Equation 2.1 (Davidovits, 1991, Van Jaarsveld et al., 1998).

$$M_n[-(Si-O_2)_z-Al-O]_n.wH_2O \text{ .... } (2.1)$$

Where M is the alkaline element, z is 1, 2 or 3 and n is the degree of polycondensation. The types of polysialates distinguished are illustrated in Figure 2.5 (Davidovits, 1988).

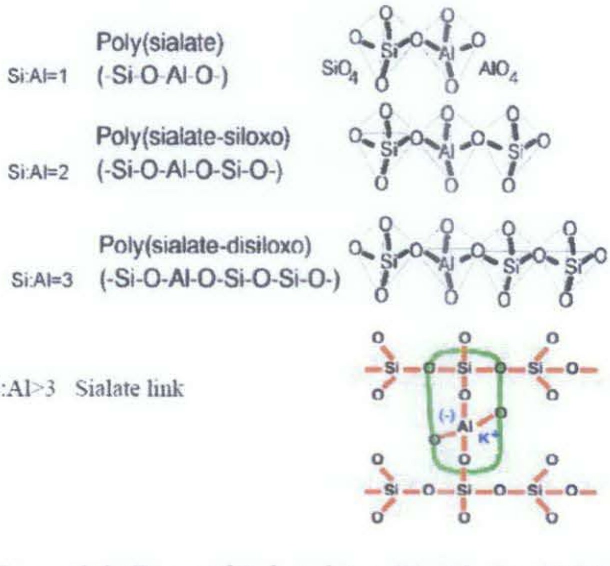


Figure 2.5: Types of Polysialates (Davidovits, 1988)

In this work however, the raw material which is POFA will be studied for the purpose of having a better understanding about its composition. Based on literatures, POFA is believed to contain percentage amount of aluminium oxide (AlO_4) which could be a good supplier of Al^{3+} ions for the geopolymer process. Hence, the addition of inactive filler is not necessary.

2.2.3 Geopolymer Liquor

Phair (2009) defined the geopolymer liquor as an alkali hydroxide which is required to dissolve the raw material whereas sodium or potassium silicate solution functions as a binder, alkali activator and dispersant or plasticiser. The alkali component includes the element of the first group in the periodic table which is also knows as alkali activated alumina-silicate binders or alkali activated cementitious material (Xiong CJ et al., 2004).

A study by Hardjito D et al. (2004) concluded that strong alkalis are required to activate the silicon and aluminium present in fly ash and setting additives in order to allow the transformation of glassy structure either partially or totally into a very compacted composite. In theory, any alkali and alkali earth cation can be used as the alkali element in geopolymerisation reactions. However, most of the studies have focused on the effect of potassium and sodium ions (Kostas et al., 2007). In addition, NaOH, Na_2SO_4, water-glass, Na_2CO_3, K_2CO_3, KOH, K_2SO_4 or a little amount of cement clinker (Xiong CJ et al., 2004).

The choice of type of alkali metal cation used during geopolymer synthesis depends on many factors. One of the most important influences is the type of source materials as well as the application purpose of the resultant geopolymers (Van Jaarsveld, 2000). For instance, sodium silicate has been used for more than a century for the production of commercial products such as special cements, coatings, moulded articles and catalysts. He also added that the alkali metal cations control and affect almost all stages of geopolymerization especially during gel hardening and crystal formation since it contributes to the structure formation of geopolymers.

2.3 Synthesis Parameters

The properties of geopolymer are influenced by how the parameters during the synthesis process are being controlled. For instance, high compressive strength geopolymer can be produced by using high reactivity source material (Alonso S, 2001). A study by Divya et al. (2007) presents the factors that affect unconfined compressive strength; curing temperature, curing time, silicate and hydroxide ratio, alkali concentration and pH. It can be concluded that the properties of the geopolymer is determined by the variations in the synthesis parameters.

This work will use the similar concept of study but it will concentrate on the effects of synthesis parameters towards the setting time of the geopolymer system. However, regardless of any raw material, the investigations into this underlying chemistry of the processes of setting and hardening development of geopolymer mixtures at the very early stage of geopolymerization are still rare in literature. Such understanding is indeed important for geopolymer formation, which can be extremely sensitive to the type of raw materials used in its processing.

As discussing in the aspect of setting time of geopolymer, the period of time is basically depends on dozen of synthesis parameters. For example, De Silva et al. (2007) varied SiO_2/Al_2O_3 ratios in the initial mixture to observe its effect on the setting time. They discovered that the content of alumina controls the setting time of geopolymerization by shortening the time as the ratio decreased. However, increasing Al_2O_3 content will result in low strength products (De Silva et al., 2007).

Another study by TW Cheng and JP Chiu (2003) shows that the setting time of geopolymer shortens as the temperature increased since higher temperature tends to increase the rate of water loss during geopolymerization. Based on the literature, it is believed that the water content plays a big role in controlling the setting time of the geopolymer. For further understanding, both studies are explained in details in the next subchapter.

2.3.1 Silicate and Aluminium Ratio

In general, inorganic geopolymers can be synthesized by alkali activation of materials rich in SiO_2 and Al_2O_3. The mechanism involves the dissolution of Al and Si in the alkali medium, transportation (orientation) of dissolved species, followed by a polycondensation, forming a 3D network of silica-aluminate structures. The setting (hardening) of geopolymer is believed to be due to the polycondensation of hydrolysed 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).

In brief, low Si/Al ratios mixture (≤1) results in single polysialate polymer structures due to primary condensation occurs only between aluminate and silicate species. Similarly as the Si/Al increases (>1), the silicate species formed as a result of the hydrolysis of SiO_2 tend to condense among themselves to form oligomeric silicates. These oligomeric silicates in turn condense with $Al(OH)_4^{4-}$ forming a rigid 3D network of polymer structures [poly(sialate–siloxo) and poly(sialate–disiloxo)]. The rate of condensation between silicate species is believed to be slower than that between aluminate and silicate species (Davitovits, 1991).

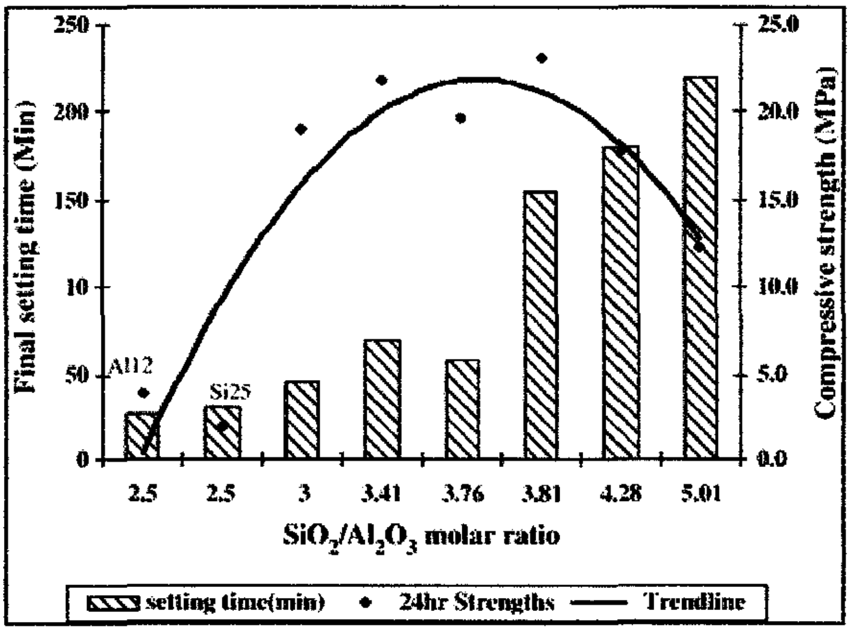


Figure 2.6: Setting Times vs. SiO_2/Al_2O_3 Ratio (De Silva et al., 2007)

De Silva et al. (2007) studied the effect of initial Si/Al ratio on the setting time based on metakaolin since the raw material is a good source of Al_2O_3 and SiO_2 which is highly reactive with alkaline activators. Typically, a mixture with SiO_2/Al_2O_3 ratios in the range of 3.4-3.8 with a Na_2O/Al_2O_3 ratio of about 1 provides better properties. Changes in the SiO_2/Al_2O_3 ratio beyond this range have been found to result in low strength systems.

However, these initial ratios can be expected to change when materials other than metakaolin are used as the Al_2O_3 and SiO_2 sources. Figure 2.6 shows their studies on the setting time with respect to SiO_2/Al_2O_3 ratios at a constant H_2O/Na_2O ratio of 13.6. From the result, it can be concluded that higher SiO_2/Al_2O_3 ratios increased the setting time but decreased the compressive strength of resulting geopolymer.

2.3.2 Temperature

Another parameter that affecting the setting time of geopolymer is temperature. Many studies have been done regarding this matter to investigate its effect towards the synthesis of geopolymer. One of the studies done discussed on setting time of different KOH concentration both at ambient temperature and 60°C temperature (TW Cheng and JP Chiu, 2003). Figure 2.7 presents the graphs of their findings, left at ambient temperature and right at 60°C.

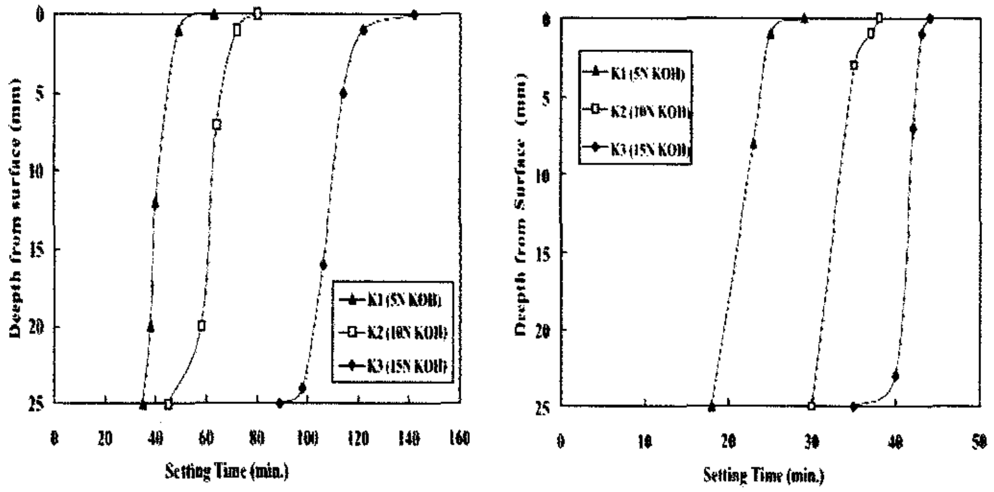


Figure 2.7: Setting Time of Both Temperatures (TW Cheng and JP Chiu, 2003)

Based on the result of the setting time measurement, it can be seen that the geopolymer setting time is faster at 60°C than at ambient temperature. At higher temperature, the rate of water loss increased due to high degree of water evaporation. It is believed that the amount of water used in the initial mixture will result in different measurement to the geopolymer setting time.

2.3.3 Roles of Waters in Geopolymerization

As mentioned earlier, water plays an important role in the whole process of geopolymer synthesis. A study on this subject matter has been discussed in details by Zuhua Zhang et al. (2009). Figure 2.8 shows one of their results regarding the water role in synthesis of geopolymer. By using calcined kaolin as the raw material, they vary the solution concentration from 3-12 mol/L of NaOH. They concluded that at higher concentration, the calcined kaolin is activated quicker, thus shorten the setting time.

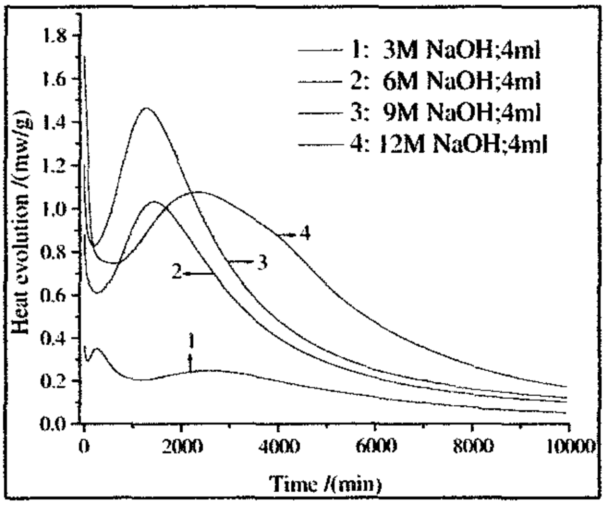


Figure 2.8: Time Curve of Calcine Kaolin (Zuhua Zhang et al., 2009)

As a matter of fact, Van Deventer (2003) stated that high alkalinity is necessary to activate the raw material. Zuhua Zhang et al. (2009) also studied the effect of liquid/solid ratio on the same raw material. It is found that higher ratio will result in faster setting time due to increase of reaction rate since higher water content will accelerate the rate of polycondensation. In other words, lower liquid/solid ratio has higher polycondensation rate. However, dilution effects of geopolymer might be reduced if too much water is used.

2.4 Steel Coating Material

Steel is one of the most common materials that being used widely in utmost engineering applications. Fire resistance is an example of important properties related to steel since it loses half of its ambient temperature yield stress at approximately 550°C (Jadambaa et al., 2011). The steel properties however could be enhanced by applying a layer of coating. Coating is defined as a covering that is applied to the surface of a substrate. In many cases coatings are applied to improve surface properties of the substrate.

In application of steel coatings, research development in geopolymer-based coatings is being conducted since it exhibits greater properties compared with the existing coatings. In fact, geopolymers are also very promising material for protective coating of different surfaces including metal due to their superior mechanical, chemical and thermal resistance properties (Jadambaa et al., 2010).

2.4.1 Type of Coatings

Coatings are basically an applied layer to expand the durability and sturdiness of certain substrate. Thus, its anticorrosion, water resistance, fire resistance, adhesiveness and other related properties are important to perform as a good coating function. In general, the coatings for fire coating materials are divided into different group namely cementitious materials, intumescent paints, fibrous material etc. However, the most commonly used materials for coating are cementitious materials and intumescent paints.

a. Cementitious Materials

In general, the cementitious materials are inorganic and unlikely combust when exposed to fire. Many studies have been done to improve its durability and wear resistance since these materials are low in cost. In its most basic form, the principle of cementitious materials is the normal mixing of producing Portland cement. Nowadays, the mixtures contain supplementary cementitious materials that are added up as a proportion during mixing. These materials are generally by-product or waste from other industrial processes or natural materials.

Some of these materials are called pozzolans, which do not have any cementitious properties but somehow it reacts with Portland cement to form cementitious compounds. However, other materials than those pozzolans do exhibit the cementitous properties (NRMCA, 2007). Supplementary cementitious materials can be used to improve coating performance in its fresh and hardened state. They are primarily used to improved workability, durability and strength.

Figure 2.9: Example of Cementitious Materials (SCA, 2011)

However, as they are made from ordinary Portland Cement (OPC), they are likely to lose strength and adversely affected by spalling when exposed to fire; spall are flakes of a material that are broken off a larger solid body and can be produced by variety of mechanisms as a result of projectile impact, corrosion weathering, cavitation etc. Spalling describes the process of surface failure in which spall is shed. In providing sufficient fire protection, cementitious coatings need to be thick, therefore it is likely to be heavy (Jadambaa et al., 2011).

b. Intumescent Paint

Thin film intumescent coatings are manufactured from organic materials and are inert at low temperatures. They swell (or intumesce) to provide a charred layer of low conductivity foam when exposed to high temperatures. This char layer reduces the rate of temperature rise in the steel and prolongs the steels load bearing capacity. It exhibits light, aesthetic and smooth properties, and can be used as thin coatings (Guojian and Jiayun, 2010).

Intumescent coatings can be applied off-site. This takes the application of fire protection off the critical path and helps to reduce the overall construction programme. A range of fully tested topcoats can be specified for use with intumescent coatings that offer a wide choice of finish in terms of colour and level of gloss. In addition, top coats can easily be repaired and redecorated. One of the most commonly used intumescent coating is a sodium silicate based paint (Signs, 2007).

The used of sodium silicate as a basis to produce a harder char which is suitable for the utilization for exterior steel fireproofing has been notified. In this application, it is necessary to produce a more substantial char, with a quantifiable expansion pressure. In the case of the exterior fireproofing, a hydrocarbon fire must be held off with quite potentially more kinetic energy than a house fire. Intumescent that produce hard chars are not typically used for interior spray fireproofing as they are not suitable for that application.

Figure 2.10: Pipes Covered With a Thin-Film Intumescent

However, the intumescent paint is more expensive and often requires extensive surface preparation before applying coating. Additionally, it has poor water resistance, low fire rating and may combine with carbon dioxide to revert back to its original constituents of silicon dioxide and sodium carbonate (Jadambaa, 2010).

2.4.2 Geopolymer-type Coating

There exists a novel class of materials called geopolymer or alkali activated alumina-silicate. Geopolymer is a man-made material with many exceptional properties including impressive fire resistance and capacity to encapsulate hazardous material (Davidovits, 2008). In the development of geopolymer coating, studies towards understanding this green novel technology is being extensively conducted. There are limited literatures on this subject matter with most of current studies been focused on the thermal and corrosion properties of the geopolymer-type coating.

Jadambaa et al. (2011) studied the fire resistivity properties of geopolymer-type coating by using the basis of metakaolin. The geopolymer-type coatings were prepared by using an industrially available silicate solution and metakaolin which was then applied to steel substrates. By taking H_2O and cement ratio as manipulated variable, they examined the coatings on the metal substrates on the basis of curing and hardening properties.

The studies showed that by using a geopolymer-type composition with a H_2O and cement of 0.41 shows improved water stability when compared with samples with a H_2O and cement of 0.5 which lost 34% of its weight after 72 hours static leaching in the water. Figure 2.11 presents the reduced weight changed for each coating samples. It can be concluded that even though the prepared coatings showed reduced water stability, their adhesion to metal substrates and thermal resistance were excellent.

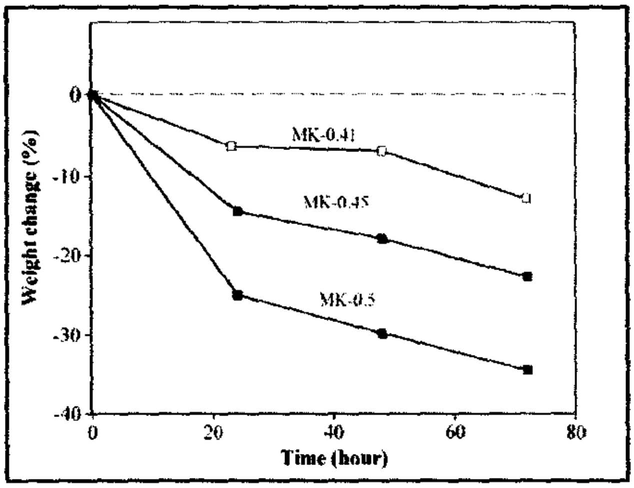


Figure 2.11: Weight Change vs. Time Curves (Jadambaa et al., 2011)

Another study on geopolymer-type coatings by Zhang et al. (2010) exposed the potential application of the materials for marine concrete. By using granulated blast furnace slag and metakaolin as raw materials, they studied the influence of microstructure to the anticorrosion property of geopolymers. The results revealed the mechanism accounting for the low water permeability, good anticorrosion in sea water and high bonding strength to paste and mortar. The physical anticorrosion was caused by the compact microstructure of geopolymer. The geopolymers were stable when immersed in sea water or exposed in air (unlike the hydration product of OPC), giving marine concrete a chemical protection.

A review on preparation of geopolymer-type coatings believed that water content of initial formulation plays a big role in the properties of resultant geopolymer. Based on synthesizing process of geopolymer from metakaolin, much water may be required due to porosity increase and therefore become too soft which is suitable for applications as adhesives, coatings and hydro-ceramics (Duxson et al., 2007). Van Jaarsveld et al (2002) also concluded that water content affected the properties of geopolymer. Further study by van Jaarsveld et al (2003) showed that the source materials determine the properties of geopolymers, especially the water ratio.

The above literatures suggested that the geopolymers can be used as coating materials based on its excellent properties. In this work however, the adhesive property of geopolymers will be tested against the different composition. As the coatings will be applied on steel substrates, it is essential for the coating to have high adhesion strength for it to perform its fire resistant function. In fact, the fireproof effect of coating material is generally due to the formation of a heat insulating layer, a protective atmosphere and to the endothermic processes that lower the surface temperature (Jadambaa et al., 2009).

3. CHAPTER 3

METHODOLOGY/PROJECT WORK

3.1 Project Activities

The research methodology for this project is divided into two phases where phase one mainly involves literature review. The second phase is the most important part of the entire study where the actual work on identifying the relationship between setting time and adhesive property are conducted. This project was mainly focus on synthesizing the geopolymer by using the raw material which is palm oil fuel ash (POFA). This research project was conducted in several stages which begin with raw material preparation and characterization, geopolymer process and ends with determination of the adhesive property of geopolymer produced. Figure 3.1 presents the simplified version of project activities for this work.

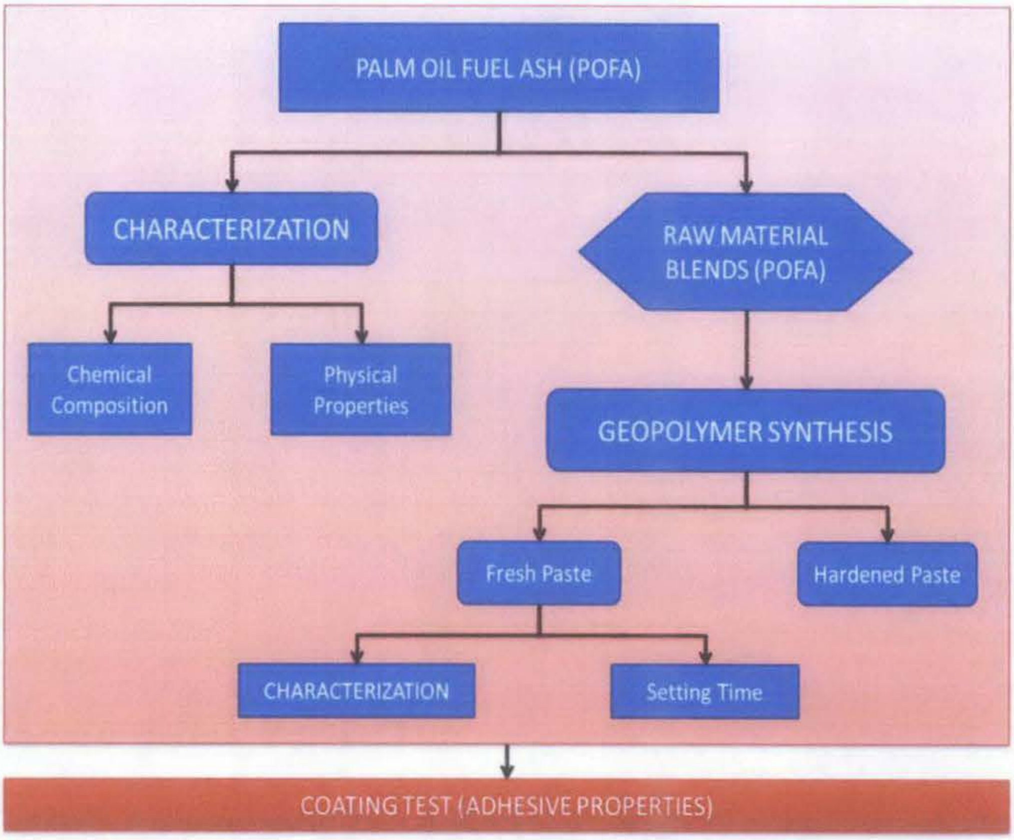


Figure 3.1: Flowchart of Project Activities

3.2 Raw Material Preparation and Characterization

First activity was involved with preparation and characterization of the raw material. The raw material which is POFA was obtained from the local industry and representatively sampled for characterization work. The sample was dried under the temperature of 120°C for 24 hours before further work is done. For this characterization work, the chemical compositions and physical properties of this waste material was determined by using X-ray Fluorescence (XRF), Particle Size Analyser, CHNS Analyser and Fourier Transform Infrared (FTIR) Spectrometer.

3.3 Experimental Setup

This experiment will study on the effect of setting time due to POFA addition in the formation of fly ash-based geopolymer at different weight percentage ranging. Since the resultant geopolymer will be used in application of coating, the setting time should be prolonged to a range within an hour. In order to observe the changes in the setting time, another process parameter was introduced which is solid to liquid ratio.

3.3.1 Solid/Liquid Ratio

The study for this particular parameter was began with the used of 100% fly ash as the raw material which is also functioned as the control mix for the whole experiment. A series of fresh paste with different solid to liquid ratios was prepared. The solid to liquid ratios was varied from 2.0 to 3.0. The geopolymer was prepared by first weighing the corresponding amount of fly ash needed. Table 3.1 summarizes the proportion of geopolymer mixture under discussion. Later the material was mixed with alkaline activating solution using mechanical mixer at low mixing speed for 15 minutes. The samples were then casted in 50-mm cube moulds as shown in Figure 3.2.

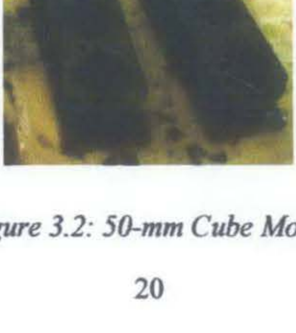


Figure 3.2: 50-mm Cube Mould

Table 3.1: Proportion of Mixture by Weight

Series	**Proportion by weight (kg)**			**Solid-liquid Ratio**
	Solid	**Liquid**		
	Fly ash	**NaOH**	**Na_2SiO_3**	
1	1.21	0.296	0.309	2.00
2	1.21	0.241	0.309	2.20
3	1.21	0.195	0.309	2.40
4	1.21	0.156	0.309	2.60
5	1.21	0.123	0.309	2.80
6	1.21	0.094	0.309	3.00

The alkaline activating solution was prepared by blending a fixed amount of commercial sodium silicate solution with certain weight percentage of water and sodium hydroxide to reach the desired modulus. The solid to liquid ratio was calculated by fixing the amount of solid (fly ash) and varying the amount of liquid (alkaline activating solution) whiles other parameters are set constant. The ratio was calculated as in equation 3.1.

$$r = \frac{m_s}{m_1 + m_2} \dots\dots\dots (3.1)$$

In which:

r solid/liquid ratio;
m_s mass of fly ash (kg);
m_1 mass of NaOH (kg);
m_2 mass of Na_2SiO_3 (kg).

In this study, the solid/liquid ratio was set in a range of 2.0-3.0 and the amount of sodium silicate is fixed at 309 grams. Thus, by rewriting the equation 3.1 as shown in equation 3.2, the amount of sodium hydroxide is calculated precisely according to the desired ratio.

$$m_1 = \frac{m_s}{r} - m_2 \dots\dots\dots (3.2)$$

3.3.2 Setting Time Measurement

The setting time for each sample was determined by using Vicat apparatus. A Vicat needle was used to measure the geopolymer setting time. After the paste was mixed, it was poured into the apparatus mould. By recording the time of a 1 mm needle penetration in the softening specimen, the time of a penetration of 25 mm was determined. This is the initial setting time. The final setting time is when the needle does not sink visibly into the paste. Total time taken for the paste to reach it's harden state is measured as setting time.

3.3.3 Compressive Strength Measurement

The casted moulds of samples (as shown in Figure 3.3) were left for 24 hours curing time before being tested for its compressive strength. The test was carried out by an ELE ADR Compression Machine 2000KN/s.

Figure 3.3: Casted Moulds

The machine was operated according to its procedure. Initially, it began the operation as both of power supplies are switched on. The sample was then put in the centre of the upper and lower platen. Later, the safety door was closed for safety purpose. After setting the machine accordingly to the sample, the compressive strength test was ran. The machine will compress the sample until certain limit before the result is shown on the display.

Figure 3.4: Compression Machine

3.3.4 Palm Oil Fuel Ash (POFA) Addition

With the data obtained from the experiment, this study was furthered to observe the effect of setting time towards the addition of POFA in the initial composition. A series of fresh paste consisting different percentage of POFA was produced. The percentage is ranging from 5% to 25%. In addition of this study, three variations of solid/liquid ratio was as well investigated; 2.0, 2.4 and 3.0. Similarly, POFA and fly ash were weighed correspondently with the calculated amount required. Table 3.2 gives the summary of the geopolymer mixture proportion.

Table 3.2: Fly Ash and POFA Mixture Composition by Weight

Series	**Description**	**Proportion by weight (kg)**			**NaOH (kg)**	**Solid/liquid ratio**
		Fly ash	**POFA**	**Na_2SiO_3**		
1	Control mix (100% Fly ash)	1.21	-	0.309	0.296	2.0
					0.195	2.4
					0.094	3.0
2	95% Fly ash + 5% POFA	1.145	0.0605	0.309	0.296	2.0
					0.195	2.4
					0.094	3.0
3	90% Fly ash + 10% POFA	1.089	0.121	0.309	0.296	2.0
					0.195	2.4
					0.094	3.0
4	85% Fly ash + 15% POFA	1.029	0.182	0.309	0.296	2.0
					0.195	2.4
					0.094	3.0
5	80% Fly ash + 20% POFA	0.968	0.242	0.309	0.296	2.0
					0.195	2.4
					0.094	3.0
6	75% Fly ash + 25% POFA	0.908	0.303	0.309	0.296	2.0
					0.195	2.4
					0.094	3.0

By using the similar procedure as producing geopolymer with variations of solid/liquid ratio, both setting time and compressive strength of the sample were determined. Both results were compared to study further on its effect towards setting time. The results and discussions on the subject will be discussed in details in the next chapter.

3.3.5 Adhesive Properties Measurement

Geopolymer pastes prepared from the respective POFA and fly ash mixture were then applied to steel substrates by dipping the metal into the geopolymer mix. Initially, the steel plates (550x300x2 mm) were lapped and polished in order to keep an uniform steel substrate. Later, the substrates were cleaned by sand paper, followed by detergent, distilled water and acetone washing.

The adhesive strength of the coated sample was measured with an Elcometer 106 Adhesion Tester. Basically, the tester uses the concept of pull-off test where dolly functioned as a medium. The surface of the dolly and metal substrate should be free from dust, moisture and oil in order to ensure a good bond is formed. Then a small quantity of adhesive was mixed and applied to the surface of the dolly. The dolly was placed at the surfaced of metal substrates and pressure applied to squeeze out excess adhesive. The adhesive was cured for 24 hours before testing the adhesive properties of the coating. Figure 3.5 shows the allocated dolly on the metal substrates.

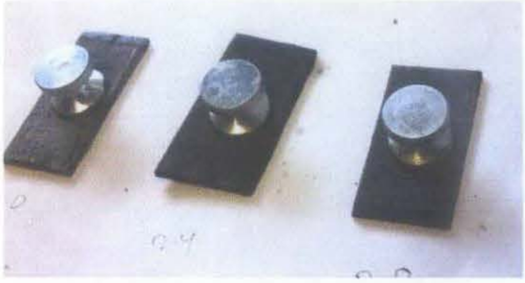


Figure 3.5: Dolly on Metal Substrates

As the adhesive was properly cured, the base around the dolly was carefully cut with dolly cutter in order to create some space for the pull-off test. The test was carried out until the dolly was pulled off from the metal substrate. Result for the adhesion strength was captured and tabulated in table.

4. CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Characterization of Raw Material

POFA consists of crystalline and amorphous components where the amorphous composition is expected to readily react with alkaline solutions. Thus, the amorphous composition of POFA is used as the reactive components. The amorphous composition of POFA is determined by XRD and FTIR spectrometer. The chemical composition of the bulk POFA is shown in Table 4.1 and Figure 4.1.

Table 4.1: Chemical Composition of POFA (Khairun Azizi et al., 2010)

Component	Chemical Composition (mass %)
SiO_2	61.85
Al_2O_3	5.65
Fe_2O_3	5.45
CaO	5.09
MgO	2.79
SO_3	0.28
Na_2O	0.1
K_2O	5.09
Ti_2O	0.32
MnO	0.11
P_2O_5	3.32
LOI	9.88

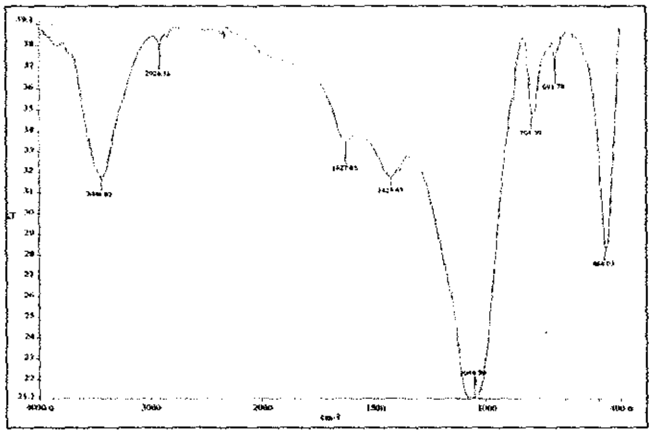


Figure 4.1: FTIR Analysis of POFA

XRD and FTIR revealed that POFA can be classified as Class F pozzolanic materials since it satisfies the requirement standard by American Society of Testing and Materials (ASTM). According to ASTM C618 specification table, the percentage requirement for the sum of SiO_2, Al_2O_3 and Fe_2O_3 should be at minimum of 70%. The table shows that POFA is suitable to be utilized as raw material for geopolymerization process.

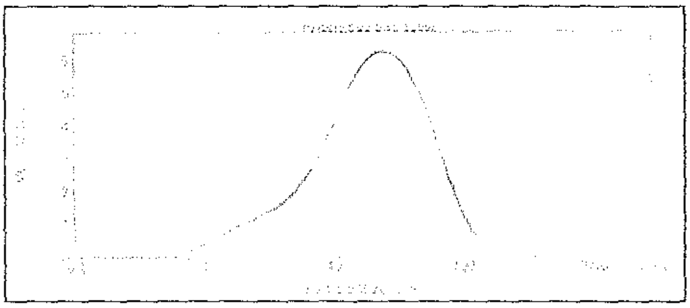


Figure 4.2: Particle Size Analysis

The particle size for POFA is determined by using the Particle Size Analyser. Figure 4.2 shows the graph of the analysis. By computing the graph, it shows that the average particle size of POFA is 21.125 µm. As for carbon content, Table 4.2 presents the data taken from the use of CHNS equipment. Carbon shows the highest value which is 52.26 by mass percentage. High carbon content in POFA reduces the fluidity of paste; however it can be treated at temperature of 500°C (Khairun Azizi et al., 2010). Further study on this subject is somehow needed to investigate the parameter.

Table 4.2: CHNS Analysis

Sample	C	H	N	S
POFA	52.260	4.891	20.270	11.710

4.2 Solid/Liquid Ratio

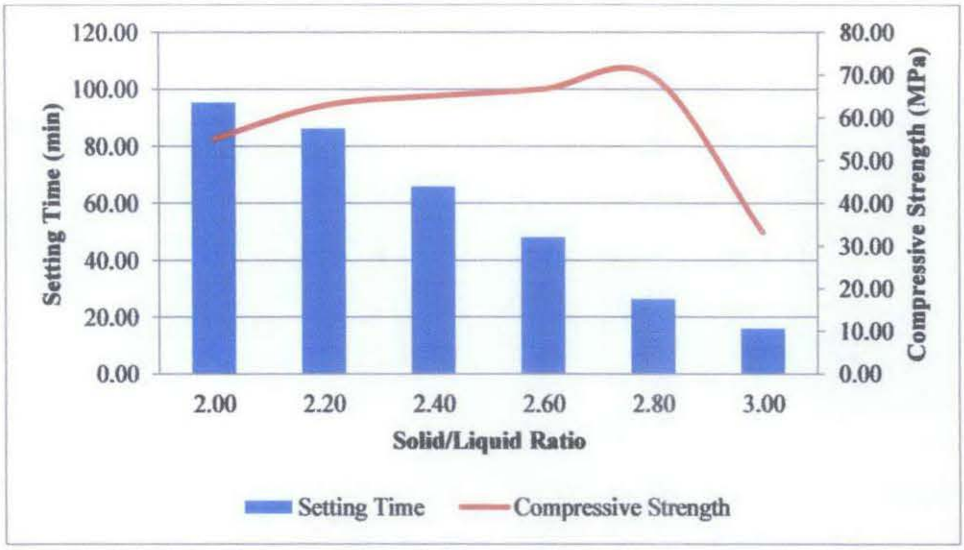


Figure 4.3: Setting Time and Compressive Strength (Different Solid/Liquid Ratio)

Figure 4.3 shows the setting time and compressive strength at different solid/liquid ratio ranging from 2.0 to 3.0. The setting time shows gradual reduction as higher ratio is used. It indicates the setting time is influenced by water content in the initial mixture. Higher solid/liquid ratio will result in faster setting time due to increase of reaction rate. Lower solid/liquid ratio will accelerate the process of polycondensation instead, thus slower the time taken for the geopolymer to harden.

Basically, process of geopolymerization can be approximately partitioned into two phases namely hydrolysis and polycondensation. In hydrolysis phase, the dissolution process requires water and the main reaction may change into polycondensation where the water is released. The exact change of phases is hardly been seen and the partitions is only from the view point of thermodynamics (Zuhua Zhang et al., 2009). It is observed that system with high water content has higher polycondensation rate but too much water will hinder the polycondensation kinetically.

On the other hand, the compressive strength increased at lower water content but somehow exhibit significant decrement as reaching the solid/liquid ratio of 3.0 due to rapid formation of geopolymer. Geopolymers at ratio of 2.0 have lower compressive strength than latter four ratios. The reason may be too much water content which may account for the slow compressive strength development.

4.3 POFA Addition

As for the addition of POFA in the mixture composition, the result showed similar trends on the solid/liquid ratio part. Table 4.3 summarizes the findings for the addition of POFA. There is slight decrement of setting time as percentage of POFA added increased. Likely, the compressive strength also shows significant changes. At higher water content, the adhesive strength of geopolymer produced is higher instead. As the amount of POFA added increased, the resulting strength was much improved.

Table 4.3: Summary of POFA Addition

Series	Description	Solid/liquid ratio	Setting Time (min)	Compressive Strength (Mpa)	Adhesive Strength (MPa)
1	Control mix (100% Fly ash)	2.0	95.35	55.10	1.5
		2.4	65.88	65.07	<1
		3.0	15.98	33.27	<1
2	95% Fly ash + 5% POFA	2.0	93.21	51.45	2.5
		2.4	61.45	60.11	<1
		3.0	12.11	25.18	<1
3	90% Fly ash + 10% POFA	2.0	92.11	45.78	5.0
		2.4	62.36	53.53	<1
		3.0	6.05	10.99	<1
4	85% Fly ash + 15% POFA	2.0	90.32	39.79	8.5
		2.4	60.12	46.26	<1
		3.0	-	-	-
5	80% Fly ash + 20% POFA	2.0	89.95	28.30	10.0
		2.4	57.48	34.61	1.0
		3.0	-	-	-
6	75% Fly ash + 25% POFA	2.0	87.65	16.03	12.5
		2.4	54.35	23.60	1.5
		3.0	-	-	-

As discussing under the subject of setting time, the result shows gradual decrement as compared with 100% fly ash mixture. It is may be due to the different percentage of iron composition between those raw materials. In addition, previous research has shown that iron rich material particles inhibit the dissolution of alumina-silicate during geopolymerization (William D. A. Rickard et al., 2011). In other word, higher iron content tends to disrupt the geopolymer synthesis, thus prolonged the setting time.

Particle size determines the surface area that is initially available for dissolution by the alkaline solution. It is also known that smaller ash particles (<20µm) are more likely ideal for geopolymerization since small particles quench faster than large particles (William D. A. Rickard et al., 2011). It is expected that the particle size of POFA is smaller than the fly ash, hence quicker the setting time due to higher rate of dissolution in alkaline solution.

The addition of POFA in initial mixture resulted in lower compressive strength as the percentage of POFA increased. Figure 4.4 presents the curve of compressive strength in different percentage of initial mixture. Geopolymeric materials designed for high temperature applications do not necessarily require high mechanical strength. For instance, in application of fire resistance steel coating, high compressive strength is not essential, whereas the stability during and after high temperature exposure is accounted.

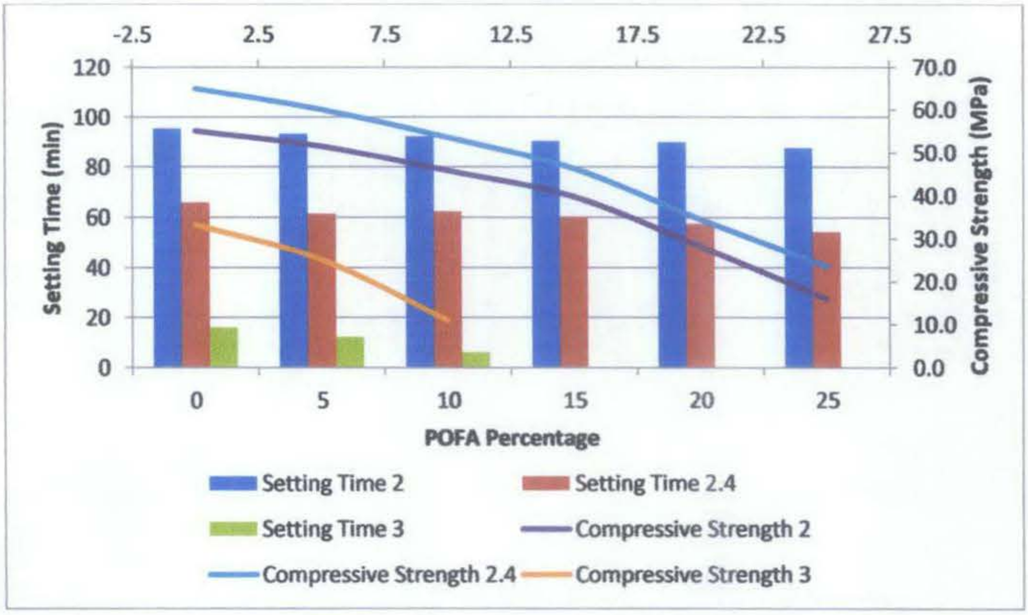


Figure 4.4: Setting Time and Compressive Strength (Different POFA Percentage)

It is believed by the author that that the variation in compressive strength between the geopolymer mixes is largely due to differing levels of geopolymerization between mixes. It means that the greater the conversion of the amorphous alumina-silicates from the fly ash into geopolymer gel, the stronger the sample. The decrement also may be due to slow compressive strength development for higher percentage of POFA added.

High adhesion strength of the coating to the metal substrate is important so that the coating can perform its fire resistance function. As shown in Table 4.3, the adhesive strength increased as higher percentage of POFA added is used, regardless of its solid/liquid ratio. In addition, the strength shows significant changes at the ratio of 2.0 where the water content is high. However, the actual adhesive strength could not be accurately determined because the large scale measurement of the Elcometer. Even though, these values are in very good agreement with previous result on adhesion strength of other raw material geopolymers to steel substrates (Jadambaa et al., 2011).

Apart from the discussion, the geopolymer samples with the addition of POFA higher than 15% and lower water content were quickly harden thus preventing measurement of those parameters (as shown in Figure 4.5 and Figure 4.6). It is believed that the POFA addition increased the reaction rate due to high water absorption from the POFA particle which leads to a very short setting time. Therefore, it is not possible for the POFA to be used at high solid/liquid ratio where there is limited amount of water for material dissolution. It is also observed that only part of the fly ash and POFA mixture reacted with the alkaline solution while other remains as excess.

Figure 4.5: Harden Geopolymer in Mixer

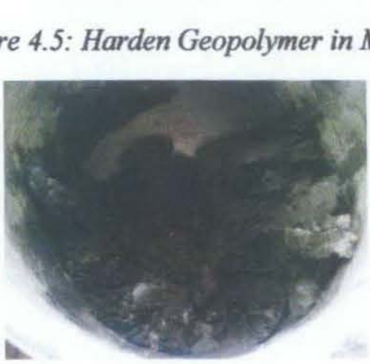


Figure 4.6: Unreacted POFA and Fly Ash Mixture Due to Short Setting Time

On the other hand, stronger adhesion strength of geopolymer is observed on metal substrate (approximately 12.5MPa) as more POFA is added. Jadambaa et al. (2010) suggested that the adhesive strength of geopolymeric gel to metal substrate is clearly depends on chemical composition and experimental procedures for preparing the geopolymer paste, raw material and substrate types etc. There is speculated that the bonding of the geopolymer to mild steel may have the component of chemical adhesion. From these references, there is no clear consensus on the mechanism responsible for the adhesion of geopolymer to steel substrate. In fact, the author does not have direct evidence of its chemical bonding between geopolymer composition and metal substrates. The detailed mechanisms of the geopolymer bonding to steel substrates are subject to further investigation.

As extend of study in coating application, it is generally recommended that the thermal expansion should match the substrate in order to maintain structural integrity during heating and cooling. Additionally, the geopolymer compositions that exposed to very high temperature exhibited shrinkage and expansion behaviour (W. Rickard et al., 2011). This behaviour however is in reverse with the metal substrate. As heated, the metal is likely to expand while geopolymers generally shrink which result in thermal mismatch, thus could lead to cracking of the coating and loss of adhesion. Therefore, geopolymer composition at high water content as at solid/liquid ratio of 2.0 is preferable for thermal expansion coatings.

5. CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

The raw material which is POFA is characterized using XRD, particle size analyser, FTIR spectrometer, and CHNS analyser. Geopolymers have been prepared by using fly ash as the main starting constituent to study the effect of the setting time. Shorter setting time is shown as the solid/liquid ratio increased. It reveals that water content in the initial mixture affects the resulting setting time. Lower water content could accelerate the dissolution and hydrolysis however it could hinder the polycondensation process when the ratio is too high. The addition of POFA in the initial mixture is believed to shorten the setting time. The resulting geopolymer is tested for its adhesive strength towards metal substrates as in application of steel coating. The adhesive strength of the coating to steel strongly depends on the chemical composition of the geopolymer. The best adhesive strength was observed for high addition of POFA at 2.0 solid/liquid ratio which is 12.5MPa. Increasing the water content will result in greater thermal coating expansion.

For further research of the project, it would be best if a detail study is carried out on the process of geopolymer specifically during the period of fresh paste to have better understanding on its microstructure evolutions. Besides, it also suggested that the discussed parameters of geopolymer are measured at higher temperature to observe the effect on geopolymer produced. In fact, it is expected that the addition of POFA would give a greater geopolymer properties at high temperature.

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