CHARACTERIZATION AND MECHANICAL PROPERTIES OF GEOPOLYMER MATERIALS USING KAOLIN AND WHITE CLAY FOR COATING APPLICATION

by

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TABLE OF CONTENT

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS

Al	Alumina
Al_2O_3	Aluminum Oxide
ASTM	American Society for Testing and Materials
Ca	Calcium
CaO	Calcium Oxide
CO_2	Carbon Dioxide
CSH	Calcium Silicate Hydrate
GGBS	Ground Granulated Blast Slag
K	Potassium
KOH	Potassium Hydroxide
M	Molar Ratio
MgO	Magnesium Oxide
mm	Milimeter
MPa	Megapascal
Na	Sodium
Na_2SiO_3	Sodium Silicate
NaOH	Sodium Hydroxide
OH	Hydroxide
OPC	Ordinary Portland Cement
S/L	Solid/Liquid
SEM	Scanning Electron Microscopy
Si	Silicon
SiO_2	Silicon Dioxide
XRF	X-Ray Fluorescence
XRD	X-Ray Diffraction

Pencirian dan Sifat-Sifat Mekanikal Tentang Bahan Geopolymer Menggunakan Kaolin dan Tanah Liat Putih Dalam Aplikasi Salutan

ABSTRAK

Geopolimer memperlihatkan kepelbagaian ciri didalam pelbagai aplikasi termasuk di dalam industri salutan. Sebagai salutan bukan organik, geopolimer adalah polimer amorfus bukan organik yang mempunyai ciri-ciri struktur ikatan yang baik terutamanya pada peringkat suhu yang rendah. Penggunaan sumber bahan baru seperti kaolin dan tanah liat putih mempunyai potensi sebagai salutan geopolimer disamping dapat mengurangkan penggunaan simen biasa. Kebolehan kaolin dan tanah liat putih dalam geopolimer salutan telah diuji pada paip epoksi gentian bertetulang yang dibekalkan dari Arab Saudi. Parameter terbaik diperolehi pada reka bentuk campuran kaolin dan tanah liat putih ditetapkan pada nisbah cecair/pepejal, 1.0 dan kepelbagaian nisbah Na_2SiO_3/NaOH dikaji. Semua campuran diuji pada suhu bilik, 80°C, 200°C, dan 400°C bagi mendapatkan lapisan yang stabil berdasarkan ciri-ciri salutan sebelum ujian kekuatan dilakukan. Mikrostruktur sumber bahan (kaolin dan tanah liat putih) dan produk geopolimer salutan diuji dibawah analisis komposisi kimia, analisis fasa, dan analisis morfologi. Selepas memperolehi geopolimer salutan yang stabil pada nisbah Na_2SiO_3/NaOH (0.40 - 0.60), kajian terhadap kekuatan mekanikal iaitu kekuatan lenturan, kekuatan perekat, kadar penyerapan air, dan kekuatan kekerasan (Vickers) diteruskan bagi mencari formulasi geopolimer salutan yang terbaik. Morfologi lapisan permukaan antara substrat (epoksi kaca gentian bertetulang) dan lapisan geopolimer (kaolin dan tanah liat putih) telah dikaji dengan menggunakan mikroskop optik. Formulasi terbaik untuk geopolimer salutan kaolin pada nisbah Na_2SiO_3/NaOH adalah pada 0.45 dengan kekuatan lenturan maksimum 33.88 MPa. Manakala kekuatan maksimum perekat untuk formulasi terbaik ini ialah 55 MPa dimana kadar peratus penyerapan air mencapai kadar resapan terendah iaitu 1.91 %. Bagi ujian kekerasan, bacaan yang paling tinggi iaitu 229.8 MPa juga diperolehi hasil daripada formulasi terbaik ini. Namun, formulasi terbaik untuk geopolimer tanah liat putih pada Na_2SiO_3/NaOH adalah pada 0.50 dengan memperolehi kekuatan lenturan maksimum iaitu pada 33.89 MPa. Formulasi terbaik ini juga berkait rapat dengan memberi kekuatan maksimum pada kekuatan perekat, kadar peratus penyerapan air, dan kekuatan kekerasan (Vickers) iaitu masing-masing pada 55 MPa, 1.93 %, dan 232.1 MPa. Daripada analisis morfologi, hampir keseluruhan zarah bertindak balas dalam proses pengeopolimeran dan kawasan yang dipadatkan lalu membentuk geopolimer gel melalui analisis mikrostruktur yang dijalankan pada kedua-dua produk geopolimer salutan (kaolin dan tanah liat putih) ke atas paip GRE. Daripada analisis fasa yang dijalankan ke atas produk geopolimer salutan kaolin dan tanah liat putih, kewujudan sampel illite, dickite, calcite, dan sodalite membuktikan pembetukan gel aluminosilikat. Berdasarkan keputusan ini, kedua-dua produk geopolimer salutan ini mempunyai keputusan yang hampir sama kerana diperolehi daripada kumpulan mineral tanah liat yang sama tetapi dari tempat yang berbeza dimana bahan-bahan ini mempunyai potensi untuk digunakan sebagai geopolimer salutan.

Characterization and Mechanical Properties of Geopolymer Materials using Kaolin and White Clay for Coating Application

ABSTRACT

Geopolymer exhibit a wide variety of properties in various applications including coating. Geopolymer as inorganic coating has good bonding structure of amorphous inorganic polymer which has excellent bonding agent properties and form at low temperature compare to organic coating. The use of new source materials such as kaolin and white clay has potential as geopolymer coating plus can reduce the use of existing cement as main material in existing cementitious coating. The performance of kaolin and white clay geopolymer coating has been tested on glass reinforced epoxy (GRE) pipe sample which provided from Saudi Arabia. The parameter to find the best mix design for kaolin and white clay is by fixing the solid/liquid ratio at 1.0 while the ratio of Na_2SiO_3/NaOH ratio is verified and has been cured at room temperature, 80°C, 200°C and 400°C to get the stable coating surface based on coating properties appearance before proceed to the strength testing. The microstructure of kaolin and white clay geopolymer coating were testing under chemical composition analysis, phase analysis and morphology analysis for raw materials (kaolin and white clay) and geopolymer coating products (kaolin and white clay). After sample of Na_2SiO_3/NaOH ratio from 0.40 – 0.60 can stand cured at room temperature, 80°C, 200°C and 400°C, sample then is proceed to mechanical strength testing by flexural strength, adhesive strength, water absorption, and hardness to get the best formulation. The morphology of the interfacial layer contact between substrate (glass reinforced epoxy sample) and geopolymer coating (kaolin and white clay) layer is studied using optical microscope. The best mix design for kaolin geopolymer coating was at 0.45 ratio Na_2SiO_3/NaOH with maximum flexural strength at 33.88 MPa. The adhesive strength at this mix design was among the highest strength which is 5.5 MPa as well as the water absorption achieved the lowest percentage at this mix design which is 1.91 %. During hardness test, the highest strength (229.8 MPa) was identified in the best mix design kaolin geopolymer coating. However, the best design for white clay geopolymer coating was at 0.50 ratio of Na_2SiO_3/NaOH by maximum flexural strength of 33.89 MPa. This best mix design also correlate with the highest result obtained in adhesive strength, water absorption, and Vickers hardness which is 5.5 MPa, 1.93 % and 232.1 MPa respectively. From morphology analysis almost all particle has take part in geopolymerization process and the compacted area has represent the form of geopolymer gel through microstructure analysis that has carried out both kaolin and white clay geopolymer coating product on GRE pipe. From the phase analysis on kaolin and white clay geopolymer product, the existence of illite, dickite, calcite and sodalite sample proved the formation aluminosilicate gel. Based on the result, both kaolin and white clay geopolymer coating has comparable result due to the materials come from same group of clay mineral but come from different area which make these materials has potential to be use in geopolymer coating.

CHAPTER 1

INTRODUCTION

1.1 Research background

Coating is a covering material with thin film of functional materials which is practically used towards surface of an existing object, infrastructure or product, normally called as substrate to allow the lifespan as well as reducing additional maintenance cost during service life. Application of the coating has been agreed a wide range in enhanced the properties of the substrates in term of adhesion, appearance, wet ability, thermal resistance, wear resistance, and corrosion resistance. The coating material in coating application can be classified as solid, liquid or gas; metallic or non-metallic; organic or inorganic. Nowadays, the use of inorganic coating looks like an alternative way to the organic coating mainly due to the lack of thermal resistant which limits their applications in coating application. Inorganic coating has advantages of exhibit excellent thermal resistance, high mechanical properties, acid resistant, and environmental friendly (Davidovits, 1994; Wallah et al., 2006; Duxson et al., 2007; Daniel et al., 2007). Therefore, geopolymer as inorganic polymer or alkali activated binder (Davidovits, 1994) has expanded international interests and its high performance makes it a new coating material.

Geopolymer is binder contrived of aluminosilicate materials which has been investigated, reviewed, and used for several decades by several researchers throughout world. The geopolymer chemistry concept was invented in 1979 (Davidovits, 1979) and the idea of geopolymer concept is an aluminium silicate inorganic polymer formed by geochemistry (Davidovits, 1991). Geopolymerization process can be defined as dissolution of aluminium (Al) and silicon (Si) species from by-product materials such as fly ash, silica fume, slag, kaolin, etc. which can form geopolymer source materials followed by the polymerization of active surface group as well as soluble species to form a gel and consequently hardened geopolymer product (Xu et al., 2000).

Geopolymerization process is involved the synthesized of geopolymer by polycondensation reaction of geopolymeric precursor and alkali polysilicate. The geopolymerization process involved three separated but inter-related stages which are: (1) dissolution of Si and Al atoms from the source material all the way through the action of hydroxide ions, (2) condensation or orientation or transportation of precursor ions into monomers, (3) setting or polymerisation/polycondensation of monomers into polymeric structures (Cheng et al., 2003; Mustafa et al., 2011).

The potential of source materials in a wide range of slag, waste and natural Al–Si minerals possibly will provide as potential source materials for the production of geopolymer has been studied previously (Davidovits, 1999; Van Jaarsveld et al., 1997, Van Jaarsveld et al., 1999; Xu et al., 1999, Xu et al., 2000). The characteristic and performance of source materials such as metakaolin, fly ash and granulated furnace slag has proved for the fire resistance panels and metal coatings application (Zuhua et al. 2010a; Zuhua et al. 2010b; Temuujin et al. 2009; Cheng et al., 2011; Temuujin et al. 2011). Kaolin is natural clay in one of our natural world resources that has potential to be use as geopolymer sources materials since it has high silica (Si) and alumina (Al) which is considered both as clay mineral and rock. Kaolin is contained of mineral or uncontaminated kaolinite for example illite, dickite and nacrite which is related towards mineral grouping which consist of micas, feldspars, smectites and quartz (Georges-Ivo, 2005). Kaolin has developed in industrial application such as the plastic, ceramic, rubber, paint and paper industries. Another application include iron smelting, cosmetics, cat litter, polish, fertilizers, oil absorbers, pencils and crayons, fungicides, pesticides, insecticides, vegetable clarifiers and wine and pharmaceutics (Murray et al., 1986; Ekosse, 2001; Al-Shameri et al., 2009). Kaolin has huge advantage in to be one of main source materials in geopolymer coating because of its abundance, whiteness, fine particle size, plate-like structure, low cost, environment friendly and has suitable properties for multiple usages. Furthermore, white clay as raw materials has potential in geopolymer coating which is has same chemical composition with kaolin but still little research on this raw material.

Besides source materials, the alkaline activator is also the main component in synthesis of geopolymer. The merger of sodium hydroxide solution and sodium silicate solution as the binder materials in previous studied enhanced the reaction between the source material and alkaline activator. The common used of alkaline liquid in geopolymerization is a combination of sodium silicate or potassium silicate and sodium hydroxide (NaOH) or potassium hydroxide (KOH) (Palomo et al., 1999; Davidovits 1999; Xu et al., 2000; Barbosa et al., 2000; Swanepoel et al., 2002). The type of alkaline liquid plays an important role in the polymerisation process (Palomo et al., 1999). Plus, the reactions occur at a high rate as the alkaline liquid which contains soluble silicate with those combinations compared using single alkaline hydroxides.

1.2 Problem Statement

Nowadays a broad range of cementitious coating products is widely used in modern society. The performance of cement due to the flexibility of onsite casting or prefabrication at all ambient temperature make Ordinary Portland Cement (OPC) has become one of the mainly used cementitious sources materials within the world. Nevertheless, most of OPC products are organic coatings and by manufacturing of most organic coating was harmful to both humans and the environment. Harmful and hazardous materials used in the production process or in and after preparation of the organic coating might also volatilize into the atmosphere. The use of organic coating materials lead the increasing of CO_2 emission during manufacturing process has led to the development of new formulations such as inorganic coating materials (Davidovits, 1994; Duxson et al., 2007). Geopolymer sources materials can present equivalent performance towards traditional cementitious materials in a several main applications, other than with the additional improvement of considerably in reducing greenhouse emissions (Gartner E, 2004).

Geopolymer is a novel invention of construction materials, a new binder for new cement for concrete, new material for coatings and adhesives, waste encapsulation and fibre composites (Cioffi et al., 2003). Hence, these geopolymer coating can be one of the solution to reduce the risk or lack of workability such as on glass fibre-reinforced epoxy (GRE). Since the consumption of these material raise, therefore to improve the design limits in terms of performance is needed. It is important to consider the short and long term behaviour of GRE pipe for 20 to 30 years by complex loading based on failure testing. GRE pipes are generally designed towards high pressure resistance. However, as with all pipelines, GRE pipes face significant risks of external interference of pipeline failures and has to spend millions of money in maintenance. Therefore, by applying geopolymer coating it can improvise the mechanical and physical properties of the GRE pipe based industrial needed.

1.3 Research Objective

The prime objective of this research is to study the design and microstructure of geopolymer materials for coating application. Several geopolymer source materials were prepared in order to study:

1. To determine best formulation of Na_2SiO_3/NaOH for kaolin and white clay geopolymer depend on strength for coating application
2. To identify the microstructure of kaolin and white clay geopolymer coating product on GRE pipe.
3. To analyze the morphology of the interfacial layer between substrate and geopolymer coating

In order to fulfil the objective of this research, these several testing has been used to analyze which are morphology analysis, chemical composition analysis, phase analysis, adhesive strength test, flexural strength test, water absorption test and hardness test.

1.4 Scope of Study

The scope of study for this research is focused on two main source materials; kaolin and white clay. The performance of this research is covered on characterization study which are morphology analysis, chemical composition analysis, phase analysis. Mechanical study for this research is covered by adhesive strength test, flexural strength test, water absorption test and hardness test. Testing age for sample for conducting mechanical testing is 3 days constant for all mechanical testing. The alkaline solutions used in this research are sodium hydroxide (NaOH) and sodium silicate (Na_2SiO_3).

NaOH in pellet from with (99%) purity and Na_2SiO_3 consists of SiO_2 = 29.4%, Na_2O = 14.7% and H_2O = 55.9%.

1.5 Thesis Outline

This thesis is clarified separately into five chapters. Chapter 1 describe the background study of this research, problem statement, objectives of research, scope of study and the thesis outline.

Chapter 2 discuss on the literature review based on the geopolymer as a coating and geopolymer coating technology as another alternative to conventional organic coating. The literature review is focused on design of coating process, design and mix proportion of geopolymer coating, coating method and geopolymer coating properties.

Chapter 3 describes the planning and the methodology according this research. This chapter elaborate more on research materials (kaolin, white clay, alkaline activator, and substrate used), materials proportion, mixing process, and method used in geopolymer coating application. Furthermore, this chapter also explained detail on the characterization and mechanical testing for geopolymer coating follows the ASTM requirement.

Chapter 4 elaborates the results and discussion from the characterization and mechanical testing that has been carried out for this research. The best mix design for kaolin and white clay are also discussed in this chapter.

Lastly, chapter 5 states the conclusions of this research and proposed some recommendations for the future work. The end of this thesis is complete by a bibliography and appendices.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

The coating or surface protection system used to the surface of an object or substrate towards enhance properties of the substrate, such as extend their service life, thermal resistance, scratch resistance, wear resistance, corrosion resistance, adhesion and appearance. The coating industry is a material demanding in manufacturing industry. The organic coating and inorganic coating are two types of coating commonly used in coating industry. Based on behaviour of anticorrosion, high chemical resistance and strong adhesion to the metal surface, the organic coatings have become a common used as protecting coating for metal. Organic coating can be applied on both metallic and non-metallic substrate. Materials which might be unsafe towards both human and the environment are used in the manufacturing of most organic coatings.

Therefore, the using inorganic coatings as protective coating materials look like as an alternative choice in coating application. Inorganic coatings have many advantages. They are much resistant than concrete and environmentally friendly. The corrosion and abrasion resistance of inorganic coating can be significantly increased as protective coatings and this is a growing industry of substantial economic importance. Geopolymer is aluminosilicate inorganic polymer materials as inorganic coating has potential to be use as alternative to the organic coating. This chapter has review the geopolymer coating as coating in term of advancing the substrate that used in this research which is the glass fibre-reinforced epoxy (GRE) by conducting several mechanical testing to get the best formulation of geopolymer coating.

2.2 Glass Fibre-reinforced Epoxy (GRE)

Glass fibre-reinforced epoxy (GRE) composite is one of the commonly used in pipeline system underground and underwater transportation of fluid materials, marine application, building and automotive industries. GRE pipes are normally designed to withstand high pressure. Their limitation of GRE performance in heat resistance, fracture failure pressure and also impact performance for long-term behaviour which results in reduced performance of GRE pipe (Gibson, 1989; Gibson et al., 1991; Frost, 1999). GRE pipe sample withstand to temperature up to 225°F (107.2°C) when used with oil and gas, and up to 275°F (135°C) for industrial and chemical applications (API, 1980; ASTM D 2992-91). The maximum pressure for these pipes and fittings is 4000 psi (27.58 MPa).

The rupture failure pressure of GRE pipes is a critical problem that needs to be focused on, considering the fact that they may subjected to various loads during their service life period (Tarfaoui et al., 2007). These loads could possibility damage the layer of the composite pipes, which usually unseen by visual inspection. Therefore, this research used GRE pipe sample as substrate which is supplied by Saudi Arabia from oil and gas industry pipe. The capability of geopolymer form at low temperature and excellent mechanical properties has good potentials to create an innovative coating application in term of advancing the properties of the GRE pipe by using new geopolymer source materials.

2.3 Basic Geopolymer Coating

Geopolymer has received much attention as green alternative to ordinary Portland cement (OPC), with most of the work focused on various applications in nuclear waste disposal, membrane materials, coating, metallurgy, emergency repairs and transportation (Van Jaarsveld et al., 1999; Hua et al., 2000; He et al., 2013; Zhang et al., 2014; Zhang et al., 2015). The workability of geopolymer and manufactured at normal temperature has made geopolymer increasingly being used in adhesiveness, coating for pipeline and floors, mending interfaces, and fireproofing covers (Davidovits, 1991; Davidovits, 2008).

Geopolymer has displayed an opportunity all together to improve both environmental and engineering performance compared to traditional technology (Palomo et al., 1999; Duxson et al., 2007). Due to the excellent resistance to sulphate and seawater attack (Bakharev, 2005; Fernandez et al., 2009), geopolymer as a novel coating material has been studied for protective marine concretes (Zuhua et al., 2010a, Zuhua et al., 2010b). Geopolymer coating application has been studied to advance the performance in aircraft (G.P. Bierwagen et al., 2001), construction (Balaguru et al., 1997). Besides, geopolymer have properties of anti-aging and anti-ultraviolet capability that make geopolymer suitable for fabricating inorganic exterior wall building coating (Liu et al., 2008; Li et al., 2013).

In geopolymer coating, geopolymer source material acted as aluminosilicate source towards produce geopolymer coating material using sodium hydroxide (NaOH) and sodium silicate (Na_2SiO_3) as alkaline activator (Temuujin et al., 2009; Temuujin et al., 2010; Mustafa et al., 2011; Mustafa et al., 2013). Geopolymer source materials such as kaolin, silica fume, ground granulate blast slag (GGBS), boiler ash, volcano ash and fly ash reactivated via alkaline solution has potential to be use as geopolymer coating. Previous research in geopolymer studied has proved that fly ash was possesses good quality mechanical properties and durability in aggressive environments (Davidovits et al. 1994) while silica fume has been research as one of the source materials by adding the silica fume content and test based on the geopolymer porosity, water absorption and strength (Dutta et al., 2010). Besides that, kaolin as source material in geopolymer has improved mechanical strength (Xu et al., 2001). According to the past research, GGBS activated with alkaline solution be able to improve strength properties and slag concrete with satisfactory workability (Douglas et al., 1991).

2.4 Geopolymer as a Coating

Geopolymer is produced by aluminosilicate source materials dissolve with alkaline solution which alter into tridimensional tecto-aluminosilicate materials. Geopolymer source materials commonly used geopolymer source materials such as granulated blast furnace slag (GBFS), kaolin, metakaolin and fly ash which contain mostly high content in silica (Si), alumina (Al), calcium (Ca) and ferum (Fe). Geopolymer source material reacted as aluminosilicate source dissolved by alkaline solution in geopolymerization process to produce geopolymer coating. Previous research has used the merger of sodium hydroxide and sodium silicate to use as alkaline activator (Temuujin et al., 2009; Temuujin et al., 2010; Mustafa et al., 2011; Mustafa et al., 2013) was prepared coating paste by mixing fly ash with alkaline activator solution with the ratio of fly ash/alkaline activator to NaOH/ Na_2SiO_3 was used at 2.5 for all mixture in this process (Mustafa el al., 2013). The combination of 12 M concentration of sodium hydroxide (NaOH) and sodium silicate (Na_2SiO_3) is prepared before mixed with the fly ash. After adding the alkaline solution to fly ash powder, the mixture paste was applied to ceramic substrates by dipping method. The ceramic plates were placed in plastic bag cured at 70°C for 24 hours before sintered and coating thickness is controlled from 0.3 to 0.5 mm (Mustafa et al., 2013).

Geopolymer is known as a group of three-dimensionally networked by synthetic alumina-silicate materials which is similar to natural zeolite minerals, and first developed by Joseph Davidovits in 1978 (Comrie et al., 1988; Davidovits, 1991). According to Geopolymer Chemistry and Applications book (Davidovits, 2011), geopolymerization process with involves 3 phases. The first phase is alkaline depolymerization of the poly (siloxo). The second phase involve the formation of the ortho-sialate $(OH)_3$-Si-O-Al-$(OH)_3$ particle followed by polymerization (polycondensation) into polymers and higher oligomers. The chemical composition of geopolymer is rather similar to zeolites other than with an amorphous microstructure. Geopolymer application depends on chemical composition within geopolymer source materials as stated by Davidovits (1999) in Table 2.1. It is different with ordinary Portland/pozzolanic cements, geopolymer do not form calcium-silicate-hydrates (CSHs) for matrix formation and strength, but utilize the polycondensation of alumina and silica precursors towards achieve structural strength. Hence, geopolymer coating illustrated a new concept and excellent potential of cementitious coating in coating application.