UNIVERSITI PUTRA MALAYSIA

EFFECTS OF NANOCLAY ON PROPERTIES OF RICE HUSK ASH/ KAOLIN-BASED GEOPOLYMER COATING COMPOSITES

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By

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Thesis submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Master of Science

October 2017

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the Master of Science

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October 2017

Chairman : Norkhairunnisa Mazlan, PhD
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Research was done to investigate whether the addition of nanoclay influenced the properties of the rice husk ash/kaolin based geopolymer coating composite in fire resistance and bond strength. This geopolymer coating composite that mostly consists of silicon and aluminium are activated by alkaline activator which are the combination of sodium silicate (Na_2SiO_3) solution and sodium hydroxide (NaOH) solution to produce the coating resin.

The preliminary works were initially done in order to obtain the best mixture proportions of geopolymer coating composite. The sodium hydroxide molarity of 8 M, 1.0 ratio solid to liquid and 5.5 ratio of alkaline activator were chosen as the control parameters while the ratio between rice husk ash and kaolin was varied.

The fire-retardant test results showed that with 20:80 of rice husk ash to kaolin, better fire performance was obtained as the temperature at equilibrium of that coating is 230°C. The fire performance of geopolymer coating composite improved with nanoclay addition and the maximum of bond strength obtained was 3.48 MPa. These performances were seen in samples with 3 wt. % of nanoclay addition. However, the adhesion strength of the geopolymer coating composites were not majorly affected by nanoclay addition.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia Sebagai memenuhi keperluan untuk Master Sains

KESAN SAMPINGAN NANO-TANAH LIAT TERHADAP SIFAT-SIFAT KOMPOSIT SELAPUT GEOPOLIMER ASAS ABU SEKAM PADI/KAOLIN

Oleh

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Penyelidikan telah dilakukan untuk menyiasat sama ada penambahan nano-tanah liat mempengaruhi sifat abu sekam padi/kaolin berasaskan komposit lapisan geopolimer dalam rintangan api dan kekuatan ikatan. Komposit selaput geopolimer yang kebanyakannya terdiri daripada silikon dan alumina diaktifkan oleh pengaktif alkali yang merupakan gabungan larutan natrium silikat dan larutan natrium hidroksida untuk menghasilkan selaput geopolimer.

Penyelidikan awal dilakukan untuk mendapatkan campuran terbaik komposit selaput geopolimer. Kemolaran natrium hidroksida 8 M, nisbah 1.0 padat kepada cecair dan nisbah pengaktif alkali 5.5 dipilih sebagai parameter kawalan manakala nisbah antara abu sekam padi dan kaolin berbeza-beza.

Keputusan ujian kalis api menunjukkan bahawa dengan nisbah 20:80 abu sekam padi ke kaolin, prestasi kebakaran yang lebih baik diperolehi dengan mencapai suhu keseimbangan pada 230°C. Prestasi kebakaran komposit selaput geopolimer bertambah baik dengan penambahan nano-tanah liat dan maksimum kekuatan ikatan yang diperolehi ialah 3.48 MPa. Penambahbaikan ini dilihat dalam sampel dengan 3 wt. % tambahan nano-tanah liat. Walau bagaimanapun, kekuatan lekatan komposit selaput geopolimer tidak banyak dipengaruhi oleh tambahan nano-tanah liat.

ACKNOWLEDGEMENT

I would like to thank you my supervisor Dr Norkhairunnisa Mazlan and my co-supervisor Dr Azmah Hanim and Dr Noorazline for their invaluable support, guidance and suggestions throughout this research.

The technical assistances provided by the technical staff are gratefully acknowledged. I would like to thank Mr Salahuddin for his kind help in various ways throughout the research work.

I would also like to thank Miss Afiqah Musa for her caring assistance during the experimental work.

Many thanks to friends for their tremendously support throughout this research work. Last but not least, special thanks go to my *Mak* & *Abah* and *You* for their love, support, encouragement especially in difficult times which enabled me to complete this research work.

This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the Master of Science. The members of the Supervisory Committee were as follows:

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

DTGA	Derivative Weight
FA	Fly Ash
KA	Kaolin
RHA	Rice Husk Ash
rpm	Revolution Per Minute
SEM	Scanning Emission Morphology
TGA	Thermogravimetric Analysis
wt. %wt.	Weight Percentage
µ	Micron

CHAPTER 1

INTRODUCTION

1.1 Introduction

The development of geopolymer materials has drawn interest from researchers all over the world and the application of geopolymer has been expanded in many areas. Usually, pozzolanic materials like granulated blast furnace slag, fly ash, rice husk ash, metakaolin, and kaolin are used in cement and concrete because of their high compressive strength (Davidovits, 2002; Mustafa Al Bakri et al., 2012). This unique material called geopolymer is obtained from mixing of aluminosilicate sources with activated by alkaline activator solutions. When an aluminosilicate source is readily dissolved in alkaline activator solution, a process called as geopolymerization takes place to produce hydrated product (Zarina et al., 2016). Geopolymerization process is also known as geo-synthesis which is the reaction that chemically integrated minerals that involved the raw geopolymer material (Khale & Chaudhary, 2007). In other words, any sources of silica and alumina or pozzolan compound that activated by alkaline activator solution, acts as a source of aluminosilicate undergoes a geopolymerization.

The alkaline solution acted as an activator in geopolymerization is a compound from the element of first group in the periodic table which is commonly sodium and potassium. This alkaline solution also called as alkaline activated aluminosilicate binders (Khale & Chaudhary, 2007; Mustafa Al Bakri et al., 2012). The most common alkaline activator solutions used are sodium silicate, sodium hydroxide and potassium hydroxide (Bakharev, 2005). The mechanism of geopolymerization process involved the polycondensation reaction of geopolymeric precursors (aluminosilicate structure) that yields the polymeric Si-O-Al bond (Zarina et al., 2016; Khale & Chaudhary, 2007; Mustafa Al Bakri et al., 2011). This geopolymerization process is one of research field for utilizing the solid waste and by-products by producing a cost-efficient geopolymer materials and solved environmental problems where hazardous materials have to be treated.

Rice production is one of main agriculture activity in Malaysia. From the production of rice, it produces a major waste called rice husk. Rice husk is agricultural residues obtained from the outer covered of rice grains during the milling process and by burning the rice husk under controlled conditions (time and air flow) at high temperature ranging from 400° - 1000°C, the remained ashes are named RHA (RHA) (Xiong et al., 2009; Kumar et al., 2013). This RHA is contained mostly with silica approximately about 98% in mass. Silica is porous in nature and it has hydrophilic Si-OH groups which make it to have higher tendency to absorb moisture (Xiong et al., 2009). Since, RHA is highly content with silica, the structure and property of the RHA were also influenced by the nature of silica. Highly porous structure of RHA lead to its low-density property, large surface area and thermal resistivity.

Another raw pozzolanic material which is suitably used in making geopolymer is kaolin. Kaolin clay is technically known as hydrated aluminosilicate and structurally unmodified. The physical form of kaolin is powder and it is mainly consisting of silica (47.0 – 53.0 wt. %) and alumina (32.0 – 38.0 wt. %). However, there is lack of study done on using kaolin as based for geopolymer. Purpose addition of kaolin is to produce a good ratio balance of Si to Al when combined with RHA.

Nanofillers are usually added into composite system to improve the flammability resistance, good thermal stability, decreased water absorption and increased electrical properties (Subasri & Hima, 2015; Miltner et al., 2010; Šupová et al., 2011; Baniassadi et al., 2011). Only small amount of nanofillers (<10 wt. %) are needed to disperse in polymer matrix due to their small size in nature and its high aspect ratios properties (Sibeko & Luyt, 2013; Subasri & Hima, 2015). As it has high surface area, the interaction with the polymer matrix can be improved thus helps in uniform distribution of the nanoparticles. Examples of nanofillers are nanoclay, nanofibers, carbon nanotubes (SWCNT) and multi- walled (MWCNT), metal oxide nanoparticles.

The application of geopolymer has been mainly focused on cement and concrete production. The other potential application for geopolymer material is in coating application. Pozzolanic materials such as metakaolin, fly ash and granulated blast have been experimented as main source for the geopolymer coating and these aluminosilicate sources proved that geopolymer material has good adhesive with steel. Therefore, this research is conducted to develop the rice husk ash/kaolin based geopolymer coating composite with nanoclay addition. In this research, the main materials are rice husk ash/kaolin as geopolymer binder and nanoclay as reinforcing fillers. In order to determine the optimum mixture proportions of geopolymer coating composite, the composition of rice husk ash: kaolin is studied along with the fire performance and the morphology of the geopolymer coating samples. Prior to that, a study on water absorption behaviour of RHA based geopolymer samples are first observed.

The geopolymer material is able to act as heat reflective insulation coating that potentially reduce the exterior wall surface temperature. It is expected that the geopolymer coatings which is applied on the building exterior wall can productively reduce the temperature at the wall surface. Further, the development of alternative binders that have high in fire resistance is important in order to produce great thermal stability material.

The morphology of RHA and kaolin are viewed under scanning electron microscope (SEM) for further understanding of their shapes and structure. The morphology study on RHA based geopolymer and geopolymer coating composite samples are also observed under SEM too. This is to provide the information on samples structure after the water absorption test and fire-retardant test. The thermal stability of RHA based geopolymer and RHA/kaolin based geopolymer coating composite is analyzed by thermogravimetric analysis (TGA). TGA test provided on the analysis of weight degradation of the samples as the temperature increasing until 500 °C. Then, the relationship between fire resistance performance and thermal stability analysis can be established. All the findings obtained

from the experimental tests are able to characterize the geopolymer samples and fulfilled their potential application.

1.2 Problem statements

Rice is an essential food sources in worldwide and mostly in Southeast Asia. In Malaysia alone, the rice yields are estimated at 4.04 tons per hectare and due to the subsidies of crop inputs, the Malaysia government wants to increase the rice production throughout the years (*Booklet Statistik Tanaman*, 2014). This is because rice production is one of main agriculture activity in Malaysia. Production of rice leaved residues called rice husk is one of main agricultural residues obtained from the outer covering of rice grains during milling process. These waste products known as rice husk which is hardly used and neglected. As the rice production increased so as the waste product coming from the rice production also increased. The rice husk usually being dumped and left into water stream or in landfills thus causing pollutions (Davidovits, 2002; Mustafa Al Bakri et al., 2011; Kumar et al., 2013). Utilization of these waste product from agricultural sector might solved the disposal issues and also could minimized the cost of waste treatment (Kumar et al., 2013).

Moreover, since Malaysia is one of the major countries that produced rice, by utilizing the rice husk which is the most widely available agricultural wastes could have contributed in job sector for farmers particularly. This is because RHA can be used as a valued raw material for different purposes such as cement and concrete (Kumar et al., 2013; Davidovits, 2002; Zarina et al., 2016; Palomo et al., 1999). Many published literatures agreed that geopolymer coating could reduce defects cause by environmental contaminations and also improved engineering properties (Bakharev, 2005; Palomo et al., 1999). However excessive amount of RHA could be an environmental threat to the land and surrounding area. This crisis in the environmental health requires an innovative solution. There is much attention has been focused on utilized the plant biomass by producing engineering worthy materials. In amongst various agricultural wastes, RHA is selected due to its mass production in worldwide and it possessed unique chemistry-related features.

Rice husk is an agricultural residue obtained from the outer covered of rice grains during the milling process and by burning the rice husk under controlled conditions (time and air flow) at high temperature ranging from 400 - 1000 °C, the remained ashes are named RHA (RHA) (Xiong et al., 2009; Kumar et al., 2013). Therefore, in this research is focused on the development of geopolymer by using RHA as the main raw material. However, study on RHA based geopolymer not well published as others raw materials and it is limited to refer to. The idea of this research is to investigate the properties of the combination of RHA and kaolin when adding nanoclay as a filler. The geopolymer coating composite is fabricated with addition of nanoclay into rice husk ash/kaolin based geopolymer coating. The geopolymer coating composite is expected to have high fire resistance and good adhesion strength with mild steel plate. Thus, when a plane crash-lands and catches fire, the number of survivals could be increased.

Another advantage of geopolymer is it can have gained 70% of the final compressive strength in the first 4 hours of setting and can withdraw thousands of years weathering attack without too much function loss (Zhen et al., 2004). This is due to the statement from the Federal Aviation Administration (FAA) stated that geopolymer material had been selected as the best material for low cost, environmentally friendly and fire-resistant material for aircraft composites and cabin interior applications (Davidovits, 2002). The geopolymer composite has proven to be a better material than ceramic-matrix material and plastics because geopolymer composite offer better properties than others. Not just the geopolymer is very easy to make and handle but it also does not require high heat. In facts, future aircraft demands the use of green materials due to its renewable resource and concern for the environment.

It has been known that various parts in aircraft are vulnerable to high temperature conditions especially the seat cushion, carpeting, walls and luggage bins are all combustible (Davidovits, 2002). However, it is yet to be studied on whether the nanoclay addition in geopolymer coating composite is able to improve the fire resistance performance and adhesion strength of geopolymer coating. The optimum loading of nanoclay that helps producing the best fire performance and adhesion strength is studied. Researches on geopolymers are widely published and well-known to most researchers but research about RHA based geopolymer is limited and also the research on combining RHA with others geopolymer raw materials. Moreover, the fire resistance properties and adhesion properties of geopolymer coating in general were not well established. Other than that, a study on intumescent of geopolymer coating also not sufficiently covered.

1.3 Scope and Limitations

This research is about the development of geopolymer coating composite. The main material for the geopolymer coating composite is the RHA and kaolin as geopolymer binder, nanoclay as reinforcing fillers. The scopes in this research are the fabrication of RHA based geopolymer, fabrication of rice husk ash/kaolin based geopolymer coating and fabrication of rice husk ash/kaolin based geopolymer coating composite with nanoclay addition. The geopolymer material need to have high water resistance in order to proceed with the addition of nanoclay to produce high fire resistance geopolymer material. Therefore, water absorption test is conducted at early stage of the research. Then the selected geopolymer mixture will be used to fabricate the geopolymer composite by combining with kaolin.

However, before adding the nanoclay fillers, optimum ratio of mixed RHA and kaolin need to be study beforehand by analysed the fire properties obtained from combined RHA and kaolin. Then, by using the optimum ratio of RHA and kaolin, the nanoclay fillers are added to improve the fire properties. Several tests such as water absorption test, fire retardant test, adhesion test, scanning emission microscope and thermogravimetric analysis had been carried out in order to determine the characteristics and properties of the geopolymer coating composites. The hypothesis in this research is with optimum weight percent (wt. %) of nanoclay addition in rice husk ash/kaolin based geopolymer matrix, the fire and adhesion properties of the geopolymer coating will be improved.

1.4 Research Objective

The objectives of the research are stated as below:

i. To study the water absorption properties of the RHA based geopolymer with different ratio of solid to liquid, ratio of Na_2SiO_3 solutions to NaOH solutions and molarity of NaOH solutions

ii. To analyse and investigate the effect of nanoclay addition in fire resistance performance and adhesion strength of rice husk ash/kaolin geopolymer coating composites.

1.5 Thesis Arrangement

The remainder of the thesis is arranged as follows:

Chapter 2 explains on the review of RHA and kaolin based geopolymer material. This chapter mainly to explain on thermal stability and workability of coating resins, availability of the geopolymer materials. This chapter also discuss the properties and performance of nanoclay addition in geopolymer material. In addition, current geopolymer technology is discussed in this chapter too.

Chapter 3 describes the experimental procedure carried out to develop the mixture proportions, the mixing techniques and the curing conditions for geopolymer coating composite. Several tests are performed to study the characteristics of the RHA and kaolin. The procedure of water absorption test, fire retardant test and adhesion test for rice husk ash/kaolin geopolymer coating composites are also explained in this chapter.

Chapter 4 presents and discusses the results obtained from the tests conducted. At initial, this chapter discussed on the water resistance performance of RHA based geopolymer followed with the fire-retardant test results on geopolymer coating and geopolymer coating composite. This chapter 4 continued with adhesion strength obtained from geopolymer coating composite. The morphologies and thermal analysis of all samples are discussed in this chapter too.

Chapter 5 states the summary and the conclusion of this study and also the recommendations for future work. The thesis ends with a Reference List and several Appendices.

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PUBLICATIONS

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