UTILIZATION OF GLYCERINE PITCH AS A BINDER IN THE PRODUCTION OF GREEN ROOFING TILE

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A project report submitted in partial fulfilment of the requirements for the award of Bachelor of Engineering (Honours) Environmental Engineering

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DECLARATION

I hereby declare that this project report is based on my original work except for citations and quotations which have been duly acknowledged. I also declare that it has not been previously and concurrently submitted for any other degree or award at UTAR or other institutions.

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APPROVAL FOR SUBMISSION

I certify that this project report entitled **“UTILIZATION OF GLYCERINE PITCH AS A BINDER IN THE PRODUCTION OF GREEN ROOFING TILE”** was prepared by **Branda Yap Jian Tong** has met the required standard for submission in partial fulfilment of the requirements for the award of Bachelor of Engineering (Hons.) Environmental Engineering at Universiti Tunku Abdul Rahman.

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ABSTRACT

Global warming has always been a serious problem for us due to the excessive amount of greenhouse gases emission especially carbon dioxide. Also, the waste generation has increased year by year due to the increase of human population and resource consumption. The conventional way of disposing wastes are through landfill and incineration which contributes to more carbon dioxide emission. 33% from the 73% of total carbon dioxide emission is from the construction sector and 31.7% is from the landfill waste services. If the problem persists it is going to be harming the environment. In this study, glycerine pitch, a waste from the oleo chemical plant which is normally dispose through incineration is used as a binder in the production of green roofing tiles. This helps in the waste reduction, also on increasing the value of glycerine pitch as it serves as a negative cost waste all the time. Moreover, other waste like pulverized fly ash as a filler and waste cooking oil as an additional binder and protective layer have been included in the production in order to enhance the strength of the green roofing tiles. A series of test has been conducted based on the ASTM standards to ensure that the green roofing tiles produced achieve the minimum requirements. Throughout this study it has been proven that glycerine pitch has its potential on becoming a binder as the highest dry strength obtained was 5385.40 N with a wet strength and water absorption of 1139.96 N and 4.66% respectively.

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LIST OF SYMBOLS / ABBREVIATIONS

C=O	Carbonyl Group
$C_{12}H_{22}O_4$	Dodecanedioic Acid
C-O	Carbon-Oxygen Bonds
CO_2	Carbon Dioxide
H_2SO_4	Sulphuric Acid
-OH	Hydroxyl Group
d	Diameter of Sample, mm
L	Span Length, mm
P	Maximum Force Applied, N
w	Width of Sample, mm
W_d	Dry Weight of Specimen before Submersion, g
W_w	Wet Weight of Specimen after 24 hours of Submersion, g
σ	Flexural Strength, MPa
ASTM	American Society for Testing and Materials
ATR-FTIR	Attenuated Total Reflectance Fourier Transform Infrared Spectrometry
BS	British Standards
CNN	Cable News Network
DDDA	Dodecanedioic Acid
DOE	Department of Environment
EC	Embodied Carbon
EE	Embodied Energy
En-O Roofing Tiles	Engine Oil Roofing Tiles
EPA	Environmental Protection Agency

EU	European Union
FA1	Fly Ash with size 16.256 µm
FA2	Fly Ash with size 115.014 µm
FFA	Free Fatty Acids
GHG	Green House Gases
GP	Glycerine Pitch
GP-GRT	Glycerine Pitch- Green Roofing Tile
LCA	Life Cycle Assessment
N	Newton
PVC	Polymerizing Vinyl Chloride
TPM	Total Polar Material
UK	United Kingdom
US	United States
USA	United States of America
UV	Ultraviolet
WCO	Waste Cooking Oil

CHAPTER 1

INTRODUCTION

1.1 Background of Global Warming

Global warming has always been a concerning problem for all the governmental and non-governmental agencies. This is because of the rapid improvement and innovation in technology and industrial development which leads to an excessive amount of Green House Gases (GHG): carbon dioxide, methane and nitrous oxide being emitted into the atmosphere. When sunlight penetrates into our Earth surface, the oceans, air and land will absorb 70% of the heat in order to make the surface of the earth warm and liveable. Warming up of the atmosphere will then lead to the radiation of solar energy by infrared rays and thermal radiation that tend to send back to outer space (Shazad and Riphah, 2015). By having this mechanism, our Earth will be at an ambient temperature which is comfortable and suitable for the living things on Earth. However, due to the excessive amount of GHG, the solar energy that were supposed to be released will be reflected back to the Earth surface (Shazad and Riphah, 2015).

The consequences of this phenomena is caused by human actions and selfishness, the global temperature on our Earth is increasing gradually each year which leads to several severe situations. The most common effect of global warming is the melting of iceberg at the North Pole that has caused the rising of sea level. According to Cable News Network (CNN) on January 16, 2019 the temperature in South Australia’s Port Augusta has hit the highest of 48.5°C since 1962 (Regan and Westcott, 2019). This hot weather has brought serious effects to human health, also to wildlife.

1.2 Conventional Roofing Tiles

Among the three types of GHG, carbon dioxide, CO_2 has the highest percentage of emission which is 76% mentioned in the Intergovernmental Panel on Climate Change (IPCC) 2014. Recently updated in 2017 the share of CO_2 in the GHG emission is 73% (Olivier and Peters, 2018). According to Teoh, et al. (2018) a total of 33% originates from the constructions sector. Adding on, roofing materials happens to be one of the construction materials that is irreplaceable whether it is made by clay or cement (Kuruppuarachchi, Ihalawatta and Kulatunga, 2014). 1.84- 2.8 kJ/kg of energy is consumed to produce clay tiles at 1000 ˚C high temperature for a period of 5 - 24 hours, such energy consumption tends to release a large amount of carbon dioxide and therefore it is concluded that the production of conventional roofing tiles is one of the contributors of global warming (Humayun et al., 2017 & Nadeem et al., 2017).

Furthermore, the conventional roofing tiles are clay tiles and asbestos fibre roofing sheets, both of them are widely in used due to their advantages in strength and durability. However, the conventional roofing tiles tend to cause harm and bring threat to the environment and human health be it directly or indirectly at different stages from extraction of raw materials to the disposal of waste. For instance, the inhalation of asbestos fibre will bring asbestos-related diseases like lung cancers which are lethal to humans and these types of diseases tend to have a long time delay that would not show the effect immediately (Kuruppuarachchi, Ihalawatta and Kulatunga, 2014 &Udagama and Kulatunga, 2014). Therefore, other alternatives has to be investigated and studied so that there is a possibility in reducing the GHG emission and minimize the health problem brought by the conventional roofing tiles.

1.3 Waste Management

Waste is generated when there is resource consumption which will be affected by the industrialization, urbanization and increase in human population. These four aspects are tightly related because when there is an increase in human population, the resource consumption will follow which then lead to the improvement in industrialization and urbanization and eventually causes more waste to be generated. 2.01 billion metric tonnes per year is said to be the current global waste generation level, however recently a new prediction has been calculated and said that it will soon be reached to 3.40 billion metric tonnes per year by 2025 (Ellis, 2018). According to the Environmental Protection Agency (EPA), the landfills and waste services have contributed to a total of 31.7% in the GHG emission which can be seen from Figure 1.1.

There are two main decisions that is normally done to dispose the waste that has been generated which are incineration and transfer to landfill. Landfill simply means by collecting our waste and bury in underground. Most of the landfill around the world might not be properly designed which has the possibility of leakage and contaminating the groundwater. It will release CO_2 and methane gas when the waste undergoes decomposition. Incineration process is defined as burning of waste at a high temperature for size reduction so that it can be nicely compacted for better arrangement of compacted waste. However, the consequences of incineration is that it contributes to the global warming as CO_2 is emitted during the combustion process. Also, it reduces the air quality of the surrounding as incineration will definitely generate dust particles. Adding on, for the incineration process to take place, a large amount of energy is required.

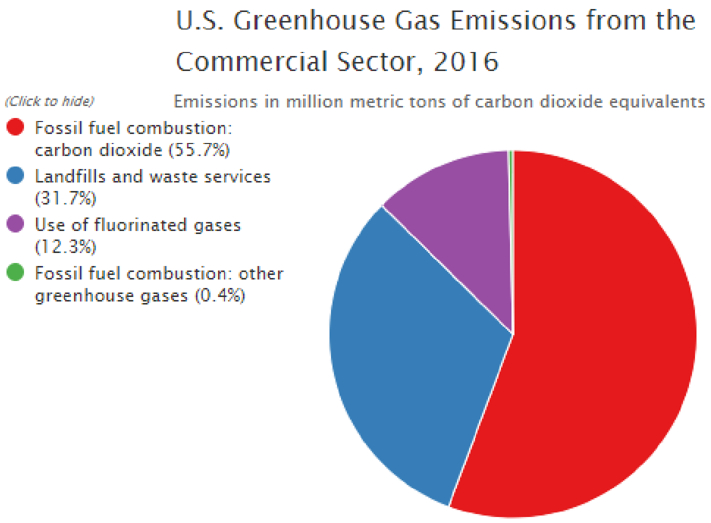


Figure 1.1: Percentage of GHG Emission from Commercial Sector (United States Environmental Protection Agency, 2016).

Pulverized fly ash which is a by-product from a power plant due to the combustion process of coal to produce energy. Every year there will be approximately 140 million tons being produced and most of them are disposed in the local dry landfills (United States Affiliate of International Physicians for the Prevention Nuclear War, n.d.) which has the possibilities in causing cancerous diseases to the neighbouring residents. Glycerine pitch, a listed Schedule Waste generated during the process of refining sweet water has not only contribute to some of the carbon dioxide emission but also has the tendency to bring impacts towards human health. This is because the only way to dispose of glycerine pitch is through incineration which leads to the emission of carbon dioxide and a highly volatile carcinogenic compound called acrolein that would bring significant threat to the humans. Currently the only authority in Malaysia that can handle this waste is Kualiti Alam Malaysia (Hazimah, Ooi & Salmiah, 2003).

1.4 Problem Statement

According to the records of United States Environmental Protection Agency (EPA) there has been an increase of GHG emission since the year 1990. However, around 2015, the United States' emission has reduced as shown from Figure 1.2, this is due to the awareness of communities on the critical condition of the Earth and alternatives strategies have been introduced to decrease the emission. For instance, introduction of biodiesel and replacement of coal and natural gas. Although there is a sign of decrease in the GHG emissions, further improvements can still be done to achieve a more pleasant results to save the world or to recover the balance of the ecosystem before it is disrupted by human activities.

Not only that, as mentioned the harm that has been brought by conventional roofing tiles, incineration of glycerine pitch and disposal of pulverized fly ash, communities have to take initiative on solving the problem in order to protect both the human race and the environment. A lot of studies had been investigating various types of alternatives on producing roofing tiles such as EnO-Roofing Tiles (Teoh et al., 2018), roofing tiles using waste cooking oil as a binder (Humayun et al., 2017) in order to reduce the waste generation and the greenhouse gas emission to the atmosphere. In addition, there are also studies on handling glycerine pitch for other application like recovery of glycerol (Hazimah, Ooi&Salmiah, 2003), involvement in the production of soap (Solihin et al, 2017) and production in masonry units (Vu, Forth and Toropov, 2017).

With all the studies that have been done, there are still no studies on the involvement of glycerine pitch as a binder and pulverized fly ash as a filler in contributing to the strength during the production of green roofing tiles. This study aims to provide another additional solution or mitigation on the reduction of the global greenhouse gas emission and glycerine pitch, also to prevent the harm brought by conventional roofing tiles. Preliminary studies have been done that glycerine pitch is able to act as a binder in roofing tiles. However, due to the natural hygroscopic effect of glycerine pitch and fly ash, further improvements will be needed in order to achieve higher standard. It is also can be another alternative of the application of glycerine pitch to ease global warming crisis.

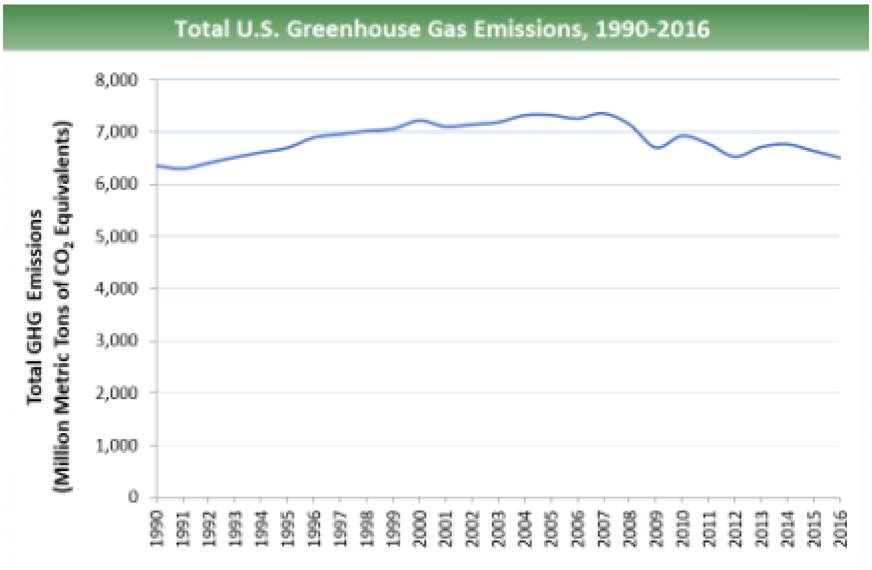


Figure 1.2: The GHG emissions between year 1990-2016 (United States Environmental Protection Agency, 2016).

1.5 Objectives

The main objectives in this current study are:

1. To produce a novel environmental friendly roofing tile.
2. To investigate the feasibility of using glycerine pitch as binder in the production of roofing tile.
3. To characterize the roofing tile produced from the mixture of glycerine pitch, waste cooking oil, sand and fly ash.
4. To identify the possible mechanism on the hardening of roofing tile produced from the mixture of glycerine pitch, waste cooking oil, sand and fly ash.

1.6 Scope of Study

This research is carried out to determine the feasibility of using glycerine pitch as a binder in the production of roofing tiles. The main material that will be used is fly ash, sand, waste cooking oil and glycerine pitch. The roofing tiles samples produced will undergo a series of flexural strength test, water absorption test and permeability test. All of the test parameters are based on the requirements of the American Society for Testing and Materials (ASTM C 67-07a, C1167-03 and C1492-03). Each test carried out is based on the literature reports and experimental approach.

CHAPTER 2

LITERATURE REVIEW

2.1 Green Roofing Tiles

Roofing tiles are building materials that requires a massive energy while it is being manufactured. Roofing plays an important role in the buildings because it serves as a function of preventing rain and excessive UV rays from entering the building. Products that can be defined as green products need to fulfil either four requirements which are as follows:

i. The product must ensure that it is able to save energy either during the manufacturing process or during its using life.
ii. It is able to be recycle or it is made by using recycling materials.
iii. The product could reduce the earth's pollution and lowering down the impacts by reducing the emission of carbon dioxide
iv. It uses local materials whereby there will be no need of transportation of materials on site which helps in saving energy, reducing the pollution and prevent extra cost for the transportation.

Due to the high emission of greenhouse gases while producing conventional roofing tiles, test are being carried out in order to reduce the impacts brought by producing roofing tiles. Studies have been made on using palm oil, waste vegetable oil and waste engine oil as a binder to produce the green roofing tiles which tend to perform better comparing it with the conventional roofing tile which will be further discussed.

The first type of green roofing tile is the involvement of crude palm oil. Malaysia is known to be the second largest producer of crude palm oil in the world (Humayun et al., 2017). Saturated and unsaturated fats are contained inside the palm oil that were extracted from the oil palm trees. The crude palm oil can not only be served as the usage of cooking oil it has several functions too. Palm oil can be used in non-food applicants for instance production of cosmetics or detergent. Other than that, palm oil has been used in the production of biodiesel and has shown better results and condition than the normal diesel fuel. Moreover, during the past few years research has been carried out on using vegetable oil as a binder together with waste or recycle aggregates to produce green block named as Vege blocks. The research on Vege block has shown quite successful results whereby the blocks have a high compressive strength that is close to ordinary concrete blocks. Due to the research, palm oil has been considered to be used as a binder in the production of building material and using palm oil requires a lower level of embodied energy and carbon dioxide level which are 11MJ/kg and 2.8kilograms carbon dioxide equivalent (kgCO_2e) during processing, cropping and plantation. (Humayun et al., 2017). Experiments had been carried out with different content of palm oil and fly ash has come to a result that the embodied energy for a green roofing tile is 1.64MJ. The value shows that using of palm oil has 64% less than conventional concrete tile, 265% less than for clay tile and 631% less than ceramic tile based on the embodied energy. Also, having palm oil as a material in producing roofing tiles, the total carbon emissions per piece of roof tile is 0.378 kgCO_2e. It is much lower by comparing it with the concrete, clay and ceramic tiles. (Humayun et al., 2017).

The next green roofing tile is the usage of catalysed waste engine oil mixed together with coal-fired ash named as EnO-roofing tiles (Teoh et al., 2018). It has been tested that when waste engine oil is heated at a certain temperature, it will transform from liquid state to solid state and this is due to the process of oxy-polymerization. This research has been proven that it has a relatively lower value of embodied carbon and embodied energy compared with the conventional roofing tiles. Although it has been proven that the functional group which is used to contribute strength in waste engine oil is lesser compared to the utilization of the vegetable oil, waste engine oil was able to reduce the total porosity of the tiles whereby having lower porosity means that the percentage of water absorption of the tiles is relatively lesser which then increases the durability of the roofing tiles. Other than that, having lower porosity inhibits the penetration of sodium chloride solution. Roof tiles that are produced using palm oil or waste engine oil can be considered as green roofing tile as it helps in reducing the embodied energy and the carbon emission which can at least ease the pollution level on the earth.

2.2 Waste Cooking Oil

Every year there will be an increase of waste in the world due to the increase in population. Waste cooking oil is one of the materials that have contributed to the world's waste which creates quite a problem to the environment. It has been estimated that there will be at least 50-90 million litres and 300 million gallons of cooking oil being wasted in the United States (US) and the United Kingdom (UK) every year (Nadeem et al., 2017). Adding on, in China, there will be at least 500 million tons of waste cooking oil that will be produced annually and this amount of waste oil is only focusing on the catering industry of China (Zhang et al., 2012).

Waste cooking oil are formed due to continuously of heating of the oil at high temperature with the presence of air and moisture which causes the degradation of the cooking oil. There are three processes of degradation of the cooking which the first one is hydrolysis whereby in this process free fatty acids (FFA), mono- and diglycerides are formed due to the moisture content of fried food. Moreover, when it has contact with oxygen the process of oxidation will occur and produces oxidized monomeric, dimeric and oligomeric triglycerides and volatile materials such as aldehydes and ketones. (Şanli et al., 2011)**.** The last process of degradation is polymerization which happens due to the above reaction stated with high temperature whereby dimeric and polymeric triglycerides with ring structures were produced in this process. Due to the above degradation processes, the physical and chemical properties of the cooking oil will change such as the increasing of its viscosity, density, free fatty acids content, total polar material (TPM), polymerized triglycerides, and decreasing of the number of double bonds and smoke point.(Şanli et al., 2011)**.** If the processes continue, the cooking oil will degrade until it reaches a state whereby it is not suitable for using and it needs to be discarded which we term it as waste cooking oil.

Waste cooking oil is known as oils and fats that are used for the purpose of cooking such as frying for household, restaurants or even food processing factories. It can be considered as a pollutant if it is not taken care of or being disposed properly. This is because the waste cooking oil can pollute and reduce the water quality of the streams or even worse affecting the marine life when people disposed them irresponsibly. Not only that, there are many irresponsible households that dispose their waste cooking oil through the sink which have led to the blocking of drainage system and affecting the wastewater treatment system as it will be requiring extra energy to treat the unwanted waste oil. By needing extra energy to treat means it requires a higher processing costs. From a study that has been carried out in the United States of America (USA), it shows that the blockage of the sewerage system that caused by the waste cooking oil took a percentage of 40% and this is because the local citizens have a habit of pouring their waste cooking oil into their sink. Furthermore, the waste cooking oil can also be contaminating the soil and damaging the plants due to their eco-toxic properties. Moreover, waste cooking oil can also be a threat to human health because in China there are a lot of restaurants that allows the flowing back of the waste cooking oil to the dining table with the amount of 200-300 million tons according to the statistics that were carried out (Zhang et al., 2012).

Due to the excessive amount of waste cooking oil that contributes to the world’s waste, there were some studies that had been carried out and had successfully utilized the characteristics of the waste cooking oil to transform it into useful substances for other purposes. Using waste cooking oil as a low cost feedstock to produce biodiesel was one of the method. In the current situation of the world, the most critical parameter that can affect the social and economic development of a country is energy and it is increasing gradually with the population of the world. Present, fossil fuels uses a total of 90% of the world’s energy and petroleum held a total of 45% in the fossil fuel. Although petroleum holds energy sources used in the world, there are still countries like USA and the European Union (EU) countries that needs to import their energy requirements (Şanli et al., 2011). Although they have imported their energy requirements, there were still too little that they can do as their petroleum production was only half of the amount of the petroleum consumption which is shown in the Table 2.1 below. Therefore research has been carried out to solve the problem and have come out with an alternative that would not cause harm to the environment which is using vegetable oils and animal fats as feedstock to produce a fatty acid alkyl monoesters called biodiesel.

Table 2.1: The production and consumption amounts of petroleum of some countries (Şanli et al., 2011).

Country	Petroleum Consumption (barrel/day)	Petroleum Production (barrel/day)
USA	18,690	9,056
EU	13,680	2,383
China	8,200	3,991
India	2,980	879
Russia	2,850	9,932
Germany	2,437	157
France	1,875	71
Turkey	580	53
Greece	414	7

The production of biodiesel shows a superior properties over the normal diesel fuel based on its renewability, lubricity, ability of biodegradation and etcetera (Şanli et al., 2011). However, the production of biodiesel using vegetable oil requires a higher amount of cost compared with the normal diesel fuel therefore waste cooking oil was used to replace the vegetable oil as a feedstock which is more economic while comparing it with vegetable oil. By using waste cooking oil is not only reduces the cost of the biodiesel to 60%, it is also cheaper compared with normal diesel fuel (Şanli et al., 2011). Waste vegetable oil has been used to produce vege-roofing tiles when the waste vegetable oil is heated where the fatty acids in it will form di-acids or trimers with more than one carboxylic acid group (Nadeem et al., 2017). Therefore, poly-esterification can occur between di-acids and diols that are in the waste vegetable oil that forms a solid polyester which will become a good binder to bind all the materials together during the process of heating. However, before using the waste vegetable oil, it needs to be catalysed by using a small amount of sulphuric acid, H_2SO_4 and it can only be stored for three days after it has been catalysed. Other than that, the mixing fly ash with catalysed waste vegetable oil helps in binding the tile materials together and increasing the flexural strength of the roofing tile while comparing with the ordinary roofing tile. (Nadeem et al., 2017)

2.3 Pulverized Fly Ash

Fly ash is defined as a by-product from the combustion of pulverized coal in electric power generating plants. The process of obtaining fly ash is during combustion the minerals impurities in the coal will be suspended and float out of the combustion chamber together with the exhaust gases. When it went out from the combustion chamber the fused material will rise and cooled down then solidifies forming a spherical glassy particle that are called fly ash and they are collected using electrostatic precipitators or bag house. (Basham, et al., 2007). Fly ash works similarly like cement whereby it can react with water and form cement due to the presence of aluminous and siliceous material. If fly ash are mixed with lime and water there will be a formation of a compound that has similar properties as the Portland cement. (Rodriguez, 2018).

Fly ash can be categorized into two classes, class C and class F. the difference between the classes are due to the level of calcium fly ashes with carbon content. For class C fly ash, it often contains higher level of calcium fly ash with carbon content less than 2%, it is normally obtained from the combustion of sub-bituminous or lignite coals. As for class F, it contains a lower level of calcium fly ash with carbon content less than 5% or sometimes it will reach up to 10% of carbon content (Basham, et al., 2007). Class F is formed from ashes bituminous or anthracite coals. Both classes react differently due to their variation of the chemical and physical properties. For instance, class C reacts faster when it meets with water whereby it will become as hard as cement. As for class F it normally will only react with the byproduct that were formed by cement when it reacts with water.

Fly ash is considered as a dangerous pollutant according to the Environmental Protection Agency (EPA). It is estimated that 140 million tons of fly ash are produced every year and more than a third of the total amount of fly ash are not being handled carefully and are disposed in the local dry landfills. The EPA has also stated that living near to a fly ash disposal site can increase the chances of getting cancer or other lethal diseases. It adds on saying that if the water supply happens to be near an unlined wet ash pond, the possibilities of getting cancer is 1 in a 50 people due to the consumption of contaminated water (United States Affiliate of International Physicians for the Prevention Nuclear War, n.d.).

There is research done by utilizing fly ash as a filler in producing roofing tiles or construction buildings whereby it serves as a substitute of cement due to its cementitious properties. It has been stated that having a percentage of between 30% and 60% of fly ash filler in the production of concrete is able to achieve good durability and mechanical properties. However, it must be known that higher percentage of fly ash may also reduce the compressibility strength of the concrete, therefore the percentage of fly ash used in concrete must be tested until it reaches its optimized percentage to achieve the best condition of the concrete (Nadeem et al., 2017).

2.4 Glycerine Pitch

1,2,3-propanetriol which has a commercial name called Glycerol is known as a type of alcohol with three hydroxyl group (-OH) in liquid form that is colourless, viscous and odourless which is normally resulting from both natural and petrochemical feedstock (Chow, Chan & Chong, 2014 & Solihin et al, 2017) and possesses a sweet taste. Glycerol has a very unique properties whereby it has a low melting point of 18.2℃ and a high melting point of 290℃ when it is in a condition of the absence of water. However, at low temperature, crystals may be formed and it will be easily melted at the temperature of 17.9℃. The structure and the overall chemical and physical properties of Glycerol are as shown in the Figure 2.1 and Table 2.2 below. As for Glycerin or Glycerine, it is commonly a solution of Glycerol with water which contains a percentage of 95 or more of Glycerol. It has the same physical properties as with Glycerol and is able to react with alcohol, at the same time being stable at most of the conditions, which is known as a trihydric alcohol (Pagliaro& Rossi, 2008). Glycerine is a very popular chemical that can be utilized in over 1500 applications ranging from foods to urethane foams (The Soap and Detergent Association, 1990). The consumption of Glycerine is able to reach up to 1.1 to 1.2 billion pounds per year and still at a rising pace due to the urbanization of the rural or less developed countries. For instance, United States uses an approximation of 300 million pounds per year, Japan with the consumption of 100 million pounds annually (Pagliaro & Rossi, 2008).

Figure 2.1: Structure of Glycerol (Pagliaro & Rossi, 2008).

Although glycerol is able to be widely used in various applications, it is still contributing to a serious environmental issue whereby a waste will be generated during its production called glycerine pitch. Normally, glycerine pitch is formed during the refining of sweet water to pure glycerol from fatty acid of the plants (Hazimah, Ooi & Salmiah, 2003). This process normally takes place in oleo-chemicals industries, and Figure 2.3 below shows the amount of glycerine pitch formed per month in an oleo chemical industry (Chow, Chan & Chong, 2014).

Glycerine pitch has been listed as one of the schedule waste by the Malaysian Department of Environment (DOE) as it falls under the category of First Schedule of the Environmental Quality (Scheduled Wastes) Regulation 1989. The current solution on the disposal of glycerine Pitch is through incineration. However, this may bring negative impacts to small areas and places that has high populations. In addition, during the combustion of glycerine pitch there may be possibilities on the emitting of highly hazardous and lethal gas called acrolein. Not to mention the price is quite high for the glycerine pitch to be incinerated or thrown to the landfill. Hazimah, Ooi and Salmiah (2003) have stated that the cost for landfill is approximately RM 500 whereas for incineration a range of RM810 to RM3600 per tonne. In this present situation, Kualiti Alam Waste Management Centre is the only organization that has the authority to handle schedule waste (Hazimah, Ooi & Salmiah, 2003).

Table 2.2: Physiochemical Properties of Glycerol (Pagliaro & Rossi, 2008).

Properties	Quantity
Chemical formula	$C_3H_5(OH)_3$
Molecular mass	92.09382 gmol^{-1}
Density	1.261 g cm^{-3}
Viscosity	1.5 Pa.s
Melting point	18.2℃
Boiling point	290℃
Food energy	4.32 kcal g^{-1}
Flash Point	160℃ (closed cup)
Surface tension	64.00 mN m^{-1}
Temperature coefficient	-0.0598 mN (mK)$^{-1}$

Table 2.3: By-products and waste generation on monthly basis by an oleo chemical industry (Chow, Chan & Chong, 2014).

	Tonne/month		
	Range	**Average**	**Standard Deviation**
Raw material (palm kernel oil)	11688 – 25884	21841	3983
Water	18896 – 18950	18484	–
By-products			
a) Fatty acids	–	25203	–
b) Refined glycerine	1794 – 3368	2645	450
Wastewater			
a) Glycerine pitch	–	899	–
b) Oleo chemical effluent	–	12121	–
c) Wash Water	–	12400	–

The formation of glycerine pitch as mentioned is through the refining process whereby according to Hazimah, Ooi and Salmiah, 2003 the sweet water needs to undergo a series of chemical treatment in order to remove oxidized fatty acids, dissolved or suspended fatty acids, colour materials and various nitrogenous materials prior to the evaporation stage. From the splitting unit, the sweet water is then transferred to a settling tank so that the suspended fatty acids can be skimmed off. Then the remaining solution will proceed to remove the insoluble materials for instance adsorbed fatty acids, metal salt and others through the process of air-agitation and other chemical treatments. Later on, there will be a formation of concentrated aqueous fraction which then a pure and refined glycerol will be extracted from it using a high vacuum distillation. The leftovers from the concentrated aqueous fraction are what it is called as glycerine pitch.

Due to the worrying problems brought by the increasing of glycerine pitch production, there are studies that have been carried out to test on its possible application in different types of field. Researches are doing experiments hoping to reduce the amount of glycerine pitch being sent to the landfill or allowing it to be incinerated. One of the research done by Hazimah, Ooi and Salimiah on 2003 has focused on recovering glycerol and diglycerol from glycerine pitch. The main steps were to use acid and separate it into two layers and the upper are the ones called fatty acid layer, the aqueous later will then need to undergo a series of procedures in order to extract the crude glycerol and inorganic salts. Each different type of glycerine pitch varies due to their composition. The results from the recovery of glycerine pitch are as shown below and it can been seen that glycerine pitch, a waste can still be used to extract extra glycerol, di-glycerol which can be used in the recovery of useful chemicals.

Table 2.4: Composition of Glycerine Pitch (%)

Glycerol	**Fatty Acids**	**Inorganic salts**	**Diglycerol-rich fraction**
55 to 65	< 10	< 10	15 to 25

Studies carried out by Vu, Forth and Toropov have shown that using pure and glycerine pitch, clean and wasted cooking oil, pulverized fuel ash and aggregates are able to produce masonry production that fulfils the requirements set by the British Standards. In their experiment, a mixing ratio of 1:3 was used for glycerol and cooking oil both for pure and used ones (Vu, Forth and Toropov, 2017). The strength that they were able to obtain was relatively high comparing it with the conventional masonry blocks that they are using. Their results are as shown below in Table 2.5, whereby pure binder refers to the mixture of pure glycerol and clean cooking oil and waste binder is glycerine pitch with used cooking oil.

It has been stated in their reports that although they have achieved the requirements needs to produce masonry units, improvements are still needed to overcome the problem whereby the saturated strength of masonry units using waste binder has decreased a range of 25-50% of its original strength. Is may be the possibilities that glycerol having a hydrophilic properties has caused the glycerol to leach out from the samples during the immersion period. Having this problem solved, might be a great achievement on improving the saturated strength of the masonry units.

From the application above, there are studies that show interest in experimenting the possible uses of glycerine pitch since it is a schedule waste and that brings harm to the humans and environment. Although there are studies relating the involvement of glycerine pitch in masonry units, there are still no studies showing its involvement in the production of roofing tiles. Therefore, this research is carried out and hoping that it can be applied or include in the production process so that the excessive amount of this waste can be reduced and able to help the world in providing a cleaner and more environmental friendly Earth. Similar problems as the masonry units might be faced and improvements are needed in order to achieve the requirements of being qualified as a roofing tile.

Table 2.5: Compressive strength of control sample, pure binder and waste binder samples (Vu, Forth and Toropov, 2017).

Properties	**Natural Aggregates (Mix A)**	**Pure Binders (Mix B)**	**Waste Binders (Mix C)**	**Recommended value**
Compressive Strength (MPa)	38.4	33.6	31.3	≥ 5 for Damp proof course 1,2 (BS 3921: 1985)
Water adsorption (%)	7.26	8.03	8.15	No limits for other types of bricks (BS 5628 part. 3: 1985)
Initial rate of water absorption (kg/m^2min)	0.067	0.117	0.083	≤ 1.5 (BS EN 772-11:2000)

2.5 Basic Requirement of Roofing Tiles

2.5.1 Transverse and Flexural Strength

Transverse strength which can also be meant by compression strength whereby the roofing tile samples will need to withstand an axially exerted load when it is being compressed. The yielding strength to break the roofing tile samples will be the transverse strength in terms of Newton (N). There are two different transverse strengths, which are dry and wet. Wet transverse requires roofing tile samples to submerge into water for 24 hour prior to testing. Different profiles or grades of roofing tiles have different requirement as shown in Table 2.6, the requirements are according to the ASTM C 1492-03. As for flexural strength, it is derived from the transverse strength having the unit MPa which is the capability of the roofing tile samples to tolerate a load without bending.

Table 2.6: Minimum Transverse Breaking Strength (ASTM C 1492-03)

Type (All Grades)	**Dry Transverse Strength (N)**		**Wet Transverse Strength (N)**	
	Individual Tile	**Average 5 tiles**	**Individual Tile**	**Average 5 tiles**
High Profile	1556	1779	1157	1334
Medium Profile	1112	1334	890	1001
Low Profile	1112	1334	890	1001

2.5.2 Water Absorption

It is very important to check for the water absorption ability for construction materials, as when the construction materials that have a high water absorption rate, it might affect its overall strength. This is crucial for roofing tiles as they are exposed to rainwater, if their water absorption is too high, the roofing tiles might someday giveaway and collapse. Selection of materials comes important at this section whereby choosing of less water absorption or hydrophilic materials are more desirable. However, if the materials chosen have high water absorption rate, a layer of water resistance coating could be apply in order to stop the rate of absorption. In this test, there is a maximum limit of water absorption percentage where the roofing tiles must remain within the range set by ASTM C 1167-03.

Table 2.7: Maximum Percentage of Water Absorption

Type (All Grade)	Cold Maximum Water Absorption Percent
1	6
2	11
3	13

2.5.3 Permeability

Permeability is the ability for water to penetrate through the material. It is important to note that the fulfilment of this criteria is a must for roofing tiles as it is put at the top of the house, it needs to prevent water from entering into the house. Factors that mostly affect the permeability of the construction material is the porosity and the density. Porosity and permeability directly proportional, when there is more voids within the material, it gives chances for water to enter. As for density, it is directly proportional with the permeability whereby when it is highly dense means that the roofing tiles are well-compacted and minimal voids are present. To undergo the permeability test, it is to observe that no water droplets are present at the bottom part of the roofing tiles following the standards of ASTM C 1167 – 11. It is said to have failed if water droplets are found at the bottom of the roofing tile samples.

CHAPTER 3

RESEARCH METHODOLOGY

3.1 Introduction

The experimental setup and the methodology of the experiment is discussed in this chapter and a summary of the study is shown in a flowchart in Figure 3.1. It can be seen from the flowchart below has three main parts of process in the production of green roofing tiles, which are (i) mechanical mixing of raw materials, (ii) compaction of mixture into shaped of prototype roofing tiles and (iii) lastly is the curing process in the oven to harden the roofing tiles (Teoh et al., 2018).

3.2 Materials and Chemicals

Materials and chemicals used, its source and purposes will be listed clearly in Table 3.1. The main ingredients that will be used in the production or fabrication of roofing tiles are sand, fly ash, glycerine pitch and waste cooking oil. The remaining ingredients that will be used are for the optimization or improvement on the strength of the roofing tiles.

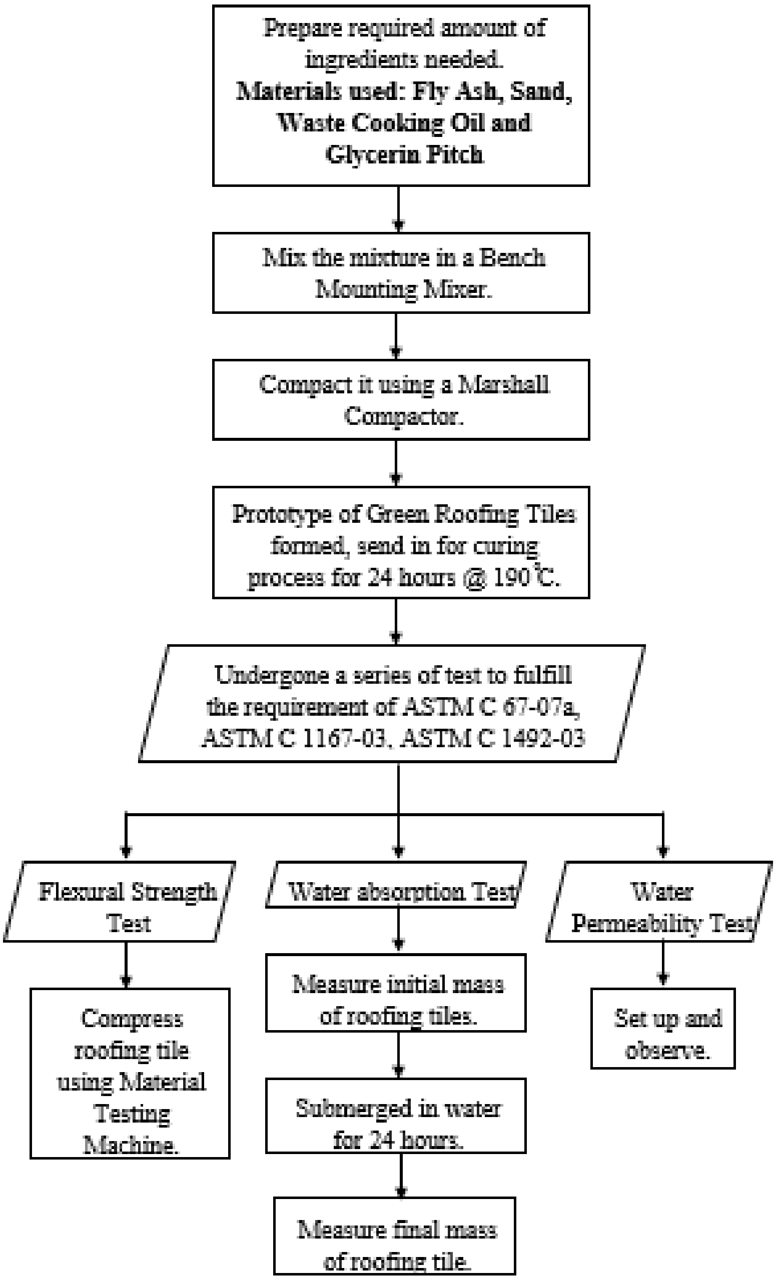


Figure 3.1: Flow Chart of Experimental Procedures.

3.2.1 Glycerine Pitch

Glycerine Pitch that is used in this production of roofing tiles are collected from an oleo-chemical company called KL-Kepong Oleochemical Sdn. Bhd. located at Kepong. Glycerine pitch is selected as an alternative binder is due to the excessive amount of generation each year and also due to the effects of it when it is being disposed. So far there is no study that involves in having glycerine pitch as a binder in the production of roofing tiles.

Table 3.1: List of Materials and Chemicals Used.

Material/ Chemical	Purity (%)	Supplier	Purpose of Use
Coal Fly Ash	-	TNB Janamanjung Sdn. Bhd.	Used as a filler
Sand	-	Mining and River	Strength enhancement
Waste Cooking Oil	-	Household	Used as a binder
Glycerine Pitch	-	KL-Kepong Oleochemical Sdn. Bhd.	Used as a binder
Sulphuric Acid (H_2SO_4)	95-98%	Synertec	Used as a Catalyst
Dodecanedioic Acid ($C_{12}H_{22}O_4$)	-	Chem Soln	A diacids used to react with –OH groups in glycerine pitch

There are two types of glycerine pitch that is used throughout the experiment which are raw glycerine pitch without any modifications and adding of dodecanedioic acid (DDDA) in testing to remove additional –OH groups in glycerine pitch. Both materials are as shown below in figures. The physical difference based on observation are the colour changing and the stickiness, the raw glycerine pitch tends to be stickier compared with the one that has been mixed with di-acid.

Figure 3.2: Glycerine Pitch

Figure 3.3: Glycerine Pitch Mixed with Dodecanedioic Acid

3.2.2 Waste Cooking Oil

Waste cooking oil is defined as used or unwanted cooking oil that has been used for cooking and discharged. The source of waste cooking oil for this research is collected from a household which the oil is derived from palm oil. Waste cooking oil in this research also serves as an alternative binder due to a reaction between the di-acids and di-ol to form solid polyester called poly-esterification that helps to bind the materials together. Also, the viscosity of waste cooking oil will increase due to the heat curing process during the production of roofing tile sample.

Raw waste cooking oil and catalysed waste cooking oil are used in this research. The catalysed waste cooking oil was catalysed using sulphuric acid, H_2SO_4 which prior to mixing for 10 minutes before using it. It has been found out that having a catalyst present in the cooking oil tends to help in the reaction of oxy-polymerization and accelerating the curing process (Humayun et al., 2017). Both waste cooking oil and catalysed waste cooking oil are shown below. There is no significance difference between both based on appearances.

Figure 3.4: Waste Cooking Oil.

Figure 3.5: Catalysed Waste Cooking Oil

3.2.3 Sand Aggregate

Sand aggregate used in this study is a mixture of river and mining sand. Throughout the research experiment it helps to enhance the strength of the roofing tiles. ASTM C 136/136M-14 is referred in order to determine the size distribution of the aggregate.

Figure 3.6: Sand Aggregate

3.2.4 Pulverized Fly Ash

Pulverized fly ash, an unwanted schedule waste produced during the generation of electricity through the burning of coal. It has been listed as one of the world’s highest level of raw material resources (Dasgupta, et al., 2012). Fly ash is a type of finely-grained amorphous alumino-sillicate with different components such as calcium which is able to react with calcium hydroxide when mixed with Portland cement and water. The process tends to create various calcium-silicate hydrates (C-S-H) and it is classified as a pozzolanic material. However, there is no water involved in the production of roofing tiles so the pozzolanic effect on this project is negligible. Basically there are two main classes of fly ash which are class F and class C, the different between these two classes are identified through the ASTM C 618. The percentage of the components that is within the fly ash are the ways to differentiate them. For instance, SiO_2 + $Al2O_3$ + $Fe2O_3$ $\geqslant$70% is for class F whereas for class C is more than 50 % (Thomas, n.d.).

The coal-fired ash of this study are collected from TNB Janamanjung Sdn. Bhd. at Sitiawan. Fly ash is being used as a filler in this research as it has a very small particle size which can help to fill up the voids in the mixture so that the tiles produced could be more compacted and at the same time the strength could be improved. There are two groups of fly ash that had been used throughout the research whereby both of their particle sizes and number were analysed using a particle size analyser. The results were 16.256 µm and 115.014 µm in terms of particle size and 2.141 µm and 6.333 µm in terms of particle number respectively.

Figure 3.7: Fly Ash with Particle Size and Number 16.256 µm and 2.141 µm

Figure 3.8: Fly Ash with Particle Size and Number 115.014 µm and 6.333 µm

3.2.5 Catalyst

The catalyst that was used in this research were sulphuric acid and dodecanedioic acid (DDDA). Sulphuric acid, H_2SO_4 was used as a catalyst to lower down the activation energy in order to speed up the reaction process. Same function, the catalyst that is used is to enhance the polymerization process so that the transverse strength of the roofing tiles is able to be increase. The amount of the catalyst will be in between 3-4% as the optimized value for the catalyst to work according to Humayun et al. (2017). Having excessive amount of catalyst will not contribute to more strength on the roofing tiles but will interrupt the interaction between the fly ash with the oil polymers. Only a small amount of acid is needed for the enhancement, the acid used was diluted prior being used with a ratio of 1:20 (Teoh et al., 2018). Sulphuric acid was chosen for this study because it is readily available.

Other than sulphuric acid, DDDA was added to react with glycerine pitch. A glycerine pitch contains a component of glycerol, diglycerol, fatty acids and inorganic salts. As mentioned, glycerine pitch has the hygroscopic effect that tends to absorb water at surrounding which will contribute to the decrease of strength in roofing tiles. This happens is due to the presence of –OH group in glycerine pitch, therefore DDDA is added into glycerine pitch so that the di-acid works to eliminate the –OH group by reacting with it to form ester.

Figure 3.9: Diluted Sulphuric Acid

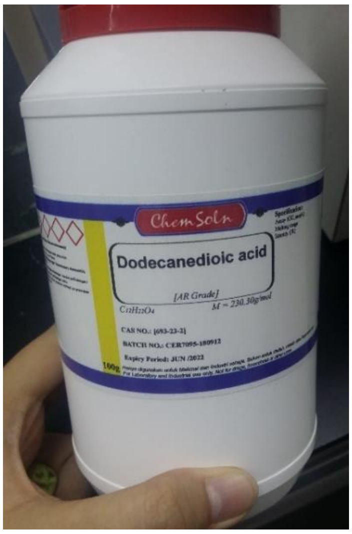


Figure 3.10: Dodecanedioic Acid

3.3 Experimental Procedure

3.3.1 Preliminary Analysis of Selected Materials

The materials that had been used in this research study is analysed and characterized in order to understand better on how it works during the production of roofing tiles.

3.3.1.1 Attenuated Total Reflectance Fourier Transform Infrared Spectrometry (ATR-FTIR)

ATR-FTIR is a useful tool in determining the chemical reaction/ structure at both solid and liquid interface. It works by measuring the variation of reflected infrared beam when the beam hits the sample. The operation of the machine was to first clean the ATR crystal using isopropanol with cotton in one direction, this was to prevent possible cotton residue got stuck in the ATR crystal. Then a small amount of sample was put on the ATR crystal, it was important to ensure that the sample tested fully covers the ATR crystal before the starting of the test. The functional group of glycerine pitch, fly ash and waste cooking oil are determined by using this machine.

Figure 3.11: Attenuated Total Reflectance Fourier Transform Infrared Spectrometry (ATR-FTIR)

3.3.1.2 Sieve Analysis

A sieve analysis was carried out according to the ASTM C 136/ C 136M- 4 in order to determine the size distribution of the sand aggregates that is going to be used in the research. The machine used is a Mechanical Sieve Shaker where it works by creating a constant rate of motion on the sieve that will cause the particles inside the sieve to tumble into their respective sizes of openings.

A total amount of 1 kg of sand aggregate is prepared and washed with tap water prior to the test in order to prevent any impurities present within the sand aggregate to interrupt with the binding of roofing tiles. After the washing of sand aggregate, it undergoes the drying process in the oven at a temperature of 110 ± 5 ˚C. The sieves were then arranged in the order from large to small according to the size of the opening from top to bottom and the sand aggregates were then put at the highest sieve, after that the machine was started and the sand aggregates were sieved for approximately 15 minutes time to ensure that there were no leftover small particles trapped in the larger sieve openings. The sieve size used in this analysis are 4, 1, 0.85, 0.71, 0.50 mm.

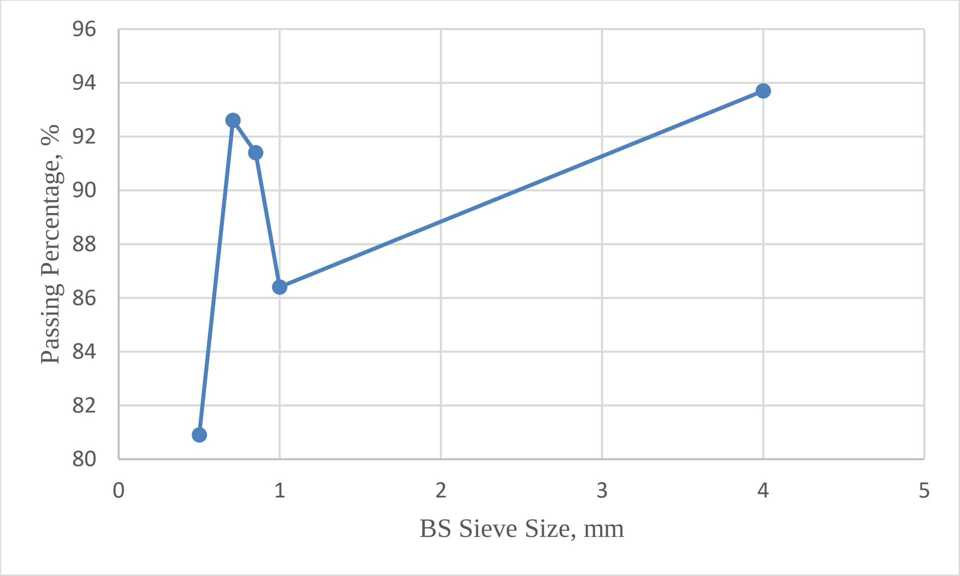


Figure 3.12: Size Gradation of Sand Aggregate

3.3.1.3 Particle Size Analysis

In this analysis the particle size of the coal-fired ash was determined using a *Malvern Mastersizer 2000* particle size analyser matched with the *Malvern Panalytical Software* for the data extraction. To carry out this analysis, the coal-fired ash were put into the tap water bits by bits until it reaches its required amount by the machine. After that the solution will be injected into the analyser to be analysed. The results shown will be in terms of the volume and number of the average particle size of coal-fired ash.

Figure 3.13: Particle Size Analyser

3.3.2 Production of Roofing Tile Samples

3.3.2.1 Manufacturing Processes of Roofing Tile Samples

As mentioned from above, the production of the roofing tile samples required three main steps which are (i) the mixing of ingredients in a bench mounting mixer, (ii) compaction of mould into desire shape of roofing tile samples using a Marshall compactor and last (iii) heat curing process in the oven for 24 hours at $190^{o}C$.

Before having the three main steps carried out, there are some preliminary steps that were taken for the preparation of the ingredients to be used in the production. First, the sand aggregate used was collected and cleaned with tap water to wash away any possible dust or unwanted particles, it was then dried using an oven at the temperature of 110 ± 5 ˚C to ensure that there were no remaining water contained between the sand particles. The sand aggregate were then sieved under a sieve size of 1.68mm (No. sieve 12) to make sure that the sizes of the sand aggregate were maintained below the size. Also, the coal-fired ash were sieve beforehand with the sieve size of 850 µm to remove any possible incomplete pulverized coal particles during the combustion process or any unwanted substances from the power plant. All ingredients that were required were all sealed and covered in a container to prevent any direct sunlight and any dust particles from affecting it.

After the preliminary steps had been taken, the first step for preparing the roofing tiles was to first prepare the required amount of materials needed. The sand aggregate and coal-fired ash were first mixed together manually and next was the addition of the glycerine pitch and waste cooking oil. After that the mixture was mixed using a bench mounting mixer for a period of 35 ± 5 minutes to ensure that there were no clumps left in the mixture of ingredients. It is also need to make sure that the ingredients were all well mixed together. After that, the mixture of ingredients were transferred into a 100mm Marshall Mould and compacted using the Marshall compactor for 20 blows. The sample were then taken out from the mould and the roofing tile samples' shape will be formed as below in Figure 3.2. To ensure that the roofing tile samples are able to achieve the desire strength and also in order to maintain its shape, the tiles were sent to a curing process in the oven for a period of 24 hours at the temperature of 190 ± 5 ˚C.

Figure 3.14: Example of Roofing Tile Sample before Curing Process

3.3.2.2 Optimization of Parameters

Optimization process involves the determination of the highest strength of the roofing tiles. In order to achieve the optimized roofing tile using alternative binder, the composition of the material used needs to be formulated. Some of the material components are fixed throughout the experiment and there are the optimized percentage based on other studies carried out by researchers. Table 3.2 shows the composition of each materials that were involved in the production of roofing tiles. Materials that requires optimization was the percentage of glycerine pitch and waste cooking oil.

Table 3.2: Initial Selected Composition of Materials for Optimization

Parameters	**Range of composition**
Sand Aggregate	65%
Fly Ash	35%
Glycerine Pitch	3-9%
Waste Cooking Oil	3-5%
Sulphuric Acid	4% with respect to the weight of waste cooking oil
Dodecanedioic Acid	4% with respect to the weight of glycerine pitch
Number of Compactions	20 bowls
Mixing time	30-40 minutes (ensure that there are no materials clump together)
Curing Temperature and Duration	190 °C
Curing Duration	24 hours

3.3.3 Physical and Chemical Analysis of Roofing Tile Samples

3.3.3.1 Transverse/ Flexural Strength Test

Transverse Strength test is also known as transverse rupture test whereby it is used to determine the maximum stress that the sample can sustain when it is bent by the load. The testing method for the roofing tile samples are following the standard testing method by ASTM C 1167 – 11(2017) and 1492 – 03(2016). There are two different types of transverse strength tests that the tiles need to undergo which are dry and wet transverse strength tests respectively. For the dry transverse strength test, the roofing tile samples to undergo a heating process at 190 ± 5 ˚C for a period of 24 hours in the oven and it was cooled for at least 4 hours before the test was carried out. For the wet transverse strength test, the roofing tile samples need to be submerged in water for 24 hours at an average temperature of 24 ± 6 ˚C before the test can be taken place.

The transverse strength test of the sample will be tested using a Material Testing Machine *T-Machine*.The data and results of the test can be obtained from the software *Universal Testing Manager*. The roofing tiles had been tested using a three-point bending mode in a horizontal plane whereby there will be two lower support members supporting the lower base of the tile. The load will be applied perpendicularly to the plane of the tile with the third member located at the mid-span of the tile. It is important to note that the distance between the two lower span must be at least 2/3 of the length of the tile. The crosshead of the third member was adjusted using the software so that it is located right above the tile. The testing of tiles is shown in Figure 3.3. After the tile has been secured in its correct place, specifications of the tile such as diameter, height, area and the naming of the tile are inserted into the software accordingly before the test is carried out. The results obtained is in the unit of of Newton (N).

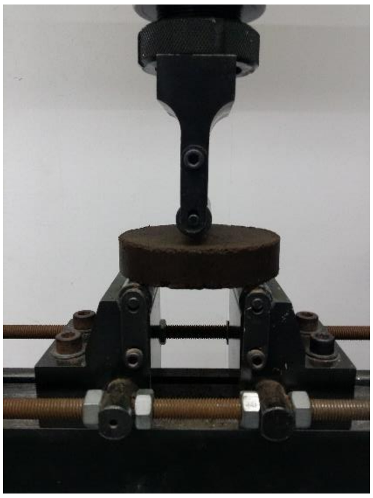


Figure 3.15: Sample Testing of Transverse Strength

Once the yield strength is obtained from the material testing machine, the dry and wet flexural strength, σ in terms of MPa can be calculated using the formula as shown below for the three-point bending mode.

$$Flexural\ Strength\ (MPa) = \frac{3PL}{2wd^2}$$

where,

P = maximum force applied, N

L = span length, mm

w = width of the sample, mm

d = diameter of the sample, mm

3.3.3.2 Water Absorption Test

Water absorption test is also an important test to ensure that the roofing tiles is able to withstand the excessive amount of rain. The testing method and calculations will be following the ASTM C 67-07a. The first step for the testing method was preparation of cooled down roofing tile samples and its initial weight was recorded. After that the roofing tiles were submerged into clean water (soft, distilled or rain water) for 24 hours at the temperature between 15.5 to 30.0 ° C. After 24 hours of submerging the tiles in the water, the roofing tiles are taken out while the surface of the tiles are wiped using a damped cloth. The final wet weight of the tile must be measured within 5 minutes after being removed from the water. The percentage of water absorption is calculated according to the formula as shown below. The demonstration of water absorption test is shown in Figure 3.16.

$$Water\ Absorption\ (\%) = \frac{Ww - Wd}{Wd} \times 100\%$$

Where,

W_w = wet weight of the specimen after 24 hours of submersion, g

W_d = dry weight of the specimen before submersion, g

Figure 3.16: Demonstration of Water Absorption Test.

3.3.3.3 Permeability Test

The permeability test is taken place in order to ensure that the roofing tiles are able to prevent the penetration of water during rainy days so that there is no leakage of rainwater into the house as the roofing tiles are served as a cover for the house. There is also a standard for the permeability test which is according to the ASTM 1167 – 11(2017). The roofing tile samples are placed on a round PVC pipe with a diameter that is at least 4/5 of the diameter of tile. It is important that the gap between the specimen and the pipe is sealed using a watertight sealant material so that there are no chance of water leakage during the test. Later on water is poured into the pipe with the height of approximately 5mm and it is observed for a period of 24 hours to check if there is any water penetrate through the samples. If there is no penetration of water through the samples, the roofing tiles are said to be impermeable.

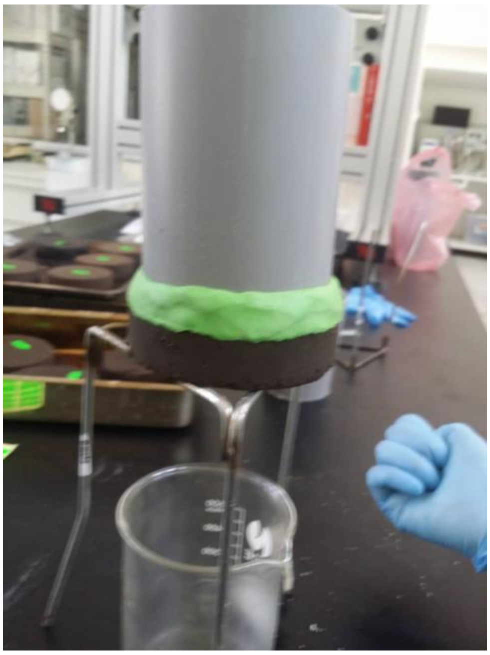


Figure 3.17: Demonstration of Permeability Test

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Raw Materials Analysis using Attenuated Total Reflectance Fourier Transform Infrared Spectrometry (ATR- FTIR)

For this study, unwanted glycerine pitch and waste cooking oil were used as binder for the production of roofing tiles. It is believe that, waste cooking oil that undergoes a high temperature of curing process will have an increase of viscosity due to oxy-polymerization that helps to bind materials together and eventually hardens after the curing process. Formation of solid polyester that contributes to the strength of the roofing tiles happened is because of the poly-esterification process (Humayun, et al., 2017 and Nadeem, et al., 2017). The occurrence of the above mentioned process is may be due to the presence of di-ols and di-acids in the oil. The ATR-FTIR results are as shown in Figure 4.1.

As for glycerine pitch, there are previous studies which use pure glycerine in the production of masonry units and glycerine pitch has shown to have similar properties as pure glycerine especially with the presence of 55- 65% of glycerol. Therefore the FTIR-ATR is used to investigate the functional group presence in both the binders so that it is easier to understand the chemical reactions while producing the roofing tiles. Figure 4.2 shows the ATR-FTIR result of glycerine pitch. As for fly ash, it is also used as one of the material in the production of green roofing tiles. Therefore it has also undergone the ATR-FTIR analysis to identify its possible mineral present which is shown in Figure 4.3 and Figure 4.4.

4.1.1 Glycerine Pitch Analysis using Attenuated Total Reflectance Fourier Transform Infrared Spectrometry (ATR- FTIR)

From Figure 4.1, it can be seen that there is a broad peak of 3307.49 cm^{-1} which indicates the existence of O-H alcohol which is due to the presence of high percentage (55-65%) of glycerol in the glycerine pitch. It is also the main contributor to the hygroscopic effect of the glycerine pitch that will cause weakening of strength of the roofing tiles by having high water absorption rate. At 2877.42 cm^{-1}, shows a C-H bond contributed by alkane compounds. A very small peak at 1736 cm^{-1} shows that there is the existence of C=O compound of ester. There is also COO^{-} functionalities of soap existed at a small peak of 1627 cm^{-1} which represents that glycerol contain a certain amount of mineral salts (Hidawati and Sakinah, 2011). 1585.74cm^{-1} and 1412.17 cm^{-1} show a medium-weak with multiple bands which represent the presence of C=C stretch contributed by the aromatic compound. Ether compound has contributed to C-O stretch at 1333.15 cm^{-1}. 925.74 cm^{-1}, 857.33 cm^{-1} and 656.34 cm^{-1} shows strong =C-H bending by alkene compound.

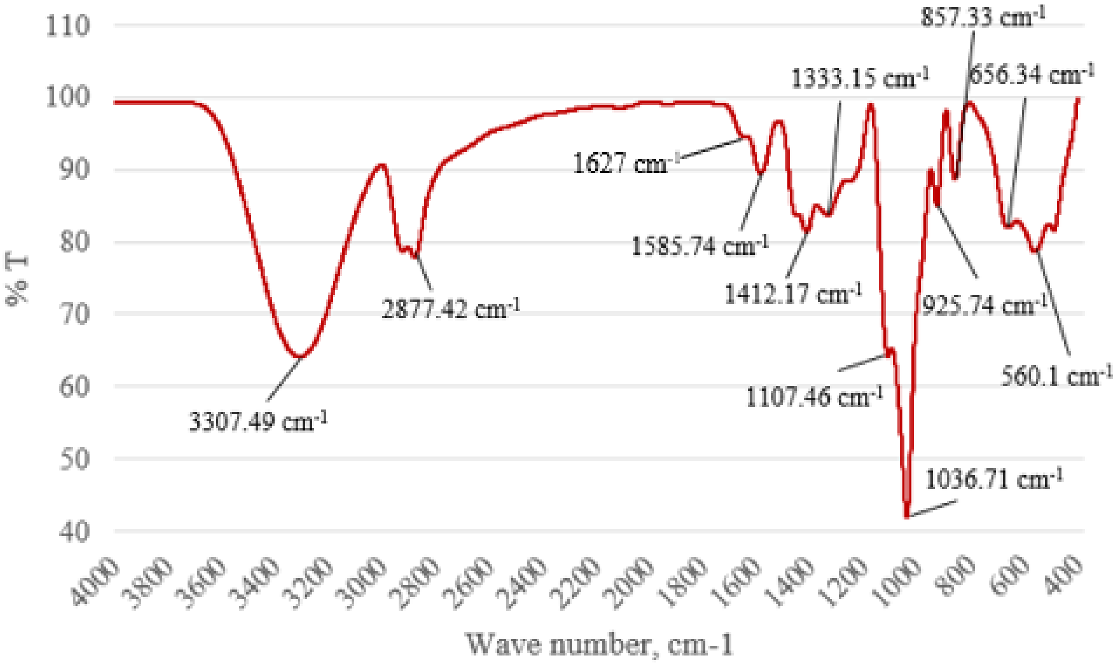


Figure 4.1: ATR- FTIR Spectrum of Glycerine Pitch

4.1.2 Waste Cooking Oil Analysis using Attenuated Total Reflectance Fourier Transform Infrared Spectrometry (ATR- FTIR)

From the results, it can observed that at peak 2922.22 cm^{-1} and 2853.91 cm^{-1}, there are asymmetrical and symmetrical C-H stretch bonds contributed by alkane compounds. Adding on there are also asymmetrical and symmetrical C-H bending bond at two absorption peaks of 1459.19 cm^{-1}and 1371.08 cm^{-1} which are contributed by those hydrocarbon components. Moreover, there are also signs of carbonyl group (C=O) contributed by ester compounds at the absorption peak of 1743.85 cm^{-1}. Other than that, ester compound has also contributed to carbon-oxygen bonds (C-O) at the peak of 1158.78 cm^{-1}. The process of oxy-polymerization occurs which may be due to the presence of carbonyl group (C=O), the process is initiated through the thermal treatment whereby chemical reaction happened between carboxylic acid with glycol or H_2O_2 at high temperature for the formation of larger molecular species.

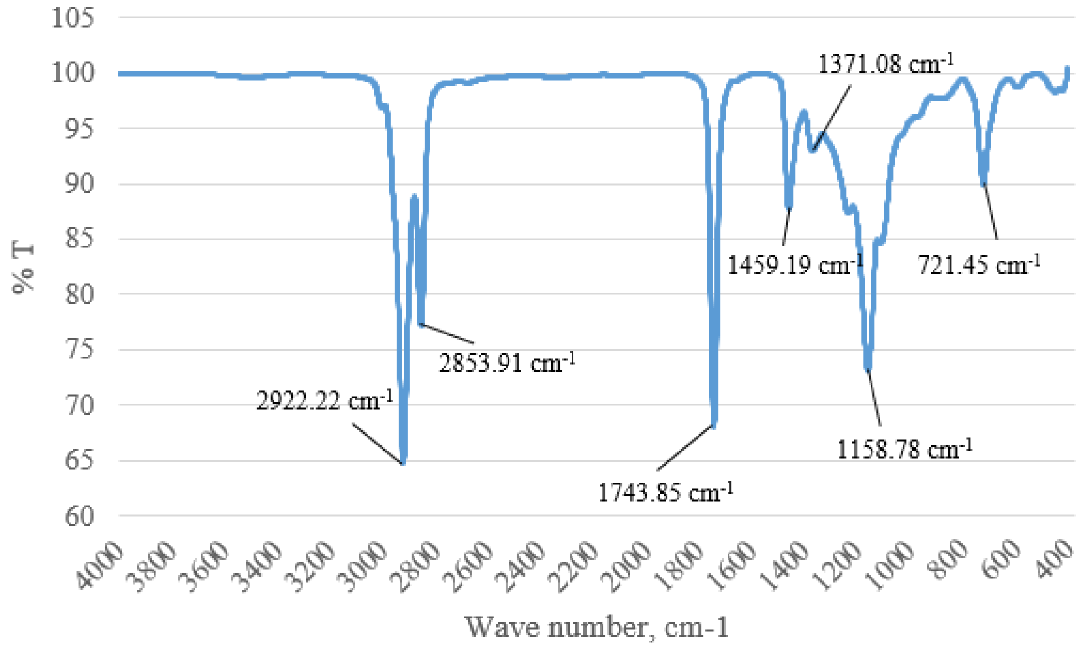


Figure 4.2: ATR- FTIR Spectrum of Waste Cooking Oil.

4.1.3 Fly Ash Analysis using Attenuated Total Reflectance Fourier Transform Infrared Spectrometry (ATR- FTIR)

Throughout this study, two different sizes of fly ash were used during the fabrication of green roofing tiles, so both of the fly ash had also undergone the ATR-FTIR analysis. By comparing both the results, they have shown similar peaks. From the figures below, it can be seen that there are two large peaks for each size of fly ash, which are 998.84 cm^{-1} and 445.52 cm^{-1} for smaller size fly ash and 1048.31 cm^{-1} and 450.50 cm^{-1} for larger particle size fly ash. From the results there are also a small peak at 786 cm^{-1} present for both sizes of fly ash together with the absorption wavelength of 445.52 cm^{-1} and 450.50 cm^{-1} which indicates the presence of symmetric Si-O-Si stretch (Dasgupta, et al., 2012). As for the big broad band at 1048.31 cm^{-1} and 998.84 cm^{-1}, it represents the presence of anti-symmetric Si-O-Si stretch.

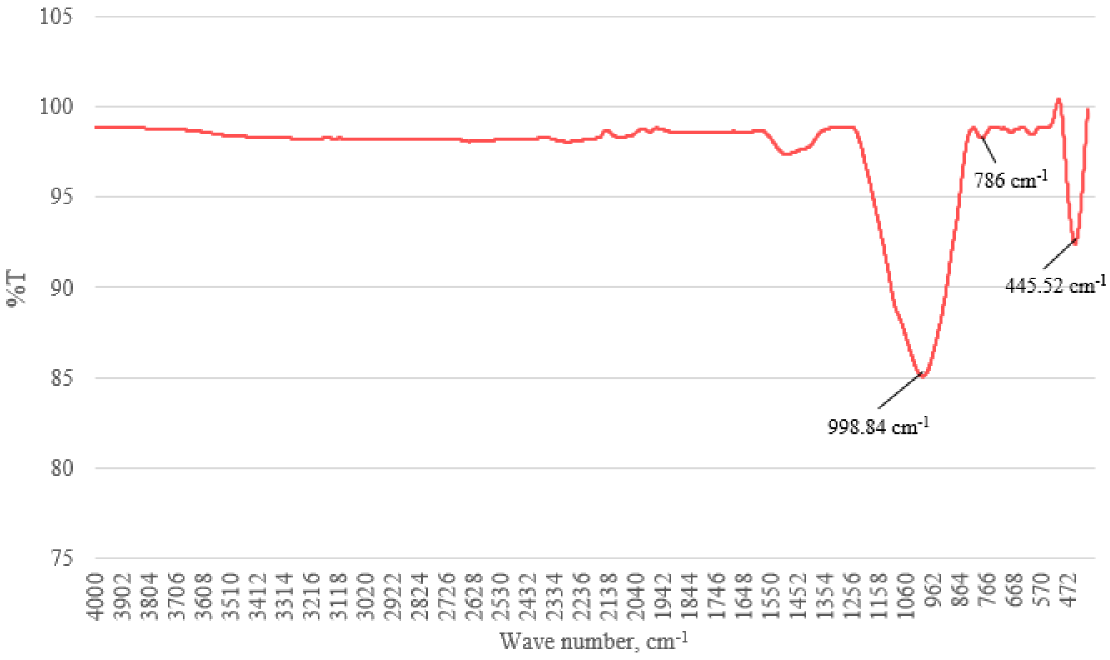


Figure 4.3: ATR-FTIR Spectrum of Smaller Particle Size Fly Ash (16.256 µm).

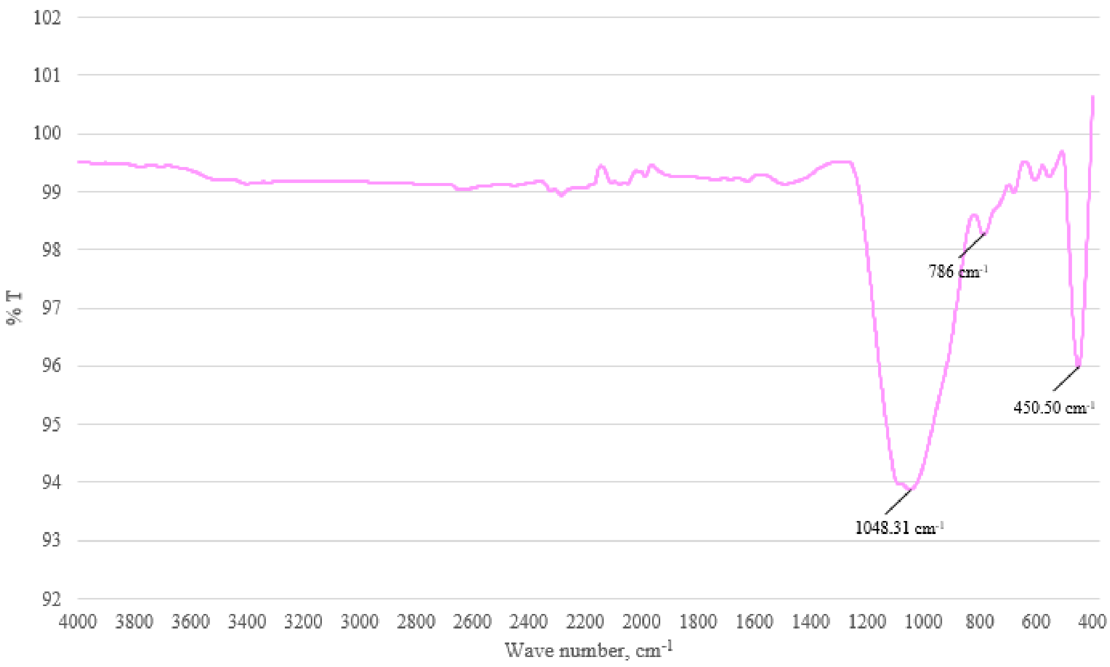


Figure 4.4: ATR-FTIR Spectrum of Larger Particle Size Fly Ash (115.014 µm).

4.2 Optimization Process of Glycerine Pitch Green Roofing Tiles (GP-GRT)

This part covers the investigation of the optimised parameters for the green roofing tiles. It was determined by comparing their dry and wet flexural strengths, water absorption and permeability. The glycerine pitch green roofing tiles that have the highest value in both the flexural dry and wet strengths are also not exceed the maximum limit of water absorption and being impermeable are said to be the optimized composition for producing the glycerine pitch green roofing tiles. This section is separated into three (3) main parts as follows:

4.2.1 Parameters Used in Glycerine Pitch Green Roofing Tiles

Throughout the study, there are some initial compositions for the filler and sand aggregate based on previous studies that were carried out in producing alternative green roofing tiles. Other than that, the range of the binders is listed in Table 4.1 as below.

Table 4.1: Initial parameters for the optimization process

Material	Selected Range (%)	Reference
Sand Aggregate	65%	Humayun et al., 2017 Nadeem et al., 2017
Fly Ash (16.256 µm & 115.014 µm)	35%	Humayun et al., 2017 Nadeem et al., 2017
Glycerine Pitch	1- 9%	
Waste Cooking Oil	1- 9%	
Sulphuric Acid, H_2SO_4	3-4% of waste cooking oil percentage	Humayun et al., 2017
	Dilution into 1:20	Teoh et al., 2018
Dodecanedioic Acid,	3-4% of waste cooking oil percentage	Humayun et al, 2017

4.2.2 Optimization of Glycerine Pitch Green Roofing Tiles using Pulverized Fly Ash with Smaller Particle Size

The type of filler used in this study is pulverized fly ash with its particle sizes are16.256 µm in volume and 2.141 µm in number. Since the percentage of filler and sand aggregate had been fixed, the main focus for the optimization process was on the percentage of the binder used which are glycerine pitch and waste cooking oil. In this section it is separated into three (3) parts:

i. The determination of glycerine pitch to be used as a binder in GP-GRT;

ii. The determination of WCO percentage in GP-GRT and

iii. The optimization of GP-GRT using different materials.

4.2.2.1 Determination of Glycerine Pitch to be used as a binder in Glycerine Pitch Green Roofing Tiles (GP- GRT)

In this determination process, a series of triplicate roofing tile prototypes were produced using the initial estimated appropriate proportion. Other production parameters are also fixed, for instance mixing time of 30 minutes or at least there are no lumps present within the mixture, 20 times of Marshall compaction to ensure that the mixture is well compacted and able to form a secure prototype shape, lastly, the curing process at 190˚C for 24 hours so that the roofing tiles are not under-cured nor over-cured to affect the strength of the roofing tiles. The percentage that had been set for this determination process are 3, 5, 7, 8 and 9% of the glycerine pitch.

The results that were obtained are as shown in Table 4.2. It can be seen clearly that the increase in the percentage of glycerine pitch will not increase the strength of the roofing tile from Figure 4.1, whereby the strength increased gradually at first and when it reached a certain peak percentage the strength started to drop. The most suitable percentage of glycerine pitch used for GP-GRT is 7% when it is compared among the five (5) different percentages. It had the transverse strength of 2149.63 ± 263 N which had exceeded the requirements of the high profile roofing tile set by ASTM C 1167 and C 1492. The percentage of the glycerine pitch is not directly proportional to the strength of the roofing tile. This may be due to insufficient heat cure of the roofing tiles (Humayun et al., 2017) as the core of the roofing tile requires more time to be cured completely.

However, none of the glycerine pitch percentage prototype had achieved the minimum requirement of the wet transverse strength set by the standards in ASTM C 1167 and C 1492. This was predicted as it is due to the natural hygroscopic effect of the glycerine pitch and filler. This effect led to the increased of water absorption and weaken the strength of the roofing tiles. Therefore, an alternative solution had been made whereby an additional binder- waste cooking oil was added in the production process, hoping to restrict or reduce the hygroscopic effect of glycerine pitch and fly ash. The waste cooking oil was predicted to work as a protective layer for the filler and glycerine pitch. The oil tends to block the material from absorbing more water into the roofing tile. In that way the roofing tiles are able to achieve the requirements. This study shows that glycerine pitch is able to act as a binder in the production of roofing tiles, however its hygroscopic effect problem needs to be addressed.

Table 4.2: Results of GP-GRT using different Glycerine Pitch Percentage

Name	Percentage of glycerine pitch (%)	Transverse Strength (N)		Water Absorption (%)
		Dry	Wet	
G3	3	407.03 ± 59	24.16 ± 4	7.81 ± 0.3
G5	5	1030.71 ± 76	27.29 ± 8	6.72 ± 0.3
G7	7	2149.63 ± 263	184.41 ± 16	6.63 ± 0.3
G8	8	1081.70 ± 70	198.17 ± 4	6.69 ± 0.4
G9	9	1633.09 ± 70	151.38 ± 49	6.98 ± 0.2

Table 4.3: Flexural strength of GP-GRT using different glycerine pitch percentage

Name	Percentage of glycerine pitch (%)	Flexural Strength (MPa)	
		Dry	Wet
G3	3	0.92 ± 0.13	0.05 ± 0.01
G5	5	2.34 ± 0.17	0.06 ± 0.02
G7	7	4.87 ± 0.60	0.42 ± 0.04
G8	8	2.45 ± 0.17	0.45 ± 0.008
G9	9	3.70 ± 0.5	0.34 ± 0.11

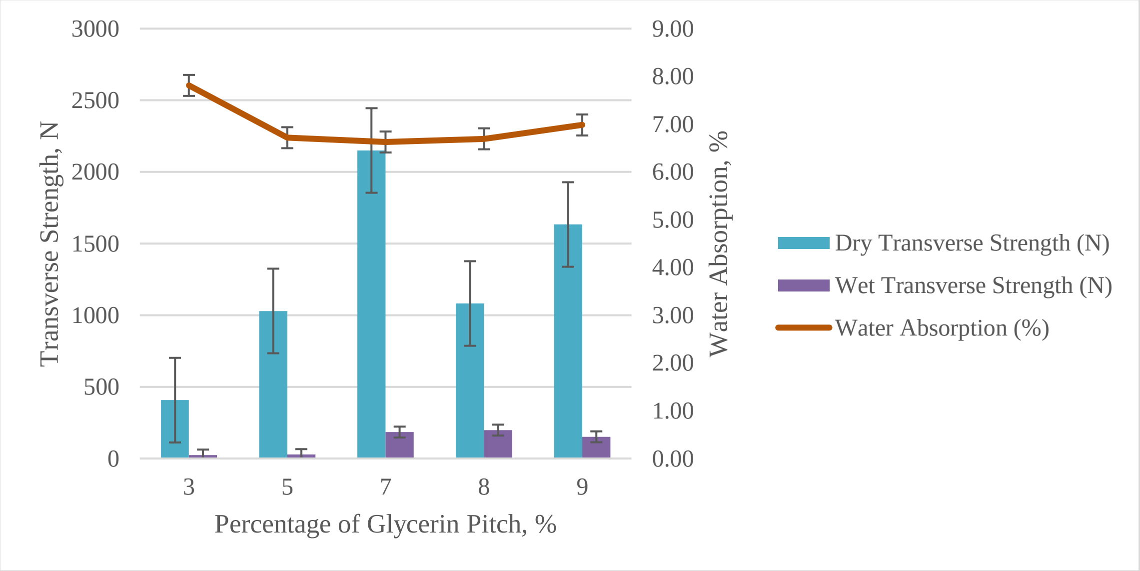


Figure 4.5: Results of Strength and Water Absorption at different Percentage of Glycerine Pitch

4.2.2.2 Determination of Waste Cooking Oil (WCO) Percentage in Glycerine Pitch Green Roofing Tiles (GP- GRT)

As mentioned from the previous section, WCO is required in order to act as a protective layer that limits the hygroscopic effect of the other materials. In this section, glycerine pitch with 3.5% was mixed with WCO which percentage between 2.5 to 5.5%. The results were tabulated in Table 4.3. Figure 4.2 shows that increased oil percentage in the mixture would raise the overall dry and wet transverse strength of the GRT. The results show that with the percentage of glycerine pitch of 3.5% together with waste cooking oil at 3.5 %, both dry and wet strength achieved by the tile are the highest. Not only that, G3.5O3.5 had achieved the minimum requirement of dry and wet strengths needed in the ASTM C 1167 and C 1492 for a medium profile roofing tiles. The tile also passed water absorption test according to the ASTM C 1167-11. The level achieved was a high profile roofing tile based on water absorption. The values obtained was 1971.03 N for dry strength, 1053.25 N of wet strength with the water absorption of 2.18%. The results had exceeded the minimum requirement by 47% and 5.2% in terms of dry and wet strength.

The reason that the percentage of WCO can never be too high nor low was explained whereby when at low WCO percentage the oil was unable to cover most of the hygroscopic material of the filler and glycerine pitch. As for the higher percentage of WCO, it might be due to excessive percentage that leads to the aggravation of compaction problem whereby the mixture gets sticky and eventually the strength of the roofing tiles were effected. Although most of the roofing tile samples were still unable to achieve the minimum requirement of wet strength, it had proven that by the addition of another binder was able to help in contributing to the strength as the reaction between di-ols and di-acids forming poly-esters and acted as a protective layer for water prevention.

Table 4.4: Results of GP-GRT using different WCO percentage

Name	Percentage of waste cooking oil (%)	Transverse Strength (N)		Water Absorption (%)
		Dry	Wet	
G3.5O2.5	2.5	1080.78 ± 116	240.38 ± 20	4.96 ± 1.0
G3.5O3.5	3.5	1971.03 ± 125	1053.25 ± 96	2.18 ± 0.8
G3.5O4.5	4.5	1090.87 ± 41	647.73 ± 20	2.61 ± 1.0
G3.5O5.5	5.5	1385.38 ± 20	660.58 ± 20	3.64 ± 1.0

Table 4.5: Flexural strength of GP-GRT using different WCO percentage

Name	Percentage of waste cooking oil (%)	Flexural Strength (MPa)	
		Dry	Wet
G3.5O2.5	2.5	2.45 ± 0.26	0.55 ± 0.02
G3.5O3.5	3.5	4.47 ± 0.28	2.39 ± 0.22
G3.5O4.5	4.5	2.47 ± 0.09	1.47 ± 0.05
G3.5O5.5	5.5	3.14 ± 0.05	1.50 ± 0.03

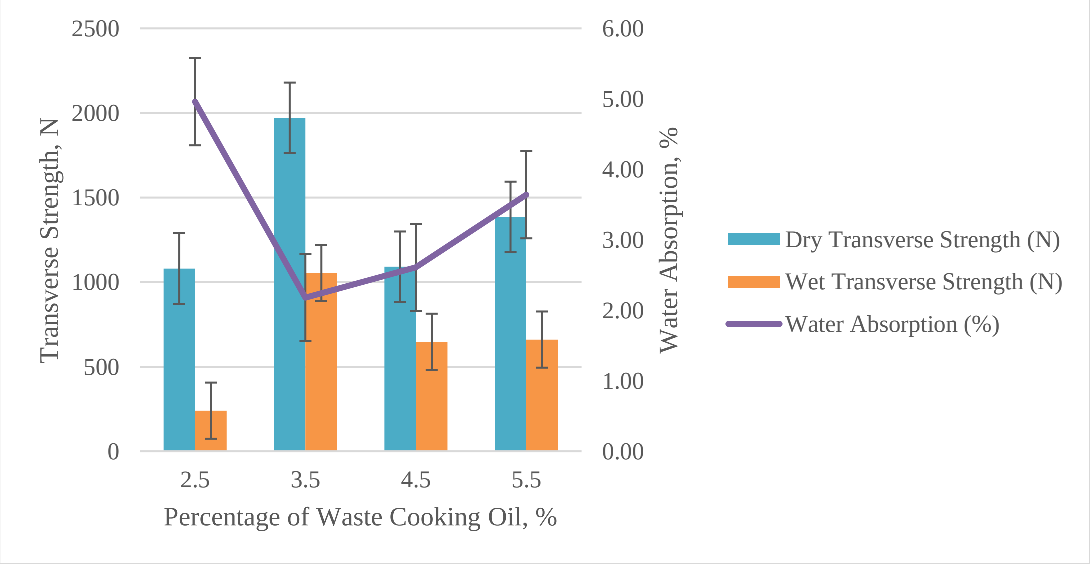


Figure 4.6: Strength and water absorption at different percentage of WCO

4.2.2.3 Optimization of Glycerine Pitch Green Roofing Tiles (GP- GRT) using Different Materials

In this section four (4) different conditions of green roofing tiles were produced which are:

a. Without any additional materials which act as a control among the other three components;
b. Addition of sulphuric acid, H_2SO_4 in hoping to act as a catalyst that is able to speed up and lower the activation energy;
c. WCO coating layer is applied in order to reduce the water absorption of the roofing tiles and
d. The tile was added with acid and coated with oil. The results can be seen clearly from Table 4.4 and Figure 4.3.

The roofing tile composition that has the highest strength among the four different types of roofing tiles is the one with the addition of acid. The usage of acid is able to enhance the oxy-polymerization process. When the viscosity of the binder increased, the materials were able to bind more effectively and efficiently which then contributed in the increased of the tile strength. The strength achieved by the tile was 2573 N and 1062 N in terms of dry and wet strength.

The roofing tiles prototype that had a layer of oil coating was expected to have better water absorption, but it shows that it has a higher percentage of water absorption and lower wet strength. This might be due to the overheated curing process. Studies has shown that by having excess cuing process, crack will be formed within the roofing tiles which then explained that weaker strength and high percentage of water absorption as the presence of cracks within the tile allows the water to enter and weaken it from the inside. Other than that, there might be the possibility that the voids were not expanded for the oil to fill up as the oil coating process was taken place after the roofing tiles were cooled down.

Table 4.6: Results of GP-GRT at different type of alternatives

O= Original; A= Acid; B= Acid & Coating; C= Oil Coating

Name	Alternatives	Transverse Strength (N)		Water Absorption (%)
		Dry	Wet	
G3.5O3.5O	Blank	2566.47 ± 121	875.88 ± 53	2.95 ± 0.15
G3.5O3.5A	H_2SO_4 added	2573.19 ± 92	1062.92 ± 71	2.22 ± 0.17
G3.5O3.5B	H_2SO_4 + oil coat	2239.54 ± 10	847.74 ± 49	3.09 ± 0.01
G3.5O3.5C	Oil coat	2159.42 ± 93	709.50 ± 132	3.28 ± 0.34

Table 4.7: Results of GP-GRT at different type of alternatives

O= Original; A= Acid; B= Acid & Coating; C= Oil Coating

Name	Alternatives	Flexural Strength (MPa)	
		Dry	Wet
G3.5O3.5O	Blank	5.82 ± 0.27	1.99 ± 0.12
G3.5O3.5A	H_2SO_4 added	5.84 ± 0.21	2.41 ± 0.16
G3.5O3.5B	H_2SO_4 + oil coat	5.08 ± 0.16	1.92 ± 0.11
G3.5O3.5C	Oil coat	1.92 ± 0.11	1.61 ± 0.3

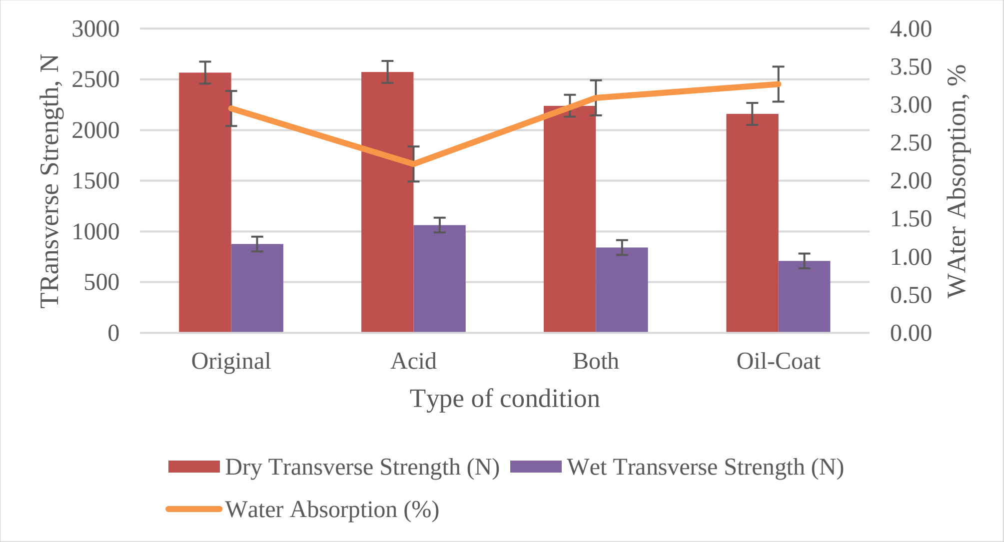


Figure 4.7: Strength and water absorption of different condition

4.2.3 Optimization of Glycerine Pitch Green Roofing Tiles (GP- GRT) using Pulverized Fly Ash with Larger Particle Size

Referring to the previous experiment, both the binders were required in order to achieve a sufficient strength so that it exceeds the minimum requirements therefore the initial composition for the optimization process will include both the binders. In this section the particle size in volume and number of the pulverized fly ash is 115.014 µm and 6.333 µm respectively. The percentage of fly ash and sand aggregate will remain constant together with the same number of Marshall Compactions and curing criteria as the previous section of the test. There will be two (2) main parts in this section:

a. The variation of ratio between glycerine pitch and waste cooking oil in terms of 7% of the total weight of the roofing tiles and

b. Comparison of different materials used to produce GP-GRT.

4.2.3.1 Variation of Ratio between Glycerine Pitch and Waste Cooking Oil

The ratio used between glycerine pitch and waste cooking oil is 1:9, 2:8, 3:7, 4:6, 5:5, 6:4, 7:3, 8:2, 9:1 respectively. From Figure 4.4, the best ratio among them is 1:9 and 2:8 of GP: WCO, whereby three of requirements set by ASTM was able to be fulfilled. Other than that, from the result below, it was observed that the water absorption and wet transverse strength were interconnected. When there was a higher percentage of water absorption there will lead to a decrease of wet transverse strength and vice versa. For instance, the ratio of 7:3, the water absorption percentage is the highest among all and has a relatively low transverse strength. This condition happened might be due to the infiltration of water into the voids of the roofing tiles which would then led to the saturation of the materials, when materials get saturated they tend to expand thus making the possible formation of internal cracks within them which is the reason the tiles were unable to perform well and a weak strength was obtained.

Table 4.8: Results of GP-GRT at different ratio of GP with WCO

Name	GP: WCO	Transverse Strength (N)		Water Absorption (%)
		Dry	Wet	
G1O9	1:9	2908.99 ± 264	1245.92 ± 94	5.99 ± 0.65
G2O8	2:8	3106.86 ± 222	724.28 ± 86	8.79 ± 1.7
G3O7	3:7	2495.82 ± 74	677.40 ± 39	7.65 ± 0.43
G4O6	4:6	2117.21 ± 167	432.13 ± 183	8.87 ± 0.82
G5O5	5:5	1394.86 ± 34	462.71 ± 85	12.78 ± 1.15
G6O4	6:4	1140.41 ± 95	380.44 ± 93	13.37 ± 0.38
G7O3	7:3	1597.31 ± 122	31.19 ±1.83	14.98 ± 0.70
G8O2	8:2	1504.34 ± 42	17.43 ± 4.71	13.67 ± 0.96
G9O1	9:1	160.56 ± 4.71	23.85 ± 3.31	13.32 ± 1.59

Table 4.9: Flexural Strength of GP-GRT at different ratio of GP with WCO

Name	GP: WCO	Flexural Strength (MPa)	
		Dry	Wet
G1O9	1:9	6.60 ± 0.6	2.83 ± 0.21
G2O8	2:8	7.05 ± 0.50	1.67 ± 0.34
G3O7	3:7	5.66 ± 0.17	1.54 ± 0.09
G4O6	4:6	4.80 ± 0.38	0.98 ± 0.42
G5O5	5:5	3.16 ± 0.08	1.05 ± 0.19
G6O4	6:4	2.59 ± 0.21	0.86 ± 0.21
G7O3	7:3	3.62 ± 0.28	0.07 ± 0.004
G8O2	8:2	3.41 ± 0.10	0.04 ± 0.01
G9O1	9:1	0.36 ± 0.01	0.05 ± 0.01

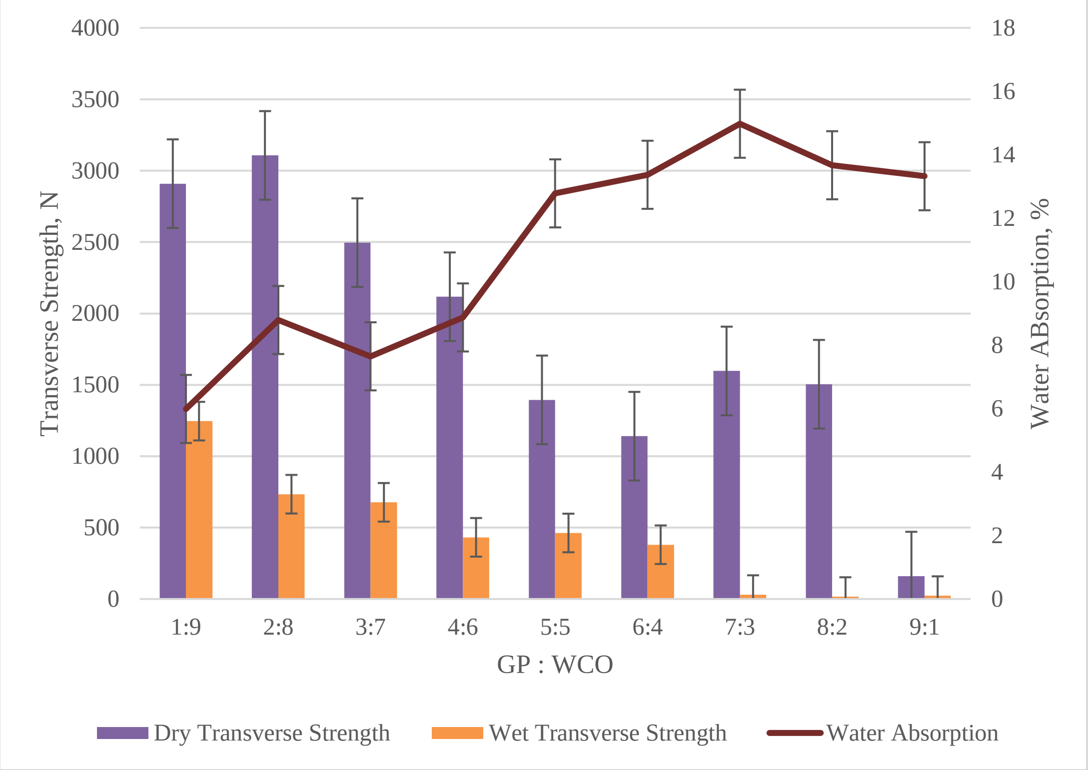


Figure 4.8: Strength and Water Absorption of Different ratio of GP with WCO

4.2.3.2 Comparison of Glycerine Pitch Green Roofing Tiles (GP- GRT) using Different Materials

The final optimization process for larger particle size of fly ash includes the addition of acids and coat a layer of oil on the surface of tiles. Other than that, the percentages of glycerine pitch (GP) and waste cooking oil (WCO) were halved based on their total percentage, therefore the total percentage of GP and WCO involved in this section is in the range of 3-10%. The results are shown in Tables 4.10 and 4.11 and Figures 4.5, 4.6 and 4.7.

It can be seen from the results, the best result based on the three different conditions in producing GP-GRT is the oil-coated catalysed GP-GRT. One of the highest dry strength achieved is 5385.40 ± 79 N with a flexural strength of 12.21 ± 0.18 MPa and with the composition of 3% GP and 3% WCO. This result is even better than the results of previous studies of using waste cooking oil alone as a binder in producing roofing tiles with the maximum strength obtained is 10.1 MPa. The wet strength 1139.96 ± 54 N of the roofing tile is still relatively low although it had achieved the minimum requirements of a medium profile tile as per ASTM standard. This might be due to the non-uniform coating of WCO on the surface of the tiles as this can be explained by studying oil coated catalysed GP-GRT, the wet transverse strength for G3O3 is the lowest and the water absorption is the highest which is 4.66 ± 0.6%, meaning that there was higher amount of water that had penetrated into the roofing tile. The wet strength of the tiles could be improved if the coating process can be carried out more effectively.

Table 4.10: Results of GP-GRT with Different Additives

Situation	Name	GP & WCO (%)	Transverse Strength (N)		Water Absorption (%)
			Dry	**Wet**	
Original	G3O3	3.0	1297.91 ± 40	499.41 ± 13	7.02 ± 0.19
	G3.5O3.5	3.5	1394.86 ± 34	462.70 ± 85	12.78 ± 1.15
	G4O4	4.0	1377.73 ± 263	815.94 ± 36	7.37 ± 0.02
	G4.5O4.5	4.5	1411.37 ± 142	552.95 ± 89	7.60 ± 0.47
	G5O5	5.0	2770.08 ± 176	853.25 ± 55	7.46 ± 0.55
Catalyzed	**G3O3**	**3.0**	**578.62 ± 24**	**547.12 ± 89**	**6.51 ± 1.96**
	G3.5O3.5	**3.5**	**563.33 ± 143**	**313.16 ± 53**	**9.37 ± 1.01**
	G4O4	**4.0**	**793.92 ± 54**	**86.54 ± 23**	**9.04 ± 0.33**
	G4.5O4.5	**4.5**	**600.02 ± 37**	**148.63 ± 39**	**8.74 ± 0.38**
	G5O5	**5.0**	**3154.86 ± 525**	**925.72 ± 100**	**5.32 ± 0.9**
Catalyzed + Oil-coating	G3O3	3.0	5385.40 ± 79	1139.96 ± 54	4.66 ± 0.6
	G3.5O3.5	3.5	2070.71 ± 1087	1119.01 ± 146	2.80 ± 0.35
	G4O4	4.0	2650.57 ± 127	1332.78 ± 91	1.74 ± 0.15
	G4.5O4.5	4.5	3068.63 ± 50	1454.50 ± 309	3.63 ± 1.18
	G5O5	5.0	1752.37 ± 150	1901.30 ± 200	1.94 ± 0.77

Table 4.11: Flexural Strength of GP-GRT with Different Additives

Situation	Name	GP & WCO (%)	Transverse Strength (N)	
			Dry	**Wet**
Original	G3O3	3.0	2.94 ± 0.09	1.13 ± 0.03
	G3.5O3.5	3.5	3.16 ± 0.08	1.05 ± 0.19
	G4O4	4.0	3.12 ± 0.06	1.85 ± 0.08
	G4.5O4.5	4.5	3.20 ± 0.32	1.25 ± 0.02
	G5O5	5.0	6.28 ± 0.4	1.93 ± 0.12
Catalyzed	**G3O3**	**3.0**	**1.31 ± 0.06**	**1.24 ± 0.20**
	G3.5O3.5	**3.5**	**1.28 ± 0.32**	**0.71 ± 0.12**
	G4O4	**4.0**	**1.80 ± 0.21**	**0.20 ± 0.05**
	G4.5O4.5	**4.5**	**1.36 ± 0.08**	**0.34 ± 0.09**
	G5O5	**5.0**	**7.15 ± 1.19**	**2.10 ± 0.23**
Catalyzed + Oil-coating	G3O3	3.0	12.21 ± 0.18	2.59 ± 0.12
	G3.5O3.5	3.5	4.70 ± 2.46	2.54 ± 0.33
	G4O4	4.0	6.01 ± 0.29	3.02 ± 0.21
	G4.5O4.5	4.5	6.96 ± 0.7	3.30 ± 0.11
	G5O5	5.0	1.84 ± 0.3	4.31 ± 0.45

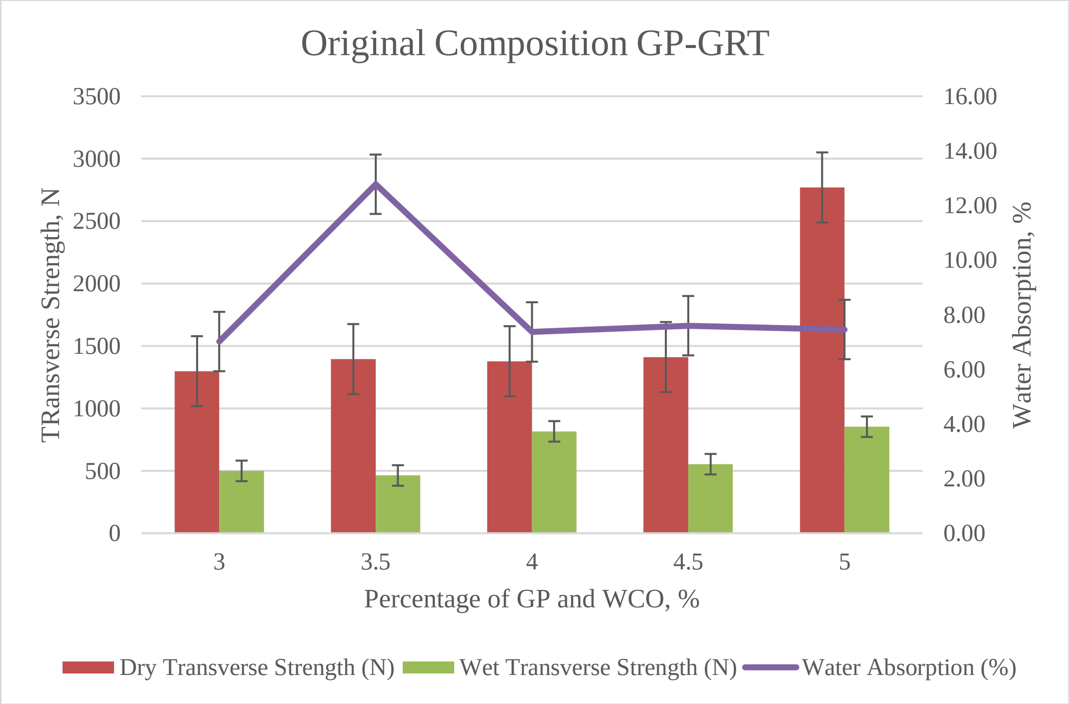


Figure 4.9: Strength and Water Absorption of Original Composition GP-GRT

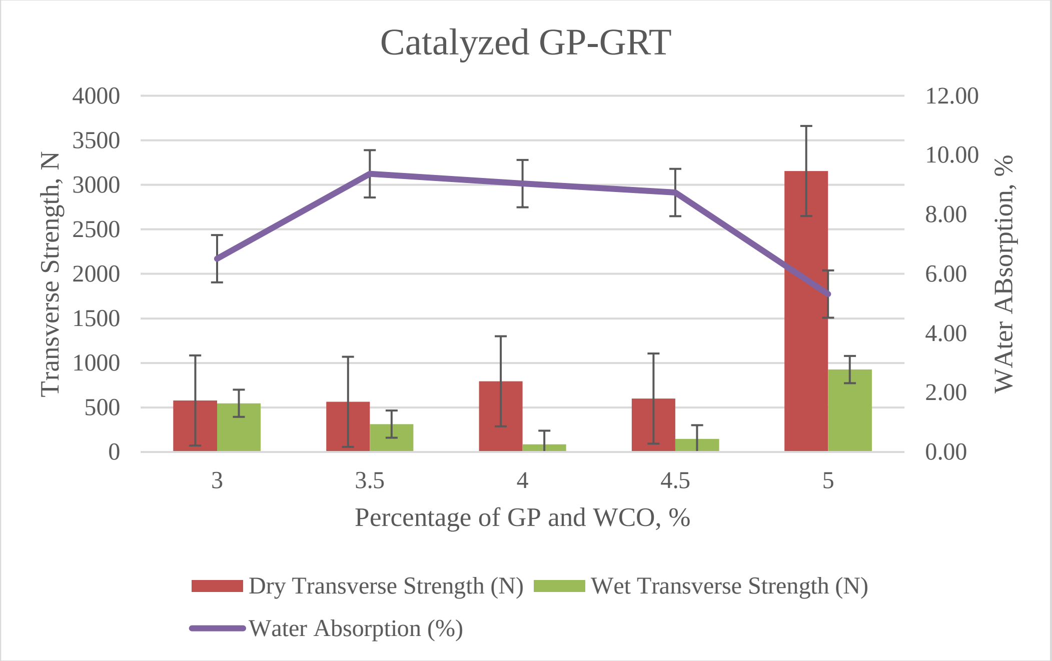


Figure 4.10: Strength and Water Absorption of Catalyzed Composition GP-GRT

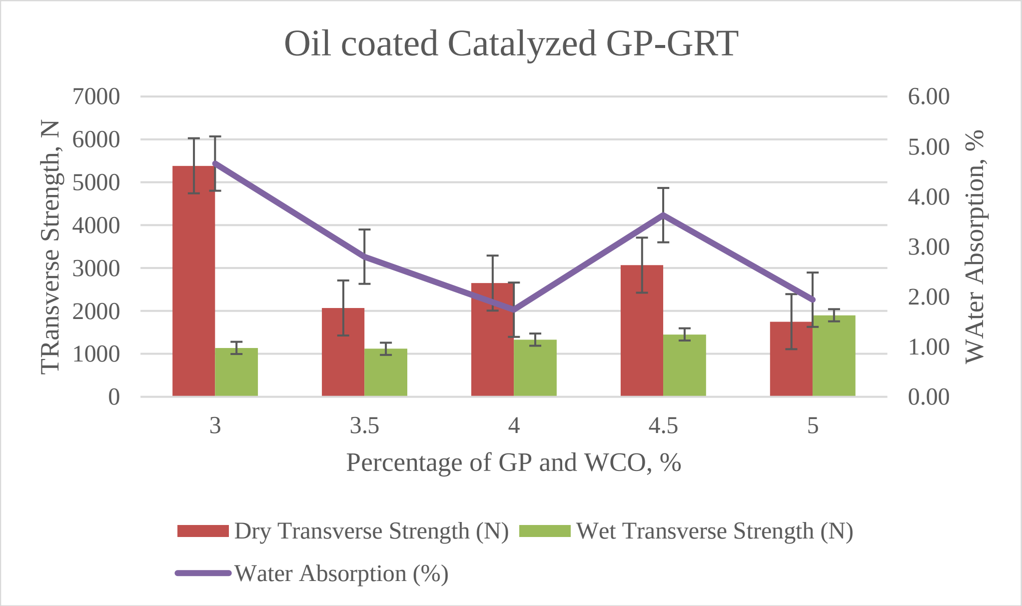


Figure 4.11: Strength and Water Absorption of Oil Coated Catalyzed Composition GP-GRT

4.2.4 Effect of Using Different Particle Sizes of Pulverized Fly Ash in the Production of Glycerine Pitch Green Roofing Tiles (GP- GRT)

From the previous experiment there are two different fly ash with different particle sizes of 16.256 µm (FA1) and 115.014 µm (FA2). The composition of materials that were used to compare the difference between both sizes are 65% of sand aggregate, 35% of filler, each 3.5% of glycerine pitch and waste cooking oil. The prototypes are triplicated and the results are shown in Tables 4.12, 4.13 and Figure 4.12.

It can be clearly seen that by comparing the dry strength of smaller sizes of pulverized fly ash with larger size of pulverized fly ash, small particle size pulverized fly ash had shown a relatively higher dry strength of 1971 ± 216 N which is 141% of the strength of bigger size of pulverized fly ash. The dry strength that uses FA1 had contributed to almost 1.5 times higher of the one using FA2. As for the comparison of wet strength, the roofing tiles using FA2 had failed to fulfil the minimum requirement of 1001 N and had exceeded the maximum water absorption percentage of 6%, whereas FA1 has a fairly better results as both the requirements of wet strength and water absorption percentage are able to be achieved. The wet strength of roofing tiles that used FA1 was 1053 ± 203 N with a water absorption percentage of 6%.

Table 4.12: Results between Two Different Sizes of Pulverized Fly Ash

Fly Ash	GP: WCO	Transverse Strength (N)		Water Absorption (%)
		Dry	Wet	
FA1	3.5 : 3.5	1971.03 ± 125	1053.25 ± 117	5.53 ± 1.06
FA2	3.5 : 3.5	1394.86 ± 34	462.71 ± 85	12.78 ± 1.99

Table 4.13: Flexural Strength between Two Different Sizes of Pulverized Fly Ash

Fly Ash	GP: WCO	Transverse Strength (MPa)	
		Dry	Wet
FA1	3.5 : 3.5	4.47 ± 0.28	2.38 ± 0.27
FA2	3.5 : 3.5	3.16 ± 0.08	1.05 ± 0.19

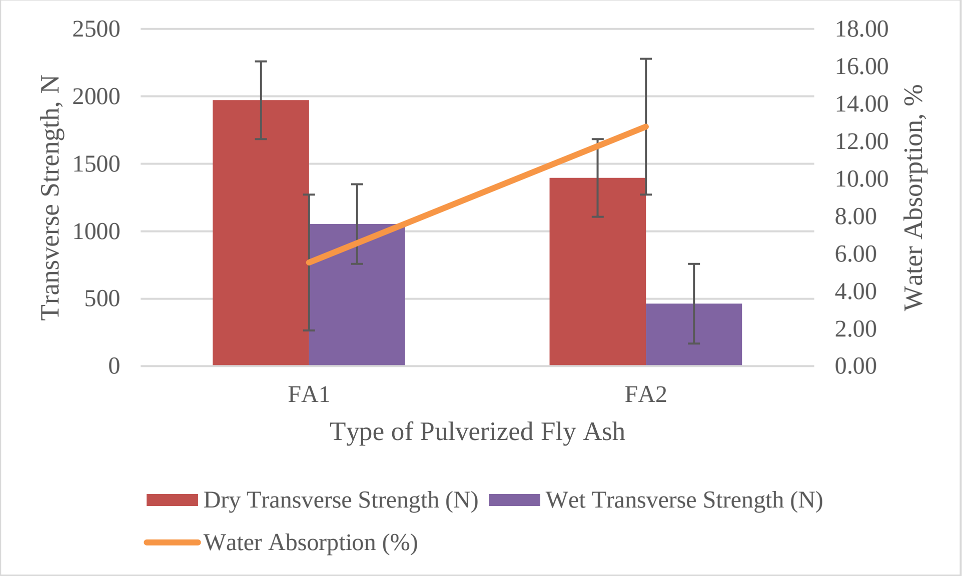


Figure 4.12: Results between Different Sizes of Fly Ash

4.3 Discussion of Mechanism

After going through the above mentioned experiments, the possible mechanism involves in the hardening process is as follows:

4.3.1 Formation of Propylene Glycol

The possible explanation for the strength contribution of glycerine pitch as a binder in the green roofing tile may be due the formation of a compound called propylene glycol which is also known as 1, 2-propanediol. Propylene glycol has two alcohol groups (-OH). It is normally used as an emulsifier that helps in the mixing of immiscible solutions for instance in this case it is glycerine pitch and waste cooking oil (Chuang, 2006). With the mixing of these two products the waste cooking oil can help to cover a thin layer outside and help in the reduction of water absorption and thus preventing to have low wet transverse strength. Moreover, the propylene glycol is a type of monomer for the production of polyester which is able to help in the contribution of strength for the green roofing tiles (Aziati and Sakinah, n.d.).

Studies had been carried out through experiments on using glycerol on obtaining propylene glycol. This might be possible in this research, as glycerol are present in glycerine pitch with a percentage between 55-65% and more will be released during the heat curing process of the roofing tiles as the bonds of triglyceride will be broken. The synthesis of propylene glycol involves two steps: dehydration to form an intermediate product called acetol from glycerol and hydrogenation of the acetol to the final product which is propylene glycol. The figure shown below is the reaction of glycerol to propylene glycol.

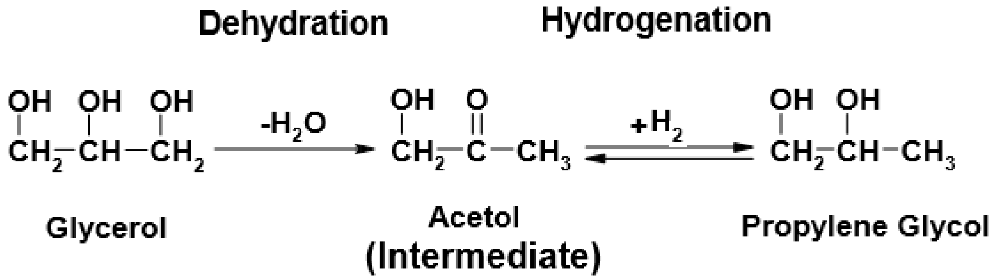


Figure 4.13: Chemical reaction of glycerol to propylene glycol (Chuang, 2006).

The requirement for the hydrogenation to take place requires the presence of hydrogen atom. Although there were no hydrogen added into the mixture throughout the experiment, the hydrogen contributor in this research was predicted to be dodecanedioic acid as it is a di-acid where initially plan to allow the reaction between the hydrogen ion with the alcohol group -OH, so that reaction of the acid and alcohol to form ester in order to stop the hygroscopic effect of glycerine pitch. This addition of chemical has gain a chance for the strengthening of the roofing tile as there might be a possibility of the formation of propylene glycerol.

4.3.2 Absorption Prevention

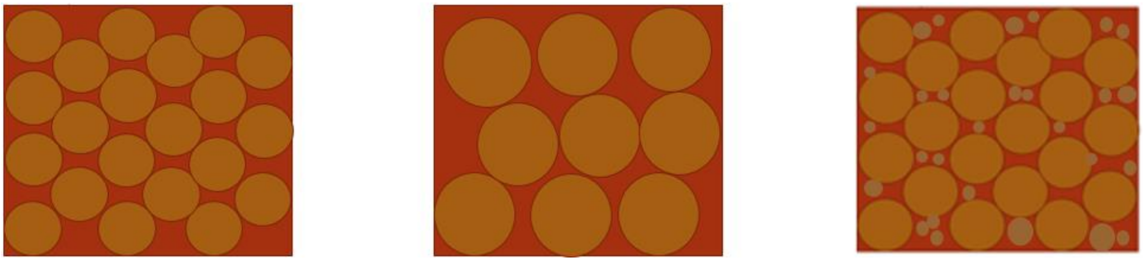
One of the main challenges throughout this study was the hygroscopic effect of glycerine pitch, whereby this effect tends to allow water to be absorbed into the green roofing tiles which will then affect its wet strength and increase the water absorption. This problem can be solved by applying a layer of waste cooking oil on the outer part of the green roofing tiles. Oil was applied after the first four hours of curing, this is because after four hours the shape of the roofing tile was fixed.

The mechanism behind the coating process was that it had to be taken place when it is at high temperature. This was due of the expansion of particles within the roofing tiles when it is hot. The pores were opened up and allowing the flow of the oil to fill up the pores to form coating layer. After the coating process, the green roofing tiles were then sent back for the remaining 20 hours of heat curing. This not only ensure that the void were covered up by the oil but also ensure that the roofing tiles are not over-cured. The oil coating process serves as a protective layer to prevent the penetration of water. It is able to achieve a lotus effect at the surface of the roofing tile, also to fill up the remaining voids to order to achieve a higher strength when the pores are filled up. There would be a good interlocking between the particles and the binding effect would be greater and thus providing greater strength.

4.3.3 Size of Filler

Another possible mechanism that was able to enhance the strength was the size of the filler. Throughout the study, two different sizes of filler were used and tested. It can be seen that the smaller particle size had relatively higher strength compared with the one with the bigger size. This might mainly due to the arrangement of the particle within the mixture. An illustration is shown in Figures 4.10 (a) and (b), it was assumed that the particles were all in circular shape. It can be seen that the voids in the smaller particle sizes were relatively smaller compared to the larger one, this is because the arrangement of the large particle size was limited as for the one with the smaller particle size, they have the ability to be nicely packed together making them well arranged and provide higher strength.

Furthermore, by having bigger voids means higher chances of allowing the intrusion of water into the roofing tiles. And which had been explained above, the higher the water penetration, the lower the wet strength of the roofing tile. However, although the small particle size has greater strength, it can be still improved by having a larger range of size distribution of the fly ash. This is because by having different sizes of particles tend to help in filling up the voids in between, for instance the void between the small particles can be filled up by even smaller ones which can help to have better and more secure arrangement between the particle which then enhances both the dry and wet strength as shown in Figure 4.10 (c)



(a) (b) (c)

Figure 4.14: Illustration of particle size within the roofing tile mixture (a) smaller particle size (b) larger particle size (c) a range of different particle size

4.4 Life Cycle Assessment

Life cycle assessment (LCA) is an analysis known as "cradle to grave analysis" that is used to evaluate the total possible environmental impacts of a product throughout its entire product life from the extraction of raw materials to manufacturing and purchasing by consumers then its product life until its end life and its disposal. It is used to assist in environmental management in sustainable development (Jensen, et al., 1997). This includes the determination the rate of carbon emission and total energy usage of different products for instance in this project is the green roofing tiles so that the embodied energy (EE) and embodied carbon (EC) of glycerine pitch- green roofing tile (GP-GRT) can be compared with conventional roofing tiles and identify the environmental suitability of GP-GRT.

4.4.1 Life Cycle Assessment of Glycerine Pitch- Green Roofing Tile (GP-GRT)

For the life cycle assessment the embodied carbon (EC) and embodied energy (EE) need to be considered. EC is defined as the total carbon footprint of the material from its raw materials extraction to its end of life. Therefore there are three processes for EC to identify the total carbon emission of GP-GRT which are "cradle to gate", "cradle to site” and “cradle to grave”. Cradle to gate means the processes starting from the extraction of raw materials, transporting, refining and processing until the materials which are suitable to be transported out of the factory. As for cradle to site means the transportation of the material to the site to be used. Lastly, cradle to grave means the usage and maintenance of the product until end of its life. EE is defined as the total energy required to produce the material.

The embodied carbon and embodied energy of GP-GRT are 0.1439 kg CO_2/kg and 0.73 MJ/kg which are extremely low compared with the conventional roofing tiles. This is due to the utilization of waste materials during the production of the roofing tiles, the embodied carbon of waste materials will always be lower when it is compared with crude or original material. Waste cooking oil is being one of the waste material used has shown no carbon dioxide released during its manufacturing process (0.00 kg CO_2/kg). Moreover, the embodied energy found from waste cooking oil is 2.00 MJ/kg. As for fly ash which is being a by-product produced through the burning of coal at high temperature for the generation of electricity, the total embodied carbon is 0.004 kg CO_2 per equivalent. As glycerine pitch is a waste produced through the extraction of sweet water and it is being a negative cost waste, its EC and EE are relatively low and therefore can be neglected throughout the calculation process. The transportation distance for all calculations is based on assumption. The total mass per roofing tile sample is 3kg.

The embodied energy is compared with the conventional roofing tiles and the results are shown in Table 4.16. It can be seen that there are 71.96%, 87.83 % and 93.92 % lower when it is compared with tiles that are made by concrete, clay and ceramic tiles respectively in terms of embodied energy. It can be seen that the EE and EC obtained are relatively low which means that GP-GRT is able to be an alternative binder in terms of the environmental aspects.

Table 4.14: Embodied Carbon of GP-GRT

Cradle to Gate – Materials Extraction and Manufacturing					
Materials Extraction Process					
Material	Quantity	Emission Factor, kg CO_2/eq	Estimated Transportation distance, km	Transport Emission, kg CO_2/km	Total Emission
Glycerine Pitch	0.135	0.00	100	0.0001	0.01
Waste cooking oil	0.135	0.004	100	0.0001	0.01
Fly Ash	0.954	0.00	60	0.0001	0.0098
Sand	1.773	0.00	60	0.0001	0.006
Manufacturing Process					
Operation	Curing time, hour	Electricity Usage, kWh		Emission Factor, kg CO_2/eq	Total Emission
Heat Curing	24	0.533		0.63	0.336
Mixing	0.5	0.008		0.63	0.005
Cradle to Site - Distribution of Products					
Material	Estimated transportation distance, km			Transport Emission, kg CO_2/km	Total Emission
Tile	500			0.0001	0.05
Cradle to Grave- End of Life Management					
Material	Estimated Transport Distance, km		Transport Emission, kg CO_2/km		Total Emission
Tile	50		0.0001		0.005
Total Carbon Emission per Tile, kg CO_2					0.4318
Carbon `Embodied, kg CO_2/kg					0.1439

* Emission factor were obtained from Ecoinvent 3.3 and ICE Ver. 1.6a

Table 4.15: Embodied Energy of GP-GRT

Materials	**Embodied Energy, MJ/kg**	***Material Required per tile, kg**	**Total embodied energy per tile, MJ**
Waste Cooking Oil	2.00	0.135	0.27
Glycerine Pitch		0.135	
Sand	0.20	1.773	0.35
Fly Ash	0.12	0.954	0.11
Total Emission per tile, MJ			0.73
Embodied Energy, MJ/kg			0.243

*** Humayun, et al., 2017**

Table 4.16: Comparative Analysis of Embodied Energy

Sample Number	**Tile**	**Total embodied energy, MJ**
1	Concrete	2.70
2	Clay	6.00
3	Ceramic	12.00
4	GP-Green	0.243

4.5 Economic Evaluation

Economic evaluation is also an important step that needs to be considered as it also serves as a criteria on becoming a feasible green roofing tile. The total costing per tile is calculated as below from Table 4.17. The price rate for glycerine pitch is RM 0.00, as it is a negative cost waste, which it has zero value.

Table 4.17: Economic Evaluation of GP-GRT

Glycerine Pitch- Green Roofing Tile (GP-GRT)				
Description	**Rate (RM)**	**Input power (kW)**	**Amount used(kg)/ Time used (hr)**	**Rate per Tile (RM)**
Glycerine pitch	0/ metric ton	N/A	0.01812	0.00
Fly ash	80/ metric ton	N/A	0.1268	0.01
Sand	40/ metric ton	N/A	0.2536	0.01
Waste cooking oil	400/ metric ton	N/A	0.018	0.01
Sulphuric acid	500/ metric ton	N/A	0.0008	0.0004
Dodecanedioic acid	1120/ metric ton	N/A	0.0008	0.0009
Oven	0.37/kWh	1.5	24	0.37
Mixer	0.37/kWh	0.5	0.5	0.03
Compactor	0.37/kWh	0.8	0.2	0.06
Total cost per tile				RM 0.49

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Throughout this study it is proven that glycerine pitch which is being a schedule waste is able to be used as a binder in the production of green roofing tiles. The maximum dry strength of the roofing tiles made throughout this study can go up to 5385.40 N for transverse strength which is 403% higher than the minimum requirement set by the ASTM standards. Not only that, the highest wet strength achieved is 1901.30 N and is approximately 190% higher than the minimum requirement of wet strength. In the end, the green roofing tiles has succeeded in achieve all three requirements according to the ASTM C1167-03, C1492-03 and C1167-11 standards after they had undergone a series of strength, water absorption and permeability tests.

Although glycerine pitch has a natural hygroscopic effect that tends to weaken the wet strength of the roofing tiles and increase the water absorption, it was able to be solved through another alternative which is through the addition of waste cooking oil in in the production of the green roofing tiles. The addition of waste cooking oil not only helps to act as a protective layer in covering the fly ash and glycerine pitch, it also helps in contributing to more strength of the roofing tiles. As it is explained previously, waste cooking oil tends to block away the water from infiltrating into the roofing tiles. During heat curing process, oxy-polymerization occurs which leads to the increase of its viscosity that helps in binding of the materials. Poly-esterification would happen between the di-acids and diols that are present inside the waste cooking oil which had led to the formation of a solid polyester.

Furthermore, it is also an important aspect in identifying the particle size distribution of the fly ash as the size affects the arrangement of the particles within the roofing tiles. As explained in Chapter 4, having large particle sizes tends to achieve a well-arranged sequence but it tends to create larger voids between the particles that enables and gives a higher chances for water to infiltrate into the roofing tiles that have led to the decreasing of wet strength and increasing of the water absorption. As for particles size that are smaller, it is able to fill up more space and they were able to be more nicely compacted with each other, which will then prevent the chances of water getting into the roofing tiles. The best way of having high strength and low water absorption, a vast range of particle sizes of fly ash should be used so that different sizes are able to have better interlocking within each other and the smaller sizes are able to fill up any possible voids present between the particles. With that, it is able to decrease the porosity and increase the density of the roofing which made it more durable and safe.

As glycerine pitch is a negative cost waste whereby its generators require to pay a certain amount of money for special waste handlers in order to dispose the waste. Throughout Malaysia the only organization that is able to handle glycerine pitch is Kualiti Alam. Even though several studies have been carried out on recovery of glycerine pitch for glycerol, but the production and manufacturing cost were too high which makes it impractical as a long term solution. Therefore, having it to be used as a binder in the roofing tiles production tends to be the most suitable and novel way so that it is able to reduce the waste generation and disposal cost. Also, this step helps in adding value to glycerine pitch instead of being a negative cost waste. In terms of conventional roofing tiles, having glycerine pitch in the production of roofing tiles has a lower embodied carbon (EC) and embodied energy (EE) as it only requires a day of heat curing at a lower temperature comparing it with the conventional roofing tiles.

This is not only helps in reducing the production cost of roofing tiles, but also helps in easing the carbon dioxide emissions which at the end of the day helps in reducing or easing the condition of the global warming. In a nutshell, by having glycerine pitch as a binder in the production of green roofing tiles is able to reduce waste production, improve and save the environment and also to safeguard the humans and the wildlife. Throughout this project, all of the objectives are able to be achieved but further improvements are still required to further enhance the strength of the green roofing tiles.

5.2 Recommendations

Although the green roofing tiles are able to achieve the minimum requirements of the ASTM standards, there is always more rooms for improvements. Further investigations are required for the possible leachates are released from the roofing tiles when it is exposed to water. It is important to determine the composition that are contained within the leachate so that it can be fully ensured that the roofing tiles are safe and would not bring harm to both the environment and the humans. Further enhancement on the best composition of glycerine used in the roofing tiles is still required as the roofing tile that had achieved the strength of 5385 N still has a relatively low wet strength although it has passed the minimum wet strength requirement. The next milestone is to achieve a strength and water absorption that is able to fulfil the Grade 1 standard in the ASTM to become high profile roofing tile.

As mentioned throughout the study, the utilization of waste cooking oil is well needed in preventing the water penetration in the roofing tiles, the coating method still needs improvement so that the waste cooking oil can be fully utilized for its purpose on stopping the penetration of water. The roofing tiles were heated for 4 hours for fixing its shape prior to the spraying or coating of waste cooking oil and further heat cured for 20 hours after the coating process. It is suggested to determine the best temperature for the coating of the cooking oil so that the oil is able to fill up all of the pores that are present within the roofing tiles. In addition for the coating procedure, further investigation is required for the number of oil coating layers required in order to achieve the best coating condition of the roofing tiles. It can also be observed that whether the number of layers of oil coat will affect the strength of the roofing tiles and the reason behind the reaction. Last recommendation is to further investigate the mechanism behind the reaction of the glycerine pitch that had contributed to the strength of the green roofing tile.

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