RHEOLOGICAL AND STRUCTURAL CHARACTERIZATION OF EMULSIFIED MODIFICATION BITUMEN SYNTHESIZED FROM INDUSTRIAL WASTE

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Report submitted in fulfilment of the requirements for Fundamental Research Grant Scheme (FRGS)

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FEBRUARY 2020

ACKNOWLEDGEMENT

The authors wish to express their gratitude and appreciation for the financial support from the Ministry of Higher Education (MOHE), Malaysia for the Fundamental Research Grant Scheme (FRGS KPT – RDU160129, Reference Number: FRGS/1/2016/TK02/UMP/03/2 entitled Rheological and Structural Characterization of Emulsified Modification Bitumen Synthesized from Industrial Wastes) and the Universiti Malaysia Pahang for the Internal Grant (RDU160324). The support from the Faculty of Chemical and Process Engineering Technology and University Malaysia Pahang, Malaysia are also acknowledged.

ABSTRACT

The cooler surface temperature than surrounding air may result in condensation which will propagate the growth of mould and fungi. This problem also occurs in the public health sector such as in the operation theatre of a hospital. The operation theatre has to maintain the temperature lower than the ambient condition which may result in condensation and lead to fungi problems. The aim of this study is to eradicate the fungi problems through coating and insulation by formulating Emulsified Modified Bitumen (EMB) using three types of emulsifier (anionic, cationic, and non-ionic). The industrial grade bitumen (60/70) will be modified with recycle used oil and mix with three different types of emulsifier producing three different formulated (EMB A, EMB B, and EMB C). In this research project, industrial waste such as recycle used oil was being used as other alternative to reduce the usage of raw bitumen in the formulation of EMB and also to reduce the excessive environmental issue in Malaysia. EMB A is using the anionic emulsifier, EMB B is using cationic emulsifier and EMB C is using non-ionic emulsifier. The formulated EMB samples being analysed for their characterization and performance test on a dry wall substrate. From the analysis, EMB B shows the best performance among all three formulated EMB with the best characterization in terms of viscosity, rheological behaviour and flash point and also resulting in the fastest drying rate at 8 hours and good adhesiveness properties with no flaking occurs except for the emulsion stability, EMB A showing the best stability performance of only 1.69% water separated from the original volume of water. It can be concluded that in terms of characterization and performance, cationic emulsifier (EMB B) is the most suitable for EMB formulations for coating purpose meanwhile anionic emulsifier (EMB A) will contribute to the stability of emulsion. %. The accelerated, natural and cooling ageing period are 296days, 1107 days and 893days. The total heat transfer (q) at temperature of 60°C, 45°C, 30°C and 27°C are 1.14W, 0.79W, 0.70W and 0.65W. It can be concluded that the ageing period and insulation effect are directly proportional to the bitumen composition.

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CHAPTER 1

INTRODUCTION

1.1 Research Background

Emulsified Bitumen (EB) is a mixture of water and bitumen. Ironically, water and bitumen cannot be mixed as bitumen is an oil based product from the fractional distillation process of crude oil. So, the addition of emulsifier into the water facilitates the breaking of bitumen into smaller particles and allowing the dispersion of bitumen in the liquid suspension (Arab, D., Kantzas, A., & Bryant, S. L., 2018). Therefore, EB is a combination of water, emulsifier and bitumen. In the meantime, the main raw materials for production of EB is bitumen itself. However, most of the EB available in the market are using the industrial aggregate of bitumen as their source of raw material whereby the production of EB by using modified bitumen is still minute. In the meantime, the research on the development of modified bitumen from waste as their source of raw materials is still limited. Thus, the needs for the production of Emulsified Modification Bitumen (EMB) from waste as an alternative to the current products is very important.

The major application of EMB is for coating and insulation on or in the interior surfaces of the wall. The liquid properties of the EMB will assist the coating and insulation process because it can be sprayed on the surface of the wall by using the airless spray painting equipment. This is a substantial role in the coating and insulation procedure as it can reduce the time needed for the process and maintaining the uniformity of the mixture on or in the surface of the wall. The uses of EMB in the coating and insulation of interior surface of the wall is vital due to facts that it is able to prevent the infiltration of moisture into the wall, reduce the heat losses to the surrounding during rainy seasons and assisting in the reduction of heat transfer to the building during hot weather. The presence of moisture content in the inner wall will become the catalyst for the growth of fungi and mould. Exposure to fungi and mould may result in allergy, asthma, hypersensitivity, respiratory infections, cognitive defects and difficulties in concentration (Haleem Khan & Mohan Karuppayil, 2012).

The existing research focusing on the performances and qualities of the EB on the road application, waterproofing and anticorrosion coating of oil and gas pipelines. This research is focusing on the performance and quality of emulsified modified bitumen as interior surface coating and insulation in the operation theatre.

1.2 Problem Statement

Nowadays, the substantial needs for quality indoor air environment is very important because populations spend a significant fraction of time within buildings. In operation theatre, medical healthcare, residences, day-care centres, retirement homes and other special environments, indoor air pollution affects population groups that are particularly vulnerable due to their health status or age. Indoor air pollution is recognized as important risk factors for human health around the globe. The sources of indoor air pollutions are the presence of biological agents with hundreds of species of bacteria and fungi or mould. The main factors that lead to the growth and spread of this biological agents are the existence of water, nutrients and appropriate temperature (Haleem Khan & Mohan Karuppayil, 2012).

Microorganisms are ubiquitous. Microbes propagate rapidly in the presence of water. In the meantime, most moisture enters a building in incoming air, including that infiltrating through the building envelope or that resulting from the occupant's activities. Besides, the dust and dirt normally present in most indoor environment provide sufficient nutrients to support extensive microbial growth. On top of that, by allowing the surface temperature to become cooler than the surrounding air may result in condensation. Thermal bridges (such as metal window frames), inadequate insulation and unplanned air pathways, or cold water plumbing and cool parts of air-conditioning units can result in surface temperatures below the dew point of the air and in dampness (Soldatova, Sansone, Stephens, & Shah, 2011). This condition will propagate the growth of fungi or mould in the building structure or on the interior surfaces of the wall. This statement is supported by the facts that, the inner wall materials used in operation theatre buildings like prefabricated gypsum board, highly favours the growth of Stachybotrys chartarum which is one of the fungi species (Haleem Khan & Mohan Karuppayil, 2012). According to this findings, the high airborne levels of fungal particulates in the operation theatre had caused hypersensitivity where patients exhibited pneumonia-like symptoms. Hypersensitivity pneumonitis or extrinsic allergic alveolitis is a granumalomatous lung disease due to exposure and sensitization to antigens inhaled. This disease can be acute or chronic. Exposure to buildings contaminated with fungi may develop hypersensitivity pneumonitis.

Thus, the application of Emulsified Modification Bitumen (EMB) as interior surface coating and insulation in the operation theatre will be the best alternative to eradicate the problems. The EMB that will be studied for this research is the formulation of EMB from industrial waste. The reason for this selection are to reduce the resources dependency and simultaneously leading to the reduction of industrial waste from the environment. This EMB is waterproof which can act as a barrier to dampness and moisture during the rainy season or leakage from the piping system. In term of thermal insulation, EMB can reduce the heat transfer from the surrounding environment to the buildings during hot weather and reducing the heat transfer rate from the building during rainy seasons. In addition, this EMB is developed from waste materials which are cheaper, efficient and more environmentally sustainable mixture. This EMB also shows low viscosity level performance compared to the conventional one. This significant properties is due to the fact that this product is mixed with water during the process. Hence, this EMB can be produced at lower temperature as low as 80ºC (Alex K. Apeagyei, Gordon D. Airey 2011). The production of EMB at lower temperature will help to decrease the consumption of energy during the process which subsequently will reduce the operational cost and the emission of greenhouse gases to the environment. Likewise, the mixing of emulsifier (surface active agent) into the water before adding to the modified bitumen help to blend the mixture well and maintain the product in a liquid form. This properties will make the coating and insulation process easier and faster as there is no need for further mixing with water before applying on or in the interior surface of the wall.

1.3 Research Objectives

1) To formulate bitumen emulsion from industrial waste.
2) To investigate the coating performances of bitumen emulsion on the surface of wall.
3) To study the effect of different emulsifier on the performances of bitumen emulsion

1.4 Scopes of Study

1) Characterization of raw material from industry and industrial wastes using physical and chemical test.
2) Determine the best ratio of Emulsified Modification Bitumen (EMB) from industrial waste.

3) Conducting rheological characterization of emulsified bitumen from industrial waste.
4) Simulate the actual condition of operation theatre by developing suitable models.
5) Analyse the effects of Emulsified Modification Bitumen (EMB) on heat transfer and thermal insulation of the wall.
6) Evaluate the effectiveness of Emulsified Modification Bitumen (EMB) in preventing infiltration of moisture into the wall.
7) Performance testing, characterization of formulated EMB for three different type of emulsifier (anionic, cationic and non-ionic)

CHAPTER 2

LITERATURE REVIEW

2.1 Bitumen

Approximately 5.6 trillion barrels of bitumen and heavy-oil resources are produced worldwide (Schamel et al., 2015). From that amount, the remaining bitumen reserve is approximately 360.99 billion barrels. This data is shown as in Table 2.1.

Table 2.1: Major world heavy-oil and bitumen estimated remaining recovery reserve (Alberta Energy Regulator, 2016).

Region	Heavy Oil (bbl)	Bitumen (bbl)	Total (bbl)	Heavy oil (%)	Bitumen (%)	Total (%)
Africa	7.2	43	50.2	1.5	11.91	5.97
Asia	29.6	42.8	72.4	6.17	11.86	8.61
Canada (Alberta)	2.71	165	167.71	0.565	45.71	19.94
Europe	4.9	0.2	5.1	1.02	0.055	0.606
Middle East	78.2	0	78.2	16.29	0	9.29
Russia	13.4	33.7	47.1	2.79	9.34	5.6
Venezuela	265.7	0.1	265.8	55.35	0.027	31.6
U.S.A Total	78.33	76.19	154.52	16.32	21.11	18.37
Alabama	0	6.36	6.36	0	1.76	0.756
Alaska	0.14	19	19.14	0.029	5.26	2.28
California	62.85	5.34	68.19	13.09	1.48	8.11
Texas	11.84	5.44	17.28	2.47	1.5	2.05
Utah	0.06	32.33	32.39	0.012	8.96	3.85
Other States	3.44	7.72	11.16	0.716	2.14	1.33
Grand Total	480.04	360.99	841.03	100	100	99.99

Despite of continues decline in the oil price, the world interest continued in bitumen. Bitumen is an oil based non-crystalline solid or viscous substance derived from petroleum that exists in the natural or as a by-product of refinery processes; has adhesive properties, and substantially soluble in carbon disulphide. It is a mixture of organic liquids that are highly viscous, black, sticky, and composed primarily of highly condensed polycyclic aromatic hydrocarbons. Similarly, bitumen is denser than water, with a minimum viscosity similar to honey or molasses, with a gas-free viscosity > 10,000 cP; and, in general, an API gravity <10° (Hein, 2017). Bitumen is obtained by removing the lighter fractions (such as liquid petroleum gas, petrol and diesel) by distillation of blends of heavy crude oil during the refining process (Ehinola, Felode, & Jonathan, 2012). The contents of the bitumen are hydrocarbons with small amounts of sulphur, nitrogen and oxygen and traces of metals like vanadium and nickel. The hydrocarbons may be described by a number of core structures consisting of polyaromatic structures containing different number of fused rings, saturated polycyclic structures also with different number of rings and combinations of these. All these core structures contain saturated hydrocarbon side chains of different chain length and different substitution pattern. The number of possible isomers is almost unlimited (Redelius & Soenen, 2015).

The size of the bitumen is determined by the cut point at the distillation of the crude oil. It is possible to estimate that the smallest size of the molecules is around 20 carbons and goes up to the largest size in the residue. Based on the latest findings it seems unlikely that there are any significant quantities of molecules larger than about 1500 g/mol (about 110 carbons). There are 5 major properties of bitumen. First, bitumen is elastic as it has the ability to return to a length close to its original length when one takes a thread of bitumen, stretches and elongates it. Secondly, bitumen is plastic. When temperature is increased, as well as when a load is applied to bitumen, the bitumen will flow, but will not return to its original position when the load is removed. Applying the loads means that a weight is put on the bitumen in order to subject it to stress. Next, Bitumen is also visco-elastic (Behzadfar & Hatzikiriakos, 2013), it can behave either viscous or elastic depending on the temperature or the load it is carrying. At high temperature, there is more flow or plastic behaviour of bitumen while the bitumen tends to be stiff and elastic at lower temperature and it tends to be a combination of the two forms at the intermediate temperature. Furthermore, bitumen also can age over time, due to external conditions. The bitumen molecules react with oxygen when it is exposed to the atmospheric conditions which results in a change of the structure and composition of the bitumen. This process is called oxidation that will cause the bitumen to become brittle and hard and to change colour from dark brown or black to grey. This change usually referred to as oxidative hardening or age hardening. The ageing process occurs more frequently during warmer climates or warm seasons. Finally, when it is exposed to ultraviolet (UV) rays, the bitumen will be evaporated and become harder (Liang, 2007).

2.2 Applications of Bitumen

Roadways were the largest application segment in 2015, estimated at USD 39.29 billion (Size & Summary, 2018). Road connectivity is the most crucial feature of any developed economy. This factor has resulted in market expansion on account of growing need for roads in emerging economies. The efficient transportation system in various countries including India, China, and the U.S. will stimulate product demand in the near future. Rising demand for paving applications across different regions of the world especially in Asia Pacific and the Middle East will promote product growth over the next eight years. Growing modern construction systems having waterproofed flat roofs will stimulate bitumen demand over the forecast period. Asia Pacific was the dominant market in 2015 and accounted for over 33.0% of the global volume and will show growth on account of rising construction industry growth in India, China, Thailand, and Vietnam (Size & Summary, 2018). Moreover, the presence of the major market players in the region including ExxonMobil, Shell Bitumen, and British Petroleum will augment industry expansion over the next eight years. Also, Asia Pacific will increase its bitumen consumption owing to the extensive road network in the region. North America bitumen market was valued over USD 19.00 billion in 2015 and is expected to witness significant expansion on account of the growing need for rebuilding existing assets such as bridges, highways, and buildings.

MEA is expected to show significant volume gains with CAGR of 2.0% from 2016 to 2024 as a result of growing construction sector primarily in UAE and Qatar coupled with rising infrastructure activities in the region (Size & Summary, 2018). Also, increasing government spending on construction will further propel industry growth in the near future. The global bitumen industry is characterized by integration through raw material supply to the manufacturing stages. Companies including Valero Energy Corporation, NuStar Energy, Suncor Energy, Athabasca Oil Corporation, Imperial Oil Limited, Syncrude are engaged in producing crude bitumen from oil sands. Companies including Sinopec, Indian Oil Corporation, Nippon Oil Corporation, ExxonMobil, Shell Bitumen, Petróleos Mexicanos (PEMEX) Nynas AB, Marathon Oil Corporation captively consume crude bitumen, refine it and then use it in various applications. Companies including Imperial Oil Limited, Valero Energy Corporation, Petróleos Mexicanos (PEMEX) and Shell are integrated across three stages of the value chain. Kraton Performance Polymers has developed a Highly Modified Asphalt Technology (HiMA) to cater to the ever-increasing demand from the paving and roofing sectors. This technology offers a broad range of modification options including styrene-isoprene-styrene, styrene-butadiene-styrene for high performance and superior quality (June, 2013). Kraton Performance Polymer and British Petroleum are engaged in various grades of cost effective waterproofing applications that provide with high water resistance and ability to withstand extreme temperatures. Cenovus Energy Inc. and Suncor Energy Inc. are some of the companies which have cut down their capital expenditures owing to the declining oil prices. The Canadian bitumen has a huge demand in the U.S. due to the presence of a vast number of processing units and refineries.

2.3 Grade / Standard of Bitumen

Penetration Grade Bitumen is a standard bitumen usually used as a Paving Grade Bitumen essential for road construction, civil construction and surface dressing. Penetration Grade Bitumen is classified into different groups and ranges according to the penetration test. This penetration test is conducted to measure the hardness of the bitumen by measuring the depth (in tenths of mm) to which a standard and loaded needle will vertically penetrate the bitumen sample in 5 seconds of time while maintaining the temperature at 25°C. The greater the number of penetration unit, the softer the bitumen. Penetration grading was developed to characterise the consistency of bitumen. The specification covered by this test are bitumen penetration at 25°C, flash point temperature, ductility at 25°C, solubility in trichloroethylene and thin film oven test(Chin, 2005). The result for Penetration test for two common Asian bitumen is shown in Table 2.2 below.

Table 2.2: Penetration test results of two typical Asian bitumen (Chin, 2005)

Properties	**80/100**		**60/70**	
	Min	**Max**	**Min**	**Max**
Penetration at 25°C, 0.1mm	80	100	60	70
Softening point, °C	45.0	52.0	45.0	52.0
Flash point, °C	276	-	276	-
Ductility at 25 °C, cm	100	-	100	-
Loss on heating (LOH), %wt	-	0.75	-	0.75
Penetration of residue, after LOH, % of original	70	-	70	-
Wax content, %wt	-	-	-	2.0

In correspondence to ASTM D946-09, there are 5 different class of Bitumen Penetration Grade Standard. The grades are classified as follows:

Table 2.3: Classification of Bitumen Penetration Grade Standard (Roberts et al, 1996)

Type of bitumen	Comments
Bitumen Penetration Grade 40-50	Hardest grade
Bitumen Penetration Grade 60-70	Typical grade used in Asia
Bitumen Penetration Grade 85-100	
Bitumen Penetration Grade 120-150	Medium grade
Bitumen Penetration Grade 200-300	Softest grade

2.4 Modified Bitumen

Modified Bitumen (MB) is bitumen with additives. Among all of the additives, polymer has been one of the most popular approaches. The polymer is incorporate in bitumen by mechanical mixing or chemical reaction. Generally, polymer modifiers can be divided into two categories which are elastomers and plastomers. The elastomers are natural and synthetic rubbers, styrene-butadiene-styrene, reclaimed crumb rubber modifiers harvested from scrap tires and the plastomers include low density polyethylene, ethylene-propylene-diene- monomer and ethyl vinyl acetate (Yaacob et al., 2013). This elastomeric polymers exhibit a low modulus elasticity which can give the polymer matrix to expand without failure about up to 10 times when it is stretched and will return to its original position once the load removed. While for plastomeric polymers, it exhibits the same physical properties as elastomeric but it will not return to its original position once the load removed (Roque et al, 2005). Furthermore, the polymers can respond in three ways; elastically, time- dependent elasticity and viscously (plastically). Besides that, these additives help in further enhancing the properties of bitumen such as better resistance to deformation and tear, increase adhesion between aggregates and binder and increase fatigue life. The limited oil resources to produce such good quality bitumen as well as the driving force to earning maximum economic benefits has made industries pay more attention on bitumen modified for the past 40 years (Zhu, 2014).

2.5 Emulsifier

Emulsifier is a chemical agent that helps to emulsify the bitumen in water in order to produce the emulsion form. The choice of the emulsifier is crucial in the formation of the emulsion to ensure it has the stability over time and also it sets when applied on a particular aggregate (Tadros, 2013). There are numerous natural compounds that act as emulsifier, but more commonly chemical compounds are synthesized to produce the desired characteristics such as amine class chemicals that are of a liquid or paste consistency not soluble in water. Furthermore, it can be group by the type of ion that it will yield during the emulsion process which are anionic, cationic, and nonionic. Also, emulsifier will functions in 4 ways which the first one is it will reduce the interfacial tension between bitumen and water. Secondly, it will determine whether the emulsion formed is W/O or O/W type. Emulsifier will also stabilise the emulsion by preventing coalescence of droplets. Flocculation and coalescence can result from settlement, shear, and boiling or freezing of the emulsion. Lastly, it dictates the performance characteristic of the emulsion such as adhesivity and setting rate. These emulsifying agents are similar to soap which allow the particles and water to form a uniform mixture (Yaacob et al., 2013).

The emulsifier molecule is having both hydrophilic (water-loving) and lipophilic (oil-loving) properties derived from renewable sources such as fats and vegetables oil. Upon emulsion, the ionic portion of the emulsifier will impart a charge to the bitumen droplets, and create a repulsive force when the droplets approach each other thus making the bitumen droplet and water is homogenously mix together as the emulsifier and bitumen is firmly attached. In a simpler word, the emulsifier will be act like this; the attraction of both positive and negative will act up so that the droplet will be deposited on the surface of the aggregate. Further, the emulsifier molecules will be oriented and adsorbed to bond them together and ultimately prevent them stripping from the surface of the aggregate. Both figure below illustrate the emulsifier molecule and how did it works in emulsion while table 2.4 emphasize on example of emulsifier that can be used for this purpose.

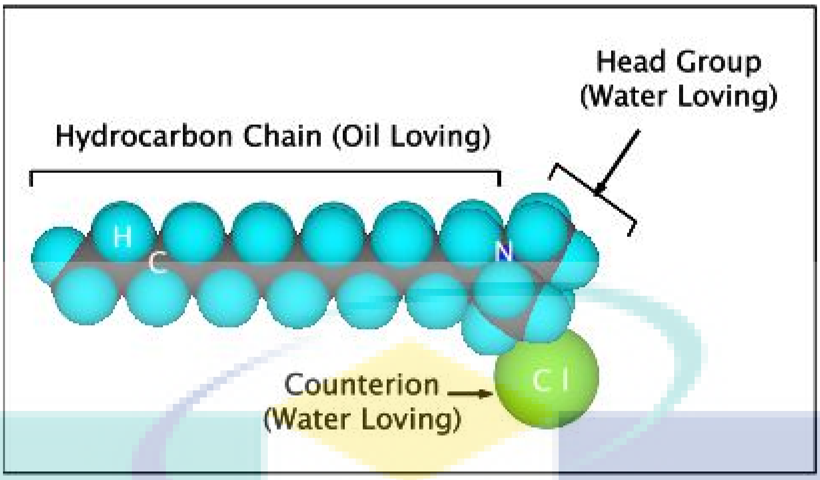


Figure 2.1: Cationic Emulsifier Molecule

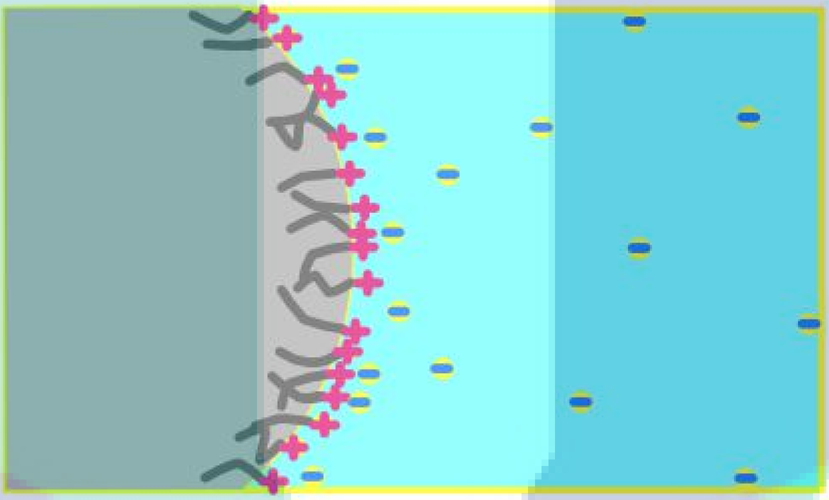


Figure 2.2: Charge Particle in Bitumen Emulsion

Table 2.4: Example of Emulsifier Use in Bitumen Emulsi

Anionic	Nonionic	Cationic
• Carboxylates • Sulphonates • Petroleum Sulphonates • Alkylbenzenesulphonates • Naphthalenesulphonates • Olefin Sulphonates • Alkyl Sulphates • Sulphates • Sulphated Natural Oils & Fats • Sulphated Esters • Sulphated Alkanolamides • Alkylphenols, Ethoxylated & Sulphated	• Ethoxylated Aliphatic Alcohol • Polyoxyethylene Surfactants • Carboxylic Esters • Polyethylene Glycol Esters • Anhydrosorbitol Ester • Glycol Esters Of Fatty Acids • Carboxylic Amides • Monoalkanolamine Condensates • Polyoxyethylene Fatty Acid Amides.	• Quaternary Ammonium Salts • Amines With Amide Linkages • Polyoxyethylene Alkyl & Alicyclic Amines • N,N,N',N' Tetrakis Substituted Ethylenediamines • Alkyl 1- Hydroxethyl 2-Imidazolines.

Anionic surfactant is when it is dissolved in water, negatively charged particles are created. In contrast, cationic surfactants ionise in water into the positively charged Non-ionic surfactants neither form cations nor anions in water. Their solubility in water is based on the binding of the hydrophilic parts to the water molecules (J. Beringer, 2011). The most effective emulsifiers are nonionic surfactants that can be used to emulsify O/W or W/O. In addition, they can stabilize the emulsion against flocculation and coalescence. Surfactant mixtures, for example, ionic and nonionic, or mixtures of nonionic surfactants can be more effective in emulsification and stabilization of the emulsion (Tadros, 2013).

2.6 Bitumen Emulsion

Bitumen emulsions are two-phase system consisting of bitumen, water one or more additives added to assist in formation and stabilisation and to modify the properties of emulsion. The bitumen is dispersed throughout the water phase in the form of discrete droplets, which are held in suspension by electrostatic charges stabilised by an emulsifier (Read, 2010). Bitumen commonly can be emulsified in two-ways; oil-in-water (O/W) emulsions are those in which the continuous phase is water and the dispersed (droplet) phase is a water-insoluble ‘oily’ liquid whereby water-in-oil (W/O) emulsions are those in which the continuous phase is oil and the dispersed phase is water (Shojaei et al., 2013). However, more complicated emulsions such as O/W/W are also possible to be emulsified.

For good quality of bitumen emulsion, the droplets are in range 1 to 30 μm in diameter with majority < 1μm and the largest volume or mass between 5 to 10 μm. In this emulsion, bitumen content normally in the region of 60 to 70% but it can also be as low as 40% or as high as 80% (Hebishy et al., 2017). The dispersion of emulsion droplet size is dependent on the interfacial tension between the bitumen and the aqueous phase (the lower the interfacial tension, the easier the bitumen dispersed) and on the energy used in dispersing the bitumen (Malakasiotis et al., 2010). This instability emulsion can leads to the requirement of higher energy input to form and increased interfacial area. However, the stability of this system can be improved by addition of appropriate agents such as surfactants to the system that will play their role to adsorb at the phase interface and lowering the interfacial tension. As a result, this energy can be reduced.

Surfactant and some polymer of steric stabiliser, also certain clay mineral can also kinetically stabilise an emulsion against re-coalescence. Generally surfactants are relatively more soluble in water rather than oil (Malakasiotis et al., 2010). Therefore, it tend to promote the formation of O/W compared to formation of W/O. Normally the surfactant that is used in bitumen emulsion production are cationic in nature such as alky diamines, amidoimidazolines and quaternary ammonium chlorides.

Bitumen emulsions are classified according to the sign of the charge on the droplets either it is cationic emulsion in which the droplets carry a positive charge, anionic emulsion that has negatively charged droplets or non-ionic emulsion that is neutral in charge. This system use a fundamental law of electricity in which the like charge repel, unlike charge attract(Xiao, 2010). As an illustration, in cationic emulsion, the positively charge of bitumen will migrate to the cathode as well as negatively charge particle in anionic emulsion will move to anode. There are also another one class of bitumen emulsion which is non-ionic emulsion. The bitumen particle in non-ionic emulsion will not move to either anode or cathode pole due to its neutral charge.

Table 2. 5: Difference between O/W and W/O emulsions(Poyato et al., 2013)

DIFFERENCES BETWEEN O/W AND W/O EMULSIONS	
Oil in water emulsion (O/W)	**Water in oil emulsion (W/O)**
Water is the dispersion medium and oil is the dispersed phase.	Oil is the dispersion medium and water is the dispersed phase.
They are non greasy and easily removable from the skin surface	They are greasy and not water washable.
They are used externally to provide cooling effect e.g. vanishing cream.	They are used externally to prevent evaporation of moisture from the surface of skin e.g. Cold cream
Water soluble drugs are more quickly released from O/W emulsions.	Oil soluble drugs are more quickly released from W/O emulsions.
They are preferred for formulations meant for internal use as bitter taste of oils can be masked.	They are preferred for formulations meant for external use like creams.
O/W emulsions give a positive conductivity test as water is the external phase which is good conductor.	W/O emulsions not giving a positive conductivity test as oil is the external phase which is a poor conductor of electricity.

The most important properties of bitumen emulsions are stability, viscosity (rheology), breaking point and adhesiveness. Emulsion is one of the examples of Non-Newtonian fluid hat has the shear thinning behaviour in which the viscosity value is actually depends on the shear stress applied. The properties also depend on the molecular weight and the structure, the temperature, as well as the concentration of additives and filler used (Wang et al., 2018). Normally for this type of complex fluid, it can be done by using the rheological test because the minimum number of function that are needed to relates stress with the strain rates are being characterize. For the stability of emulsions, it is depends on several factors which are types of bitumen emulsifier and its quantity, water evaporation rate, bitumen quantity, bitumen globules size and last one is the mechanical forces applied(Ronald & Luis, 2016).

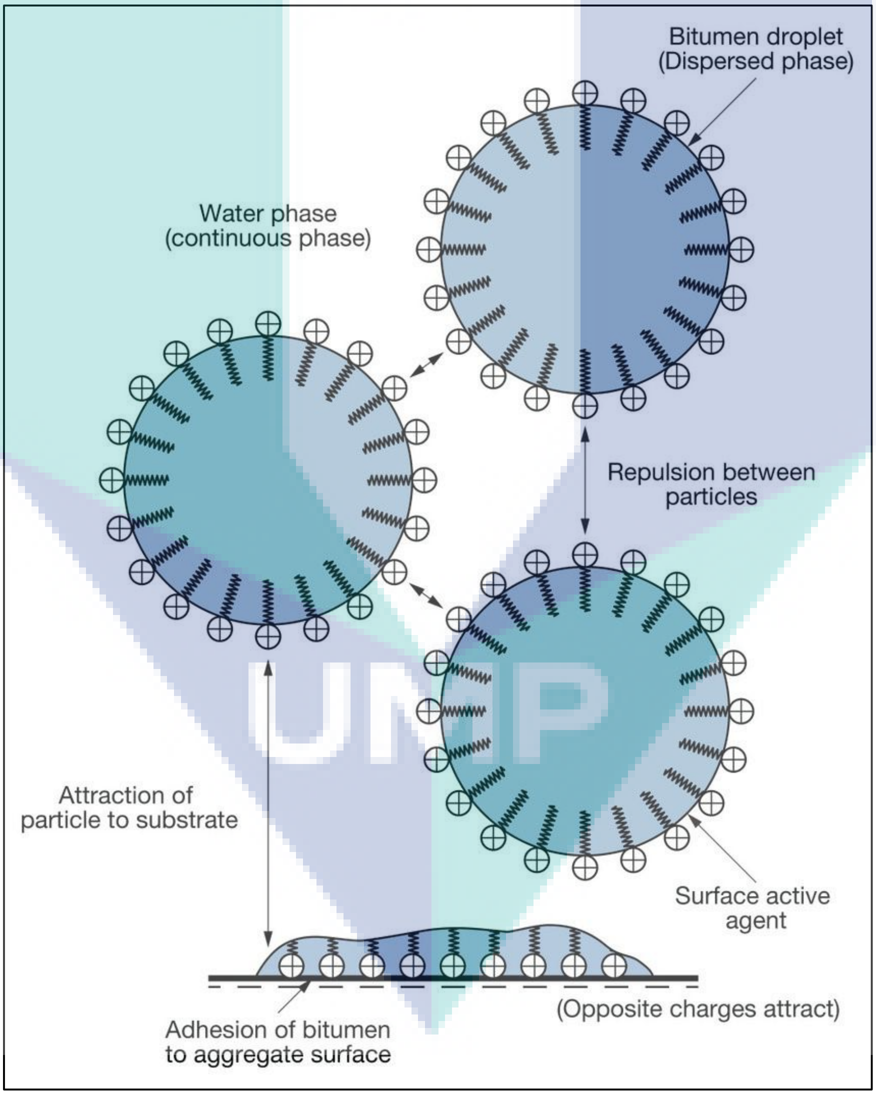


Figure 2. 3: Attraction of water and bitumen particle

2.7 Application of Bitumen Emulsion

Normally bitumen emulsions are used for road maintenance and repairs such as surface dressing application, wall insulator, and also as slurry seals. Bitumen emulsion also has been used for part of structural pavement for example like primary coating and cold mixes (Suda et al., 2017). It is applied to create a layer in order to retain its strength by preventing water infiltrate into the layer. Thus, the water absorption is reduced and at the same time the resistance to environmental aggression is improved (Borziak et al., 2018). Bitumen emulsion as a wall insulator will acts to reduce the flow of heat to the building during hot condition, while during cold climate, it will reduce the heat flow out of the building. Since the bitumen emulsion is in liquid form, it just need to be sprayed onto the surface of the wall.

Bitumen emulsion is an important building material, especially in highway pavement construction. It is a mixture of bitumen (asphalt), water and emulsifying agent, dispersed in tiny particles in an aqueous medium. It is an important material widely used in the pavement construction ever since the first introduction since the year 1900's. Bitumen emulsion can be manufactured in a batch plant or in-line plant. Being water based, it is capable to be applied under ambient temperature besides being more environmental friendly. Categorizing the bitumen emulsion is simple but the naming may differs slightly according to local specification. Continuous research also has end up in the modification of conventional bitumen emulsion using polymers to produce polymer modified bitumen (PMB) emulsion which decreases thermal susceptibility and permanent deformation (rutting). It has resulted in even wider application of bitumen emulsion as in microsurfacing, slurry seal and cape seal (Yaacob et al., 2013).

In the present study bitumen is replaced by bitumen emulsion for the construction of flexible pavement. The conventional method of road construction involves the burning of bitumen which produces toxic gases which degrades the environment. In colder region it is difficult to maintain the paving temperature of hot mix. To overcome these problems and conserve the energy bitumen emulsion is considered as good option. Likewise emulsion can be used in the areas having higher rate of rainfall where the hot mix plant is closed most of the time because of rain. Emulsified bitumen can be used during rainy season and colder regions(Suda et al., 2017). Road construction is not the only sphere of bitumen emulsion application. This material is also used for protection of concrete structures, for subsoil penetration, as well as for painting of metal parts. In industrial engineering, bitumen emulsions are used to make heat and electric insulation materials. Paper industry uses bitumen emulsion for production of waterproof cardboard, while agriculture uses it for quick sand strengthening, as well as for support of soil temperature and water balance. This wide application of bitumen emulsion became possible due to the capability to be used in cold state. Due to increase in energy costs and emission problems in hot mix asphalt usually used, it brought a great interest to the researchers to develop the warm mix technology for pavement constructions. Commonly known as warm mix asphalt (WMA), it is a typical method in the bituminous paving technology, which allows production and placement of bituminous mixes at lesser temperatures than that used for hot mix asphalt (HMA). The WMA involves an environmental friendly production process that utilises organic additives, chemical additives and water based technologies(Panda et al., 2017)

2.8 Emulsified Modification Bitumen (EMB) Formulation

Bitumen emulsion is an important building material, especially in highway pavement construction. It is a mixture of bitumen (asphalt), water and emulsifying agent, dispersed in tiny particles in an aqueous medium. It is an important material widely used in the pavement construction ever since the first introduction in the year 1900's (Yaacob et al., 2013). The emulsifier is an amphiphilic substance with a hydrophilic head and a lipophilic coil. It resides at the interface between the bitumen droplet and the water phase, acting as a stabilizer which reduces the interfacial tension between both phases and facilitates the emulsification process. In terms of the surface charge of the hydrophilic end, cationic emulsifiers are used, by far, in a larger scale than anionic or non-ionic emulsifiers in the bitumen emulsion industry (Yuliestyan et al., 2017). Due to the high viscosity of bitumen, bitumen can rarely be used in its raw form so several technique can be used to reduce the viscosity such as heating but heating generally will use a lot of energy consumption. So the other alternative to reduce the viscosity is by using additives. It also can improve the mechanical performance of modified emulsified bitumen in terms of tensile strength, resistance to permanent deformation and stiffness (Ayar, 2018).

According to the current literature review, most of the emulsified modified bitumen (EMB) available in the market is formulated by using the industrial grade bitumen where the crude oil as the main source of the raw materials. Generally, just a few products has been developed by using modified bitumen.

Table 2.6: Emulsifier and additives used for emulsified bitumen available in the market

Researchers	Type of Emulsion /Additives	Raw Material	Ratio	Findings	Application
Kwang Hoon Baek .,et al (2018)	**Anionic** Emulsifier: Triethylenetetramine (TETA) Acid: NaCl	Bitumen penetration modified with organic alkali	30-80 wt% Bitumen 0.5-90 wt% TETA 0.5-5.6 ml Acid brine	• Oil-in-water (o/w) emulsions created by TETA can be an effective bitumen carrier with a low viscosity and high bitumen content in the emulsion. It is possible to create o/w emulsions by adding a small amount of TETA to Athabasca bitumen and NaCl brine. • In comparison to the original bitumen, o/w emulsions were 4–5 orders of magnitude less viscous at 298 K, 2 to 3 orders of magnitude less viscous at 323 K, and 1 to 2 orders of magnitude less viscous at 353 K.	Petroleum application
(Yuliestyan et al., 2018)	**Cationic** Emulsifier: Kraft Lignin (KL) Tetra-ethylene-pentamine (TEPA) + Formaldehyde	The emulsifiers are used for producing cationic modified lignin (MKL). Bitumen penetration grade 60/40 modified with MKL	Droplet size distribution (DSD) of 60/40 bitumen emulsions 1.5% modified lignin emulsifier	• Asphalt mixes with maximum recycling and minimum impact to environment may be manufactured, between 80 and 130 °C, with a 100% reclaimed asphalt pavements (RAP) as aggregates and a bitumen emulsion stabilized by modified lignin. • The assessment of aqueous phase containing modified lignin suggests that MKL can play roles of emulsion stabilizer along with RAP coating agent.	Construction and building materials

(Cuadri et al., 2016)	**Cationic** Emulsifier: Recycle low density Polyethylene Alkyltrimethylene diamine Acid: HCl	Bitumen penetration grade 160/220 & 70/100 Modified with recycled polyethylene	4 wt% emulsifier in solution with pH 1 Polyethylene Modified Bitumen concentrations between 50 and 63 wt% and LPDE up to 5 wt%)	• Compared to non-emulsified binders, the finer and more homogeneous Recycled low density polyethylene (LDPER)polymer distribution found in the emulsion residues may improve bitumen performance at high service temperatures, increasing the resistance to rutting deformation in pavements	Road and civil construction
(Ziyani et al., 2016)	**Cationic** Emulsifier: Diamine –for rapid setting bitumen emulsions Acid: HCl Emulsifier: Polymamine-for medium setting emulsions Acid: HCl Quaternary ammonium emulsifier-for slow setting emulsions	Paraffinic bitumen grade 160/220 Modified with three type of different emulsions	4 doplets of each bitumen emulsions In 20 ml bitumen mixture.	• The aim of this work was to assess bitumen emulsion wetting on mineral substrates. • Wetting kinetics was followed and emulsion/substrate contact angles were measured, with varying different parameters such as the nature of the emulsifier, the nature and the roughness of the mineral. • • Regarding emulsions, polyamine and quaternary ammonium were found to have the highest surface tension • Concerning minerals, quartzite has the highest surface energy, and gneiss the lowest	Road materials and pavement
(Mallawarachchi et al., 2016)	**Cationic** Emulsifier: Chitosan	Bitumen with penetration value of 81 modified with	Chitosan to bitumen ratio at critical point was	• A stable emulsion could be formed without hindering its compliance to ASTM	Construction and building materials

	Additives: Calcium chloride	chitosan and $CaCl_2$	found to be 0.0028	standards for storage stability as all samples were within ±1% difference. • Comparison of the results of 5 day settlement and storage stability indicated a notable change in settling behaviour of the emulsion from a floating tendency (within 24 h) to a settling tendency (after 5 days) in the presence of Chitosan.	
(Zhang et al., 2018)	**Anionic** Emulsifier: 3, 5, 7-trimethyl decanolpolyoxyethylene ether carboxylate	Branched alcohol polyoxyethylene ether carboxylic acids were adjusted to the pH of 3 to ensure full conversion of alcohol ether carboxylic acids.	99% purity of branched alcohol polyoxyethylene ether	• Adsorption efficiency of branched A13EC5-H at the air/water interface is the fastest and the formation of micelles is the easiest. • From contact angle and dynamic surface tension measurements, the wetting ability is stronger, diffusion rate to the interface is faster and the time of surface tension • reaching equilibrium is shorter.	Colloids and surfactants
(Li et al., 2015)	**Non Ionic** Emulsifier: nano-ZnO Acid: Acetic acid	Bitumen penetration grade 60/70 modifed with nano-ZnO and acetic acid to adjust the pH value	- None	• FTIR shows that the nano-ZnO particles were graft polymerized through a chemical bonding, so that the nano-ZnO were uniformly dispersed in the bitumen matrix. • SEM analysis indicates that surface modification can improve the compatibility of nano- ZnO and bitumen significantly.	Construction and building materials

				• Compared with the unmodified nano-ZnO, the surface modified nano-ZnO substantially increased the softening point and viscosity of binder, as well as improved the ductility of bitumen.	
(Neto et al., 2019)	**Anionic** Emulsifier: Sodium chloride (NaCl)	Bitumen penetration modified with deionized water, formation water and NaCl	55 g L^{-1} NaCl Sat. Water 270 g L^{-1}	• It was observed that heavy oils generally form stable water-in-oil emulsions with a significant amount of emulsified water, up to 50% w/v. - The optical microscopy analysis shows that all emulsions prepared had a homogeneous appearance and average droplet diameter between 1 and 10 µm.	Road and civil construction
(Carrera et al., 2014)	**Cationic** Emulsifier: alkyltrimethylene diamine Acid: HCl	Bitumen penetration grade 160/220 modify with polypropylene glycol groups	1.4 wt% emulsifier in solution with pH 2 Different concentration from 14wt% of polymerbitumen	• Low experimental temperature below 100°C and presents enhanced resistance to permanent deformation at high temperatures if compared to standard non-modified bituminous emulsions	Road and civil construction
(Isa, 2017)	**Non-ionic** Polyethylenimine 80% ethoxylated solution from Sigma Aldrich	Bitumen grade 200/300 modify with HDPE, waste oil, waste sludge	39% bitumen 60% water 1% emulsifier	• HDPE 1 was chosen as the thickener for modified bitumen since it can tolerate with the formulation better than the other polymer and Base oil 3 was chosen for its high flash point and stable properties. -modified bitumen with 200/300 grade was chosen for the emulsification process.	Wall coating and insulation

2.9 Application of Emulsified Modification Bitumen (EMB)

Emulsions are extremely versatile material. It can be used as corrective and preventive maintenance depending on their aggregate (Yaacob et al., 2013). In Malaysia, majority of the EMB are used for surface dressing applications and wall insulator. It is applied to create a membrane between layers of wall in order to retain its strength by preventing water infiltrate into the layers. During cold climate, it will reduce the heat flow out of the building while on hot condition it will minimize the heat flow to the building. The EMB is in liquid form and will be sprayed onto the top surface of the wall. Moreover, liquid applied membrane is becoming a popular choice nowadays (Nafici, 2011). Figure 2.6 below shows the application of the EMB formulated which to be use as wall insulator.

Figure 2.4: The Application of EMB as Wall Insulator

2.10 Materials of Emulsified Modification Bitumen (EMB)

2.10.1 Bitumen

Bitumen is obtained by removing the lighter fractions (such as liquid petroleum gas, petrol and diesel) by distillation of blends of heavy crude oil during the refining process (Ehinola et al., 2012). The contents of the bitumen are hydrocarbons with small amounts of sulphur, nitrogen and oxygen and traces of metals like vanadium and nickel. The hydrocarbons may be described by a number of core structures consisting of polyaromatic structures containing different number of fused rings, saturated polycyclic structures also with different number of rings and combinations of these. All these core structures contain saturated hydrocarbon side chains of different chain length and different substitution pattern.

2.10.2 Crude Oil

Unrefined petroleum product that are composed of hydrocarbon deposits and other organic materials are known as crude oil. This crude oil later can be refined to turn it into usable products such as gasoline, asphalt and various forms of petrochemicals or petroleum distillates such as olefins include propylene and butadiene, and aromatics including toluene and xylene isomers. (Bergmann, 2013) The process to obtain the crude oil typically is by drilling.

This non-renewable resource that is generally called black gold has ranging viscosity and differ from yellow to black colour depends on the composition of hydrocarbon in it (Hughes, 2009). It also known that crude oil can exhibit regional trends in chemical composition which make it fall in the following groups:

- Paraffinic
- Naphthenic
- Aromatic

Paraffinic

Paraffinic is a group of hydrocarbon consisting of linear molecules. Crude oil from this group have high viscosity index stock since it containing a lot of wax starting at about C_{18}. Paraffinic also have good thermal and oxidative stability as well as good high temperature viscosity characteristics. General formula for paraffin is C_nH_{2n+2}

Napthenic

Naphthenic is a one type of organic compound that contain one or more saturated cyclic (ring) structures of carbon and hydrogen as a major portion of the molecule. This compound also known as naphthenes, cycloparaffins or hydrogenated benzenes. Napthenic crude oil are inexpensive and very available. It naturally low pour points and only have low viscosity index due to its containing a little of wax. However, naphthenic have poor thermal and oxidative stability.

Aromatics

Aromatic hydrocarbons are arranged in a symmetrical 6-carbon ring structure with single(C-C) and double(C=C) bonds alternating around the ring. It is unsaturated hydrocarbon but very stable and frequently behave as saturated hydrocarbon. The name ‘’aromatic’’ refers to the fact that the hydrocarbon are commonly fragrant compounds.

Like coal, the quality ranges are depending on the maturation of the crude itself. The younger crude shows the low quality of the crude oil. One of the easy way to know the quality of crude oil is by looking at the colour since the variations of oil colour can be dramatic (Bergmann, 2013). The best quality of oil can be a golden or amber in colour. As in Figure 2.1 below, is shows that “old deep’’ oil is the higher quality if crude oil.

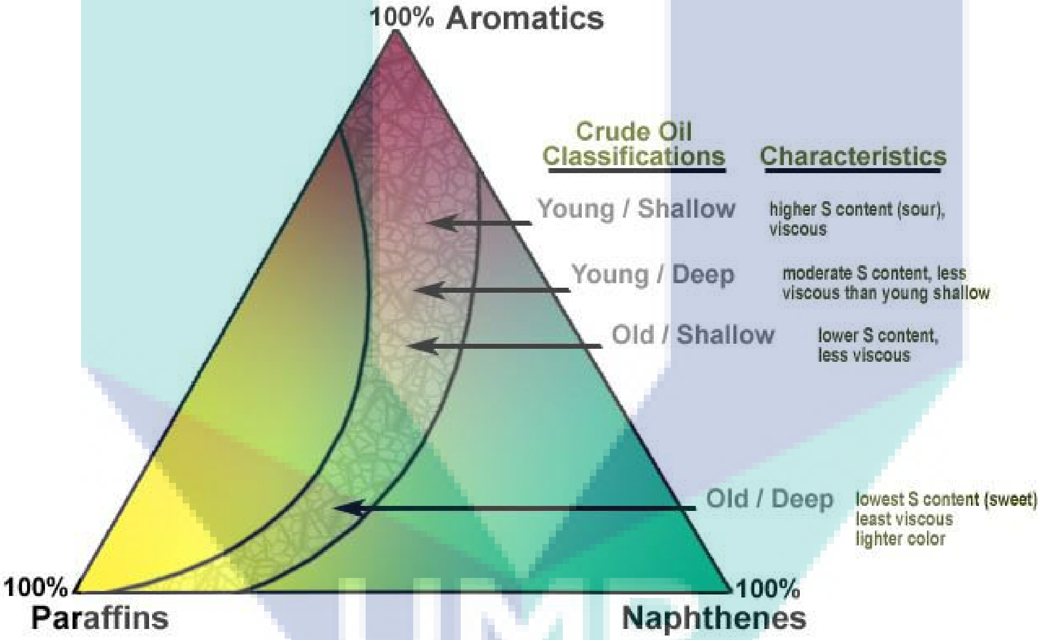


Figure 2.5: Ternary diagram of relative percentage of three components in crude oil. (Bergmann, 2013)

In this study, crude oil will act as base oil in order to mix the other materials.

2.10.3 Used Oil

Used oil is a waste oil which is derived from petroleum or synthetic oil that have been used before for lubricating, heating, corrosion protecting or other purposes but no longer meet the requirements of these applications due to the loss of original and presence of contaminants or impurities (Norhasmi et al, 2009). In Malaysia, there are 22 million vehicles contribute to this waste oil which leads to the environmental pollution as it is discarded into the landfill without any treatment (Hidayah et al, 2012). This used oil will act as base oil in order to mix the polyethylene. So by using it as the base oil, it will help in reduce of the recycling industry value.

2.10.4 Waste Sludge

Waste oily sludge is a mixture of oil, solids, and water deposited at the storage tank bottom. Oil storage tanks which include stationary storage tanks, tank cars, and ocean going tankers, barges, pipelines or other structures for storing or transporting crude oil or petroleum products accumulate large amounts of sludge over a period of time which made up of chemical or hydrocarbon deposits (Naggar, 2010) . Sludge is a combination of hydrocarbons, sediment, paraffin and water which can accelerate corrosion, reduce storage capacity and disrupt operations. It is actually the heavy ends that separate from the crude oil. A huge amount of oily sludge is generated from petroleum refineries during their storage operations and through on-going operations. This sludge contains a reasonable amount of oil (hydrocarbons). It could contain not only organic and inorganic matter, but also bacteria and viruses, oil and grease, nutrients such as nitrogen and phosphorus, heavy metals and organochlorine compounds (Hu, Li, & Zeng, 2013) (Ramaswamy, 2007). It is removed during tank cleaning operations where all these wastes are removed and dumped in a nearby pit. The typical composition of sludge is solids 10–12%, water 30–50% and oil 30–50% by weight (Ramaswamy et al, 2007). Table 2.7 describe the characteristic of fresh sludge from petroleum processing industry.

Table 2.7: Physico-Chemical Properties of Fresh Sludge from Petroleum Processing Industry

Properties	Unit	Values
Density at 293K	g/cm^3	958
Specific viscosity at 373K	-	3.8
Content of mechanical impurities	wt%	traces
Water content	wt%	0.6

Sulphur content	wt%	1.34
Flash point	K	468
Ash content	wt%	0.38
Fractional content: **Boiled till 623K**	wt%	8.2

2.10.5 High Density Polyethylene (HDPE)

Polyethylene is one of the types of polymer that already being used widely in bitumen to enhance its properties. It is derived mainly either from crude oil or through modifying natural gas such as methane, ethane and propane. In industry, it can be found as a plastic packaging including bottles. Besides, although plastic has become major issue that contribute to many environmental problem, Malaysian plastic industry is a promising industry as it is continue to accelerate in 2014 with a total turnover is RM20 billion, which RM12 billion were exported (Petronas, 2015). Moreover, bitumen in its nature itself is possess a plastic behaviour as when temperature is increased and a load is applied to bitumen, the bitumen will flow, but will not return to its original position once the load is removed so with the help of polyethylene, EMB tends to resist a permanent deformation at high temperature (Carrera et al., 2015).

2.10.6 Crump Rubber

Crumb rubber is a black colour in the form of powder. It can obtained from the truck tyres or automobile tyres because every year the vehicle tyres in the world that are discarded are about more than one billions (Razali et al., 2016). This crumb rubber can be produced by two methods which is grinding the tyres at ambient temperature that will produce the grain size of the crumb rubber from 5 mm to 0.5 mm. As it name, this mechanical grinding process will occur at or above the room temperature, 25˚C by rotating the blade and knives to separate of the fibre. This process then will comes out with the irregular shaped, tone particles with larges surface area products in order to promote interaction with the bitumen. The second method is grinding cryogenically cooled tyre rubber. This process will use liquid nitrogen to chill and freeze it until it become brittle before it is fractured by using the hammer mill into smooth particles (Presti, 2013). The crumb rubber have low surface area when it is obtained by cryogenic grinding than those produced by ambient temperature. However the most commonly method used is ambient grinding due to the most cost effective method of processing of end life tyres. Another methods that can be used as an addition techniques to the ambient grinding and cryogenic grinding processes is by wet grinding and hydro jet size reduction.

In wet grinding, usually water is used as a liquid medium where the tiny rubber particle is grinding into, for further size reduction to make it suitable to use as bitumen modifier. Same goes to the hydro jet size reduction, but this techniques used pressurised water around 55.000 psi in high speed array (Presti, 2013). By using the crumb rubber to formulate the bitumen emulsion, it tend to increase the strength and quality of bitumen emulsion and also provide a better adhesion with aggregate, become more flexible and more elastic. The increasing of physical properties of crumb rubber will be indicated by reduction in penetration and ductility, otherwise will increase the softening point (Lee, 2008).

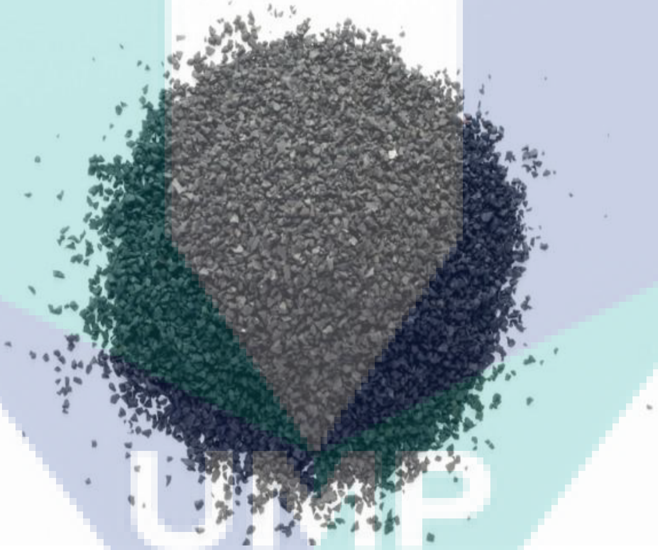


Figure *2.6*: Crumb rubber

2.10.7 Latex

As the one types of polymer, latex already being used extensively in bitumen emulsion to enhance its mechanical and physical properties in terms of cohesion, resistance to crack at low temperature and resistance to flow at high temperatures (Xia, 2017), (M.A.Shafii, 2011). Latex polymers can be cationic, anionic or non-ionic types, which depends on the charge of the particles. In water bitumen emulsion, latex will improves the strength and elasticity of the material. Latex polymer can be combined with water phase and are emulsified with bitumen directly during preparation of bitumen latex emulsion. This latex also can be used to modify bitumen directly or it can be post added into bitumen emulsion as an independently mixed emulsion. (Stasiukaitis, 2014). Besides road construction industry, it is used as waterproofing materials, protecting structures from water and its destructive effects because this “liquid rubber” is a unique waterproofing material based on bitumen emulsion with no solvent.

2.10.8 Polyethylenimine 80% Ethoxylated Solution

Ethoxylate solution is a non-ionic surfactant that have both lipophilic tails and polar head group. It is used widely as emulsifying agent due to its properties that are soluble in the water and can demonstrate a significant resistance during deformation.

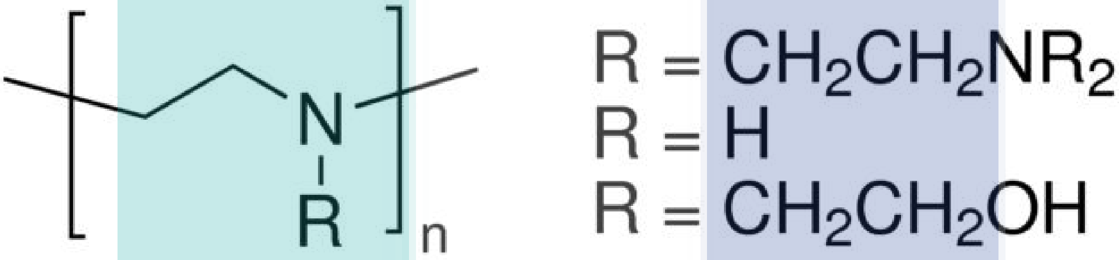


Figure 2.7: Structure of Polyethylenimine 80% Ethoxylated Solution

2.10.9 Abietic Acid

Abietic acid is an extraction product of tree rosin, a solid form of resin from pine, conifer and some other plants. This non-hazardous natural substances is belongs to the organic compound that are derived from four isoprene units (Yi-Qiu, 2007). Figure 2.8 shows the structure of abietic acid whereas table 2.8 shows the properties of abietic acid.

Table 2.8: Properties of Abietic acid

IUPAC name: Abieta-7,13-dien-18-oic acid Others name: Sylvc acidi	
Properties	
Molecular formula	$C_{20}H_{30}O_2$
Molar mass	302.46 g/mol

Density	1.06g/mL
Appearance	Yellow resinous powder, crystal or chunks. Colourless solid when pure.
Melting point	172-175˚C
Solubility in water	Insoluble
Solubility in other solvents	Very soluble in acetone, petroleum ether and ethanol

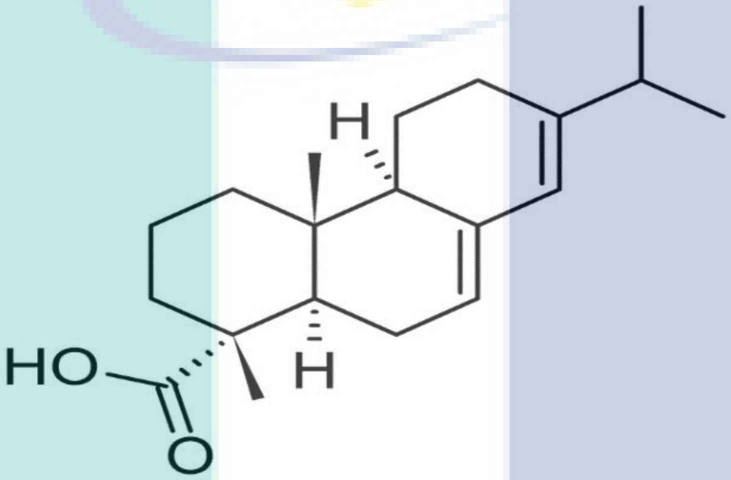


Figure 2.8: Structure of Abietic acid

2.10.10 Sodium Dodecylsulphate

Sodium Dodecylsulphate is an anionic surfactant. Also known as sodium lauryl sulfate (SDS or SLS), it is a synthetic organic compound that widely used in many cleaning and hygiene product. The sodium salt in sodium dodecysulphate is an organo sulphate class of organic. It consist of a 12-carbon tail that are attached to a sulphate group.

Table 2.9: Properties of Sodium Dodecylsulphate

IUPAC name: Sodium Dodecylsulphate Others name: Dodecyl Alcohol, Hydrogen Sulphate	
Properties	
Molecular formula	$NaC_{12}H_{25}SO_4$

Molar mass	288.372 g/mol
Density	1.01 g/mL
Appearance	White or cream coloured solid
Melting point	206˚C

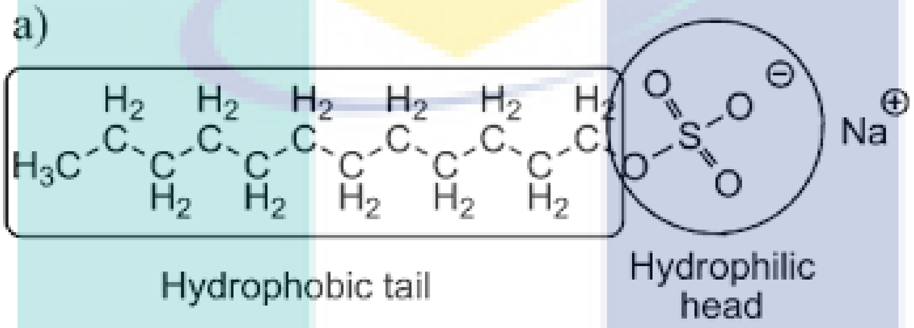


Figure 2.9: Structure of Sodium Dodecylsulphate

2.10.11 2-Bromostearic Acid

2-bromohexadecanoic acid is a bromo fatty acid that is hexadecanoic (palmitic) acid carrying a single bromo substituent at position 2. It has a role as a fatty acid oxidation inhibitor. It is a bromo fatty acid, a straight-chain fatty acid, a long-chain fatty acid and a 2-bromocarboxylic acid. It derives from a hexadecanoic acid.

Table 2. 10: Properties of 2-Bromostearic Acid (Source: Chemwatch)

IUPAC name: 2-Bromostearic Acid	
Properties	
Molecular formula	$C_{18}H_{35}BrO_2$
Molar mass	363.38 g/mol
Topological surface area	37.3 A^2
Chemical safety	Irritant
Odour	Odourless

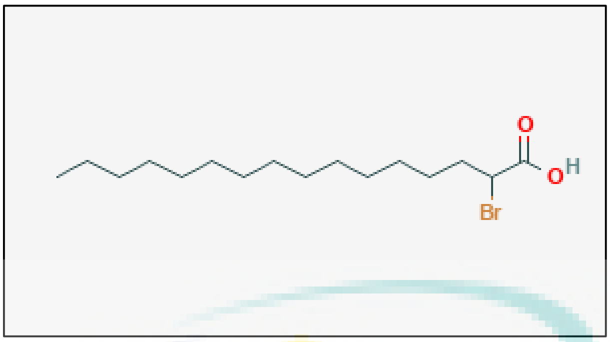


Figure 2.10: Chemical structure of 2-bromostearic acid

2.10.12 Didodecyldimethylammonium bromide

Dimethyldioctadecylammonium bromide is a double-chained quaternary ammonium surfactant that forms unilamellar vesicles (ULVs) in water. Among various preparation methods, the ‘‘hot-water” method offers a simple procedure to prepare DODAB cationic vesicles by simply dissolving the DODAB in hot water above 50 °C.

Table 2. 11: Properties of Didodecyldimethylammonium bromide

IUPAC name: Dimethyldioctadecylammonium bromide Other name: Distearyldimethylammonium bromide	
Properties	
Molecular formula	$C_{38}H_{80}BrN$
Molar mass	630.969 g/mol
Density	1.05 g/cm^3
Melting point	160° C
Solubility	Soluble in water, ethanol, methanol, acetonitrile, and acetone.
Appearance	White solid

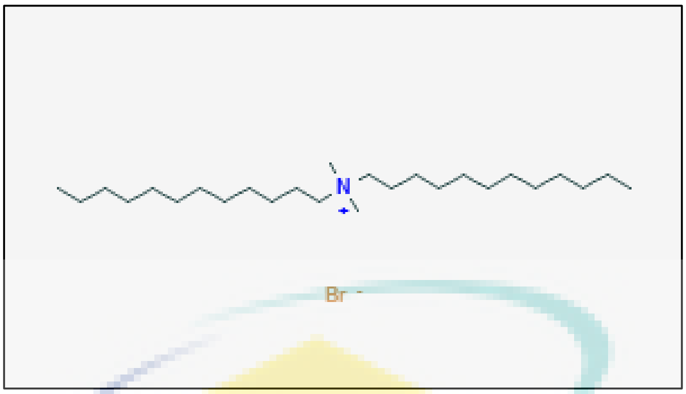


Figure 2. 11: Chemical structure of didodecyldimethylammonium bromide

2.10.13 Polyethylene Glycol Hexadecyl Ether

Polyethylene glycol hexadecyl ether, or Brij 58, has been used in a study to assess properties of gemini-conventional surfactant mixtures and their effects on solubilisation of polycyclic aromatic hydrocarbons. It has also been used as a surface active agent in cosmetics. It is a compound of derivatives of cetyl, lauryl, stearyl, and oleyl alcohols mixed with ethylene oxide. It is a non-ionic surfactant of the polyethylene glycol family. It is used as a solubilizer and emulsifying agent in foods, cosmetics, and pharmaceuticals, often as an ointment base, and also as a research tool.

Table 2. 12: Properties of Polyethylene glycol hexadecyl ether

IUPAC name: Polyethylene glycol hexadecyl ether	
Properties	
Molecular formula	$C_{56}H_{114}O_{21}$
Molar mass	1123.507 g/mol
Melting point	41-49 °C
Density	0.978 g/mL at 25 °C
Appearance	White Pellets

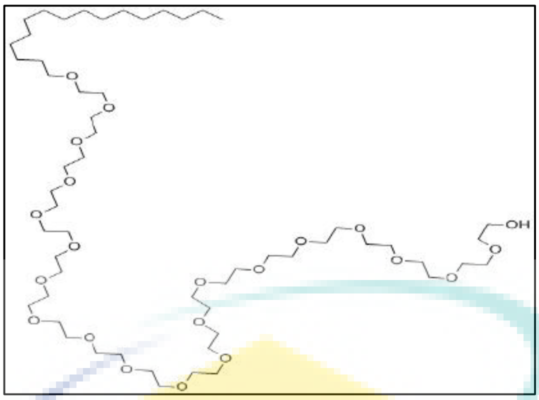


Figure 2. 12: Chemical structure of Polyethylene glycol hexadecyl ether

2.11 Water Resistance

Water can be found in three states: liquid, solid, and vapor. Depending on its state, it can be moved or transported through or within an exterior wall assembly through various mechanisms. Building materials have physical properties which impact liquid moisture movement and accumulation including absorption, sorption, liquid water permeance, air flow, and vapor permeance. In vapor form, water is moved by differences in vapor pressure and air flow. Water vapor migration through a material by differences in vapor pressure across the material is a process known as diffusion. Vapor pressures are elevated by temperature and the amount of moisture vapor in the air. As a result, the water vapor will want to move from the warm and more humid side of a building envelope (higher vapor pressure) to the cold and dry side (lower vapor pressure) as the water vapor molecules seek to reach equilibrium as in Figure 2.13.

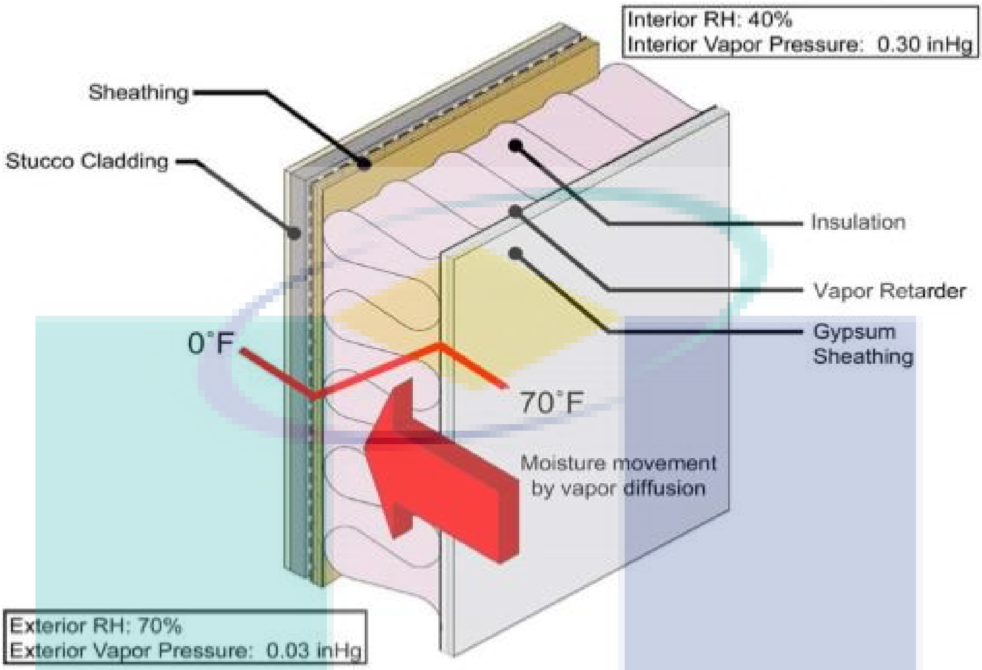


Figure 2.13: Moisture movement through a wall (Garth D. Hall, Senior Architect, AIA, Kenneth M. Lies, Principal, AIA, n.d.)

The needs for a coating material that is water resistance and can prevent the permeability of the vapor into the inner wall of operation theatre is very important. Moisture content is an ambient condition for the growth of mould and fungi. The present of mould and fungi may lead to various adverse health effect to the patients while simultaneously will lead to the degradation of the building's structure. All materials have different resistance properties to the flow of vapor through them. For example, some coatings have been developed that are "breathable" which means that they provide little resistance to the movement of moisture vapor, while others are considered "impermeable". Vapor permeance of a material is formally defined as, the time rate of water vapor transmission through unit area of a flat material induced by unit water vapor pressure difference between its two surfaces. This property is commonly given in units referred to as perms (Garth D. Hall, Senior Architect, AIA, Kenneth M. Lies, Principal, AIA, n.d.). In simple terms, it is the rate that water vapor moves through a material under specific controlled steady state test conditions. The vapor permeance of a material is given for a prescribed thickness of the material. The permeability of a material standardizes the value according to a thickness, specifically one-inch thickness for English units or one centimetre for metric units.

Vapor permeance of coatings can be measured using several test procedures and analytical methods. Historically, vapor permeance of materials has been evaluated by the ASTM E96, “Water Vapor Transmission of Materials.” This test method was originally published in 1954 and serves to measure the rate of vapor transmission through either a dry cup method or wet cup method. Different perm values may be possible depending on the material and which of these two methods was used. For this reason, when comparing perm values of different coatings, it is important to recognize the method under which a product was tested, and results were reported. For example, hygroscopic materials store moisture and therefore, behave differently under the wet cup method. The characteristics of hygroscopic materials result in a vapor permeance range that is dependent on the relative humidity of the surrounding environment. This can portray a material as more vapor permeable than may be achievable in the environmental conditions of a particular wall construction in which the product is used. Liquid applied coatings must be adapted to be tested under the ASTM E 96 protocol. ASTM specifically evaluates permeance of organic coatings with the D1653 method. This method provides techniques for the coating material to be adapted into a sheet format in order to perform similar test methods to those in the E96 (Garth D. Hall, Senior Architect, AIA, Kenneth M. Lies, Principal, AIA, n.d.).

So, in this scope of research EMB will be tested to verify and validate the performances of EMB as a coating and insulation material in preventing the infiltration of moisture into the wall. This verification and validation process is significantly important since EMB is widely used for surface dressing applications and wall insulator. Generally, it is applied to create a membrane between layers of wall to retain its strength by preventing water infiltrate into the layers. During cold climate, it will reduce the heat flow out of the building while on hot condition it will minimize the heat flow to the building. The EMB is in liquid form and will be sprayed onto the top surface of the wall. Moreover, liquid applied membrane is becoming a popular choice nowadays (Nafici, 2011)

2.12 Coating

2.12.1 Wetting

Wetting is the measurement of spreadness and contact of the liquid (adhesive) on the surface of solid (substrate). In this dissertation, the adhesive will be EMB and the substrate will be the bricks and the container. The basic principle of wetting process is when the two phases contacting within sufficient period of time which subsequently develop physical attraction between these phases due to the inter-molecular forces. As a result, the adhesive will conform on the surface of the substrate, displacing air and minimizing interfacial flaws. Good wettability is a prerequisite for good adhesion. The factor that lead to the good wettability of EMB on a substrate is its surface energy. Surface energy is defined as the work necessary to separate two surfaces beyond the range of the forces holding them together. The wetting ability of the EMB on the substrate will occur when its surface energy is lower than surface energy of the substrate (Restricted, 2006). Force balance or equilibrium at the solid-liquid boundary is given by Young's equation for contact angles greater than zero.

$$\gamma_{\mathrm{lv}} \cos \theta = \gamma_{\mathrm{sv}} - \gamma_{\mathrm{sl}} \qquad \text{Eq. 2.1}$$

where θ is the contact angle, and γlv, γsv and γsl are the surface free energies of the liquidvapour, solid-vapour and solid-liquid interfaces, respectively. The lower the contact angle, the greater the tendency for the liquid to wet the solid, until complete wetting occurs (contact angle $\theta = 0$, $\cos\theta = 1$). For complete wetting to occur the surface tension of the liquid should be less than or equal to the critical surface tension of the substrate (γsv-γsl). Large contact angles are associated with poor wettability. Finally, the wetting ability will be measured by using water-break test (ASTM F22-02)(ASTM, 2002).

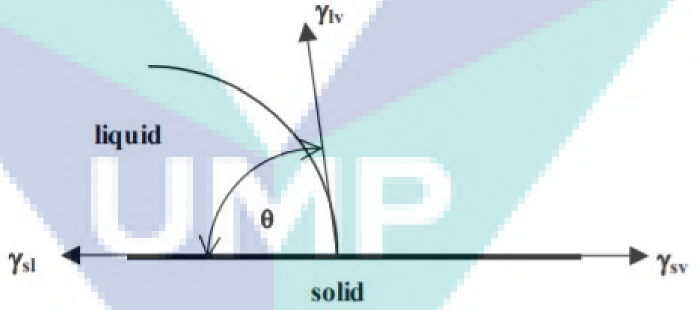


Figure 2.14: Contact angle of an adhesive on a substrate (Restricted, 2006)

2.12.2 Adhesion

Resin is a substance that give the adhesive properties of a material to be applied on the substrate (Mereco, 2016). In EMB, the resin is found abundantly in the bitumen which will give the adhesion properties for EMB in coating processes. The availability of resin in a coating material is very crucial as it will ensure the material to adhere and stick on the surface of the substrate. The excellent adhesive properties of resins are due to the attractive forces between the resin and the surface of the substrate. These forces usually known as polar forces which will be formed between the reactive sites in the resin and polar sites on the surface of the substrate. Typical resins are consisting of hydroxyl group which can form polar bonds to oxide or hydroxyl surfaces (Mereco, 2016). The key factor that determines the adhesive strength of a material is how close the surface energy of the substrate to the surface energy adhesive substance (Restricted, 2006). On most of the surfaces, the forces between the adhesive and the substrate are higher compared to the forces between the resins itself. This condition, will assist the adhesion between the adhesive and the substrate. However, if the substrate has low surface energy compared to the adhesive, then it will lead to the attraction between the adhesive itself rather than to the surface of the substrate (A, Rowland, 1998). This phenomenon is characterized by having the adhesive bead up on the surface rather than wetting the surface of the substrate. The measurement for adhesion properties of the adhesive on the substrate will be conducted according to adhesion test (ASTM D3359-09)(ASTM, 2013).

2.12.3 Drying

There are various factors that affecting the drying rate of EMB during the coating application. Firstly the weather or air conditions. High relative humidity which correlates to high moisture will slow down the drying process. This is because the moisture content in the air will obstruct the evaporation process of liquid from the EMB (Rohm and Haas, 2018). The surrounding temperature also play a significant role as painting under direct sunshine will subsequently increase the surface temperature of the EMB which will shorten the drying time of the coating material. The black colour of the EMB also give extra advantages as the black colour is a good heat absorber. The air movement also help to increase the drying rate of the coating material as the fresh air flow over a wet EMB helps the water in the EMB to evaporate. Secondly, the characteristic of the surface or substrate. The drying rate of EMB will increase when it is coated on the porous surface rather than a sealed surface (Rohm and Haas, 2018). This is due to the fact that the liquid will be absorbed by the porous surface and speed up the drying time of the EMB. Similarly, a warm or hot surface also contribute to the reduction in the drying time. Finally, the drying rate of EMB also been determined by the painting or coating composition. The composition of the EMBs’ in this dissertation are the combination of bitumen modified with waste material, water and emulsifier (Razali, Nur, Mohd, & Salehan, 2018). Different ratio in the composition of the EMB will give different drying rate of the substance. The higher the water composition in the EMB the longer the drying time for the substance as there is more liquid to be evaporated. The drying rate of the EMB will be measured according to drying of coating test (ASTM D1640-03)(ASTM, 2003).

2.13 Microorganism and Fungi

Most water damage indoors is due to natural disaster (e.g., flooding) or human error (e.g., disrepair). Water can seep into a building because of melting snow, heavy rain, or sewer system overflow. Water vapour can be produced by human activities like cooking, laundering, or showering and then condense on cold surfaces like outer walls, windows, or furniture. The present of moisture can damage building materials and components. Besides, the present of moisture content environment will predominantly lead to the high risk of fungal growth (mould growth). This problem will possibly be resulting in health problems for the occupants and the deterioration of the buildings. The negative health effects of damp building materials and fungal growth in homes, institutions, and workplaces have been reported in many publications, including the WHO guidelines *Dampness and Mould*, which concluded that there is sufficient epidemiological evidence to show that occupants of damp or mouldy buildings are at increased risk of respiratory problems, respiratory infections, and the exacerbation of asthma (Soldatova, Sansone, Stephens, & Shah, 2011). In the meantime, various researchers have proven that the present of fungi lead to the adverse health effect and deterioration of buildings design. The details of the finding are illustrated in Table 2.13.

Table 2.13: Studies on airborne fungi on different countries (Haleem Khan & Mohan Karuppayil, 2012)

Location	Country	Predominant Fungi	Analysis	Health concerns	Reference
Hotel rooms	**Asia** China, Taiwan, Malaysia, Vietnam Thailand, Japan, Cambodia and Iran **Europe** Spain, Italy, Sweden, France, Portugal, UK, Norway, Denmark, Germany, Poland, Estonia, Iceland	Aspergillus versicolor, Stachybotrys chartarum, Penicillum spp.	Analysis of fungal DNA in 69 hotel rooms in 20 countries of Asia & Europe		Norback and Cai (2011)
Child day care centers, Uppsala	Sweden	Aspergillusspp ,	To investigate the relationship between building construction and indoor quality and	To reduce allergies levels and protect allergic children	Cai et al. (2011)

		Stachybotrys chartarum, Penicillium sp	exposure to fungi by qPCR		
Air conditioning in Adult & Neonatal Intensive treatment units, Culaba city	Brazil	Aspergillas spp., Penicillum spp., Cladosporium spp.	To evaluate fungi in A/C units of hospitals	This study showed the risk factor for the acquisition of infection in ICU's	Simoes et al. (2011)
Child care centers, Singapore	Singapore	Aspergillas, Penicillum, Geotrichum, Cladosporium	Concentration of culturable fungi were examined	Information provided was useful to determine etiology wheeze and rhinitis	Zuraimi et al. (2009
Hospitals, Zarqa	Jordan	Aspergillus, Penicillium, Alternaria, Rhizopus	To investigate air quality and microbial quantity To evaluate the levels of microorganisms To investigate the distribution patterns of airborne fungi	To assess level of airborne pathogens To minimize the biological hazards	Qudiesat et al. (2009)

One of the main source of moisture content in the wall is surrounding air. Both indoor air and outdoor air contains water vapor. Wherever air goes, water vapor goes. When humid air contacts a surface that is cold enough, the water vapor in the air will condense onto that cold surface. The concept of the air dew-point temperature is very useful in understanding when, why and how much condensation will occur—and how to avoid it. The dew point is the temperature of the air at which condensation occurs. The higher the dew point, the greater the risk of condensation on cold surfaces. The dew point depends on how much water vapor the air contains. If the air is very dry and has few water molecules, the dew point is low, and surfaces must be much cooler than the air for condensation to occur. If the air is very humid and contains many water molecules, the dew point is high, and condensation can occur on surfaces that are only a few degrees cooler than the air. Consider hot weather condensation inside a building. Condensation can be prevented if the indoor air dew point is below the temperature of surfaces that are likely to be cold. If the dew point rises, moisture will begin to condense on cold surfaces. For example, humid outdoor air leaking into a building in Miami will have a dew point above 70°F throughout most of a typical year. During normal operation of an air-conditioned building, there are many surfaces that have a temperature below 70°F. For example, a supply air duct carrying air at 55°F will have a surface temperature near 55°F. If the infiltrating outdoor air has a dew point of 70°F, its moisture will condense on the outside of that cold duct, and possibly on the supply air diffuser (U.S. Environmental Protection Agency, 2013).

Condensation may be the result of excessively high dew point, unusually cold surfaces, or a combination of the two. The indoor dew point is a balance between the addition and subtraction of water vapor from the air. A building has both indoor and outdoor sources that add water vapor, and its mechanical systems must have adequate dehumidification capacity to remove it, to keep the dew point within reasonable limits (Haleem Khan & Mohan Karuppayil, 2012). Inside residential buildings, people and their activities, especially cooking and washing of floors and clothes, are usually the leading sources of humidity. In humidified commercial and institutional buildings such as hospitals, museums and swimming pool enclosures, indoor humidity is very high by design or necessity. In low-rise buildings of all types, damp basements or crawlspaces may add as much water vapor to the air in a day as all the other internal sources combined. During the cooling season, humidity loads from outdoor air are far larger than loads generated inside commercial and institutional buildings. The largest sources of humidity are the ventilation air, the makeup air that compensates for exhaust air, and the air that infiltrates into the building through air leaks in the enclosure. If the ventilation and makeup air is kept dry and the building is tight so that it does not allow much leakage, the contributions from outdoor air will be low. Water vapor may be removed from indoor air by dehumidification (e.g., air conditioners or dehumidifiers) or by ventilation air when the outdoor air is dry. Ventilating air only dehumidifies the indoors when the outdoor air dew point is lower than the indoor air dew point. Exhaust air is a special case. When an exhaust fan rids a building of highly humid air, from showers or cooking, for example, the indoor humidity loads are reduced. On the other hand, if the outdoor air that replaces that exhaust air has a dew point above the indoor dew point, the incoming outdoor air represents a humidity load that must be removed by the mechanical system.

2.14 Heat Transfer / Heat Losses

2.14.1 Malaysian Climate

A building in tropics means a confrontation of construction and function with intense climatic condition. Tropical climate regions characterized as high humidity, excessive rainfall and considerable sunshine. Typical features of tropical climate have the negative impact and positive impact to the building design. The extreme impacts caused by the tropical climate through its climatic parameters such as temperature, heat transfer, humidity, and air velocity. Malaysia is a tropical country characterized as warm and humid located within the Tropic of Cancer and Capricorn. The latitude of 1° - 7°N and longitude 100° - 119°E. The climatic elements categorized as high temperature and uniform diurnal pattern throughout the year. The annual mean temperature is 26.4°C with average daily maximum temperature is 34°C and average daily minimum at 23°C (AlTamimi & Syed Fadzil, 2011). The annual relative humidity value ranges within 74% to 86%. Malaysia also experiences high solar intensity and duration. Weather data analysis in term of building design for warm humid climate is overheating is not as great as in hot–dry areas but it is aggravated by high humidity and small diurnal temperature variation (Haase & Amato, 2009). There are several factors which influence room thermal comfort, namely thermal loads from occupants, equipment, lights/lamps, and thermal load coming from sun rays. In tropical area, the main thermal load is due to the average temperature of ambient air exceeding the thermal comfort temperature, as well as sun shine which hits buildings continue into the rooms. Solar radiation which reaches the wall surface partly continues through the wall and a part is reflected as shown in Figure 2.15.

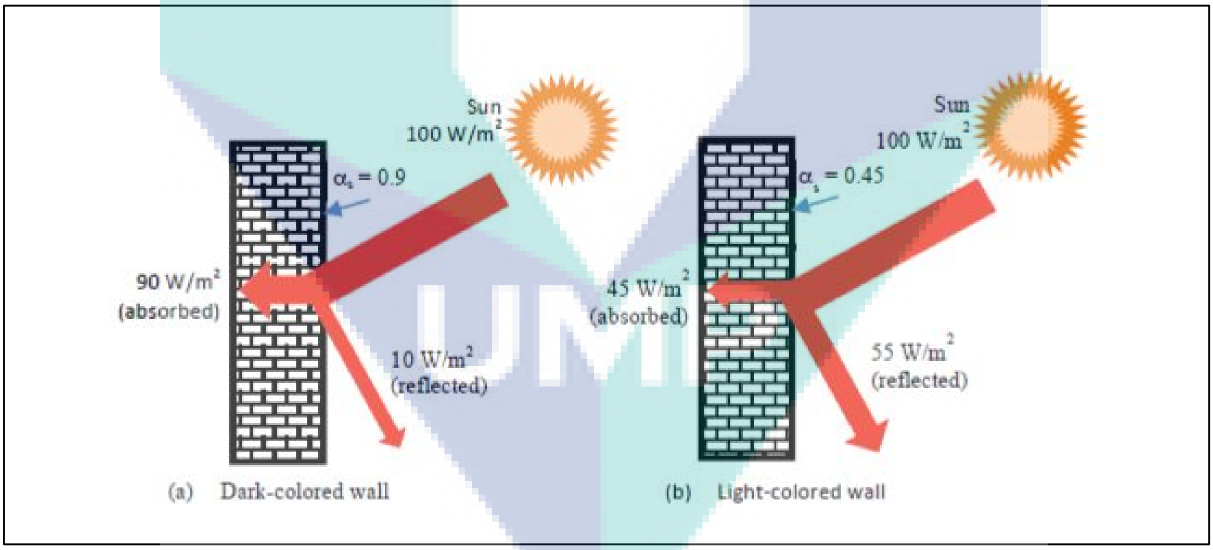


Figure 2.15: Distribution of heat transfer on wall receiving solar radiation (Science, 2017)

The heat transfer on the wall is also influenced by wall thermal conductivity. The varied thermal conductivity of wall material is as shown in Table 2.6.

Table 2.14: Properties of wall materials (Science, 2017)

Material	Thermal conductivity [W/m.K]	Specific heat capacity [kJ/kg K]	Mass density [kg/m^3]
Tuff	0.630	1.300	1500
Concrete	1.263	1.000	2000
Brick	0.500	0.840	840
Plaster	0.900	0.910	1800
Insulating material	0.170	0.920	1200

Thermal load which enters the room is solar radiation energy received by wall surface and then through conduction is continued to the surface of the inside part of the wall. Solar radiation energy which can be continued to the inside surface of the wall can reach 90%, depending on the darkness level of the wall. With this condition, the use of air conditioning system is highly necessary to acquire room thermal comfort.

2.14.2 Equation

To simplify analysis, the two-plate room model is used, and this model has been validated before for building indoor environment simulations (Jiang et al., 2012; Wang et al., 2014). Figure 2.16 gives the heat transfer process of building external walls.

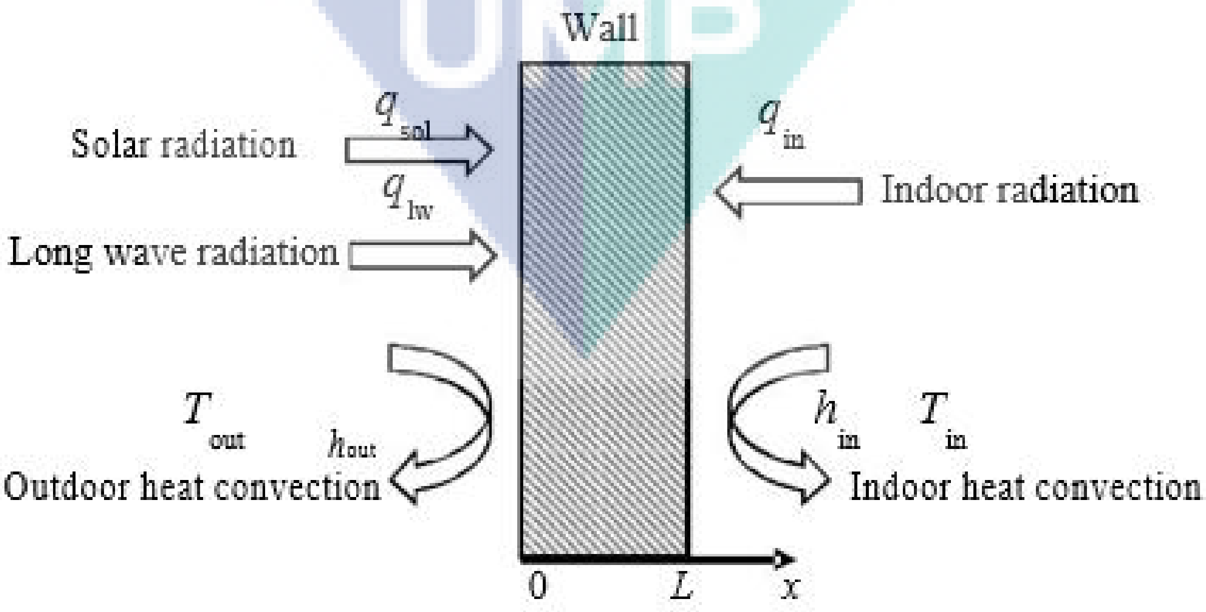


Figure 2.16: Heat transfer process of external walls (Zhang, Long, Li, & Li, 2017)

The transient heat transfer equations for the external wall are as follows

$$\rho_{w c_{p,w}} \frac{\partial T_w}{\partial \tau} = k_w \frac{\partial^2 T_w}{\partial x^2} \qquad \text{Eq. 2.2}$$

Boundary conditions

$$h_w\left(T_{out} - T_{w,out}\right) + q_{r,out} = -k_w \frac{\partial^2 T_w}{\partial x^2} \mid_{x=0} \qquad \text{Eq. 2.3}$$

$$h_{in}\left(T_{in} - T_{w,in}\right) + q_{r,in} = k_w \frac{\partial T_w}{\partial x} \mid_{x=L} \qquad \text{Eq. 2.4}$$

Table 2.15: Symbols and definition for heat transfer equation

Symbols	**Definition**
w	wall density (kg/m^3)
$c_{p,w}$	specific heat (J/(kg C))
k_w	thermal conductivity (W/ (m C))
$q_{r,in}$	Indoor heat gains of people, equipment and solar radiation penetrated from windows (W/m^2)
$q_{r,out}$	Outdoor heat gains of solar radiation, long wave radiation from the ground and sky (W/m^2)

According to available research (Fang and Li, 2000), the equivalent temperature of solar radiation is related to the thermal–physical properties of the external surface material of building envelopes, which determines the ratio of solar absorption (a_{sol}) and reflection (r_{sol}) for the wall surface

$$T_{sol,eq} = \frac{a_{sol} q_{sol}}{h_{out}} = \frac{(1-r_{sol}) q_{sol}}{h_{out}} \qquad \text{Eq. 2.5}$$

The long wave radiation contains two parts: sky radiation and ground radiation. According to the heat radiation principle, there is

$$h_{lw,out} = q_{sky} + q_g = \sigma\varepsilon_{w,sky}\varphi_{w,sky}\left[T_{w,out}^4 - T_{sky}^4\right] + \sigma\varepsilon_{w,g}\varphi_{w,g}[T_{w,out}^4 - T_g^4] \quad \text{Eq. 2.6}$$

Then the equivalent temperature of long wave radiations can be obtained

$$T_{sky,eq} = \frac{\sigma\varepsilon_{w,sky}\varphi_{w,sky}\left[T_{w,out}^4 - T_{sky}^4\right]}{h_{out}}$$

Eq. 2.7

$$T_{g,eq} = \frac{\sigma\varepsilon_{w,g}\varphi_{w,g}\left[T_{w,out}^4 - T_s^4\right]}{h_{out}}$$

Based on the equivalent radiation temperatures, equation (2) can be changed into the following form

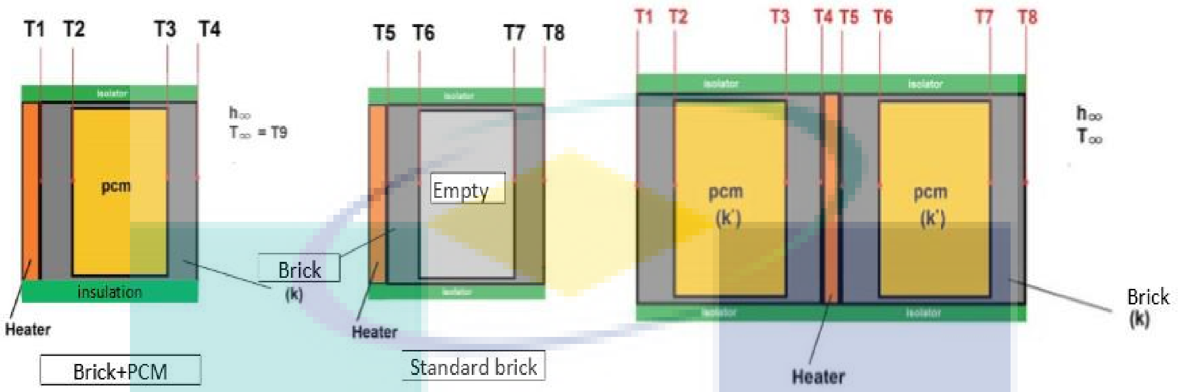
$$h_{out}\left[T_{out} - T_{w,out} + \left(T_{sol,eq} - T_{sky,eq} - T_{g,eq}\right)\right] = -k_w \frac{\partial T_w}{\partial x} |_{x=0} \quad \text{Eq. 2.8}$$

The convective heat transfer coefficient of wall external surface can be regarded as a constant value, h_{out} ¼ 23.3 W/(m^2 C) (Zhang et al., 2013). For the internal surface, convective heat transfer coefficient can be obtained by using Eq. 2.9.

$$h_{in} = 1.31\ (\Delta T)^{\frac{1}{3}} = 1.31\left(T_{w,in} - T_{in}\right) \quad \text{Eq. 2.9}$$

2.14.3 Models

There are two sample models that have been referred for this study. The first model is illustrated as in Figure 2.17 and 2.18.



(a) Heat transfer time (b) thermal conductivity

Figure 2.17: Test equipment scheme of heat transfer characteristics in brick (Science, 2017)

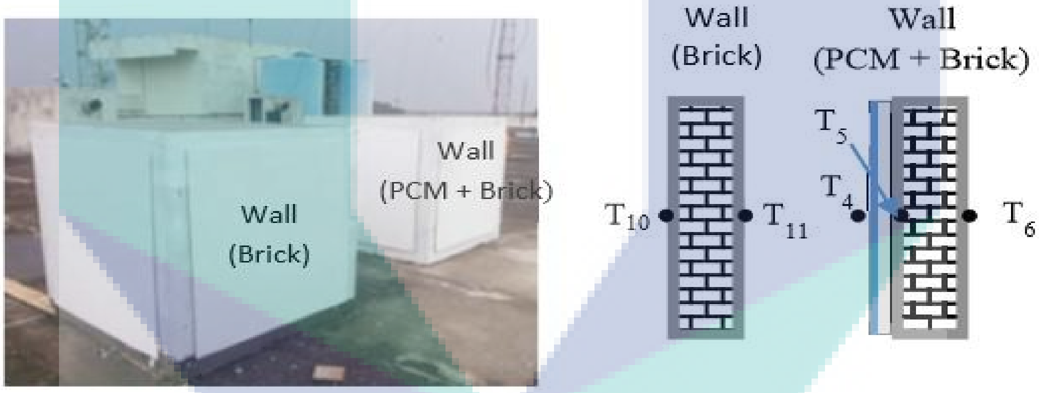


Figure 2.18: Heat transfer test on walls in building models (Science, 2017)

In this study, heat transfer characteristics were tested for bricks added with encapsulated PCM, and building wall made of bricks with the inner side coated with PCM were conducted. In brick test, temperature was measured at several points by using thermocouple and data logger lutron type 224SD either for standard brick or brick containing encapsulated PCM (Figure 2.17 a). Heat source was from heater and surface temperature of 80ºC was maintained by using thermo controller. Besides that, thermal conductivity test in standard brick and brick containing encapsulated PCM was conducted (Figure 2.17 b). While in the building model wall test, points with thermocouple are outer and inner wall surfaces, PCM container surface, ambient temperature. At the same time, a standard building model has been tested as a comparison. Test equipment is shown in Figure 2.17. PCM used was Barco brand coconut oil.

The second sample model is illustrated as in Figure 2.19. The inside environmental temperature of the wall is controlled by the HVAC system, and which is kept 26°C consistently. The consecutive ten-day outside environmental temperatures are considered, representative of a hot climate. So, the meteorological data from July 24th to August 2nd in Xi'an are chosen and obtained from meteorological data for Chinese building thermal environment analysis.

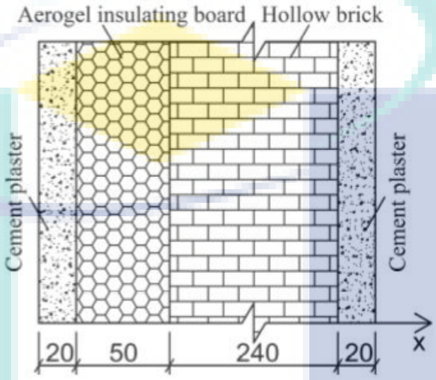


Figure 2.19: Structural model of a wall (Kong, He, Cao, Sun, & Chen, 2017)

From the references model, an appropriate model for this study has been proposed to measure the performances of Emulsified Modification Bitumen (EMB) according to the parameters that have been stated which are heat transfer, temperature, air velocity, water resistance and moisture content. The proposed model is illustrated as in Figure 2.20.

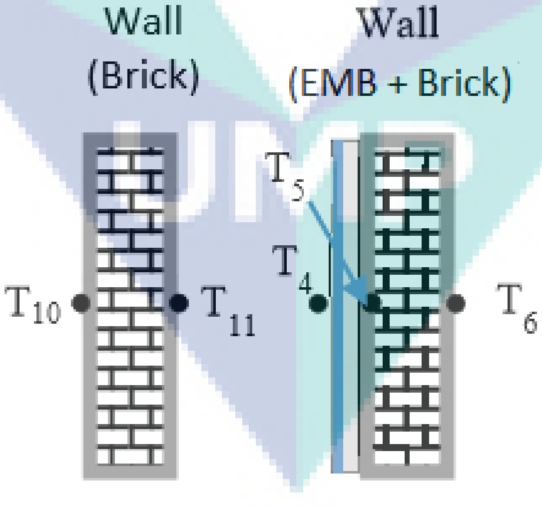


Figure 2.20: The control model of brick wall and brick wall coated with EMB

By using these proposed model, the samples of coating and insulation products will be tested on the surface of the models. There are EMB formulation A, EMB formulation B, EMB from industrial C and EMB from industrial D. In the meantime, a sample on the surface of each model will be left uncoated as a control variable in this study. Then, the performances of the samples will be measured and compared according to the parameters that been listed before.

CHAPTER 3

RESEARCH METHODOLOGY

3.1 Overview

This chapter describe and discuss about the raw materials, chemicals, equipment, and experimental procedure, testing for characterization of raw material and American Society for Testing Materials (ASTM). A proper experimental procedure will be conducted where it involves formulation and emulsifying the bitumen through heating and continuously mixing. The experimental procedure include the preparation of waste sludge, polystyrene, crump rubber, latex, polyethylene, crude oil and used oil.

3.2 Materials

Table 3.1: List of raw materials for this research

No.	Type of Raw Materials	Source
1	Bitumen grade 80/100	Kemaman Bitumen Corporation (KBC)
2	Bitumen grade 60/70	Kemaman Bitumen Corporation (KBC)
3	High Density Polyethylene (HDPE)	Landfill
4	Polystyrene	Landfill
5	Crump rubber	Landfill
6	Latex polymer	Lembaga Getah Malaysia (LGM)
7	Waste sludge	Kemaman
8	Crude oil	Kerteh
9	Used oil 1	Banting
10	Used oil 2	Kemaman
11	Used oil 3	Kuantan

3.3 Chemicals

Table 3.2: List of chemicals for this research

No.	Type of Chemicals	Name	Source
1	Non-ionic emulsifier	Polyethylenimine 80% ethoxyated solution	Sigma Aldrich
2		Polyethylene glycol hexadecyl ether	Sigma Aldrich
3	Anionic emulsifier	Sodium dodecylsulphate	Sigma Aldrich
4		2-bromohexadecanoic acid	Sigma Aldrich
5	Cationic emulsifier	Abietic acid	Sigma Aldrich
6		Dimethyldioctadecylammonium bromide	Sigma Aldrich
7	Bitumen emulsion	Atlaskote bitumen emulsion	Atlaskote

3.4 Methods

3.4.1 Pre-Treatment of Waste Sludge

Waste oily sludge is a mixture of oil, solids, and water deposited at the storage tank bottom. In order to obtain the bottom part of the sludge, the waste need to be pretreat 2 days before the experiment began to ensure all the component of waste sludge is fully separated. The method is called liquid-liquid separation, where the mechanism depends upon the difference in solubility, density and specific gravity of a compound (Razali, 2016). However, since this waste is completely concentrated, it can’t be treated only by using this liquid-liquid separation but it needs to undergo centrifuge process for approximately 10 minute at 1000 rpm. Below is the method and summary of the pre-treatment process.

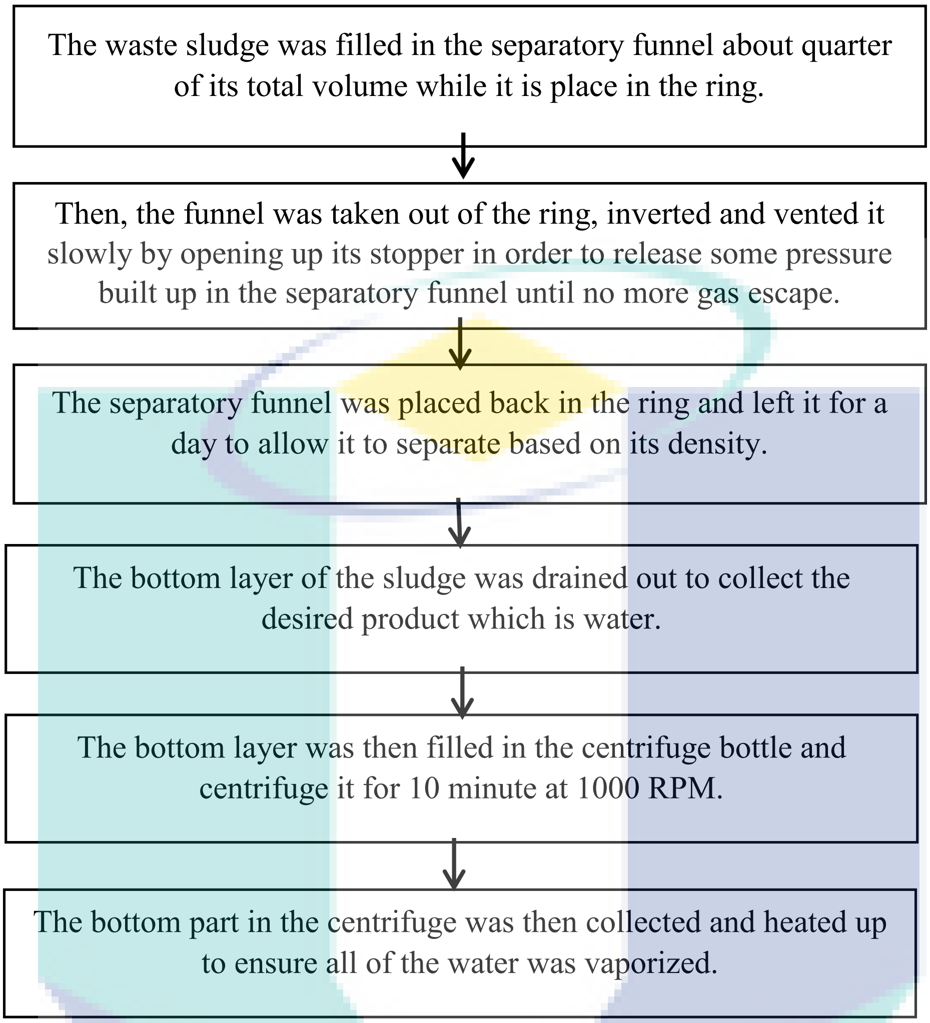


Figure 3.1: Pre-treatment of Waste Sludge Procedure

3.4.2 Characterization of Raw Materials

The raw materials was characterized for a total of 6 testing before the experiment was started. The test involved include thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), density test, flash point, moisture content and FTIR.

3.4.2.1 Thermogravimetric Analysis (TGA)

TGA was performed to determine the decompose temperature and the composition in a sample. This analysis measures the percent weight loss of a test sample while it is heated at 10ºC/min until approximately 900 ºC under inert air. Firstly, 2.5 mg pf test specimen is weight and placed in an aluminium pan and sits upon a constantan disc on a platform in the TGA cell and it is hangs off a hook which is connected by a microgram arm to a tare pan. The loss in weight over specific temperature ranges provides an indication of the composition of the sample.

3.4.2.2 Differential Scanning Calorimetry (DSC)

This analysis was done to determine its melting temperature (Tm). Approximately 2.5 mg of test specimen is weight and placed in a aluminium pan and sits upon a constantan disc on a platform in the DSC cell with a chromel wafer immediately underneath. A chromel-alumel thermocouple under the constantan disc measures the sample temperature. An empty reference pan sits on a symmetric platform with its own underlying chromel wafer and chromel-alumel thermocouple. Heat flow is measured by comparing the difference in temperature across the sample and the reference chromel wafers. The sample was running for about 33 minute by specifying the final temperature of the sample at 350ºC.

3.4.2.3 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR analysis was measured to determine the material's molecular composition and structure. The first step is to collect a background spectra to subtract from the test spectra to ensure the actual sample is all that is analyzed. A simple device called an interferometer is used to identify samples by producing an optical signal with all the IR frequencies encoded into it. Then, the signal is decoded by applying a mathematical technique known as Fourier transformation which generates the absorbance spectra showing the unique chemical bonds and the molecular structure of the sample material.

3.4.2.4 Flash Point Test

A flash point test was performed. Approximately 70 ml test specimen is placed into a test cup. The temperature of the test specimen is increased rapidly at first and then at a slower constant rate as the flash point was approached. At specified intervals a test flame was passed across the cup. The flash point is the lowest liquid temperature at which application of the test flame causes the vapors of the test specimen to ignite. To determine the fire point, the test is continued until the application of the test flame causes the test specimen to ignite and sustain burning for a minimum of 5s.

3.4.2.5 Density Test

Density test was performed by using gas pycnometer device to determine the density of each samples. To conduct the testing, the liquid sample is filled in a steel cup and then placed in the device. A sealed sample chamber of known volume is pressurized to a target pressure with the displacement gas. Once stabilized, this pressure is recorded. A valve is then opened allowing the gas to expand into a reference chamber whose volume is also known. Once stabilized, this second pressure is recorded. This pressure drop ratio is then compared to the behavior of the system when a known volume standard underwent the same process.

3.4.2.5 Moisture Content Test

Moisture content analysis was performed to check on any moisture in each samples. About 2g of the sample is filled in its pan evenly and placed on the platform. The drying temperature was set to standard drying temperature which is 105 ºC and the lid was closed.

3.5 American Society for Testing Material (ASTM)

The industrial grade bitumen and the formulated modified bitumen are analysed to compare between them. In this research there are nine ASTM standard for testing the industrial grade bitumen, formulated modified bitumen and emulsified modification bitumen.

3.5.1 Softening Point Test (ASTM D36)

Softening point of bitumen was determined by using American Standard Testing Methods ASTM D36. The apparatus used in this experiment include shouldered ring, ball centering guide, ring holder and assembly, bath (beaker) and thermometer. The heated sample was poured into two shouldered ring and allow to a cool in ambient temperature for at least 30 min. Then the rings was put in a water bath for 1 hour at 25°C and once it was cooled, the sample was immersed in the bath and placed in a freezer at 15°C for 45 minutes. After that, the apparatus with rings, ball and thermometer in the bath was assembled. While the bath was heated from below, the temperature of the bath was recorded every minutes until the sample soften and slightly touch the bottom of the ring apparatus.

3.5.2 Penetration Test (ASTM D5)

Hardness and grade of bitumen was determined by using American Standard Testing Methods ASTM D5. The apparatus used include penetrometer with needle and timer, sample container and thermometer. The melted sample was poured into the sample container and allows cooling in air for 45 minutes. Then the sample was placed in the water bath at 25°C for about 1 hour. After that, the needle was assembled at the penetrator and was positioned until the tip just make contact with the surface of the sample. The needle holder then was released for 5 seconds.

3.5.3 Differential Scanning Calorimetry (ASTM D314)

Differential Scanning Calorimetry (DSC) is a thermoanalytical technique was used to assess the stability and kinetics of emulsions by materials' thermal transition through the changes of temperature. The analysis was performed according to ASTM D314 by using a TA instrument DSCQ100 system of type DSC-50 with heating rate of 5ºC/min from -60 °C to 100 °C.

3.5.4 Viscosity Test (ASTM D4402)

Viscosity test (D4402) was measured using a rotational viscometer equipped with a plate geometry of 1mm in Malvern Instruments set up with rotational speed of 50 rpm. The average viscosity was calculated from the overall data as temperature increases.

3.5.5 Oscillatory Test (ASTM D7271)

Oscillatory test (ASTM D7271) was performed through Malvern Instruments which carried out controlled shear stress rheometer equipped with a parallel geometry of 1 mm within temperature range of 0 to 30 for temperature control aimed at investigating material phase transition using temperature sweep tests. This non-destructive test examine the viscoelastic characteristics (elastic-solid and a viscous-fluid like behaviour) and rigidity of the formulated bitumen when external deformation force is applied to its micro structure.

3.5.6 Standard Test Method for Thickness of Compacted Bituminous Mixture Specimen (ASTM D 3549-03)

The standard test method for thickness of compacted bituminous mixture specimen (ASTM D 3549-03) is conducted as a construction check to ensure that the proper amount of bitumen emulsion has been placed on the substrate. This test method is performed by preparing a caster with a thickness of 1 mm. Next, the samples of bitumen emulsion are placed on the surface of the drywall. The bitumen emulsion samples are flattened in accordance with the thickness of the caster. Finally, the caster will be detached to leave behind the bitumen emulsion coated on the surface of the drywall.

3.5.7 Standard Test Method for Drying of Organic Coatings

The drying test is applied according to ASTM D1640-03. The EMB will be poured on a clean glass panels. The test films shall be cast with a doctor blade to give the recommended dry film thickness. Then, separate a number of individual fibres from a mass of absorbent cotton with the aid of tweezers. After that, at a constant time interval, several cotton fibres will be dropped upon the marked film from a height of 25 mm (1 in). The film is considered to have dried dust free when the cotton fibres can be removed by blowing lightly over the surface of the film.

3.5.8 Standard Test Method for Measuring Adhesion by Tape Test (ASTM D 3359-09)

The standard test method for measuring adhesion by tape test (ASTM D3359-09) is used to establish whether the adhesion of a coating material (bitumen emulsion) on a substrate (drywall) is at an adequate level. If a coating is to fulfil its function of protecting or decorating a substrate, it must adhere to it for the expected service life. Because the substrate and its surface preparation (or lack of it) have a drastic effect on the adhesion of coatings, a method to evaluate the adhesion of a coating to different substrates or surface treatments, or of different coatings to the same substrate and treatment must be investigated. This testing method is executed by applying and removing pressure-sensitive tape over cuts made in the film. Then, the rate of adhesion will be measured according to the illustrated scale in the testing method.

3.5.9 Ageing (ASTM G 154)

After all of the standard test methods have been carried out, the analysis is continued with ageing. Ageing is one of the most influential factors that change the properties of the bitumen emulsion on the substrate. The ageing process is measured at three different temperatures (55°C, 27°C and 10°C). The ageing process at 55 °C is tested by using Accelerated Weathering Tester. Accelerated Weathering Tester is conducted in accordance to ASTM G 154 with the irradiance intensity of 0.89 $\frac{W}{m^2}$, step time of 8 hours, setting temperature of 55°C and a test time of 168 hours. This process is equivalent to actual conditions of 10343 hours or 431 days [3]. Ageing at 27°C is conducted by placing the bitumen emulsion samples in the laboratory and leaving them for 7 days. For the ageing process at 10°C, the bitumen emulsion samples are left in the chiller for seven days. The weights of all the bitumen emulsion samples at these three different temperatures are measured and recorded daily.

3.6 Heat Transfer

Heat transfer analysis will be conducted to determine the insulation capacities of the bitumen emulsion. The apparatus includes a 10 cm x 5 cm x 1 cm drywall, aluminium foil tape, non-contact digital laser infrared thermometer, and an oven. The bitumen emulsion will be poured on the top surface of six drywall samples and a drywall sample will be left uncoated as a control variable. Then, the sides and back of the drywall sample will be covered with aluminium foil tape to prevent the loss of heat to the surroundings. The samples are then placed inside the oven at four different temperatures (60°C, 45°C, 30°C and 27°C) for three hours. Next, the temperatures of the coating (bitumen emulsion), top and back surfaces of the drywall are taken by using a non-contact digital laser infrared thermometer. The amount of heat, q in watt will be calculated according to the governing equations as follows :

$$\text{Conduction: } q = \frac{k\,A\,(\Delta T)}{t} \qquad \text{Eq. 1.1}$$

$$\text{Convection: } q = hA\,(\Delta T) \qquad \text{Eq. 1.2}$$

where,

q = amount of heat (W)

k = thermal conductivity of material ($\frac{W}{m\,K}$)

h = convective heat transfer coefficient ($\frac{W}{m^2\,K}$)

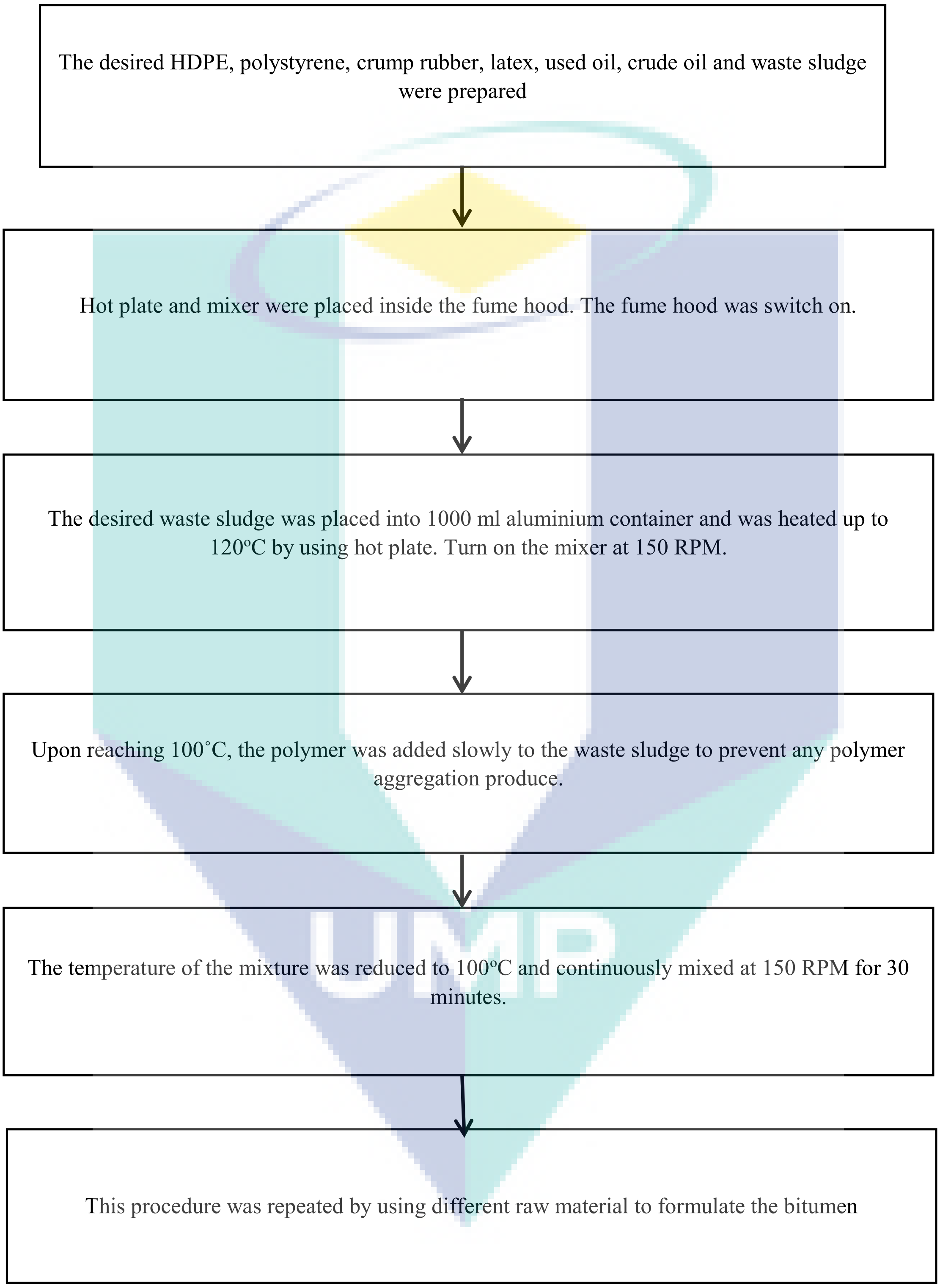
ΔT = temperature difference (K)

t = thickness (m)

A = area (m^2)

3.7 Modified Bitumen Formulation

3.7.1 Procedure



The desired HDPE, polystyrene, crump rubber, latex, used oil, crude oil and waste sludge were prepared

Hot plate and mixer were placed inside the fume hood. The fume hood was switch on.

The desired waste sludge was placed into 1000 ml aluminium container and was heated up to 120ºC by using hot plate. Turn on the mixer at 150 RPM.

Upon reaching 100˚C, the polymer was added slowly to the waste sludge to prevent any polymer aggregation produce.

The temperature of the mixture was reduced to 100ºC and continuously mixed at 150 RPM for 30 minutes.

This procedure was repeated by using different raw material to formulate the bitumen

Figure 3.2: Modified Bitumen Formulation Procedure

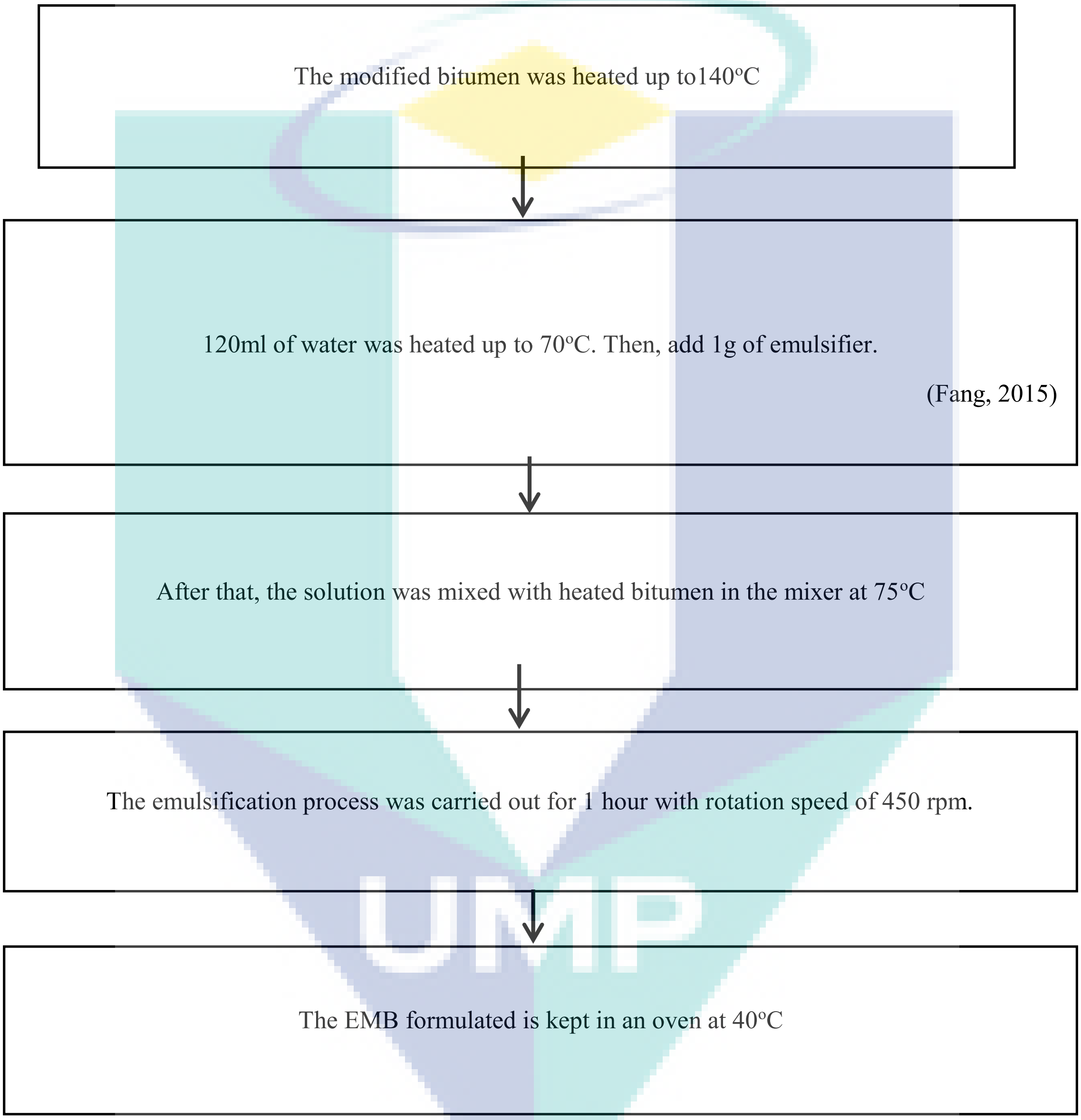
3.7.2 List of Modified Bitumen Formulation

Table 3.3: General formulae for Modified Bitumen (MB) formulation

Code	Ratio Weight (wt. %)						
	Bitumen 80/100	Bitumen 60/70	HDPE	Latex	Crump Rubber	Crude Oil	Used Oil
A	80		7				13
B	80		5				15
C	60		7				38
D	60		5				35
E	40		7				53
F	40		5				55
G	20		7				73
H	20		5				75
A1	20		5	5		70	
B1	20		4	6		70	
C1	20		2	8		70	
D1	20		5	15		60	
E1	20		4	16		60	
F1	20		2	28		60	
G1	20		5	25		50	
H1	20		4	26		50	
I1	20		2	28		50	
J1	20			5	5	70	
K1	20			6	4	70	
L1	20			8	2	70	
M1	20			15	5	60	
N1	20			16	4	60	
O1	20			28	2	60	
P1	20			25	5	50	
Q1	20			26	4	50	
R1	20			28	2	50	
S1	20		2			39	39
EMB 01		40					60
EMB 02		45					55
EMB 03		50					50
EMB 04		55					45
EMB 05		60					40

3.8 Emulsified Modification Bitumen Formulation

3.8.1 Procedure



The modified bitumen was heated up to140°C

120ml of water was heated up to 70°C. Then, add 1g of emulsifier.

(Fang, 2015)

After that, the solution was mixed with heated bitumen in the mixer at 75°C

The emulsification process was carried out for 1 hour with rotation speed of 450 rpm.

The EMB formulated is kept in an oven at 40°C

Figure 3.3: Emulsified Modification Bitumen Formulation Procedure

3.8.2 Ratio of EMB, Water and Emulsifier

Table 3.4: Weight Percent of EMB Formulation

	Modified Bitumen (wt %)	Water (wt %)	Emulsifier (wt %)
Sample	39	60	1

The key parameters for this process was the temperature, weight of each material and the speed of mixer. The continuous mixing is important to ensure the mixture was homogenously mixed. Besides that, the mixture need to be added to each other at the right temperature. Water and emulsifier was first heated up till 70°C. After that the bitumen at 140°C was added onto the mixture. In this experiment, only 1wt% of emulsifier was used as Glady et al (2016) and Cai et al (2010) both reported that only 1wt% of emulsifier is enough to emulsify a bitumen. Furthermore, the speed of the mixture need to be control throughout the emulsifying process. When the bitumen already added to the mixture, the speed of the mixture need to be high as to fasten the reaction between bitumen and the mixture. The water used must be deionised water as the emulsifier cannot tolerate with any mechanical impurities present in the water (Kornetova, 2016).

3.9 Model development

The proposed model is illustrated as in Figure 2.20.

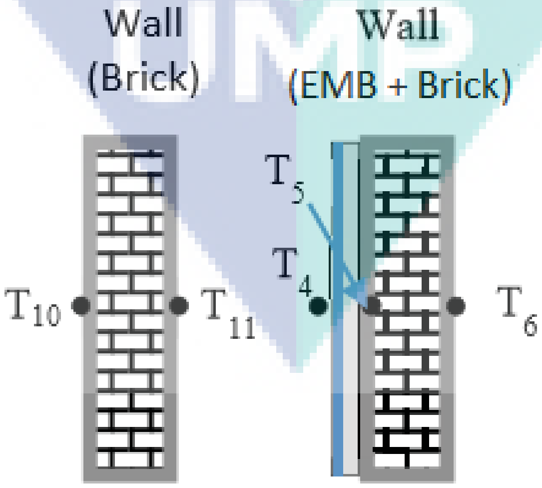


Figure 2.20: The control model of brick wall and brick wall coated with EMB

By using these proposed model, the samples of coating and insulation products will be tested on the surface of the models. The model will be developed from dry wall with dimension of 5 cm x 10 cm. In the meantime, a sample on the surface of each model will be left uncoated as a control variable in this study. Then, the performances of the samples will be measured and compared according to the parameters that been listed before.

3.10 Workflow of Development of EMB from Waste

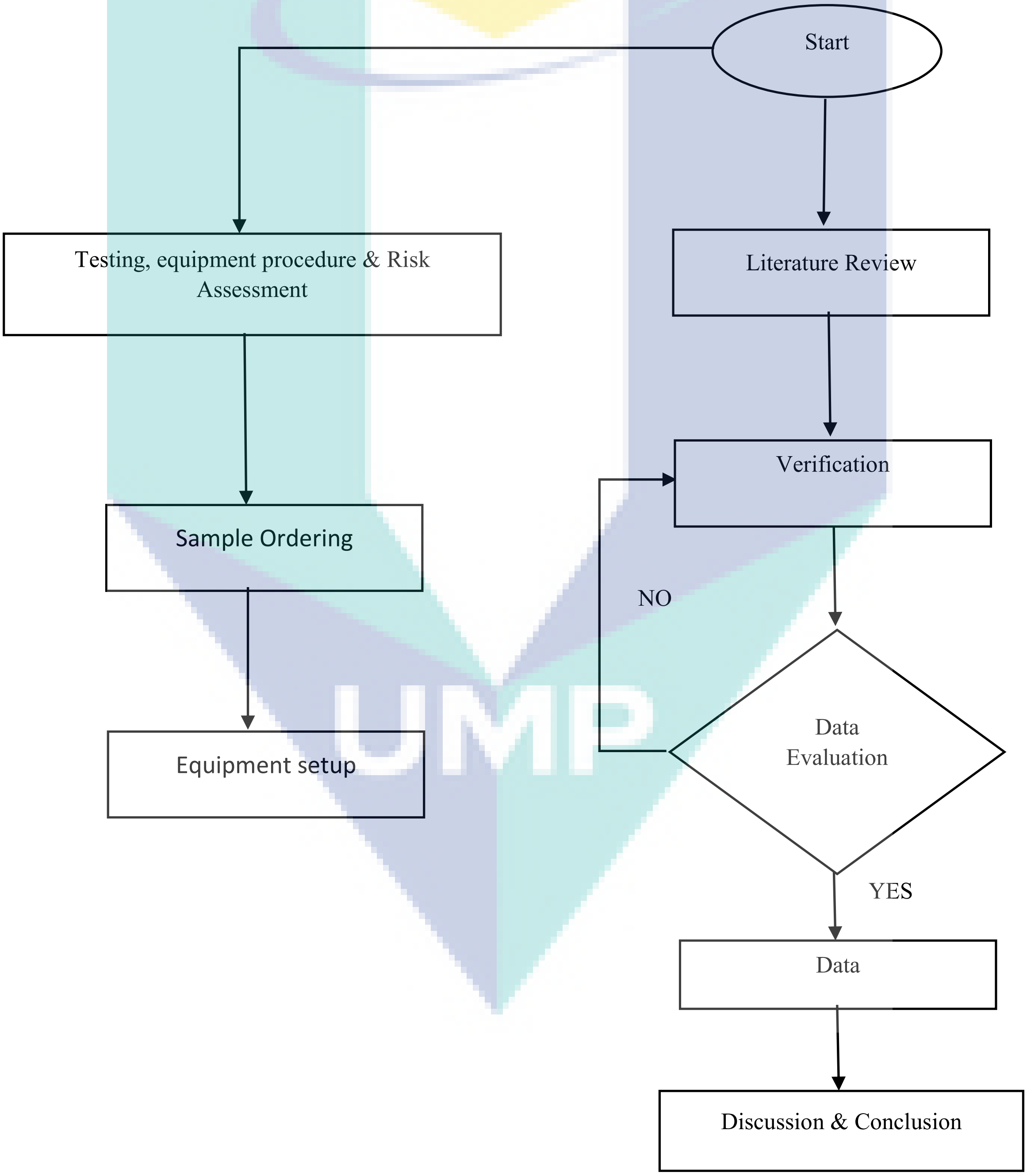


Figure 3.4: General workflow for this research

3.11 General Experimental Procedure

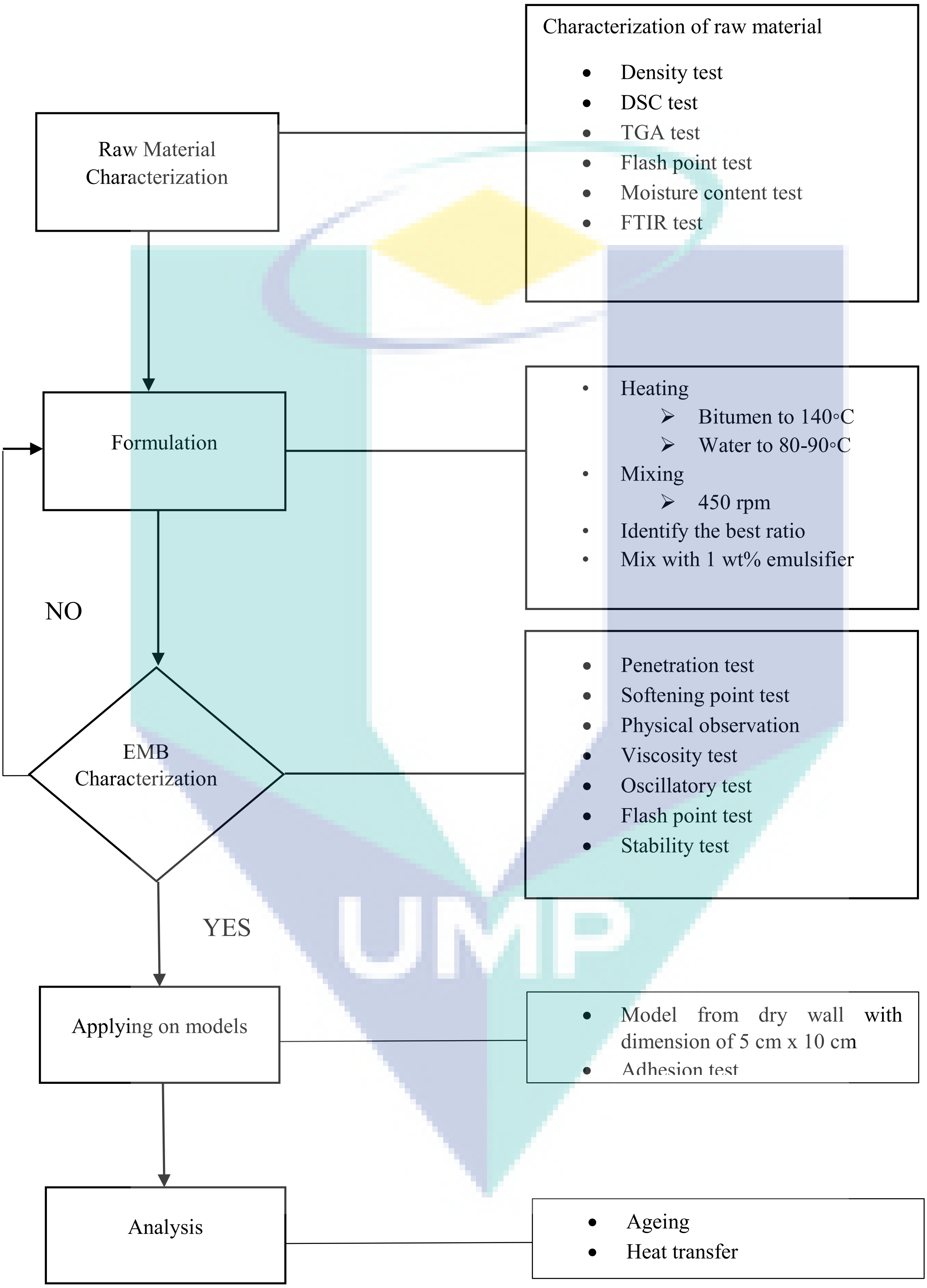


Figure 3.5: General experimental procedure for this research

CHAPTER 4

RESULT AND DISCUSSION

4.1 Chapter Overview

In this research, there were four stages of experiment in order to complete this research. Firstly, the raw material was characterized in terms of its chemical and physical properties by using eight different testing which were DSC, TGA, FTIR, moisture content analyzer, density test, flash point test, softening test and penetration test. Secondly, the bitumen is formulated using industrial waste which were crude oil, used oil and polymer. Then, they were compared with the existing bitumen emulsion from industry. Then, the formulated bitumen was emulsified using cationic, anionic and non-ionic emulsifier. Finally, the formulated EMB were compared with bitumen emulsion from industry.

4.2 Preliminary Study

Firstly, the experiment was conducted to know the polymer melting temperature. 5g of polymer was heated up at 70°C and the temperature was increased gradually until all the polymer was melted at 180°C. Next, the sludge was tested for its suitability to mix with the other raw materials then the percentage of polymer that was not suitable in the formulation was found out. Ratio of 10% polymer was introduced to control the polymer percentage before further experiment was performed to formulate the bitumen.

Table 4.1: Preliminary Formulation of Bitumen

Ratio Weight (wt%)	8:1:1 (A)	6:1:3 (B)
Bitumen	176.0	132.0
Polymer	22.0	22.0
Used oil	-	75.7
Sludge	11.0	-

Upon adding the sludge in the A formulation, the mixer of bitumen become completely harden and cannot be stirred by the head stirrer anymore. The solubility of polymer also dropped which makes the mixture become very low of liquid content. For the B formulation, the solubility of polymer was very low upon adding it in that ratio even it was being added slowly in a 5 minutes interval until all the polymer was used to allow the mixture mixed together homogeneously. Both of A and B formulation was in completely solid state. This 10% content of polymer was introduced as Nalini (2012) state that when bitumen is mixed with 10% of polymer, bitumen will exhibits the best behavior however Lu & Isacsson (2000) reported polymer content in modified bitumen cannot go beyond 9wt% in fact 6wt% is the most sufficient one

4.3 Characterization of Raw Material

Characterization of raw material is important before further experiment was performed in order to understand the behaviour of the raw material used. For example, three different polymers were compared based on its behaviour using TGA, DSC, FTIR, moisture content analyser. Three different sources of used oil was analysed based on its flash point and density. These were all done to check on its nature in order to pick the best material to use in this research.

4.3.1 Thermo Gravimetric Analysis (TGA)

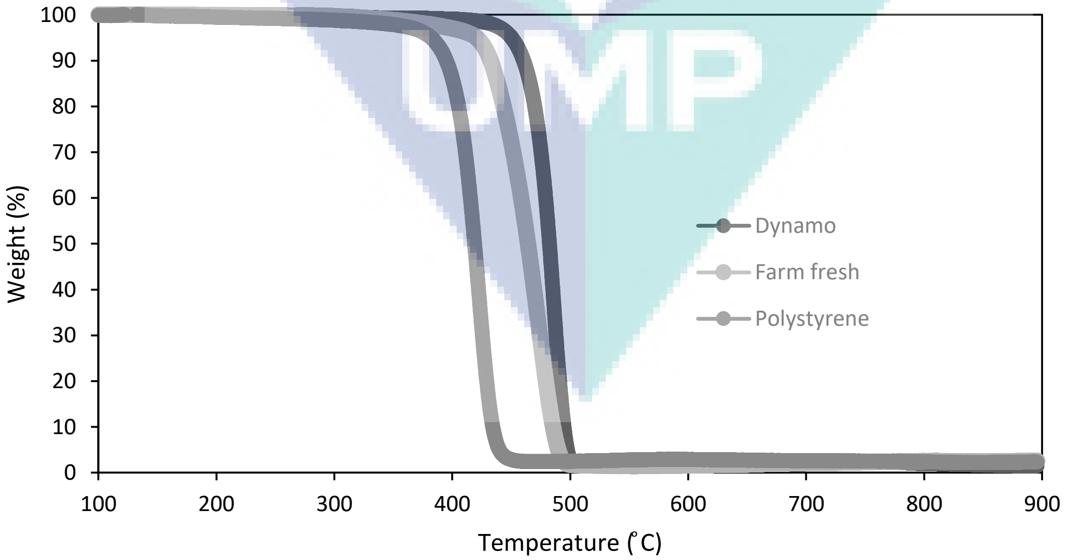


Figure 4.1: Graph of Weight Loss (%) against Temperature (ºC)

Based on Figure 4.1, the curves showed continuous mass loss steps relating to the loss of volatile components, such as moisture and additives, the decomposition temperature of the polymers, and the combustion of final residues, such as ash and fillers (Turi, 1997). According to Joseph (2009), the multicomponent materials in one polymer, which are low-molecular mass compounds, polymeric materials, and inorganic additives can be divided by temperature. Thus, each composition and degradation temperature can be known.

Based on the figure, all samples showed the same degradation temperature, but different weight losses, namely, polystyrene sample, with 0.4476% of its components degraded at lower than 200 °C, 97.16% at 402.9 °C, and 2.355% at 900 °C. Meanwhile, the high density polyethylene 2 (HDPE 2) had 0.0852% of its components degraded at lower than 200 °C, 97.33% at 402.9 °C, and 2.606% at 900 °C. Lastly, the high density polyethylene 1 (HDPE 1) was 0.3235% degraded at lower than 200 °C, 98.17% at 402.9 °C, and 1.510% at 900 °C. These results showed that these samples had consisted of low-molecular-mass components, such as water and additives because they completely lost their mass at a low temperature. Furthermore, the major weight loss of approximately 80% of each sample had occurred at 402.9 °C. At 350-500 °C, all carbon-carbon bonds were typically ruptured by undergoing three possible mechanisms; random scission, depolymerisation, and side group elimination (Crompton, 2012). In addition, the residues, which were about 3% of the samples at the end of analysis, can be classified as additives or fillers because inorganic additives are usually stable in an inert atmosphere up to 900 °C or higher. The residues that remain at higher than 600 °C are normally associated with inorganic compounds, such as silica particles, glass fibres, and calcium carbonate (Joseph, 2009).

Therefore, based on these results, it was concluded that HDPE 1 was the best sample that would be able to tolerate the bitumen formulation because it contained the least amount of filler and the highest purity of polymer, with 98.17% of its total weight was the hydrocarbon component.

4.3.2 Differential Scanning Calorimetry (DSC)

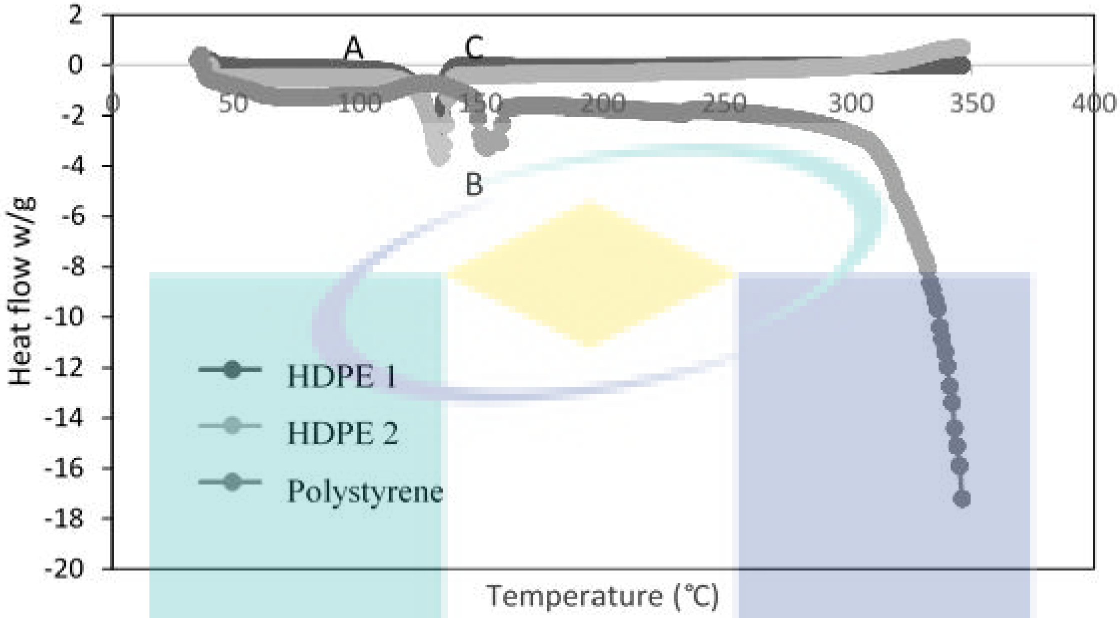


Figure 4.2: Graph of Heat (w/g) Flow against Temperature (ºC)

From Figure 4.2, samples of HDPE 1 and 2 showed approximately the same trend, which deviated from the polystyrene sample. This was because both samples came from the same group of polymer. The DSC graph showed three different melting values for each material, which were denoted as A, B, and C. At point A, the materials began to melt. Point B depicted the peak melting temperature, where it indicated the maximum rate of melting. Lastly, the real melting point was at point C, when the curves reached steady-state before they continued down the endotherm (Joseph, 2009). Therefore, to formulate bitumen, the melting point of each sample was determined in order to develop a method for this study, which could ensure all materials used were melted according to their melting temperature.

4.3.3 Fourier Transform Infrared Spectroscopy (FTIR)

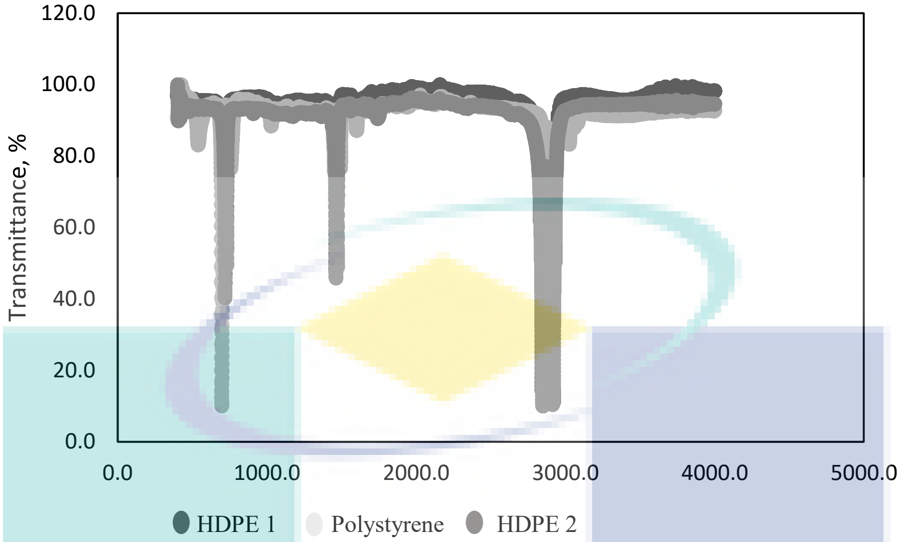


Figure 4.3: Graph of Transmittance (%) against Wavelength (cm^{-1})

Figure 4.3 Figure 3 shows the spectra of the three types of polymer used in this study, namely, HDPE 1, HDPE 2, and polystyrene. FTIR is a technique based on the vibrations of the atoms of a molecule. An IR spectrum is commonly obtained by passing IR radiation through a sample and determining what fraction of the incident radiation is absorbed at a particular energy. This energy is determined at any peak in an absorption spectrum that appears to correspond to the frequency of the vibration of a part of a sample molecule. This test was conducted to determine the actual group of the three samples, especially the HDPE 1 and 2 samples, as they were used for the same application, which was as detergent bottles. From the figure, it was noted that all samples had presented the same absorption, varying only in terms of intensity, which can be attributed to their degree of branching, i.e., the number and size of ramifications. The samples of HDPE 1 and HDPE 2 showed the exact same trend because they both came from the same group. For the HDPE or LDPE group, significant bands can be seen in the regions of 3000–2800, 1550–1400, and 750–650 cm^{-1} (Gulmine, 2002) because they have nearly similar spectra. When the HDPE-LDPE spectra were compared, no noticeable difference was observed. The only exception would be the inclusion of additional thickness or length of the peaks due to additional branching in some samples (Petrovich, 2015). FTIR also allows the determination if any water molecule that exists in a sample. If the sample has water molecules, the spectrum will resonate around the 3450 cm^{-1} region. Amongst the three samples, none of them showed significant resonances around 3450 cm^{-1}. It can be said that the water contents in all these samples were negligible. Thus, moisture content analysis was performed to determine the exact amount of moisture content in a sample.

4.3.4 Flash Point (ASTM D93-08)

Table 4.2: Flash Point Temperature for liquid samples

Sample Name	Flash Point Temperature (°C)
Base oil 1	132.5
Base oil 2	20.0
Used Oil	65.0
Sludge	145.5
Crude Oil	32.5

Table 4.2 shows the flash point temperatures for four different samples that mainly contained different blends of oil, which were collected from different sources. Flash point is defined as the lowest temperature of a liquid at which its vapours will form a combustible mixture with air (Gharagheizi, 2008). Generally, the more viscous and higher additive content in the oil, the higher the flash point. From the table , base oil 1 has the highest flash point at 132.5°C, while base oil 2 has the lowest flash point at 20 °C. Physically, base oil 2 was more watery-like compared to the other samples. This could be the effect of the addition of other components that diluted the oil. In order to formulate modified bitumen, the oil needs to have a high flash point since this experiment was conducted at the maximum temperature of 180 °C, and the oil was used as the medium for the polymer to melt.

4.3.5 Density

Table 4.3 shows the density results for four different oil samples that mainly contained different blends of oil. This test was conducted to determine the physical behaviour of the oils. Generally, in order to mix different materials into one mixture, the density of all materials involved must be closed enough to homogeneously mix the mixture. In a comparison of the density of the oil samples, base oil 1 showed the highest density of 0.9304 kg/m^3, whereas the lowest density belonged to base oil 2 at 0.8070 kg/m^3. In this case, used oil 3 was chosen because the supplier for base oil 1 no longer produce it and used oil 3 has a higher density compared to base oil 2.

Table 4.3: Density for liquid samples

Sample Name	Density (kg/m^3)
Base oil 1	0.9304
Base oil 2	0.8070
Used Oil	0.8720
Sludge	1.1831

4.3.5 Moisture Content

Table 4.4: Moisture content for all solid and liquid samples

Sample Name	Moisture Content (%)
Base oil 1	1.019
Base oil 2	0.504
Used Oil	0.311
Sludge	14.479
HDPE 1	0.266
HDPE 2	0.389
Polystyrene	0.757
Crump rubber	0.392
Crude Oil	0.130

Table 4.4 shows the moisture content of all raw materials, which consisted of oil and polymer. A moisture content analyser was run to determine any moisture that could exist in the

samples because a standard for moisture content in raw materials needs to be developed in order to control the quality of the final products. Amongst the three polymeric materials, HDPE 1 sample has the least moisture content at 0.266%, followed by HDPE 2 sample at 0.389% and polystyrene sample at 0.757%. Meanwhile, for the base oil samples, base oil 1 has the highest moisture content at 1.02% and the lowest moisture content was for used oil at 0.311%. The formulated bitumen was then emulsified using a suitable emulsifier to dilute the bitumen into liquid form. Therefore, the bitumen sample would not necessarily have the exact same performance as the original pavement bitumen, which is more viscous compared to the formulated bitumen in this study.

4.3.6 Summary of Analysis

Table 4.5: Summary and result of all the test conducted

Sample Test	HDPE 1	HDPE 2	Poly-styrene	CR	Base oil 1	Base oil 2	Used oil	Crude oil	Sludge
TGA (°C)	468.68	439.54	402.90	395.56	-	-	-	-	-
	Solid sample only								
DSC (°C)	131.24	133.19	151.90	140.22	-	-	-	-	-
	Solid sample only								
Flash Point (°C)	-	-	-	-	20	132.5	65.0	32.5	145.5
					Liquid sample only				
Density (kg/m^3)	-	-	-	-	0.807	0.9304	0.872	-	1.1831
					Liquid sample only				
Moisture Content (%)	0.266	0.389	0.757	0.392	0.504	1.019	0.311	0.130	14.48

***CR=Crump rubber**

Table 4.5 summarizes the results for each test. TGA and DSC had only allowed solid samples to be tested, while the flash point and density testing had only allowed liquid samples.

On the other hand, moisture content analysis had allowed both liquid and solid samples to be tested using the analyser. TGA measured the decomposition temperature and composition one of each sample, so the exact amount of filler can be determined from this analysis. Furthermore, DSC was applied to determine the melting point of each sample because it is an important parameter for establishing a method for bitumen formulation. In addition, it is also important that the oil used in this formulation has a high flash point.

4.4 Formulation of Modified Bitumen

There are 32 different formulations of modified bitumen comprise of different ratio content. These sample are classified into three different type which are phase 1, phase 2 and phase 3.

4.4.1 Phase 1: Formulated Modified Bitumen (Bitumen 80/100, Polymer, Used Oil)

The result shows eight formulation of bitumen sample produced using different ratios of bitumen, polymer and used oil.

Table 4.6: Physical Properties of Polymer Modified Bitumen Formulated

Sample	Ratio (B:P:U)	Colour	Solubility of polymer	Phase	Liquid content
A	8:0.7:1.3	Pure black	Low	Solid	Low
B	8:0.5:1.5	Pure black	High	Liquid semi-solid	Medium
C	6:0.7:3.8	Pure black	High	Solid	Low
D	6:0.5:3.5	Pure black	Medium	Liquid semi-solid	Medium
E	4:0.7:5.3	Pure black	Low	Liquid semi-solid	Medium
F	4:0.5:5.5	Pure black	High	Liquid semi-solid	High
G	2:0.7:7.3	Pure black	High	Solid	Low
H	2:0.5:7.5	Pure black	High	Liquid semi-solid	High

*B: P: U=Bitumen: Polymer: Used oil

This formulation process involved melting, mixing and dissolving of three materials namely bitumen, polymer and used oil in one system. Used oil was used as the medium to dissolve the polymer when it was added to the system. The polymer need to undergo depolymerisation which means the polymer was dissolved completely in the system. Figure 4.2 shows the melting temperature of the chosen polymer was 131.24℃. However, all type of polymer will degrade gradually which it is not massively depolymerize until it reached 180℃ (Nguyen et al, 2006). Hence, the temperature of the mixture was set to 180℃ in order to melt the polymer completely. The speed of the mixer played an important role as it stirred and mixed the mixture until it was mixed homogenously. Then, three ratios was chosen as the best combination and undergo softening point test and penetration test. The three samples are B (8:0.5:1.5), F (4:0.5:5.5) and H (2:0.5:7.5) due to no lump and irrequlaties.. Moreover, these samples was containing 5% of bitumen thus remarks that the mixture of bitumen and used oil was able to tolerate with 5% of polymer better than the other polymer percentage. Amongst the three sample, sample (8:0.5:1.5) was the most viscous. Increased viscosity indicates the stiffening effect of polymer (Nalini, 2012). The less viscous was H (2:0.5:7.5) sample since this sample contained the highest amount of used oil compared to the others but still, modified bitumen will shows a high elasticity properties (Nalini, 2012) .

4.4.2 Phase 2: Formulated Modified Bitumen (Bitumen 80/100, Polymer, Crump Rubber, Latex, Used Oil and Crude Oil)

Table 4.7: Ratio of formulation of modified bitumen (B: P: L: C)

Sample Code	Ratio (B:P:L:C)	Colour	Solubility of polyethylene	Phase
A1	20:5:5:70	Pure black	Low	Liquid semi-solid
B1	20:4:6:70	Pure black	High	Liquid semi-solid
C1	20:2:8:70	Pure black	High	Liquid semi-solid
D1	20:5:15:60	Pure black	Low	Liquid semi-solid
E1	20:4:16:60	Pure black	High	Solid
F1	20:2:28:60	Pure black	High	Solid
G1	20:5:25:50	Pure black	Low	Liquid semi-solid
H1	20:4:26:50	Pure black	High	Solid
I1	20:2:28:50	Pure black	High	Solid
Standard Bitumen	-	Pure black	-	Semi solid

*(B: P: L: C)-(Bitumen: Polyethylene: Latex: Crude oil)

Table 4.8: Ratio of formulation of modified bitumen (B: CR: L: C)

Sample Code	Ratio (B:CR:L:C)	Colour	Solubility of crumb rubber	Phase
J1	20:5:5:70	Pure black	Low	Liquid semi-solid
K1	20:4:6:70	Pure black	High	Liquid semi-solid
L1	20:2:8:70	Pure black	High	Liquid semi-solid
M1	20:5:15:60	Pure black	Low	Liquid semi-solid
N1	20:4:16:60	Pure black	High	Solid
O1	20:2:28:60	Pure black	High	Solid
P1	20:5:25:50	Pure black	Low	Liquid semi-solid
Q1	20:4:26:50	Pure black	High	Solid
R1	20:2:28:50	Pure black	High	Solid
Standard Bitumen	-	Pure black	-	Semi solid

*B: CR: L: C=Bitumen: Crumb Rubber: Latex: Crude oil

Table 4.9: Ratio of formulation bitumen (B: P: C: U)

Sample Code	Ratio (B:P:C:U)	Colour	Solubility of polyethylene	Phase
S1	20:2:39:39	Pure black	High	Liquid semi-solid

*(B: P: C: U)-(Bitumen: Polyethylene: Crude oil: Used oil)

This formulation process involved melting, mixing and dissolving of four materials which bitumen itself, polymer either polyethylene or crumb rubber powder, latex, crude oil and used oil in one system. All the sample formulation then being observed according to physical properties include colour, solubility of crumb rubber or solubility of polyethylene and phase. From the observation of all sample starting with sample A1 to sample R1, there are only two sample was chosen as the best combination before undergo the penetration test and softening point test according to the American Standard for Testing and Materials (ASTM) to compare the formulated bitumen with the industrial grade bitumen (KBC). This two sample are quite similar to the industrial grade bitumen from the appearance like have shiny surface and smooth compared to others which was lumpy and have uneven surface. The two samples are B1 (20:4:6:70) and C1 (20:2:8:70).

4.4.3 Phase 3: Formulated Modified Bitumen (Bitumen 60/70, Used Oil)

Table 4.10: Ratio of neat bitumen and used oil for modified bitumen (EMB) 01 to 05

Sample	Type	Ratio	Colour	Phase
EMB 01	B: U	40:60	Pure Black	Liquid-Semi Solid
EMB 02	B: U	45: 55	Pure Black	Liquid-Semi Solid
EMB 03	B: U	50 : 50	Pure Black	Liquid-Semi Solid
EMB 04	B: U	55 : 45	Pure Black	Liquid-Semi Solid
EMB 05	B: U	60 : 40	Pure Black	Liquid-Semi Solid

* B: U = Bitumen: Used Oil

Bitumen and used oil were prepared by heating and mixing at five different ratios as shown in Table 4.10. The formulated samples were prepared by heating the neat bitumen until liquefied before used oil was slowly added at 120˚C. The mixture was further heated at temperature of 190 ˚C and were stirred at 450 rpm by using the overhead stirrer for one hour until homogenously paste formed.

This 5 formulations are neglecting the composition of polymer inside the formulation. This formulations are utilizing the bitumen as main component due to the adhesive capabilities. The used oil in this formulation play a vital role as a solvent to the bitumen in order to develop a suitable modified bitumen for coating purposes.

4.4.4 Selection of Formulated Modified Bitumen

From 32 formulated modified bitumen of phase 1, 2 and 3, 11 formulations have been selected for further investigation which are shown as in table 4.11.

Table 4.11: Selection of formulated modified bitumen

Code	Type	Ratio	Colour	Solubility of Polymer	Phase
B	B: P: U	8:0.5:1.5	Pure Black	Medium	Liquid-Semi Solid
F	B: P: U	4:0.5:5.5	Pure Black	High	Liquid-Semi Solid
H	B: P: U	2:0.5:7.5	Pure Black	High	Liquid-Semi Solid
B1	B: P: L: C	20:4:6:70	Pure Black	High	Liquid-Semi Solid
C1	B: P: L: C	20:2:8:70	Pure Black	High	Liquid-Semi Solid
S1	B: P: C: U	20:2:39:39	Pure Black	High	Liquid-Semi Solid
EMB 01	B: U	40: 60	Pure Black	High	Liquid-Semi Solid
EMB 02	B: U	40: 60	Pure Black	High	Liquid-Semi Solid
EMB 03	B: U	40: 60	Pure Black	High	Liquid-Semi Solid
EMB 04	B: U	40: 60	Pure Black	High	Liquid-Semi Solid
EMB 05	B: U	40: 60	Pure Black	High	Liquid-Semi Solid

*B: U = Bitumen: Used Oil
*B: P: U = Bitumen: Polymer: Used Oil
*B: P: L: C = Bitumen: Polymer: Latex: Crude Oil
*B: P: C: U= Bitumen, Polymer, Crude Oil, Used Oil

4.5 ASTM Analysis

The five polymer modified bitumen and industrial grade bitumen were characterized using American Standard for Testing and Materials (ASTM) method which includes softening point and penetration test to know the type of bitumen that was used in this research and to compare the formulated one with the industrial grade bitumen.

4.5.1 Penetration Test (ASTM D5)

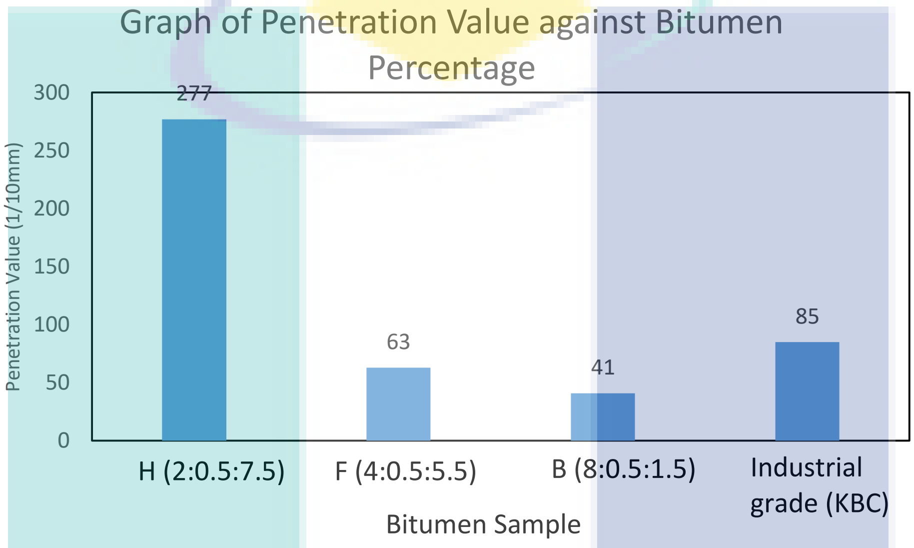


Figure 4.4: Graph of Penetration value (1/10mm) against Bitumen Percentage (%) for B, F and H

Figure 4.4 shows the comparison of penetration value of bitumen from KBC and the bitumen formulated from industrial waste. The penetration value indicates the grade and the hardness of bitumen. Moreover, different grade of bitumen presents different application in different climatic conditions and types of construction. In high temperature regions, lower penetration grades were chosen to prevent grease softening while higher penetration grades were used in colder regions to limit the cracking deformation. Figure 4.3 shows the bitumen from industry was in grade 80/100 whereas the rest were B (40/50), F (60/70) and H (200/300) grades. This proved that even with the mixed of 5% polymer and the amount of bitumen content was reduced down to 20%, all the samples are still possessed the behaviour of original bitumen although resulting in different grade of bitumen. As bitumen content increased, the penetration value is decreased. A lower penetration value indicates the sample can withstand high temperature environments and by this property deformation, fatigue cracking of the binder mixture during performance can be avoided (Sekar,2015). The application of bitumen as waterproofing insulator not require a high grade of bitumen as it needs to be emulsify later on.

Carrera (2015) reported the selection of high grade bitumen (160/220) was vital in order to formulate bitumen emulsion. Therefore, in this study, bitumen with H (200/300) grade was chosen for the emulsification process.

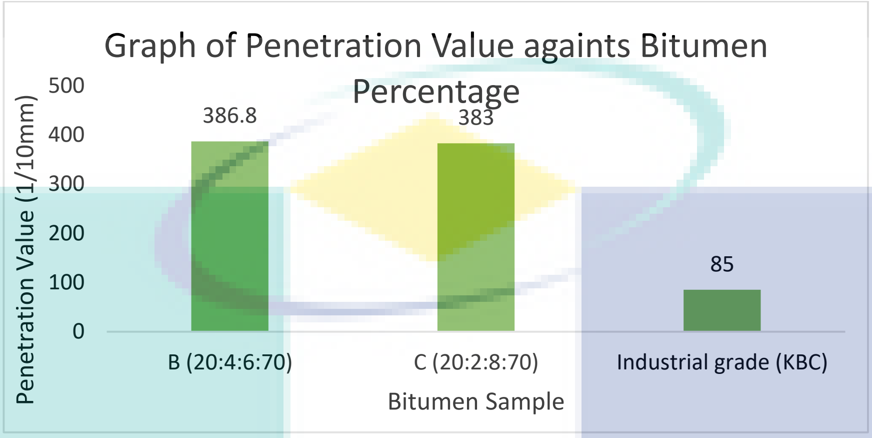


Figure 4.5: Graph of Penetration Value (1/10mm) against Bitumen Percentage (%) for B1 and C1

Figure 4.5 shows the comparison of penetration value of formulated bitumen from industrial waste and the industrial grade bitumen (KBC). Penetration value indicates grade and hardness of bitumen. From this two test, the bitumen that is formulated have almost the same properties with the industrial bitumen but it differ in terms of the grade of bitumen. This different types of bitumen grade will be used for different application in different climatic condition as well as different types of construction. In colder area, higher penetration grades were used in order to limit the cracking deformation whereas lower penetration grades usually were used in high temperature area to prevent grease softening.

However, this two formulation as bitumen cannot be used further in order to formulate the bitumen emulsion due to their characteristic have changed when the latex is added. Latex tends to increase the strength and quality of the bitumen itself and thus make it less interaction with others materials especially water. It only have cohesive properties and not adhesive. This two sample, B1 and C1 can be used for another application such as for road paving because the latex make it bind more stronger than the unmodified bitumen (Ruggles, 2005). So in this study, another formulation, S1 (20:2:39:39) is formulated using the same material and method but the latex is replace with the used oil. The appearance of the sample S is smooth and shiny and have a texture as the industrial grade bitumen.

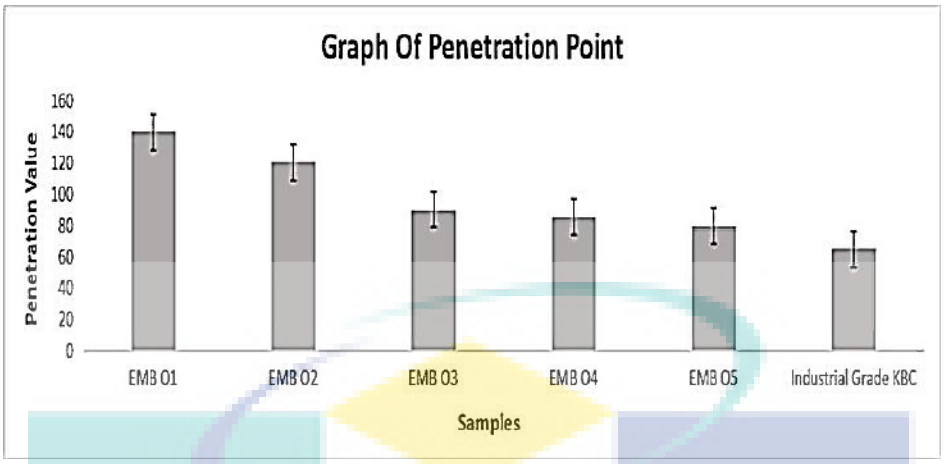


Figure 4.6: Graph of Penetration Point for EMB 01-EMB 05

The penetration value indicates the grade and hardness of bitumen. Figure above shows as bitumen percentage increases varying recycled oil from EMB01 to EMB05, the harder the emulsified bitumen to be penetrated due to its hard consistency resulting decrease in penetration point. Literature shows that for most of the higher temperature regions, lower penetration grades were chosen to prevent grease softening while higher penetration grades were recycled in colder regions to limit cracking deformation (Ali M, 2011). A lower penetration value as EMB05 can withstand higher temperature environments and by this property deformation, fatigue cracking of the binder during performance can be avoided. Moreover, EMB05 was selected due to its lower penetration point because it has a lower value of 80 mm compared to industrial grade KBC which is 65mm. Hence for the coating purposes, the application of bitumen as waterproofing insulator requires higher percentage bitumen to prevent cracking or deformation in structure as it dries on later. Moreover, formulated EMB (EMB01to EMB05) was done before emulsification process where it was not mixed with water resulting in exhibiting pure bitumen properties. Hence, it was only compared with industrial grade KBC instead Atlas bitumen which contains traces of water.

4.5.2 Softening Point (ASTMD36)

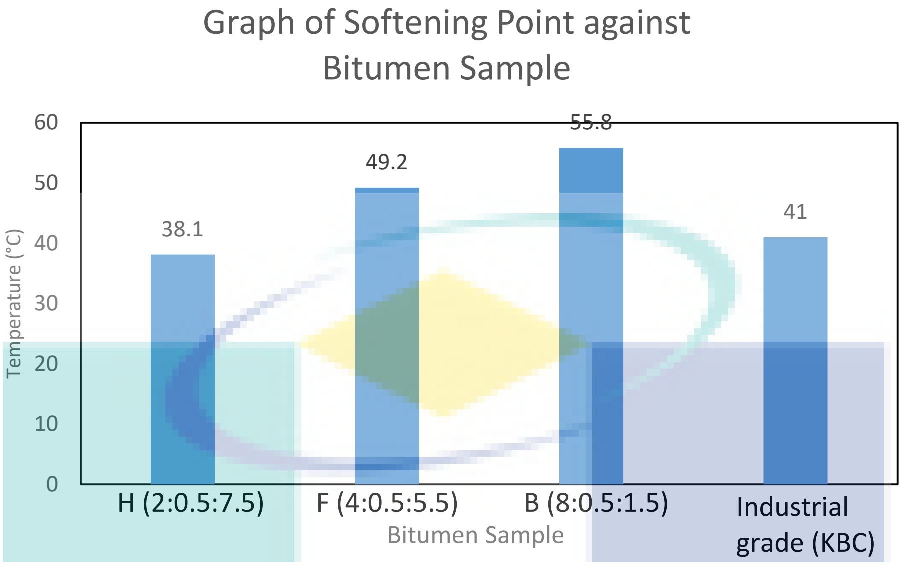


Figure 4.7: Graph of Softening Point (°C) against Bitumen Percentage (%) for B, F and H

Figure 4.6 shows the comparison of softening point of bitumen from industry and the bitumen formulated from industrial waste. It shows the temperature of the bitumen attains a particular degree of softening point under the specifications of test (Rao, 2007). Softening point also indicates the grade of bitumen which higher softening point is suitable for high temperature application. From figure 4.4, lower content of bitumen gave a low softening point. It shows the formulated bitumen were very fragile and easily pourable when it was heated up. Out of all the samples, the sample with 20wt% of bitumen (H) was the most sleet since it contained the highest amount of used oil so the polymer was easier to mix with the mixture. Thus, it was the most suitable sample for the emulsification process.

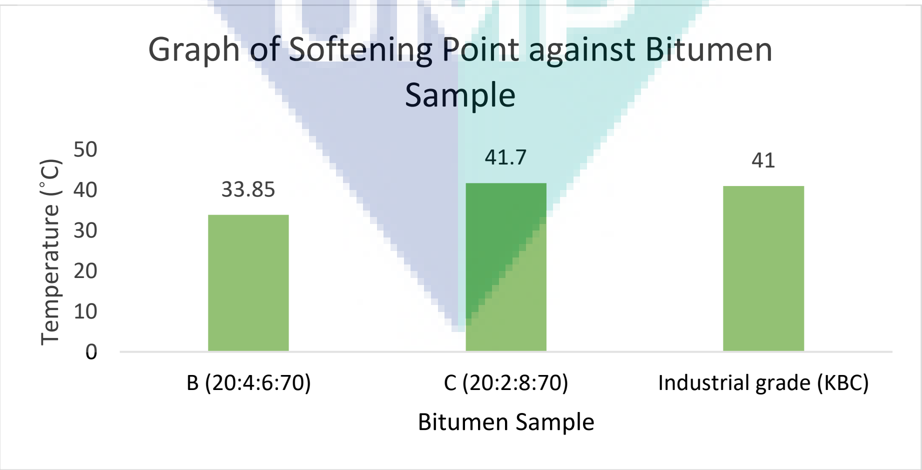


Figure 4.8: Graph of Softening Point (˚C) against Bitumen Sample Percentage (%) for B1 and C1

Figure 4.7 shows the comparison of softening point of industrial grade bitumen (KBC) and the formulated bitumen from the industrial waste. It shows the temperature of bitumen soften after its arbitrary softness point is reached under the specifications of test. Softening point also illustrate at which temperature the bitumen should be heated for various use applications. From figure 4.7 higher content of polyethylene gave a low softening point. It shows that the formulated bitumen were very fragile and easily pourable when it was heated up.

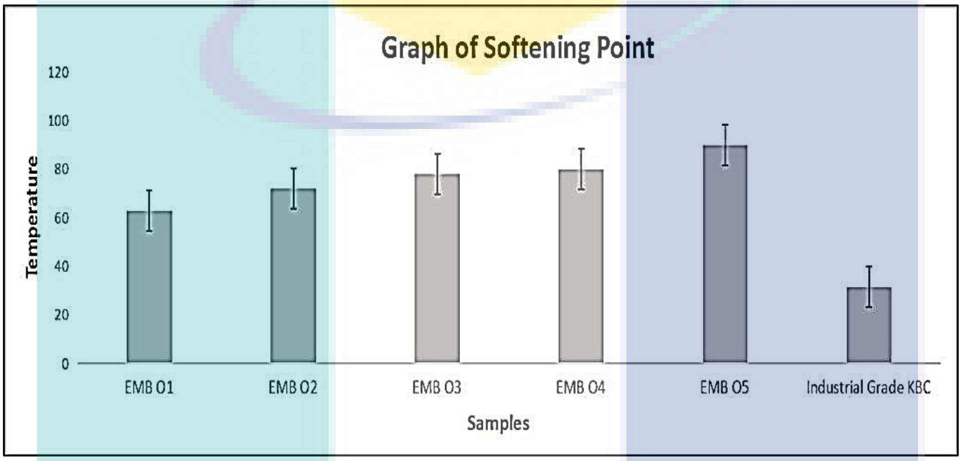


Figure 4.9: Graph of Softening Point for EMB 01-EMB05

Figure 4.6 showed the comparison of softening point of bitumen from industry and the formulated bitumen from industrial waste (EMB01 to EMB05). It shows that the temperature attains a particular degree of softening point under a specification of test. Softening point indicated the grade of bitumen in which higher softening point is suitable for higher temperature applications. From figure 1, the trend shows as the bitumen percentage increases from EMB01 to EMB05, the harder for the bitumen emulsion to get soften as temperature increases. It proved that the formulated bitumen EMB05 was viscous and has good texture when heated up resulting in efficiency for the coating and insulation purposes. Moreover, EMB05 was selected due to its higher softening point because it has a higher value of 90°C compared to industrial grade KBC which is 31.4 °C.Generally, by having a higher softening point specifies lesser temperature vulnerability make it more preferable in hot climate application (Cheng Y et al., 2018). Moreover, formulated EMB (EMB01 to EMB05) was done before emulsification process where it was not mixed with water resulting in exhibiting pure bitumen properties.

4.6 Formulation of Emulsified Modification Bitumen

From the list of characterization of modified bitumen as in phase 1 phase 2 and phase 3, seven types of modified bitumen have been selected for emulsification process to form Emulsified Modification Bitumen (EMB) which are formulation H, S1, EMB 01, EMB 02, EMB 03, EMB 04 and EMB 05. These seven formulation are chosen based on physical appearances, high penetration test value and low softening point.

The emulsification process for formulation H will be using non-ionic type emulsifier, polyethylenimine 80% ethoxylated solution to mix the bitumen with water whereby formulation S1 will be emulsified with three different types of emulsifier which are polyethylenimine 80% ethoxylated solution (non-ionic), abietic acid (cationic), and sodium dodeclsulphate (anionic) and all of this samples denoted as S1a, S1b and S1c. Similarly, formulation of modified bitumen EMB 01 to EMB 05 will be emulsified with abietic acid (cationic). Then the formulated EMB samples were compared with industrial grade bitumen emulsion from Atlas Kote. The sample then was observed on its colour, solubility of polymer and viscosity of the sample based on physical observation as shown in Table 4.11.

Table 4.12: Physical Properties of EMB Formulated

	Ratio	Emulsifier	Colour	Solubility	Viscosity
Industrial Grade (KBC)	-		Pure black	Medium	Low
EMB H (B: P: U)	20:5:75	Non-ionic	Brown	High	High
EMB S1a (B: P: C: U)	20:2:39:39	Non-ionic	Dark Brown	High	High
EMB S1b (B: P: C: U)	20:2:39:39	Cationic	Dark Brown	High	High
EMB S1c (B: P: C: U)	20:2:39:39	Anionic	Dark Brown	High	High
EMB 01 (B: U)	40: 60	Cationic	Dark Brown	High	High
EMB 02(B: U)	45: 55	Cationic	Dark Brown	High	High
EMB 03 (B: U)	50: 50	Cationic	Dark Brown	High	High
EMB 04 (B: U)	55: 45	Cationic	Dark Brown	High	High
EMB 05 (B: U)	60: 40	Cationic	Dark Brown	High	High

The emulsifying process required a continuous mixing and the right mixing temperature at 70°C. The continuous mixing was important factor to ensure the mixture was mixed homogenously. When polymer is used as a modifier, modified bitumen emulsion is prepared through the process of polymer mixing with bitumen by means of high shear and emulsification of polymer-modified bitumen. It is known that the difficulty of emulsification of modified bitumen increases with the concentration of emulsifier in base bitumen (Sitz & Maysville, 1991). Chai (2010) reported when the concentration of polymer is at 3–5%, the modified bitumen can be emulsified, but the product is not perfect in term of its storage stability. However, the modified bitumen was added with used oil so that it can improves its properties and make it easier to emulsify by using 1% wt emulsifier. In this experiment, the EMB was obtained with the content of 39, 60 and 1wt%. of modified bitumen, water and emulsifier. All the formulated EMB samples were more viscous and soluble than industrial bitumen emulsion. Hence, it can be easily applied on an inclined surface (it is one of bitumen emulsion limit)(Glady et al, 2016).

Table 4.13: Physical Properties of selected EMB Formulation

	Ratio	Emulsifier	Colour	Solubility	Viscosity
EMB 01 (B: U)	40: 60	Cationic	Dark Brown	High	High
EMB 02(B: U)	45: 55	Cationic	Dark Brown	High	High
EMB 03 (B: U)	50: 50	Cationic	Dark Brown	High	High
EMB 04 (B: U)	55: 45	Cationic	Dark Brown	High	High
EMB 05 (B: U)	60: 40	Cationic	Dark Brown	High	High

From all the formulated bitumen emulsion samples EMB H, EMB S1a, EMB S1b and EMB S1c are neglected for further investigation. This is due to the shortage and change in demand towards raw material. Kemaman Bitumen Corporation (KBC) had stop the production of 80/100 grade of bitumen due to lower market demand. Instead, KBC just focusing on the production of 60/70 bitumen as its core product. The procurement of 80/100 bitumen from overseas will incur high cost due to the shipping fess. Thus, the needs of changing and altering the composition of the formulation by substituting 80/100 bitumen with 60/70 bitumen is crucial. Hence, only 5 formulations are considered for further analysis which are EMB 01, EMB 02, EMB 03, EMB 04 and EMB 05 as shown in Table 4.13.

4.7 Characterization of Emulsified Modification Bitumen

Table 4.14 summarized five EMB formulation with varying ratios of bitumen (60/70) and used oil. The samples are examined by using standard empirical tests such as Differential Scanning Calorimetry (DSC), viscosity test and oscillatory test to evaluate the properties of Emulsified Modification Bitumen (EMB).

Table 4.14: Ratio of Emulsified Modification Bitumen (EMB) formulation (362 g).

Ratio weight (wt.%)	33:50:0.8:16.2 (B: U: AA: DI)	37:46:0.8:16.2 (B: U: AA: DI)	41:41:0.8:16.2 (B: U: AA: DI)	46:37:0.8:16.2 (B: U: AA: DI)	50:33:0.8:16.2 (B: U: AA: DI)
Sample code	EMB 01	EMB 02	EMB 03	EMB 04	EMB 05
Bitumen (60/70) (g)	120.0	135.0	150.0	165.0	180.0
Used Oil (g)	180.0	165.0	150.0	135.0	120.0
Abeitic Acid (g)	3.0	3.0	3.0	3.0	3.0
Deionised Water (g)	59.0	59.0	59.0	59.0	59.0

*B: U: AA: DI = Bitumen: Used oil: Abeitic Acid: Deionised water

4.7.1 Differential Scanning Calorimetry (ASTM D314)

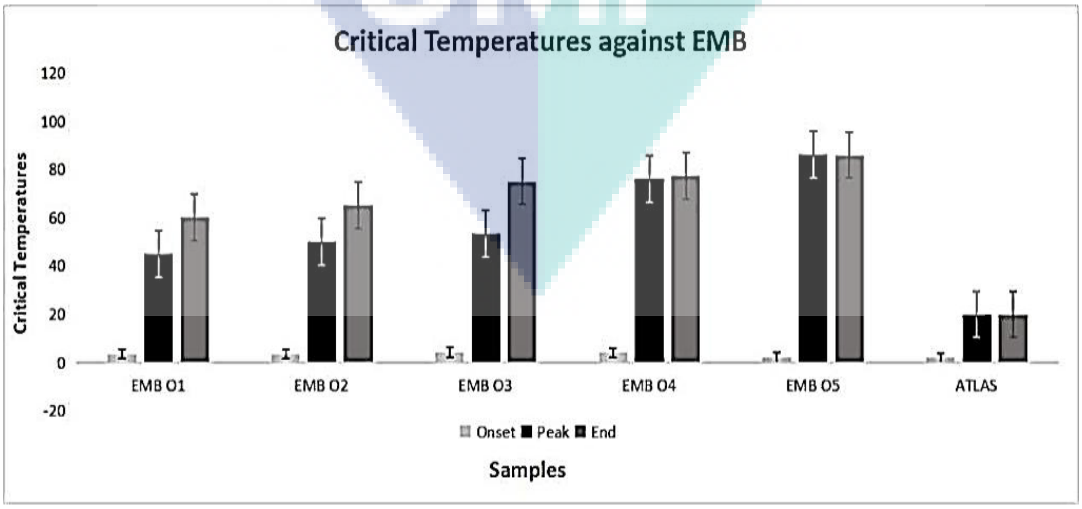


Figure 4.10: Critical Temperatures against EMB

Demulsification of emulsified bitumen may form with the increase of temperature or heat. Differential scanning calorimeter is used to study material temperature change against heat flow (Hou S et al., 2018) and the analysis was performed on emulsified bitumen to characterize its thermal transition and thermal stability. The ascending peak describes exothermic and descending peaks designate endothermic process with the area of the peak indicates enthalpy change (ΔH). Figure 4.10 showed the critical temperatures for EMB01 to EMB05, with industrial Atlas bitumen as benchmark include onset, peak, and end temperatures for all the samples. Onset is the start of demulsification process, peak indicates maximum rate of breaking for oil, water structures and end is where the demulsification process ends.

From EMB01 to EMB05 emulsified bitumen formulation, the temperature interval of demulsification from onset to end was from 60 °C increasing gradually to 80°C which shows that as bitumen percentage increases in sample EMB01 to EMB05, demulsification occurs at higher temperatures. Demulsification indicates separation of water from the oil and the graph shows at which temperature the demulsification occurs. EMB05 has higher demulsification process temperature at 80°C as compared to other formulated bitumen emulsion meanwhile comparing with Atlas which occurs at 20°C. In addition, the temperature difference between peak and end is approximately from 20 °C to 2 °C as the trend increases from EMB01 to EMB05. This implied how fast the demulsification process would terminate after the peak temperature. The lower the temperature difference between peak and end, the faster the demulsification process stops as it prevents O/W structures from destroyed during demulsification process (Hou S et al., 2018). Hence, emulsified bitumen EMB05 with 2 °C which has lower temperature difference yielded the highest critical temperatures, indicate lowest temperature susceptibility as it has shorter period of time of demulsification so that it is suitable for stable structure of coating purposes. By comparing with Atlas Bitumen which has 0 °C of temperature difference, EMB05 shows slightly lower performance than Atlas Bitumen. Moreover, the emulsified modified bitumen (EMB01 to EMB05) after mixed with water exhibits coating application properties. Hence it was only compared with Atlas bitumen which has similar application properties instead of raw bitumen KBC.

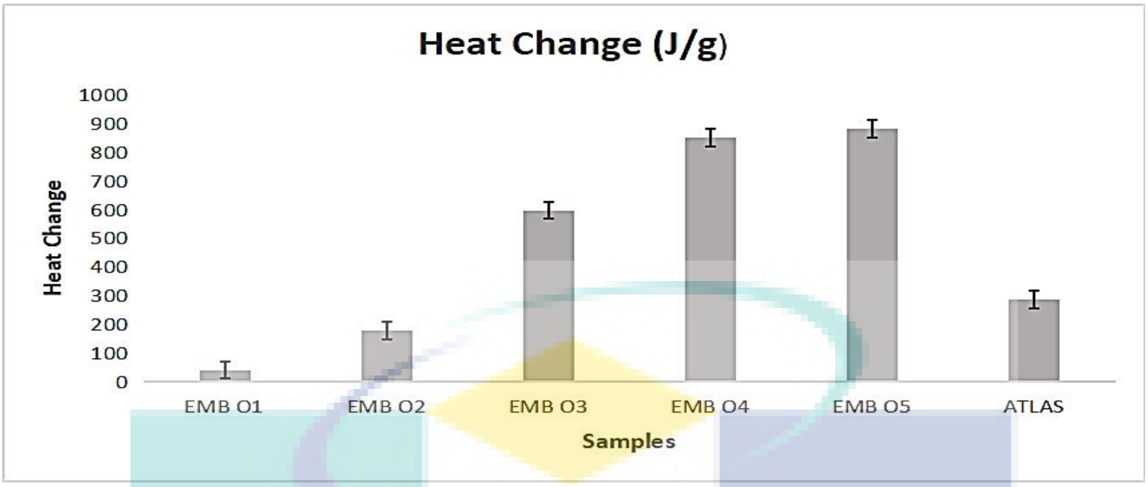


Figure 1.11: Graph of Heat Change

Additionally from Figure 4.11, as bitumen percentage increases from EMB01 to EMB05, the absolute ΔH value ((|ΔH|) heat change increases since higher content of bitumen withstand higher temperatures. Heat change indicates the energy required for demulsification process (Amman S et al., 2018). The higher the absolute ΔH value ((|ΔH|) heat change from EMB01 to EMB05, the higher energy required for demulsification process. This showed that EMB05 which has 1000 J/g had a higher thermal stability due to the increase in H value from EMB01 to EMB04 and even compared to Atlas bitumen which has lower ΔH value of 286 J/g. Hence, the EMB05 can withstand higher temperature in terms of heat changes. The heat changes in coating are important to prevent degradation of coating and substrate via embrittlement, lower melting temperatures, and lower creep resistance ("National Research Council", 1996).

4.7.2 Viscosity Test (ASTM D4402)

Table 4.15: Average Viscosity of Sample

Sample	Viscosity (pa.s)
EMB 01	7.191
EMB 02	10.367
EMB 03	12.72
EMB 04	16.063
EMB 05	19.617
ATLAS	20.212

The viscosity test of the formulated bitumen was conducted to measure and evaluate its resistance to flow and it to deformation by internal and external force (Yero S & Hainin M, 2011). The deformation that may varies with load and it may effect uneven spraying by avoiding run off during spraying for coating and insulation purposes. Hence to control the quality of end product, this test was conducted to determine the viscosity of the samples and made a comparison with Atlas bitumen for its similar application. Table 4.15 showed the viscosity of all the emulsified bitumen samples formulated and industrial Atlas Bitumen. The table showed increasing trend from EMB01 to EMB05. As the bitumen percentage increases, the emulsion become more viscous. Hence, EMB05 was selected since it showed higher viscosity around 19.617 pa.s and by bench-marking Atlas Bitumen which has similar industrial applications, it shows nearest reading around 20.212 pa.s. Moreover, the emulsified modified bitumen (EMB01-EMB05) after mixed with water exhibits coating application properties. Hence it was only compared with Atlas bitumen which has similar application properties instead of raw bitumen KBC.

4.7.3 Oscillatory Test (ASTM D7271)

Fundamental measurements of performance based tests are related with the physicochemical properties such as flow and deformation characteristics of EMB (Rosato D V., 2003) (Remisova E & Holy M, 2017). Rheological properties can be described by material's deformation properties in response to a certain load (Murata H, 2012). Oscillatory rheology used for studying the mechanical behaviour as viscoelastic strength of emulsified bitumen for detecting large strain deformations, stability and resistance (Zapata et al., 2015; Macosko, 1994). Figure 5 showed temperature sweep results from EMB01 to EMB05 bench-marking with ATLAS. G' showed elastic modulus (solid-like) and G'' showed viscous modulus (liquid-like). As the temperature increases, there was an intersection which is crossover point (G'=G" or tan δ =1 or δ = 45°) where the viscoelastic behaviour changes from a dominant elastic solid-like behaviour (G'>G") to a dominant viscous, liquid-like (G">G'). This crossover point is also called the gel point or the characteristics modulus, and has been used in emulsion rheology to correspond to the change of behaviour from a more solid-like to a liquid-like different emulsions (Zhai et al., 2006). The gel point may be related to the interaction of particles in emulsified bitumen. As bitumen percentage increases from EMB01-EMB05, gel point temperature increase as the emulsion is harder to melt. The highest gel point in EMB05, 28°C known as adequate room temperature indicated that before gel point it behaved like solid to prevent sedimentation and after gel point it behaved as a flow as fluid of spray nozzle and can evenly be sprayed. The gel point reduced as EMB04, 03, 02 and 01 sequentially and these emulsions are inefficient due to its gel point lower than room temperature. Moreover, it also indicated that the lower gel point may shorten breaking time of emulsion which eventually causes fast separation of the material. Hence, higher gel point EMB 05 indicated viscoelastic stability at room temperature.

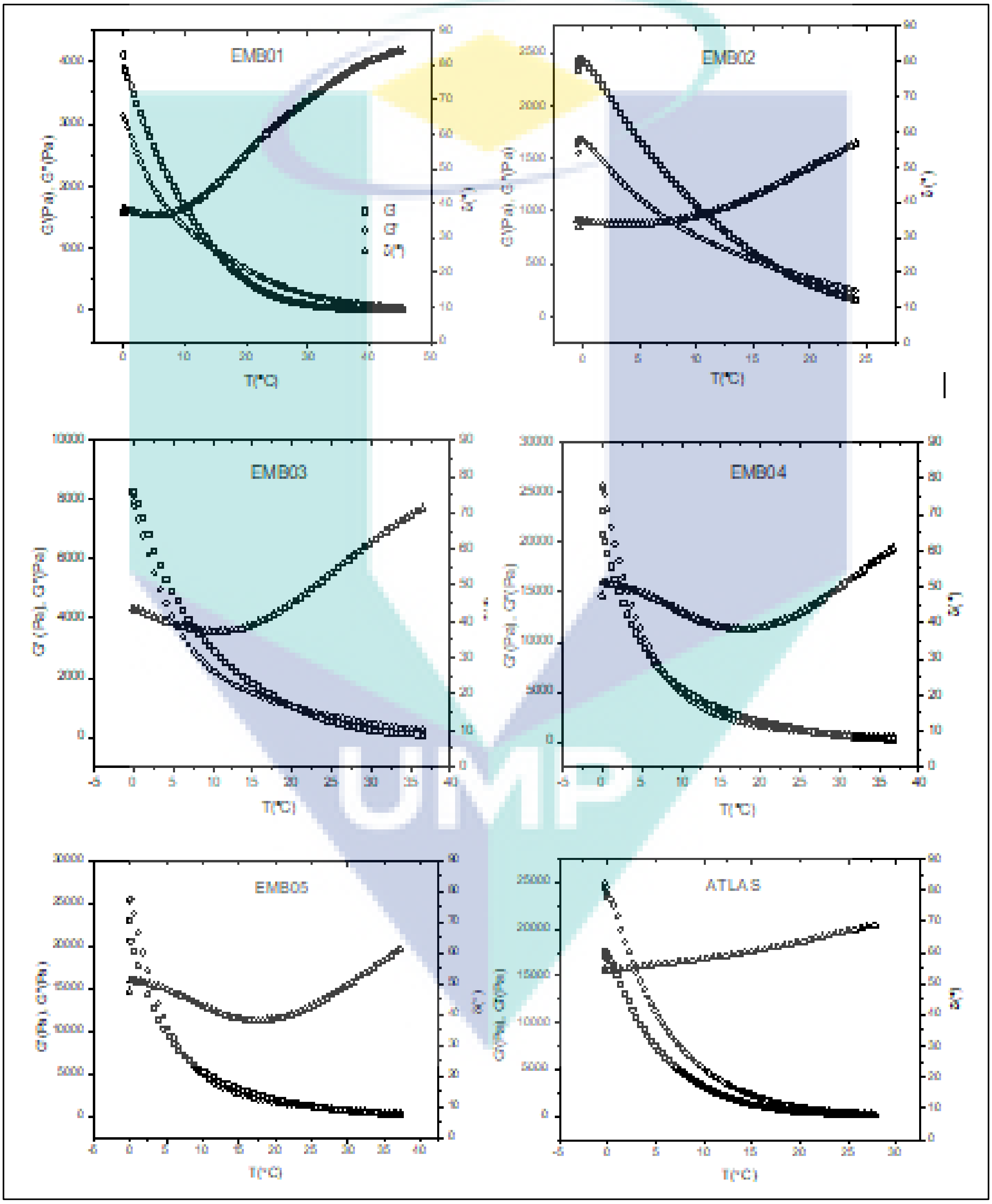


Figure 4.12: Graph of Oscillatory Test

4.8 Performance Test

4.8.1 Adhesion Test (ASTM D 3359-09)

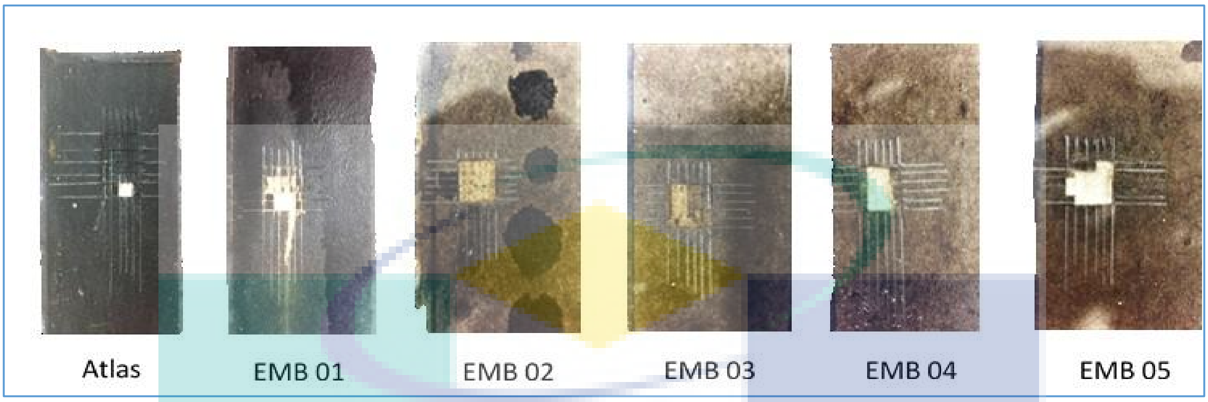
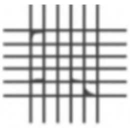
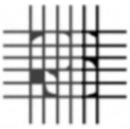
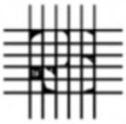
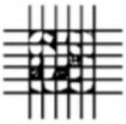
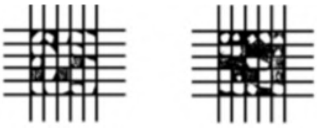
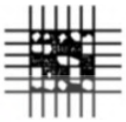


Figure 4.13: Standard test method for adhesion (ASTM D 3359-09) for formulated bitumen emulsion and Atlas.

Figure 4.13 showed the result of adhesion test for five formulated bitumen emulsion and industrial grade of bitumen emulsion (Atlas). The classification of the adhesion test result will be classified according to Table 4.16.

Table 4.16: Classification of adhesion test where 5B is the best and 0B is the worst (Weishaar, 2018)

Classification of Adhesion Test Result		
Classification	Percent area removed	Surface of cross-cut area from which flaking has occurred for six parallel cuts and adhesion range by percent
5B	0% None	
4B	Less than 5%	
3B	5-15%	 
2B	15-35%	 

1B	35-65%	
0B	Greater than 65%	

From Table 4.16, the classification of industrial grade bitumen emulsion (Atlas) was 3B where the total area that has been removed is between 5%-15%. Meanwhile, the classifications of EMB 01, EMB 02, EMB 03, EMB 04 and EMB 05 are the same which are 0B where the total area that has been removed is greater than 65%. From this result, it is clearly shown that industrial grade bitumen emulsion (Atlas) has the best adhesion towards the substrate (drywall). In the meantime, the best formulated bitumen emulsion in term of adhesiveness is EMB 04 where the percentage of removal area was approximately 66%. The result also suggested that EMB 02 has the poorest adhesion towards substrate as approximately 90% of the coated area has been removed through this standard test method. Table 4.4 summarized the adhesion test results for all samples.

Table 4.17: The summary of adhesion test results for all samples

Samples	Classification	Percent Area Removed (%)
EMB 01	0B	72
EMB 02	0B	90
EMB 03	0B	90
EMB 04	0B	66
EMB 05	0B	80
Atlas	3B	5-15

Poor adhesion is a property of coatings that can lead to the damage of the substrate as it is not able to protect the substrate from the surrounding environment such as water and heat. The poor adhesion of the material is due to the inadequate bonding between the coating and the substrate (Weishaar, 2018) (ASTM D3359, 2013). This factor can cause the coating material to flake off from the substrate. The ideal coating to protect the substrate from water and heat need to have even and consistent adhesion (Weishaar, 2018) (ASTM D3359, 2013). This is the property that shall be optimized for the Emulsified Modification Bitumen (EMB) been adopted for coating purposes.

4.8.2 Ageing

Ageing is one of the vital influential factor that alter the properties of bituminous materials. In a simple word, ageing will help to understand and describe the changes of the coating material (EMB) when it is exposed to the external effects with respect to time such as heat and sunlight. The external effects are vary according on location, altitude and season. Hence, simulation in the laboratory is critical to simulate the condition as closest possible to the real condition. To fulfil this criteria, the ageing test for the samples will be conducted at three different temperature which are 55 °C, 27 °C and 10 °C.

4.8.2.1 Accelerated Weathering Tester

The purpose of this machine is to simulate the external weather conditions inside a control chamber. There are 4 controllable factors inside this machine which are UV lamps, heater, water and condensation. Heat is the only factor that can be combined with other factor. For the purposes of this experiment only 3 factor will be considered which are heat, condensation and UV light. The effect of water is neglected due to its complexity in analysing moisture damage with ageing (Tauste et al., 2018). Table 4.5 and Figure 4.2 highlighted the results of weight loss (%) of six bitumen emulsion samples within seven days in the accelerated weathering tester. Based on graph in Figure 4.2, the weight loss (%) for all bitumen samples are showing increasing trend. The results also provide an information that after seven days of testing, the EMB 01 is showing the highest weight loss (2.72%) followed by EMB 02 (2.42%), EMB 03 (2.34%), EMB 04 (2.25%), EMB 05(2.22%) and Atlas (2.09%). The ageing period for the bitumen emulsion also can be predicted by setting linear correlation from the graph in Figure 3. For this purposes, the best formulated bitumen emulsion in term of weight loss (EMB 05) will be chosen as a comparison to the industrial grade bitumen (Atlas). The linear equation for EMB 05 and Atlas are $y=0.339x-0.3231$ and $y=0.2341x-0.2386$. By setting the y-axis (weight loss) to 100%, the ageing period (days) can be determined. After a thorough calculation, the ageing period for EMB 05 is 296 days whereby the ageing period for Atlas is 428 days

Table 4.18: The weight loss (%) of formulated bitumen emulsion and Atlas in cooling within 7 days

Sample	Day 1 (g)	Day 2 (g)	Day 3 (g)	Day 4 (g)	Day 5 (g)	Day 6 (g)	Day 7 (g)
EMB 01	0.57	1.38	1.50	1.91	2.11	2.59	2.72
EMB 02	0.52	0.91	1.07	1.31	1.63	1.83	2.42
EMB 03	0.44	0.60	1.03	1.23	1.43	1.55	2.34
EMB 04	0.23	0.32	0.95	1.17	1.40	1.53	2.25
EMB 05	0.16	0.20	0.65	1.13	1.37	1.49	2.22
Atlas	0.08	0.08	0.50	0.67	1.00	1.17	1.38

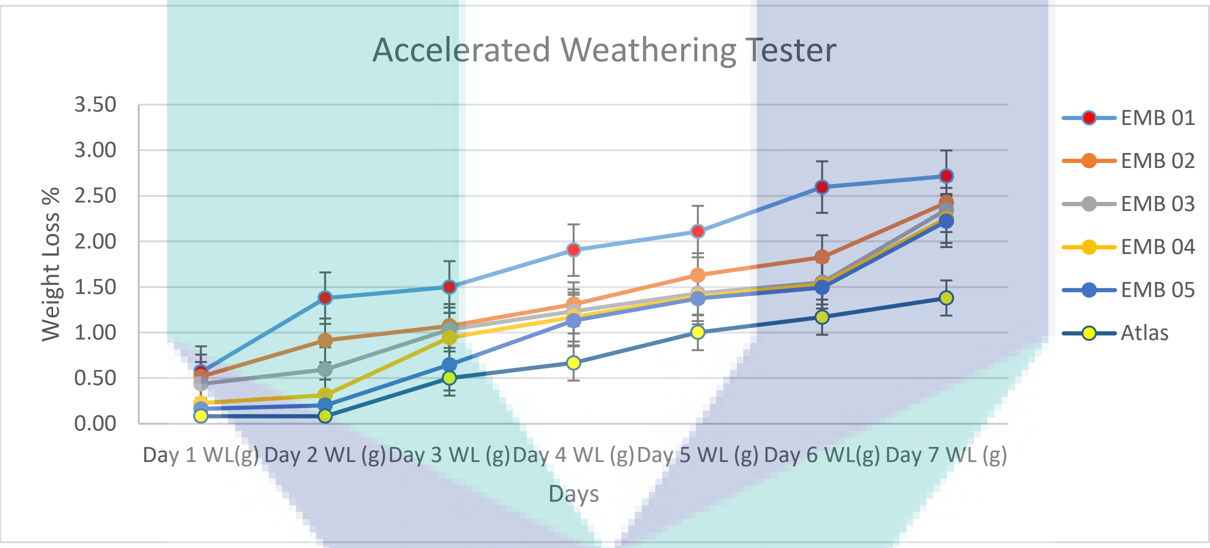


Figure 4.13: The graph of weight loss (%) against days for accelerated weathering tester

4.8.2.2 Natural Weathering at 27 °C

The ageing at 27 °C is chosen to study the effect of the EMB at ambient condition. This temperature has been chosen to correlate the ambient condition outside the building of operation theatre. Table 4.19 and Figure 4.14 highlighted the results of weight loss (%) of six bitumen emulsion samples within seven days for natural weathering at 27 °C. From Figure 4.14, the weight loss (%) for all bitumen samples are showing increasing trend. After seven days of testing, the EMB 01 is showing the highest weight loss (1.10%) followed by EMB 02 (0.98%), EMB 03 (0.86%), EMB 04 (0.78%), EMB 05(0.71%) and Atlas (0.42%). The ageing period can be predicted by setting linear correlation from the graph in Figure 4.14. The best formulated bitumen emulsion (EMB 05) will be chosen as a comparison to the industrial grade bitumen (Atlas). The linear equation for EMB 05 and Atlas are y=0.0905x-0.1484 and y=0.0595x-0.1191 which correlates to ageing period for EMB 05 at 1107 days and Atlas at 1683 days.

Table 4.19: The weight loss (%) of formulated bitumen emulsion and Atlas in natural weathering within 7 days

Samples	Day 1 (g)	Day 2 (g)	Day 3 (g)	Day 4 (g)	Day 5 (g)	Day 6 (g)	Day 7 (g)
EMB 01	0.04	0.20	0.35	0.43	0.55	0.67	1.10
EMB 02	0.04	0.15	0.26	0.41	0.49	0.64	0.98
EMB 03	0.04	0.12	0.20	0.27	0.43	0.59	0.86
EMB 04	0.04	0.12	0.17	0.25	0.41	0.54	0.78
EMB 05	0.04	0.04	0.04	0.12	0.25	0.46	0.54
Atlas	0.00	0.00	0.02	0.09	0.19	0.33	0.32

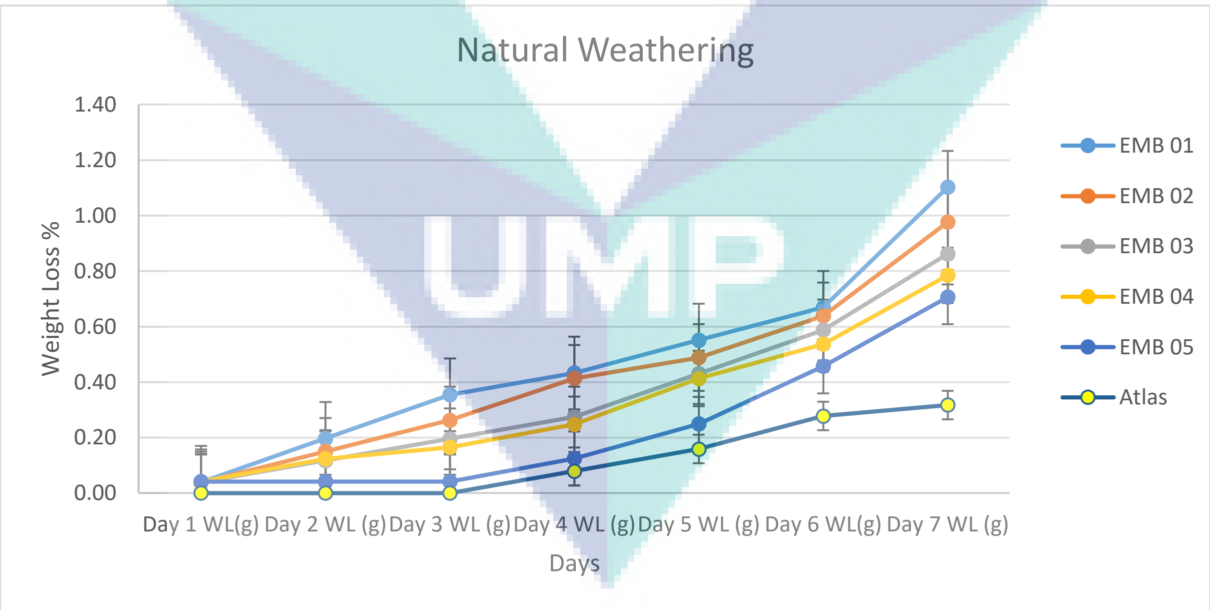


Figure 4.14: The graph of weight loss (%) against days for natural weathering.

4.8.2.3 Cooling at 10 ℃

The ageing test at 10 ℃ has been chosen to correlate the condition of operation theatre which normally operated at 16 ℃. Table 4.20 and Figure 4.15 highlighted the results of weight loss (%) of six bitumen emulsion samples within seven days for cooling at 10 ℃. Based on the graph, the weight loss (%) for all bitumen samples are showing increasing trend. The results also provide an information that after seven days of testing, the EMB 01 is showing the highest weight loss (1.15%) followed by EMB 02 (1.07%), EMB 03 (0.91%), EMB 04 (0.55%), EMB 05(0.45%) and Atlas (0.37%). The ageing period for the bitumen emulsion also can be predicted by setting linear correlation from the graph in Figure 4. For this purposes, the best formulated bitumen emulsion in term of weight loss (EMB 05) will be chosen as a comparison to the industrial grade bitumen (Atlas). The linear equation for EMB 05 and Atlas are y=0.1123x-0.2594 and y=0.0673x-0.1559. By setting the y-axis (weight loss) to 100%, the ageing period (days) can be determined. After a thorough calculation, the ageing period for EMB 05 is 893 days whereby the ageing period for Atlas is 1488 days.

Table 4.20: The weight loss (%) of formulated bitumen emulsion and Atlas in cooling within 7 days

Sample	Day 1 (g)	Day 2 (g)	Day 3 (g)	Day 4 (g)	Day 5 (g)	Day 6 (g)	Day 7 (g)
EMB 01	0.03	0.03	0.24	0.38	0.45	0.87	1.15
EMB 02	0.00	0.00	0.21	0.36	0.43	0.79	1.07
EMB 03	0.00	0.00	0.07	0.10	0.26	0.46	0.91
EMB 04	0.00	0.00	0.06	0.10	0.22	0.35	0.87
EMB 05	0.00	0.00	0.00	0.06	0.16	0.32	0.78
Atlas	0.00	0.00	0.00	0.03	0.10	0.20	0.46

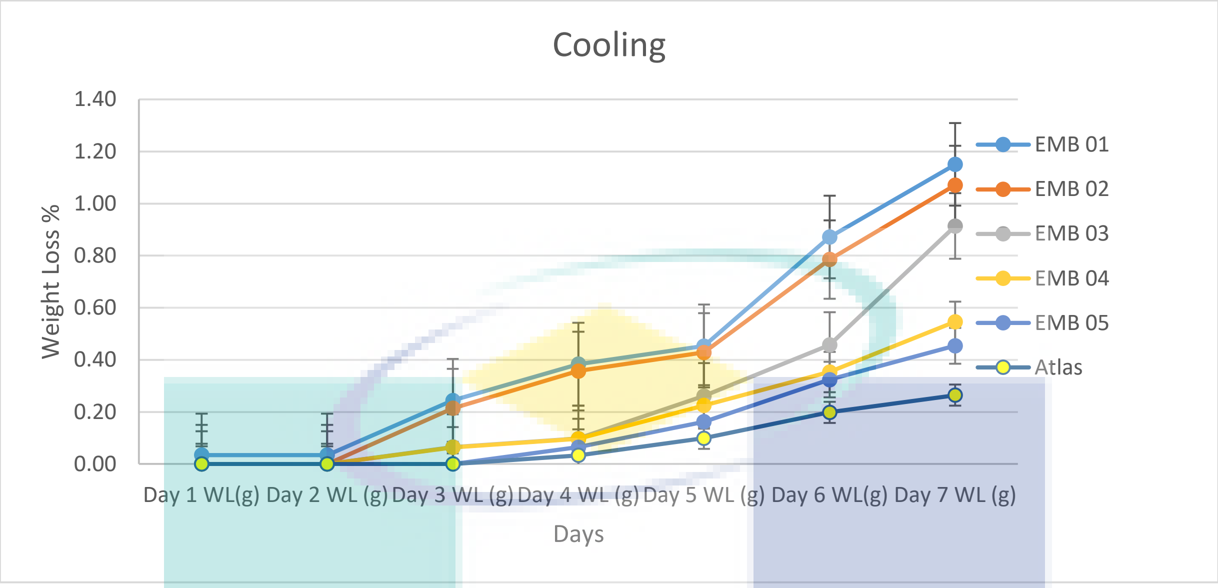


Figure 4.15: The graph of weight loss (%) against days for cooling.

Based on the ageing analysis at three different conditions, the industrial grade bitumen emulsion (Atlas) last longer compared to the best formulated bitumen emulsion EMB 05. This statement is supported by the fact that the ageing period for Atlas by using accelerated weathering tester, natural weathering and cooling are 428 days, 1683 days and 1488 days significantly. As a contrary, the ageing period for EMB 05 are 296 days, 1107 days and 893 days consecutively. This result also showing a trend where the ageing period under natural weathering will last longer followed by cooling and accelerated weathering tester. However, the ageing period by using natural weathering and cooling are not accurate as this condition neglect the effect of heating and condensation simultaneously. In the meantime, the result from accelerated weathering tester combined different ageing factors to bring the coated material on the substrate to similar external conditions but obtain results in a much shorter timeframe (Sadeq et al., 2017). Hence, the result from accelerated weathering tester will be the best option to measure the coating performances of the bitumen emulsion on the substrate.

There are three main factors that influence the ageing phenomena of bitumen emulsion which are physical (steric) hardening, evaporation and oxidation (Zaidullin et al., 2013) (Bell, 1989). The physical (steric) hardening is a process that responsible to the alteration of the rheological properties in the bitumen emulsion without changing its chemical composition (Santagata et al., 2016). This phenomenon develops rapidly at a lower temperature where the inner restructuring of the binder molecules happen (R.N. Hunter & A. Self, 2015). Even though its effects are moderate and comprise of the hardening effect yet its impact on the final characterization of the binder shall not be neglected (R.N. Hunter & A. Self, 2015)(Dessouky et al., 2015). The evaporation of volatile components in the bitumen emulsion such as saturates and aromatic is also the contributing factor for the ageing process (R.N. Hunter & A. Self, 2015) (Haleem & Mohan, 2012). It is mostly depending on temperature where most of the evaporation process occur at the mixing and laying on the substrate. Besides, when the operating temperature shows an increment 10-12 ℃ above the mixing temperature will double the emission of volatiles component (R.N. Hunter & A. Self, 2015). Other than that, the diffusion rate and the length or thickness of the diffusion path also play a substantial role in the evaporation of the volatiles component. However, the effects of evaporation of volatile components towards ageing is lower compared to oxidation. This is due to the facts that the amount of volatiles component in the bitumen have been restricted at the refining phase. This action is to ensure that the dosage of the volatiles is in a limited amount and to reduce the potential toxic fume emission during heating process (Tauste et al., 2018). The third ageing factor is bitumen oxidation. This phenomenon is mainly contributed by the thermal reaction between atmospheric oxygen and the bitumen components (Thur & Ston, 1941). This reaction results in the modification of the chemical structures. Similarly, it also affected by the photo-oxidation reaction occurs on the surface of the upper part of the bitumen emulsion. The effects of oxidation is faster and significance at high temperature compared to lower temperature (Thur & Ston, 1941).

4.8.3 Heat Transfer

Table 4.21 shows the value of heat transfer (q) in watt at four different temperatures. The condition is at steady state as it is hard to calculate at a transient condition. The flow of the heat transfer is assumed to be in 1D model. The effect of radiation in the calculation also been neglected as the effect of radiation on the samples is insignificance. Then, the heat transfer through the drywall is calculated based on equation 3.1 and 3.2 with $K_{\mathrm{bitumen}} = 0.5\frac{\mathrm{W}}{\mathrm{m\,K}}$, $K_{\mathrm{drywall}} = 0.27\frac{\mathrm{W}}{\mathrm{m\,K}}$, $h_{\mathrm{air}} = 0.27\frac{\mathrm{W}}{\mathrm{m^2\,K}}$, $t_{\mathrm{bitumen}} = 0.001\mathrm{m}$, $A = 0.005\mathrm{m}^2$ and $t_{\mathrm{drywall}} = 0.009\mathrm{m}$ (Zhang et al., 2017).

Table 4.21: Value of heat transfer, q for bitumen emulsion at varying temperature (℃)

Material	T_{oven} (℃)	$T_{bitumen}$ (℃)	$T_{drywall,top}$ (℃)	$T_{drywall,bottom}$ (℃)	q_{total} (W)
Uncoated	60.00	0.000	58.37	57.33	1.54
EMB 01		56.83	56.67	56.30	1.50
EMB 02		57.60	57.10	56.60	1.35
EMB 03		57.20	56.70	56.20	1.31
EMB 04		56.70	56.20	55.70	1.26
EMB 05		55.50	55.00	54.50	1.14
Atlas		58.17	57.80	57.27	1.09
Uncoated	45.00	0.00	40.20	35.30	0.98
EMB 01		41.67	41.50	36.70	0.91
EMB 02		41.83	41.77	37.90	0.91
EMB 03		42.07	41.93	38.23	0.87
EMB 04		42.17	42.07	38.23	0.80
EMB 05		42.00	41.90	39.93	0.79
Atlas		42.00	41.93	39.33	0.71
Uncoated	30.00	0.00	25.40	20.37	0.99
EMB 01		28.80	28.47	28.33	0.90
EMB 02		28.83	28.60	28.27	0.85
EMB 03		28.67	28.43	28.17	0.84
EMB 04		28.83	28.63	28.30	0.77
EMB 05		28.87	28.70	28.23	0.70
Atlas		27.83	27.65	27.19	0.64
Uncoated	27.00	0.00	22.40	17.47	0.97
EMB 01		25.28	24.97	24.47	0.88
EMB 02		25.57	25.33	24.67	0.81
EMB 03		25.58	25.37	25.10	0.77
EMB 04		25.10	24.90	24.53	0.69
EMB 05		25.95	25.80	25.07	0.65
Atlas		25.47	25.33	24.30	0.57

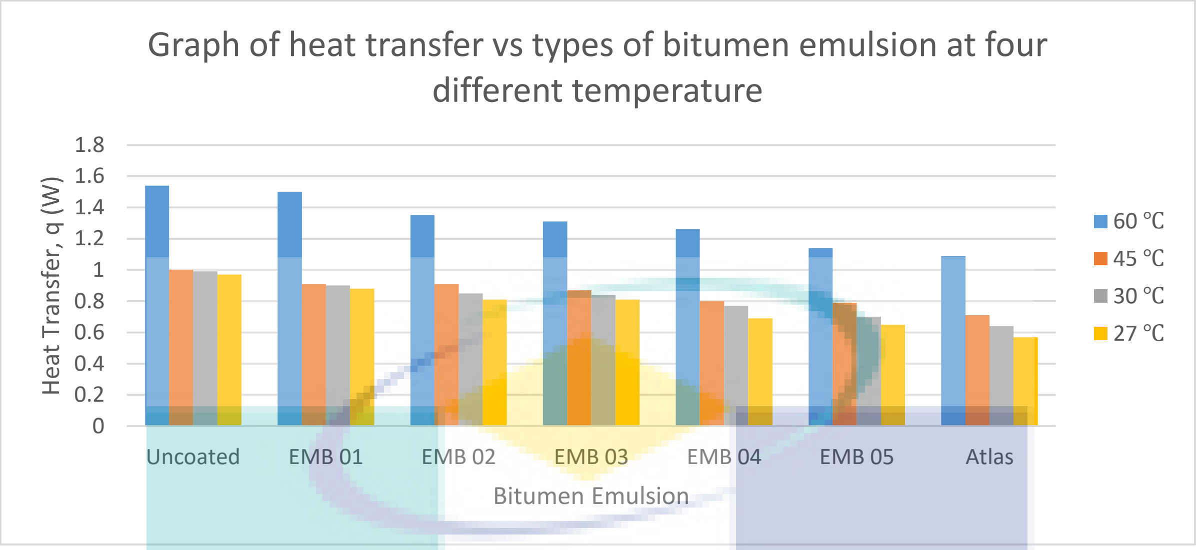


Figure 4.16: The graph of heat transfer, q (W) for different types of bitumen emulsion at four different temperature (°C)

Figure 4.16 showed a downward trend for the amount of heat transfer through the drywall. The graph also stated that the coated material (bitumen emulsion) do help in reducing the amount of heat transfer (q) through the drywall. Atlas is showing the best performances as heat insulator at all temperatures followed by EMB05, EMB04, EMB03, EMB02 and EMB01. From the trend it can be concluded that the ability to insulate heat is increasing with the increment of bitumen composition. There are two mode of heat transfer being focus in this study which are conduction and convection. According to the governing equation 1.1 and 1.2, the value of heat transfer (q) is directly proportional to the change in temperature (Zhang et al., 2017). According to the data, the higher composition of bitumen (EMB 05) help to minimize the changes in the temperature (ΔT) significantly compared to the lower composition of bitumen coating and uncoated drywall. Thus, the experimental value supports the theoretical evidence.

4.9 The Effect of Different Types of Emulsifier on EMB

To further understand the effect of emulsifier on the performance of the bitumen emulsion, 3 new emulsifiers have been tested which are 2-bromostearic acid, didoceldimethylammonium and polyethylene glycol. These are clearly shown as in Table 4.22.

Table 4.22: The formulation of EMB from 3 different types of emulsifier

EMB types	Type of Emulsion	Raw Material	Ratio
EMB A	**Anionic** 2-Bromostearic acid	• Bitumen grade 60/70 • Recycle used oil • Anionic emulsifier • Deionized water	Bitumen: 180g Used oil: 120 g Emulsifier: 3g Deionized water: 59 ml
EMB B	**Cationic** Didodecyldimethylammonium bromide	• Bitumen grade 60/70 • Recycle used oil • Cationic emulsifier • Deionized water	Bitumen: 180g Used oil: 120 g Emulsifier: 3g Deionized water: 59 ml
EMB C	**Non-ionic** Polyethylene glycol hexadecyl ether	• Bitumen grade 60/70 • Recycle used oil • Non-ionic emulsifier • Deionized water	Bitumen: 180g Used oil: 120 g Emulsifier: 3g Deionized water: 59 ml
Control sample	**No emulsion**	Bitumen grade 60/70 only mix with used oil	Bitumen: 180g Used oil: 120 g
Atlas	Industrial bitumen emulsion	ATLASKOTE	-

4.9.1 EMB Characterization

4.9.1.1 Viscosity

Table 4. 13: Viscosity data

Type of formulation	Viscosity (cP)
EMB A (Anionic)	47980.68
EMB B (Cationic)	41433.72
EMB C (Non-ionic)	46138.06
Control sample (without emulsion)	63346.29
Atlaskote	367.75

Table 4.23 above shows the viscosity data for all three types of EMB formulations, control sample and also industrial bitumen emulsion from Atlaskote. The viscosity of bitumen is its internal resistance to flow or measure of it resistance to deform either shear stress or tensile stress. The lower the viscosity reading of the EMB formulations, the better the performance for the coating application as the internal resistance to flow is lower (Yero & Hainin, 2017). The deformation characteristics may varies with load and it may give effect in uneven spraying by avoiding run off during spraying for coating and insulation purposes. Hence to control the quality of end product, this test was conducted to determine the viscosity of the samples and made a comparison with Atlas bitumen for its similar application. Table 4.23 shows a very high reading of all three EMB formulations using different type of emulsifiers. Among all of the three type of EMB formulations, EMB B showing the lowest reading of viscosity with the value of 41433.72 cP. However, when it being compared to the bench-marked industrial bitumen emulsion from Atlaskote, the EMB B is still very far away from the reading which is at low value of 367.75 cP. This high value of viscosity will result in difficulties to apply for coating because of high internal resistance to flow and not feasible to be used especially for spray coating purpose (C.J. Li et al., 2010). High viscosity also will result in uneven coating. For further improvement on the EMB formulations for its very high reading of viscosity, another additional solvent will be added to reduce its viscosity and make if feasible enough to be applied for the coating purpose.

4.9.1.2 Moisture Content

Moisture content of the samples were being analyzed through conventional method of oven-dried method. The oven-drying methodology consists of heating by convection with forced or circulating hot air. The accuracy and moisture range that oven-drying techniques offer is very similar to other thermogravimetric methods. Table 4.24 below shows the moisture content data of formulated EMB, control sample and industrial bitumen emulsion (Atlaskote).

Table 4. 24: Moisture content in the formulations

Sample	Moisture content (%)
EMB A	21.88
EMB B	21.88
EMB C	21.22
Control sample	14.81
Atlaskote	40

The relationship of moisture and viscosity can be summarized as the moisture content increase, the viscosity decrease (Yanniotis et al,. 2006). From Table 4.24, it can be observed that the sample having the highest moisture content is the sample from industrial bitumen emulsion (Atlaskote) while the lowest moisture content is the control sample. The highest moisture content in Atlaskote bitumen emulsion sample is having the lowest viscosity value of 367.75 cP while the lowest moisture content of control sample is having the highest viscosity value as high as 63346.29 cP.It is proven that the higher the moisture content in a sample, the lower the viscosity value. So, in further improvement for the EMB formulations, the moisture content need to be increased by adding more solvent in order to sustain low value of viscosity so it would be feasible for coating application.

4.9.1.3 Oscillatory Test

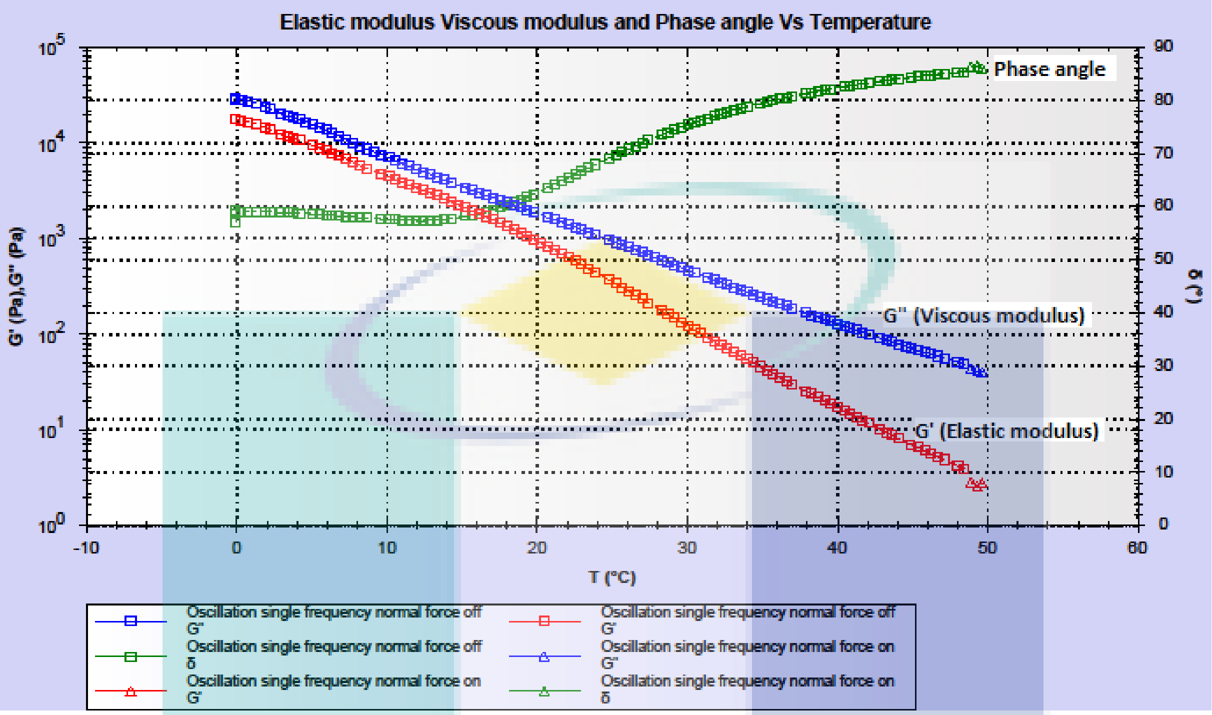


Figure 4. 17: Elastic-viscous modulus data for EMB A over temperature

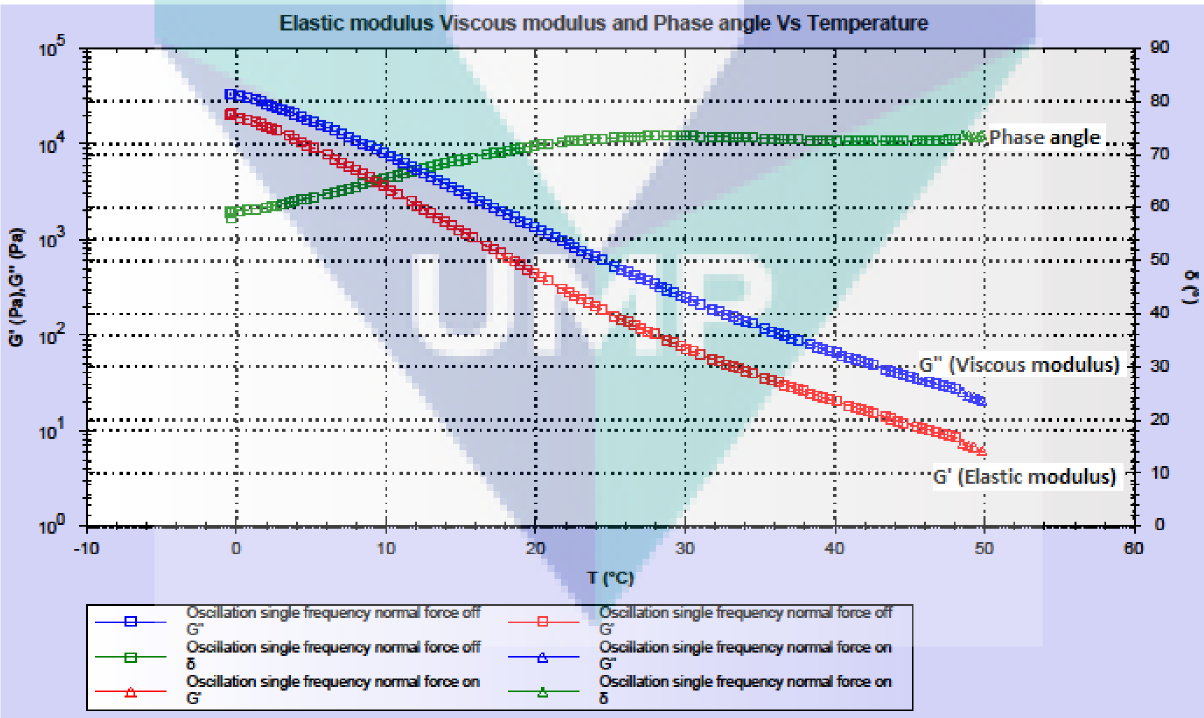


Figure 4. 18: Elastic-viscous modulus data for EMB B over temperature

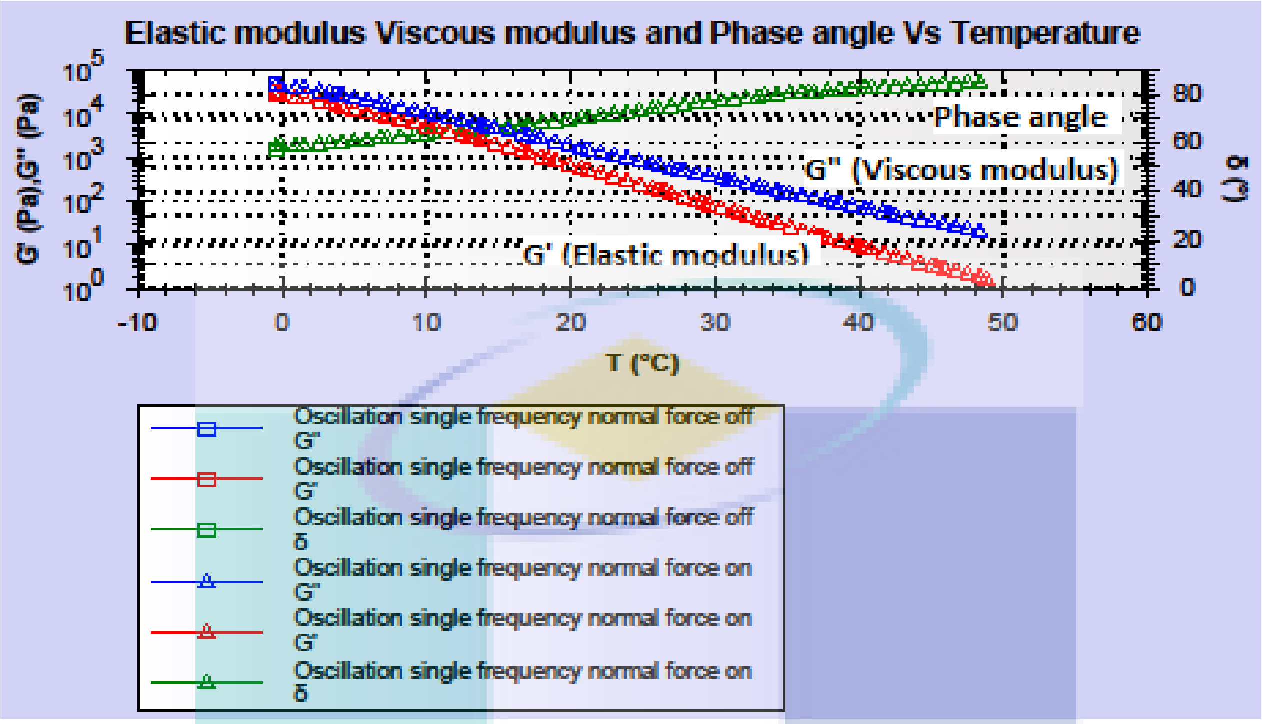


Figure 4. 19: Elastic-viscous modulus data for EMB C over temperature

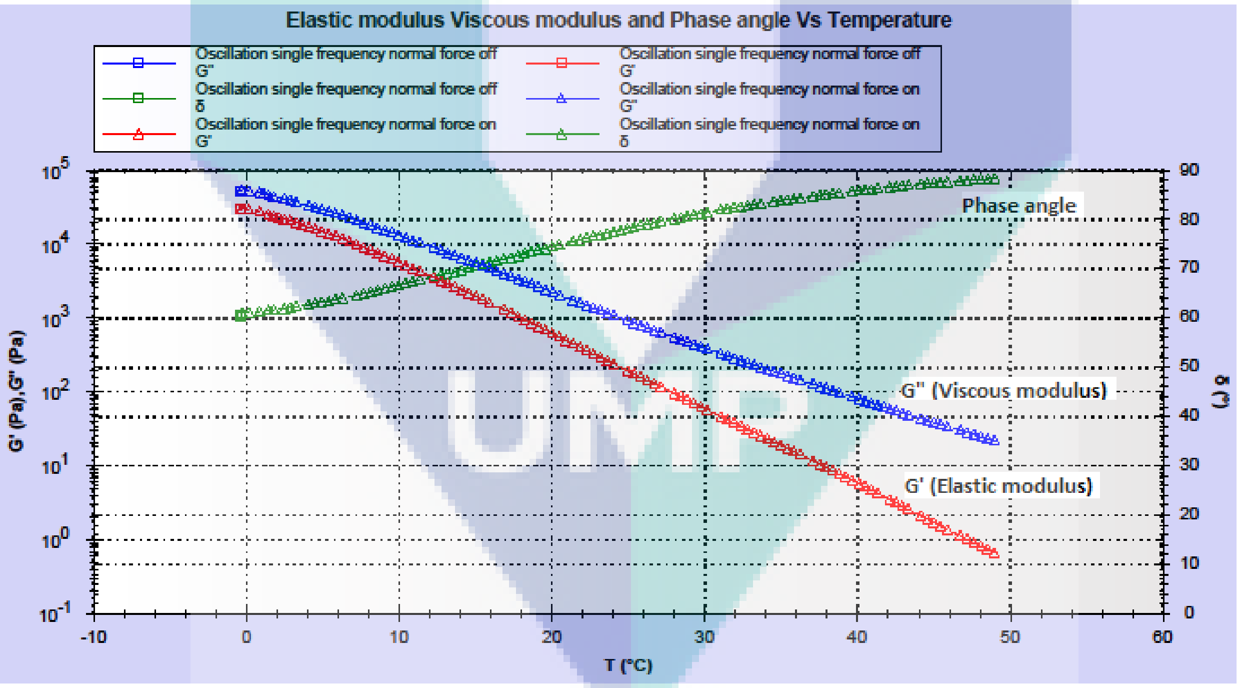


Figure 4. 20: Elastic-viscous modulus data for control sample over temperature

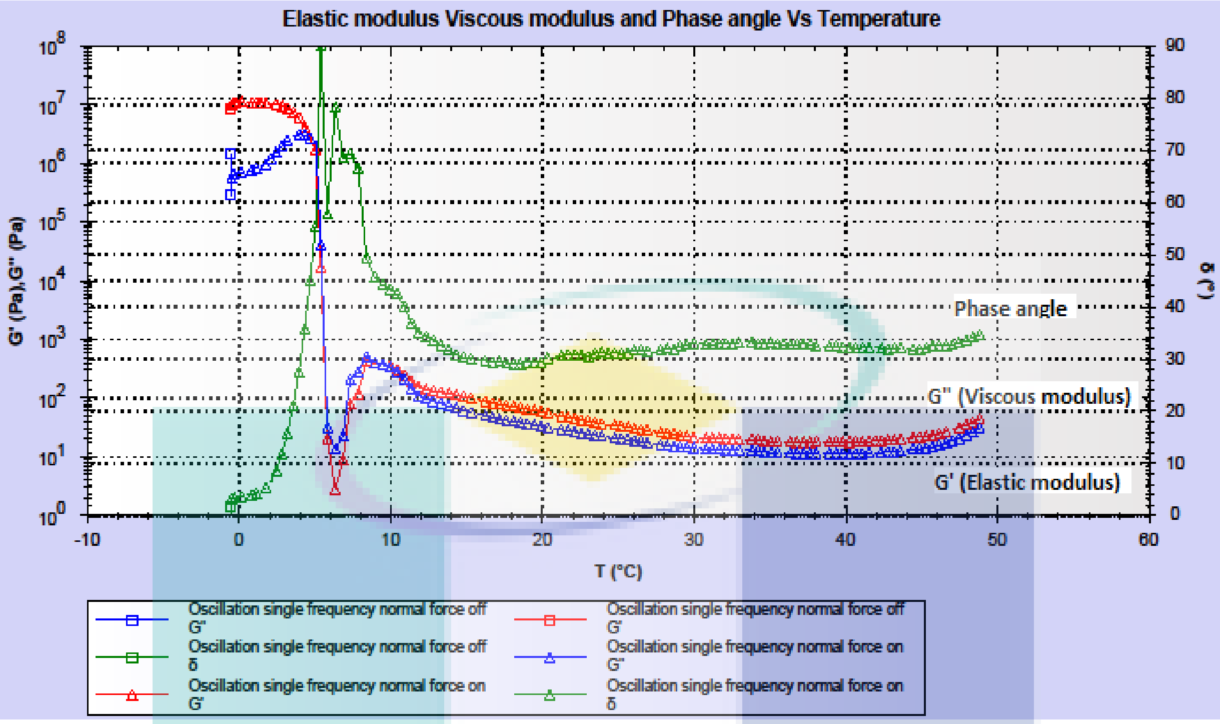


Figure 4. 21: Elastic-viscous modulus data for Atlaskote over temperature

Oscillatory rheological is used for studying the mechanical behavior as viscoelastic strength of emulsified bitumen for detecting large strain deformations. Figure 4.17-4.21 above shows temperature sweep results from three types of EMB formulations, control sample and bench-marking with Atlas. From the trend in the graph, G' is representing elastic modulus (solid-like) and G'' is representing viscous modulus (liquid-like). As the temperature increases, there was an intersection which is crossover point (G'=G" or tan δ =1 or δ = 45°) where the viscoelastic behavior changes from a dominant elastic solid-like behavior (G'>G") to a dominant viscous, liquid-like (G">G') (Zhai, 2006). This crossover point is also called the gel point or the characteristics modulus, and has been used in emulsion rheology to correspond to the change of behaviour from a more solid-like to a liquid-like different emulsion (Zhai, 2006). Among the three types of EMB formulations, EMB B showing the best result as the temperature increase, the slope of G' with G" getting closer as compared to EMB A and EMB C showing that it will deform to solid faster at certain extent and it is the closest trend to Atlas.

4.9.1.4 Flash Point

All three type of Emulsified Modified Bitumen (EMB) were being tested for their flash point together with the control sample and bitumen emulsion from the industry (Atlaskote). Table 4.4 below shows the reading of flash point for all of the samples. From the flash point readings, it shows that all of the samples having a very high flash point reading which all of it having flash point above 200°C and EMB B gives the highest reading of flash point from all those three type of formulated EMB. It is very important for the formulated EMB to have a very high reading of flash point in order to sustain the application for coating at normal room temperature and normal atmosphere temperature for exterior coating purpose.

Table 4. 25: Flash point data of formulated EMB

Sample	Flash point (°C)
EMB A (Anionic)	200.2
EMB B (Cationic)	208.1
EMB C (Non-ionic)	202.0
Control sample (without emulsion)	250.0
Atlaskote	267.3

4.10 Performance test

Performance test is the main part analysis of this research in order to determine which emulsifier works the best for the EMB formulation. Three type of analysis have been conducted which are stability test, drying rate performance and lastly the adhesiveness properties.

4.10.1 Stability performance

The stability test was being analyzed by observing the volume of water separated from the water-in-oil (W/O) mixture after three days. The percentage of water separated is the best indicator of emulsion stability (Nour & Rosli, 2006). The amount of water separation in percent was calculated as separation efficiency (e) from the volume of water observed in the measuring cylinder and calculated as equation (1) as follow:

$$\%\ water\ separation, e = \frac{Volume\ of\ water\ resolved, mL}{Original\ volume\ of\ water, mL}\ x\ 100\ (1)$$

Table 4. 26: Stability result for emulsion analysis

Sample	Volume of water resolved, mL	% water separation, e
EMB A (Anionic)	1	1.69
EMB B (Cationic)	16	27.11
EMB C (Non-ionic)	30	50.85
Control sample (Without emulsion)	0	0
Atlaskote (Industrial)	0	0

*(Original volume of water = 59 mL)

Table 4.26 above shows the stability data which indicating the emulsion stability in the bitumen emulsion mixture. Emulsifiers work by forming physical barriers that keep droplets from coalescing. An emulsifier contains both hydrophilic (water-loving) head group and a hydrophobic (oil-loving) tail (Jhalani, 2019). Therefore, emulsifiers are attracted to both polar and non polar compounds. For a w/o emulsion mixture, the emulsifier's orientation is the non polar tails extend outward into the oil phase, while polar head groups point into the water droplet. In this way, emulsifiers functioning by lowering the interfacial tension between the oil and water phases, stabilizing the droplets and preventing them from coalescing. Emulsifiers generally categorized into two types which are ionic (with charge) and non ionic (without charge). The ionic emulsifier can be cationic (positively charged polar head group) and anionic (negatively charged head group). When charged emulsifiers (ionic) coat droplets in an w/o emulsion mixture, the positive or negative charges on the outside of the oil droplets electrostatically repel each other, helping to keep the oil droplets to form tiny particles and separated in the liquid suspension. Non-ionic emulsifiers tend to have large, bulky head groups that point away from the oil droplet. These polar head groups clash and tangle with head groups on other water droplets, sterically hindering the droplets from coming together so the oil-water mixture may not be mixed properly because of that phenomenon. The unsuitable selection of emulsifier type will lead to the instability of emulsion in the mixture which resulting in separation of water from the mixture after a certain extent of time. Based on the percentage of water separation shows in Table 6 above, from the three type of emulsifier used in the formulation, EMB A (anionic) formulation showing the most stable result which is only 1.69% of water separated from the water-oil mixture after three days of observation. The selection of different surfactants in the preparation of either O/W or W/O emulsions is often still made on an empirical basis. A semi empirical scale for selecting surfactants is the Hydrophilic–Lipophilic Balance (HLB) number developed by Griffin. This scale is based on the relative percentage of hydrophilic to lipophilic (hydrophobic) groups in the surfactant molecules. For an O/W emulsion droplet, the hydrophobic chain resides in the oil phase, whereas the hydrophilic head group resides in the aqueous phase. For a W/O emulsion droplet, the hydrophilic groups reside in the water droplet, whereas the lipophilic groups reside in the hydrocarbon phase (Malakasiotis & Androutsopoulos, 2010). Water-in-oil emulsions (w/o) require low HLB surfactants while oil-in-water (o/w) emulsions require higher HLB surfactants(Acids & Zheng, 2015). So in this research study, the anionic emulsifier used which is 2-bromostearic acid is having HLB value of 13.8 while the cationic emulsifier which is didodecyldimethyl ammonium bromide is having higher value of 18.1 (Schulz et al., 2003). It shows that emulsifier having lower HLB value is more suitable for this emulsified bitumen formulation which support the result of anionic emulsifier formulation is the most stable one and gives the nearest stability rate with the bench-marked industrial bitumen emulsion (Atlaskote).

4.10.2 Drying rate performance

Drying process usually is one of most important factor in coating application. It can affect the time efficiency during the application purpose. The faster the drying rate of a coating on the wall, the better the performance and quality of that coating. This can be related with the rheological characteristic from the oscillatory test which is how fast a substrate deforms to solid at certain extent. From the rheological test, EMB B (cationic) emulsifier shows the fastest extent of deformation and it also has resulting for a faster drying rate as shown in Table 4.6 below. The drying rate is depending on how fast the evaporation of moisture from the samples coating. As shown in the table, Atlaskote sample coating perform a very fast dying rate as compared to the other samples coating because it has the highest moisture content hence giving the lowest viscosity which helping in faster drying effect.

Table 4. 27: Drying rate for the EMB coating

Sample	Time take to completely dried (at room temperature)
EMB A (Anionic)	24 hours
EMB B (Cationic)	8 hours
EMB C (Non-ionic)	20 hours
Control sample (without emulsion)	32 hours
Atlaskote	0.83 hours

4.10.3 Adhesiveness performance

The classification of the adhesion test result classified according to ASTM D3359-09 as summarized in Table 4.28 below. From that table, the percent of area removed can be categorized into several grading classifications. The classification of industrial grade bitumen emulsion (Atlas) was 3B where the total area that has been removed is between 5%-15%. Meanwhile, the classifications of EMB A, EMB B and EMB C are the same which are 5B where the total area that has been removed is 0%. All of the adhesiveness results have been tabulated in Table 4.28 below. From this result, it is clearly shown that industrial grade bitumen emulsion (Atlas) not having the best adhesion towards the substrate (drywall). In the meantime, all of the three types of emulsified modified bitumen shown the best performance in term of the adhesion.

Table 4. 28: Classification of adhesiveness according to ASTM D3359-09

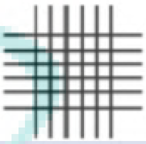
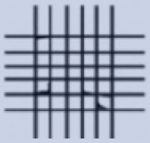
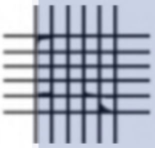
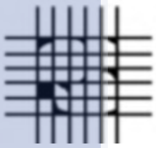
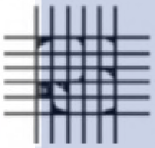
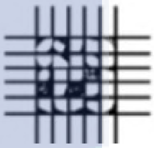
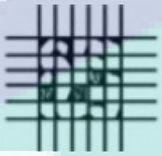
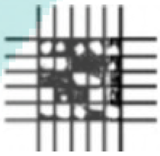
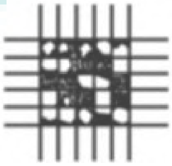
Classification of adhesion test result		
Classification	Percent area removed	Surface of cross-cut area from which flaking has occurred for six parallel cuts and adhesion range by percent
5B	0% None	
4B	Less than 5%	
3B	5-15%	 
2B	15-35%	 
1B	35-65%	 
0B	Greater than 65%	

Table 4. 29 Summary of adhesion test for all samples

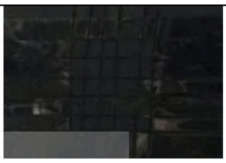
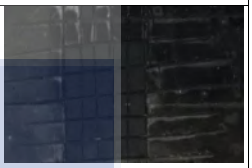
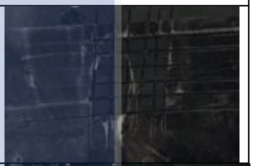
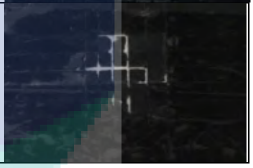
Samples	Classification	Percent Area Removed (%)	Result
EMB A	5B	0	
EMB B	5B	0	
EMB C	5B	0	
Control sample	3B	10	
Atlaskote	3B	15	

Table 4.29 above summarizes the adhesion test results for all samples. From these results, it is clearly shown that industrial grade bitumen emulsion (Atlas) not having the best adhesion towards the substrate (drywall) while all of three types of emulsified modified bitumen have shown the best performance in term of the adhesion. Poor adhesion is a property of coatings that can lead to the damage of the substrate as it is not able to protect the substrate from the surrounding environment such as water and heat. The poor adhesion of the material is due to the inadequate bonding between the coating and the substrate (Weishaar et al., 2018). This factor can cause the coating material to flake off from the substrate. The ideal coating to protect the substrate from water and heat need to have even and consistent adhesion (Weishaar et al., 2018). This is the property that shall be optimized for all formulations that have been adopted for coating purposes.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

From the analysis that have been conducted on the Emulsified Modification Bitumen (EMB) on adhesion, ageing and heat transfer, here are the conclusions that can be made:

1. It is found that the EMB 05 with ratio of 5.0:3.3:0.08:1.62 is the best formulated bitumen emulsion and resembles the industrial bitumen emulsion (Atlas).
2. The total coated area for EMB 05 been removed from drywall is more than 65%. This shows that the adhesion ability of the EMB 05 on the substrate is lower compared to Atlas. This analysis answer the first objective of this dissertation which is to investigate the coating performances of EMB on the surface of drywall.
3. The coating performances of EMB also been investigated through ageing analysis. The analysis highlighted that the ageing period of EMB 05 for accelerated weathering tester, natural weathering and cooling is 296 days, 1107days and 893 days. This value also showing the same trend as Atlas where the ageing period is temperature dependant.
4. The results show that the heat transfer values (q) in EMB 05 for the temperature at 60℃, 45℃, 30℃ and 27℃ are 1.14W, 0.79W, 0.70W and 0.65W. The analysis also showing a trend that the higher the composition of bitumen in the bitumen emulsion, the higher the ability for the bitumen emulsion to insulate heat.
5. The emulsifier used in the emulsified modified bitumen (EMB) that gives the best performance is EMB B which is using cationic type of emulsifier. The cationic emulsifier is didodecyldimethyl ammonium bromide.
6. EMB B shows the best characterization in terms of viscosity value, rheological behaviour and flash point reading. The viscosity value of EMB B which having the lowest value among those three type of EMB formulations however still very far away from the bench-marked industrial bitumen emulsion (Atlaskote). In terms of

rheological behaviour, EMB B shows the trend of fastest deformation to solid compared to the other two formulations which will effect in faster drying rate. Lastly, the highest flash point value among all three formulations showing that it is feasible enough to be applied for coating industry.

7. In terms of performance, EMB B also showing the best performance in term of drying and adhesiveness. Drying rate and adhesiveness properties are two major characteristics for a coating substrate. The adhesiveness properties of EMB B is at the highest rate with zero flaking effect which beating the bench-marked industrial bitumen emulsion which occur some flaking. In terms of emulsion stability, anionic emulsifier is leading the performance because it is having lower HLB value compared to cationic one.
8. In overall of characterization and performance, using cationic emulsifier in the formulations (EMB) is the best one.

5.2 Recommendations

Recommendations are made to suggest for future work in order to give a better improvement on the formulation of EMB from industrial wastes. Below are some recommendations for future work:

1. Injection of special adhesion additives are required to improve the adhesion properties of the formulated bitumen emulsion.
2. Solvent such as thinner can be added into the formulated bitumen emulsion to speed up the drying time of the coating material
3. The uses of Bentonite will help to improve the insulation properties of the formulated bitumen emulsion.
4. Methylene Chloride shall be used as a solvent to remove the bitumen residues from equipment.
5. The mechanical strength of the EMB shall be analysed after the ageing process to understand better the coating performances and behaviour of the EMB.
6. Health and hazard consideration should be taken seriously because of the sulphur contain in the main raw material of bitumen itself or maybe the ratio of bitumen used can be reduced more.

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