DEVELOPMENT OF BITUMEN FROM INDUSTRIAL WASTES

MOHD NAJIB BIN RAZALI

RDU160324

UNIVERSITI MALAYSIA PAHANG

DEVELOPMENT OF BITUMEN FROM INDUSTRIAL WASTES

MOHD NAJIB BIN RAZALI

Faculty of Chemical and Natural Resources Engineering

UNIVERSITI MALAYSIA PAHANG

SEPTEMBER 2018

ACKNOWLEDGEMENTS

With great honour, I wish to express my sincere appreciation to God for the blessing and giving me strength to move on during the hard times,

I would also like to show my gratitude to all grant members, Prof. Abdulrahman Hamid Nour, Dr Mohd Aizudin bin Abd Aziz, Prof. Dato' Dr Rosli Mohd Yunus, En Musfafikri bin Musa, Dr Saidatul Shima binti Jamari, and Dr Anwaruddin for their full support, patient guidance, infinite suggestions, comments guidance and encouragement to complete this project.

Besides, I would like to take this opportunity to thank the administrative and technical staff in the faculty for their valuable help. I also want to express my gratitude to all my students who had given their full commitment to complete this project especially during run the experiment.

Last but not least, thanks to my lovely friends who played the important role in giving me all the guidance and support that I need.

Thank you.

ABSTRAK

Bitumen dihasilkan daripada minyak mentah yang diekstrak dari tanah maka, minyak mentah dikategorikan sebagai salah satu sumber yang tidak boleh diperbaharui. Isu masalah alam sekitar yang semakin meningkat di Malaysia adalah disebabkan oleh aktiviti pengilangan yang berlebihan yang membawa kepada ketidakteraturan pengurusan sisa industry. Sisa industri seperti polistirena, polietilena dan minyak automotif boleh digunakan sebagai alternatif lain untuk merumuskan bitumen. Kebiasaannya, sejenias agen kimia yang sesuai akan digunakan untuk menghasilkan produk terakhir yang dinamakan EMB. Agen tersebut akan menghasilkan caj bergantung kepada sifat-sifatnya untuk mengikat bitumen berminyak dengan air. Analisis fizikal dan kimia seperti TGA, DSC, FTIR, analisis ketumpatan, analisis kandungan air dan analisis titik penyalaan telah dijalankan untuk mengetahui sifat dan struktur bahan dan bagi memilih bahan yang akan digunakan di dalam uji kaji ini . Kaedah yang digunakan untuk merumuskan produk ini adalah pemanasan dan pencampuran itu lakukan dalam hud wasap supaya ia boleh menyerap wasap yang dikeluarkan semasa eksperimen dijalankan. Parameter utama untuk proses ini adalah berat sampel, suhu, masa, kelajuan pengadun dan jenis agen yang digunakan. Pertama, semua bahan perlu dikategorikan menggunakan beberapa analisis untuk mengetahui sifat-sifat setiapnya. Apabila formulasi telah dihasilkan, sampel perlu di analisis berdasarkan ujian, penembusan @ 25^{o}C kaedah ASTM D5 dan ujian titik lembut, kaedah ASTM D36. PMB seterusnya di larutkan dalam air untuk menjadi EMB dan akan dibanding dengan EMB gred perindustrian (80/100) daripada Syarikat Kemaman Bitumen. Daripada kajian menunjukkan, nisbah emulsi bitumen yang terbaik adalah (2: 0.5.7.5) untuk formulasi tanpa serbuk getah dan (20: 2: 39: 39) dengan serbuk getah kerana pkedua-dua bahan sangat larut dalam campuran dan ia mempunyai 200 / 300 nilai penembusan, 34 ℃ titik pelembutan. Oleh itu, ia adalah yang paling sesuai untuk aplikasi kalis air di dinding.

ABSTRACT

Bitumen is produced from crude oil extracted from the ground, which categorizes crude oil as one of the non-renewable fossil fuels. Various environmental issues that have risen in Malaysia are caused by the excessive manufacturing activities and the miss-management of industrial wastes. In an effort to mitigate these issues, industrial wastes are being used in various EMB formulations. Industrial wastes, such as polystyrene, polyethylene, and used automotive oil can be used as alternatives to formulate bitumen. Normally, a suitable emulsifier is needed to produce the final product, which is EMB. The emulsifier will yield a charge, depending on its properties, to bind the oily bitumen with water. In this current study, physical characteristic studies were performed using thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), flash point test, density test, and moisture content test. Fourier Transform Infrared Spectroscopy (FTIR) analysis was also performed to determine the material's molecular composition and structure. These tests was performed in order to choose the best material for the experiment The method that was used to formulate this product was heating and mixing that was done inside the fume hood. So that it can absorb the fume released while the experiment was conducted. The key parameters for this process are weight of the sample, temperature, time, speed of the mixer and the emulsifier used. Firstly, the raw materials were characterized by using analytical method such as TGA, DSC, Density test and Flash point test. Once the polymer modified bitumen was produced, the sample was analyse based on penetration @ 25^{o}C test using ASTM D5 method and softening point test, ASTM D36 method. The polymer modified bitumen formulated was then being emulsified to become EMB and was compared with industrial grade bitumen emulsion (80/100) from Kemaman Bitumen Company. From the result, the best ratio of bitumen emulsion is (2:0.5.7.5) for formulation without crumb rubber and (20:2:39:39) formulation with crumb rubber since both substance was perfectly soluble in the mixture and it is having 200/300 penetration value, 34°C of softening point. Thus it is the most suitable one for waterproofing wall application.

TABLE OF CONTENT

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

g/m^3	Density
g	Gram
%wt	Weight Percentage
mm	milimeter
Pa.s	Pascal.seconds
Cm	Centimeter
^oC	Degree Celcius

LIST OF ABBREVIATIONS

MS	Malaysian Standard
W/O	Water in Oil Emulsion
O/W	Oil in Water Emulsion
ASTM	American Society for Testing and Materials
EMB	Emulsified Modified Bitumen
RPM	Revolutions per Minute
HDPE	High Density Polyethylene
LDPE	Low Density Polyethylene
EVA	Ethylene Vinyl-Acetate
TGA	Thermogravimetric Analysis
DSC	Differential Scanning Calorimetry
FTIR	Fourier Transform Infrared Spectroscopy
KBC	Kemaman Bitumen Company

CHAPTER 1

INTRODUCTION

1.1 Background

Bitumen is a sticky, black, highly viscous liquid or semi-solid form of petroleum. It is primarily obtained by fractional distillation of selected crude oil. It is comprised of non-distillable fraction, which technically referred as residue. Upon manufacturing, crude oil will be separated to the lighter, low boiling point of fractions resulting in product with high boiling point, high molecular weight and low volatility called as bitumen (Paliukaitė et al, 2014). The properties and quality of bitumen depend wholly on the crude oil use in its manufacturing. Bitumen can be produce by crude oil refining or by natural deposits. Natural bitumen is usually used as an additive to other base product such as traditional bitumen to improve the physical properties for road construction material.

Bitumen is used mainly in road paving, roofing application, roads construction, waterproofing products, building materials and industrial coatings. It is estimated that the current world consumption of bitumen is 102 million tonnes per year which 85% from it is used as binder for pavements, 10% for roofing application and the rest is used for other variety kind of purposes (Asphalt Institute and Eurobitume, 2011)

In Malaysia, the urge to solve the environmental issue is getting crucial. Significantly, the industrial waste such as plastics, waste sludge and used oil has been contributed to this problem. These wastes can be formulated to become modified bitumen and essentially with the help of suitable emulsifier, it can become emulsified modified bitumen (EMB).

1.2 Motivation

Bitumen is considered as one of the non-renewable product when it is produced from crude oil. In order to prevent this non-renewable source replenished from earth as well as to maximize the use of waste produce by the industry, EMB can be formulated from industrial waste by using plastics, waste sludge and used oil to replace the existed bitumen from crude oil. The EMB formulated will solve the dependency to the natural resources as well as the vast environmental problem that consequently happen because of the overused of natural resources. The EMB formulated will be used for insulation and coating of building. Not only that, most EMB shows a better performance than unmodified one (Carrera et al, 2015). It is formulated in the form of liquid so that it can be sprayed or applied easily to the surfaces. This EMB will provide an extra weather barrier in case of blow offs or water penetration through roofing or flashings. This coating layer is important to retain the wall during raining season in Malaysia and reduce the heat transfer into the building during hot weather. Besides, to compare with the conventional bitumen, it has higher ability to work in adverse weather conditions and low ambient temperatures while using less bitumen to complete a job as it is diluted with a solution containing water and emulsifier. The EMB produced also can reduce the risk of hydrocarbon pollution of waterways and to the atmosphere.

Since the viscosities of the bitumen emulsion is in the range of 0.5-10 Poise at 60˚C is considerably lower than the bitumen itself (100-4000 Poise), it is allowed to be used at low temperature (Sola, 2013). The bitumen emulsion formulated then will be use as insulation and coating of building. Since it is in a liquid form, therefore it can be applied easily or sprayed to the surface. This new bitumen emulsion formulation will have tough film with flexible waterproofing properties which has the ability to damp-prove water barrier (Iwanski & Chomicz-Kowalska, 2016). This coating layer is important as it will used in medical industry specifically in operation theater which it will be applied on the wall and ceiling. Besides, the purpose is to prevent the external wall and also the ceiling of the operation theater from being growth with the moss and thus figure out the fungal problems. Considering hygiene is the crucial part in medical field, using this formulation will be a point due to it waterproofing, easy to clean and long lasting in which will reduce costs to be spent. By using this bitumen emulsion formulation, the present of microbes and fungus on the wall can be avoided and thus, promoting a clean and sterile environment (Ministry of Health and Social Services, 2015). The bitumen emulsion produced also will be applied the ‘eco-efficiency’ technique which will make less environmental impacts than the conventional bitumen. In addition most of formulated bitumen emulsions that have been modified shown better performance to be compared with the unmodified bitumen (Ariffin et al., 2016) and (Carrera et al., 2014).

1.3 Problem Statement

The increasing quantities of industrial waste in Malaysia have led to many serious environmental problems which require a better solution to handle it. The solid waste in Malaysia increased from 16,200 tonnes/day in 2001 to 19,100 tonnes/day in 2005 or an average of 0.8 kilogram per capita/ day (Tarmudi et al, 2009). In 2014, the Environmental Protection Expenditure (EPE) was reported at a total of RM2.244 billion where the manufacturing sector was the highest contributor to this EPE at RM1.619 billion (Department of Statistics Malaysia, 2016) and since the solid wastes generated are exceeding the maximum amount, these generated wastes are finally disposed in landfills as the current implemented waste management is poorly managed. This method is not sustainable and need to be improved or else it would affect our environment, social and lead to economic lose (Sin et al, 2012). Industrial waste such as crumb rubber and high density polyethylene plastics have contributed to this massive problem (Amin, 2013) and at the same time, the rapid demand for crude oil due to the increasing world population and industrialization can make this non-renewable resources gone as the main source in the earth. Moreover, with the growing demand of crude oil at a rate of 4.5 % annually during 2000-2005 to 6.2 % per annum during 2006-2010 (Rahim & Liwan, 2012), it is consequently decrease the rate of natural resources in Malaysia. Thus, the development of emulsified modified bitumen from industrial waste is one of the alternative ways to reduce this problem.

As the EMB will be formulated through recycling technology, many environmental aspects that will lead to serious effect can be decreased such as energy consumption, high level of CO_2 emission to the environment during work construction, maintenance operation and worker’s health (Yaacob et al, 2013). Besides, bitumen emulsion presents much lower viscosity as it is diluted with water and can be applied at lower temperature as low as 80 ^{o}C. Conventional binders are sprayed at 160-200 ^{o}C so there is much more additional risk of fire and explosion (Carrera et al, 2015).

In this project, the raw materials from industrial waste will be first characterized using physical and chemical testing. Then bitumen from industry will be modified using industrial waste and non-ionic type of emulsifier will be used on it in order to emulsify the bitumen.

1.4 Objectives

The following are the objectives of this research:

1) To develop emulsified modified bitumen from industrial waste
2) To formulate the bitumen emulsion from industrial waste
3) To verify the formulation of bitumen emulsion for insulation and coating purpose

1.5 Scope of study

In order to achieve the objectives stated above, several scopes of work have been identified.

1) To characterize the raw material from industry and industrial wastes using physical and chemical test
2) To find the best ratio of emulsified modified bitumen from industrial waste
3) To analyse the emulsified modified bitumen properties by using physical test
4) To investigate the properties of bitumen emulsion using chemical and physical test
5) To verify the application of bitumen emulsion for insulation and coating purpose

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter will explain the properties and mechanism of the bitumen and bitumen emulsion. Besides, the formulation and application of materials used are explained and compared. In this chapter, mechanism, characteristics and usage of the material used is also discussed.

2.2 Bitumen

Bitumen is a black, viscous liquid or solid which consists a mixture of hydrocarbons and their derivatives. It is having a waterproof, adhesive property and substantially non-volatile and softens gradually when heated and since it is possesses a non-polar properties, it is soluble in organic solvents such as tri-chloro-ethyelene and toluene. As a residue that is obtained from a fractional distillation of a crude oil, bitumen which can be define as a mixture of various organic liquid have an API gravity less than 10° and have a viscosity greater than 10,000 centipoise which consists a mixture of hydrocarbons and their derivatives. This black and extra heavy oil have adhesive and cohesive properties, waterproof and substantially non- volatile. Besides softens gradually when it was heated.

Bitumen is a complex chemical mixture of molecules that are predominantly hydrocarbons with a small amount of structurally analogous heterocyclic species and functional group containing sulphur, nitrogen and oxygen atoms (David, 2003). It is so full with carbon that it cannot be used for combustion (unlike gasoline, diesel and jet fuel). In fact it has so much carbon that unless it is kept heated to a temperature of about

150℃, it solidifies into a rock-hard wax. Table below shows the chemical component contained in bitumen.

Table 2.1 Component of Single Bitumen

Chemical Component	Percentage Contained (%)
Carbon	82-88
Hydrogen	8-11
Sulphur	0-6
Oxygen	0-1.5
Nitrogen	0-1

Bitumen also contains trace quantities of metals such as vanadium, nickel, iron, magnesium and calcium which occur in the form of inorganic salts and oxides or in porphyrine structures. By its properties, bitumen behaves in five ways. 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.

Moreover, 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. 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. Lastly, when it is exposed to ultraviolet (UV) rays, the bitumen will be evaporated and become harder (Liang, 2007). Bitumen's versatility as a construction material is limitless. It is used for many applications; adhesive, sealant and waterproofing agent including roofing, pool linings, pipe coatings, paints and many others. Not only does the sticky nature of the product quite literally glue all the construction material together, its water-proofing characteristics are unparalleled, which means that rain water does not permeate into wall and simply runs off (Biofuels, 2015).

Since the versatility of bitumen as a construction material is endless, it is used for wide variety applications such as an adhesive, sealant and waterproofing agents including roofing, paints, pipe coating, and pool linings (M.Chappat, 1994). The bitumen become the most highly demanded construction materials in the world due to its multi-functional, easy to maintain, water resistance, durable and also cost effective. Normally, condition for every type of application need bitumen to behave as a mobile liquid, thus there are three ways on how to make a low viscosity of bitumen from highly viscous bitumen which is heat it, dissolve it in solvents or emulsify it (Hunter, 2016).

Table 2.2 Component of Single Bitumen (Praveen Kumar, 2009)

Properties	**60/70 Grade**	**80/100 Grade**	**Permissible Limits**
Penetration (25^{o}C, 100g, 5s) dmm	63	94	80-100
Softening Point ^{o}C	49.5	47	35-50
Ductility at 27^{o}C, cm	100+	100+	75 (min)
Specific Gravity at 27^{o}C, gm/cc	1.01	1.02	0.99 (min)

2.2.1 Production of Bitumen from Petroleum Refineries

An oil refinery is a series of manufacturing processes designed to yield a physical and chemical changes in crude oil to convert it into everyday products. In petroleum refineries process, bitumen is obtained as the last residue in fractional distillation of crude oil petroleum. This crude oil is extracted from the ground, on land or under the oceans by sinking an oil well and are transported by pipeline or ship to refineries where the crude oil will be processed or separated further. As crude oil comes from the well it contains a mixture of hydrocarbon compounds and relatively small quantities of other materials such as oxygen, nitrogen, sulphur, salt and water. Throughout this process, most of these non - hydrocarbon substances are removed and the oil is broken down and blended into useful products like LPG, naphtha, kerosene and diesel in the distillation process based on their boiling point and density. There are several manufacturing methods available to produce bitumen depending on the crude oil source and processing capabilities available.

The most common method is by introduced the crude oil to two distillation columns; atmospheric distillation and then to vacuum distillation column before the bitumen product is obtained. To summarize the flow of the process, first crude oil will be heated up to 300-350^{o}C near atmospheric pressure where it is partly vaporized into the first column. Here, the liquid falls to the bottom and the vapour rises, passing through a series of perforated trays (sieve trays). Heavier hydrocarbons condense more quickly and settle on lower trays and lighter hydrocarbons remain as a vapour longer and condense on higher trays.

Liquid fractions are drawn from the trays and removed. In this way the light gases, methane, ethane, propane and butane pass out the top of the column, petrol is formed in the top trays, kerosene and gas oils in the middle, and fuel oils at the bottom. Residue drawn of the bottom may be burned as fuel, processed into lubricating oils, waxes and bitumen or used as feedstock for cracking units. As the boiling point of bitumen is very high which is 525^{o}C, so it does no rise in the distillation chamber. In order to recover the heavy residue which contain bitumen, it is then pass through a vacuum distillation column to allow the heavy hydrocarbons with boiling points of 450^{o}C and higher to be separated further and the final bitumen product is obtained (James, 2007). Figure 2.1 describe the two processes in a much simpler way where the crude oil entering the atmospheric distillation first before the non-distilled fraction consisting bitumen is fed to the vacuum distillation.

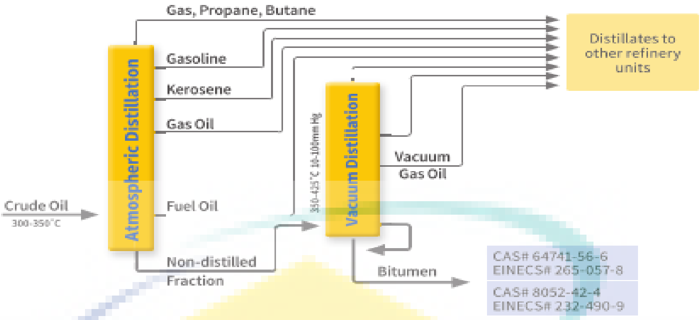


Figure 2.1 Distillation Process for Bitumen Production

2.2.2 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).

Table 2.3 Comparison of Properties Modified and Unmodified Bitumen (Yaacob et al., 2013)

Properties	Unit	*A-70 Bitumen	Polymer Modified Bitumen (PMB)
Penetration (25^{o}C, 100g, 5s)			
Penetration Index	-	-1.35	0.24
Ductility 5^{o}C, 5cm/min	Cm	-	25.2
Density 15^{o}C	g/cm^3	1.043	-
Solubility (trichloroethylene)	%wt	1.86	-
Flash Point	^{o}C	312	304
Dynamic Viscosity 60^{o}C	Pa.s	233	-
Elastic Recovery, 60^{o}C	%	-	93.7
Viscosity 135 ^{o}C	Pa.s	0.39	1.78

*A-70 is a Chinese standard bitumen grade which having penetration of 70 and quality level A

2.2.3 Bitumen Emulsion

Generally, emulsions is a thermodynamically unstable heterogeneous system consisting of two immiscible liquids, which one of the substance is the dispersed in the least amount in the form of droplets with a diameter greater than 00.1 micro meter (Glady,2016). The stability of this system can be increased by promoting a special agent such as surfactants.

Bitumen emulsions are two-phase systems consisting of bitumen which called as a binder, water and one or more additives to assist in formation and stabilisation to modify the properties of the emulsion. The bitumen is dispersed throughout the water phase which is held in suspension by electrostatic charges stabilised by an emulsifier. As in Malaysian Standard (MS) 161, bitumen emulsion is defined as a liquid product in which a substantial amount of bitumen is entirely suspended in a finely divided condition in an aqueous medium by means of one or more suitable emulsifying agents (Yaacob et al., 2013). Furthermore, bitumen 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 an oil and the dispersed phase water (Shojaei et al, 2013).

Standard bitumen emulsions are normally O/W type and the limit of bitumen content is in the range of 70% to 80%, 1% to 2.5% emulsifier, 25% to 60% water plus some minor components based on the emulsifier used (Salomon, 2006). The binder for this purpose can be either bitumen, cutback bitumen or modified bitumen. The most important properties of bitumen emulsions are stability, viscosity, breaking and adhesivity. Moreover, the ideal emulsion would be the one that stable under storage and during transportation and possessed a low viscosity for ease of handling (Yang et al., 2013). The rate for which bitumen emulsion gain strength is proportional to the rate of water losses from the bitumen emulsion itself. This process is closely related to environmental conditions such as ambient temperature, humidity and the presence of wind movement besides the material properties itself. Figure 2.2 shows the final state of bitumen emulsion which is in liquid form.

Figure 2.2 Bitumen Emulsion

In good quality of bitumen emulsion, the droplets are in range 1 to 30 μm in diameter with majority < 1 μm and the largest volume or mass between 5 and 10 μm. In this emulsion, bitumen content normally in the region of 60 to 70% but can it can also be as low as 40% or as high as 80% (Needham, 1996). 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 (Read, 2010). This instability emulsion can leads to the requirement of higher energy input to form an 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 lower 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 surfactant are relatively more soluble in water rather than oil (Read, 2010). Therefore it tend to promote the formation of O/W compared to formation of W/O. Ordinarily surfactant that is used in bitumen emulsion production are cationic in nature such as alkyl diamines, amidoimidazolines and quaternary ammonium chlorides (Salomon, 2006).

Bitumen emulsions are classified according to the sign of the charged on the droplets either it is a cationic emulsion in which the droplets carry a positive charge or anionic emulsion that have negatively charged droplets. This system use a fundamental law of electricity in which the like charges repel, unlike charge attract (Sola, 2013). As an illustration, in cationic emulsion, the positively charge particle of bitumen will migrate to the cathode as well as negatively charge particle in anionic emulsion will move to the anode. There are also another two classes of bitumen emulsion which are non-ionic emulsion, also clay stabilised emulsion. The bitumen particle in non-ionic emulsion will not move to either anode or cathode pole due to the neutral charge.

The most important properties of bitumen emulsions are stability, viscosity (rheology), breaking and adhesively. Emulsion is one of the examples of non-Newtonian fluid that has the shear thinning behaviour in which the viscosity value is actually depend on the shear stress applied. The properties also lean on the molecular weight and the structure, the temperature, as well as the concentration of additives and fillers used (Derkach, 2009). Normally for this type of complex fluid, it can be done by using the rheology test because the minimum number of function that are needed to relate stress with the strain rates are been characterize. (Michelle, 2014). For the stability of emulsion, it is depends on the several factors which is the types of bitumen emulsifier and its quantity, water evaporation rate, bitumen quantity, bitumen globules size and the last one is mechanical forces that are applied.

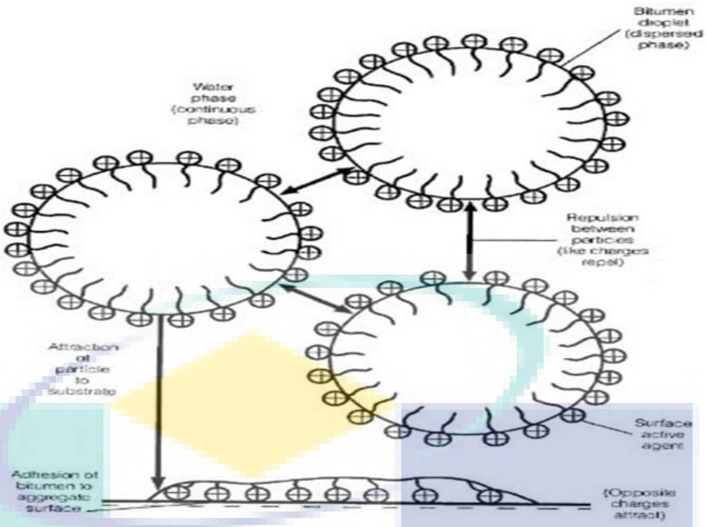


Figure 2.3 Attraction of water and bitumen particle

2.3 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.

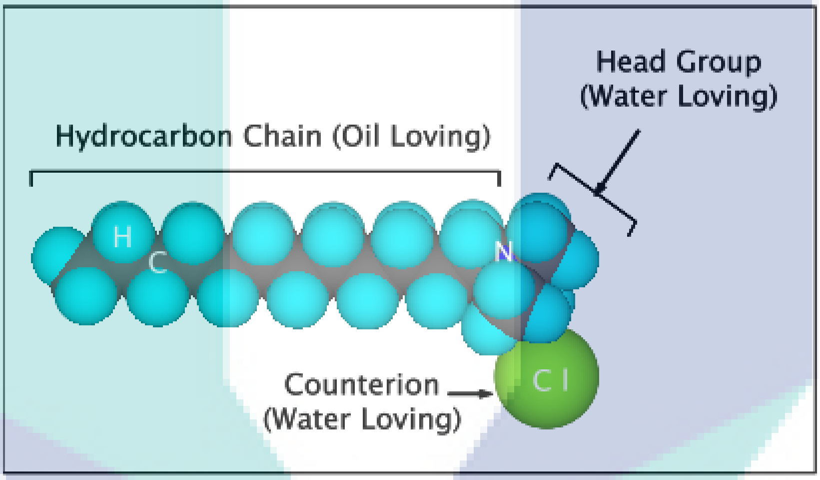


Figure 2.4 Cationic Emulsifier Molecule

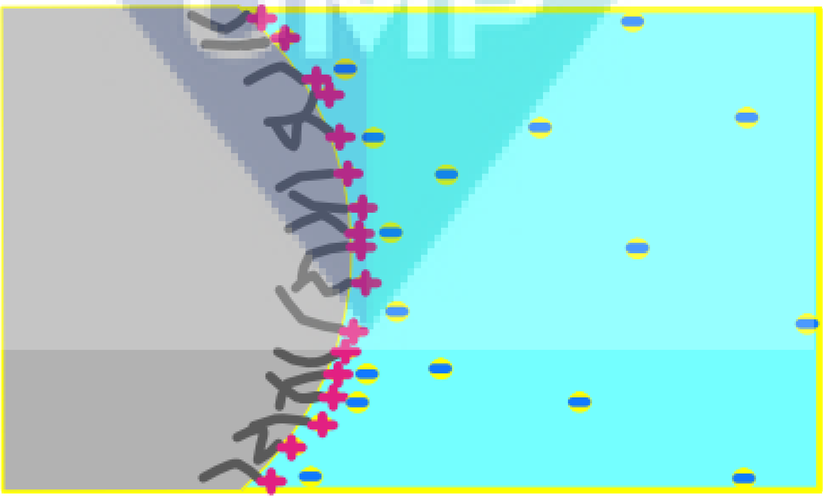


Figure 2.5 Charge Particle in Bitumen Emulsion

Table 2.4 Example of Emulsifier Use in Bitumen Emulsion

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).

Ethoxylate solution is actually a non-ionic surfactant. It features both lipophilic tails, indicate by the alkyl group abbreviation, R and relatively polar headgroups. Furthermore, it is used as emulsifying agent from the fact that it is soluble in water and can demonstrate a significant resistance during deformation (Glady et al., 2016b).

Usually bitumen emulsion 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 like prime coat and cold mixes (Hunter, 2016). 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 (Boltryk et al., 2017). 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 (M.Chappat, 1994). Nowadays bitumen emulsion also have been used for the medical purpose especially for the operation theatre. It is applied to the wall to solve the fungal problems. Since the bitumen emulsion is in liquid form, it just need to be sprayed onto the top of the wall or surface. 2010 World Emulsion Congress have updated that the total production of bitumen emulsion produce in 2009 was roughly 8 million tonnes and it is represent around 10% to 12% of the total global road bitumen demands. It is also a similar volume to that use in previous five years (Le Bouteiller, 2012).

2.3.1 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 2.4 shows the structure of abietic acid whereas table 2.6 shows the properties of abietic acid.

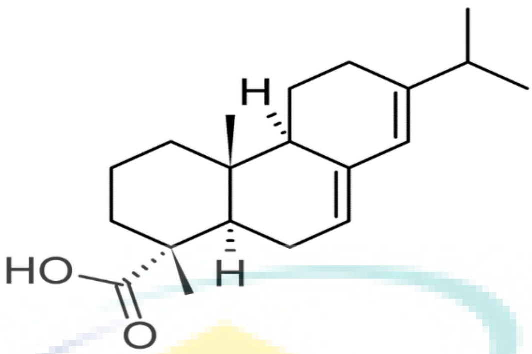


Figure 2.6 Structure of Abietic Acid

Table 2.5 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	Very soluble in acetone, petroleum ether and ethanol

2.3.2 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.

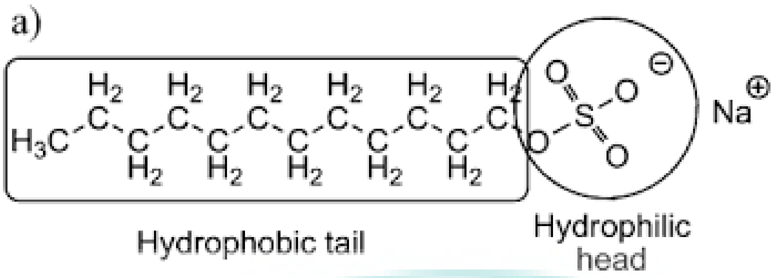


Figure 2.7 Structure of Sodium Dodecylsulphate

Table 2.6 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

2.4 Comparison of EMB

From previous research, most of the emulsified bitumen develop is by using the industrial grade bitumen which is they are using crude oil as the raw material. Only a few of them is made by using modified bitumen. This can be referred in table 2.6.

Table 2.7 Comparison of Emulsified Modified Bitumen EMB

No	Journal	Type of Emulsion	Raw Material	Emulsifier Solution	Composition	Novel	Application
1	E. Glady et al., 2016	Nonionic	Bitumen penetration grade 60/90	Emulsifier: Alcohol Ethoxylation Stabilizer: Calcium Chloride Acid: HCl	30-80wt% Bitumen 15-70wt% Water 0.1-1.0wt% Acid 0.05-0.5wt% Stabilizer	▪ Viscous consistency that used to solve application to an inclined surface without use of adhesion additives. ▪ Increased resistance to delamination and coalescence of emulsion during storage.	Road and civil construction
2	A.A Cuadri et al., 2016	Cationic	Bitumen penetration grade 160/220 & 70/100 Modify with recycled	Emulsifier: alkyltrimethylenediamine Acid: HCl	4wt% emulsifier in solution with pH 1 Ranging Polyethylene Modified Bitumen	▪ 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	Road construction and civil construction

			polyethylene		concentrations between 50 and 63 wt% and LPDE up to 5 wt%)	temperatures, increasing the resistance to rutting deformation in pavements.	
3	Z.Liu et al., 2016	Cationic	Kraft Lignin from Pine Woods	Emulsifier: Lignin Amine	-	▪ Lignin is burned as fuel or disposed of as waste which results in increased greenhouse gases and also the loss of a valuable biomass resource. ▪ The conversion of technical lignin to surfactant is an important utilization of this renewable resource as a functional material	Road maintenance
4	F.Xing et al., 2015	Anionic	A stable anionic bitumen emulsion for use in highway	Emulsifier: Abietic acid Filler: Limestone Alkali: Potassium	6% bitumen & 6% filler, 1:1 ratio	▪ Viscous, stable, homogeneous, liquid-like	Road construction and civil construction

				Hydroxide			
5	V. Carrera et al., 2014	Cationic	Bitumen penetration grade 160/220 modify with polypropylene-glycol groups	Emulsifier: alkyltrimethylenediamine Acid: HCl	1.4 wt% emulsifier in solution with pH 2 Different concentration from 1-4 wt% of polymer-bitumen	▪ 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 construction and civil construction
6	H.M.Cai et al 2010	-	Bitumen penetration grade 80/100	Emulsifier: JQT, OP-10, rosin potassium soap Stabilizer: Polyacrylamide Coagulant: Styrene	Weight ratio 3:1:1 of emulsifier mixture	▪ The emulsifier is mixture of three surfactants. (cationic, anionic, non-ionic) ▪ Some properties improved; thermal stability, high- and low-temperature performance, durability, as well as adhesive property with aggregates, better crack resistance than pure bitumen emulsion at low temperature. ▪ Styrene-butadiene-	Surface dressing

	*Toluene is use to dissolve SBS (Styrene-butadiene-styrene) latex	styrene (SBS) block copolymers can increase the elasticity of

2.5 Material of EMB

2.5.1 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).

2.5.2 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.

2.5.3 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 differs 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 three groups paraffinic, naphthenic, and aromatic.

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 C18. Paraffinic also have good thermal and oxidative stability as well as good high temperature viscosity characteristics. General formula for paraffin is $C_n H_{(2n+2)}$. 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.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.

2.5.4 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 2.8 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

2.5.5 Crumb 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).

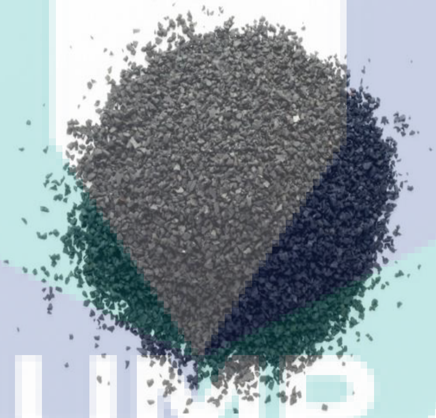


Figure 2.8 Crumb rubber

2.5.6 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.

2.5.7 Application of 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 2.9 The Application of EMB as Wall Insulator

2.5.8 American Society for Testing Materials (ASTM)

American Society for Testing Materials (ASTM) is an international standards organization that develops and publishes voluntary consensus technical standards for a wide range of materials, products, systems and services. Approximately over 12,000 ASTM standards are develop and used around globally to enhance the performance and quality of the product, improve safety system and boost confidence and satisfactory in consumer. In this experiment, there a two ASTM tests that are used which are softening point test (ASTM D36) and penetration test (ASTM D5).

2.5.8.1 Softening Point Test (ASTM D36)

Softening point denotes the temperature at which the bitumen attains a particular degree of softening under the specifications of test. The test is conducted by using Ring and Ball apparatus. A brass ring containing test sample of bitumen is suspended in liquid like water or glycerine at a given temperature. A steel ball is placed upon the bitumen sample and the liquid medium is heated at a rate of 5◦C per minute then the temperature is noted when the softened bitumen touches the metal plate which is at a specified distance below. A higher softening point indicates lower temperature and is preferred in hot climates (Pavement Materials, 2007).

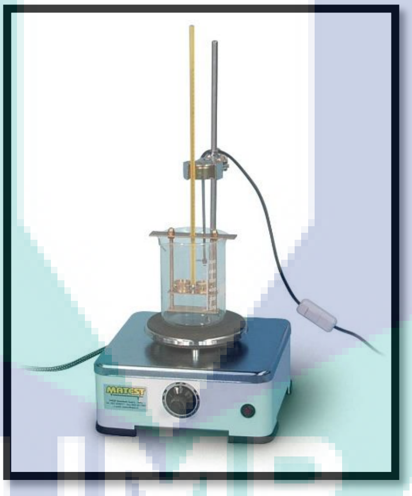


Figure 2.10 Equipment for Softening Test

2.5.8.2 Penetration Test (ASTM D5)

It measures the hardness or softness of bitumen by measuring the depth in 10mm to which a standard loaded needle will penetrate vertically in 5 seconds. The penetrometer consists of a needle assembly with a total weight of 100g and a device for releasing and locking in any position. The bitumen is softened to a pouring consistency, stirred thoroughly and poured into containers at a depth at least 15mm in excess of the expected penetration. The test should be conducted at specified room temperature. For this test, a grade of 40/50 bitumen means the penetration value is in the range of 40 to 50 at standard test conditions (Pavement Materials, 2007).

Figure 2.11 Equipment for Penetration Test

CHAPTER 3

MATERIALS AND METHODS

3.1 Overview

This chapter describe and discuss about the raw materials, chemicals, equipment, experimental procedure, testing for characterization of raw material and American Society for Testing Materials (ASTM). In order to accomplish the objectives and scope of this research, 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, polyethylene and used oil. It also include an analysis parameter for the EMB that will be produced.

3.2 Materials

The raw materials that are used for this research are bitumen grade 80/100 from Kemaman Bitumen Company (KBC), high density polyethylene and polystyrene from landfill. Lastly, the waste sludge is from Kemaman.

3.3 Chemicals

The chemicals used in this research are three type of used oil obtained from Kemaman, Banting and Kuantan. Three different chemicals will be used as an emulsifier which are polyethylenimine 80% ethoxyated solution, abietic acid, and sodium dodecylsulphate from Sigma Aldrich. Lastly, the industrial bitumen emulsion later will compare with the bitumen emulsion that will be formulated.

3.4 Workflow of Development of EMB from Waste

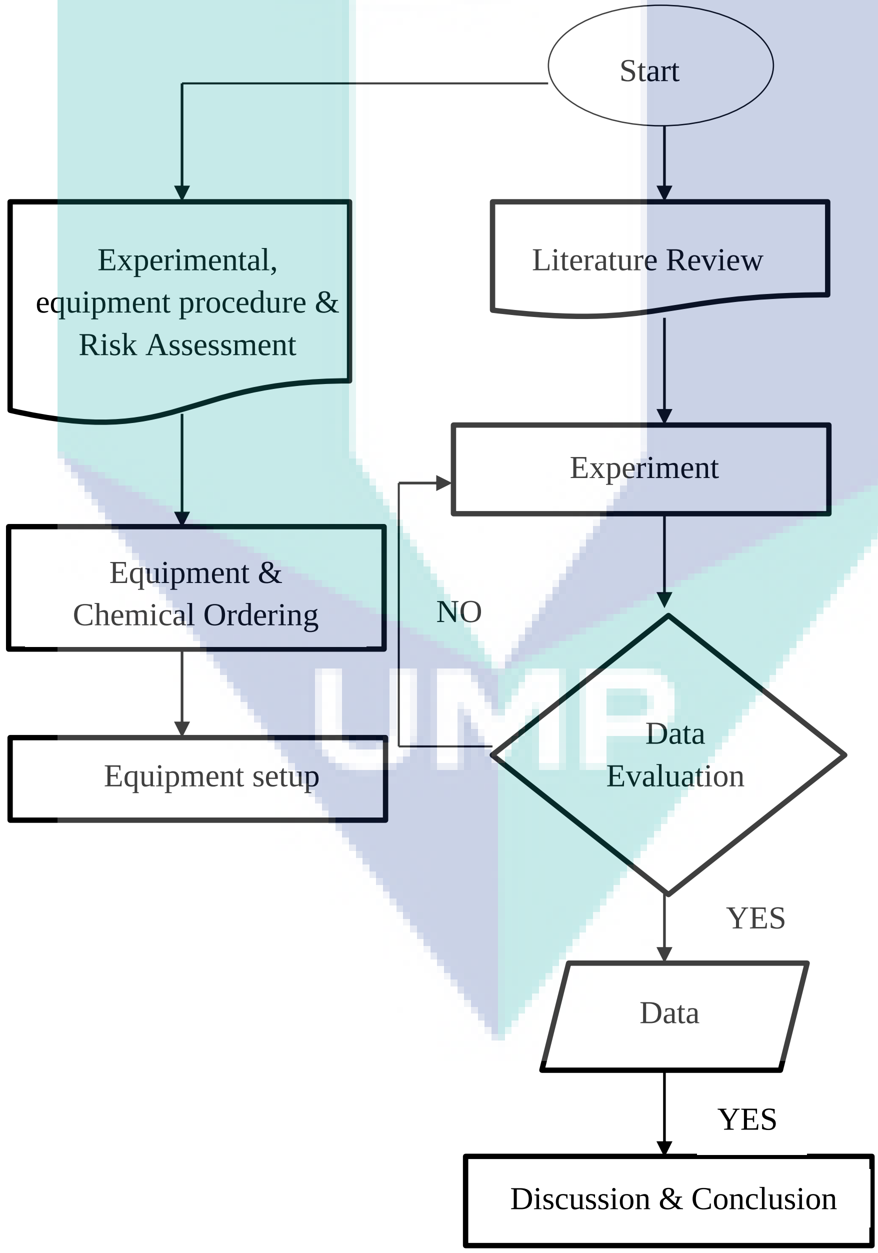


Figure 3.1 General Workflow for this Research

3.5 General Experimental Procedure

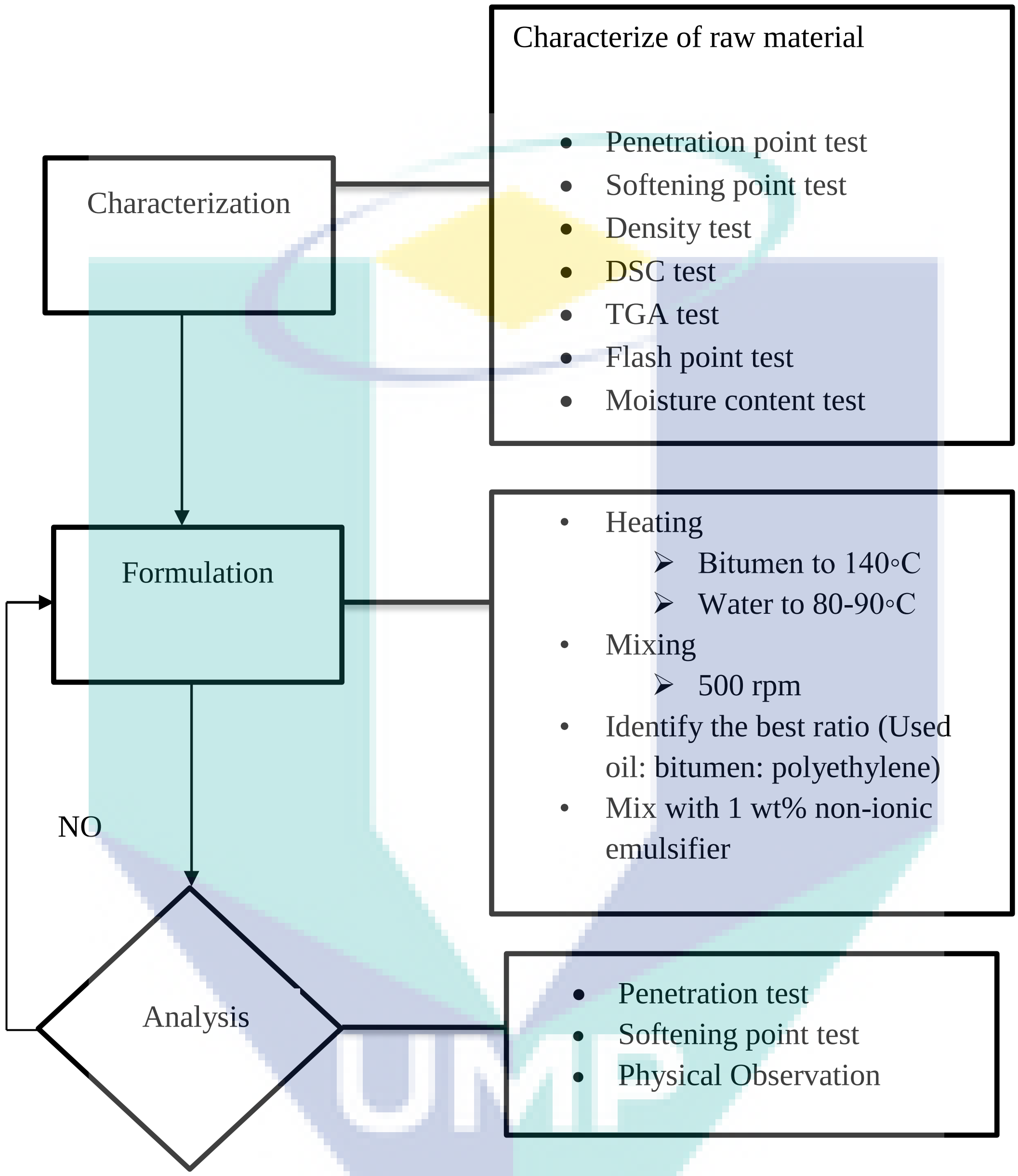


Figure 3.2 Overall Workflow for this Research

The waste sludge was filled in the separatory funnel about quarter of its total volume while it is place in the ring.

↓

Then, the funnel was taken out of the ring, inverted and vented it slowly by opening up its stopper in order to release some pressure built up in the separatory funnel until no more gas escape.

↓

The separatory funnel was placed back in the ring and left it for a day to allow it to separate based on its density.

↓

The bottom layer of the sludge was drained out to collect the desired product which is water.

↓

The bottom layer was then filled in the centrifuge bottle and centrifuge it for 10 minute at 1000 RPM.

↓

The bottom part in the centrifuge was then collected and heated up to ensure all of the water was vaporized.

Figure 3.3 Pre-treatment of Waste Sludge Procedure

3.6 Characterization of Raw Material

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.

3.6.1 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 10^{o}C/min until approximately 900 ^{o}C 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.

3.6.2 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 350^{o}C.

3.6.3 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.

3.6.4 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.

3.6.5 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.

3.6.6 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 ^{o}C and the lid was closed.

3.6.7 American Society for Testing Materials (ASTM)

The industrial grade bitumen and the formulated modified bitumen is analyse to compare between them. In this research there are two ASTM test are perform which is penetration and softening test.

3.6.8 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.

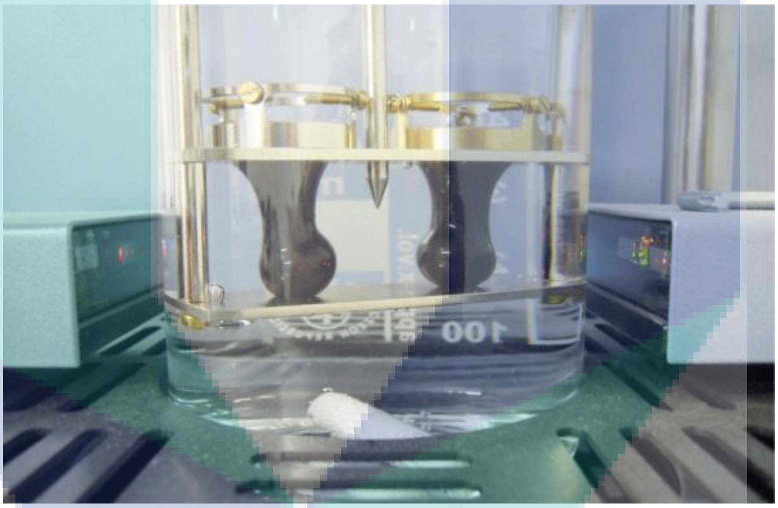


Figure 3.4 Steel ball with bituminous coating touches bottom plate

Heat the material to a temperature between 75-100˚C above its softening point and stir until it is completely fluid and pour into heated ring placed on a metal plate.

Coat the sample with solution of glycerine and dextrin to avoid the sticking bitumen sample to metal plate.

Cool the sample for 30 minutes in air then level the material in the ring by removing and trimming the excess material with a warmed sharp knife.

↓

Assemble the apparatus with the rings, thermometer and ball guides in position.

↓

Fill the bath with distilled water until 50 mm above the upper surface of the rings.

↓

Apply heat to the bath and stir the liquid to uniform the rate of temperature increase at 5˚C per minute. Start temperature with 35˚C until the bitumen soften and touches the bottom plate by sinking of

↓

Record the temperature when any of steel ball with bituminous coating touches the bottom plate.

↓

Record the temperature when second ball touches the bottom plate. The averages of two readings to the nearest 0.5˚C is softening

Figure 3.5 Softening point test procedure

3.6.9 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.

Figure 3.6 Penetration test equipment

Heat the sample at temperature not more than 90˚C above approximate softening point and stir it thoroughly until it homogenous and free from bubble and water.

Pour the sample in a container to a depth such when a cooled, the depth of sample is at least 10 mm greater than the expected penetration.

Allow the sample to cool in an atmospheric pressure at a temperature between 15˚C to 30˚C for one hour.

Fill the transfer dish with water from the water bath to a depth sufficient to cover the container completely and place the sample in it and put in upon the stand of the penetration apparatus.

Clean the needle with benzene and load it with the weight

Adjust the needle until it make a contact with the surface of sample.

Start the stopwatch and allow the penetration needle to penetrate freely for five seconds.

↓

Measure the distance penetrated.

Figure 3.7 Penetration test procedure

3.7 Bitumen Formulation

The desired HDPE, polystyrene, used 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 120°C 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 100°C and continuously mixed at 150 RPM for 30 minutes.

↓

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

Figure 3.8 Bitumen Formulation Procedure

3.8 Bitumen Emulsion

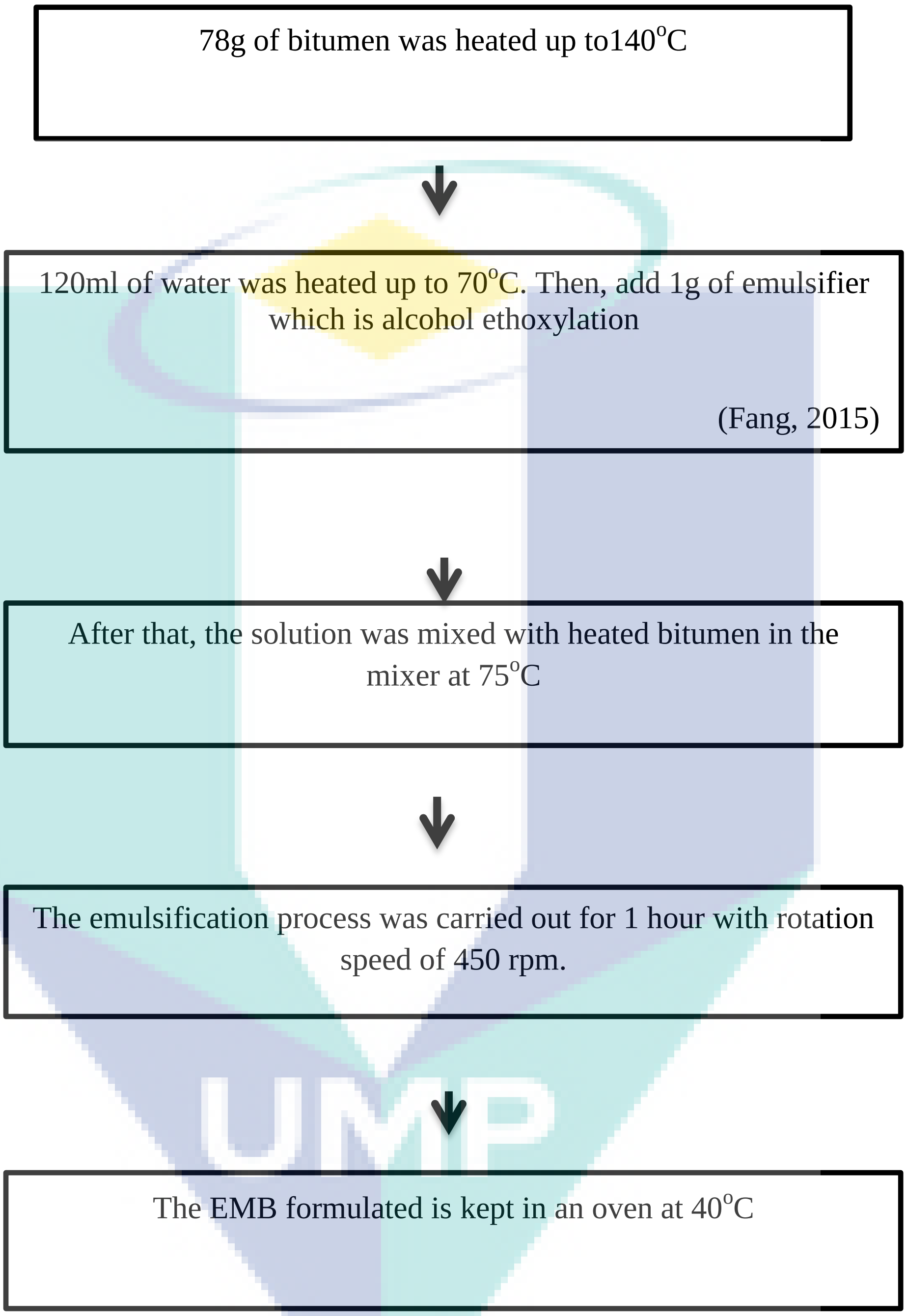


Figure 3.9 Bitumen Emulsion Procedure

3.9 Ratio of Bitumen, Polymer and Used oil-Part 1

Table 3.1 General Formulation of 220g of Bitumen

Ratio **Weight (wt%)**	8:0.7:1.3	8:0.5:1.5	6:0.7:3.8	6:0.5:3.5
Sample code	A	B	C	D
Bitumen	176.0	176.0	132.0	132.0
Polymer	15.4	11.0	33.0	22.0
Used oil	28.6	33.0	55.0	66.0

Table 3.2 General Formulation of 220g of Bitumen (continue)

Ratio **Weight (wt%)**	4:0.7:5.3	4:0.5:5.5	2:0.7:7.3	2:0.5:7.5
Sample code	E	F	G	H
Bitumen	88.0	88.0	44.0	44.0
Polymer	15.4	11.0	15.4	11.0
Used oil	116.6	121.0	160.6	165.0

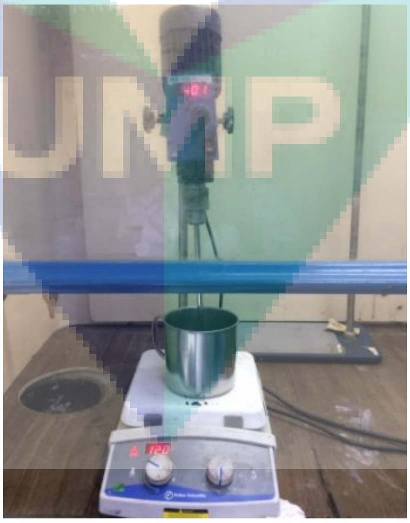


Figure 3.10 Experiment was conducted inside Fume hood

3.10 Ratio of Bitumen, Water and Emulsifier-Part 1

Table 3.2 shows the ratio of EMB formulation using bitumen, water and a chemical agent known as emulsifier.

Table 3.3 Weight Percent of EMB Formulation

	Bitumen (wt %)	Water (wt %)	Emulsifier (wt %)
Industrial Grade (Kemaman Bitumen Company)	39	60	1
Sample (H)	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℃. After that the bitumen at 140℃ 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).

3.11 Ratio of Bitumen, Polymer, and Latex, Crude Oil and Used Oil-Part 2

Table 3.4 Ratio of formulation bitumen (of 300g)

Sample Code	**Ratio Weight (wt%) (B:P:L:C)**	**Bitumen**	**HDPE**	**Latex**	**Crude Oil**
A	20:5:5:70	60	15	15	210
B	20:4:6:70	60	12	18	210
C	20:2:8:70	60	6	24	210
D	20:5:15:60	60	15	45	180

E	20:4:16:60	60	12	48	180
F	20:2:28:60	60	6	54	180
G	20:5:25:50	60	15	75	150
H	20:4:26:50	60	12	78	150
I	20:2:28:50	60	6	84	150
J	20:5:5:70	60	15	15	210
K	20:4:6:70	60	12	18	210
L	20:2:8:70	60	6	24	210
M	20:5:15:60	60	15	45	180
N	20:4:16:60	60	12	48	180
O	20:2:28:60	60	6	54	180
P	20:5:25:50	60	15	75	150
Q	20:4:26:50	60	12	78	150
R	20:2:28:50	60	6	84	150

*(B:CR:L:C)-(Bitumen : Crumb Rubber: Latex : Crude oil)

Table 3.5 Ratio of formulation bitumen (of 100g)

Sample	Ratio (B:P:C:U)	Bitumen	HDPE	Crude Oil	Used Oil
S	20:2:39:39	20	2	39	39

3.12 Ratio of Bitumen, Water and Emulsifier-Part 2

Table 3.4 shows the ratio of bitumen emulsion formulation using bitumen, water and three different chemical agents known as emulsifier which are polyethylenimine 80 % ethoxylation, abietic acid and sodium dodecylsulphate. S1, S2 and S3 indicate the formulated bitumen emulsion by using polyethylenimine 80 % ethoxylation, abietic acid and sodium dodecylsulphate respectively.

Table 3.6 Weight Percent of Bitumen Emulsion Formulation

	Bitumen (wt%)	Water (wt%)	Emulsifier (wt%)
Industrial Grade	39	60	1
Sample (S1)	39	60	1
Sample (S2)	39	60	1
Sample (S3)	39	60	1

Temperature, weight of each materials as well as the speed of the mixer are the key parameters for this process. It is important for the mixture to be added to each other at the right temperature. Bitumen firstly must be heated up to 140˚C. At the same time, water was heated up 75˚C before the emulsifier was poured into the water. Then the bitumen at 140˚C was added into the mixture. The type of water used also plays an important rule. It is due to the emulsifier cannot tolerate with any mechanical impurities present in the water (Glady., et al, 2016). Therefore the water used to emulsify the bitumen must be deionised water. Only 1 wt% of emulsifier was used in this experiment because it is enough amount to emulsify the bitumen (Glady., et al, 2016) and (Cai., 2010). Beside the temperature, the continuous mixing also is a crucial to secure the mixture was homogenously mixed. In term of the speed of the stirrer, it also must be control during the emulsification process to ensure it will reached a small droplet size as it can be (Ronald & Luis, 2016). The speed of the mixture need to be increase when the bitumen is already added to the mixture of water and emulsifier. It is to fasten the reaction between bitumen and the mixture.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Chapter Overview

This chapter discuss the result obtained from the experiment that is conducted based on the methodology stated in chapter 3. 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 used lubricant oil and polymer bottle and compare with the existing bitumen from industry. Then, the formulated bitumen was emulsified using non-ionic emulsifier called Polyethylenimine, 80% ethoxylated solution and lastly, the EMB formulated was compare with bitumen emulsion using industrial grade 80/100.

4.2 Preliminary Study-Part 1

The preliminary study was conducted to prove the concept of bitumen being modified using polymer. Firstly, the experiment was conducted to know the polymer melting temperature. 5g of polymer was heated up at 70℃ and the temperature was increased gradually until all the polymer was melted at 180℃. 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. It was to obtain information whether 10% of polymer could be eliminated from this research.

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-Part 1

Characterization of raw material is important before further experiment was performed in order to understand the behavior of the raw material used. For example, three different polymers were compared based on its behavior using TGA, DSC, FTIR, moisture content analyzer. Three different sources of used oil was analyze 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 Thermogravimetric Analysis (TGA)

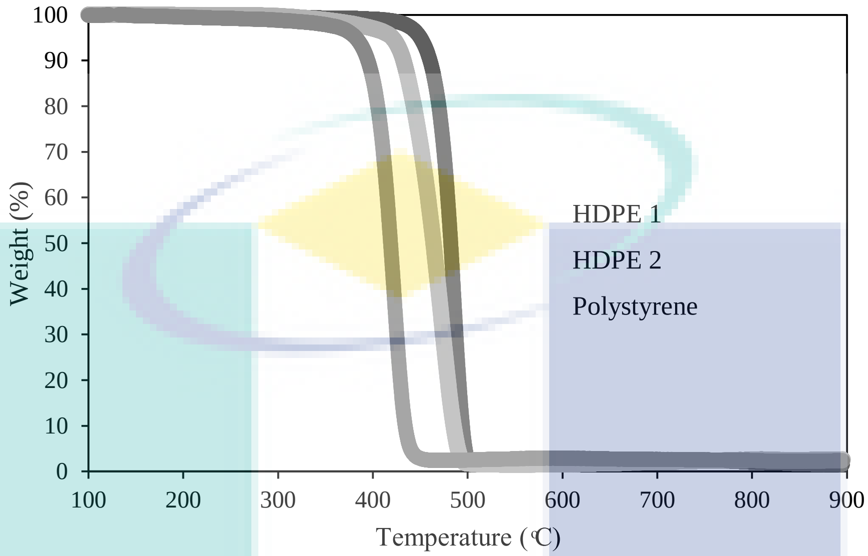


Figure 4.1 Graph of Weight Loss (%) against Temperature (°C)

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)

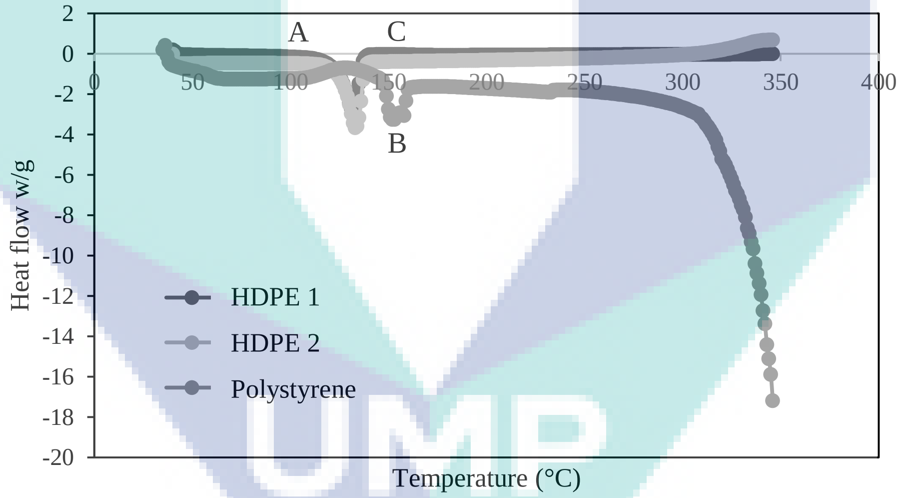


Figure 4.2 Graph of Heat (w/g) Flow against Temperature (^oC)

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)

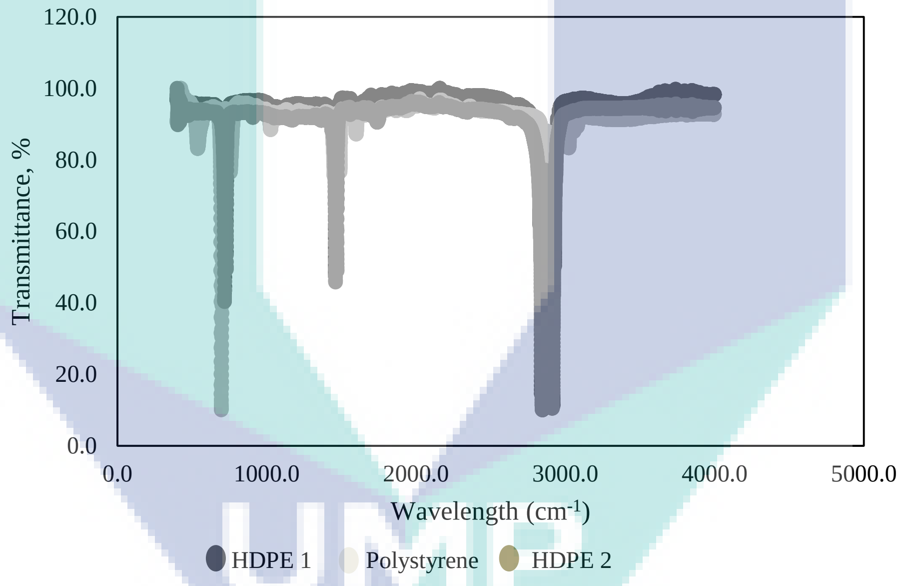


Figure 4.3 Graph of Transmittance (%) against Wavelength (cm^{-1})

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 negligeable. 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
Base oil 3	65.0
Sludge	145.5

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 Density for liquid samples

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

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 behavior 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, base oil 3 was chosen because the supplier for base oil 1 no longer produce it and base oil 3 has a higher density compared to base oil 2.

4.3.6 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
Base oil 3	0.311
Sludge	14.479
HDPE 1	0.266
HDPE 2	0.389
Polystyrene	0.757

Table 4.4 shows the moisture content of all raw materials, which consisted of oil and polymer. 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 base oil 3 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.

4.3.7 Summary of Analysis

Table 4.5 Summary and result of all the test conducted

Sample Test	**HDPE 1**	**HDPE 2**	**Polystyrene**	**Base oil 1**	**Base oil 2**	**Base oil 3**	**Sludge**
TGA (˚C)	468.68	439.54	402.90	-	-	-	-
				Solid sample only			
DSC (˚C)	131.24	133.19	151.90	-	-	-	-
				Solid sample only			
Flash Point (˚C)	-	-	-	20.0	132.5	65.0	145.5
				Liquid sample only			
Density (kg/m^3)	-	-	-	0.8070	0.9304	0.8720	1.1831
				Liquid sample only			

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 analyzer. 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 Characterization of raw Materials-Part 2

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

4.4.1 Differential Scanning Calorimetry (DSC)

Table 4.6 DCS for solid sample

Sample Test	DSC (˚C)
HDPE 1	131.24
HDPE 2	133.19
Crumb Rubber	140.22

Table 4.6 shows three different melting values for each material which is HDPE 1, HDPE 2 and crumb rubber. The melting point for HDPE 1 and HDPE 2 is not so different with the deviation of 1.95 to be compared with the crumb rubber. Melting point for each sample is important in order to formulate the bitumen emulsion because it is used to determine the method of this study and it is to ensure that all the materials used were melted to their melting temperature.

4.4.2 Flash Point Test

Table 4.7 Flash point temperature for liquid sample

Sample Name	Flash Point Temperature (˚C)
Crude Oil	32.5
Used Oil	65.0

Table 4.7 shows the flash point temperature for the crude oil and the used oil. Flash point is conduct to know the lowest temperature of both of this liquid at which its vapor will forms a combustible mixture with air and allow for ignition and the

propagation of flame when exposed to an ignition source (Gharagheiz et al., 2007) and (Collier, 2004). From the table above, used oil have high flash point than the crude oil. From the physical observation, the crude oil is more watery like compared to the base oil that is more viscous and that give an explanation why the crude oil have low flash point than the base oil. Basically any liquid especially oil that have high flash point looks more viscous and content high additives in it (Razali et al .,2018). In this study, both of crude oil and used oil is used to formulate the bitumen to be compared with the previous research that use only the used oil to formulate it.

4.4.3 Moisture Content Test

Table 4.8 Moisture content for all solid and liquid sample

Sample Name	Moisture Content (%)
Crude oil	0.130
Used oil	0.311
HDPE 1	0.266
HDPE 2	0.389
Crumb rubber	0.392

Table 4.8 shows the moisture content of all raw materials which consist of oil and polymer. To control the quality of final product, this test was conducted to determine the moisture content that could exist in the sample. Throughout the two oil sample, crude oil has least moisture content than the used oil with 0.13% and 0.311% respectively. Meanwhile for the polymer materials, the moisture content for HDPE 2 is in the middle of HDPE 1 and crumb rubber with 0.389%, 0.266% and 0.392% respectively.

4.4.4 Summary of Analysis

Table 4.9 Summary and result of all the test conducted

Sample Test	HDPE 1	HDPE 2	Crumb Rubber	Crude Oil	Used Oil
TGA (˚C)	468.8	439.54	395.56	-	-

DSC (˚C)	131.24	133.19	140.22	-	-
Flash Point (˚C)	-	-	-	32.5	65.0
Moisture Content (%)	0.266	0.389	0.392	0.130	0.311

Table 4.9 summarizes the results for each test. TGA and DSC only can be test on solid samples, while the flash point only allowed liquid samples. However moisture content analysis had allowed both solid and liquid samples to be tested. To formulate the bitumen emulsion, the exact amount of filler should be determine first and this can be done by TGA which measure the decomposition temperature and composition of each sample. The crucial parameter in this formulation is the melting point of each sample and that is the reason why the DSC was applied. By doing all this test, the key factor that affecting each materials can be determine can thus the best raw materials can be selected in order to formulate the bitumen and bitumen emulsion.

4.5 Formulation of Modified Bitumen-Part 1

The result shows eight formulation of bitumen sample produced using different ratios of bitumen, polymer and used oil. The sample was then being observed on its colour, solubility of polymer, phase and liquid content based on physical observation.

Table 4.10 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. In order to do that, the process needs to take place at the polymer melting temperature. 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. Furthermore, the speed of the mixer played an important role as it stirred and mixed the mixture until it was mixed homogenously by means bitumen, polymer and used oil had dissolved and settle down. From the observation of all the samples, three ratios was chosen as the best combination and undergo conventional bitumen tests which include 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). These three sample shows the most clean and shiny surface compared to others which was a bit bumpy and irregular. 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) .

4.5.1 ASTM Analysis

The three polymer modified bitumen and industrial grade bitumen was characterized using American Standard for Testing and Materials (ASTM) method which include 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.

4.5.1.1 Penetration Test (ASTM D5)

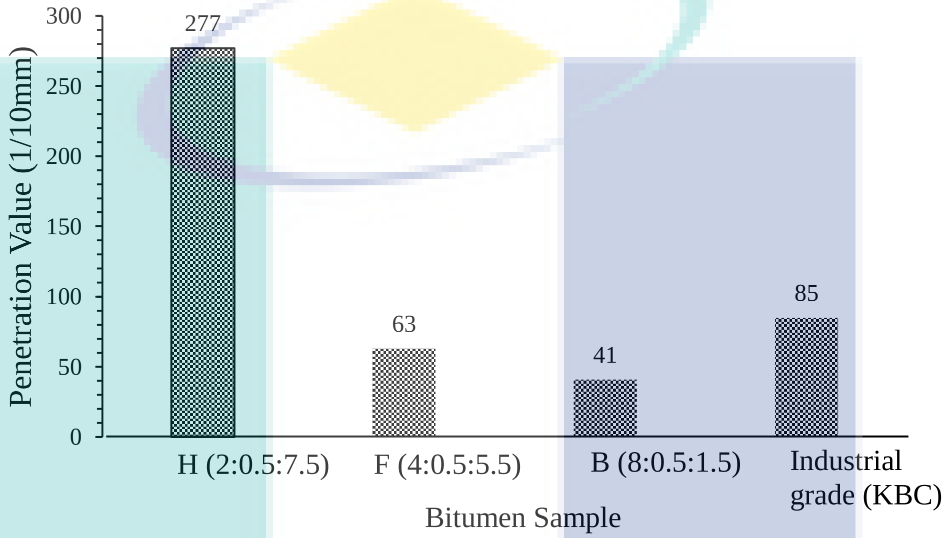


Figure 4.4 Graph of Penetration value (1/10mm) against Bitumen Percentage (%)

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.

4.5.1.2 Softening Point (ASTMD36)

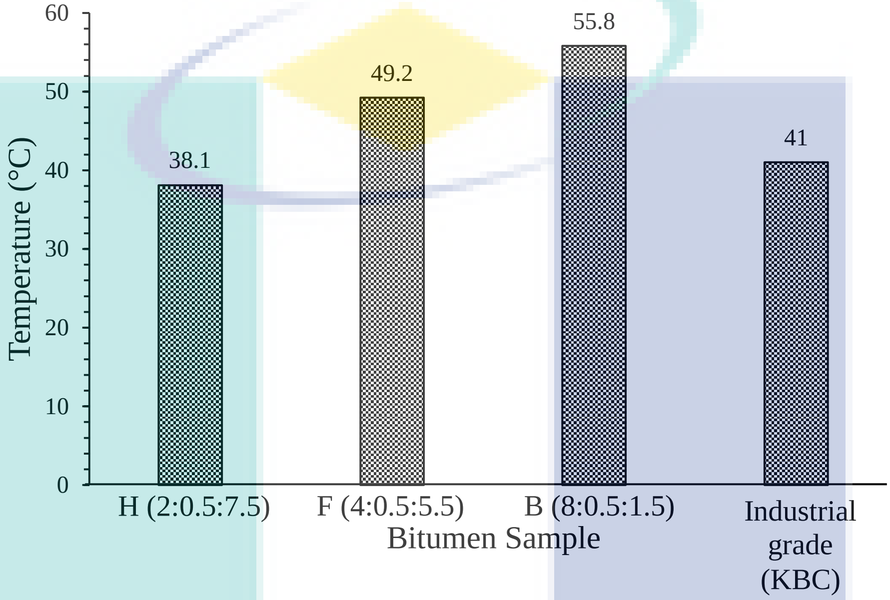


Figure 4.5 Graph of Softening Point (℃) against Bitumen Percentage (%)

Figure 4.5 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.

4.6 Formulation of Emulsified Modified Bitumen-Part 1

The emulsification process used non-ionic type emulsifier, Polyethylenimine 80% ethoxylated solution to mix the bitumen with water. Then the EMB formulated using H ratio from Table 4.11 was compared with industrial grade bitumen emulsion (80/100) from Kemaman Bitumen Company. The sample then was observed on its colour, solubility of polymer and viscosity of the sample based on physical observation. Table 4.7 shows the result of three bitumen emulsion.

Table 4.11 Physical Properties of EMB Formulated

	Ratio	**Colour**	**Solubility**	**Viscosity**
Industrial Grade (KBC)	-	Pure black	Medium	Low
EMB (H)	2:0.5:7.5	Brown	High	High

The emulsifying process required a continuous mixing and the right mixing temperature at 70℃. 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 and 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 of non-ionic emulsifier. In this experiment, the EMB was obtained with the content of 39, 60 and 1wt%. of bitumen, water and emulsifier. The EMB (H) sample was much more viscous and soluble than industrial bitumen from KBC so it can be easily applied on an inclined surface (it is one of bitumen emulsion limit)(Glady et al, 2016).

4.7 Formulation of Bitumen from Industrial Waste-Part 2

The results shows 19 formulation of bitumen sample produced using different ratios of industrial grade bitumen, waste of polyethylene, crumb rubber powder, latex, crude oil and used oil.

Table 4.12 Ratio of formulation bitumen (of 330g)

Sample Code	Ratio (B:P:L:C)	Colour	Solubility of polyethylene	Phase
A	20:5:5:70	Pure black	Low	Liquid semi-solid
B	20:4:6:70	Pure black	High	Liquid semi-solid
C	20:2:8:70	Pure black	High	Liquid semi-solid
D	20:5:15:60	Pure black	Low	Liquid semi-solid
E	20:4:16:60	Pure black	High	Solid
F	20:2:28:60	Pure black	High	Solid
G	20:5:25:50	Pure black	Low	Liquid semi-solid
H	20:4:26:50	Pure black	High	Solid
I	20:2:28:50	Pure black	High	Solid
Standard Bitumen	-	Pure black	-	Semi solid

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

Table 4.13 Ratio of formulation bitumen (of 330g)

Sample Code	Ratio (B:CR:L:C)	Colour	Solubility of crumb rubber	Phase
J	20:5:5:70	Pure black	Low	Liquid semi-solid
K	20:4:6:70	Pure black	High	Liquid semi-solid
L	20:2:8:70	Pure black	High	Liquid semi-solid
M	20:5:15:60	Pure black	Low	Liquid semi-solid
N	20:4:16:60	Pure black	High	Solid
O	20:2:28:60	Pure black	High	Solid
P	20:5:25:50	Pure black	Low	Liquid semi-solid
Q	20:4:26:50	Pure black	High	Solid
R	20:2:28:50	Pure black	High	Solid
Standard	-	Pure black	-	Semi solid

Bitumen

*(B:CR:L:C)-(Bitumen : Crumb Rubber: Latex : Crude oil)

Table 4.14 Ratio of formulation bitumen (of 100g)

Sample Code	Ratio (B:P:C:U)	Colour	Solubility of polyethylene	Phase
S	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 A to sample R, 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 B (20:4:6:70) and C (20:2:8:70).

4.7.1 Softening Point Test (ASTM D36)

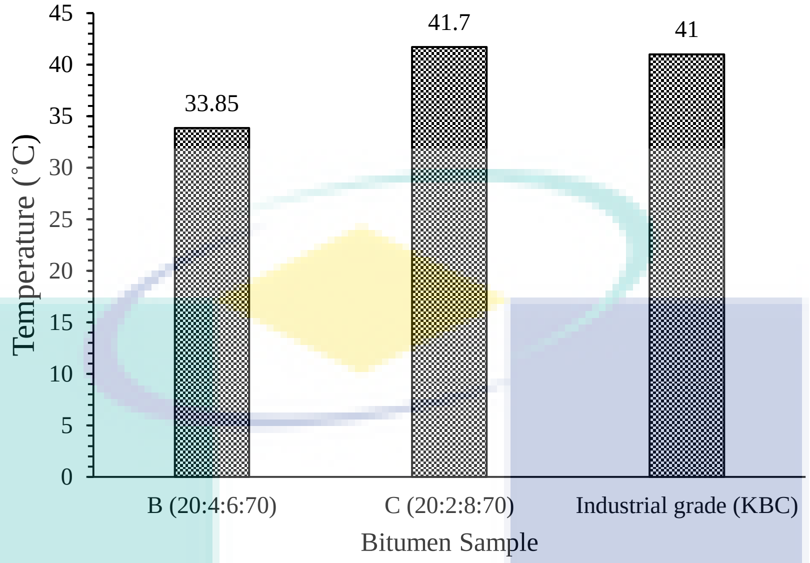


Figure 4.6 Graph of Softening Point (˚C) against Bitumen Sample Percentage (%)

Figure 4.6 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 4.1 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.

4.7.2 Penetration Test (ASTM D5)

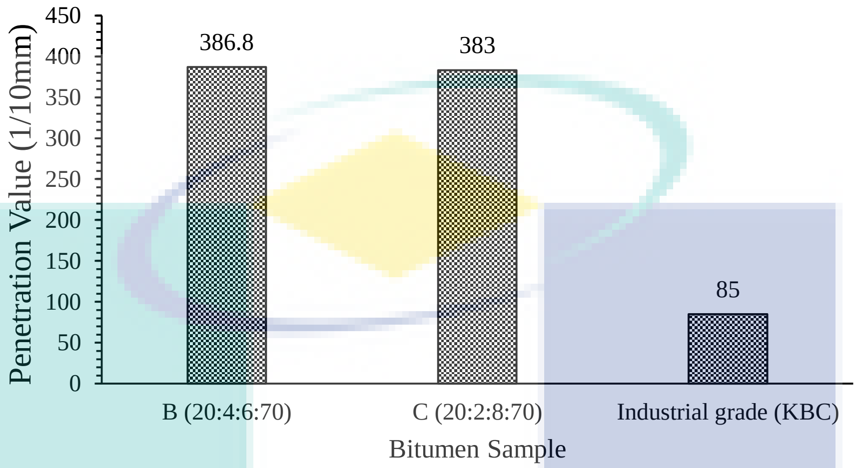


Figure 4.7 Graph of Penetration Value (1/10mm) against Bitumen Percentage (%)

Figure 4.7 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 has almost the same properties with the industrial bitumen but it differ in terms of the grade of bitumen. These 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, B and C 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, S (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.

4.8 Formulation of Bitumen Emulsion-Part 2

The sample S (20:2:39:39) then was chosen based on the physical observation. This ratio then were emulsified by using three different emulsifier; polyethylenimine 80% ethoxylated solution, abietic acid, and sodium dodeclsulphate to mix the bitumen and all of this sample are denoted by S1,S2 and S3 respectively. The bitumen emulsion produced later was observed on its colour, solubility of polymer and viscosity of the sample based on physical observation.

Table 4.15 Physical properties of bitumen emulsion formulated

Type of Bitumen	Ratio	Colour	Solubility	Viscosity
Industrial Grade Bitumen (KBC 1)	-	Pure black	Medium	Low
Industrial Grade Bitumen (KBC 2)	-	Pure black	Medium	Low
Industrial Grade Bitumen (KBC 3)	-	Pure black	Medium	Low
Formulated Bitumen Emulsion (S1)	20:2:39:39	Dark brown	High	High
Formulated Bitumen Emulsion (S2)	20:2:39:39	Dark brown	High	High
Formulated Bitumen Emulsion (S3)	20:2:39:39	Dark brown	High	High
Industrial Bitumen Emulsion (ATL)	-	Dark brown	-	High

Table 4.16 Comparison of moisture content between the formulated and industrial gred bitumen emulsion

Type of Bitumen	Moisture Content (%)
Formulated Bitumen Emulsion (S1)	62.72
Industrial Bitumen Emulsion (ATL)	47.22

From the table 4.16, it can be clearly seen that the formulated bitumen emulsion S1, S2 and S3 have the same properties like the industrial bitumen emulsion (ATL) based on the physical observation in terms of colour and solubility. All of this emulsion also have higher viscosity even though the emulsifier used is differ. For the industrial grade bitumen (KBC), when it is emulsified, it have low viscosity and pure black in colour to be compared with all of formulated sample S and ATL. In this experiment, the formulated bitumen emulsion was obtained with the content of 39,60,1 wt% of bitumen, water and emulsifier. From three different sample of formulated bitumen emulsion, S1 that are use polyethylenimine 80% solution as emulsifier was selected to be tested on moisture content analysis due to its well structure when mixed with water. The formulated bitumen emulsion S1's moisture content also not so differ with the industrial from the bitumen emulsion which is 62.72% and 47.22% respectively. Therefore it can be said that the formulated bitumen emulsion S1 is the best formulation because the formulated bitumen emulsion did not deviate much from the industrial bitumen emulsion

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusion

The characterization of raw material was conducted to study the behavior of all raw materials such as the melting point, degradation temperature, density and flash point. This is vital to choose the best raw material suitable for this research. 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 for Part 1 formulation.

Whereas, HDPE 2 and crumb rubber was chosen for Part 2 formulations to compare the differences and effect on the bitumen appearance with the previous formulation. Even though the filler more than HDPE 1 but it is not so high, so it still can undergo the depolymerisation process while being heated and mixed with the bitumen but not easy as HDPE 1. Besides, crude oil and the used oil were used as the medium for the heating process due to it has a stable supplier and has low moisture content.

For formulation Part 1, the modified bitumen with 200/300 grade was chosen for the emulsification process. EMB was formulated by using bitumen grade 200/300 with ratio of (3.9:6.0:0.1wt %), bitumen, water and emulsifier. Only 1% of non-ionic emulsifier was needed to emulsify the bitumen completely in water.

For Part 2 formulation, the best ratio was (20% of bitumen: 2% of HDPE 2: 39% of crude oil: 39% of used oil) with the water and emulsifier with the ratio (39: 60: 1

wt%). In this formulation, the best emulsifier is polyethylenimine 80% ethoxylated solution compared to the other two which are abietic acid and sodium dodecylsulphate. This is because polyethylenimine 80% ethoxylated solution have a rapid reaction in order to emulsify the bitumen and make it mix with the water that make the structure look better. The formulation of sample S1 produced is dark brown in colour and liquid in phase. The HDPE 2 in this formulation also is fully dissolve in the mixture at 190˚C. In short, the formulated bitumen emulsion is comparable and has an approximation characteristic with the industrial grade bitumen emulsion.

5.2 Recommendation

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:

i. Detail studies on the wastes to be used includes its physical and chemical properties must be done before use it to avoid any problems during reactions with emulsifier as well as to formulate higher quality of the bitumen emulsion.

ii. Different type of polymer could be mixed together to enhance the properties of modified bitumen such as mix of LDPE and EVA. García-Morales (2006) reported these combination of polymer led to the best performance of bitumen

iii. There are still many analyses available excluding for those that are mentioned in the result and discussion. If possible all test regard bitumen emulsion must be performed on the formulated bitumen emulsion to verify its quality.

REFERENCES

Ahmad, S. (2011, September). A Study on Scrap Tyres Management for Peninsular Malaysia. Putrajaya: National Solid Waste Management Department. Retrieved from National Solid Waste Management Department:

Amin, S. (2013, June). Survey on Solid Waste Composition, Characteristics & Existing Practice of Solid Waste Recycling in Malaysia. Putrajaya: Jabatan Pengurusan Sisa Pepejal Negara. Retrieved from Jabatan Pengurusan Sisa:

Arnold, G. (2014, May). General Uses of Bitumen. Retrieved from Bitumen Business:

Asphalt Institute and Eurobitume (2011). The Bitumen Industry – A Global Perspective: Production, Chemistry, Use, Specification and Occupational Exposure, 2nd Edition. Lexington, Kentucky, USA

Baghini, M. S., Ismail, A., Kheradmand, B., Hafezi, M. H., & Almansob, R. A. (2013). The Potentials of Portland Cement and Bitumen Emulsion Mixture on Soil. Jurnal Teknologi (Science & Engineering), Vol 65, 67-72. Retrieved from

Behzadfar, E., & Hatzikiriakos, S. G. (2013). Viscoelastic properties and constitutive modelling of bitumen. Fuel, 108, 391–399.

Behzadfar, E., & Hatzikiriakos, S. G. (2013, June). Viscoelastic properties and constitutive modelling of bitumen. Fuel, Vol 108, 391-399. Retrieved from Science Direct:

Bergmann, A. (2013, January). Crude Oil. Retrieved from Investopedia Academy:

Boltryk, M., Falkowski', K., & Pawluczuk, E. (2017). A Report on the Fabrication of Concrete Pavement with the Application of Anionic Bitumen Emulsion. Construction and Building Materials, 1004-1014.

Cai, H. M., Wang, T., Zhang, J. Y., & Zhang, Y. Z. (2010). Preparation of an sbs latex-modified bitumen emulsion and performance assessment. Petroleum Science and Technology, 28(10), 987–996.

Cai, H. M., Wang, T., Zhang, J. Y., & Zhang, Y. Z. (2010). Preparation of an SBS Latex–Modified Bitumen Emulsion and Performance Assessment. Journal Petroleun Science & Technology, Vol 28 Issue 10, 987-996.

Carrera, V. (2014, August 26). The development of polyurethane modified bitumen emulsions for cold mix applications. Material & Structures, 3407–3414.

Carrera, V., Cuadri, A. A., & Partal, P. (2015). The development of polyurethane modified bitumen emulsions for cold mix applications, 3407–3414.

Chan, H. (2014, February). College of Engineering Purdue University. Retrieved from Standard Operating Procedure Differential Scanning Calorimeter (DSC) in POWER Laboratory Model

Collier, M. A. (2004, June). Flashpoint. Retrieved from Standardization News:

Conference, T. S. A., Of, T., Year, T. H. E., & Biofuels, U. K. (2015). TANKER OF THE YEAR Leaders in Improving Fuel Quality Since 2005 FAST ' s fuel additives are profit rich , concentrated, (September).

Crompton, T.R. Thermal Stability of Polymer. Smithers Lapra Technology Ltd. United Kingdom

Department of Statistics Malaysia. (2016). Department of Statistics Malaysia Press Release Report on Survey of Manufacturing Industries 2015, (June), 2–6.

Derkach, S. R. (2009). Rheology of emulsions. Advances in Colloid and Interface Science, 1-23.

Engin Yener, S. H. (2014). Effects of exposure time and temperature in aging test on asphalt binder properties. International Journal of Civil and Structural Engineering, 112-124.

Farrington, D. (2016, May). Integrated Publishing. Retrieved from Grade of Asphalts and Cutbacks:

García-Morales, M., Partal, P., Navarro, F. J., & Gallegos, C. (2006). Effect of waste polymer addition on the rheology of modified bitumen. Fuel, 85(7–8), 936–943.

Gharagheizi, F., & Alamdari, R. F. (2008). Prediction of Flash Point Temperature of Pure Components Using a Quantitative Structure–Property Relationship Model. QSAR & Combinatorial Science, 27(6), 679–683.

Glady, E. A., Kemalov, R. A., Kemalov, A. F., & Kornetova, O. M. (2016a). Obtaining of bitumen emulsions using nonionic surface-active substances. Indian Journal of Science and Technology, 9(18).

Glady, E. A., Kemalov, R. A., Kemalov, A. F., & Kornetova, O. M. (2016b). Obtaining of Bitumen Emulsions using Nonionic Surface-Active Substances, 9(May), 1–6.

Glady, E. A., Kemalov, R. A., Kemalov, A. F., & Kornetova, O. M. (2016). Obtaining of Bitumen Emulsions using Nonionic Surface-Active Substances. Indian Journal of Science and Technology, Vol 9 (18), 1-6.

Globe Core. (2017). Retrieved from Latex Modified Bitumen Emulsion:

Government, N. S. (2011). A Study on Scrap Tyres Management for Peninsular Malaysia. Chemsain Konsultant Sdn. Bhd.

Gulmine, J.,Janissek P.R.(2002). Polyethylene Characterization by FTIR. Vol 21,557-563.

Hidayah, N., Rosli, M., Norhidayah, ., & Ezree, M. (2012). Faculty of Civil and Environmental Engineering, UniversitiTun Hussein Onn Malaysia,86400 Parit Raja, BatuPahat, Johor, Malaysia.

Hu, G., Li, J., & Zeng, G. (2013). Recent development in the treatment of oily sludge from petroleum industry: A review. Journal of Hazardous Materials, 261, 470–490.

Hu, J. (2017). Extraction of crude oil from petrochemical sludge: Characterization of products using thermogravimetric analysis. Fuel, 166-172.

Hughes, R. (2009, January). History: Crude Oil . Retrieved from Energy & the Environment:

Hunter, D. R. (2016). The Shell Bitumen Handbook Sixth Edition. London: ICE Publishing.

Iwanski, M., & Chomicz-Kowalska, A. (2016). Laboratory Study on Mechanical Parameters of Foamed Bitumen Mixtures in the Cold Recycling Technology. Procedia Engineering 57, 433-442.

Joseph, W. (2009). Characterization and analysis of polymers. John Wiley & sons. Hoboken,

Journal, E. P., & Journal, E. P. (2014). Postprint Polymer Modification of Bitumen : Advances and Challenges, 18–38.

Kei, H. M. (2018, April 11). Index of Industrial Production, Malysai February 2018. Retrieved from Department of Statistic Malaysia:

Klinkesorn, U. (2013). The Role of Chitosan in Emulsion Formation. Food Review International, 371-393.

Kramer, J. (2012, December). Petroleum & Petroleum Product. Retrieved from General Petroleum & Fuels:

Kumar, P., Mehndiratta, H. C., & Lakshman Singh, K. (2009). Rheological properties of crumb rubber modified bitumen-A lab study. Journal of Scientific and Industrial Research, 68(September), 812–816.

Lee, S.-J. (2008). The effect of crumb rubber modifier (CRM) on the performance properties of rubberized binders in HMA pavements. Construction And Building Materials, 1368-1376.

Lu, X., & Isacsson, U. (2000). Modification of road bitumens with thermoplastic polymers. Polymer Testing, 20(1), 77–86.

M.A.Shafii. (2011). Polymer Modified Asphalt Emulsion . International Journal of Civil & Environmental Engineering IJCEE-IJENS, 43-49. Retrieved from Polymer Modified Asphalt Emulsion:

M.Chappat. (1994, July 5). Some Applications of Emulsions. Colloids and Surfaces: A Physiochemical and Engineering Aspects, Vol 91, 57-77. Retrieved from Some applications of emulsions

Malaysian Petrochemicals Association. (2015). Malaysia Petrochemical Country Report 2014. APIC- The Asia Petrochemical Industry Conference, (May), 1–52. Retrieved from

Mallawarachi, D. (2016). Suitability of Chitosan as an emulsifier for cationic bitumen emulsions. Construction And Building Materials, 1-6. Retrieved from Suitability of Chitosan as an emulsifier for cationic bitumen emulsions:

Mansur, A. A. (2015). ecovery and Characterization of Oil from Waste Crude Oil Tank Bottom Sludge from Azzawiya Oil Refinery in Libya. Journal of Advanced Chemical Engineering.

Materials, P., & May, B. N. (2007). Pavement materials : Bitumen, 1–8.

Michelle, G. J. (2014). Understanding Rheology of Structured Fluids.

Ministry of Health and Social Services. (2015). Retrieved from Operation Theatre Manual:

Nafici, N., & Zain, M. F. M. (2011). The Role and Function of Thermal Insulation in Architecture, 4, 63–73.

Naggar, a Y. El, Saad, E. a, Kandil, a T., & Elmoher, H. O. (2010). Petroleum cuts as solvent extractor for oil recovery from petroleum sludge. Journal of Petroleum Technology, 1(November), 10–19.

Nalini Thakre, Dipak Mangrulkar, Mahesh Janbandhu, J. S. (2012). Polymer modified bitumen. Materials Research Innovations, 16(1), 1–6.

Needham, D. (1996). Nottingham eTheses. Retrieved from Developments in bitumen emulsion mixtures for roads:

New JerseyNorhasmi Binti Hassan. (2009). Recovery and recycling processes of scheduled waste in Malaysia, (November).

Paliukaitė, M., Vaitkus, A., & Zofka, A. (2014). Evaluation of bitumen fractional composition depending on the crude oil type and production technology. The 9th International Conference Environmental Engineering, (May).

Petrovich, J. (2015). FTIR and DSC of polymers films used for packaging: LLDPE, PP, PVDC. SHAPE American High School.

Praveen Kumar, H. C. (2009). Rheological properties of crumb rubber modified bitumen-A lab study. Journal of Scientific & Industrial Research, 812-816.

Presti, D. L. (2013). Recycle Tyre Rubber Modofied Bitumen for Road Asphalt Mixture: A Literature Review. Construction and Building Material, 863-881.

Rahim, K. A., & Liwan, A. (2012). Oil and gas trends and implications in Malaysia. Energy Policy, 50, 262–271.

Ramaswamy, B., Kar, D. D., & De, S. (2007). A study on recovery of oil from sludge containing oil using froth flotation. Journal of Environmental Management, 85(1), 150–154.

Razali, M. N., Effendi, M. L., Musa, M., & Yunus, R. M. (2016). Formulation of Bitumen From Industrial Waste. ARPN Journal of Engineering and Applied Sciences, 5244-5249.

Read, D. J. (2010). The Shell Bitumen Handbook. London: Thomas Telford Publishing.

Rinaudo, M. (2006). Chitin and chitosan: Properties and applications. Progree in Polymer Science, 603-632.

Ronald, M., & Luis, F. P. (2016). Asphalt Emulsion Formulation: State-of-the-Art and Dependency of Formulation on Emulsions Properties. Construction and Building Materials 123, 162-173.

Roque, R., Birgisson, B., & Drakos, C. (2005). Guidelines for use of modified binders. Test, 354(352), 99.

Ryabenko, V. S. (2016). The Preparation of the Quick-Drying Bitumen Emulsion for the. Oriental Journal of Chemistry, 3129-3134 . Retrieved from The Preparation of the Quick-Drying Bitumen Emulsion for the Protection of the Road Surface Asphalt Concrete Layer:

Salomon, D. R. (2006). Asphalt emulsion technology. Ransportation Research Board, Washington, D.C, (August), 1–24. Retrieved from

Salomon, D. R. (2006). Asphalt Emulsion Technology. Washington DC: Transportation Research Board.

Samuel, E. M. (2011). Bitumen and Binders. Retrieved from Bitumen: Sekar, A. R. C., Mahendran, M., Vasudevan, R., & Velkennedy, R. (2015). Polymer Modified Bitumen Prepared Using Abs Polymer- Characterization and Application in Flexible Pavement, 10(8), 3786–3792.

Shojaei, M., Ismail, A., Kheradmand, B., Hesam, M., & Alezzi, R. (2013). Jurnal Teknologi Full paper The Potentials of Portland Cement and Bitumen Emulsion Mixture on Soil Stabilization in Road Base Construction, 2, 67–72.

Sin, T. J., Chen, G. K., Long, K. S., Goh, I., & Hwang, H. (n.d.). Current practice of waste management system in Malaysia : Towards sustainable waste management Current Practices for Malaysia.

Sola, N. Q. (2013, July). Highly concentrated bitumen emulsions. A state of the art, review of experimental results

Stasiukaitis, T. (2014). Equipment, emulsifiers for production of bitumen emulsions. Retrieved from Bincis:

Sun, Y., Kwok, Y. C., & Nguyen, N. T. (2006). Low-pressure, high-temperature thermal bonding of polymeric microfluidic devices and their applications for electrophoretic separation. Journal of Micromechanics and Microengineering, 16(8), 1681–1688.

Suryakanta. (2015, July 23). 6 Characteristic Properties of Bitumen. Retrieved from CivilBlog.ORG:

Tadros, T. F. (2013). Emulsion Formation,Stability, and Rheology. Emulsion Formation and Stability, 1–76.

Tarmudi, Z., Abdullah, M., & Tap, A. M. (2009). an Overview of Municipal Solid Wastes Generation in Malaysia. Jurnal Teknologi, 51 (F)(November 2016), 1–15

The Bitumen Industry – The Bitumen Industry –. (2011).

The National Academic Press. (2016). Spills of Diluted Bitumen From Pipelines: A Comparatives Study of Environmental Fate, Effects and Response.

Tom V. Mathew and K V Krishna Rao (2007). Introduction to Transportation Engineering, 23, 1-8.

Turi, A. (1997). Thermal Characterization of Polymeric Materials. 1st Edition.

Wu, S. (2010, August 8). Laboratory Study on Ultraviolet Radiation Aging of Bitumen. 768-773. Retrieved from ASCE Library: Wu, S., Pang, L., & Gang Liu, J. Z. (2010, August 8). Laboratory Study on Ultraviolet Radiation Aging of Bitumen. Journal of Materials in Civil Engineering, Vol 22 Issue 8, 767-773. Retrieved from ASCE Library:

Xia, C. (2017). Modification of bitumen emulsion via heterocoagulation with SIS. Journal of Applied Polymer Science, 1-9. Retrieved from Modification of bitumen emulsion via heterocoagulation with SIS:

Yaacob, H., Hainin, M. R., Aziz, M. M. A., Warid, M. N. M., Chang, F. L., Ismail, C. R., & Hassan, N. A. (2013). Bitumen emulsion in malaysia-a conspectus. Jurnal Teknologi (Sciences and Engineering), 65(3), 97–104.

Yang, Q., Ke, D., Yang, M., Hong, J., Ran, Q., & Wang, X. (2013). Colloids and Surfaces A : Physicochemical and Engineering Aspects Effect of salt concentration on the phase separation of bitumen emulsions. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 425, 1–5.

Yi-Qiu, T. (2007). Influence And Mechanism Of Ultraviolet Aging On Bitumen Performance. 726-735.

Yi-qiu, T., Jia-ni, W., Zhong-liang, F., & Xing-ye, Z. (2007). Influence and Mechanism of Ultraviolet Aging on Bitumen Performance, (July), 726–735.

Yuliestyan, A. (2017). Assessment of modified lignin cationic emulsifier for bitumen emulsions used in road paving . Material & Design, 242-251.

APPENDIX

FORMULATION PART 1

Figure A1: Polymer was cut into smaller pieces

Figure A2: Polymer was heated up to check on the temperature at it would completely melt

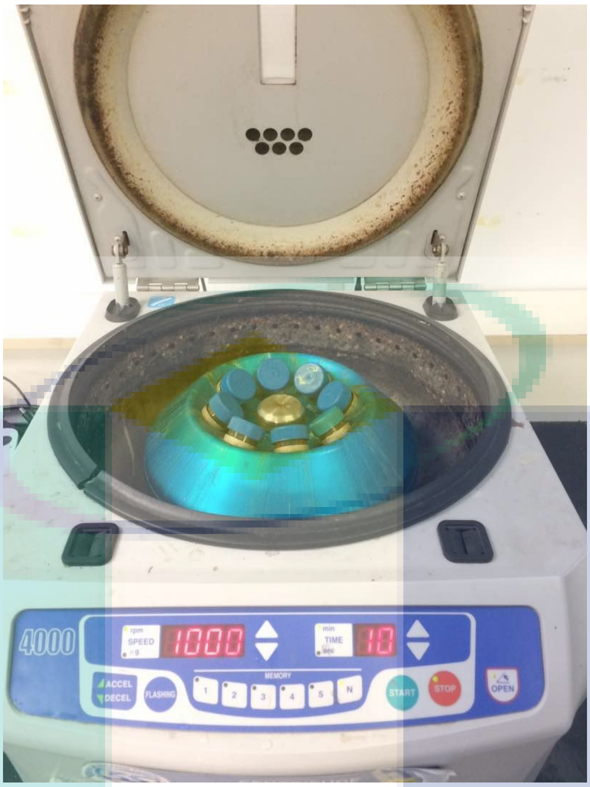


Figure A3: Sludge was separated using centrifuge at 1000 rpm

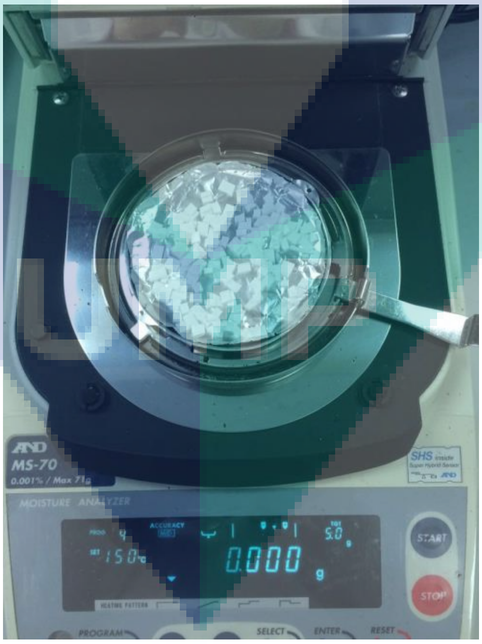
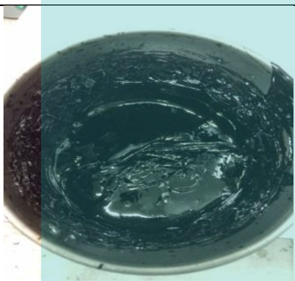


Figure A4: Moisture content analysis for polymer sample

8:0.5:1.5	8:0.7:13	6:0.5:3
		

6:0.7:3.8	4:0.5:5.5	4:0.7:5.3
		

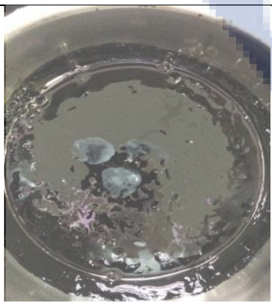
2:0.7:7.3	2:0.5:7.5
	

Figure A5: Eight formulation of modified bitumen using polymer

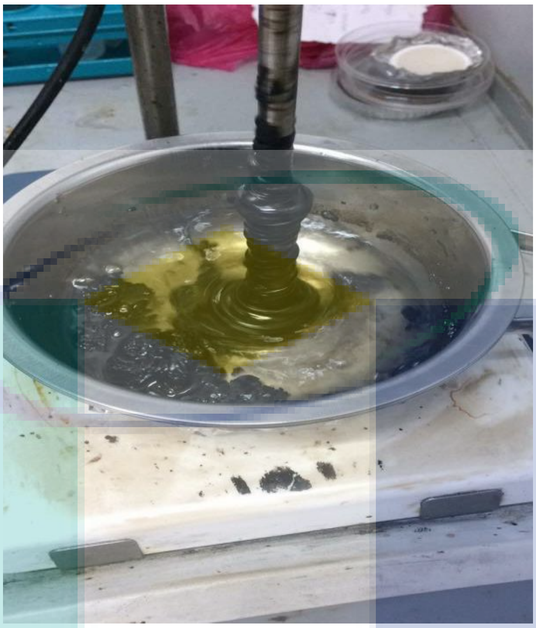


Figure A6: Initial state when bitumen was added to the water and emulsifier mixture

Figure A7: EMB Formulated from industrial waste

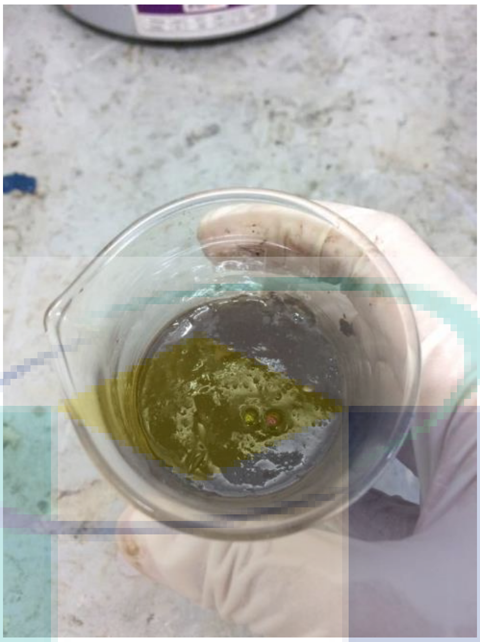


Figure A8: Surface of EMB

Figure A9: Bitumen emulsion of industrial grade bitumen

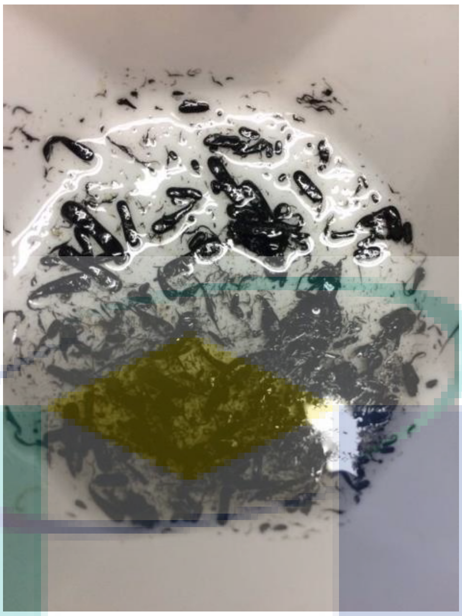


Figure A10: Closer look of bitumen emulsion using bitumen from industry