AN INVESTIGATION STUDY ON USAGE OF BORIC POWDER AND ETHYLENE GLYCOL BASED SYNTHETIC BORIC ACID POLYMER AS BITUMEN MODIFIERS

CHAI ZHEN HAO

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

Faculty of Engineering and Green Technology
Universiti Tunku Abdul Rahman

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DECLARATION

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

Signature : ______________________________

Name : Chai Zhen Hao

ID No. : 11AGB01117

Date : ______________________________

APPROVAL FOR SUBMISSION

I certify that this project report entitled "**AN INVESTIGATION STUDY ON USAGE OF BORIC POWDER AND ETHYLENE GLYCOL BASED SYNTHETIC BORIC ACID POLYMER AS BITUMEN MODIFIERS**" was prepared by **CHAI ZHEN HAO** has met the required standard for submission in partial fulfillment of the requirements for the award of Bachelor of Engineering (Hons) Environmental Engineering at Universiti Tunku Abdul Rahman.

Approved by,

Signature : _________________________________

Supervisor : Dr. Noor Zainab Habib

Date : _________________________________

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ABSTRACT

In this research ethylene glycol based synthetic boric acid polymer (EGBAP) and boric powder were used to improve the properties of 80/100 penetration grade bitumen. The ethylene glycol based synthetic boric acid polymer was synthesized in the laboratory. The percentage of additives used were 1%, 2%, 3%, 4% and 5% by weight of bitumen. High shear rate mixer was used for blending additive with bitumen. All blended samples were then tested using Empirical test namely Penetration, Softening Temperature and Ductility according to ASTM standard test methods. Morphological Analysis using Scanning Electron Microscope was done to know the compatibility of the polymer with bitumen. From the results, the penetration value of modified bitumen decreased and the softening point of modified bitumen increased. As a result, modification of bitumen with boric powder and ethylene glycol based synthetic boric acid polymer (EGBAP) induced stiffness thus would improve the fatigue resistance of pavement. Ductility of all modified bitumen was lower than virgin bitumen thus the modified bitumen might crack at low temperature. However, most of ductility of the modified bitumen was above the minimum requirement of 75cm for 80/100 penetration grade bitumen so the modified bitumen could be used in hot climatic country. The morphological analysis also reflected that the compatibility of modified bitumen was increased as proved by empirical test results.

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LIST OF SYMBOLS /ABBREVIATIONS

AASHTO	American Association of State and Highway Transportation Officials
ASTM	American Society for Testing and Materials
$B(OH)_3$	Monomeric ortho boric acid
B_2O_3	Boron Trioxide
Dmm	Penetration values
DSR	Dynamic Shear Rheometer
EGBAP	Ethylene Glycol Based Synthetic Boric Acid Polymer
EVA	Ethylene-Vinyl Acetate
HBO_2	Metaboric Acid
H_2SO_4	Sulphuric Acid
H_3BO_3	Boric Acid
OBBAC	Organic-Based Boric Acid Compound
pKa	Acid dissociation constant
PMB	Polymer Modified Bitumen
PPA	Polyphosphoric acid
PS	Polystyrene
PB	polybutadiene
R&B	Ring and Ball method

rpm	Revolution per minute
SEM	Scanning Electron Microscope
SBS	Styrene-butadiene-styrene
TEGPB	Triethylene Glycol Based Synthetic Polyboron
UV	Ultraviolet
$2CaO.3B_2O_3$	Colemanite

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Around 2600 years ago, bitumen was first known to be used to construct road by King of Babylon, Nabopolassar. The courses of burnt bricks and stone slabs are cemented by the mortar which contains bitumen. After that, there was no news about the usage of bitumen to pave an area (Lesueur, 2008). Later on refined bitumen which was produced in the USA in early of 19 century was once again used in road construction. The refined bitumen to which was basically obtained from vacuum distillation. Even today most of the bitumen used for paving the road is recently obtained from the bottom of the petroleum distillation column (Lesueur, 2008).

About 95% of the bitumen from 100 million tons of bitumen produced from all over the world is used by paving industry where bitumen acts as a binder for mineral aggregate (Nejad, et al., 2001).

Bitumen cannot last long alone due to factors like temperature, water and air. Thus, bitumen should be strong enough when the temperature is high it can still resist rutting. Fatigue of bitumen will not occur at a moderate temperature only if the bitumen is soft enough. When the temperature is low there will be no more excessive thermal stresses (Nejad, et al., 2001).

Bitumen is a type of thermoplastic material. When the temperature is low, bitumen becomes elastic solid. On the other hand, when the temperature is high, bitumen is a viscous fluid (Firoozifar, Foroutan and Foroutan, 2011).

1.2 Problem Statement

Due to increase in air traffic and vehicle numbers along with the change in the climatic land; resulting in the increase in failure mode namely rutting and fatigue. In order to take care of these failures, mode modification is this required.

Fatigue cracking which shown in Figure 1.1 starts and later accumulated is relevant to the extent of friction from vehicles.

Figure 1.1: Fatigue cracking (theconstructor.org, 2011)

Rutting of road which shown in Figure 1.2 means the permanent deformation of road after vehicles cause some forces while passing on it, the effect is obvious in asphalt layer.

Figure 1.2: Rutting (Pavement interactive, 2008)

1.3 Objective of Study

1. To know the compatibility of two additives, namely boric powder and ethylene glycol based synthetic boric acid polymer (EGBAP) with bitumen by using morphological analysis.
2. To check the enhance characteristic of modified bitumen by using empirical test.

CHAPTER 2

LITERATURE REVIEW

2.1 Bitumen

Bitumen is an engineering material that has been used for thousands of year. People who in ancient time get the natural bitumen from earth surface and directly use it without any binding process. Some applications of bitumen are preservative, adhesive, waterproofing agent (Polacco, et al., 2006). Bitumen can also help the binding of filler and aggregate combine together to form asphalt concrete. The environmental and economic factors driving the force of making more suitable asphalt pavement. The examples of those factors are petroleum resources which getting lesser and lesser cannot be renewed in nature within the short time and the cost to produce asphalt pavement is increasing every year. The programme "The Strategic Highway Research Program (SHRP)" was established to enhance some performance of asphalt concrete and asphalt binder in the year 1987. This project develops many methods to test and find the characteristic of thermal cracking and rheology of asphalt binders. However, it is very difficult to predict how the overall performance of asphalt pavements influenced by the chemical compositions of bitumen because the chemistry of asphalt binder is complicated and the methods of microscopic investigation are not advance enough (Yu, Burnham, and Tao, 2015). Different sources of crude oil and refinery processes produce different properties of bitumen (Jiqing, Bjorn and Niki, 2014).

2.1.1 Manufacture of Bitumen

Bitumen is produced by the distillation of crude oil in paving industry. Only about 10% of available petroleum can be used to produce bitumen (Read & Whiteoak, 2003).

The distillation process is used to process bitumen. The lighter component is first separated in this process at around 350℃. The heavier component is then refined at a bit higher temperature (350 to 425 ℃) with a 0.01 to 0.1 bars pressure under vacuum. The processes are shown in Figure 2.1 below. Only from refined bitumen hard grade and soft grade bitumen can be obtained. The intermediate can only be obtained by blending (Corbett, 1965). Besides that, harder bitumen can also be produced by distillation from new vacuum distillation columns provided with structured packing internals. There is another type of bitumen which has wider temperature range for operating process than normal bitumen and can also be produced by acid modification.

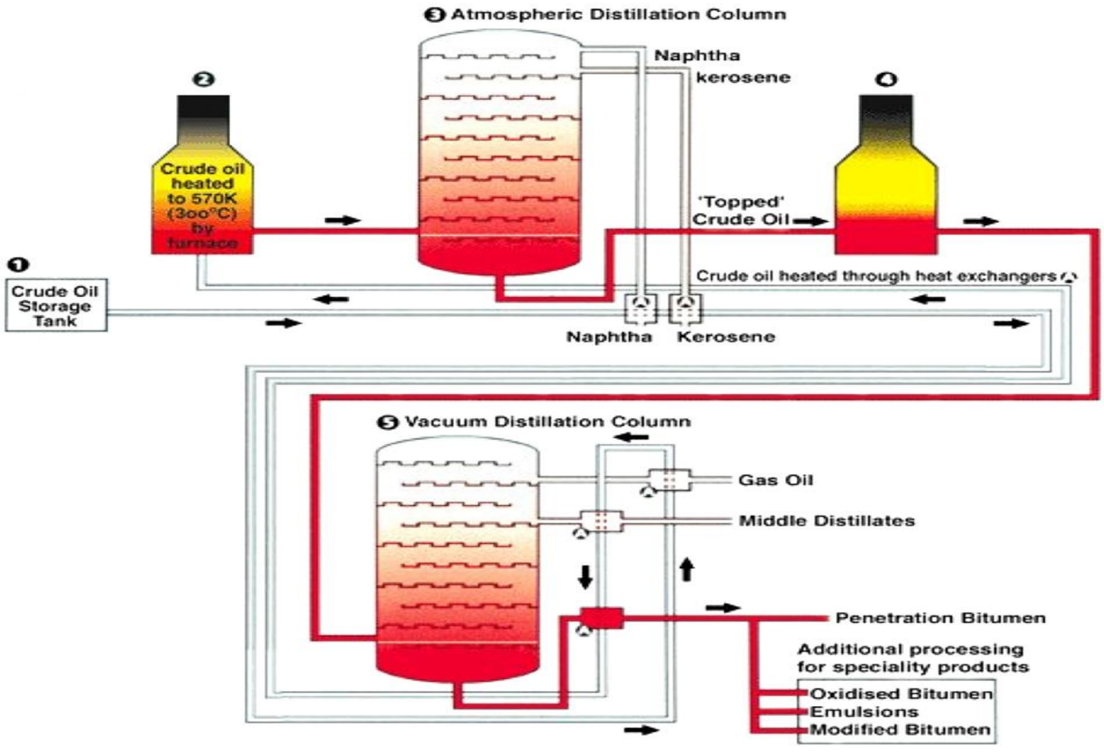

Figure 2.1 Distillation processes of Bitumen from crude oil (Read & Whiteoak, 2003)

2.1.2 Composition of Bitumen

Bituminous concrete is a type of compound that contains components with various ranges, particles from nano scale to macro scale. The nano scale and micro scale are shown in Figure 2.2 (Yu, Burnham, and Tao, 2015).

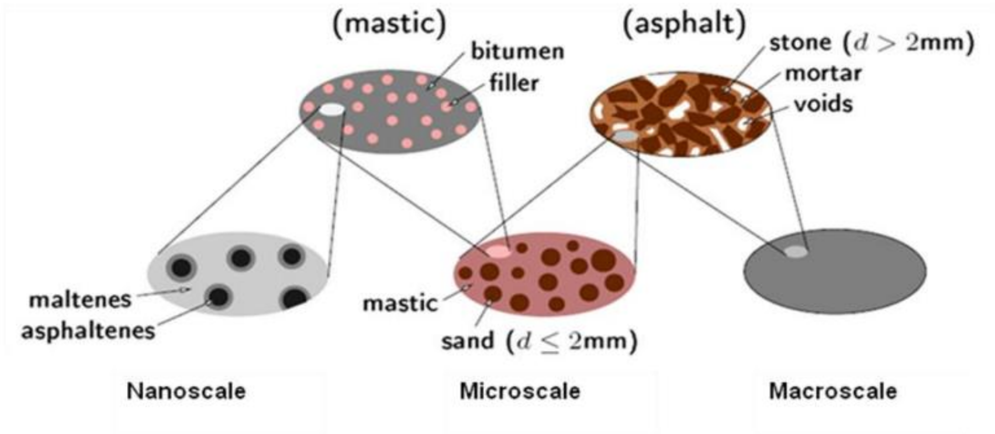

Figure 2.2 Multiscale models for determines bitumen-rock component. Besides macroscale, the other scale of observation is also shown, namely bitumen-scale, mastic-scale (bitumen and filler), mortar-scale (mastic and fine aggregate with diameter less than 2mm) and asphalt scale (mortal and aggregates with diameter more than 2 mm)

Bitumen is composed of maltene and asphaltenes. By using the chromatographic techniques, maltene can further divided into saturates, aromatics and resins. These three groups together with asphaltenes are the four generic groups (SARAs). The aromaticity, complexity, heteroatom content and molecular weight of the four generic groups decrease in order As>R>A>S (Cuadri, et al, 2011).

Asphaltenes is considered as the major component of crude oil that cannot be dissolved in the aliphatic solvent such as n- hepthane. Asphaltenes is composed of dipoles, heteroatoms and short aliphatic side groups which form the big polycyclic-aromatic sheets or typical molecular structure of the asphaltenes which shown in Figure 2.3 (Mullins, O.C., 2011). The polyaromatic fused rings in asphaltenes attract each other such that asphaltenes gather in a mass and thus become the heaviest portion of the bitumen. Polyaromatic fused rings attracted each other and may cause the asphaltenes to aggregate and precipitate out from an initially stable mixture at cold temperature (Yu, Burnham, and Tao, 2015).

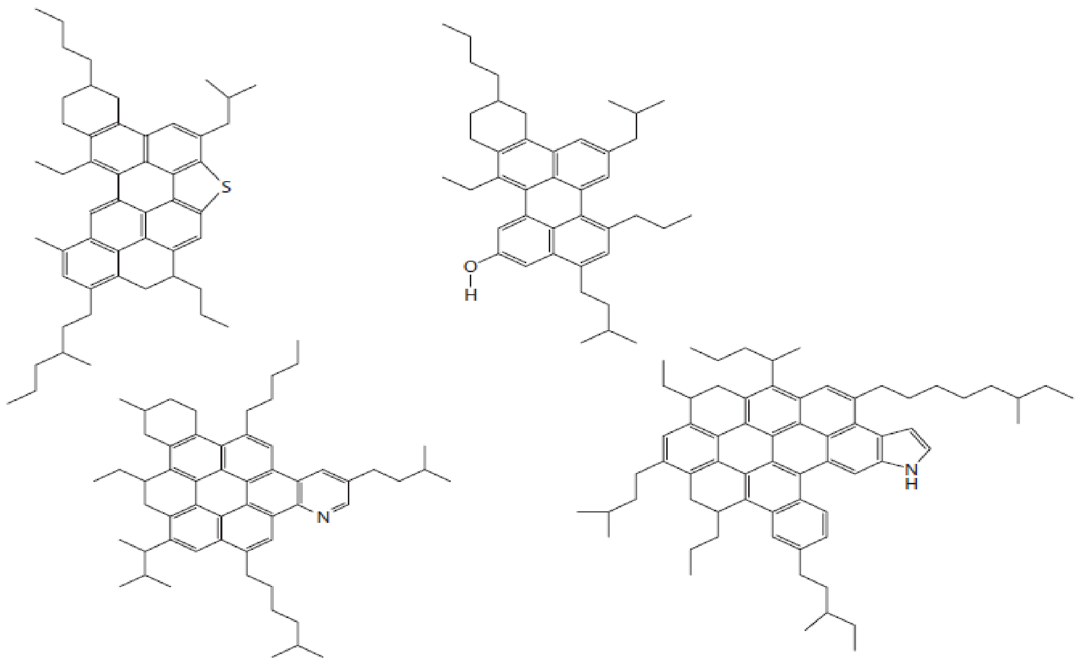

Figure 2.3 Some structures of asphaltenes containing dipoles, heteroatoms or short aliphatic side groups (Mullins, 2011)

The structures of asphaltenes fused aromatic rings, existing like a structure with 4 -5 fused rings and aliphatic chains can be detected by FTIR, U-V fluorescence, Nuclear Magnetic Resonance and X-Ray Raman spectroscopy (Mullins, 1998).

The other component bitumen molecules do not have fused aromatic structures with less condensed aromatic rings and less polar groups compared to asphaltenes. Asphaltenes can form some planar molecules and ultimately form stacks which look like graphite by linking with the π- π bond. The structure is shown in Figure 2.4.

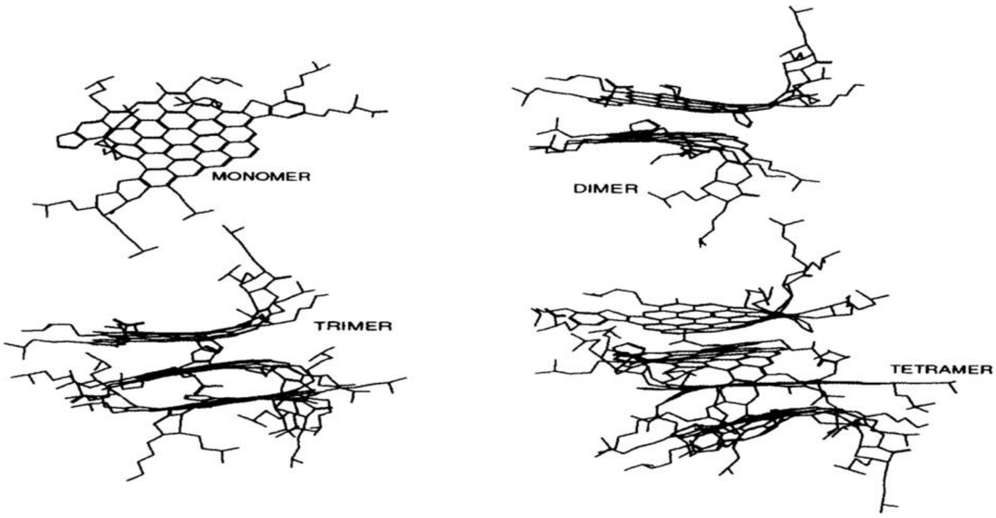

Figure 2.4 Certain structures of monomer dimer, trimer and tetramers of asphaltenes (Scotti, 1998)

It is very difficult to segregate asphaltenes even in the solvent as shown in Figure 2.4 (Scotti, 1998). After sometimes they aggregate to something generally known "micelles". Depending on alsphaltenes content, solvent nature and temperature different, sizes of micelles are formed. This was proven and can be measured by molar masses (Speight 1991). Asphaltenes provide better adhesion property and many surface activities to the mineral aggregate not only because of polar groups but also due to the presence of metal-complexes and polycyclic aromatics present in asphaltenes (Petersen, 1998).

2.1.3 Physical properties and Chemical properties of Bitumen

Most of the molecules in bitumen are hydrocarbons whereas oxygen, nitrogen, sulphur, vanadium and nickel contribute the little percentage of the bitumen. Some centre structures which composed of polyaromatic structures form the hydrocarbon of the bitumen. The saturated polycyclic structures which have varies a number of rings combine to form polyaromatic structures. Since the saturated carbon side chains are different length and pattern thus it is a possibility that they form the isomers (Redelius, P., and Soenen, H., 2014). This is the reason which makes the bitumen be difficult to isolate and characterize (Cuadri, et al, 2011).

2.1.4 Colloid Structure of Bitumen

Nellensteyn was the first to describe the colloidal structure of bitumen. He claimed that when asphaltene is in the maltene phase, a colloidal liquid can be formed (Nellensteyn, 1923). The colloidal model was later used to describe the difference between solubility and delayed elasticity in viscoelastic properties (Saal. and Labout, 1940).

In Figure 2.5, (Lesueur, 2008), asphaltenes micelles are well connected with each other, forming the structure of harder grade bitumen with lower asphaltenes content and higher aromatics content Softer grade bitumen has lesser number of asphaltenes. Besides these resins, saturate contents are also present in crude oil. The resin and aromatics in the bitumen form the surfactant so the asphaltenes micelles can be suspended in maltene (Lesueur, 2008). Some molecular recognition effects in asphaltenes micelles will prevent the resin to enter because the shapes of resin do not fit with the aromatic structure. Therefore, the resin in one type of crude oils that can stabilize the asphaltenes well cannot stabilize the asphaltenes in any other type of crude oil. Differences in polarity between asphaltenes and the maltenes were smothered by the recognition effect thus makes the asphaltenes micelles suspended in maltenes phase (Lesueur, 2008).

At high temperature asphaltenes may possess Brownian motion. Presence the Brownian diffusion explains the higher temperature, increase the electrical conductivities also higher resulting the changes on asphaltenes (Lesueur, 2008).

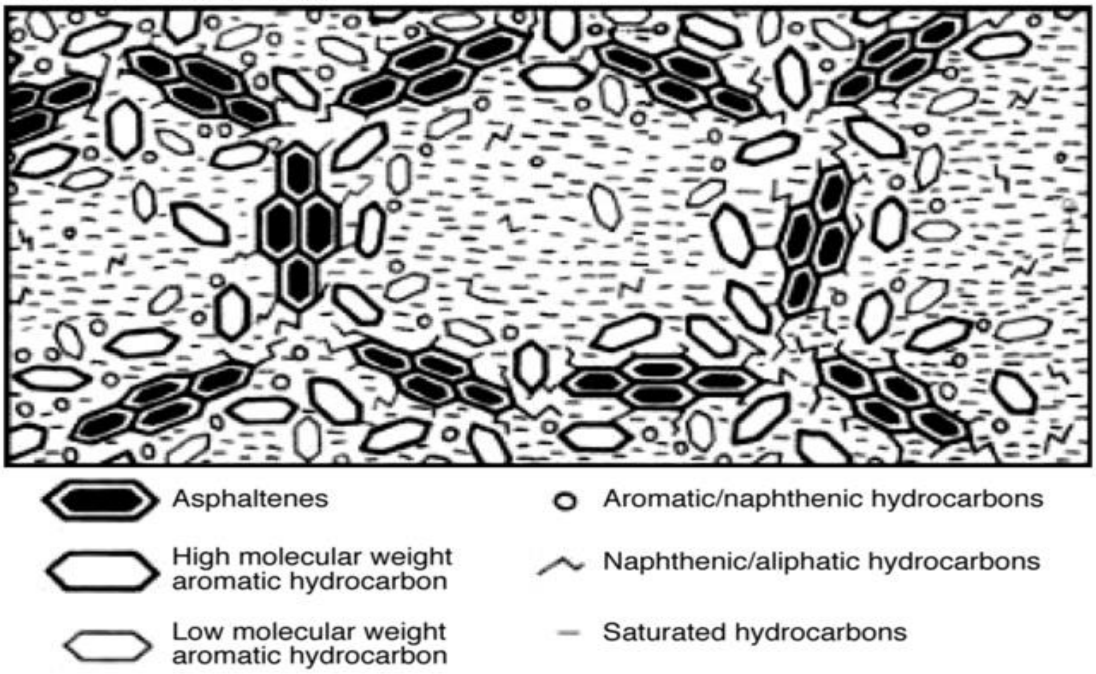

Figure 2.5 Well-connected Asphaltenes (Read & Whiteoak, 2003)

2.2 Boron

Boron is a nonmetallic element and has both amorphous and crystalline form. Boron can be used to make cleaning products and fiberglass (Adair, 2007). Boron has a good conductivity of electricity and heat at high temperature. On the other hand, boron is an electricity and heat conductor in normal temperature that the human live (Muljadi, 2011). Boron appears naturally in mineral ore, volcanic spring water and seawater in the form of borate salt or boric acid. Boron is a type of micronutrients that is a necessity for animals and plants. The range between the level of boron that is low enough to cause boron deficiency and the level that is high enough to cause toxicity of certain plants can be small. The level of boron in the aquatic environment is normally very low (1mg/L water) that cause no effect to animals and plants (Samatya, Tuncel, and Kabay, 2015).

2.2.1 Boric Acid

Boron is found to have some natural form in minerals such as colemanite (2 CaO·3 $B_2O_3 \cdot 5H_2O$), ulexite ($Na_2O \cdot 2$ CaO· $5B_2O_3.16H_2O$) and tincal ($Na_2O \cdot 2B_2O_3 \cdot 10\ H_2O$). The usage of them can be corrosion inhibitors in anti-freeze formulations for cooling systems, boron fertilizers, insecticides and buffers in pharmaceutical production (Barth, S., 1998).

Colemanite and sulphuric acid can be used to produce the boric acid by batch method:

$$2CaO.3B_2O_3 + 2H_2SO_4 + 11\ H_2O \rightarrow 6H_3BO_3 + 2CaSO_4 \cdot 2H_2O$$ (Kroschwitz, 1992)

First of all, calcinated colemanite was placed in a stirred reactor which contains sulphuric acid. The reactor is then heated to 95˚C, the diameter of calcinated colemanite chosen is about 10 mm and the high percentage (98.5%) of sulphuric acid is using in the reactor. The solution needs to be filtered. The clear solution is then cooled and put in a crystallizer to crystallize. A higher temperature, 80˚C is required to dry the wet crystallize boric acid. It may become white, waxy crystals and if the condition of the process is different the colour and appearances of boric acid will be different. The density of crystalline boric acid is 1.48 g/cm^3. Monomeric ortho boric acid, $B(OH)_3$ is the form of boric acid in water. When the temperature higher, the solubility also higher (Barth, S., 1998).

Boric acid, H_3BO_3 contain 3 OH groups connected with boron and arrange in a planar triangular shape as shown in Figure 2.6. Therefore, it is likely to become a basic unit for supramolecular hydrogen-bonded structures. Boric acid becomes tetrahedral anion $[B(OH)_4]^-$ so it acts as a lewis acid instead of becomes conjugate base anion $[BO(OH)_2]$-, a Bronsted acid. In dilute aqua solution, H_3BO_3 is a mixture of $[B(OH)_4]^-$ and acid that does not dissociate. The mixture can achieve equilibrium (Roy, Choudhury, and Rao, 2002). The monomeric borate becomes concentrated and gives many types of polymeric hydroxo (oxo) borate anions at higher concentration (Farmer, 1982).

2.2.2 Physical properties and Chemical properties of Boric Acid

Boric acid is a white crystalline solid and it is odorless. The molecular weight of the boric acid is 61.83g/cm^3 and the Specific gravity is 1.51 at 14˚C (Cheremisinoff, 1999). Boiling point and melting point of boric acid are 300˚C and 169˚C respectively (Hench, 2008). Boric acid has dissociation constant pK_a around 9.2 at the existing environment (Liang, 2005). If the pH of the solution is higher than 10, the metaborate anion dominates the solution. On the other hand, the boric acid will remain as the undissociated boric acid in solution less than pH 7 (WHO, 1998).

Boric acid, H_3BO_3 contain 3 OH groups connected with boron and arrange in a planar triangular shape as shown in Figure 2.6.

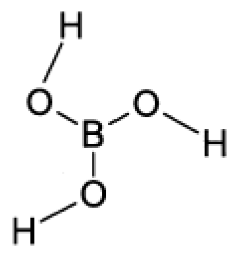

Figure 2.6 Planar triangular structure of boric acid (Roy, Choudhury, and Rao, 2002)

2.2.3 Use of boric powder as Bitumen Modifier

Boric acid was used to synthesize chemically to become organic-based boric acid compound (OBBAC) and triethylene glycol based synthetic polyboron (TEGPB). Both additives can be used to modify bitumen. The modified bitumen increase ductility and viscosity while reduce the softening point. OBBAC modified bitumen thus consider suitable to for cold climatic area (Arslan, Guru, and Cubuk, 2012). OBBAC modified bitumen shows better low temperature cracking resistance as confirmed by the indirect tensile test. OBBAC can also help to enhance the stiffness modulus and marshall stability (Arslan, Guru, and Cubuk, 2012). TEGPB also increases softening point thus TEGPB considered suitable for the hot climatic area. Marshall stability and rutting resistance also found to be improved by TEGPB modified bitumen (Aslan, et al, 2011).

Therefore, the boric powder can be effectively used in tropical countries like Malaysia where severe climatic condition adversely affect pavements in terms of rutting.

2.2.4 Ethylene glycol

Ethylene glycol is an odorless, sweet-tasting, clear, highly viscous liquid colourless and sweet-tasting. It may not easily go in our body through the nose due to its low vapor pressure at room temperature. Precautions need to be done if handle with ethylene glycol because it is acute toxic to human. The ethylene glycol is not easily absorbed by skin so normally someone is poisoned by ethylene glycol is when he/she ingested it (Committee on Curriculum Development in Environmental Medicine, Institute of Medicine, 1995).

Ethylene glycol can absorb water very well and thus prevent freezing or overheating. It can be found to be used in automobile fluids as hydraulic fluids and antifreeze. Ethylene glycol can also be used in fat extractants and cosmetics. It can be detected in fire extinguishers, inks, polish and inks because it was used as a solvent. It can also be used in solar energy system or air conditioning due to it has the properties of heat regulation (Committee on Curriculum Development in Environmental Medicine, Institute of Medicine, 1995). However, ethylene glycol is not carcinogenic and causes the birth defects. After run through Ames test, it was found also not mutagenic (Harte et al, 1991).

2.2.5 Physical properties and Chemical properties of Ethylene Glycol

Ethylene glycol has a molecular weight of 62 mg/mol and the molecular formula of it is $C_2H_6OCH_2CH_2OH$. Figure 2.7 shows the structural formula of ethylene glycol. The density of ethylene glycol at 20 ℃ is 1.1088 (Weast, 1983). The Melting point and boiling point of it are -12.69 ℃ and 197.3 ℃ respectively (Lide, 2003). Modification of Bitumen and the additive is carried out at around 160 ℃ thus the ethylene glycol will not evaporate as the boiling point is around 27.3 ℃ higher than 160 ℃. The molar volume is 55.8cm^3/mol (Rohrschneider, 1973). Ethylene glycol has the acid dissociation constant, pK_a of 14.24 and the water solubility (g/cm^3 or mg/L) at 25 ℃ is miscible (Riddick, Bunger and Sakano, 1986).

Figure 2.7 Structural formula of Ethylene glycol (Mackay et al., 2006)

2.3 Bitumen Modification

Modification of bitumen can be achieved by following methods.

2.3.1 Filler

The general description of mineral filler is "finely divided mineral matter" according to ASTM – D242. The examples are rock dust, fly ash, loess. It also should be free from agglomerations and very dry so that it can flow. Mineral filler also has to pass through 100 % the No. 230 sieve (53 µm). The filler basically refers to the material with size lesser than 75 μm for practical application (Anderson, 1996).

Different size of aggregates, filler and bitumen form the bituminous mixtures. Fillers are mineral grains that can pass through 63μm sieve (BSI, 2004). The filler is around 1/5 the weight of aggregate in the entire bituminous mixture. After crushing rocks, the more natural filler can be produced. Nevertheless, the filler like ash, cement, lime, and slag can also be produced in industry. The role of filler is to fill voids in aggregate skeleton so the mixture becomes denser. It is also found that after adding filler, asphalt cement binder will extend and stiffen (Melotti, et al., 2013). However, if too much filler added into the asphalt cement, rutting may occur because excessive extend of asphalt cement. After adding filler, asphalt mixture can prevent moisture damage (Kandhal, and Parker, 1998).

2.3.2 Acid Modification

Polyphosphoric acid (PPA) which can form chemical bonding with the bitumen molecule is one of the modifiers that used to improve rheological properties of bitumen. According to Edwards et al (2006), after adding 1% of the PPA to the bitumen, stiffness of the bitumen increased (Noemi, et al, 2012).

2.3.3 Polymer Modification

The polymers that can be used to modify bitumen separated into virgin polymers and waste polymer (Cuadri, et al, 2011).

The polymers common: plastomers and thermoplastic elastomers. Plastomers contain very less elastic portion. They are brittle so if they resist high load they will easily deform (Stroup-Gardiner and Newcomb, 1995). On the other hand, thermoplastic elastomers become soft at high temperature and become hard at low temperature (Isacsson and Lu, 1995). The thermoplastic elastomers can also withstand the deformation and able to return to original shape if the load is removed (Stroup-Gardiner and Newcomb, 1995). Therefore, the thermoplastic elastomers are better modifiers of bitumen than plastomers.

Ninety percent of total weight of polymer modified bitumen (PMB) is mainly contributed by the base bitumen. The final properties of the PMB are mainly affected by the base bitumen. The effects of polymer modified bitumen will be improved due to the present of good quality base bitumen. In order to select the appropriate base bitumen, some experiments need to be carried out as the compatibility between bitumen and polymer is different (Jiqing, Bjorn and Niki, 2014). This compatibility may be low if a number of asphaltenes is large in bitumen. The compatibility is good at a certain value of aromaticity of the maltenes (Lesueur, 2008).

The ethylene copolymers are the plastomers that used to modified bitumen, one example is Ethylene-vinyl acetate (EVA) (Sengoz, Topal and Isikyakar, 2009). The polar acetate groups in EVA interferes the crystalline small structure of the segment thus the polarity of the polymer is higher and the crystallization process is less. Therefore, the storage stability is believed to be enhanced in modified bitumen (Polacco, et al., 2006). The higher the portion of vinyl acetate in EVA will lead to the lower crystallization and more amorphous phase. The degree of crystallisation should not be too low because the modified bitumen is easily interfered. It also should not be too high because EVA has fewer interactions with bitumen.

The modified bitumen is able to resist more deformation when the EVA content increase and forms a rigid network inside (Sengoz, Topal and Isikyakar, 2009). However, there are two disadvantages of EVA. The first one is EVA are barely increased elastic recovery of bitumen. Secondly, the EVA cannot enhance the low-temperature properties of bitumen because the glass transition temperature is quite high.

Styrene-butadiene-styrene (SBS) is a thermoplastic elastomer that can be used to modify the bitumen. Rigid polystyrene (PS) linked with flexible polybutadiene (PB) to form the block chains of Styrene-butadiene-styrene (Polacco, et al., 2006). At the temperature that the bitumen is stable, PB blocks contribute elasticity to SBS while PS blocks provide strength to SBS (Lucena, Soares, and Soares, 2004).

PB and PS can also physically link together at room temperature because of the incompatibility (Zhang, et al., 2008). The elasticity of SBS will return to the original state when the temperature goes down (Masson, et al., 2003). The process of phase inversion increases with the SBS concentration. A rubbery supporting network can be found after the SBS-rich phase form in the modified bitumen. SBS modified bitumen are not easily crack at low temperature, have more complex modulus and better elastic behaviour and higher viscosity compared to virgin bitumen. SBS is famous to be used to modify bitumen due to suitable solubility and cheap in price (Chen, Liao and Shiah, 2002).

However, there are some disadvantages of modified bitumen. The compatibility is not satisfied between SBS and bitumen (Airey, 2003). SBS modification bitumen is not able to withstand oxidation, heat and Ultraviolet (UV). This is because some chemical reactions of α-H and double bonds in PB blocks (Collins, and Bouldin, 1992).

2.4 Empirical properties of Bitumen

There are different tests conducted in order to know the empirical properties of bitumen after modification.

2.4.1 Penetration Test (ASTM D5 – 97)

This penetration test used to find the penetration of semi-solid and solid bitumen. The penetration is the distance of material which is penetrated downward by a standard needle of 100g at 25˚C for 5 seconds. This distance will be shown in tenths of a millimeter. The bitumen which has a penetration greater than 150dmm and a ring & ball softening point of more than 35˚C is considered soft grade bitumen (Stopin, 2013). On the other hand, the bitumen which has a penetration less than 50dmm is classified as hard grade bitumen.

2.4.2 Softening point Test (ASTM D36-95)

The method that used to find the softening point is the ring and ball method (R&B) and the unit that measured is degree Celsius (temperature). A steel ball which has a diameter of 9.5mm is first put on a hard sample because the sample is cold. The sample is prepared in a steel ring with the diameter of 15.9mm. The temperature that the steel ball sinks down a distance of around 25mm is determined as the softening point of the sample. The soft grade bitumen has the softening point of around 40˚C while hard grade bitumen has softening point of around 63˚C (ASTM, 1998). The softening point of the different grade of road bitumen is different and it is shown in Table 2.1. One example is the range of penetration of 40/50 pen bitumen is from 40 to 50 (4-5mm).

Table 2.1 Penetration and softening point of road bitumen.

	Penetration grade			
Properties	**40/50**	**60/70**	**80/100**	**Test method**
Penetration at 25 ˚C, 1/10 mm[dmm]	**40-50**	**60-70**	**80-100**	**ASTM D5-IP49**
Softening point, [˚C].	**49-59**	**46-56**	**42-51**	**ASTM D36**

2.4.3 Ductility test (ASTM D113-07)

The ductility of bitumen is the measurement of elongation distance (cm) of bitumen until it reaching a breaking point. This is done by pulling the two end of the bitumen in the opposite direction. The condition of ductility test is around 25˚C at a speed of 5cm/min. Brittle bitumen can be determined by the ductility test and it is not suitable for the pavement of the road.

CHAPTER 3

RESEARCH METHODOLOGY

3.1 Material

3.1.1 Chemical Substance

Some chemicals are using in this project

- Sulfuric acid (H_2SO_4)
  Sulfuric acid solution with 95-98% purity was obtained from QRëC Chemical Manufacturer
- Ethylene Glycol
  Ethylene Glycol solution with 99% purity was obtained from R & M Chemical Manufacturer
- Boric acid
  Boric acid crystal powder with 99.5% purity was obtained from Fisher Scientific Manufacturer

3.1.2 Bitumen

The bitumen grade and some information are shown below:

- 80/100 penetration grade bitumen are from PETRONAS Refinery Melaka, Malaysia.

3.1.3 Equipment

Equipment used are listed below:

- Oven
- High Shear Mixer
- Heater
- Condenser
- Thermometer
- Three neck glass flask
- Magnetic stirrer
- Grinder
- Stainless Sieve
- Sieve Shaker
- Penetrometer
- Ring and Ball apparatus
- Ductimeter

3.2 Design of Experiment

Boric powder and Ethylene glycol based synthetic boric acid polymer (EGBAP) are proposed in this study to modify the bitumen.

Boric powder and EGBAP will mix with the 80/100 penetration grade bitumen with the high shear mixer at a speed of 1300 rpm. The concentration of Boric powder and also EGBAP will used as 1.0%, 2.0%, 3.0%, 4.0% and 5.0% by weight of bitumen in modified bitumen compound.

After that, morphological analysis and some empirical tests will be conducted so we could understand the micro changes of the structure and effect of adding boric powder and EGBAP in the bitumen.

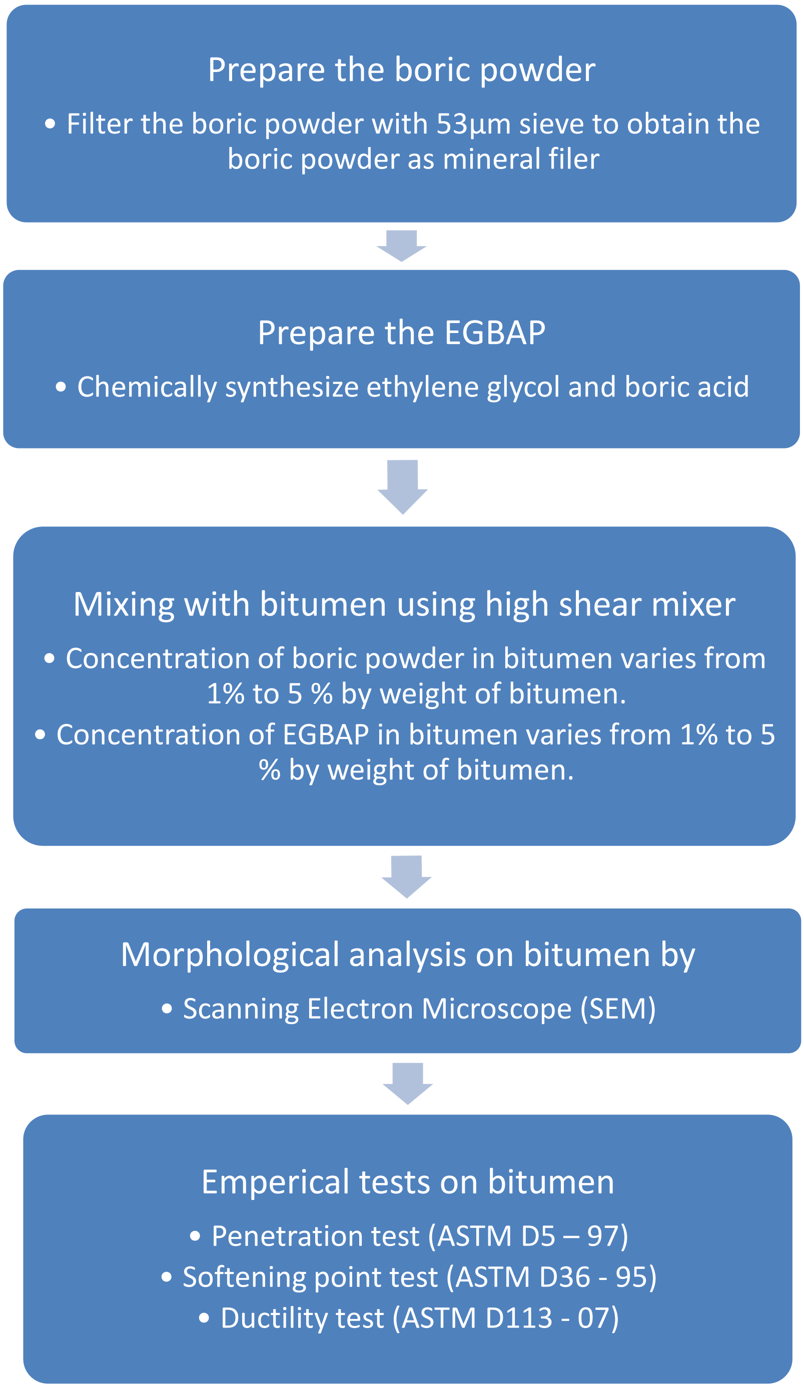

Figure 3.1 Procedure of Design Experiment

3.2.1 Preparation of Boric Powder

The boric powder was grinded by grinder as shown in Figure 3.2 and passing through sieve no. 230 (53 μm) using sieve shaker to achieve the requirement of mineral filler as shown in Figure 3.3 and Figure 3.4.

Figure 3.2 Grinder

Figure 3.3 Stainless Steel Sieves

Figure 3.4 Sieve Shaker

3.2.2 Preparation of Ethylene Glycol Based Synthetic Boric Acid Polymer

Boric acid and ethylene glycol were reacted to form polymers. Sulphuric acid (H_2SO_4) was used as a catalyst in this reaction. A three-neck glass flask, condenser and heater were used to synthesis the ethylene glycol based synthetic boric acid polymer (EGBAP) as shown in Figure 3.5. The magnetic stirrer was also put in three-neck glass flask to stir the solution. The temperature was required to be controlled in this reaction. After that, 150g ethylene glycol was poured in the three-neck glass flask. Heating and stirring of solution were started. A volume of 0.8ml H_2SO_4 was added just after beginning of the heating. After the solution reached 70˚C, 90g of boric acid was added slowly. The heating continue and would be maintained at 120˚C for 30 minutes. After that, the system was completely turned off and the polymer was cooled to room temperature. The polymer would be stored in a jar and ready to be used to modify the bitumen (Aslan, et al, 2011).

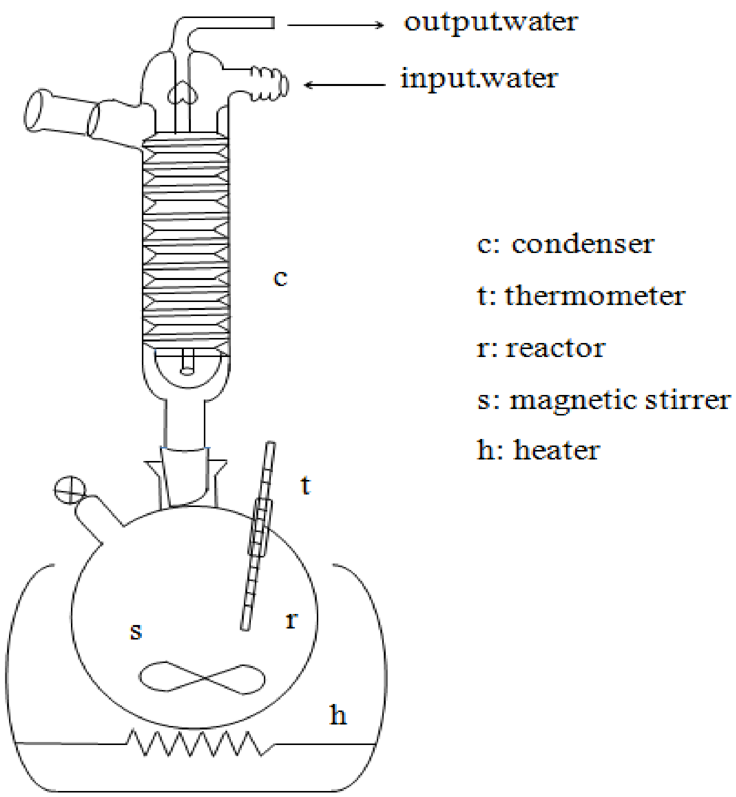

Figure 3.5 Equipment of polymer additive synthesizing

3.2.3 Preparation of Virgin Bitumen

The 80/100 penetration virgin bitumen would be placed in the oven for 2 hours to soften the bitumen. Next, bitumen would be blended using the high shear mixer shown in Figure 3.6 at 160˚C on the hot plate at a speed of 1300 rpm for 20 minutes. This blend was prepared so it was similar to boric acid modified bitumen.

Figure 3.6 High Shear Mixer

3.2.4 Preparation of Boric Powder Modified Bitumen

First of all, 80/100 penetration virgin bitumen would be placed in the oven for 2 hours to soften the bitumen. After that, 5g of boric powder was added into 495g virgin bitumen at 1300 rpm and 160℃ for 20 minutes. This produced 1% boric powder by weight of bitumen.

The same procedure would be repeated by adding dosages of 10.0g boric powder into 490.0g virgin bitumen, 15.0g boric powder into 485.0g virgin bitumen, 20.0g boric powder into 480.0g virgin bitumen and 25.0g boric powder into 475.0g in order to produce 2.0%, 3.0%, 4.0% and 5.0% boric acid by weight of bitumen. The overall preparation is shown in Figure 3.7.

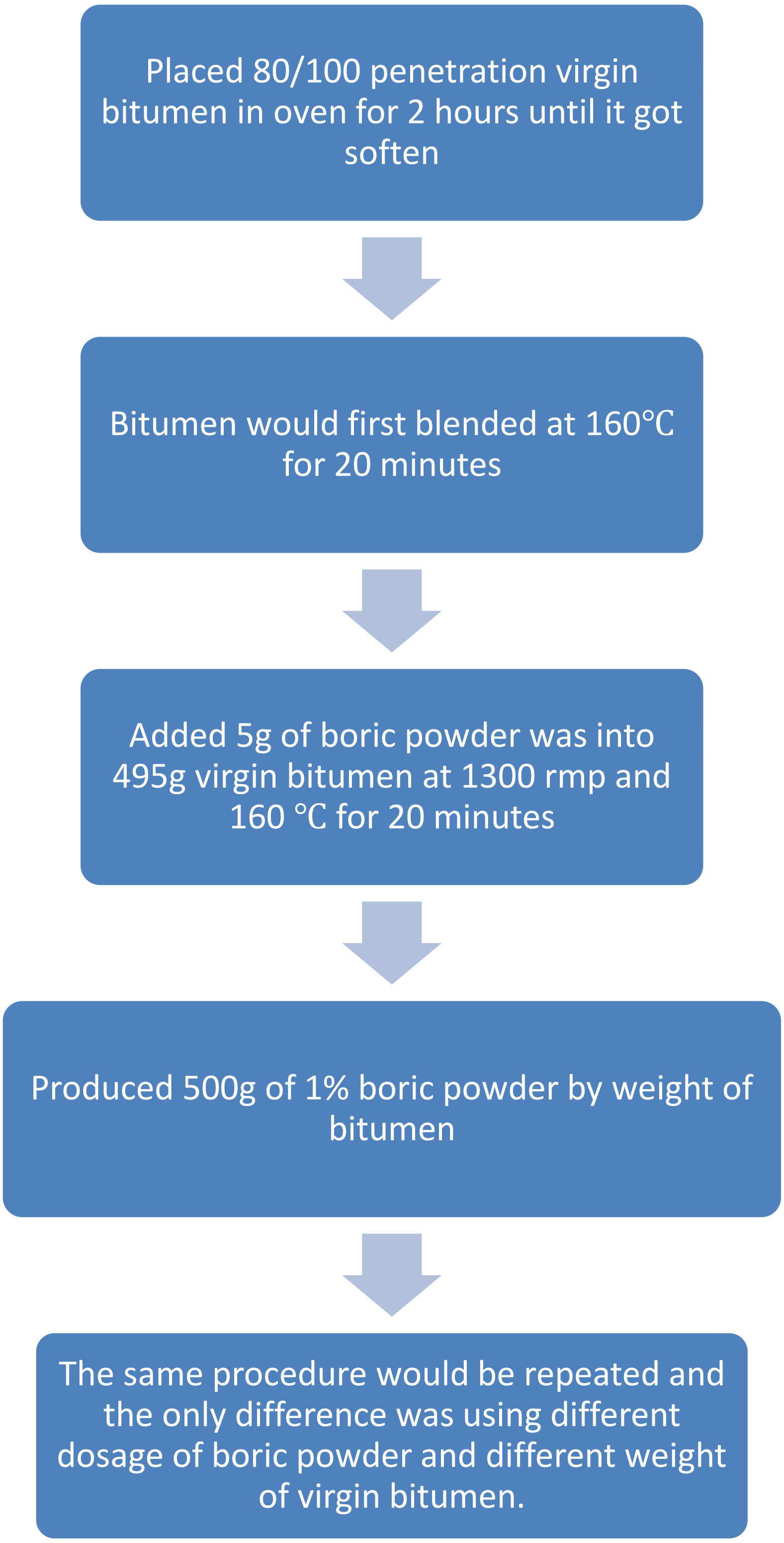

Figure 3.7 Preparation of boric powder Modified Sample

3.2.5 Preparation of Ethylene Glycol Based Synthetic Boric Acid Polymer Modified Bitumen

The ethylene glycol based synthetic boric acid polymer (EGBAP) modified bitumen was produced using the same procedure of the boric powder modified bitumen. The only difference was the boric powder would be replaced by the ethylene glycol based synthetic boric acid polymer. By adding dosages of 5.0g EGBAP into 495.0g virgin bitumen, 10.0g EGBAP into 490.0g bitumen, 15.0g EGBAP into 485.0g virgin bitumen, 20.0g EGBAP into 480.0g virgin bitumen and 25.0g EGBAP into 475.0g, 2.0%, 3.0%, 4.0% and 5.0% EGBAP by weight of bitumen could be obtained.

3.2.6 Morphological Analysis

All samples including additives, bitumen virgin and modified samples were scanned by Scanning Electron Microscope (SEM) as shown in Figure 3.8.

Figure 3.8 Scanning Electron Microscope (SEM)

3.2.7 Empirical Test

Three empirical tests performed were used to analyse the empirical properties of the virgin and modified bitumen which are Penetration test, Ring and Ball test (Softening point) and Ductility test and they will be discussed separately.

3.2.7.1 Standard Penetration Test

A penetration test is a common test to grade the hardness of the bitumen. The penetration of bitumen is lesser indicate the bitumen is harder. For example, the 40/50 grade is harder than 80/100 grade bitumen. A 100g standard needle penetrated the bitumen vertically for 5 seconds at 25˚C. The distance obtained will be the penetration value and is expressed in tenths of a millimeter.

Figure 3.9 shows the penetrometer that used to conduct the penetration test.

Figure 3.9 Penetrometer

The Table 3.1 below shows the range of the differences of the penetration test. If the difference of penetration exceeds the range, the test needs to be repeated. Each sample should be tested at least 3 times and every time the needle should change. This is because the bitumen may stick on the needle and affect the result.

Table 3.1 Maximum difference between the highest and the lowest penetration for different grade of bitumen (ASTM, 1997).

Penetration	0 to 49	50 to 149	150 to 249	250 to 500
Maximum difference between the highest and the lowest penetration	2	4	12	20

3.2.7.2 Softening Point test

The bitumen has no certain definite value of the melting point. It varies with grade and manufacturing process of bitumen. However, bitumen will change from brittle to mobile or softer liquids when heated slowly. Ring and ball method is a good method to test this kind of material.

The temperature that the 3.5g of steel ball penetrate and pass through the bitumen sample and finally touch the base plate is the softening point. The bitumen sample is first placed in the horizontal disk and emerged in the water bath. The temperature is maintained at 5 ℃ for 15 minutes. After that, the water bath is heated and the rate of heating is 5 ℃ per minute until the steel ball falls down 25mm and touch the base plate, this temperate will be immediately recorded as softening point. The ring and ball apparatus to conduct the softening point test is shown in Figure 3.10.

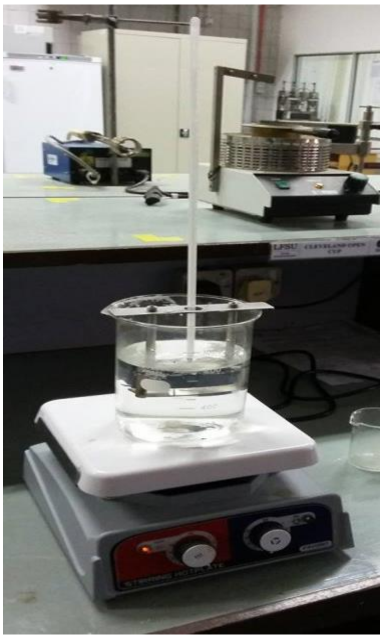

Figure 3.10 Softening Point Testing Equipment

3.2.7.3 Ductility Test

The bitumen is poured in a mould cooled at room temperature for 30 minutes. Later put the mould with bitumen in the water bath for 30 minutes. After making sure the bitumen is just full in mould, put the mould in samples in the water bath for another 90 minutes. Then take away the side pieces and start the testing.

Elongation will occur when both ends of the briquette bitumen sample are pulling in the opposite direction at a rate of 50mm/ minute and the temperature is maintained at 25 ℃. The distance that the bitumen sample break apart is measured as ductility of the bitumen and the unit is calculated in cm. The ductility value of different types of bitumen normally lies between 0 to 150 cm. Figure 3.11 and Figure 3.12 show the ductimeter using to test ductility of bitumen.

Figure 3.11 Ductimeter

Figure 3.12 View of top of Ductimeter

CHAPTER 4

RESULT AND DISCUSSION

4.1 Morphological Analysis

Samples including additives, ethylene glycol based synthetic boric acid polymer (EGBAP) modified bitumen and boric powder modified bitumen were scanned by Scanning Electron Microscope (SEM). The resolution of SEM can be smaller than 1 nanometer.

4.1.1 Scanning Electron Microscope (SEM)

The SEM images of all the samples could help to find out the changes of structure of the modified bitumen and how well the additives were dispersed in modified bitumen.

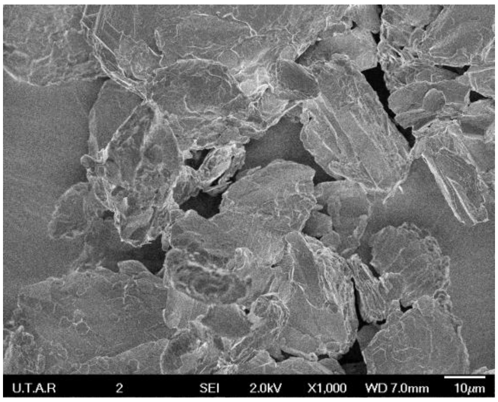

Figure 4.1 Boric powder

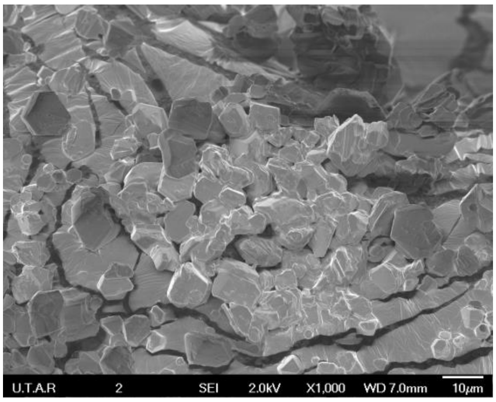

Figure 4.2 Ethylene glycol based synthetic boric acid polymer (EGBAP)

As we can see the shape of boric powder was irregular crystals shown in Figure 4.1. The shape of EGBAP was triclinic structure. The EGBAP had smaller size compare to boric powder.

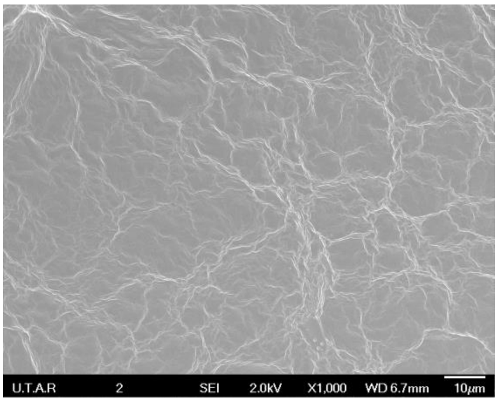

Figure 4.3 Virgin bitumen

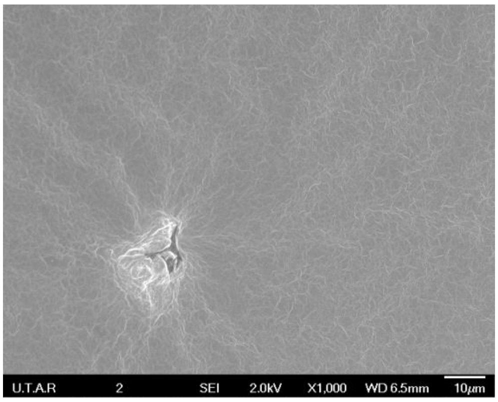

Figure 4.4 1% boric powder by weight of bitumen

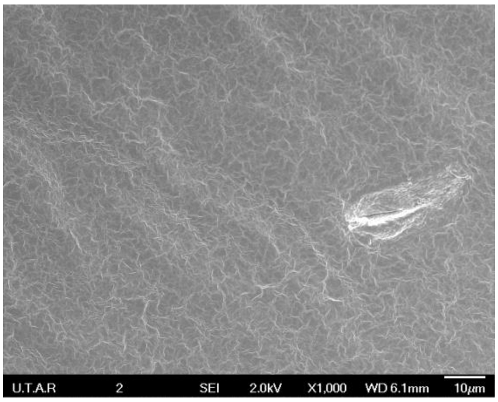

Figure 4.5 2% boric powder by weight of bitumen

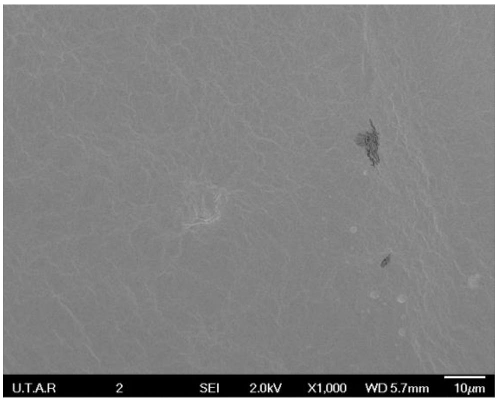

Figure 4.6 3% boric powder by weight of bitumen

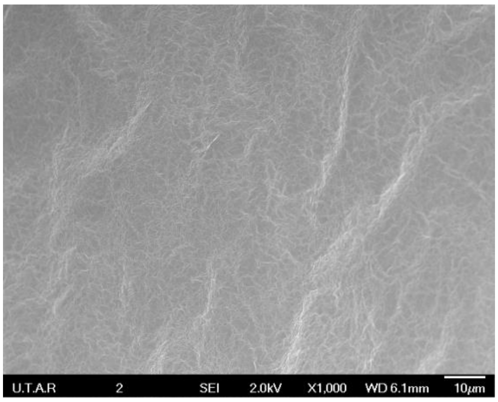

Figure 4.7 4% boric powder by weight of bitumen

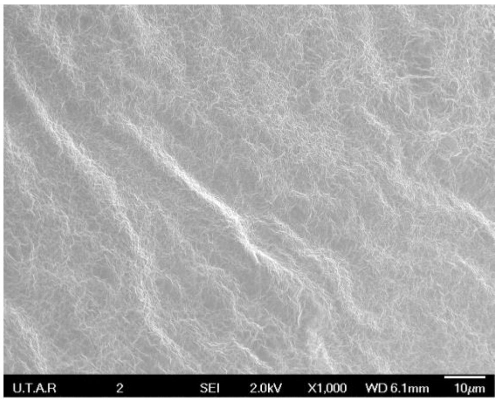

Figure 4.8 5% boric powder by weight of bitumen

SEM result of virgin bitumen was shown in Figure 4.3. The surface area of boric powder modified bitumen was rougher than virgin bitumen and became rougher as the percentage weight of the boric powder increased from 1% to 5% shown in Figures 4.4-4.8. The boric powder additive were able to be found in SEM images of 2%, 3% and 4% boric powder by weight of bitumen and the additive were very small in size. Most of the additives were swollen and disperse inside the base bitumen. The dispersion of bitumen indicated the compatibility of modifier with bitumen.

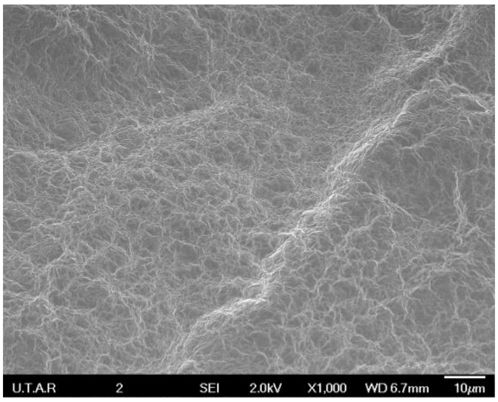

Figure 4.9 1% EGBAP by weight of bitumen

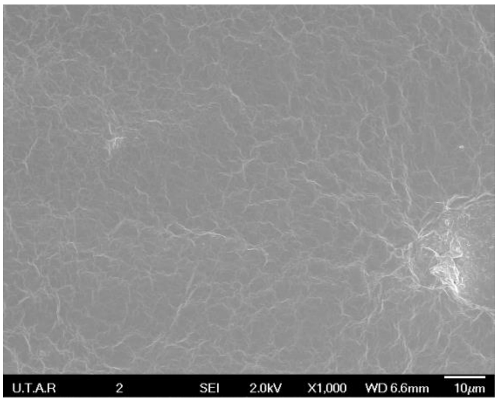

Figure 4.10 2% EGBAP by weight of bitumen

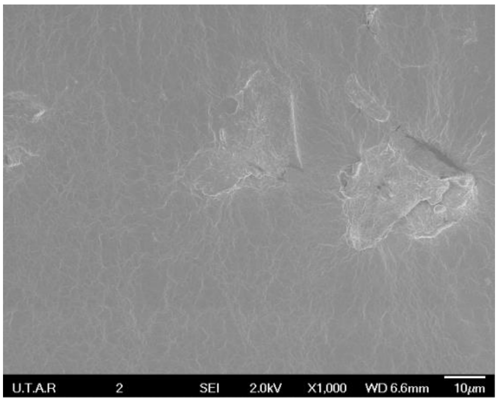

Figure 4.11 3% EGBAP by weight of bitumen

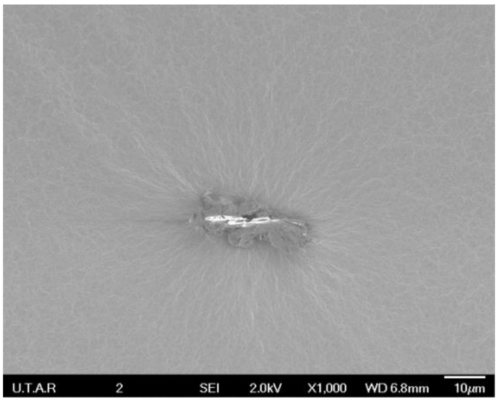

Figure 4.12 4% EGBAP by weight of bitumen

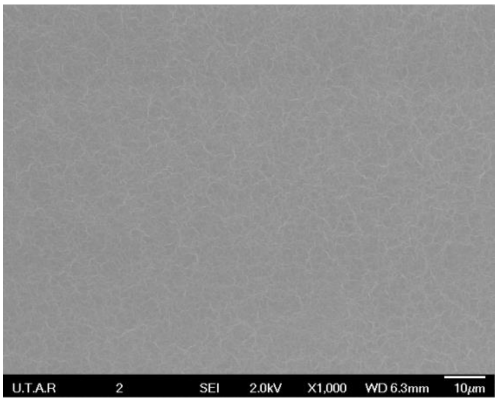

Figure 4.13 5% EGBAP by weight of bitumen

Generally the surface areas of boric powder modified bitumen were rougher than EGBAP modified bitumen by comparing the same level of percentage weight of the additive. Although the particles size of the EGBAP shown in Figure 4.2 was smaller than boric powder, the EGBAP were stick together and were liquid form during the blending process. On the other hand, the boric powder was in the dry conditions, did not stick together so had higher surface area to react with bitumen during the blending process. The EGBAP additive were able to be found in SEM images of 2%, 3% and 4% EGBAP by weight of bitumen and the particle sizes were bigger than boric powder additives. According to Airey (2003), if the polymer content in modified bitumen is lesser than 5% weight, most of the small polymers are easily swollen by some part of virgin bitumen that is compatible to polymer. On the other hand, if the polymer content is lesser than 5%, more polymer phase is formed in the modified bitumen. This might be the reason why only little additive could be seen in SEM image.

4.2 Empirical testing

The Empirical properties of samples, namely virgin bitumen, 1 %, 2%, 3%, 4%, 5% boric powder by weight of bitumen, 1 %, 2%, 3%, 4%, 5% ethylene glycol based synthetic boric acid polymer (EGBAP) by weight of bitumen were tested with Semi-Automatic Cone Penetrometer, ring and ball apparatus, and Ductimeter.

Table 4.1 Penetration, Softening Point and Ductility of Base Bitumen

Grade	80/100 penetration
Penetration(dmm)	97.5
Softening point ℃	52.5
Ductility (cm)	88.0

4.2.1 Results of Penetration

The penetration value generally decreased with the higher percentage of ethylene glycol based synthetic boric acid polymer (EGBAP) and boric powder were added in bitumen and blended. For the virgin bitumen without any additive, it had penetration value of 97.5 dmm as shown in Table 4.1. The penetration values of 1% to 5% EGBAP by weight of bitumen were decreased from 88.0dmm to 79.5 dmm and all of them were lower than virgin bitumen. From Figure 4.14, the penetration values of 1% to 5% boric powder by weight of bitumen showed similar trend compared to EGBAP modified bitumen, but the values were slightly lower, decreasing from 85.00dmm to 68.25dmm. This indicated that the bitumen was hardened when adding any of the two additives, EGBAP and boric powder.

Table 4.2 Results of Penetration Test

Additive %	EGBAP (dmm)	Boric Powder (dmm)
1	88.00	85.00
2	85.25	78.00
3	82.25	74.00
4	80.25	71.50
5	79.50	68.25

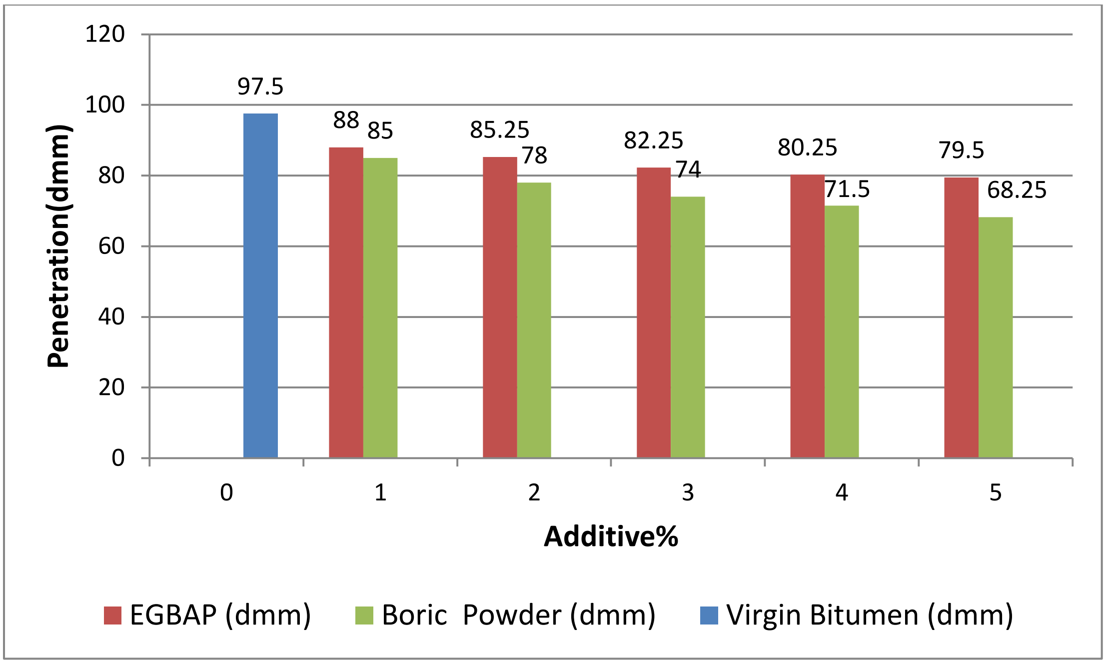

Figure 4.14 Results of Penetration of EGBAP, Boric Powder and Bitumen

4.2.2 Results of Softening Point

From Table 4.3 the softening point generally increased when the percentage of the additive of modified bitumen increased. The base bitumen without any additive had a softening point of 52.5 ℃ as shown in Table 4.1. The softening points of 1% and 2% by weight of EGBAP modified bitumen, 49.75 ℃ and 52.25℃ were first lower than the virgin bitumen. However, 3% to 5% EGBAP by weight of bitumen had the higher softening point than virgin bitumen. The softening points of 1% to 5% boric powder by weight of bitumen were all higher than virgin bitumen, ranging from 53.00 ℃ to 58.25 ℃. The difference of softening point between 1% and 2% EGBAP by weight of bitumen was quite high (2.5 ℃). It might because an insufficient amount of additives react chemically to bitumen, distributed uniformly in the bitumen. In addition, the speed of the high shear mixer which was 1300 rpm might not be fast enough to mix the additive and bitumen well.

The penetration value and softening point of EGBAP modified bitumen and boric powder modified bitumen from Table 4.2 and Table 4.3 show there was decreased in penetration and increased in softening point compared to virgin bitumen. It is believed that after the EGBAP dissolved in bitumen, the modified bitumen had the stronger bond and increased its resistant to the temperature. The modified bitumen increased its hardness may due to stiffening effect cause by the addition of the EGBAP. Therefore modified bitumen is also able to resist fatigue better than virgin bitumen (Yasreen, Madzlan and Ibrahim, 2011).

The size of boric powder was considered filler in this experiment. Adding any type of filler is able to increase the softening point of bitumen and the modified bitumen can withstand abrasion (Shell Bitumen, 1995). Besides that, the bitumen added with filler has fewer tendencies to flow. Therefore, it might be the reason that the softening points of boric powder modified bitumen was higher than the EGBAP modified bitumen as shown in the Figure 4.15. The boric powder modified bitumen appeared as a better modifier in comparison to EGBAP modified bitumen which could improve the fatigue resistance.

Table 4.3 Results of Softening Point Test

Additive %	EGBAP ℃	Boric Powder ℃
1	49.75	53.00
2	52.25	54.00
3	52.75	55.25
4	53.75	56.25
5	55.75	58.25

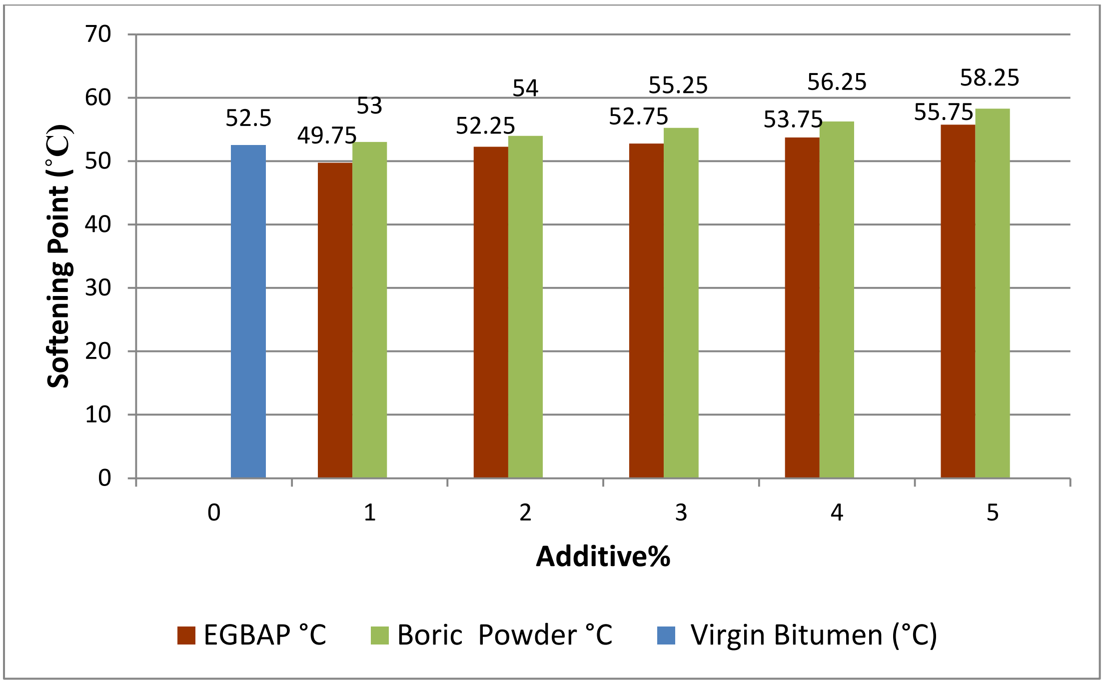

Figure 4.15 Results of Softening Point of EGBAP, Boric Powder and Bitumen

4.2.3 Results of Ductility

Generally all the ductility value of EGBAP modified bitumen and boric powder modified bitumen decreased compared to virgin bitumen as shown in Table 4.4. The range of differences of EGBAP modified bitumen and virgin bitumen were about 6cm to 13cm. Boric powder modified bitumen had lower ductility value compared to EGBAP modified bitumen as shown in the bar chart in Figure 4.16.

Ductility can be partly referred to the ability of bitumen to flow. Therefore, the low ductility of modified bitumen shows the modified bitumen has less ability to flow (Read & Whiteoak, 2003). Modified bitumen may become brittle than virgin bitumen and subject to cracking especially at low temperature. According to HP bitumen handbook (2012), minimum ductility of the 80/100 penetration grade and 60/80 penetration grade bitumen should be 75cm and 50cm respectively. The ductility of 5% boric powder by weight of bitumen was the only sample less than the minimum requirement of 80/100 penetration grade penetration grade bitumen.

Therefore, this is believed that the 1% to 4% boric powder by weight of bitumen and 1% to 5% EGBAP by weight of bitumen will not crack easily in tropical country like Malaysia.

Table 4.4 Results of Ductility Test

Additive %	EGBAP (cm)	Boric Powder (cm)
1	82.0	82.0
2	81.5	80.0
3	80.0	78.0
4	78.0	75.0
5	75.0	70.0

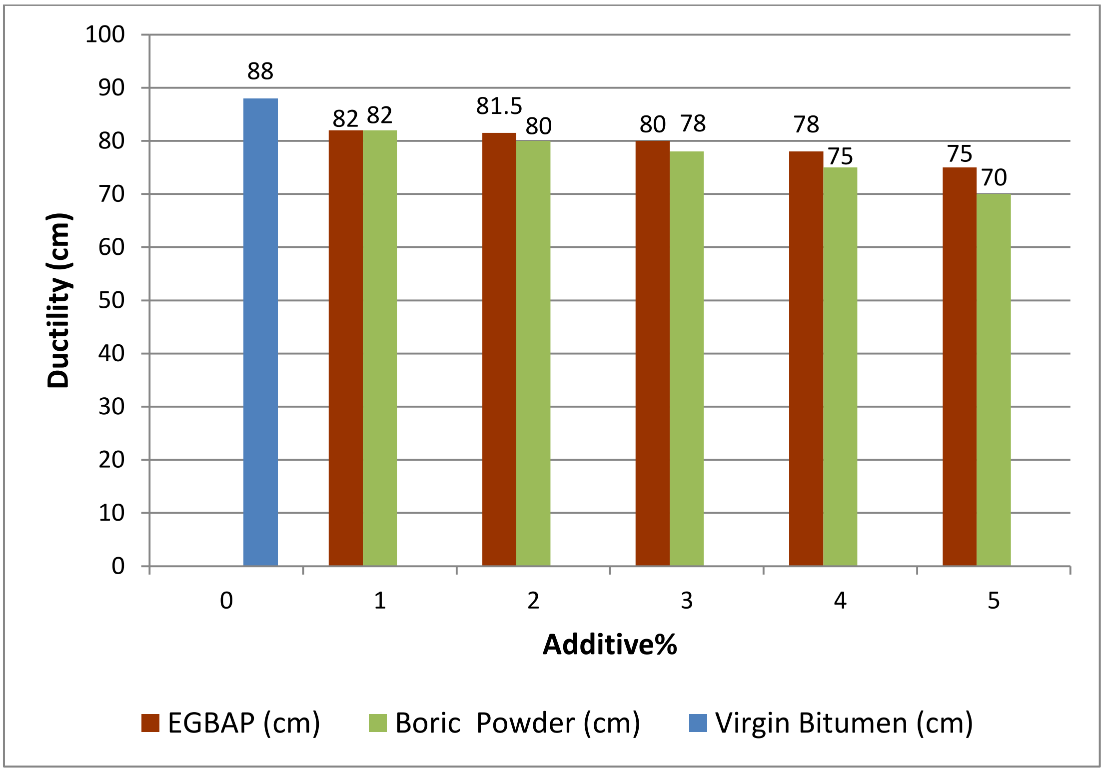

Figure 4.16 Results of Ductility of EGBAP, Boric Powder and Bitumen

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

In this project, Ethylene glycol based synthetic boric acid polymer (EGBAP) and boric powder were well dispersed in bitumen at 1300 rpm by the high shear mixer. The polymer or boric powder phase were not seen in the modified bitumen.

Ethylene glycol based synthetic boric acid polymer (EGBAP) and boric powder with their large surface areas increased the viscosity of the bitumen as reflected by rougher surfaces as observed in Scanning Electron Microscope (SEM) images.

As the concentration of modifier increased, penetration value decreased while softening point increases, which indicate stiffening of bitumen. Thus boric powder modified bitumen appeared as a better modifier in comparison to EGBAP modified bitumen which could improve the fatigue resistance while ductile behavior of 1-2% EGBAP modified bitumen offer ductile behavior, thus can be used in pavements subjected to heavy loading like climbing lanes or roundabouts more prone to fatigue cracking.

Ductility of all EGBAP modified bitumen and boric powder modified bitumen were lower than virgin bitumen. It indicated that the modified bitumen could at low temperature. However, most of ductility of the modified bitumen was above the minimum requirement of 75cm for 80/100 penetration grade bitumen so the modified bitumen could be used in tropical countries.

5.2 Recommendations

This project focused only the empirical testing and morphological analysis. The modified bitumen is also recommended to be tested by rheological testing such as Dynamic Shear Rheometer (DSR) tests to understand the rheological behaviour of the modified bitumen. Besides that, Marshall Stability test is recommended to determine the optimum content of the boric powder and EGBAP modified bitumen

Since ethylene glycol is toxic when ingested, it is recommended to look for other safer materials to replace the ethylene glycol such as triethylene glycol which is less toxic compare to ethylene glycol.

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