INVESTIGATION ON THE USAGE OF OPTIMUM CONTENT OF GRAPHITE OXIDE FOR BITUMEN MODIFICATION

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UNIVERSITI TUNKU ABDUL RAHMAN
INVESTIGATION ON THE USAGE OF OPTIMUM CONTENT OF GRAPHITE OXIDE FOR BITUMEN MODIFICATION

LAM HOU JAZZ

A project report submitted in partial fulfillment 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

January 2015
DECLARATION

I hereby to 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.

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ID No. : 10AGB05584
Date : ________________________________
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Approved by,

Signature : ________________________________
Supervisor : Dr. Noor Zainab Habib
Date : ________________________________
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INVESTIGATION OF THE USAGE OF GRAPHITE OXIDE AS A BITUMEN MODIFIER

ABSTRACT

This research project involves the preparation of Graphite oxide (GO) and used as a bitumen modifier to understand the effects of GO on the empirical testing and morphological properties of the GO modified bitumen. Graphite Nano fiber was used in the preparation of GO by using Simplified Room Temperature Hummer’s Method. There are six samples prepared in this project which are virgin bitumen, 0.1125 wt. %, 0.15 wt. %, 0.225% wt. % 0.3 wt. % and 0.4 wt. % GO modified bitumen. These six samples are analyzed by conducting Empirical Test such as Penetration Test, Softening Point Test and Ductility Test where the pure bitumen acts as reference material. On the other hand, Scanning Electron Microscope (SEM) and Fourier Transform Infrared Spectroscopy (FTIR) were conducted to know the morphological properties and spectroscopic analysis of the GO Modified Bitumen compared to the pure bitumen.
TABLE OF CONTENTS

DECLARATION iii
APPROVAL FOR SUBMISSION iv
ACKNOWLEDGEMENT vi
ABSTRACT vii
TABLE OF CONTENT viii
LIST OF TABLES xii
LIST OF FIGURES xiii
LIST OF SYMBOLS / ABBREVIATION xvi

CHAPTER

1 INTRODUCTION 1

1.1 Background of Study 1

1.2 Problem Statement 4

1.3 Objective of Study 5
2 LITERATURE REVIEW

2.1 Introduction to Bitumen

2.1.1 Extraction of Refined Bitumen from Crude Oil

2.2 Bitumen Constitution

2.2.1 Bitumen Composition – Saturates

2.2.2 Bitumen Composition – Aromatics

2.2.3 Bitumen Composition – Resins

2.2.4 Bitumen Composition – Asphaltenes

2.2.5 Bitumen Structure – Colloidal System

2.3 Graphene

2.3.1 Graphite Oxide

2.3.2 Graphite Oxide as Bitumen Modifier

2.4 Bitumen Modification

2.4.1 Polymer Modification

2.4.2 Acid Modification

2.5 Tests for Bituminous Materials

2.5.1 Penetration Test: ASTM D5-97

2.5.2 Softening Point (Ring and Ball) Test: ASTM D36-95

2.5.3 Ductility Test: ASTM D113–99
3 METHODOLOGY

3.1 Material

3.1.1 Chemical Substance
3.1.2 Bitumen
3.1.3 Graphite Nano Fiber
3.1.4 Equipment

3.2 Design of Experiment

3.2.1 Production of Graphite Oxide
3.2.2 Production of Virgin Bitumen Sample
3.2.3 Production of GO Modified Bitumen

3.3 Empirical Test

3.3.1 Penetration Test (ASTM D5-97)
3.3.2 Softening Point Test (ASTM D36-95)
3.3.3 Ductility Test (ASTM D113-99)

3.4 Morphological Test

3.4.1 Scanning Electron Microscope (SEM)
3.4.2 Attenuated Total Reflection – Fourier Transform Infrared Spectroscopy (FTIR)
4 RESULTS AND DISCUSSION

4.1 Comparison of Fourier Transform Infrared Spectroscopy

Between Graphite Nano fiber (GNF) and Graphite Oxide (GO)

4.2 Scanning Electron Microscope (SEM)

4.3 Empirical Test

4.3.1 Penetration Test

4.3.2 Softening Point Test

4.3.3 Ductility Test

5 CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

5.2 Recommendations

REFERENCES
<table>
<thead>
<tr>
<th>TABLE</th>
<th>TITLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Elemental Analysis of Bitumen</td>
<td>8</td>
</tr>
<tr>
<td>4.1</td>
<td>Fourier Transform Infrared Spectrum (FTIR) of Graphite Nano fiber and Graphite Oxide</td>
<td>41</td>
</tr>
<tr>
<td>4.2</td>
<td>Penetration Values for Virgin Bitumen</td>
<td>45</td>
</tr>
<tr>
<td>4.3</td>
<td>Penetration Values for GO Modified Bitumen</td>
<td>45</td>
</tr>
<tr>
<td>4.4</td>
<td>Softening Point for Virgin Bitumen</td>
<td>48</td>
</tr>
<tr>
<td>4.5</td>
<td>Softening Point for GO Modified Bitumen</td>
<td>48</td>
</tr>
<tr>
<td>4.6</td>
<td>Ductility Test for Virgin Bitumen</td>
<td>51</td>
</tr>
<tr>
<td>4.7</td>
<td>Ductility Test for GO Modified Bitumen</td>
<td>51</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>FIGURE</th>
<th>TITLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Global Market of Bitumen Demand 2012 vs 2005</td>
<td>2</td>
</tr>
<tr>
<td>1.2</td>
<td>Fatigue Cracking</td>
<td>4</td>
</tr>
<tr>
<td>1.3</td>
<td>Rutting</td>
<td>5</td>
</tr>
<tr>
<td>2.1</td>
<td>Process of Distillation of Refined Bitumen from Crude Oil</td>
<td>7</td>
</tr>
<tr>
<td>2.2</td>
<td>SARA fractions of Bitumen</td>
<td>9</td>
</tr>
<tr>
<td>2.3</td>
<td>Percentage by Weight of SARA fractions</td>
<td>11</td>
</tr>
<tr>
<td>2.4</td>
<td>Asphaltenes containing Heteroatoms, Dipoles or Short Aliphatic Side Groups</td>
<td>12</td>
</tr>
<tr>
<td>2.5</td>
<td>Structures of Monomer, Dimer, Trimer and Tetramers of Asphaltenes</td>
<td>12</td>
</tr>
<tr>
<td>2.6</td>
<td>SOL type Bitumen</td>
<td>14</td>
</tr>
<tr>
<td>2.7</td>
<td>GEL type Bitumen</td>
<td>14</td>
</tr>
<tr>
<td>2.8</td>
<td>Graphite Oxide</td>
<td>16</td>
</tr>
<tr>
<td>3.1</td>
<td>Procedure of Design Experiment</td>
<td>24</td>
</tr>
<tr>
<td>3.2</td>
<td>Simplified Room Temperature Hummer’s Method</td>
<td>25</td>
</tr>
<tr>
<td>3.3</td>
<td>Six Cup Standard Steel Vacuum Filter</td>
<td>27</td>
</tr>
</tbody>
</table>
# LIST OF SYMBOLS / ABBREVIATION

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>H/C</td>
<td>Hydrogen to Carbon Ratio</td>
</tr>
<tr>
<td>ppm</td>
<td>Parts per Million</td>
</tr>
<tr>
<td>rpm</td>
<td>Rotational per Minute</td>
</tr>
<tr>
<td>AASHTO</td>
<td>American Association of State and Highway Transportation Officials</td>
</tr>
<tr>
<td>GNF</td>
<td>Graphite Nano fiber</td>
</tr>
<tr>
<td>GO</td>
<td>Graphite Oxide</td>
</tr>
<tr>
<td>dmm</td>
<td>deci-millimetre</td>
</tr>
<tr>
<td>$\text{H}_2\text{SO}_4$</td>
<td>Sulfuric Acid</td>
</tr>
<tr>
<td>$\text{H}_3\text{PO}_4$</td>
<td>Phosphoric acid</td>
</tr>
<tr>
<td>$\text{KMnO}_4$</td>
<td>Potassium Permanganate</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}_2$</td>
<td>Hydrogen Peroxide</td>
</tr>
<tr>
<td>HCl</td>
<td>Hydrochloric Acid</td>
</tr>
<tr>
<td>NaNO$_3$</td>
<td>Sodium Nitrate</td>
</tr>
<tr>
<td>ASTM</td>
<td>American Society for Testing and Materials</td>
</tr>
<tr>
<td>SARA</td>
<td>Saturates, Aromatics, Resins &amp; Asphaltenes</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>------------------------------</td>
</tr>
<tr>
<td>PPA</td>
<td>Polyphosphoric Acid</td>
</tr>
<tr>
<td>°C</td>
<td>Degree Celsius</td>
</tr>
<tr>
<td>MPa</td>
<td>Mega Pascal</td>
</tr>
<tr>
<td>wt. %</td>
<td>Percentage by Weight</td>
</tr>
<tr>
<td>SBS</td>
<td>Styrene-Butadiene Copolymer</td>
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</table>
CHAPTER 1

INTRODUCTION

1.1 Background of Study

Bitumen is known as the engineering material and it has been used from the earliest times as a sealant with adhesive properties and waterproofing agent. The stone blocks in the tank’s walls are bound by the natural bitumen as well as the vertical bituminous core in the centre uses the same principle today in modern dam design (Refined Bitumen Association, 2015). Besides that, bitumen can be used now as the maintenance of the roads, constructions, roofing and airfield. There has been an increase of the material development in the 19th century until the refining of bitumen from crude oils began. The refined bitumen products now are available in many forms and grades for more variety of usages. The process of refining bitumen was started in the 1900s in United States which gives arise in producing industrial applications (Refined Bitumen Association, 2015).
Figure 1.0 shows the global market of bitumen demand 2012 vs. 2005 (World Highways, 2013)

In year 2012, Asia had higher demand of bitumen due to development of their countries while America is already a developed country and therefore, Asia’s demand of bitumen is more bitumen than America now (World Highways, 2013). These bituminous materials are widely used for construction of roadway due to their good binding properties, as a water proofing agent and low cost. Bituminous materials consists of bitumen which is either dark coloured or black, consisting of high molecular weight hydrocarbon extracted from the distillation of petroleum or natural bitumen. Besides that, bitumen is used due to its adhesive properties and solubility in carbon disulphide (Pavement Materials: Bitumen, 2007).

The desirable properties of bitumen depend on the construction and mix type. Generally, Bitumen should fulfill these conditions as the requirements for bitumen.

1. The bitumen must not be highly temperature vulnerable such as during a hot weather, the mix must not be too soft and during cold weather, the mix must not be too brittle that will eventually cause cracks. (Pavement Materials: Bitumen, 2006)
2. The mixing time and compaction of the bitumen must be adequate which can be done by emulsions of suitable grades or use of cutbacks by heating the bitumen and aggregates prior to mixing. (Pavement Materials: Bitumen, 2006)

3. The bitumen and aggregates should be adequate in the mix to enhance adhesion properties. (Pavement Materials: Bitumen, 2006)

4. Able to resist ageing, deformation and have a long term life service with lesser maintenance.

Different grades of bitumen are made for different conditions on the road, climates and even the number of traffic loading on the road. Maintaining the workability is very important during extremely cold or hot weather where the soft grade of bitumen is more acceptable for cold weather while the hard grade bitumen is more acceptable for hot weather. Cold weather might cause the bitumen cracks under frost condition so it is workable if the soft grade bitumen is used and vice versa (Pavement Materials: Bitumen, 2006).

Nowadays, bitumen modifications are widely used to increase the service life of the pavement industry where maintenance of the pavement will be lesser. The common bitumen modifications used are polymers and rubbers.
1.2 Problem Statement

Nowadays, the cost of maintenance of the pavement increases due to heavy traffic loading and changes in climate conditions that will affect the safety of the road users. Thus, there is a need of modifier which offers a greater strength by bonding the bituminous mixture, thereby reduces the fatigue cracking and rutting.

Rutting of pavement and fatigue cracks are mainly due to heavy traffic loading and excessive stress accelerated on the road as well as climate conditions. It is very common in Malaysia where hot climate conditions and amount of vehicles on the road are abundant that will cause rutting to happen. Besides that, Malaysia is a tropical country where it has a high annual rainfall. Heavy rainfall contains also force when it reaches the pavement as one of the loading as this will eventually cause the bonding between the bitumen and aggregates to shatter. After a period of time, a hole will form on the surface of the pavement. Fatigue cracks are also another road condition where excessive traffic loading on the pavement that forms irregular shape and small pattern cracks on the pavement. The cracks failure occurs at the bottom layer of the pavement. This happens because the tension stress is the highest due to excessive traffic loading similar to the deflection of the beam concept.

Figure 1.2 shows fatigue cracks on the pavement
Figure 1.3 shows the rutting on the pavement

1.3 Objective of Study

1. To determine the optimum content of Graphite Oxide Modified Bitumen which can improve rutting and fatigue properties of modified binder.

2. To perform morphological analysis and understand the compatibility of Graphite Oxide in bitumen.

3. To check whether Graphite Nano fiber is successfully converted to Graphite Oxide
CHAPTER 2

LITERATURE REVIEW

2.1 Introduction to Bitumen

Bitumen is an engineering material that is used in the earliest times due to its adhesive properties, sealant and waterproofing agent. The ship-building industry in Sumerians used bitumen during the 6000BC. Next, the binding of stone blocks between the tank’s walls are bonded with bitumen in Indus Valley, Pakistan which utilize the same concept that is used today in modern dam design. The usage of bitumen nowadays is more to paving and roofing (The Bitumen Industry, 2011).

In the 19th century, there is a little development in bituminous materials when the bitumen is available and can be refined from crude petroleum oils. Nowadays, the majority of bitumen obtained for construction such as paving and roofing are refined from crude petroleum oil. Bitumen as a product of oil refinery is available in different grades (The Bitumen Industry, 2011).
2.1.1 Extraction of Refined Bitumen from Crude Oil

Bitumen is produced from crude oil by fractional distillation. The bituminous materials obtained from the distillation of petroleum can be obtained in different forms of bitumen such as bitumen cements, slow-curing liquid bitumen, medium-curing liquid bitumen, rapid-curing liquid bitumen and bitumen emulsions (Nicholas & Lester, 2009). This was due to separation of different hydrocarbons at different boiling points during distillation process without any significant changes in the chemical composition of each material. Fractional distillation is a process in which tall steel towers were use to remove the different volatile materials in the crude oil at successively higher temperatures until the bitumen is obtained as residue (Nicholas & Lester, 2009).

In distillation tower, successive separation were made such as lighter fractions of the evaporated materials are collected on the top tray, and the heavier ones will be collected in successive trays with the heaviest residue containing bitumen at the bottom of the distillation tower. The products obtained from the first phase separation are gasoline, kerosene distillate, diesel fuel, lubricating oils and bitumen. Further processing of the heavy residue obtained after the first separation will give bitumen cement in different penetration grades (Nicholas & Lester, 2009).

Figure 2.1 shows the Process of Distillation of Refined Bitumen from Crude Oil (D. Lesueur, 2009)
2.2 Bitumen Constitution

The structure of bitumen can be determined by its chemical composition of the bitumen. Bitumen contains complex molecules consisting mostly of hydrocarbons with a small heterocyclic species and functional groups containing oxygen, nitrogen and sulfur atoms (Traxler et al., 1936). Besides that, bitumen also contains metal traces such as iron, calcium, magnesium, nickel and vanadium in form of oxides and inorganic salts or porphyrine structures (Read & Whiteok, 2003). The elementary analysis of bitumen manufactured from crude oil shows that the bitumen contains mostly:

- Carbon 82-88%
- Hydrogen 8-11%
- Sulfur 0-6%
- Oxygen 0-1.5%
- Nitrogen 0-1%

Table 2.1 shows the Elemental Analysis of Bitumen (Read & Whiteok, 2003)

<table>
<thead>
<tr>
<th></th>
<th>Carbon: %w</th>
<th>Hydrogen: %w</th>
<th>Nitrogen: %w</th>
<th>Sulphur: %w</th>
<th>Oxygen: %w</th>
<th>Nickel: ppm</th>
<th>Vanadium: ppm</th>
</tr>
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<tr>
<td>Range</td>
<td>80.2-84.3</td>
<td>9.8-10.8</td>
<td>0.2-1.2</td>
<td>0.9-6.6</td>
<td>0.4-1.0</td>
<td>10-139</td>
<td>7-1590</td>
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<tr>
<td>Average</td>
<td>82.8</td>
<td>10.2</td>
<td>0.7</td>
<td>3.8</td>
<td>0.7</td>
<td>83</td>
<td>254</td>
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</thead>
<tbody>
<tr>
<td>Range</td>
<td>5-147</td>
<td>0.1-3.7</td>
<td>1-335</td>
<td>1-134</td>
<td>6-159</td>
<td>1.42-1.50</td>
</tr>
<tr>
<td>Average</td>
<td>67</td>
<td>1.1</td>
<td>118</td>
<td>26</td>
<td>63</td>
<td>1.47</td>
</tr>
</tbody>
</table>

On the basis of complex chemical composition, bitumen can be divided into two wide chemical groups which is asphaltenes and maltenes. The maltenes can be further divided into saturates, aromatics and resins but asphaltenes considered major components of the bitumen (Read & Whiteok, 2003).
2.2.1 Bitumen Composition – Saturates

Saturates contains around 5 – 15 wt. % of a total bitumen, forming a light colourless liquid at room temperature. On the other hand, they are low in glass transition temperature at -70°C (D. Lesueur, 2009).

Besides that, their Hydrogen by Carbon H/C ratio is around 2, consisting of only hetero atoms. Besides that, only a few of crystalline linear n-alkanes are found to be 0 – 15 wt. % of overall fraction. On the other hand, their average molecular weight is about 600 g/mol (D. Lesueur, 2009). Lastly, the solubility of saturates is between 15 to 17 MPa as well as density at 20°C is 0.9 g/cm³ (Corbett, 1969).

2.2.2 Bitumen Composition – Aromatics

Aromatics also known as naphthene aromatics contained the most constituents in bitumen, same goes to resins (Mortazavi & Moulthrop, 1993). They contained around 30 – 45 wt. % in total bitumen. At room temperature, they formed a yellow to red liquid which is more viscous than saturates due to higher glass transition temperature at -20°C (D. Lesueur, 2009).
On the other hand, the carbon skeleton of aromatics consists of slightly aliphatic with lightly condensed aromatic rings and has an average molecular weight of 800 g/mol. The solubility of aromatics is around 17 to 18.5 MPa with density of 1 g/cm³ at 20°C (Mortazavi & Moulthrop, 1993).

2.2.3 Bitumen Composition – Resins

Resins also known as polar aromatics are also abundant in overall bitumen constituents around 30 – 45 wt. %. If aromatics and saturates are oily liquids at room temperature, resins will eventually form a black solid and their glass transition is not clear where it can be exhibit or not (D. Lesueur, 2009).

Koots and Speight (1975) reported that the composition of resins is almost same with asphaltenes except for their difference in molar mass which is 1100 g/mol. Besides that, resins’ Hydrogen by Carbon (H/C) ratio is about 1.38 to 1.69 with less complex aromatic structure (D. Lesueur, 2009). On the other hand, their solubility parameters are between 18.5 to 20 MPa with density of 1.07 g/cm³ at 20°C. Resins play an important role as a stabilizer for asphaltene (Mortazavi & Moulthrop, 1993).

2.2.4 Bitumen Composition – Asphaltenes

Asphaltenes are insoluble black with n-heptane or containing brown shapeless solids with carbon, hydrogen, nitrogen, sulfur and oxygen. Asphaltenes are high in polarity with complex aromatic materials. Read and Whiteok reported that different separation methods will ended up with different values of molecular weights which can be range from 600 - 300 000. However, majority test data shows that the molecular weights of asphaltenes ranges from 1000 - 100 000 which have particle size range from 5 - 30 nm and (H/C) atomic ratio of 1:1. High asphaltene content affects the rheological properties of bitumen. The higher the asphaltene content, the harder the bitumen and more viscous it will be. Therefore, the penetration grade for the bitumen will be lower, softening point increases and viscosity also increases. Bitumen consists of 5 to 25% of asphaltene content (Read &
Whiteok, 2003). Figure 2.3 shows the SARA fractions of bitumen with Percentage by Weight.

![Figure 2.3 shows the Percentage by Weight of SARA fractions (Mortazavi & Moulthrop, 1993)](image)

Besides that, asphaltenes is made up of heteroatoms, dipoles and short aliphatic groups which will form big polycyclic-aromatic sheets as shown in Figure 2.4 (Mullins & O.C., 2011). The polyaromatic rings will attract each other in the asphaltenes that shows that it is the heaviest composition in the bitumen. On the other hand, the initial stable mixture at cold temperature causes the asphaltenes to aggregate due to the polyaromatic fused rings which are attracted to each other (Yu, Burnham & Tao, 2015).

In addition, the high amount of concentrated aromatic structured rings causes asphaltenes to form planar molecules that have the ability to dissociate through π-π bonding to form structures that look like graphite stacks (Becker JR, 1997). These structures are known as monomer, dimer, trimer and tetramer as shown in Figure 2.5.
Figure 2.4 shows the Asphaltenes containing Heteroatoms, Dipoles or Short Aliphatic Side Groups (Kuznicki et al., 2009)

Figure 2.5 shows the Structures of Monomer, Dimer, Trimer and Tetramers of Asphaltenes (Dickle & Yen, 1967)
2.2.5 Bitumen Structure – Colloidal System

Bitumen is also considered as colloidal system with highly molecular weight asphaltene micelles dissolved or dispersed in low molecular weight of oily medium called maltenes (Nellensteyn, 1923). The micelles can be used as stabilizing solvating layer (Read & Whiteok, 2003). The colloidal system is developed by Pfeiffer et al to explain the difference of the rheological properties of the ‘SOL’ and ‘GEL’ type bitumen (Pfeiffer & Saal., 1940).

On the other hand, with the existing quantities of aromatics as well as resins in solvating power, the asphaltenes can be fully peptized which causes micelles to have a better mobility within the bitumen (D. Lesueur, 2008). These are regarded as ‘SOL’ type bitumen (Read & Whiteok, 2003).

Besides that, if the ratio of aromatics as well as resins fraction are insufficient to peptize the micelles or lacking of solvating power, the asphaltenes will cause irregular open packed structure of linked micelles with internal voids that contain intermicellar fluid of mixed composition. This bitumen are called ‘GEL’ type bitumen (Read & Whiteok, 2003).

The colloidal characteristics of asphaltenes in bitumen are caused by aggregation and solvation to the degree which they are peptized and influenced the viscoelastic properties of the system (Saal. and Labout, 1940). For instance, the effects of the colloidal characteristics will decrease when the temperature increases which will cause the GEL character may be lost. However, high temperature of asphaltenes may show the results of Brownian movement or motion which increases electrical conductivity of asphaltenes (D. Lesueur, 2008). The viscosities of saturates, aromatics and resins depend on molecular weight distribution. The higher molecular weight, the viscosity increases as well. As GEL character increases with lower temperature are results from asphaltenes content as well as saturates content (Read & Whiteok, 2003).
Figure 2.4 shows a “SOL” type Bitumen (Read & Whiteok, 2003)

Figure 2.5 shows “GEL” type bitumen (Read & Whiteok, 2003)
2.3 Graphene

Graphite is structured as sp2 hybridized carbon atomic layers which are bonded together by weak Van der Waals forces. The single layers of carbon atoms which are tightly packed into a two-dimensional (2D) honeycomb crystal lattice that is called graphene (Boehm et al, 1994). Graphite exhibits an extraordinary anisotropic behavior in thermal and electrical conductivity. In other words, this behavior is highly conductive in the parallel direction between the graphene layers due to the in-plane metallic character, whereas the weak Van der Waals forces between them cause poor conductivity in the perpendicular direction between the layers (Chung & D.D.L, 2002). The interplanar spacing of graphite is 0.34 nm which is not sufficient enough to occupy ions, organic molecules or other inorganic species.

On the other hand, adding oxidizing agent and strong acids creates oxygen functional groups on the surface. On the other hand, the oxygen functional groups fuse on the edges of the graphene layers to produce graphite oxide. Hummers and Offeman (Hummers & Offeman, 1958) reported that the oxidation of graphite and the production of graphite oxide in a mixture of H₂SO₄, NaNO₃, and KMnO₄ as a result of the reaction of the anions infused between the graphitic layers with carbon atoms, which break the aromatic rings. The C–O covalent bonds increase the distance between the graphene layers from 0.35 nm in graphite to about 0.68 nm in graphite oxide (Bourlinos et al., 2003). This increased in spacing and the anionic or polar character of the oxygen groups will form graphene oxide (GO) a strong hydrophilic behavior, which allows water molecules to penetrate through the graphene layers and thereby increase the distance between graphene’s interlayer. Therefore, graphite oxide becomes highly dispersible in water as surface area increases. Consequently, electrical conductivity in graphite oxide declines between 10³ and 10⁷ Ω cm depending on the amount of oxygen present (Allen et al., 2010).
2.3.1 Graphite/Graphene Oxide

Graphene/Graphite oxide (GO) is a single-atomic layered material produced by oxidation of graphite. GO is an oxidized form of graphene/graphite, fitted with oxygen-containing groups. GO is dispersible in water and other solvents, and it can even be used to make graphene/graphite. It is commonly packaged and sold in powder form, dispersed and as a coating on substrates.

Figure 2.6 shows Graphite Oxide (Ajeyan et al., 2009)

GO is produced by using four methods which are Staudenmaier, Hofmann, Brodie and Hummers. The effectiveness of an oxidation process is resulted by the carbon/oxygen (C/O) ratios of the GO. Besides that, GO has a high surface area and so it is suitable to use as electrode material for batteries, capacitors and solar cells. GO is cheaper and easier to manufacture than graphene, and therefore, GO may enter mass production in the future or even now (Young et al., 2012 & Zhu et al., 2010).

GO can be mixed with different polymers and other materials to enhance properties of composite materials as modifier like elasticity, tensile strength, conductivity and more. In solid state, GO is able to attach one to another to form thin and stable flat structures that can be wrinkled, folded, and stretched. These GO structures can be used for applications such as ion conductors, Nano-filtration membranes and hydrogen storage (Young et al., 2012 & Zhu et al., 2010).
2.3.2 Graphite Oxide as Bitumen Modifier

As mentioned above, GO is cheaper and easier to manufacture nowadays. Therefore, researchers prefer to use GO as their research to enhance properties of materials. GO can be used in many application such as sensor, energy conservation, polymer filter, cell remediation and energy storage devices (Geim, 2009).

Besides that, the high surface area of GO is around 2600 m$^2$/g (Zhu, Wenhui, Dan & Collins, 2013). Therefore, GO can be well dispersed in bitumen and effectively reinforce the bitumen due to high surface and contact area. GO is also a high thermal conductor where it can absorb large amount of heat without changing its properties due to high temperature.

2.4 Bitumen Modification

2.4.1 Polymer Modification

Modified bitumen is asphalt where the rheological or chemical properties were modified by addition of chemical compound. The earliest modifiers were sulfur and rubber and the synthetic modifiers that are commonly used nowadays is styrene-butadiene copolymer (SBS) (Jaroszek, 2012), Ethylene- vinylacetate and polyolefins (Polacco et al., 2004).

The binder and polymer have to be miscible to form homogenous mixture without changing or destroying the colloidal structure of bitumen. Miscibility depends on the structures and properties of both bitumen and polymer. Besides that, bitumen can be modified with platomeric or elastomeric polymers (Stroup-Gardiner and Newcomb, 1995). These polymers are able to improve elastic recovery after removing applied stress, broaden range of viscoelasticity, reduced the risk of rutting and reduced to fatigue and thermal cracking (Stroup-Gardiner and Newcomb, 1995). Platomers causes bitumen to be stiffer but more prone to permanent deformation such as low-temperature modified bitumen (Isacsson and Lu, 1995).
2.4.2 Acid Modification

Polyphosphoric acid (PPA) is a common acid used in bitumen modification. PPA is a polymeric product of thermal dehydration and polycondensation of orthophosphoric acid. PPA is easily hydrolyze in moist air and highly hydroscopic. Its physical form and viscosity at room temperature depends on the content of \( \text{P}_2\text{O}_5 \).

Since PPA does not oxidize bitumen, an addition of PPA into bitumen will results in increase of softening point with no effect in low temperature brittleness. This will enhance the maximum temperature range but in low-temperature properties is based on base bitumen composition (Jaroszek, 2012).

Since 1990s, researchers used PPA as well as polymers to improve quality of bitumen on the road. It has been observed for binder elasticity, thermal cracking resistance, and resistance to permanent deformation. Moreover, PPA increases adhesion properties and may remove anti-stripping agents of bitumen. In addition, the stability of binder in long-term storage in different range of temperatures is increased (Jaroszek, 2012).
2.5 Tests for Bituminous Materials

Bituminous materials tend to lose its properties through oxidation, when exposed to oxygen or air and high temperature, the bitumen tends to become harder as time goes by. This is known as age hardening. Therefore, there are few tests developed to characterize bitumen in terms of their properties. The tests are written in the following below.

2.5.1 Penetration Test: ASTM D-5

In this test, a container that contains bitumen maintained at 25°C is placed under a needle. The needle that weighed 100 g is allowed to penetrate through the bitumen for 5 second. Then, the depth of penetration is expressed in deci-millimetre (dmm) (AASHTO M20-70, 2004). This test is to show the classification of bituminous materials, checking its consistency and evaluation of overheating bituminous materials. In general, there are five different grades in bitumen available in market such as 40/50, 60/70, 85/100, 120/150 and 200/300. A 60/70 grade shows the bituminous binder that contains penetration value ranging from 60 to 70 dmm. The higher the value ranging for the penetration test, the softer the bitumen and vice versa. Therefore, a bituminous binder with low penetration grade is recommended in a warmer site whereas the high penetration grade is recommended in a colder site (Rajib & Tahar, 1966).

2.5.2 Softening Point (Ring and Ball) Test: ASTM D-36

The softening point test is used to measure the susceptibility of blown bitumen to temperature changes by determining the temperature at which the material will be softened to allow a standard steel ball to sink through it. This test is initiated by placing a sample of bitumen in the brass ring which is cooled and immersed in the water and the temperature is maintained at 5°C. In addition, the suitable paving grade of bitumen has the softening point between 35°C to 65°C (AASHTO T53, 2009). Then, the ring is immersed to a depth of 1 inch. As the temperature of the bath increases, the bitumen sample will be softened and gives the
opportunity for the steel ball to sink to the bottom of the water bath. The temperature at which the bitumen sample touches the bottom of the bath is recorded as the softening point (Nicholas & Lester, 2009).

2.5.3 Ductility Test: ASTM D113 - 99

The ductility of the bituminous materials used to measure the distance of bitumen on how long it will elongate before the two ends of bitumen are torn apart. The elongation of bitumen are pulled apart with constant temperature and speed, otherwise the test will be set at 25°C and with the speed of 50 mm/min. This test method is according to the standard ASTM D113-99 as stated.
3.1 Material

The materials used are listed as below:

3.1.1 Chemical Reagent

The chemical reagent and its general information are listed as below:

- Sulfuric acid ($\text{H}_2\text{SO}_4$)
  Sulfuric acid solution which contains 95-98% purity was obtained from QRēC Chemical Manufacturer

- Phosphoric acid ($\text{H}_3\text{PO}_4$)
  Phosphoric acid solution which contains 49-51% purity was obtained from Fluka Analytical Chemical Manufacturer

- Potassium Permanganate ($\text{KMnO}_4$)
  Potassium Permanganate powder which contains 99% purity was obtained from GENE Chem Chemical Manufacturer

- Hydrogen Peroxide ($\text{H}_2\text{O}_2$)
Hydrogen Peroxide solution which contains 35% purity was obtained from SYSTERM ChemAR Chemical Manufacturer
- Hydrochloric acid (HCl)

Hydrochloric acid solution which contains 37% purity was obtained from QRēC Chemical Manufacturer

3.1.2 Bitumen

The bitumen grade and its general information are listed as below:
- 80/100 penetration grade bitumen was obtained from PETRONAS Refinery Melaka, Malaysia.

3.1.3 Graphite Nano fiber

The type of Graphite and its general information are listed as below:
- Graphite Nano fiber was obtained from SIGMA-ALDRICH

3.1.4 Equipment

Equipments used are listed as below:
- Centrifuge
- Oven
- Six Cup Standard Steel Vacuum Filter
- Magnetic Stirrer
- High Shear Mixer
- Hot Plate
- Ductimeter
- Penetrometer
- Fourier Transform Infrared Spectroscopy
- Scanning Electron Microscope
3.2 Design of Experiment

The aim of this experiment is to verify the effect of Graphite oxide to improve the empirical and morphological properties of bitumen. Therefore, we propose to use Graphite Nano Fiber obtained from SIGMA-ALDRICH Chemistry to produce Graphite Oxide (GO) raw material. Graphite Nano Fiber is a fine powder with great dispersion as the effect and performance of GO can be verified easily. Since Graphite Nano Fiber is used, therefore the dispersion problem of GO within the bitumen matrix will not be taken into consideration.

Firstly, Graphite Nano fiber will be oxidized to GO by Simplified Room Temperature Hummer’s Method. Upon completion of GO, GO powder will be mixed with 80/100 penetration grade bitumen with high shear mixer at 2000 rpm. Upon completion of mixing, 5 mixtures with different GO content were produced excluding the pure bitumen. The Graphite oxide content was 0.1125%, 0.15%, 0.225, 0.3% and 0.4% by the weight of bitumen.

Besides that, empirical test such as Penetration Test, Softening Point Test and Ductility Test, morphological test such as Scanning Electron Microscope (SEM) and Spectroscopic Test such as Fourier Transform Infrared Spectroscopy (FTIR) will be performed to understand and enhance the effect of Graphite Oxide on empirical and morphological properties of the 80/100 bitumen sample.
Figure 3.1 Procedures of Overall Research

Production of Graphite Oxide
- Oxidation of Graphite Nano Fiber by Room Temperature Simplified Hummer’s Method

Mixing with bitumen
- High Shear Mixer
- Pure Bitumen
- 0.1125 wt. %, 0.15 wt. %, 0.225 wt. %, 0.3 wt. % and 0.4% wt. % GO Modified Bitumen

Bitumen Test
- Virgin Bitumen
- 0.1125 wt. %, 0.15 wt. %, 0.225 wt. %, 0.3 wt. %, 0.4 wt. % GO Modified Bitumen
- Morphological Test (SEM)
- Spectroscopic Test (FTIR)
- Penetration Test
- Softening Point Test
- Ductility Test
3.2.1 Production of GO – Simplified Room Temperature Hummer’s Method

- **3.2 g Graphite Nano fiber + 320 mL Sulfuric Acid + 80 mL Phosphoric Acid**
- **Slowly add 18 g of Potassium Permanganate**
- **100 mL Hydrogen Peroxide (10%) + 100 mL Distilled Warm Water**
- **Vacuum filtrated with 0.2 µm Cellulose Acetate Membrane**
- **Wash cake residue on membrane with 5% Hydrochloric Acid**
- **Centrifuge with 10,000 rpm for 20 minutes**
- **Measure the pH of upper supernatant**
  - **If pH within 4 - 5**
    - **Remove upper supernatant**
    - **Dry in oven for 70°C**
    - **Obtain Graphite Oxide**
  - **If pH not within 4 - 5**
    - **Remove upper supernatant and fill with distilled water**
    - **Repeat Centrifuge and pH Measurement**

*Figure 3.2 Simplified Room Temperature Hummer’s Method (Huang, Lim, Chia, Yarmo & Muhamad, 2011)*
The Simplified Room Temperature Hummer’s Method was conducted by oxidation of 3.2 g Graphite Nano Fiber (GNF) as shown in Figure 3.2. Firstly, 320 mL of H$_2$SO$_4$ and 80 mL of H$_3$PO$_4$ were mixed into a beaker using a magnetic stirrer. Then, 18 g of KMnO$_4$ was slowly added into stirring mixture to start the oxidation process. After finished adding KMnO$_4$, the mixtures were left stirring for 3 days. After 3 days, 100 mL of H$_2$O$_2$ solution with 10% purity was slowly added into mixtures by titration to terminate the oxidation process. Later, the mixtures were diluted with 100 mL warm distilled water and were left for settlement for another 2 days. On the other hand, 0.2 μm cellulose acetate membrane will be used to filter the settled mixtures by using Six Cup Standard Steel Vacuum Filter as show in Figure 3.3. Later, 5% of Hydrochloric acid was used to wash out the Graphite oxide from filter paper. Therefore, the beaker contains the mixtures of the filtrate and Hydrochloric acid. The mixture collected in the beaker will then go through 20 minutes of centrifuge process with 10,000 rpm by using Beckman Coulter Avanti J-E Series Centrifuge as shown in Figure 3.4. After done centrifuging, if the pH of supernatant mixture does not fall between pH 4 to 5, the supernatant will be removed and refilled with distilled water. Then, the mixtures were repeated until the supernatant falls between pH 4 to 5. The residue collected was dried in an oven for 24 hours at 70°C.
Figure 3.3 shows Six Cup Standard Steel Vacuum Filter

Figure 3.4 Beckman Coulter Avanti J-E Series Centrifuge
Simplified Room Temperature Hummer’s Method uses a highly oxidizing agent, potassium permanganate to oxidize Graphite Nano Fiber under acid condition. Unlikely Hummer’s Method, Simplified Room Temperature Hummer’s Method does not require temperature control as it can be carried out in the room temperature itself. The mixture was stirred at room temperature to obtain a high degree of oxidation as GNF is a very fine powder with large surface area. Comparing with Hummer’s method, Simplified Room Temperature Hummer’s Method does not require researcher to work for long hours in order to control temperature during oxidation of GNF as the chemicals are all poured into a beaker and being left for 3 days to complete the oxidation process at room temperature. Simplified Room Temperature Hummer’s Method is a method to convert Graphite Nano fiber to GO with a shorter duration of time. Being efficient during the experiment will lead to a faster outcome to produce GO as this method has a higher conversion rate as well as large surface area.

3.2.2 Production of Virgin Bitumen Sample

Firstly, the 80/100 pen virgin bitumen sample was left in the oven for 2 hours at 160°C to soften the bitumen as shown in Figure 3.5. Later, the virgin bitumen will be subjected to shearing rate at 2000 rpm for 20 minutes by using high shear mixer as shown in Figure 3.6. The production of the virgin bitumen sample is used to compare with the GO modified bitumen. The virgin bitumen is sheared or blended in the same rate and time with the GO modified bitumen so that the uniformity of the virgin bitumen can be compared with the GO modified bitumen under same specifications and conditions.
Figure 3.5 Production of Virgin Bitumen
3.2.3 Production of GO Modified Bitumen

Similar to the preparation of the virgin bitumen, the 80/100 pen virgin bitumen was left in oven for 2 hours to soften the bitumen. Later, the bitumen sample was blended for 10 minutes at 2000 rpm. Next, 0.5625 g of GO was added into 500 g virgin bitumen and the mixing of the GO modified bitumen will increase from 500 rpm until 2000 rpm. During mixing, a clean cloth is used to cover the opening of container to avoid GO particle disperse out from the mixer. When the mixing speed reached 2000 rpm, this mixing speed will be kept constant for 20 minutes so that the GO can be well dispersed within the bitumen. After 20 minutes, 0.1125 wt. % of GO modified bitumen was obtained.
Therefore, the other 4 samples of GO modified bitumen was produced by repeating the same procedure as mentioned above. The procedures in obtaining GO Modified Bitumen are shown in Figure 3.7.
Placed 80/100 pen virgin bitumen in oven for 2 hours

Virgin Bitumen is blended for 10 minutes at 160°C

Measure and pour 0.5625 g of GO into 500 g bitumen and gradually increase the mixing speed until 2000 rpm

Maintain mixing speed for 20 minutes at 160°C

Obtained 0.1125 wt % GO Modified Bitumen

0.15 wt %, 0.225 wt %, 0.3 wt % and 0.4 wt % were repeated with the procedure above

Figure 3.7 Production of GO Modified Bitumen
3.3 Empirical Test

The Empirical Test for bituminous material in this research consists of three methods which are Penetration Test (ASTM D5-97), Softening Ball Point Test (ASTM D-36) and Ductility Test (ASTM D113-99).

3.3.1 Penetration Test (ASTM D5-97)

Penetration Test will determine the consistency of a bituminous material expressed as the distance in tenths of a millimeter. Besides that, the standard size of the needle will penetrate through the sample under known conditions of time, temperature and loading. Firstly, the sample is melted and cooled under controlled conditions such as temperature. This test was carried out at 25°C and the reading was recorded after 5 seconds of penetration. The penetration was measured with a penetrometer where the standard size needle was applied to the sample under specific conditions as described in ASTM D5-97. This test was used to determine the consistency where higher penetration value shows softer consistency. Figure 3.8 shows the penetrometer used for the Penetration Test.

Figure 3.8 shows Penetrometer
3.3.2 Softening Ball Point Test (ASTM D36-95)

Softening Point Test is used to determine the softening point of the bitumen in the temperature range from 30°C to 157°C by using the ring-and-ball apparatus immersed in distilled water at temperature range from 30°C to 80°C, USP glycerin at temperature range from 80°C to 157°C or ethylene glycol at temperature range from 30°C to 110°C. In this research, distilled water is used as it is easier to produce than others. This test begins with the temperature of 5°C and increases at the rate of 5°C per minute. This test ends when the steel ball reached the bottom of the steel plate and the temperature is observed when the ball reached the bottom.

Bitumen contains viscoelastic properties without defined melting points as they gradually become less viscous and softer as temperature increases. Therefore, softening point must be determined by a random and defined method if the results are duplicable. Besides that, softening point is determined so that the bitumen can be classified and can be indicated of the material flow under elevated temperatures. Figure 3.9 shows the softening ball point test and Figure 3.10 shows the steel ball touching the bottom of the steel plate upon completion of the test.

![Figure 3.9 shows the setup of Softening Point Test](image)

Figure 3.9 shows the setup of Softening Point Test
Figure 3.10 shows the end of Softening Point Test
3.3.3 Ductility Test (ASTM D113-99)

The Ductility Test is used to measure the tensile properties of bitumen under specific requirements as stated in ASTM D113-99. This test is performed by elongation of the bitumen at specific speed and temperature. Firstly, the mold sample must be prepared under specifications as stated by the standard. In this standard, the speed used is 50 mm/min and temperature of water bath which is 25°C. The test ends when the bitumen sample was torn apart and the length of the bitumen when it is torn apart was measured and the characteristics of the bitumen can be determined. Figure 3.11 shows the ductimeter, Figure 3.12 shows the beginning of the test and Figure 3.13 shows the bitumen samples are being pulled apart.
Figure 3.12 shows the beginning of the Ductility Test

Figure 3.13 shows the bitumen samples are being pulled apart
3.4 Morphological Test

3.4.1 Scanning Electron Microscope (SEM)

The Scanning Electron Microscope (SEM) uses a focused beam of high-energy electrons to generate different signals at the surface of solid specimens. The signals reveal the information on texture, chemical composition and crystalline structure and orientation of materials making up the sample. The areas ranging from 1 cm to 5 microns in width can be scanned by using conventional SEM techniques with magnification ranging from 20X to approximately 30,000X and spatial resolution of 50 to 100 nm. In this study, JSM-6701F FE-SEM from JOEL (MALAYSIA) SDN. BHD. was used as the equipment to identify the surface texture morphology and surface roughness of GO in bitumen.

Figure 3.14 shows the FE-SEM used for Morphological Analysis
3.4.2 Attenuated Total Reflection - Fourier Transform Infrared Spectroscopy (ATR-FTIR)

The Attenuated Total Reflectance (ATR) revolutionized solids and liquid sample analysis as it is the most challenging aspects for infrared analysis, sample preparation and spectral reproducibility. Fourier Transform Infrared Spectroscopy is a very diverse molecular spectroscopy technique and chemical analysis method where it is used for polymer testing and pharmaceutical analysis. This includes both qualitative and quantitative analysis of wide range of organic and inorganic samples. In this project, instrument model Spectrum RX 1 from Perkin Elmer is used to investigate the functional group of Graphite Oxide (GO) and Graphite Nano Fiber (GNF).

Figure 3.15 shows the FTIR used for Spectroscopic Analysis
CHAPTER 4

RESULTS AND DISCUSSION

The Empirical Test for six samples which are virgin bitumen, 0.1125 wt. %, 0.15 wt. %, 0.225 wt. %, 0.3 wt. %, and 0.4 wt. % were tested with Penetration Test, Softening Ball Point Test and Ductility Test to determine the strength and hardness of the bitumen after adding the different percentages of graphite oxide. On the other hand, morphological testing was conducted to determine the shape and texture of the GO Modified Bitumen compared to the virgin bitumen.
4.1 Comparison of Fourier Transform Infrared Spectroscopy between Graphite Nano fiber (GNF) and Graphite Oxide (GO)

Figure 4.1 shows the FTIR of Graphite Nano fiber (GNF)
Figure 4.2 shows the FTIR of Graphite Oxide (GO)

The FTIR spectrum of Graphite Oxide in Figure 4.2 shows a very broad peak of 2400 cm\(^{-1}\) to 3400 cm\(^{-1}\) that contains O-H stretching vibrations corresponding to C-OH groups and hydroxyl group and a sharp peak at 1610 cm\(^{-1}\) indicates that the OH groups of water molecules are adsorbed on graphite oxide. Therefore, these peaks show that the GO has strong hydrophilicity property. Next, there are 2 small peaks between 2400 cm\(^{-1}\) to 2800 cm\(^{-1}\) which show the existence of aldehydes of C-H stretch.

Besides that, the presence of peak 1718 cm\(^{-1}\) indicates that the existence of C=O stretch of carboxylic acid at the edges of graphite oxide. On the other hand, the absorption peaks at 1228 cm\(^{-1}\) and 1062 cm\(^{-1}\) indicates the C=O of carboxylic acid and C-O of epoxy groups. These oxygen-containing groups showed that the Graphite Nano fiber has been successfully oxidized to Graphite Oxide. On the surface of hydroxyl groups where the hydrogen bonding that forms between graphite and water molecules will explain the hydrophilic nature of graphite oxide.

Graphite oxide contains carboxyl, carbonyl, hydroxyl and epoxy groups that contribute to strong hydrophilic nature. Therefore, graphite oxide is a stable material and able to provide strength and enhance the rheological properties as a bituminous material.
Table 4.1 Fourier Transform Infrared Spectrum (FTIR) of Graphite Nano fiber and Graphite Oxide

<table>
<thead>
<tr>
<th>Sample</th>
<th>Absorption Peak (cm(^{-1}))</th>
<th>Types of bond</th>
<th>Functional Groups</th>
<th>Citation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite Nano</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>fiber</td>
<td>2373</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1641</td>
<td>C=C stretch</td>
<td>Carbonyl</td>
<td>(Liu, et al., 2012)</td>
</tr>
<tr>
<td>Graphite Oxide</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3400</td>
<td>C-OH stretching vibration</td>
<td>Hydroxyl</td>
<td>S. Leila, et al., 2014</td>
</tr>
<tr>
<td></td>
<td>2400-2800</td>
<td>C-H stretch</td>
<td>Aldehydes</td>
<td>S. Leila, et al., 2014</td>
</tr>
<tr>
<td></td>
<td>1718</td>
<td>C=O stretch</td>
<td>Carboxyl</td>
<td>(Liu, et al., 2012)</td>
</tr>
<tr>
<td></td>
<td>1610</td>
<td>C-OH stretching vibration</td>
<td>Hydroxyl</td>
<td>S. Leila, et al., 2014</td>
</tr>
<tr>
<td></td>
<td>1228</td>
<td>C=O stretch</td>
<td>Carboxyl</td>
<td>(Liu, et al., 2012)</td>
</tr>
<tr>
<td></td>
<td>1062</td>
<td>C-O stretching vibration</td>
<td>Epoxy</td>
<td>(Liu, et al., 2012)</td>
</tr>
</tbody>
</table>
4.2 Scanning Electron Microscope (SEM)

Virgin Bitumen

0.1125 wt. % GO Modified Bitumen

0.15 wt. % GO Modified Bitumen
0.225 wt. % GO Modified Bitumen

0.3 wt. % GO Modified Bitumen

0.4 wt. % GO Modified Bitumen

Figure 4.3 shows SEM of Virgin Bitumen and GO Modified Bitumen
The morphological test for the bitumen was tested with Scanning Electron Microscope to understand and observe the morphology, surface texture and compatibility of GO in bitumen. Therefore, Figure 4.3 above shows the Scanning Electron Microscope for virgin bitumen, 0.1125 wt. %, 0.15 wt. %, 0.225 wt. %, 0.3 wt. %, 0.4 wt. % GO modified bitumen. This SEM test was conducted under 1 micron and magnification of X5,000 and X10,000. The graphite oxide is not visible from the SEM as the amount of graphite oxide used in this research is small.

On the other hand, during the shearing action during the blending, it breaks the GO into finer fragments. Therefore, as the rotational per minute of the bitumen blending with GO increases, the particles of GO are well dispersed into the bitumen as bitumen is thick and dark in colour which makes the fine GO particles difficult to be observed. Large surface area of the GO also plays an important role as a binder in bitumen. This indicates that the dispersion rate of GO is high enough to strengthen the bond of the bitumen.

From the figure above, bitumen is composed of thread-like structure with ultrathin and homogenous films. These films causes the bond within the bitumen to be strong and even it is difficult to wash away with water when intact with it. This fiber-like structures can be folded into wrinkled shape also causes the bonding between the bitumen to be strong. The strength of bitumen as well as modified bitumen were conducted based on empirical test.

Besides that, from the SEM images, as the percentage of GO increases in bitumen, the surface roughness is improved. Increases in surface roughness will increase the adhesive properties of the bitumen. Otherwise, the aggregates will slide pass bitumen which induce deformation. This shows a positive results using GO as a bitumen modifier in this research.
4.3 Empirical Test Results

The empirical results are as shown in below:

4.3.1 Penetration Test

Table 4.2 shows the Penetration Values for Virgin Bitumen

<table>
<thead>
<tr>
<th>Sample</th>
<th>Penetration Values (dmm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>80/100 Pure Bitumen</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Trial 1</td>
</tr>
<tr>
<td></td>
<td>84.0</td>
</tr>
</tbody>
</table>

Table 4.3 shows the Penetration Values for GO Modified Bitumen

<table>
<thead>
<tr>
<th>Sample</th>
<th>Penetration Values (dmm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1125 wt. % GO Modified Bitumen</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Trial 1</td>
</tr>
<tr>
<td></td>
<td>84.0</td>
</tr>
<tr>
<td>0.15 wt. % GO Modified Bitumen</td>
<td></td>
</tr>
<tr>
<td></td>
<td>83.0</td>
</tr>
<tr>
<td>0.225 wt. % GO Modified Bitumen</td>
<td></td>
</tr>
<tr>
<td></td>
<td>83.0</td>
</tr>
<tr>
<td>0.3 wt. % GO Modified Bitumen</td>
<td></td>
</tr>
<tr>
<td></td>
<td>80.5</td>
</tr>
<tr>
<td>0.4 wt. % GO Modified Bitumen</td>
<td></td>
</tr>
<tr>
<td></td>
<td>78.0</td>
</tr>
</tbody>
</table>
Figure 4.4 shows Penetration against Percentage of GO

Penetration Test was carried out to determine the consistency of the bitumen where it is expressed as the distance in tenths of a millimeter. This test will determine the grading of the bitumen sample. The sample must be melted at first at controlled temperature and cooled before the test starts. In this research, 80/100 virgin bitumen sample, 0.1125 wt. %, 0.15 wt. %, 0.225 wt. %, 0.3 wt. %, and 0.4 wt. % GO modified bitumen samples were tested and the results obtained as shown in Table 4.1 and Table 4.2.

From the results obtained, 3 sets of run were tested and the average penetration value obtained is 85 dmm. This shows that the bitumen sample is within the range of 80 to 100. Therefore, the results for virgin bitumen sample is valid and the others modified bitumen will be compared with the virgin bitumen as the reference material of this research. Next, the average penetration values obtained of 0.1125 wt. %, 0.15 wt. %, 0.225 wt. %, 0.3 wt. % and 0.4 wt. % GO modified bitumen were 84.0 dmm, 83.5 dmm, 83.0 dmm, 80.5 dmm and 78.5 dmm.
The average results show that when the percentage of modifier in the bitumen increases, the penetration value decreases. This is due to the GO particles are greatly dispersed into the bitumen and enhanced the mechanical strength of the bitumen. When the strength increases, the hardness of the bitumen increases which causes the penetration values of the GO modified bitumen decreases. In this test, higher percentage of modifier will decrease the penetration value and increase the consistency of the GO modified bitumen.
### 4.3.2 Softening Ball Point Test

Table 4.4 shows the Softening Point for Virgin Bitumen

<table>
<thead>
<tr>
<th>Sample</th>
<th>Set</th>
<th>Temperature (°C)</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>80/100 Pure Bitumen</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>53.0</td>
<td>53.0</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>53.5</td>
<td>53.5</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>53.0</td>
<td>53.0</td>
</tr>
</tbody>
</table>

Table 4.5 shows the Softening Point for GO Modified Bitumen

<table>
<thead>
<tr>
<th>Sample</th>
<th>Set</th>
<th>Temperature (°C)</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1125 wt. % GO</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GO Modified Bitumen</td>
<td>1</td>
<td>53.5</td>
<td>53.5</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>52.0</td>
<td>52.0</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>53.5</td>
<td>53.5</td>
</tr>
<tr>
<td>0.15 wt. % GO</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GO Modified Bitumen</td>
<td>1</td>
<td>52.0</td>
<td>52.0</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>52.0</td>
<td>52.0</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>52.5</td>
<td>52.5</td>
</tr>
<tr>
<td>0.225 wt. % GO</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GO Modified Bitumen</td>
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<td>52.5</td>
<td>52.5</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>53.0</td>
<td>53.0</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>53.0</td>
<td>53.0</td>
</tr>
<tr>
<td>0.3 wt. % GO</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Modified Bitumen</td>
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<td>53.5</td>
<td>53.5</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>54.0</td>
<td>54.1</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>54.5</td>
<td>54.6</td>
</tr>
<tr>
<td>0.4 wt. % GO</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Modified Bitumen</td>
<td>1</td>
<td>54.5</td>
<td>54.5</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>55.0</td>
<td>55.1</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>55.5</td>
<td>55.5</td>
</tr>
</tbody>
</table>
Figure 4.5 shows Softening Point against Percentage of GO

Softening point test is to determine when the bitumen possesses the same viscosity at a certain temperature. Bitumen does not have melting point and so this test will be carried out to indicate at which temperature, the bitumen will change its’ form, soften or melts.

The average softening point for 80/100 virgin bitumen is 53.0°C and the GO modified bitumen will be compared with the virgin bitumen. The averages softening point for 0.1125 wt. %, 0.15 wt. %, 0.225 wt. %, 0.3 wt. % and 0.4 wt. % GO modified bitumen are 53.5 cm, 52.0 cm, 53.0 cm, 54.0 cm, and 55.0 cm. There are no significant changes for 0.1125 wt. %, 0.15 wt. % and 0.225 wt. % GO modified bitumen due to the quantity of the GO used in these 3 bitumen are small. Therefore, the results show not much difference compared to the virgin bitumen.

Therefore, the comparison was made between virgin bitumen and 0.3 wt. % and 0.4 wt. % GO modified bitumen. The results show that 0.3 wt. % and 0.4 wt. % GO modified bitumen have the softening point of 54.0 °C and 55.0 °C. Comparing with the virgin bitumen, this shows that with higher percentage of GO in the bitumen will increase the softening point of the bitumen.
In addition, this is a positive result that the modified bitumen needs a higher temperature before it melts. Therefore, it can withstand a greater temperature compared to the virgin bitumen. Softening point has to be significant for the particular materials to be used as crack and joint fillers. Therefore, higher softening point will ensure that the bitumen will not flow during the service. Besides that, higher softening point indicates the temperature susceptibility to be low and preferable in warmer weathered conditions or places.
4.3.3 Ductility Test

Table 4.6 shows the Ductility Test for Virgin Bitumen

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ductility (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>80/100 Pure Bitumen</td>
<td>93.0</td>
</tr>
</tbody>
</table>

Table 4.7 shows the Ductility Test for GO Modified Bitumen

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ductility (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1125 wt. % GO Modified Bitumen</td>
<td>91.0</td>
</tr>
<tr>
<td>0.15 wt. % GO Modified Bitumen</td>
<td>91.0</td>
</tr>
<tr>
<td>0.225 wt. % GO Modified Bitumen</td>
<td>90.5</td>
</tr>
<tr>
<td>0.3 wt. % GO Modified Bitumen</td>
<td>87.0</td>
</tr>
<tr>
<td>0.4 wt. % GO Modified Bitumen</td>
<td>82.0</td>
</tr>
</tbody>
</table>

Figure 4.6 shows the Ductility against Percentage of GO
Ductility test was used to measure the tensile properties of bitumen under specific requirements and conditions. After the elongation, it turned out to be the virgin bitumen ductility test was 93.0 cm. As the reference material of the sample, virgin bitumen was used to compare with the other GO modified bitumen. The 0.1125 wt. %, 0.15 wt. %, 0.225 wt. %, 0.3 wt. % and 0.4 wt. % of GO modified bitumen sample for ductility test are 91.0 cm, 91.0 cm, 90.5 cm, 87.0 cm, and 82.0 cm.

The temperature was maintained at 25°C and the speed was maintained at 50 mm/min. As the percentage of GO modified bitumen increases, the ductility decreases. This test also indicated that as the percentage of GO modified bitumen increases, the hardness of the bitumen increases. Ductility is one of the important tests to understand the empirical properties of the bitumen. Low ductility can cause the cracking of the bitumen during cold weather whereas high ductility can cause the deformation of the bitumen during hot weather. The faster the bitumen is torn apart, the more brittle the bitumen. When the ductility of bitumen is high, the better the quality of the bitumen to resist deformation under traffic loading. Therefore, ductility test was performed to know whether the bitumen grade is suitable or not before paving them onto the road.

Besides that, according to American Standard Testing Materials (ASTM), the average standard for 80/100 bitumen of ductility is 75 cm where the condition can be fulfilled if the ductility is more than 75 cm. In this research, as the percentage of GO increases, the ductility decreases. 0.4 wt. % GO modified bitumen has the ductility of 82 cm which is more than 75 cm. Therefore, 0.4 wt. % GO modified bitumen can be used to increase the mechanical strength of the pavement.
CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

In this research, Graphite Oxide was produced from Graphite Nano fiber by Simplified Room Temperature Hummer’s Method. The blending of bitumen achieved at 2000 rpm for 20 minutes. 6 samples are produced including the virgin bitumen, 0.1125 wt. %, 0.15 wt. %, 0.225 wt. %, 0.3 wt. % and 0.4 wt. % of GO Modified Bitumen. These samples are being tested for Morphological Properties and Empirical Properties.

The morphological tests were carried out with Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscope (SEM). FTIR proves that the Graphite Nano fiber (GNF) is successfully converted to Graphite Oxide (GO). Besides that, SEM shows the morphology of the bitumen as well as GO modified bitumen. As the percentage of GO increases, the harder and more brittle the bitumen is.
Empirical properties of the bitumen were tested by Penetration Test, Softening Point Test and Ductility Test. These tests indicate the strength of the modified bitumen compared to the virgin bitumen. Besides that, these tests are able to tell the bitumen’s properties such as consistency, cracking, fatigue and deformation. These tests concluded that the higher the GO modified bitumen are able to improve the strength, consistency, deformation as well as the softening point of bitumen.

5.2 Recommendations

Although the data obtained is just briefly explain about the properties of GO modified bitumen. A rheological test must be carried out in order to know the effect of GO on bitumen. Therefore, Dynamic Shear Rheometer (DSR) is a test to determine the deformation of the bitumen under specific speed and temperature. The test will determine the Storage and Loss Modulus value under difference in temperature. Furthermore, the structures of the bitumen from SEM scanning need to be more specific in terms of the microstructure and existence of the modifier to be seen. Therefore, a few recommendations can be made as follows:-

- Increase the percentage of GO content in the bitumen and conduct rheological test to verify the effects of GO in bitumen.
- Apply low cost Graphite Nano fiber on this research as the GNF from SIGMA-ALDRICH costs very high.
- Obtain Graphite Oxide in powder form for convenience purposes.
- Prepare prototype samples with GO Modified Bitumen which can be tested for rutting performance and fatigue behavior.
- Perform other empirical testing such as Viscosity Test, Solubility Test or Specific Gravity Test and for rheological test such as Marshall Test.
REFERENCES


Crump G B. Black but such as in esteem (1981) – the analytical chemistry of bitumen, Chairman’s retiring address to the N W Region Analytical Division of the Royal Society of Chemistry.


Traxler R N and C E Coombs (1936). *The colloidal nature of asphalt as shown by its flow properties*, 13th Colloid Symp, St Louis, Missouri.


Y. Zhu , S. Murali , Dr. W. Cai , Dr. X. Li , J. W. Suk , J. R. Potts , R. S. Ruoff (2010) Graphene and Graphene Oxide: Synthesis, Properties, and Applications
