# KWAME NKRUMAH UNIVERSITY OF SCIENCE AND TECHNOLOGY, KUMASI

# **DEPARTMENT OF CHEMISTRY**



A THESIS SUBMITTED TO THE DEPARTMENT OF CHEMISTRY IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE AWARD OF MASTER OF PHILOSOPHY DEGREE (MPHIL) IN POLYMER SCIENCE AND TECHNOLOGY.

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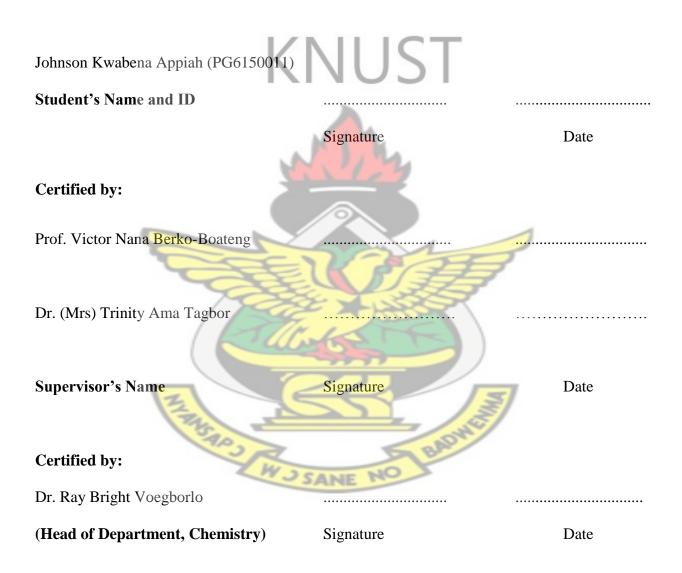
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## DR. (MRS) TRINITY AMA TAGBOR

# **JUNE 2013**

# DECLARATION

I hereby declare that this thesis submitted to the Department of Chemistry, is the result of my own work towards the MPhil degree in Polymer Science and Technology and to the best of my knowledge, it neither contains any material previously published by another person nor material which has been accepted for the award of any other degree or diploma at any institution or university, except where due acknowledgement has been made in the text.



#### ABSTRACT

The absence of efficient management of municipal solid waste (MSW), with regards to used plastic components, which have overwhelmed our major cities and towns, is a growing challenge for developing countries including Ghana. Another challenge is the deformation of our roads due to excessive traffic and binder quality used; thus, new technologies need to be adopted to improve road construction. This study examines the effect of blending waste thermoplastic polymers, namely high density polyethylene (HDPE) and polypropylene (PP) in conventional AC-20 graded bitumen, at different plastic compositions. The plastics were chopped and blended with the bitumen 'in-situ', with a shear mixer at a temperature range of 160 °C-170 °C. Basic rheological parameters such as penetration, ring and ball softening point and viscosity test were employed to determine the resulting changes from the base bitumen. FTIR spectroscopy was also employed to study the chemical functionalities present in the bitumen composite. Three prominent peaks were identified in the spectrum of the unmodified bitumen, occurring at the 3000-2850cm<sup>-1</sup> IR frequency range, typical of aliphatic –C-H symmetrical and asymmetrical stretches in alkanes. CH<sub>2</sub> and CH<sub>3</sub> bends were also observed at the characteristic frequencies of 1465cm<sup>-1</sup> and 1375cm<sup>-1</sup> respectively. A low intensity peak was observed within the 2400 cm<sup>-1</sup>-2100cm<sup>-1</sup> range, indicating the presence of a very weak -C≡C- or -C≡N group with an absorbance of precisely 0.12. The properties of the unmodified bitumen were found to be enhanced with the changes in the rheological properties of the polymer modified bitumen (PMB). The viscosity of unmodified bitumen was enhanced with the addition of the polymers and thixotropic effect was observed for both HDPE and PP at 60°C. For all modified binders prepared, the penetration values decrease as polymer ratio increases whilst, softening temperature generally increases as polymer ratio increases. The most compatible and incompatible blends for HDPE were respectively observed at 2% and 3% polymer loading. The most enhanced, homogenous blend is achieved with PP at 3% polymer loading. The use of waste commodity plastics in binder modification carries the advantage of a cheap and effective means of enhancing conventional binder performance and is an alternative way to utilise plastic waste.

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# **DEDICATION**

I dedicate this thesis to my parents, Mr. John S. Appiah and Mrs. Georgina Efua Kakraba Appiah; to Rev. Fr. Peter Addai-Mensah-my able Chaplain, to Mrs. Cecelia Ampadu and to each and every person who has offered me advice, love, care and support throughout this programme. I am most grateful!



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# LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Materials
MDG	
HDPE	High Density Polyethylene
LDPE	Low Density Polyethylene
РР	Polypropylene
РЕ	Polyethylene
	Polyethylene Terepthalate
ТРЕ	Ghana Highway Authority
GHA	Ghana Highway Authority
DFR	Department of Feeder Roads
DUR	Department of Urban Roads
НМА	
РМВ	Polymer Modified Bitumen
FTIR	
UNITAR	
BHN	Brinell hardness number
	THE SECTION
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#### CHAPTER ONE

#### **1.0 INTRODUCTION**

#### **1.1 Background**

Ghana signed to the millennium development goals (MDGs), in the year 2000. This pact, paved the way for the adoption of eight time-bound and quantifiable targets which were earmarked to be achieved by 2015. The MDGs have since been integrated into the successive medium term development plans and policy profiles across the broad spectrum of the governance structure in Ghana. It is worth applauding the effort and commitment successive governments have engineered in the realisation of some significant landmarks in the race towards the attainment of some of the targets including reduction of child mortality, improving maternal health and achieving universal primary education. With regards to some others however, this actualisation has not been solid. One of them is the promotion of environmental protection and sustainability. For well over a decade now, the country is still grappling with the proper disposal and management of its Municipal Solid Waste (MSW), especially plastic waste. Over the years, traditional waste disposal techniques including land filling and incineration have been rendered incapable of dealing with the ever increasing volumes of plastic waste generated in the various municipalities and urban centres. It is common place to come across beaches, rivers, gutters and roadsides which are choked and filled with waste plastics. Stagnant water is a danger to the human environment, primarily because of its ability to serve as a fertile breeding ground for mosquitoes and other insects; it can also house numerous types of bacteria that can be harmful to humans. It is therefore unsurprising to find high prevalence rates of malaria and other sanitation related diseases like cholera, in localities with poor sanitation systems like slums and low-income neighbourhoods (ISES, 2011)

The absence of efficient solid waste management and disposal methods is not peculiar to Ghana only, but many other developing countries as well. In several African countries, including, South Africa, Mauritania, Rwanda, Kenya and Uganda, the frustration and difficulties associated with the use and proper disposal of plastics have culminated in the adoption of very strict state laws which completely ban the use of plastic carrier bags or impose higher levies on plastic importers (Bashir, 2013).

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Thinner plastic bags, that is, those less than 30 micrometer thick (made of high density polyethylene) are the most banned, as these are more extensively used than the thicker, boutique style low density polyethylene (LDPE) plastic bags. In addition, the thicker LDPE carry bags are stronger and can be more easily reused, unlike the thinner HDPE bags which are of very poor quality and are rarely reused.

Plastic is one of the most useful materials. However, after food and paper waste, plastic waste is the third major constituent at municipal and industrial waste in cities (UNEP, 2009).

Tragically, tons of this plastic ends up in our landfills every year. Depending on the quality of the plastic, it may take a few days to several years for it to break down in the landfills, but it never breaks down completely into particles that can be used in nature. As such, plastics are among the worst offenders when it comes to environmental pollution. It is possible however to take plastic wastes and turn them into a usable energy source and many scientists are working on the best way to do this. The production of more plastic waste is mainly due to increased use of plastic packaging, in the form of plastic shopping bags, polyethylene terepthalate (PET) bottles and other goods/appliances using plastic as the major component. Fortunately, plastic waste recycling can provide an opportunity to collect and dispose of plastic waste in the most environmentally friendly way and it can be converted into a resource. In most of the situations, plastic waste recycling could also be economically viable, as it generates resources, which are in high demand. Plastic waste recycling also has a great potential for resource conservation and green house gas (GHG) emission reduction, such as producing fuel from plastic waste or using plastics as blending materials in composites. Some developed countries have already established commercial level resource recovery from waste plastics (UNEP, 2009). Therefore, having a "latecomer's advantage," developing countries like Ghana can learn from these experiences and available technologies.

The volume of road traffic on the other hand, is increasing and demands a corresponding increment in the load bearing capacities of the road and its service life span. It has been proven possible to improve the performance of bituminous mixes used in the surfacing course of road pavements, with the help of different types of additives to bitumen such as polymers, rubber latex, crumb rubber, etc. Conventional bitumen is unable to provide the performance characteristics for roads and traffic routes, which are increasingly subjected to heavy axle loads, heavy traffic and adverse environmental conditions (Lu & Isacsson, 2000). When the produced asphalt does not meet climate, traffic, and pavement structure requirements, modification has been used as one of the attractive alternatives to improve its properties. Modification offers one solution to overcome the pavement distress deficiencies of bitumen and thereby improve the performance of asphalt concrete pavement. Asphalt modifier, is defined as a material which is normally added to the binder or the mixtures to improve its properties. The choice of modifier for a particular project can depend on many factors including construction ability, availability, cost, and expected performance. The use of polymer modified bitumen to achieve better asphalt pavement performance has been observed for a long time (Isacsson and Lu, 1995).

Some limited studies have been reported on the use of recycled plastic, mainly polyethylene, in the manufacture of polymer-modified bitumen or asphalt cement. For instance, some researchers have reported that, the use of recycled polyethylene from shopping bags is useful in asphaltic (bituminous) construction and yields pavement structure which shows reduced permanent deformation in the form of rutting and reduced low-temperature cracking (Vasudevan et. al, 2012, Noor, et. al, 2011).

Waste plastics, mainly used for packaging are made up of polyethylene (PE), polypropylene (PP) and polystyrene (PS); their softening points vary between 110°C and 140°C and do not produce any toxic gases during softening. The process of modifying bitumen with plastics, promotes value addition to the waste plastics and helps to dispose of them through an eco-friendly recycling strategy for plastic waste management.

## **1.1 Problem Statement and Hypothesis**

Ghana as a developing country is experiencing genuine difficulty in the area of proper solid waste disposal and management of plastic waste. This is due to the inability of plastic materials to biodegrade and its subsequent persistence in the environment. This unfortunate situation is compounded by several factors including the poor attitude of the average Ghanaian towards waste

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disposal and the over-reliance on ineffective waste disposal techniques. It is common place to find beaches, rivers, gutters and roadsides which are choked and filled with waste plastic materials. Landfilling, incineration and haphazard littering have a negative impact on human health and the environment. The need for efficient solid waste management and alternative recycling regimes to curb this trend cannot be over-emphasized.

On the other hand, increased economic activity, urbanisation and higher traffic volumes are rapidly contributing to the deterioration of our roads. Most engineers have attributed asphaltic road failures to climatic conditions, but climatic conditions alone do not account for the deformation of roads but the choice of bituminous binder used as well. Elsewhere, the need for an enhanced binder which can better withstand adverse road conditions and provide a means to an alternative plastic recycling strategy through bitumen modification, led many researchers to explore the feasibility of blending conventional bitumen with waste plastic materials, as successfully reported by Vasudevan et al. (2012).

There is little or no reported scientific work that exists on bitumen-waste plastic modification in Ghana. Synthesis of this information is needed to break the ground for advancement in the understanding and application of established technologies to develop new materials to solve problems. In addition, research indicates that bitumen modification leads to improved binder performance (Habib et. al, 2011; Méndez et. al, 2001; Vasudevan et al, 2012)

## 1.2 Research Aim

The aim of this study is to generate scientific data which will form the basis for using plastic modified bitumen in the construction and repair of roads in Ghana; as well as provide alternative recycling options for managing plastic waste.

## 1.3 Objectives

The main objectives of this study are to:

- Conduct road condition surveys on selected highways in Ghana, in order to analyse the nature of binder associated road failures
- Collect, segregate and process waste plastics to be used in the study
- Review potential techniques for modifying bitumen as a waste management strategy
- > Prepare blends of bitumen and the various plastic waste materials
- Conduct a compositional study to determine the optimum amount of plastic for stable blending with bitumen
- Conduct different tests including; viscosity, softening point, penetration test and FTIR on the Plastic-Bitumen Blends.

# **1.4 Justification**

In spite of attaining low middle-income status, Ghana's battle with the proper disposal of solid waste lingers on. The average Ghanaian does not fully appreciate the impact of plastic waste on our environment and indirectly on our lives. Against this background, it is common place to find these non-biodegrable plastic wastes being disposed off through crude means such as being jettisoned from the windows of moving vehicles, dropped heedlessly as litter on our streets and beaches, or dumped along with household waste into drains and gutters. Eventually, the drains get choked promoting flooding during rainy season. The aquatic and terrestrial environment, such as agricultural lands may be rendered infertile by the presence of plastic residues in the soil, whilst, unsuspecting aquatic fauna, mistaking plastic materials in their environment for food may also choke and die.

Notable among the most commonly disposed plastics are packaging materials made of polyethylene, polypropylene and polystyrene. Economically viable recycling and value addition to the waste generated from plastics is of great urgency.

Ghana's vehicular traffic intensity is increasing and therefore demands an increase in the load bearing capacities of the roads.

Both bitumen and plastics are produced from petroleum or crude oil distillates and when blended as waste plastic modified bitumen, they have been found to extend the life of the road and increase the load bearing capacity substantially in comparison to the use of ordinary bitumen (García-Morales et al., 2004). In addition, the relative availability, low cost and good binding properties associated with waste plastics, makes them attractive materials for bitumen modification.



#### **CHAPTER TWO**

#### 2.0 LITERATURE REVIEW

#### 2.1 Roads in Ghana

Administratively, Ghana's total road network, which spans 109,515 kilometres (World Bank, 2010) falls under the jurisdiction of the Ministry of Roads and Highways. This includes motorways, highways, main or national roads, secondary or regional roads, and all other roads in the country. The main responsibility of oversight, construction and maintenance is shared among three main road agencies; namely, the Ghana Highway Authority (GHA); the Department of Feeder Roads (DFR); and the Department of Urban Roads (DUR). These agencies also provide specifications for all road materials and quality of road works carried out by the contractors they employ. The road sector is one of the areas where successive governments have committed tremendous amounts of money, all in a bid to construct new road ways, expand and maintain existing road networks. Sadly however, there are many roads in deplorable state due to the growing traffic density and the usual tough climatic conditions in our part of the world. These adverse conditions demand corresponding enhancements in the quality of the binder and other aggregate materials used in road making. Polymer modified binders have been used elsewhere to overcome tough road conditions and maintain superior performance to as compared to conventional binders (Vasudevan et. al, 2012). Pavement distresses and failures occur from a variety of causes including stresses from axle loads, temperature changes in the layer, or moisture and temperature changes in an underlying layer. It is worth noting that, the type of distresses which a pavement exhibits is associated with the climate and traffic volume as well. As such, fatigue cracks for instance, are more profound in areas of high temperature than lower ones (Neal, 2013).

The types of failures discussed in this report, capture those which occur in Ghana and most climatic regions of the world. They include rutting, fatigue cracking, shoving, potholes and ravelling.

# 2.1.1 Types of Road failures 2.1.1.1 Rutting

Ruts in bitumen pavements are channelized depressions in the wheel-tracks. Rutting results from consolidation or lateral movement of any of the pavement layers or the subgrade under traffic. In regions affected by frost penetration every winter, the frost in combination with winter conditions causes heavy de-compaction. Thus, in the spring, when the frozen aggregate and subgrade thaws, compaction becomes possible allowing rutting to occur. Rutting also encourage water to soak into the pavement instead of draining off the surface. This results in failure of the upper asphaltic layers. More friction is developed against the side of the tyre leading to higher rates of fuel, tyre wear and skidding (Neal, 2013). In a country like Ghana, where there is no winter, rutting can be considered to be the cause of permanent deformation of any layer due to weakened support layers, poorly compacted layers and unstable wearing surface or excessive axle loads.

Ruts are common at road sections where vehicles 'stop or start' (Neal, 2013).

Causes: Severe rutting is often caused by excessive bitumen binder in the pavement mixture. It is aggravated by hot weather which causes the softening of the bitumen binder. Again, insufficient pavement thickness; lack of compaction of the bitumen, stone base or soil; weak bitumen mixes; or moisture infiltration can also cause it.

Solution: If rutting is minor or if it has stabilized, the depressions can be filled and overlaid. If the deformations are severe, the rutted area should be removed and replaced with suitable material. Also hot mix overlay can be recommended (Neal, 2013).

Pictures of Road ruts from USA, Brazil and Scotland are shown in the Appendix A (Figures 2.1A-2.5A). Pictures of ruts observed as part of the road study are reported in chapter four.

# 2.1.1.2 Fatigue Cracking

This kind of deformation refers to as series of interconnected cracks caused by fatigue failure of the hot mix asphalt (HMA) surface (or stabilized base) under repeated traffic loading. In thin pavements, cracking initiates at the bottom of the HMA layer where the tensile stress is the highest then propagates to the surface as one or more longitudinal cracks. This is commonly referred to as

"bottom-up" or "classical" fatigue cracking. In thick pavements, the cracks most likely initiate from the top in areas of high localized tensile stresses resulting from tire-pavement interaction and bitumen binder aging (top-down cracking). After repeated loading, the longitudinal cracks connect forming many-sided sharp-angled pieces that develop into a pattern resembling the back of an alligator or crocodile (Neal, 2013). Pictures of fatigue cracks are shown in Appendix A (Figures 2.6A-2.7A). Pictures of different types of fatigue cracks observed as part of the road study are reported in chapter four.

The following are some of the defects that fall under fatigue cracking.

# i. Alligator Cracking

These cracks form a pattern similar to an alligator's skin. They are the result of repetitive traffic loads or high deflections often due to wet bases or sub-grades. They are caused by the pavement structure unable to support due to higher than normal traffic loading or loss of foundation support due to water. This type of cracking can also lead to potholes and pavement disintegration.

Alligator cracking is a load associated structural failure. The failure can be due to weakness in the surface, base or sub grade; a surface or base that is too thin; poor drainage or the combination of all three. It often starts in the wheel path as longitudinal cracking and ends up as alligator cracking after severe distress.

Solution: Chip, fog and sand sealing can be used to fill small cracks whereas full-depth patch can be used if cracks are largely interconnected (Neal, 2013).

Pictures of Alligator cracks from USA, Australia and Serbia are shown in Appendix A (Figures 2.8A-2.13A).

#### ii. Block Cracking

This refers to a pattern of cracks that divides the pavement into large, approximately rectangular, pieces that range in size from approximately 1 square foot to 100 square feet. Block cracking is not load-associated, but generally caused by shrinkage of the bitumen pavement due to an inability of bitumen binder to expand and contract with temperature cycles. This happens when the mix is placed too dry; fine aggregate mix with low penetration bitumen and absorptive aggregates; poor choice of bitumen binder in the mix design; or aging dried out bitumen.

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Solution: Less severe cracks measuring 1/2 inch or less can be sealed to prevent moisture from entering into the sub grade using crack sealing. More severe cracks should be fixed by removing the cracked pavement layer and replacing it with an overlay (Neal, 2013).

Pictures of Block cracks from USA, Australia and Mexico are shown in Appendix A (Figures 2.14A-2.17A). Pictures of block cracks observed as part of the road study are reported in chapter four.

# iii. Longitudinal (Linear) Cracking

Longitudinal cracking are cracks that are parallel to the pavements centreline or lay down direction and are usually caused by thermal stress and/or traffic loadings. These can be a result of pavement fatigue, reflective cracking, and/or poor joint construction. Joints are generally the least dense areas of a pavement. Loss of foundation support probably due to water, insufficient pavement structure or weak support material can also be responsible for the formation of these cracks. They occur frequently at joints between adjacent travel lanes or between a travel lane and the shoulder, where hot mix density is lower and voids are higher.

Solution: Less severe cracks measuring 1/2 inch or less can be sealed to prevent moisture from entering into the sub grade. More severe cracks should be fixed by removing the cracked pavement layer and replacing it with an overlay (Neal, 2013).

Pictures of longitudinal cracks from USA, Australia and Poland are shown in Appendix A (Figures 2.18A-2.21A)

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### iv. Transverse Cracking

Transverse cracks are single cracks perpendicular to the pavement's centreline or lay down direction. Transverse cracks can be caused by reflective cracks from an underlying layer, pavement expansion and contraction due to temperature changes, shrinkage of bitumen binder with aging and poor construction due to improper operation of the paver. Also when the tensile stress due to shrinkage exceeds the tensile strength of the HMA pavement surface, cracks occur.

Solution: Less severe cracks measuring 1/2 inch or less can be sealed to prevent moisture from entering into the sub grade. More severe cracks should be fixed by removing the cracked pavement layer and replacing it with an overlay (Neal, 2013).

Pictures of Transverse cracks from USA, Australia and Slovakia are shown in Appendix A (Figures 2.22A-2.25A).

# v. Edge Cracks

Edge cracks travel along the inside edge of a pavement surface within one or two feet. The most common cause for this type of crack is poor drainage conditions and lack of support at the pavement edge. As a result underlying base materials settle and become weakened. Edge cracking is usually common to pavements with unpaved shoulders. Heavy vegetation along the pavement edge and heavy traffic can also be the instigator of edge cracking.

Solution: The first step in correcting the problem is to remove any existing vegetation close to the edge of the pavement and fix any drainage problems. Crack seal/fill the cracks to prevent further deterioration or remove and reconstruct to full depth, fixing any support issues (Neal, 2013).

Pictures of Edge cracks from USA and Costa Rica are shown in Appendix A (Figures 2.26A-2.27A).

# 2.1.1.3 Ravelling

Ravelling is the on-going separation of aggregate particles in a pavement from the surface downward or from the edges inward. Usually, the fine aggregate wears away first and then leaves little "pock marks" on the pavement surface. As the erosion continues, larger and larger particles are broken free and the pavement soon has the rough and jagged appearance typical of surface erosion. Ravelling and weathering occur as a result of loss of bond between aggregates and the bitumen binder. This may occur due to hardening of the bitumen cement, dust on the aggregate which interferes with bitumen adhesion, localized areas of segregation in the bitumen concrete mix where fine aggregate particles are lacking, or low in-place density of the mix due to inadequate compaction. High air void contents are associated with more rapid aging and increased likelihood of ravelling. Increased bitumen film thickness can significantly reduce the rate of aging and offset the

effects of high air voids. Surface softening and aggregate dislodging due to oil spillage are also classified as ravelling.

Solution: Apply a thin hot-mix overlay. Other solutions could include: sand seal, chip seal, slurry seal or micro-surfacing (Neal, 2013).

Pictures of different degrees of Ravelling from USA are shown in Appendix A (Figures 2.28A-2.29A). Pictures of ravelling observed as part of the road study are reported in chapter four.

# 2.1.1.4 Potholes

Potholes are bowl-shaped openings that usually have ravelled edges and can be up to 10 inches deep. They occur when the top layer or bitumen surface of the roadway has worn away, exposing the road sub-base.

The most common cause of potholes is water seeping into cracks in the surface of the road. The water causes the roadbed to weaken. The vibration of vehicle tyres over the cracked area and stresses to the pavement by the weight of traffic causes the pavement to sink, break up and a pothole results. Potholes can be caused by deterioration of the upper pavement layer. Potholes can occur under dry conditions when trucks pass over weak spots in the subsurface causing structural failure.

Another common way of pothole formation, is when water seeps into cracks in the surface of the road and, combined with the vibration of the tyres over the cracks, causes the bitumen to fail. That explains why there are more potholes after it rains. Potholes are also created when the roadway is stressed by trucks and buses, which can cause a movement of the subsurface. Once there is a weak spot, every car that travels over it makes the problem worse, and eventually a section of the material will fail, causing a pothole (Neal, 2013).

Solution: The best-known pothole patching method is the semi-permanent repair. In this method, the pothole is completely removed of any water or debris. Next, the pothole needs to be squared. All uneven edges will be cut with a pavement saw making the hole into a square or rectangular shape. The pothole is cleaned once again before the patching mix is applied. Finally, the area is compacted with a single drum roller or a vibratory plate compactor. The semi-permanent method provides the

tightest and longest lasting patch. However, it is more time consuming and requires more workers and equipment in the field (Eaton et al, 1989).

Pictures of Potholes from USA are shown in Appendix A (Figures 2.30A-2.31A). Pictures of potholes observed as part of the road study are reported in chapter four.

# 2.1.1.5 Shoving

Shoving is the formation of ripples across a pavement. This characteristic shape is why this type of distress is sometimes called "wash-boarding". It is generally caused by braking or accelerating vehicles and is often located on hills or curves, or at intersections. Shoving occurs at locations having severe horizontal stresses, such as intersections. It is typically caused by: excess bitumen; too much fine aggregate; rounded aggregate; too soft bitumen; or a weak granular base. Shoving is aggravated by high temperatures which cause the softening and expansion of the bitumen binder. Poor mix design coupled with large horizontal pressure due to structural failure on straight stretches and turning traffic at intersections and on curves are the major causes of this deformation (Neal, 2013). Solution: A stretch of road damaged by shoving can be repaired by milling the affected area and applying a full depth patch (Neal, 2013).

Pictures of different degrees of Shoving from the USA are shown in Appendix A (Figures 2.32A-2.33A). Pictures of shoving observed as part of the road study are reported in chapter four.

### 2.2 Bitumen

The term 'bitumen' is used by European and Eastern countries, whereas the term 'asphalt' is used by Americans. The sources of bitumen can be classified into two categories. First, bitumen is derivated from petroleum crude oil and the second category includes the natural asphalt deposits (Ullmann, 1985).

Bitumen is a viscoelastic substance which behaves as an elastic solid at low temperatures or during rapid loading. At high temperatures or slow loading, it behaves as a viscous liquid. This classical dichotomy creates a need to improve the performance of bitumen to minimize the stress cracking that

occurs at low temperatures and plastic deformation at high temperatures (Wardlaw and Shuler, 1992).

In Ghana, the term 'bitumen' refers to the black, sticky, viscous binder material used in most road construction procedures whilst 'Asphalt' is reserved for the mixture and compaction of stone aggregate and bitumen. The meanings of these terms as stated above, shall apply throughout the course of this study.

## 2.2.1 Definition of Bitumen

Bitumen consists of a wide variety of reddish brown to black materials of semisolid, viscous to brittle character that can exist in nature with no mineral impurity or with mineral matter contents that exceed 50% by weight (Herbert, 1945).

The American Society for Testing and Materials (ASTM) defines bitumen as a generic class of amorphous, dark coloured, cementitious substances, natural or manufactured composed principally of high molecular mass hydrocarbons, soluble in carbon disulphide (ASTM D8-83, 1984).

For the geochemists, 'bitumen' is widely used to describe extra heavy petroleum, in conceptual agreement with the above definition. More precisely, UNITAR (United Nations Institute for Training and Research) separates between a heavy crude, defined as one having a density between 0.934 and 1 g/cm<sup>3</sup> at 15.6 °C(60°F) (between 10 and 20° in the American Petroleum Institute, API gravity scale) and a viscosity inferior to 10,000 cP at 15.6 °C. An extra-heavy crude is defined as one having a density superior to 1 g/cm<sup>3</sup> (inferior to 10° API) and a viscosity inferior to 10,000 cP and a 'tar' (used as a synonym for bitumen) as one having a density superior to 1 g/cm<sup>3</sup> (inferior to 10,000 cP (Lanier, 1998).

As exemplified by the UNITAR definition, a sandstone reservoir impregnated by viscous extra heavy crude oil is commonly called tar sand, when a more appropriate labelling would be bituminous sand (Speight, 1999). This choice of words is necessary to avoid confusion between bitumen and coal tar. The latter is the residue of the pyrolysis of coal, with very similar uses and properties than bitumen. Unfortunately, the name coal tar remains widely used in everyday language as a general term for a

black paving material when its use has almost disappeared due to economic reasons such as the decline of the coal industry and the rise of the all-petroleum era in the 1950s. Safety reasons finally ended coal tar use, as a consequence of its high content of carcinogenic polyaromatics hydrocarbons (PAH), which are only present as traces in bitumen (Burstyna et al, 2000). Preferably, the word tar should be restricted to the products of the destructive distillation (pyrogenation) of various organic sources (coal, wood etc).

## 2.2.2 Physical and Chemical Composition of Bitumen

Knowledge of bitumen chemistry has progressed rapidly as more sophisticated methods of analysis have been developed. There are a lot of techniques such as solvent fractionation, thermal diffusion, sulphuric acid precipitation, adsorption and elution or by a combination of these procedures used for determining the composition of bitumen. The study of these fractions has been made by most available methods including infrared and ultraviolet spectrometry, x-ray analysis and electron-microscope techniques (Mark, 1965).

Bitumen is a mixture of hydrocarbons and compounds of a predominantly hydrocarbon character, varying both chemically and molecular size. These hydrocarbon components change from the non-polar aliphatic wax compounds to highly polar condensed aromatics. Carbon and hydrogen compose approximately 90-95% of bitumen. The rest of the bitumen consists of heteroatoms such as nitrogen, oxygen and sulphur (Hoiberg, 1964). Bitumen density at room temperature lies typically between 1.01 and 1.04 g/cm<sup>3</sup>, depending on the crude source and paving grade (Whiteoak and Read, 2003). As a rule of thumb, the harder it is, the denser the bitumen. When referring to a natural source, a heavy crude oil is generally termed bitumen when its density overpasses 1 g/cm<sup>3</sup> at 15.6 °C (that is below 10° in the API scale), although a definite classification remains to be published (Speight, 1999).

Bitumen exhibits a glass transition around -20 °C, although it varies in a very wide range from +5 °C down to -40 °C depending essentially on the crude origin and somewhat less on the process. The transition range typically spans 30 to 45 °C and -20 °C corresponds to the typical midpoint value (Turner and Branthaver, 1997). Therefore, on a thermodynamical standpoint, bitumen is a very

viscous liquid at room temperature. The complexity of bitumen chemistry lies in the fact that many different chemicals are present. As an overall descriptor, the chemical nature of the crude oil is generally described as paraffinic, naphthenic or aromatic if a majority of saturate, cyclic or aromatic structures, respectively, are present. This classification of the petroleum is sometimes applied to the corresponding bitumen. For example, Venezuelan bitumens are generally known as naphthenic bitumens. The elemental composition of a bitumen depends primarily on its crude source and it is difficult to give geographical generalization (Turner and Branthaver, 1997; Whiteoak and Read, 2003).

A comprehensive study conducted by Lesueur (2009), brought forward some of the delicate intricacies associated with bitumen; when bitumen samples were measured by Vapour Pressure Osmometry in toluene and pyridine at 60 °C (ASTM D2503), it was found that the number-average molecular weight of bitumen falls typically in the range 600–1500 g/mol.

Yet still, the distribution extends to molecular weights up to 15,000 g/mol and the values found in the literature can vary somewhat depending on the experimental set-up, as reported by Domin et al. (1999).

The table below shows the above account as found in Lesueur, (2009).

		Z			$\leftarrow$		5		
Origin	Unit	AAA-1	AAB-1	AAC-1	AAD-1	AAF-1	AAG-1	AAK-1	AAM-1
		Canada	USA	Canada	USA	USA	USA	Venezuela	USA
С	wt.%	83.9	82.3	86.5	81.6	84.5	85.6	83.7	86.8
Н	wt.%	10.0	10.6	11.3	10.8	10.4	10.5	10.2	11.2
H+C	wt.%	93.9	92.9	97.8	92.4	94.9	96.1	93.9	98.0
H/C	Molar	1.43	1.55	1.57	1.59	1.48	1.47	1.46	1.55
0	wt.%	0.6	0.8	0.9	0.9	1.1	1.1	0.8	0.5
Ν	wt.%	0.5	0.5	0.7	0.8	0.6	1.1	0.7	0.6
S	wt.%	5.5	4.7	1.9	6.9	3.4	1.3	6.4	1.2
V	ppm	174	220	146	310	87	37	1480	58
Ni	ppm	86	56	63	145	35	95	142	36
Mn	g/mol	790	840	870	700	840	710	860	1300

Table 2.1: Elemental analysis for the core SHRP bitumens, as reported by Lesueur, (2009).

The data in Table 2.1 shows various materials from the USA or Canada with different compositions. The data in Table 2.1 originally come from the impressive work on bitumen chemistry, structure and properties realized in the USA as part of the Strategic Highway Research Program (SHRP) in the late 1980s. Eight bitumens of extreme properties (the SHRP core bitumens) were fully characterized. The coding (AAA1...etc) refers to the ones used in the SHRP materials library (Stategic Highway Research, 2001).

As described in Table 2.1, bitumen mainly consists in carbon (typically 80–88 wt.%) and hydrogen atoms (8–12 wt.%). This gives a hydrocarbon content generally superior to 90 wt.% with an hydrogen-to-carbon molar ratio H/C around 1.5. This H/C ratio is therefore intermediate between that of aromatic structures (benzene has H/C=1) and that of saturate alkanes (H/C ~2) In addition, heteroatoms such as sulphur (0–9 wt.%), nitrogen (0–2 wt.%) and oxygen (0–2 wt.%) are generally present. Traces of metals are also found, the most numerous being typically vanadium, up to 2000 parts per million (ppm), and nickel (up to 200 ppm) (Turner and Branthaver, 1997; Whiteoak and Read, 2003)

Sulfur is generally the most present polar atom. It appears in the form of sulfides, thiols and to a lesser extent, sulfoxides. Oxygen is typically present in the form of ketones, phenols and, to alesser extent, carboxylic acids. Nitrogen exists typically in pyrrolic and pyridinic structures and also forms amphoteric species such as 2-quinolones. Most of the metals form complexes such as metalloporphyrins (Speight, 1999)

Given the concentration of polar atoms, functional groups generally do not amount for more than a few 0.1 mol/l for straight-run bitumen. Their concentration can however increase upon ageing (Turner and Branthaver, 1997). In a related study conducted by Jennings et al. (1992), average molecular structures for bitumen were proposed as seen in Figure. 2.1

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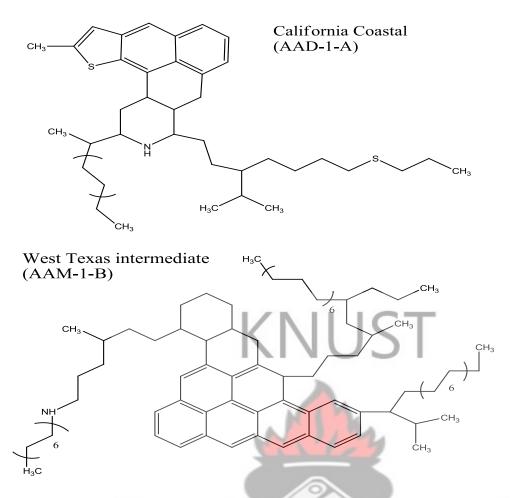


Figure 2.1: Average molecular structure for two bitumens of extreme compositions: California Coastal (AAD-1-A) and West Texas Intermediate (AAM-1-B) (Jennings et al., 1992)

In the study by Jennings et al., (1992), the molecular weight of the average structure equals the average molecular weight of the studied bitumen and the atoms are distributed in order to give a similar NMR spectrum as the one obtained for the corresponding bitumen.

Bitumen molecules are not to be regarded as macromolecules in the polymeric sense. As a consequence, care must be taken when trying to compare the properties of polymers to that of bitumen, especially when it comes to the modelling of the viscoelastic properties based on a molecular approach. Given these molecular weights and the proportion of polar atoms, it is clear that only 1–3 polar atoms are present on average in each bitumen molecule, as pictured in Fig.2.1 Still, approaching bitumen chemistry on a global basis is not sufficient when one tries to understand the properties of bitumen. Thus, the molecules are generally separated into different chemical families, depending on their size and solubility in polar, aromatic or non-polar solvents (Lesueur, 2009)

In an elaborate study on bitumen, Whiteoak and Read, (2003) confirmed the chemical composition of bitumen as extremely complex. Again, they reported that a complete analysis of bitumen (if it were possible) would be extremely laborious and would produce such a large quantity of data that correlation with the rheological properties would be impractical, if not impossible. Their work however revealed that it is possible to separate bitumen into two broad chemical groups called asphaltenes and maltenes. The maltenes can be further subdivided into saturates, aromatics and resins. The following four groups (ie: SARAs) are not well defined in the strict sense and there is some overlap between the groups.

## 2.2.2.1 Saturates

Saturates consist of straight and branch chain aliphatic hydrocarbons together with alkyl-naphthenes and some alkyl-aromatics. They are non-polar viscous oils which are straw or white in colour. The average molecular weight range is similar to that of aromatics and the components include both waxy and non-waxy saturates. This fraction forms 5 to 20% of the bitumen (Whiteoak and Read, 2003).

The Figures below show two different saturate structures.

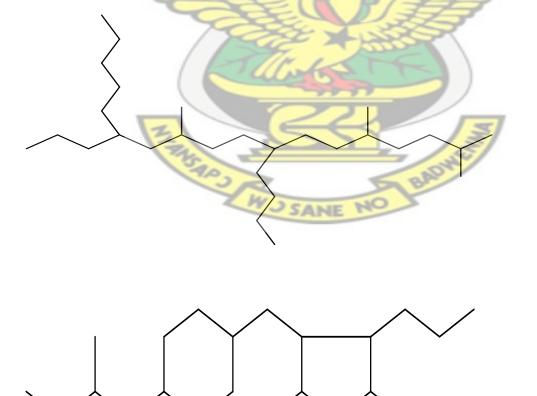


Figure 2.2: Saturate structures proposed by (Whiteoak and Read, 2003)

#### 2.2.2.2 Aromatics

Aromatics comprise the lowest molecular weight naphthenic aromatic compounds in the bitumen and represent the major proportion of the dispersion medium for the peptised asphaltenes. They constitute 40 to 65% of the total bitumen and are dark brown viscous liquids. The average molecular weight range is in the region of 300 to 2000 g/mol. They consist of non-polar carbon chains in which the unsaturated ring systems (aromatics) dominate and they have a high dissolving ability for other high molecular weight hydrocarbons (Whiteoak and Read, 2003).

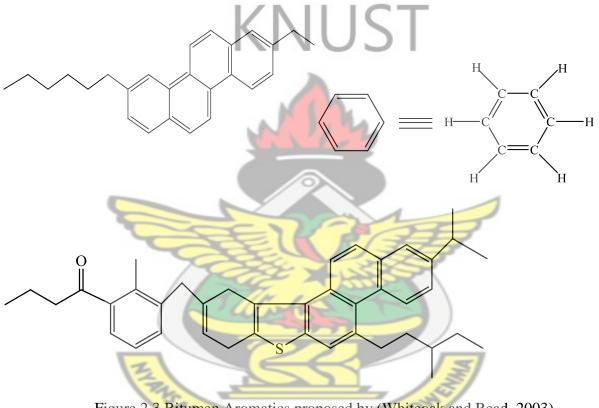


Figure 2.3 Bitumen Aromatics proposed by (Whiteoak and Read, 2003)

# 2.2.2.3 Resins

Like asphaltenes, resins are largely composed of hydrogen and carbon and contain small amounts of oxygen, sulphur and nitrogen. Resins are soluble in n-heptane, they are dark brown in colour, solid or semi-solid and being polar in nature, they are strongly adhesive. Resins are dispersing agents or peptisers for the asphaltenes. The proportion of resins to asphaltenes governs, to a degree, the solution (SOL) or gelatinous (GEL) type character of the bitumen. Resins separated from bitumens are found to have molecular weights ranging from 500 to 50000, a particle size of 1 to 5 nm and an H/C atomic ratio of 1.3 to 1.4 (Whiteoak and Read, 2003)

#### 2.2.2.4 Asphaltenes

These are n-heptane insoluble black or brown amorphous solids containing in addition to carbon and hydrogen, some nitrogen, sulphur and oxygen. Asphaltenes are generally considered to be highly polar and complex aromatic materials of fairly high molecular weight. Different methods of determining molecular weights have led to different values ranging widely from 600 to 300000 depending on the separation technique employed.

However, the majority of test data indicates that the molecular weights of asphaltenes range from 1000 to 100 000; they have a particle size of 5 to 30 nm and a hydrogen/carbon (H/C) atomic ratio of about 11. The asphaltene content has a large effect on the rheological characteristics of bitumen. Increasing the asphaltene content produces a harder, more viscous bitumen with a lower penetration, higher softening point and consequently, higher viscosity. Asphaltenes constitute 5 to 25% of the bitumen (Whiteoak and Read, 2003).

The figure below shows a typical chemical structure of an asphaltene.

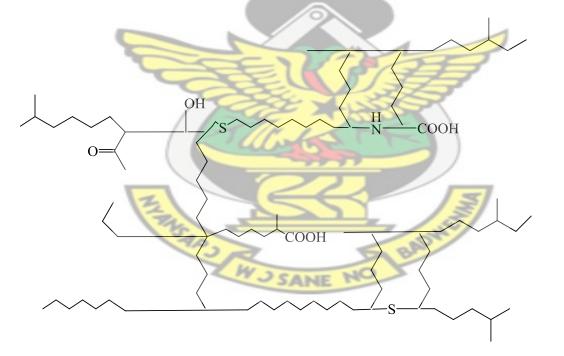


Figure 2.4 Bitumen Asphaltene as reported by Whiteoak and Read (2003)

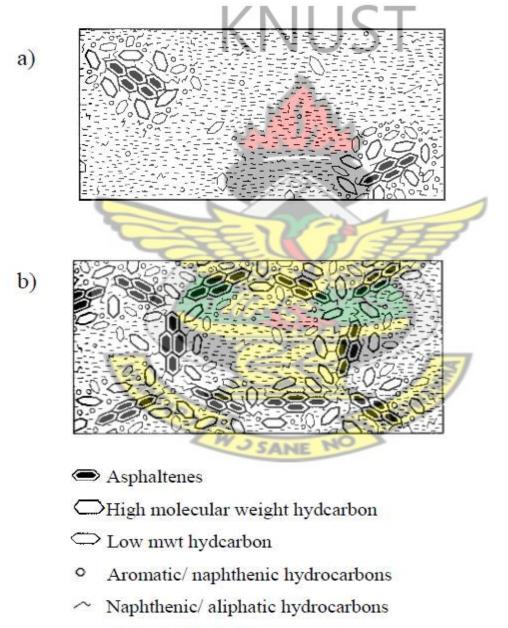
## 2.2.3 Microstructure of Bitumen

Bitumen is a highly complex residue of crude oil which most technologists consider to be a natural colloid composed of two phases, dispersed and continuous. The dispersed phase asphaltenes can be described as high molecular weight, semi-polymeric, aliphatic/aromatic complexes which are present

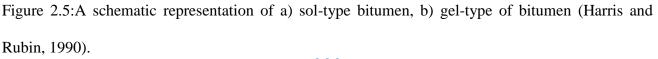
in asphalt as either discrete, uniformly dispersed particles, or flocculated or agglomerated electrostatically-bound clusters, or mixtures of both the discrete and flocculated forms.

The continuous phase, alternately referred to as the petrolene, malthene or oils and resins phase, have been the subject of some effort to analytically separate and characterize individual components (Illston and Domone, 2001).

The microstructure of bitumen is generally understood as multi-phase colloidal system. Bitumen classified into two categories sol-type bitumen and gel-type bitumen according to microstructure. In practice, most bitumens are somewhere between these two states.



- Saturated hydcarbons



In sol-type bitumens, asphaltenes bitumens well dispersed within maltene continuum. In gel-type bitumen, the asphaltene micelles are not well dispersed and form large agglomerations. The degree of dispersion asphaltenes is controlled by the relative amounts of resins, aromatics and saturated oils. As the ratio of aromatics increases, the dispersion of asphaltenes increases because the aromatics form stabilizing layer around the asphaltene micelles. The saturate oils have little solvent power in relation to the asphaltenes, so that as the saturate fraction increases, there is a great tendency for the asphaltenes to aggregate to form gel structure. However a high ratio of saturates tends to reduce viscosity because of their low molecular weight (Harris and Rubin, 1990).

# 2.2.4 Uses of Bitumen

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Bitumen, which has thermoplastic nature, water resistance and adhesion toward most other substances, is a primary engineering material. There are over one hundred different industrial applications or products in which bitumen is used. Almost every home, building or traffic area uses bitumen in different form. Bitumen has uses that range from the construction of the pavements of roads with an aggregate to water-proofing membrane in roofing and structural applications. Bitumen serves primarily as a binder in asphalt compacted mixtures which in turn are widely used in many types of road, street, runway and parking area applications. The other uses of bitumen are paints and coatings, paper, rubber products, electrical cables and other products of electrical industry (Ullmann, 1985).

# 2.2.5 Modification of Bitumen

Bitumen, as afore mentioned is a thermoplastic, viscous material carrying 'glue-like' properties which justify its use in construction and other applications as a binder. The properties of a given bituminous material are characteristic largely of the source of the crude and the processing conditions. In certain instances, the properties of the binder do not meet the requirements for certain applications, for which reason, the need arises for an 'upgrade' of the material properties or to 'modify' certain parameters. This is what is widely known as 'modification'.

Modification of bitumen can therefore be understood as the process whereby certain materials or substances which offer superior, complimentary and/or supplementary qualities to the base bitumen are incorporated into it by physical or chemical processing, to obtain a much enhanced binder material for any intended purpose.

Bitumen binders have been modified in order to:

(i) Stiffen binders and mixes at high temperatures to minimize rutting

(ii) Soften binders at low temperatures to improve relaxation properties and strain tolerance thus minimizing non-load associated thermal cracking

(iii) Improve fatigue resistance especially where higher strains are imposed on bituminous mixes(iv) Improve aggregate-bitumen bonding to reduce stripping

(v) Improve bituminous pavement durability with accompanying net reduction in life cycle costs
(vi) Permit thicker film of bitumen on aggregate in bituminous mixes (Deori et al, 2012). Majority of these modification qualities are achieved by polymer modification (Vasudevan et. al, 2012, Habib et. al, 2011 and Noor et. al, 2011)

#### 2.2.5.1 History

Processes of asphalt modification involving natural and synthetic polymers were patented as early as 1843 (Thompson and Hoiberg, 1979). Test projects were underway in Europe in the1930s, and neoprene latex began to be used in North America in the 1950s (King G et. al, 1999). In the late 1970s, Europe was ahead of the United States in the use of modified asphalts because the European use of contractors, who provided warranties, motivated a greater interest in decreased life cycle costs, even at higher initial costs. The high preliminary expenses for polymer modified asphalt limited its use in the U.S (Terrel and Walter, 1986). In the mid-1980s, newer polymers were developed and European technologies began to be used in the US (Collins, 1986).

In Australia, the current National Asphalt Specification includes guides and specifications regarding polymer modified binders (Asphalt National Specification, 2004). In India the concept of utilization of waste plastic in construction of flexible road pavement has been done since 2000 (Gawandea et al, 2012). The United States Federal Highway Administration (FHWA) has developed a life cycle cost analysis approach, which can be used to evaluate the life cycle costs of pavement containing asphalt rubber binders as well as other treatments. The findings indicated that asphalt rubber is cost effective as it is used, for example, in Arizona and California, although the estimated life of the pavement is based on interviews and engineering judgment, and can be refined as the pavement ages and longterm field performance is included in the model (Hicks and Epps, 2000).

A 1997 survey of state departments of transportation in the United States found that 47 states of the 50 reported that they would be using modified binders in the future, 35 of them saying that they would use greater amounts (Bahia, et al., 1997).

Several research teams around the world have worked on evaluating the benefits of polymer modification on pavement performance, and tests and specifications for binders are continually being developed. In a 2001 study for the Ohio Department of Transportation, Sargand and Kim, (2001), compared the fatigue and rutting resistance of three PG 70–22 binders, one unmodified, one SBS modified, and one SBR modified. It was found that the modified binders were more resistant to both fatigue and rutting than the unmodified binder, even though all three had the same performance grade.

As afore-mentioned, Ghana does not have any scientific work carried out and reported so far on the use of polymer modified binders in road making. Still, there are slight applications of the use of PMBs on a very small scale by few contractors, who generally apply them in the form of polymer modified bitumen emulsions.

# 2.2.5.2 Types of Modifiers

Based upon their strain characteristics at low temperatures, polymer modifiers are generally separated into two broad categories: elastomers and plastomers. Elastomeric polymers can be stretched up to ten times without breaking, but quickly return to original shape once the load has been removed. Typical elastomeric polymers used to modify asphalt include natural and synthetic rubbers, styrene-butadiene-styrene (SBS) and crumb rubber modifiers (CRM) reclaimed from scrap tires. Worldwide, elastomeric polymers comprise approximately 75 percent of all the asphalt polymer modifiers used (not including recycled crumb rubbers). Unlike elastomers, plastomeric polymers

attain very high strength at a rapid rate, but are brittle and resistant to deformation once set. Examples of plastomeric polymer modifiers include low density polyethylene (LDPE), ethylenepropylene-diene-monomer (EPDM), and ethyl-vinylacetate (EVA). Plastomeric polymers currently comprise about 15 percent of the global market for asphalt polymer modifiers.

Elastomeric and plastomeric polymer modifiers are further classified as either thermoset or thermoplastic, based upon their temperature-dependent structural formation and reformation characteristics. When initially heated, thermoset polymers develop a complex, cross-linked structure, which is retained upon cooling, but which cannot be reversed when reheated. In contrast, thermoplastic polymers also develop a well-defined, linked matrix when cooled, but the resultant structures can be reversed or "reset" with reheating.

Thermoplastic rubbers (TPRs) or thermoplastic elastomers (TPEs) such as SBS combine the hard, resistant characteristics and re-settable structure of plastics with the elastic recovery of thermoset elastomers like natural or synthetic rubber. TPEs exhibit this unique blend of properties through the structural integration of rigid, generally steric (i.e., styrene-containing) components with rubbery domains such as found in polybutadiene (Stroup-Gardiner and Newcomb, 1995).

The Table below presents a summary of the most commonly used polymer modifiers, classified according to their deformational and thermal properties. It is important to note that many of these polymers may be blended with other types to achieve the appropriate combination of thermal and deformational properties.

Table 2.2: Summary of the most commonly used polymer modifiers, as reported by King and Johnston (2012)

Polymer Type	Examples	Classification
Natural Rubber	Natural Rubber (NR), Polyisoprene, Isoprene,	Thermoset
(Homopolymers)	Natural Rubber Latex (NRL)	Elastomers
	Styrene-Butadiene (SBR)	
Synthetic Latex / Rubber	Polychloroprene Latex	
(Random Copolymers)	(Neoprene)	
Block Copolymers	Styrene-Butadiene-Styrene (SBS)	Thermoplastic
	Styrene-Isoprene-Styrene (SIS)	Elastomers
	Styrene-Butadiene (SB) Diblock	
	Acrylonitrile-Butadiene-Styrene (ABS)	
	Reactive-Ethylene-Terpolymers (RET)	
Reclaimed Rubber	Crumb Rubber Modifiers	Thermoset
(		Elastomers
Plastics	Low / High Density Polyethylene (LDPE /	Thermoplastic
TRAS	HDPE), Other Polyolefins.	Elastomers
	Ethylene Acrylate Copolymer	
	Ethyl-Vinyl-Acetate (EVA)	
	Ethyl-Methacrylate	
	Polyvinyl Chloride (PVC)	
	Ethylene-Propylene-Diene Monomer (EPDM)	
	Ethyl-Methacrylate Acrylates (EMA),	
	Ethyl-Butyl-Acrylate (EBA)	
Combinations	Blends of Above	Varies

There are four distinct modes of interaction between bitumen and modifiers:

- i. The modifier is present as a separate phase within the bitumen.
- ii. The bitumen is present as a separate phase in the modifier and the product will display the properties of the modifier rather than the bitumen.
- iii. The modifier will form an interface with the bitumen giving greater elasticity due to changes in the mechanical structure of the material.
- iv. The modifier will form a molecular bond with the bitumen giving greater elasticity and stiffness to the material (Asphalt Academy, 2007)

When stable polymer modification is achieved in a bitumen matrix, the polymer mostly forms an interface with the bitumen, accompanied by strong cohesion between them, giving greater elasticity due to changes in the mechanical structure of the material (Noor et. al, 2010).

#### 2.2.5.3 Modification Methods

There are two important processes for modifying bitumen for road making; namely dry process and wet process. The description of the above processes and their associated advantages and disadvantages as reported by Gawandea et al., (2012) are cited below:

#### 2.2.5.3.1 Dry Process

For flexible pavement, hot stone aggregate (170 °C) is mixed with hot bitumen (160 °C) and the mix is used for road laying. The aggregate is chosen on the basis of its strength, porosity and moisture absorption capacity. The bitumen is chosen on the basis of its binding property, penetration value and viscoelastic property. The aggregate, when coated with plastics improved its quality with respect to voids, moisture absorption and soundness. The coating of plastic decreases the porosity and helps to improve the quality of the aggregate and its performance in the flexible pavement. It is to be noted here that stones with < 2% porosity only allowed by the specification.

#### 2.2.5.3.1.1 Advantages of Dry Process

• Plastic is coated over stones - improving surface property of aggregates.

- Coating is easy and temperature required is the same as road laying temperature.
- Use of waste plastic more than 15% is possible.
- Flexible films of all types of plastics can be used.
- Doubles the binding property of aggregates.
- No new equipment is required.
- Bitumen bonding is stronger than normal.
- The coated aggregates show increased strength.
- As replacing bitumen to 15% higher cost efficiency is possible.
- No degradation of roads even after 5 -6 yrs after construction.
- Can be practiced in all type of climatic conditions.
- No evolution of any toxic gases as maximum temperature is 180°C.

# 2.2.5.3.1.2 Disadvantages of Dry Process

The process is applicable to plastic waste material only.

#### 2.2.5.3.2 Wet Process

Waste plastic is ground and made into powder; 6 to 8% plastic is mixed with the bitumen. Plastic increases the melting point of the bitumen and makes the road retain its flexibility during winters resulting in its long life. The use of shredded plastic waste acts as a strong "binding agent" for tar making the asphalt last long. By mixing plastic with bitumen the ability of the bitumen to withstand high temperature increases. The plastic waste is melted and mixed with bitumen in a particular ratio. Normally, blending takes place when temperature reaches 45.5°C but when plastic is mixed, it remains stable even at 55°C. The vigorous tests at the laboratory level proved that the bituminous concrete mixes prepared using the treated bitumen binder fulfilled all the specified Marshall mix design criteria for surface course of road pavement. There was a substantial increase in Marshall Stability value of the mix, of the order of two to three times higher value in comparison with the untreated or ordinary bitumen. Another important observation was that the bituminous mixes prepared using the treated binder could withstand adverse soaking conditions under water for longer duration (Gawandea et al., 2012).

#### 2.2.5.3.2.1 Advantage of Wet Process

• This Process can be utilized for recycling of any type, size, shape of waste material (Plastics, Rubber etc.)

#### 2.2.5.3.2.2 Disadvantages of Wet Process

• Time consuming; more energy needed for blending.

- Powerful mechanical stirring is required.
- Additional cooling is required as improper addition of bitumen may cause air pockets in roads.
- The maximum % of waste plastic that can be added is around 8 %.

#### 2.2.6 Incorporation of Polymers into Bitumen

Two methods are commonly used to incorporate polymers into bitumen:

• Addition of latex polymer to the bitumen. This method is relatively easy and trouble free.

• Addition of solid polymers to bitumen. This method normally requires substantial mixing and shearing in order to uniformly disperse the polymers, particularly when SBS or SIS block copolymers are used.

# 2.2.7 Aspects that Influence the Properties of Polymer-Bitumen Blends 2.2.7.1 Polymer characteristics

To be effective, a polymer must be blended with the bitumen and increase its rutting resistance at high temperatures without rendering it too viscous for the mixing procedure or too brittle at low temperatures. It should also be capable of being processed in bitumen conventional equipment. The modifying polymer should be sufficiently compatible with the bitumen as not to cause phase separation during the storage, transportation, application and service. Moreover, the modified polymer must be cost effective, *i.e.* the polymer should improve the rheology and strength of the bitumen with which it is mixed in such a way that any increased road costs imposed by its use are recovered through performance and reduced resurfacing costs. Polymer content ranges between 2 and 10% by weight; however, the most common proportions were about 5 or 6% a few years ago. Now the polymer content has been reduced to 2 or 3%. Sometimes waste materials (due to their low

cost they might be added in higher proportions), or mixes of two different polymers are used. Polymer parameters affecting the modification process include polymer content, chemical composition, structure, average molecular weight, molecular weight distribution, degree of branching, crystallinity, etc. (Morgan and Mulder, 1995)

Ali et al., (1994) found that, at low temperatures, the mechanical properties of all paving mixtures seem to be affected primarily by the original grade of the bitumen used in making the binder, while the addition of the modifier is not statistically significant in adversely affecting low temperature stiffness. Thus, low temperature cracking should not be adversely affected by the addition of modifiers. However, as the temperature is increased, the stiffening effect of the modifier on the binder's properties increased, resulting in a significant increase in the modulus value of the mixtures, as compared to conventional paving mixtures. Thus, the use of modifiers can actually improve the temperature susceptibility of the binders.

# 2.2.7.2 Bitumen Characteristics

The nature of the bitumen greatly influences the binder micromorphology as well as some of its properties such as penetration and mechanical properties. It has also a very large influence on the stability of the blend. As a rule of thumb, the polymer must be compatible with the bitumen and maintain this compatibility during storage and use. This is a difficult task, because the PMA constituents are very different in molecular weight and structure, viscosity and density. Moreover, bitumen differences depend not only on the composition of the original crude, but also on the production process. In all cases, there is a close connection between polymer type and bitumen composition, especially with the content of bitumen components, which act as solvents or swelling agents for the modifier. Even though not many studies have been made on the nature of the bitumen, some general conclusions have been drawn. Bitumen should contain enough oil fractions to dissolve and expand the polymer. It should also have a high content of condensed ingredients (*e.g.* aromatic hydrocarbons are often condensed and mix especially well with polar aromatic polymers) in order to guarantee the PMB blends endurance (Méndez et al., 2001).

For a binder to be effectively modified, two cases have to be considered.

• In the first case, if the bitumen binder exhibits a high aromaticity, the polymer can be solubilised.

• In the second case, when the polymer is not soluble in the molecular sense of the term (elimination of all polymer-polymer interactions to replace them by polymer solvent interactions), it can be swollen by the oily fraction of the bitumen.

For low polymer content, the continuous bitumen phase is enriched with resins and asphaltenes, thus leading to an increase in the consistency and the elastic properties of the binder. In general, thermoplastic polymer modified bitumen (resulting from physical mixing of the constituents without chemical interactions between them) can consequently be regarded as a diphase system made up of a swollen polymer and a phase grouping the constituents of the bitumen not intervening in the solvation. If the polymer content is increased, the inversion point is observed. This transition is accompanied by a major modification in the physical properties of the blend. This results essentially in a significant increase in the plasticity interval, in tensile strength and elastic properties, and a reduction in thermal sensitivity over the utilization temperature range (Brûlé, Brion, and Tanguy, 1988).

Studies by Vonk and Bull (1989), have shown that when a thermoplastic rubber copolymer is in contact with bitumen, the elastomer absorbs, almost proportionally, all the bitumen components, with the exception of the asphaltenes. The asphaltenes, however, require support from the presence of the maltenes to avoid their precipitation. Thus, if the asphaltene content of the bitumen is too high, addition of a thermoplastic rubber can result in asphaltenes precipitation or gelation and the blend becomes unworkable. Conversely, if the asphaltene content is low the polymer is able to absorb more maltenes after which even a single phase blend may be obtained. When phase separation occurs in a bitumen-SBS material, the thermoplastic rubber phase rises to the surface of the bitumen and the asphaltene phase falls to the bottom. The top section of the mixture thus becomes soft and elastic, while the bottom becomes hard and brittle. The ratio of penetration at the top versus, penetration at the bottom quantifies the extent to which separation of the binder has taken place.

The softening point of the bitumen-thermoplastic rubber blends is largely governed by the aromaticity and average molecular weight of the base bitumen and tend to be little influenced by the hardness of the base bitumen. The viscosity of the blends at 180°C is predominantly affected by the average molecular weight of the base bitumen (Morgan and Mulder, 1995).

The asphaltene content of the bitumen-thermoplastic rubber blend must also be carefully balanced as, at low concentrations, the asphaltenes interact with the thermoplastic rubber molecules forming beneficial associations, which result in higher flow resistance and higher softening points. Conversely, too high asphaltene content will result in phase separation leading to a lower proportion of the thermoplastic rubber being available in the continuous phase. The permissible level of the asphaltene concentration is dependent upon:

• Polymer content

- Polymer molecular weight
- Asphaltene molecular weight
- Aromaticity.

Careful balancing of the aromatic content and the aromaticity in relation to polymer content is necessary in order to produce a bitumen-thermoplastic rubber blend which is stable, and in which the thermoplastic rubber is present as a continuous phase to the maximum extent possible, in order to achieve the maximum possible benefit from the polymer. Such blends are termed as "compatible" blends (Morgan and Mulder, 1995).

# 2.2.7.3 Mixing conditions

Studies conducted by Zielinski et al. (1995) and others reported the following parameters as influencing the mixing process:

# i) Nature of the polymer

The time required to achieve a homogeneous blend of the polymer and the bitumen will vary with the type of polymer, its molecular weight, and (for thermoplastic rubbers) with the chemical composition of the polymer. A higher molecular weight will give rise to longer blending times, and vice versa (Morgan and Mulder, 1995).

ii) Physical form of the polymer (powder, crumbs, pellets).

The physical form of the polymer, influences the blending process in two ways. The smaller the particle size of the polymer, the lesser it has to be reduced in order to achieve a good dispersion. In addition, since smaller particle size means larger surface area per unit mass of polymer, penetration of the bitumen and swelling of the polymer is facilitated and thus more rapid dissolution is completed. Powdered polymers will therefore disperse and dissolve more rapidly than porous pellets (Morgan and Mulder, 1995).

# iii) Nature and grade of the bitumen.

Bitumen plays a complex role in the mixing process as both its composition and viscosity affect the blending process in more than one way. The way constituents affect the mixing process has not been very extensively studied. General observations drawn included that bitumen should contain big oil fractions to dissolve and expand the polymer and has a high content of condensed ingredients in order to guarantee the PMA blends endurance (Zielinski et al., 1995).

On the other hand, low viscosity bitumen is beneficial in aiding pre-dispersion of the polymer in the bitumen, and will subsequently speed the penetration and swelling of the polymer particles. A low bitumen viscosity at the blending temperature will improve the disintegration of the polymer at the mill and result in a more rapid particle size reduction (Morgan and Mulder, 1995).

iv) Type of mixing equipment.

Two main methods exist for the dissolution of polymer in the bitumen; high shear and low shear mixing. For low shear mixing a simple mixing tank with a paddle stirrer can be used with powdered modifier, the action being confined to the swelling and dissolving by the bitumen. The mixer serves to maintain homogeneity of composition and uniformity of temperature, proving little or no heat input itself. In high shear mixing, polymer particles are physically reduced in size by mechanical and hydrodynamic shear in a rotor-stator combination accompanied by significant input of heat energy to the mix.

v) Time-temperature profile during mixing.

The ideal mixing process should be undertaken at the lowest possible temperature for the shortest possible time, corresponding to the complete incorporation of the polymer into the bitumen both from an economic stand point and to minimize any thermal effect on the polymer.

In practical terms however, the time-temperature profile is a function of the bitumen chosen, and its requirement to achieve mobility and initial swelling of the polymer. For SBS, for example, temperatures higher than 190°C should be avoided to minimize thermal effects on the polymer. Blending conditions have an important impact on the structure and properties of modified binders: the longer the mixing time, the finer the microstructure. There is however, a starting point beyond which polymer degradation leads to a decrease in mechanical properties and, more precisely, in low temperature deformation possibilities. The higher the temperature, the more rapidly this threshold is reached (Brûlé et al., 1988).

# 2.2.8 Compatibility and Stability

A polymer may be incompatible, slightly compatible or compatible with bitumen.

• Incompatible polymers, when mixed with bitumens, result in heterogeneous mixtures without cohesion or ductility. The polymer affects the colloidal equilibrium of the bitumen and, therefore, the cohesion of the material.

• Slightly compatible polymers require special mechanical, thermal or chemical processes to successfully improve bitumens.

• Compatible materials yield physically stable blends, using conventional mixing techniques, and they may or may not improve the physical properties of the bitumen.

A proper degree of compatibility between polymer and bitumen is necessary in order to avoid separation during storing, pumping and application of the bitumens and to achieve the expected properties in the pavement. Poor storage stability will render the polymer modified bitumen unsuitable for use in paving binder applications, roofing applications, and other industrial specialty products.

The extent to which a stable system is formed when the bitumen is modified by the addition of thermoplastic rubber is dependent upon a number of factors which include:

- the amount and size of the asphaltenes
- the amount and size of the polymer molecules
- the aromaticity of the maltene phase.

With reference to the complexity of the inter-relationships between these factors, (Morgan and Mulder, 1995) deduced that too high aromaticity should be avoided as this leads to a weakening of the polymer domains causing low softening points and low flow resistance. Still, at low aromaticity levels, however, insufficient polymer will be incorporated into the bitumen, which also leads to low flow resistance.



# 2.2.9 Challenges and Benefits of bitumen modification

Polymer	Advantages	Disadvantages	Uses
Polyethylene (PE)	High temperature resistance	Hard to disperse in the	Industrial uses eg.
	Aging resistance	bitumen	packaging
	High modulus	Instability problems	Road applications
	Low cost	High polymer contents are	
	KN	required to achieve better properties	
		No elastic recovery	
Polypropylene	No important viscosity	Separation problems	Atactic PP is used
(PP)	increase even though high	No improvement in	for roofing
	amounts of polymer are	elasticity	
	necessary	Low thermal fatigue	
	Widens the plasticity range	cracking	
	Improves the binder's load	- The second	
	resistance		
	Low penetration resistance	ST I	
	High Ring and Ball softening	BADHE	
	point WOSAN		
Ethylene-vinyl-	Outstanding compatibility in	No improvement in elastic	Paving and roofin
acetate (EVA)	some cases	recovery	
Ethylene-	Minimal viscosity changes		
methacrylate			

Table 2.3: Characteristics of polymers used to modify bitumens as reported in Méndez et al., (2001).

Polymer	Advantages	Disadvantages	Uses	
EVA, EMA	Thermally stable at normal			
	mixing and handling			
	temperatures.			
	Low cost, as compared to			
	block Copolymers			
	Increased tack			
PVC	Lower cracking PVC disposal	Acts mostly as filler	Not commercially	
	KN	UST	applied	
Styrene-butadiene	Higher flexibility at low	High cost	Paving and roofing	
block copolymer	temperatures	Reduced penetration		
(SBS)	M.	resistance		
Styrene-isoprene	Better flow and deformation	Higher viscosity at layout		
block copolymer	resistance at high	temperatures		
(SIS)	temperatures	Resistance to heat and to		
	Strength and very good	oxidation is lower than that		
	elasticity	of polyolefins (due to the		
	Increase in rutting resistance	presence of double bonds in		
	Higher aging resistance	the main chain)		
	Better bitumen-aggregate	Bitumens suitable for SBS		
	adhesivity	blends, need an bitumen		
	Good blend stability, when	with a high aromatic and a		
	used in low proportion	low asphaltene content		
EPDM	Higher dispersion capacity	Miscibility with the bitumen	Roofing	
	(due to their lateral olefinic	is not easy		
	groups, with double bonds			
	and great volume)			

Polymer	Advantages	Disadvantages	Uses
EPDM (cont'd)	Improved elastic behaviour as	Sometimes air blowing is	
	compared to PE	necessary to produce less	
	High proportions needed in	unstable PMB (through	
	order to appreciate a	formation of some	
	performance improvement	crosslinking).	
Epoxy resins	They don't exhibit viscous	High cost	Used in a variety of
	flow	Blended with bitumens, the	special applications
	Very resistant to chemical	binders display the	such as airport
	attack	behaviour of thermosetting	paving and bridge
	Less temperature susceptible	resins rather than those of	surfacing
	Higher flexibility	bitumens	
	Cracking resistance		
	Better adhesivity		
Natural rubber	Better rutting resistance	Sensitive to decomposition	Paving
	Higher ductility	and oxygen Absorption	
	allot	Too high molecular weight	
	Higher elasticity and	(low compatibility).	
	properties under cyclical	Therefore, it must be	
	loads	partially decomposed and	
	WJ SAN	mechanically homogenized	
Polydiolefins	Easier to disperse than	The double bonds in all	Paving
(polybutadiene,	polymonoolefins	chains can lead to a partial	Roofing
polyisoprene)	They confer characteristics of	decomposition of the	
	elasticity more evident than	polymer chain by heating or	
	other thermoplastic materials	in the presence of oxygen.	

Polymer	Advantages	Disadvantages	Uses
Reclaimed tire	Rubber disposal	Lower physical resistance if	Paving
rubber	Low material cost	used as an extender	
	Potential fatigue resistance	Use of proprietary products	
	improvement	It needs high T and long	
	Reduced reflective cracking	digestion times in order to	
	Longer durability using	be dispersed in the bitumen	
	thinner lifts	If not partially	
	Lower rutting resistance	devulcanized, it produces a heterogeneous binder with	
		the rubber acting mainly as	
	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	a flexible filler	
Mixed systems	Improvements that may not	Compatibility and instability	Paving
(most used	be possible with a single	problems	
systems include	modifier	FI	
SBS in their	THE Y		
formulation.	allot	STE )	
Systems with PE		2	
have been also	AT REAL		
used).	THE APS W SAN	E NO BADHE	

In spite of the exciting prospects and breakthroughs of polymer modification in the paving industry,

- it is not without challenges. Three main problems are cited below:
- a) Poor bitumen polymer compatibility (which influences the stability of the system),
- b) Higher viscosities during bitumen processing and application
- c) Higher cost.

#### 2.3 Recent works

Vasudevan et al. (2012) have obtained a patent in India, where they utilized the dry process to produce a plastic coated aggregate (PCA) as a new modified raw material for road making. When hot bitumen is added to this PCA, the polymer-bitumen interaction leads to an in-situ modification of the bitumen structure. The results of field studies conducted on several sites across India confirm claims that the waste plastic modified binder yields superior field performance as compared to the conventional type. These roads were described by the authors as having "increased strength and performance" and were functioning well without pothole, ravelling and rutting. Their work again reports this technique as being an eco-friendly method of disposing up to 80% of waste plastics obtained from domestic and industrial packing materials usefully, which otherwise would have been disposed-off by incineration and land filling. Again, the use of polymers helps to avoid the use of anti stripping agents and also reduce needed quantity of bitumen, thus reducing the cost of the road-laying by around 10%. The authors pegged the savings at Rs. 30,000/km (~\$500/km of single lane road). This study has been accepted by the Central Pollution Control Board, India. They have already released a guideline on the technique of the road-laying by dry process and its advantages.

A related study by Habib et al. (2010), presents the effect of thermoplastic polymers namely linear low density polyethylene (LLDPE), High density polyethylene (HDPE) and Polypropylene (PP) modified on 80/100 penetration grade bitumen, using rheological tools such as penetration, ring and ball softening point and viscosity test. Their work presented modified blends made up to 5% with 0.5% increments of the respective polymers and suggested that the modification of bitumen by the use of polymers enhances its performance characteristics but significantly affects its rheological properties. Morphological analysis carried out through field emission scanning electron microscopy (FESEM) to investigate the compatibility of bitumen with polymer, also revealed that the solvency of PP and LLDPE are better as compared to HDPE, because of their lower molecular weight and less branched structure, which offers less resistance while blending with bitumen.

In a separate study by Firoozifar et al. (2010), different types of polymers such as styrene butadiene styrene block copolymer (SBS), polyethylene, polypropylene and rubbers were used to modify

bitumen in Iran. To cure the usual problems of low compatibility and poor storage stability, the researchers added some amounts of maltene-like molecules to improve the storage stability of the mixture. Different oil based materials such as oleic acid; aromatic oil, base oil (B-Oil) and vacuum bottom (VB) were added. The outcome produced a homogenous mixture where the oils serve as a dispersion agent.

Dimonie et al. (2011) have worked on investigating the differences between the properties of bitumen composites obtained by modifying two thermoplastic elastomers, by their work on SBS and EVA. Each of these polymers had different content of rigid (physical cross-links) and soft blocks, with SBS characterised by an amorphous matrix of polybutadiene and EVA having domains of polyethylene crystals (physical cross-links), distributed in soft domains represented by the amorphous material formed by the chain segment with the vinylacetate groups or those of noncrystallized branched polyethylene. This study reported great differences between the properties of the bitumen-polymer composite depending on the modifier used and related to the plastic properties (ring and ball softening point and penetration), elastic properties(elastic recovery) and morphology. The values of the plastic properties of the bitumen composites were in agreement with the rigid domain content (physical cross-links) of the polymeric modifier and the elastic properties with the content of amorphous polymer. The elastic properties and the plastic properties were found to favour SBS, as a consequence of the fact that this polymer is amorphous at temperature ranges from approximately -90°C to 250°C, while EVA is a semi-crystalline polymer in the range -42.15°C to 2 BA approximately 50°C, when its crystals are melting. WJSANE NO

## 2.4 Polymers

A polymer is a large molecule built up from numerous smaller molecules. These large molecules may be linear, slightly branched, or highly interconnected. In the latter case the structure develops into a large three-dimensional network. The small molecules used as the basic building blocks for these large molecules are known as *monomers*.

For example, polyethylene; a polymer is formed by repeated linkage of simple ethylene molecules (monomers):



Where 'n' is the number of repeat units

Again, the commercially important material polyvinyl chloride is made from the monomer vinyl chloride. The repeat unit in the polymer usually corresponds to the monomer from which the polymer was made. There are exceptions to this, though Poly(vinyl alcohol) is formally considered to be made up of vinyl alcohol (CH<sub>2</sub>CHOH) repeat units but there is, in fact, no such monomer as vinyl alcohol. The appropriate molecular unit exists in the alternative tautomeric form, ethanol CH<sub>3</sub>CHO. To make this polymer, it is necessary first to prepare poly (vinylethanoate) from the monomer vinyl ethanoate, and then to hydrolyse the product to yield the polymeric alcohol.

The size of a polymer molecule may be defined either by its mass or by the number of repeat units in the molecule. This latter indicator of size is called the *degree of polymerisation*, DP. The relative molar mass of the polymer is thus the product of the relative molar mass of the repeat unit and the DP.

The vast majority of polymers in commercial use are organic in nature that is they are based on covalent compounds of carbon. As is characteristic of covalent compounds, in addition to primary valence forces, polymer molecules are also subject to various secondary intermolecular forces. These include dipole forces between oppositely charged ends of polar bonds and dispersion forces which arise due to perturbations of the electron clouds about individual atoms within the polymer molecule. Hydrogen bonding, which arises from the particularly intense dipoles associated with hydrogen atoms attached to electronegative elements such as oxygen or nitrogen, is important in certain polymers, notably proteins (Nicholson, 2006).

#### **2.4.1 Classification of Polymers**

On the basis of different chemical structures, physical properties, mechanical behaviour, thermal characteristics, stereochemistry, polymers can be classified into following ways:

#### 2.4.1.1 Natural and Synthetic Polymers

Depending on their origin, polymers can be grouped as natural or synthetic. Those isolated from natural materials are called natural polymers, *e.g.*, cotton, silk, wool and rubber. Cellophane, cellulose rayon, leather and so on are, in fact, chemical modification of natural polymers.

Polymers synthesized from low molecular weight compounds are called synthetic polymers, *e.g.*, polyethylene, PVC, nylon and terylene.

## 2.4.1.2 Organic and Inorganic Polymers

A polymer whose backbone chain is essentially made of carbon atoms is termed as organic polymer. The atoms attached to the side valencies of the backbone carbon atoms are, however, usually those of hydrogen, oxygen, nitrogen, etc. The majority of synthetic polymers are organic. In fact, the number and variety of polymer units are so large, that's why we refer to them as 'polymers'; on the other hand, inorganic polymers generally contains no carbon atom in their chain backbone. Glass and silicone rubber are examples of inorganic polymers.

# 2.4.1.3 Thermoplastic and Thermosetting Polymers

Some polymers soften on heating and can be converted into any shape that they can retain on cooling. The process of heating, reshaping and retaining the same on cooling can be repeated several times. Such polymers, that soften on heating and stiffen on cooling, are termed 'thermoplastics'. Polyethylene, PVC, nylon and sealing wax are examples of thermoplastic polymers. Some polymers, on the other hand, undergo some chemical change on heating and convert themselves into an infusible mass. They are like the yolk of egg, which on heating sets into a mass, and, once set, cannot be reshaped. Such polymers, that become infusible and insoluble mass on heating, are called 'thermosetting' polymers.

#### 2.4.1.4 Plastics, Elastomers, Fibres and Liquid Resins

Depending on its ultimate form and use, a polymer can be classified as plastic, elastomers, fibre or liquid resins. For instance, when a polymer is shaped into hard and tough utility articles by the application of heat and pressure, it is used as a 'plastic'. Typical examples are polystyrene, PVC and polymethylmethacrylate. When vulcanised into rubbery products exhibiting good strength and elongation, polymers are used as 'elastomers'. Typical examples are natural rubber, synthetic rubber, silicone rubber.

If drawn into long filament-like material whose length is at least 100 times its diameter, polymers are said to have been converted into 'fibre' *e.g.* nylon and terylene. Polymers used as adhesives, potting compound sealants, etc. in a liquid form are described liquid resins. Commercially available epoxy adhesives and polysulphide sealants are typical examples.

# 2.4.1.5 Atactic, Isotactic and Syndiotactic Polymers

On the basis of the configurations, (stereochemistry) polymers can be classified into three categories viz., atactic, isotactic (cis-arrangement) and syndiotactic (trans-arrangement). Those polymers, in which arrangement of side groups is at random around the main chain, are termed as 'atactic' polymers. Those polymers in which the arrangement of side groups are all on the same side are known as 'isotactic' polymers. Whereas, those polymers in which the arrangement of side groups is in alternating fashion is termed as 'syndiotactic' polymers.

# 2.4.1 Properties of High Density Polyethylene Resin

This polymer has one of the simplest molecular structures [-CH<sub>2</sub>CH<sub>2</sub>-] and is at present the largest tonnage plastic material, having first been produced commercially in 1939 for use in electrical insulation. There is a difficulty over the nomenclature of this polymer. The IUPAC recommended name for the monomer is ethene, rather than the older ethylene. Hence the IUPAC name for the polymer is polyethene. However, this name is almost never used by chemists working with the material; rather this polymer is known as by its more widespread name, polyethylene.

There are four different industrial routes to the preparation of polyethylene, and they yield products having slightly different properties. One of the routes to the production of HDPE is the Ziegler Process, discovered by Karl Ziegler in Germany and developed by G. Natta at Milan in the early 1950s. Reaction is carried out at low pressures and low temperatures, typically no more than 70 °C, with rigorous exclusion of air and moisture, which would destroy the catalyst. The polyethylenes produced by such processes are of intermediate density, giving values of about0.945 g cm<sup>3</sup>. A range of relative molar masses may be obtained for such polymers by varying the ratio of the catalyst components or by introducing a small amount of hydrogen into the reaction vessel. The polymer is a very familiar material in the modern world. It is a waxy solid which is relatively low in cost, easily processed, and shows good chemical resistance. Low relative molar mass grades have the disadvantage that they suffer from so-called 'environmental stress cracking', ie. they suddenly fail catastrophically for no apparent reason after exposure to sunlight and moisture. Despite this drawback, the various grades of polyethylene have a wide range of uses. These include pipes, packaging components for chemical plant, crates, and items for electrical insulation (Nicholson, 2006).

## 2.4.2 Properties of Polypropylene Resin

Polypropylene, with basic structure ( $C_3H_6$ )n is a low-density, hard, stiff, creep-resistant plastic with good resistance to chemicals; good wear resistance, low water absorption, and is relatively low cost. Polypropylene can be spun into filaments, converted into weaves; injection moulded, and is commonly produced in a large variety of forms. Glass-filled Polypropylene is widely enhanced mechanical properties. It is used for food and chemical containers, domestic appliances, furniture, car parts, twine, toys, tubing, cable sheath, and bristles.

# 2.4.3 The Aim of Using Polymers with Bitumen

Many types of polymers are typically used in bitumen modification in different forms such as plastics, elastomers and reclaimed rubbers. Elastomers such as styrene butadiene-styrene copolymer (SBS), styrene-butadiene rubber (SBR) and natural rubber can be used with bitumen. SBS is used as

an elastomer in this study. A plastic such as polyethylene (PE), polypropylene (PP), polystyrene and ethylene vinyl acetate (EVA) are used with bitumen. EVA and low density polyethylene (LDPE) are used as thermoplastics (Mark, 1965).

Mixing polymers into bitumen has important consequences on the engineering properties of bituminous materials. The extent of modification and the improvements in the performance characteristics depend on bitumen nature, polymer chemical nature, its dosage and chemical compatibility, molecular weight, particle size, as well as blending process conditions such as type of mixing/dispersing device, time and temperature play important role in determining the modified bitumen properties (Perez-Lepe et al., 2003).

Bitumen modification by polymers improves its mechanical properties, increases the viscosity, allows an expansion of temperature range of service and improves the deformational stability and durability of bitumen (García-Morales et al., 2004).

Elastomer modification of bituminous materials is manifest in the following ways; softening temperature is increased, cold flow is reduced, change in penetration with temperature is reduced, brittleness temperature is lowered, elastic recovery is imparted, resistance to deformation under stress is increased markedly, ductility is increased, particularly at low temperatures (Hoiberg, 1964). The main reasons to modify bitumens with polymers could be summarized as follows

- To obtain softer blends at low service temperatures and reduce cracking
- To reach stiffer blends at high temperatures and reduce rutting
- To reduce viscosity at layout temperatures
- To increase the stability and the strength of mixtures
- To improve the abrasion resistance of blends
- To improve fatigue resistance of blends
- To improve oxidation and aging resistance
- To reduce structural thickness of pavements
- To reduce life costs of pavements.

The rheological behaviour of bitumen-polymer blends is of great interest because it is closely related to the performance of pavements. Furthermore, the addition of small amounts of polymer dramatically changes the rheological properties of the bitumen. The addition of polymer introduces an additional difficulty to the bitumen complexity, because of its high molecular weight. The formation of a homogeneous system is not easy and incompatibility problems arise (Lewandowski, 1994).

# 2.4.4 Interaction between Bitumen and Polymer

The morphology of polymer modified bitumen is the result of the mutual effect of polymer and bitumen, consequently is influenced by bitumen composition, polymer nature and ratio (Lu and Isacsson, 2000).

Most polymers are insoluble to some degree, in the bitumen matrix, resulting eventually in gross separation of both phases. These phases may become a continuous phase or a dispersed one depending on polymer nature, concentration and its ability to swell with maltene molecules (Perez-Lepe et al., 2003).

Bitumen phase is artificially enriched in asphaltenes by a physical distillation of the lighter species from the original bitumen because the polymer is swelled by the maltenes. This is the case of many elastomers and thermoplastics such as EVA, SBS, PE etc. (García-Morales et al., 2004).

In general at low polymer content, the small polymer spheres swollen by bitumen compatible fractions are spread homogeneously in a continuous bitumen phase. By increasing polymer content, a continuous polymer phase may be obtained. The minimum percentage of polymer to ensure the formation of its continuous phase depends to a great extent on the base bitumen, the polymer itself and its ability to swell with maltene molecules (García-Morales et al., 2004). Polymer stabilization can be achieved by mechanical dispersion of the modifier, swollen by compatible components in the maltene fraction. It is well known that the polymer may dissolve and/or disperse into maltenic medium enhancing the mechanical properties of mixtures (Lu and Isacsson, 2000).

Polyolefins are produced from olefinic monomers; the resulting homopolymers have nonpolar, nonaromatic nature. The typical range for their solubility parameter is 15.6-17.4 MPa  $^{1/2}$ . This low solubility parameter reflects its incompatibility with a bitumen dispersion medium which is polar and aromatic. Polyolefins can also be copolymerized as either block or random copolymers such as SBS, EVA. The solubility parameter can be modified by the addition of a more polar comonomer yielding a more compatible system (Wardlaw and Shuler, 1992). High molecular weight polymers have profound effects on the properties of bitumen. As the molecular weight of polymers increases, their compatibility with bitumen sharply decreases (Yousefi et al., 2000)

The blend of the bitumen thus lowers the extent of crystallization of the polymer by retaining a proportion within the amorphous bitumen-rich phase and it lowers the melting point of the crystalline regions within the polymer-rich phase by making the crystallites smaller (Fawcett et al., 1999).

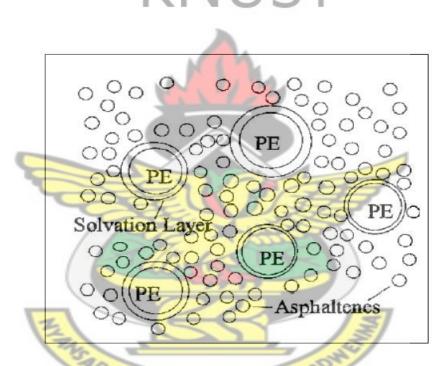


Figure 2.6: Schematic representation of the structure of PE-bitumen suspension as illustrated in Fawcett et al., (1999).

Polymer particles behave as physically active fillers that interact with the bitumen medium by absorption and adsorption mechanisms. This results in the penetration of bitumen into PE particles. PE absorbs the maltene phase of bitumen so that a swollen layer forms around the PE. The low molecular weight species of PE dissolves in the maltene phase. After the bitumen is washed out, there are a lot of hollows seen on polymer particles (Fawcett et al., 1999).

# **2.5 Characterization of Plastics**

Plastics materials are usually generally characterised by their lightweight, resistance to breakage, insulating capacity (electrical, thermal and acoustic) and versatility among others. For modification purposes, their thermal behaviour, binding properties, moisture absorption etc. is usually measured. The thermal behaviour of plastics refers to the unique transformations which occur within the material when taken through a heating cycle. Differential scanning calorimetry (DSC) is usually employed to study the thermal behaviour of a material. By the method, thermal properties of a sample are compared against a standard reference material which has no transition in the temperature range of interest, such as powdered alumina.

Polymers namely PE, PP and PS get softened easily around 130-140°C without evolution of any gas. Above 270°C they either decompose or burn to produce gaseous products (Vasudevan et al., 2012). Other tests to characterise plastics include melt flow index, plasticity index etc.

## 2.6 Characterization of Polymer Modified Bitumen Binders

There are a number of tests to assess the properties of bituminous materials. The following tests are usually conducted to evaluate different properties of bituminous materials, including PMBs (Mathew and Rao, 2006)

#### 1. Penetration Test

It measures the hardness or softness of bitumen by measuring the depth in tenths of a millimeter to which a standard loaded needle will penetrate vertically in 5 seconds. The penetrometer consists of a needle assembly with a total weight of 100g and a device for releasing and locking in any position. The bitumen is softened to a pouring consistency, stirred thoroughly and poured into containers at a depth at least 15 mm in excess of the expected penetration. The test should be conducted at a specified temperature of 25°C (Mathew and Rao, 2006). It may be noted that penetration value is largely influenced by any inaccuracy with regards to pouring temperature, size of the needle, weight placed on the needle and the test temperature. A grade of 40/50 bitumen means the penetration value

is in the range 40 to 50 at standard test conditions. In hot climates, a lower penetration grade is preferred. The figure below shows a schematic Penetration Test setup.

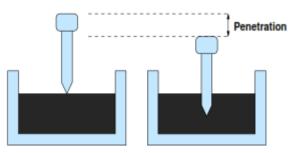


Figure 2.7: Schematic Penetration Test setup

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## 2. Softening Point Test

Softening point denotes the temperature at which the bitumen attains a particular degree of softening under the specifications of test. The test is conducted by using Ring and Ball apparatus. A brass ring containing test sample of bitumen is suspended in liquid like water or glycerine at a given temperature. A steel ball is placed upon the bitumen sample and the liquid medium is heated at a rate of 5°C per minute. Temperature is noted when the softened bitumen touches the metal plate which is at a specified distance below. Generally, higher softening point indicates lower temperature susceptibility and is preferred in hot climates. The Figure below shows Softening Point test set-up.

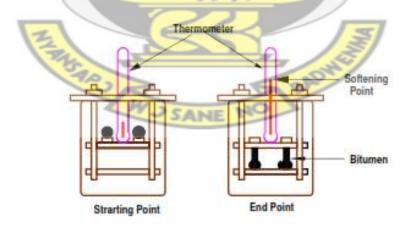


Figure 2.8: Schematic Softening Point Test setup

#### 3. Specific Gravity Test

In paving jobs, to classify a binder, density property is of great use. In most cases bitumen is weighed, but when used with aggregates, the bitumen is converted to volume using density values. The density of bitumen is greatly influenced by its chemical composition. Increase in aromatic type or mineral impurities can cause an increase in specific gravity.

The specific gravity of bitumen is defined as the ratio of mass of given volume of bitumen of known content to the mass of equal volume of water at 27°C. The specific gravity can be measured using either pycnometer or preparing a cube specimen of bitumen in semi solid or solid state. The specific gravity of bitumen varies from 0.97 to 1.02.

#### 4. Viscosity Test

Viscosity denotes the fluid property of bituminous material and it is a measure of resistance to flow. At the application temperature, this characteristic greatly influences the strength of resulting paving mixes. Low or high viscosity during compaction or mixing has been observed to result in lower stability values. At high viscosity, it resists the compactive effort and thereby resulting mix is heterogeneous, hence low stability values. And at low viscosity instead of providing a uniform film over aggregates, it will lubricate the aggregate particles. Two standard temperatures are specified for most bitumen viscosity work, namely, the kinematic viscosity at 135°C and the absolute viscosity at 60°C. Absolute viscosity is a measure of the tangential force per unit area with respect to the other at unit velocity, when maintained at unit distance apart by the fluid. It is a measure of internal resistance to flow. Kinematic viscosity is the ratio of absolute viscosity to density and therefore does not have a force component. The CGS units for absolute viscosity is dyne.s/cm<sup>2</sup> or poise and the SI-system unit for kinematic viscosity is m<sup>2</sup>/s (stoke) (Whiteoak and Read, 2003).

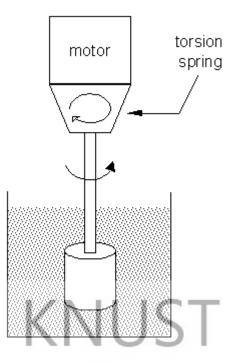


Figure 2.9: Brookfield viscometer setup

This study used the Brookfield viscometer. These employ the principle of rotational viscometry, where an applied torque turns a spindle in a fluid sample to estimate its viscosity. Here, the amount of viscous drag of the fluid is proportional to the amount of torque required to rotate the spindle and thus the viscosity characteristics of the given fluid. In Brookfield engineering, a viscometer is designated with a code that describes the maximum torque range of the instrument. For example, a viscometer labelled as HA, has a torque range appropriate for measuring medium to high viscosity materials; it's 100% torque reading corresponds to14, 374 dyne/cm. Brookfield viscometry was adopted into bitumen rheological testing for determining the viscosity of the bitumen binder at high temperatures, above 135°C, to ensure that the binder is sufficiently fluid for pumping and mixing. A maximum viscosity is specified at 135°C to ensure pumpability during storage, transport, and at the mixing plant. Most bitumen binders behave as Newtonian fluids (stress response not dependent on shear rate) and have a totally viscous response at such high temperatures. Therefore, a viscosity measurement is sufficient to represent workability of the binder. The Brookfield Viscometer is more suited for testing modified bitumen binders, such as those containing crumb rubber modified, compared to the Capillary Viscometer because the latter can get clogged up, partially inhibiting flow. The Performance Grade binder specification limits the viscosity to 3 Pa.s at 135°C (Roberts et al., 1996).

#### 2.7 Solid Waste Management

Solid-waste management may be defined as the discipline associated with controlling the generation, storage, collection, transfer and transport, processing, and disposal of solid waste in a manner that is in accordance with the best principles of health, economics, engineering, conservation, aesthetics, and other environmental considerations, and that is also responsive to public attitudes. In its scope, solid-waste management includes all administrative, financial, legal, planning, and engineering functions involved in the solutions to all problems of solid waste. The solutions may involve complex interdisciplinary fields such as political science, city and regional planning, geography, economics, public health, sociology, demography, communications, and conservation, as well engineering and materials science.

For instance, if waste is wet or has a low heating value, it would not be possible to incinerate it without adding supplemental fuel. If a portion of the waste stream consists of organics and can be easily separated from other waste materials, bioconversion of the waste may become a viable strategy. On the other hand, the waste generated by industrialized countries may be different from those generated by non-industrialized countries. Non-industrialized societies may have more organic waste than those generated by industrialized countries. If this is the case, composting or anaerobic digestion may be more suitable for organic waste management.

The activities associated with managing solid waste from the generation point to final disposal normally include generation, reduction, reuse, recycling, handling, collection, transfer and transport, transformation (e.g., recovery and treatment), and disposal. Depending on site specific conditions, a sound waste-management program can be established by combining some of the necessary activities into integrated solid-waste management. On the other hand, legislative efforts and effective implementation are vital for the safe management and disposal of solid waste. Incentives may be provided for the development and practice of safe treatments, harmless manufacturing processes and methods for converting solid waste into valuable resources by recycling and reuse (Asian Productivity Organization, 2007).

#### 2.7.1 Solid Waste Management in Ghana

Solid waste constitutes a major problem in Ghana and affects both the urban and peri-urban areas on a much similar scale of importance. Whilst in the urban areas the task is largely collection, storage, transport and disposal of municipal solid waste (MSW), in peri-urban areas the task is reduced to removal from homes. In Accra for example, the rate of generation of MSW is estimated at 0.4 kg/capita/day (Carboo and Fobil, 2005). For a city that has over 3 million residents, this rate of waste generation is an obvious challenge. Many other communities, towns and cities in Ghana are no exception to this challenge.

Waste generated in Ghana is mainly constituted of organic and inorganic wastes. The organic wastes are biodegradable and do not offer much of a problem as compared to plastic waste for instance, which take a longer time to decompose. The prevalence of these waste plastics in the environment causes several health challenges ie: sanitary diseases like Cholera.

Everyday methods used to manage solid wastes include Combustion, landfilling and haphazard littering. Neither of these methods is environmentally friendly. As Combustion, releases carbon dioxide to the atmosphere, leaching of toxic chemicals from landfills contaminates ground water and haphazard littering results in the blocking of drains and gutters, causing flooding and serving as breeding sites for mosquitoes.

Plastics are primarily used in the packaging industry. Plastics are used in the food industry for packaging certain foods. Containers used in packaging food are produced from polypropylene and polyethylene (PE) by the process of injection moulding. These containers are used to store frozen, fresh, cold or hot foods. They are also used in packaging cereals, fruits, oily foods as well as some acidic ones too. These ready packaged foods are usually found in the supermarkets and malls otherwise food is usually packaged immediately when the consumer buys them.

In many places, drinking water is mostly packaged in sachets and bottled water is not common. The general public have developed a strong like for sachet water due its portability and affordability. Unfortunately, most people openly litter the streets or throw them out of moving vehicles, upon

emptying the contents. As such, these sachets constitute a large proportion to the waste generated in many of the urban centres in Ghana.

One of the 'best practises' when it comes to managing plastic waste is by recycling. This method is environmentally friendly, as compared to the other means of plastic waste disposal aforementioned. The Recycling of plastics generates a means of employment and bears massive economic potential to the nation. The recovery and reuse of once 'waste material' creates the avenue for the generation of new energy sources and materials for diverse applications.



#### **CHAPTER THREE**

#### **3.0 METHODOLOGY**

#### **3.1 Materials and Equipment**

The following materials and equipment were used for the study:

i. Bitumen: AC-20 grade base bitumen was used in this study, obtained from V-Shabouh Construction Ltd, a Kumasi-based road construction firm.

ii. Plastics: The plastics used for modification were collected from a yoghurt stand at the Department of Chemistry, KNUST and from residential areas on KNUST campus. High density polyethylene (HDPE) and Polypropylene (PP) were in the form of used yoghurt bottles and used disposable cups and were identified by their resin codes.

iii. The basic equipment used for the bitumen modification comprises a sharp scissor for hand cutting the plastics, a stainless steel bucket as the mixing vessel and labelled 'used' Milo tins as storage vessels. The blending set-up, as shown in Figure 3.1, was powered by an air compressor (shown in Figure. 3.3). For the road condition survey, a Samsung<sup>TM</sup> 16.0 Megapixel digital camera was used to capture digital photographs of the various deformations for identification and analysis.

#### **3.2 Road Condition Survey**

The road condition survey was conducted by taking observations from the side and rear window of a moving vehicle travelling from a marked starting point. At points where traffic conditions permit safe alighting, the crew determined the particular failures at that segment of the road on foot, being careful to not endanger themselves or the motoring public.

• The condition survey data was mainly collected in the form of digital photographs, for later review and characterisation.

• The highway was marked with a starting and finishing point (ie: 0 - 220 Km in the case studies considered). The results of the study are displayed and discussed in Chapter four.

#### **3.3 Sample Preparation**

i. Bitumen: the bitumen samples were freed of any foreign matter like wood and other solid matter. It was then heated in an electric oven at 160°C.

ii. Plastics: the plastic materials were washed thoroughly in a detergent for fifteen (15) minutes. The plastics were rinsed with tap water and soaked in distilled water for one (1) hour. They were sundried in the open to remove any odour. The plastics were manually chopped with a sharp scissor to smaller pieces of approximately 5mm dimensions.

# 3.4 Preparation of Plastic-Bitumen Composite

Melt blending technique was employed for preparing the Samples. 400g of the bitumen was weighed on an analytical balance and heated in a tin can immersed in used-motor oil in a stainless steel bucket on a Sybron Thermolyne HP-A1915B Hot plate (set-up shown in Figure.3.1). At fluid condition, the polymer was slowly added, while the speed of the mixer was maintained at 120 rpm and temperature was kept between 160°C and 170°C. The concentration of PP and HDPE used were 0.5%, 1.0%, 1.5%, 2.0%, 2.5% and 3% by weight of the blend. Mixing was carried out for 1 hour to produce homogenous mixtures. The unmodified and modified bitumen were then transferred to tin containers, labelled and stored for further testing. Empirical tests such as penetration, softening point and viscosity were then conducted on the prepared samples. The preparation conditions are illustrated in Table 3.1 (Appendix B).





Figure 3.1: Set-up for Bitumen Blending



Figure 3.2: Stirrer blade

Figure 3.3: Air Compressor

# **3.5 Laboratory Tests Conducted**

Test on the prepared samples were conducted according to established Standards to characterize the properties of PMBs. The different percentages of polymer concentration employed in the modification process, provides a wider range of results which helps in analysing each type of the polymer blend at that particular concentration. The rheological tests include penetration at 25°C, softening point and viscosity test.

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The GHA specifications and test results of unmodified bitumen are presented in Table 3.2A and B respectively in the Appendix B.

#### **3.5.1 Penetration**

The standard penetration test was performed on an Analis Penetrometer P734, on base bitumen and PMB with the concentration of polymer varying between 0.5%- 3% by weight of the bitumen according to ASTM D-5. Penetration test machine is shown in Figure.3.4

A sample of about 100g of bitumen was heated in an oven between 30 minutes to 1 hour, enough time to completely soften the bitumen to pouring consistency. This was stirred thoroughly and transferred into a 15mm penetration test cup and allowed to cool to room temperature. The bitumen filled cup was then placed in a temperature controller set to 25°C and allowed to condition for about 1 hour. It was then removed, dried quickly and placed under the needle of the penetrometer. The average of three readings were taken for each sample and recorded.

Precautions: The tip of the penetrometer needle was set precisely at the surface of the filled penetration cup before the instrument was started. The samples were returned to the temperature controller in between readings. The needles were cleaned with gasoline.



Figure 3.4: The Analis Penetrometer P734

The results of the Penetration test are shown in Tables 3.3 and 3.4 (Appendix B)

The Brinell hardness number (BHN), a quantity obtained from the Brinell hardness test, typical for metals, gives an expression of the applied load, P, as a ratio of the surface area of the indentation; this was employed to simulate the hardness of the different proportions of the bitumen-plastic composites on the metallic scale (Dieter, 1961). According to ASTM Standard E10-66, the simplified expression for BHN is shown below:

# $BHN = \frac{P}{\Pi Dt}$

Where P= applied load, Kg

D=diameter of ball or indenter, mm

t=depth of the impression, mm

The parameters of the penetration test, where the applied load (P) =0.10 kg, D=diameter of the penetration needle, 1mm t=depth of penetration in mm, were employed to simulate the hardness of the bitumen-plastic composite on the metallic scale. The BHN tables for HDPE and PP modified bitumen are shown in Tables 3.3A and 3.4B in Appendix B.

# **3.5.2 Softening Point**

Ring and ball is the standard test to determine the consistency of the bitumen, which represents the temperature at which a change of phase from solid to liquid occurs. It is the temperature at which standard 3/8 inch steel ball weighing 3.55g fall and touches the base plate which is 2.5mm away (Mathew & Rao, 2006).

According to ASTM D-36, freshly softened bitumen samples were poured into two small brass rings and allowed to cool. A heated knife blade was used to trim the surface of the samples to the level of the brass rings. The prepared samples were then conditioned in a temperature controller at 4°C for at least 30 minutes before the test. A steel ball bearing (weighing 3.55 g) is centered on each specimen and placed in transparent glass jar. An electric heater and thermometer is fitted into the beaker filled with clean, distilled water. The temperature at which each bitumen specimen touches the base plate is recorded to the nearest degree. The average of the two readings were taken and rounded to the nearest whole degree. The Softening test set-up is shown in Figure.3.5-3.7





Figure 3.7: Softening point set-up

The results of the Softening point test are shown in Tables 3.5 and 3.6 (Appendix B)

# 3.5.3 Viscosity

Viscosity test was conducted using a DV-III Brook Field Ultra Programmable viscometer on virgin and polymer modified bitumen. The absolute and dynamic viscosity measurements were made at 60 °C and 135 °C respectively according to ASTM D-4402.

The tests were carried out on all polymers up to the concentration of 3%.

A sample of bitumen was heated in an oven between 30 minutes and 1 hour, to completely soften the bitumen to pouring consistency. After thorough stirring, the sample holder of the viscometer was filled <sup>3</sup>/<sub>4</sub> full, cooled and set in place in the instrument. The thermostat was first set to 60 °C for the

absolute viscosity readings and later 135 °C for the dynamic viscosity readings. Two different spindles were used for this test, that is: spindle 7 for absolute viscosity and spindle 27 for dynamic viscosity (these are shown in Figure.3.9-3.11).

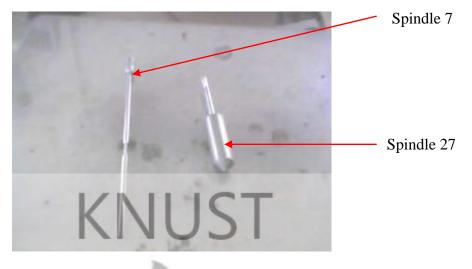


Figure 3.9: Standard Brookfield Viscometer Spindles

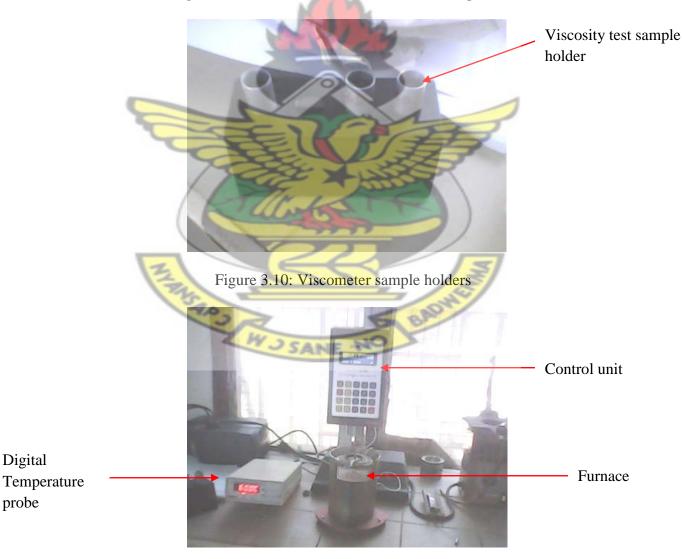


Figure 3.11: DV-III Brookfield Viscometer

The results of the viscosity test are shown in Tables 3.7 and 3.8 (Appendix B)

The specific gravity test was conducted in ambient temperature of 28°C, on unmodified and modified bitumen samples, with 25 ml Specific gravity bottle according to ASTM 1429. Mass readings were made on an analytical balance.

A clean, dry 25 ml specific gravity bottle was weighed along with the stopper (Weight 'A'). The specific gravity bottle was filled with freshly boiled distilled water and the stopper inserted firmly and weighed at room temperature (Weight 'B'). After this, the specific gravity bottle was weighed about half-filled with the material (Weight 'C') and about half-filled with the material and the other half with distilled water (Weight 'D').

The Specific gravity of the various samples was estimated from the formula below:

Specific gravity (Solids and semi-solids) =

[(B-A) - (D-C)]

The results of the test are displayed in Table 3.9 (Appendix B)

# 3.5.5 Fourier Transform Infra-Red Spectroscopy (FTIR) Test

FTIR analysis was conducted on the virgin bitumen and bitumen-plastic composites in order to determine if a chemical change occurred for the dispersion of the waste plastics within the bitumen binder. Fourier transform infrared spectroscopy (FT-IR) spectra were measured by using an Interspec 200-X Fourier transform infrared spectrometer (shown in Figure 3.12). The scanning frequency of each spectrum was 32 times per minute.

The FTIR spectrophotometer was switched on and allowed to warm for about an hour. The various binders were heated in an oven till fluid condition and 0.2g of each sample measured on an analytical balance into fourteen (14) clean, dry beakers. Each of these samples was dissolved in 2 ml Analar grade n-hexane, accurately measured with a 5 ml measuring cylinder. Due to the volatility of the solvent, FTIR readings were taken before other samples were mixed. Blank solvent and sample scans were performed using circular sealed cells  $CaF_2$  windows and 1 mm thickness. All spectra were

obtained by 32 scans with 5% iris and 4 cm resolution in wavenumbers ranging from 4000 to 400  $\text{cm}^{-1}$  (Lu & Isacsson, 2002).

The concentrations of unmodified and modified bitumen, prepared for the FTIR Analysis are shown in Tables 3.10 (Appendix B)



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### **CHAPTER FOUR**

#### 4.0 RESULTS AND DISCUSSIONS

### 4.1 Road Condition Survey

Bitumen deformation is a transcontinental construction phenomenon. Ghana has a fair share of bitumen failures as catalogued by the surface condition survey carried out on some major highways in Ghana. The road ways studied are the Tamale-Paga, Kumasi-Dormaa-Ahenkro Highway and city and town roads in Accra and Kumasi respectively. Several heavy axle trucks were observed to ply the two major highways studied and may be leading contributors to the majority of the binder associated failures encountered, that is, the failures which occur as a result of deformation in the binding characteristics of the bitumen. The most predominant failures observed comprise fatigue cracks and shoving.

#### 4.1.1 Accra Town Roads

Accra is the capital city of Ghana and is home to over two million Ghanaians. The city is well noted for its brisk commercial activities and heavy traffic congestion. The road network spans over one thousand kilometres (1000 km). Owing to the growing pressure on the existing road infrastructure, the roads in the city and its environs are exhibiting signs of deformation and defects. The results are shown below in Figures 4.1-4.4



Figure.4.1: Fatigue cracks on a patched

Figure.4.2: Alligator cracks

road





Figure 4.3: Shoving along a wheel path

Figure 4.4: Rutting along a wheel path



# 4.1.2 Tamale - Paga Highway

The highway from Tamale to Paga spans 207 km. This road serves as the main link road for carting goods from the southern sector and to and from Tema port and by, neighbouring landlocked countries like Burkina Faso and Mali. The road survey was started from the Central Mosque in Tamale, through Bolgatanga, to the Ghana-Burkina Faso border at Paga. The road was observed to be heavily patronised by several heavy axle vehicles, which can easily be pointed for the road failures identified. In the course of this road survey, the team sighted a movable axle load station belonging to the Ghana Highway Authority, a few kilometres from Bolgatanga town.

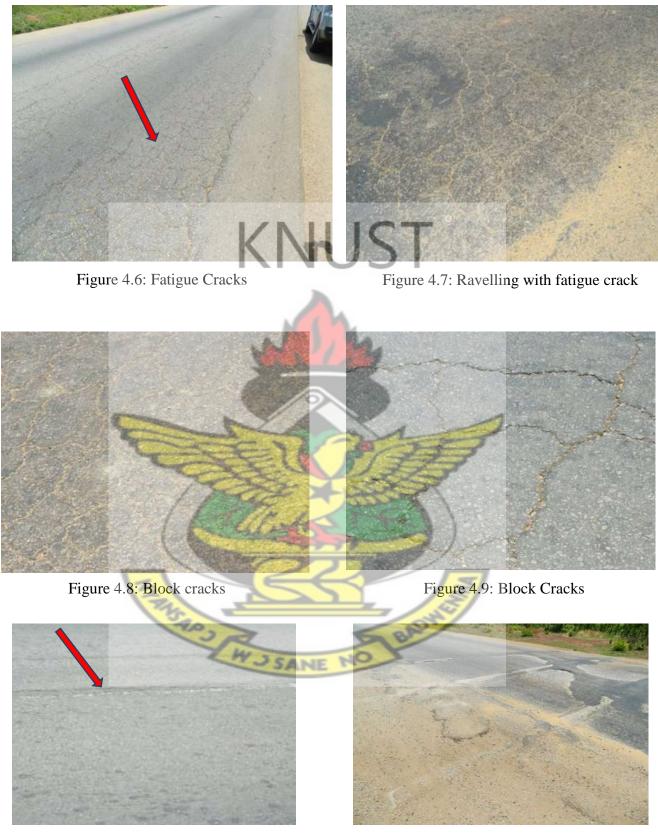


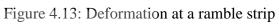
Figure 4.10: Cracking at Asphalt

Figure 4.11: Fatigue Cracks



Figure 4.12: Deformation patch







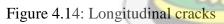


Figure 4.15: Edge Cracks





Figure 4.16: Pothole

Figure 4.17: Edge cracks, shoving and I potholes





Figure 4.18: Severe Shoving Figure 4.19: Patch with Alligator Cracks Carsus W SANE N

# 4.1.3 Kumasi-Dormaa-Ahenkro Highway

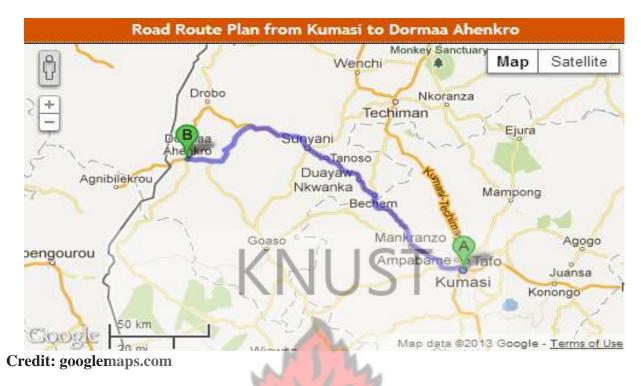


Figure 4.20: Road Route plan from Kumasi to Dormaa Ahenkro

The survey on this highway began from the Abuakwa Shell filling station all the way to the Ghana-Cote d'ivoire border at Dormaa Ahenkro, a metered distance of 202 km. This road serves the transportation needs of the middle belt of Ghana, carting foodstuffs and other inland cargo. Various degrees of failures were observed, the most dominant being fatigue cracks.

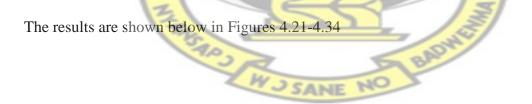




Figure 4.21: Severe Shoving and Rutting



Figure 4.22: Heavy truck on a section of the highway



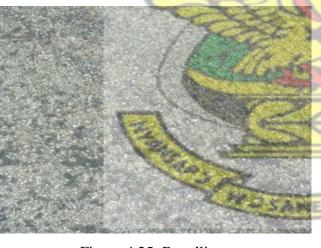


Figure 4.25: Ravelling



Figure 4.26: Alligator cracks (close up



Figure.4.27: Severe Potholes at Mankranso bypass



Figure 4.28: Severe fatigue cracks with patches



Figure 4.29: Severe Shoulder damage



Figure 4.30: Severe Shoulder damage



Figure 4.31: Severe Block and Seam cracks

Figure 4.32: Severe Block cracks (close up)





Figure 4.33: Moderate Longitudinal cracks

Figure 4.34: Low Severity Shoving and Pothole

# 4.1.4 Kumasi Town Roads

According to the Kumasi Metropolitan Assembly (KMA), Kumasi has a total of 1,921 km length of road networks linking residents to virtually all parts of the Metropolis. The road network in Kumasi can be categorized into arterials, collectors and local roads. It has the Trans Saharan roads linking the country to the landlocked countries in the West Africa sub region, which is the Accra–Kumasi–Tamale road. Furthermore, it has eight arterial roads which carry in-coming and out-going traffic from Kumasi. These roads are Barekese route, Bosomtwe route, Buokrom route, Ejisu route, Obuasi route, Sunyani route, Mampong route and Offinso route. In addition to these arteries Kumasi has a number of collector roads which collects traffic from local roads to primary roads as well as distribute traffic from the arterial roads to the access roads, Below are some the defects found during the surface condition survey, shown in Figures 4.35-46



Figure 4.35: Low Severity shoving



Figure 4.36: Severe Shoving (close up)

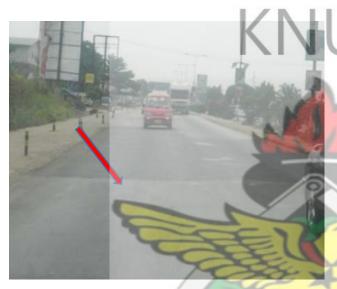


Figure 4.37: High Severity Patching

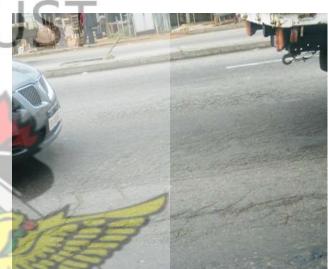


Figure 4.38: Moderate Slippage cracks



Figure 4.39: High Severity Alligator cracks



Figure 4.40: Moderate Block cracks



Figure 4.41: Alligator cracks with Potholes



Figure.4.42: Severe Alligator cracks with

Potholes



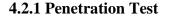
Figure 4.45: Shoving in wheel path with

Rutting

Figure 4.46: Very Severe Surface

deformation

Rheological analysis was performed in order to characterize the flow characteristics of the bituminous composites.



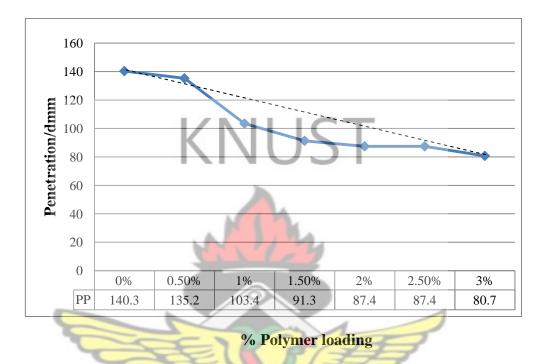


Figure.4.47: Penetration test results of Unmodified and Polypropylene modified bitumen

Figure 4.47, represents the effect of variable concentrations of polypropylene waste plastic modification on the penetration properties of the unmodified bitumen. From the graph, the addition of the polymer can be observed to slightly decrease the penetration value of the unmodified binder from 140.3 dmm to 135.2 dmm with 0.5% PP modification( $\Delta P = 5.1 \, dmm$ ). Still, as the modification ratio approaches 3%, the degree of penetration decreases drastically as its value becomes 80.7 dmm; representing an overall change in penetration of 59.6 dmm, ( $\Delta P =$ 59.6 dmm). The dotted trend line illustrates this observation and predicts that the material will show further decreases in penetration value as polymer ratio increases; an observation confirmed by the work of Noor et al., (2010) and Vasudevan et al., (2012). The hardness of a material is a composite property combining the concepts of resistance to penetration, scratching, marring among others. For most plasticised materials, the hardness test is based on resistance to penetration by an indentor pressed into the material under constant load (Junior, 1970). The penetration test shows the measure of resistance the layers of the binder offer to vertical weights. This constitutes the hardness or brittle properties of the binder. As such, the successive decrease in the penetration ability of the modified binder as the polymer ratio increases implies a corresponding increment in the hardness of the material. The hardening of the bitumen can be beneficial as it increases the stiffness of the material, thus the load spreading capabilities of the structure but also can lead to fretting or cracking (Habib et al., 2011)

The addition of polypropylene polymer to unmodified bitumen progressively increases the hardness properties of the binder.

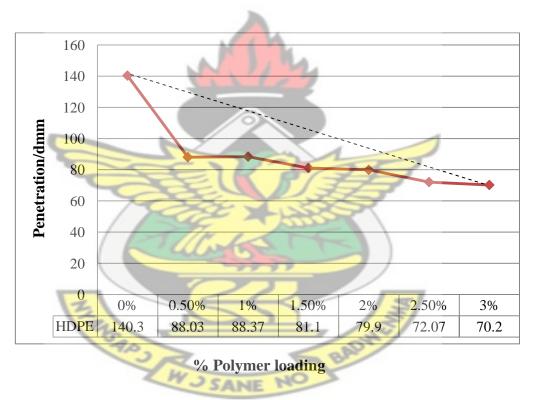
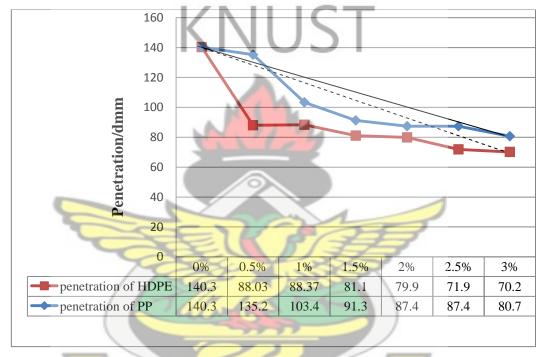


Figure.4.48: Penetration test results of unmodified and high density polyethylene modified bitumen

Figure 4.48 above, illustrates the effect of variable concentrations of high density polyethylene waste plastic modification on the penetration properties of the unmodified bitumen. The addition of just 0.5% HDPE can be observed to produce a very drastic decrease in the penetration value of the unmodified binder from 140.3 dmm to 88.03 (ie.  $\Delta P = 52.27 \text{ dmm}$ ). This change alone accounts nearly for the entire penetration degree achieved by modifying the unmodified bitumen with PP up to

3% (an eventual value of 80.7 dmm). The change in penetration value,  $\Delta P$  through the entire process is 70.1 dmm. This represents nearly 50% increment in the hardness and load resistance at 3% polymer ratio. As the modification ratio approaches 3%, the degree of penetration also decreases drastically as its value becomes 70.2 dmm. The dotted trend line depicts that the material will show further decreases in penetration value should the polymer ratio be increased. Nonetheless, such further plastic modification will affect the workability of the binder, as it becomes very hard and its flow properties decrease.



% Polymer loading

Figure 4.49: Penetration test results of Unmodified, PP and HDPE modified bitumen

SANE

From figure 4.49 for unmodified bitumen, PP and HDPE modified bitumen, the sharp decrease in the penetration value of 140.3 dmm for unmodified bitumen to 88.03 dmm for HDPE and 135.2 dmm for PP at 0.5% concentration of polymer shows the increase in the hardness of the PMB. The more drastic decrease in the penetration value of the HDPE modified bitumen suggests that the commodity HDPE plastics employed in the modification process is of relatively high molecular weight as compared to PP. A decrease in the extent of penetration of a binder is associated with increased viscosity and molecular weight (Whiteoak and Read, 2003). The melting temperature of HDPE and

PP is 135°C and 165°C respectively; both Polypropylene and Polyethylene polymers at temperature above 160°C are in melt state; they absorb some of the maltene fraction (the oily dispersing medium of the bitumen) and release its low molecular weight fractions into the bitumen which eventually increases the viscosity of the PMB (Yousefi et al., 2000). Thus, by the end of mixing process, and by the time it cools, a hardened mixture is formed. The hardening of the bitumen can be beneficial as it increases the stiffness of the material, thus the load spreading capabilities of the structure but also can lead to fretting or cracking (Whiteoak and Read, 2003). Thermoplastics generally impart increased plasticity to most binders. Penetration of a bituminous material is related to its viscosity and empirical relationships have been developed for Newtonian materials. When the Penetration Index is estimated (ie. when penetration is measured over a range of temperatures) the temperature susceptibility of the bitumen can be established.

# 4.2.1.1 Brinell hardness Number (BHN)

i) PP-Modified bitumen Graphs

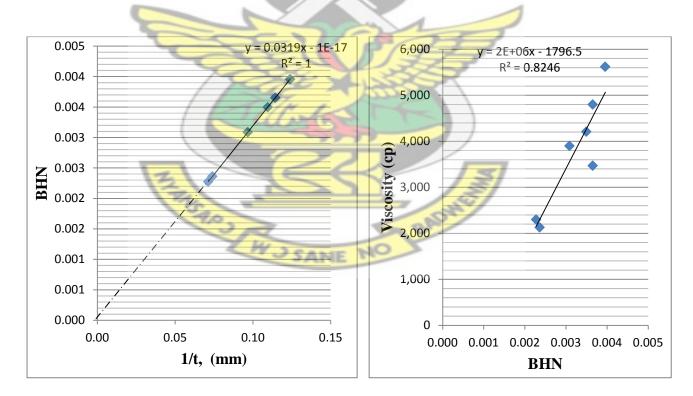


Figure 4.50: Graph of BHN versus inverse of

# penetration depth

Figure 4.51: Graph of Viscosity versus BHN

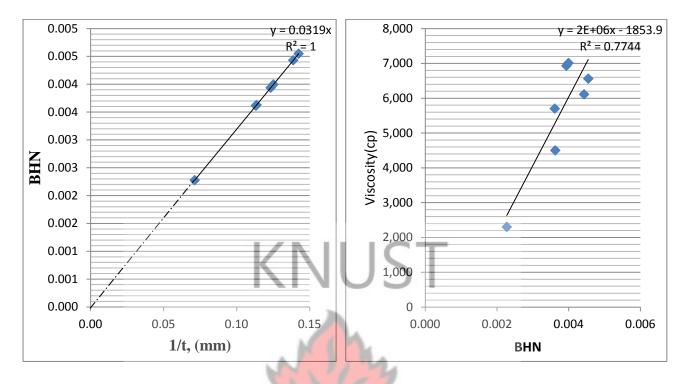


Figure 4.52: Graph of BHN versus inverse ofFigure 4.53: Graph of Absolute viscosity

#### penetration

From figure 4.50 and 4.52, the plot of BHN against the inverse depth of penetration (1/t) yields a perfect linear correlation whose slope is a ratio of the applied load to the diameter of the indentation. At unit diameter (1 mm), as applies to the penetration test indenter, the slope can be manipulated to estimate the pressure (force per unit area) involved in the indentation. The BHN increases as the depth of the indenter penetration (t) decreases (as 1/t increases). An increase in BHN corresponds to an increased hardness of the test material. Therefore, the observed trend of decrease in penetration value as the polymer loading was increased, confirms the enhancement in the hardness properties of the bitumen with plastic modification. Figure 4.51 and 4.53, shows a graph of viscosity against BHN for PP and HDPE-modified bitumen; again, it is observed from the positive correlation that, as the viscosity of the polymer modified bitumen increases, the BHN value increases. This applies in practical situations as highly viscous materials show corresponding resistance of indentation, that is, they yield low penetration values, which theoretically corresponds to high BHN and increased hardness. (Table 3.4A and Table 3.4B show values for PP and HDPE-modified bitumen BHN in Appendix B).

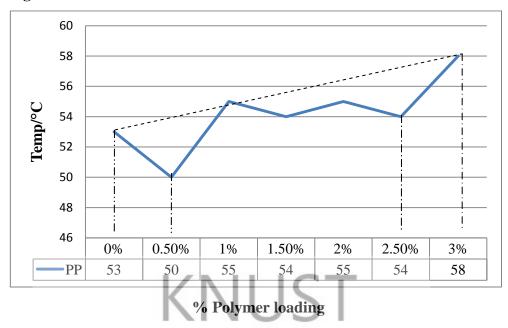


Figure.4.54: Softening point test results of Polypropylene modified bitumen

From Figure 4.54, it can be observed that Polypropylene thermoplastics offer lesser variation in the softening point of the unmodified binder. In the plot above, the softening temperature can be observed to dip at 0.5%, 1.5% and 2.5%. This deviation from the general increment in softening temperature with corresponding increase in polymer loading can be attributed to ageing in those test specimens. Ageing or hardening of bituminous binder occurs during mixing and lay down process and during service. The complex process of ageing has been studied by several authors and it is established that bitumen ageing is one of the principal factors causing negative change of physical structures and chemical compositions, and results in the deterioration of its physical behaviours including softening temperature (Lu & Isacsson, 2002). Up to 3% PP modification, the binder's softening temperature is enhanced by only 5  $^{\circ}$ C. Even though this is attributable to the homogeneity achieved during blending of PP with base bitumen, modification with thermoplastic materials generally does not significantly affect the softening point as compared to the penetration. Habib et al., (2011), explained this observation as being the cause of the internal structure formed by the polymer which seems to be thermodynamically stable and does not significantly affect the softening point of the PMB. Increases in the softening point have however been found to reflect in better rutting resistance at higher temperature (Noor et al., 2011).

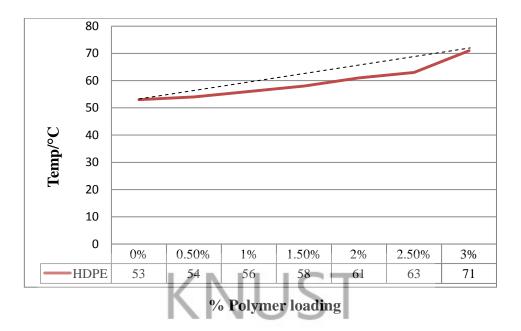
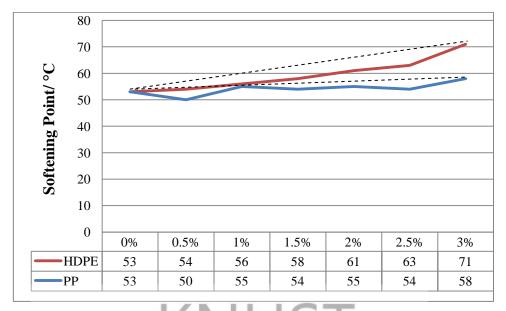


Figure.4.55: Softening point test results of High density polyethylene modified bitumen

Figure 4.55 shows a rather improved softening point profile for the modification conducted with HDPE plastic. The trend line depicts that the softening temperature steadily rises from 53°C to 71°C, that is,  $\Delta Ts = 18°C$ . As mentioned earlier, HDPE when blended with bitumen is able to swell more of the maltenes, leaving behind a mixture of maltene-rich polymer strands and the solid dispersants in the bitumen. The oily fractions of the bitumen are responsible for the volatile properties of the binder, so when much of it is lost to the polymer swelling, the binder finally takes on more of the behaviour of these solid dispersants, resulting in a more thermodynamically stable structure with fewer volatile fractions and hence an increased softening temperature. Generally, higher softening point indicates lower temperature susceptibility and is preferred in hot climates (Mathew and Rao, 2006).



# % Polymer loading

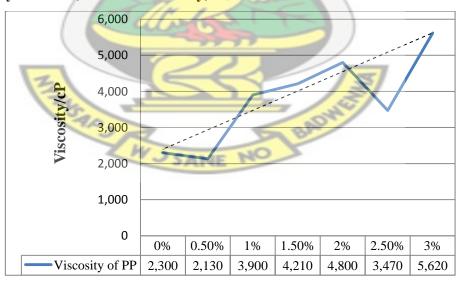
Figure 4.56: Penetration test results of Unmodified, PP and HDPE modified bitumen

Figure 4.56 compares the softening point results obtained for unmodified, PP and HDPE modified bitumen.

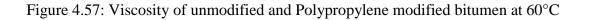
HDPE plastic modification can be observed to affect the softening temperature properties of the binder more as compared to PP.

# 4.2.3 Viscosity Test





# % Polymer loading



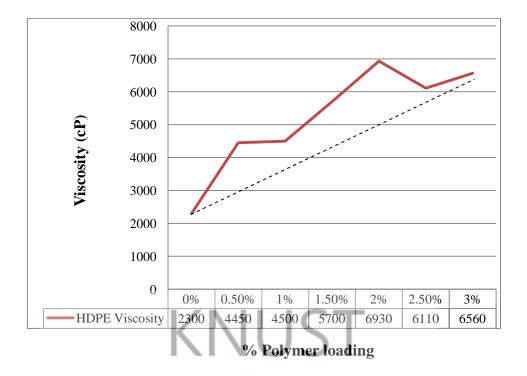
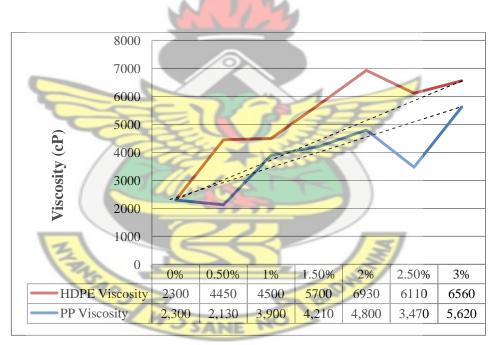


Figure 4.58: Viscosity of Unmodified and High density polyethylene modified bitumen at 60°C



% Polymer loading

Figure 4.59: Viscosity of Unmodified, PP and HDPE modified bitumen at 60°C

The Viscosity of a fluid denotes the measure of resistance it offers to flow. As seen in Figure. 4.57, PP modification of bitumen yields more than two-fold increment in the viscosity of the unmodified binder up to the 3% modification level. Again, the progressive addition of PP to the unmodified bitumen corresponds to a successive loss of the oily fractions to further polymer swelling which

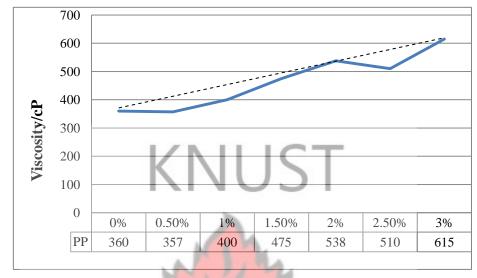
stiffens the binder internally. PP plastics melt completely within the range of 160°C-170°C; the reduction in the viscosity of the binder at the 0.5% PP modification range can be attributed to the complete solubilisation of the plastic into the bitumen. On the other hand, Figure. 4.58 shows a more drastic viscosity enhancement for HDPE, where just 0.5% modification doubles the viscosity of the unmodified binder. There is a strong relationship between the molecular weight and viscosity of materials, ie. High molecular weight materials display corresponding higher viscosity properties. Most commodity HDPE plastics are of high molecular weight and when blended with bitumen, they impart the observed enhancement to the overall viscosity of the PMB.

Figure 4.59 also shows the non-Newtonian behaviour of thermoplastic modified bitumen with the decrease in viscosity with increase in shear rate (refer to viscosity Tables 3.8 and 3.9 in Appendix). The fluctuation of viscosity was observed more for both HDPE and PP till 2.5% concentration of polymer. When bitumen is blended with polymers it forms a multiphase system; a phase rich in asphaltenes not absorbed by the polymer, which enhances the viscosity by the formation of more complex internal structure. The flow behaviour of a bituminous material described in terms of viscosity, exhibits Newtonian and non-Newtonian characteristics depending on the composition and source of the crude, temperature and loading, as well as the internal structure of the base bitumen (Noor et al., 2011). The dip in the viscosities at 2.5% polymer modification for PP and HDPE respectively in the Figures above is as a result of thixotropic effect. This denotes the non-Newtonian, mixed behaviour of decrease in viscosity with increase in shear rate and again increase in viscosity. The thixotropic behaviour of modified bitumen may be due to reversible breakdown of structure which is commonly found in the multiphase system of polymer modified bitumen (Bhattacharya Sati, 1997).

There are a number of deductions which can be drawn from the overall viscosity of a bituminous material. At the field application temperature of 160°C-170°C, viscosity greatly influences the strength of the resulting paving mixes. Low or high viscosity during compaction or mixing has been observed to result in lower stability values. High viscosities resist the compactive effort and thereby

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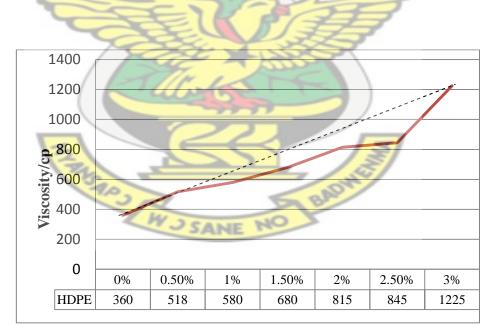
result in a heterogeneous mix, hence low stability values. At low viscosity, instead of providing a uniform film over aggregates, it will lubricate the aggregate particles, which is equally undesired.



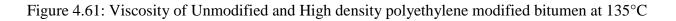
4.2.3.2 Viscosity at 135°C (Dynamic Viscosity)

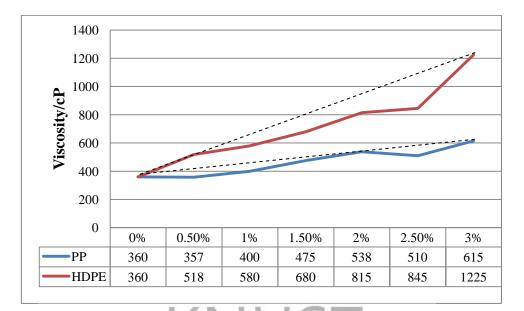
% Polymer loading

Figure 4.60: Viscosity of Unmodified and Polypropylene modified bitumen at 135°C



# % Polymer loading

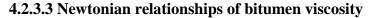




# % Polymer loading

Figure 4.62: Viscosity of Unmodified, Polypropylene and High density polyethylene modified bitumen at 135°C.

The unmodified Bitumen with viscosity of 357 CSt at 135 °C shows increase in viscosity with the increase in polymer concentration, a similar trend as seen in the absolute viscosity profiles (ie. Figure.4.57-4.59). At 135 °C further thixotropic behaviour is observed for PP modified bitumen but not HDPE. This may be due to the complete melt-breakdown of structure of the polymer chains in the HDPE, as it reaches its melting temperature at 130°C. Bituminous binders are assumed to behave like Newtonian fluids at high temperatures (>>100°C) where shear rate is proportional to applied shear stress and the viscosity is independent of shear rate. These same binders can assume shear-thinning behaviour at lower temperatures (<100°C) where the viscosity decreases with an increase in shear rate. The PP-bitumen blend is more homogenous and offers less fluctuation as can be observed for all concentration of polymer in the blend as shown in Figures 4.60-4.62. HDPE on the other hand is more heterogeneous and relatively unstable due to its high molecular weight. One of the main causes of this instability is the tendency of PMB to morphological phase separation which is due to Brownian coalescence followed by gravitational flocculation and creaming (Noor et al., 2011). The addition of PP and HDPE at high temperature resulted in the decrease in viscosity, which should show increase resistance to rutting and thermal cracking at high and low temperatures, respectively.



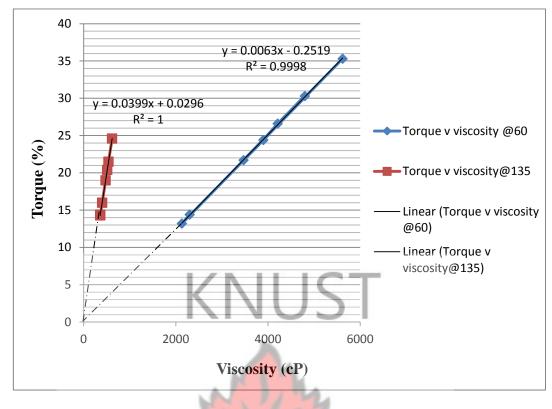


Figure 4.63: Graph of Torque versus viscosity for PP-modified bitumen

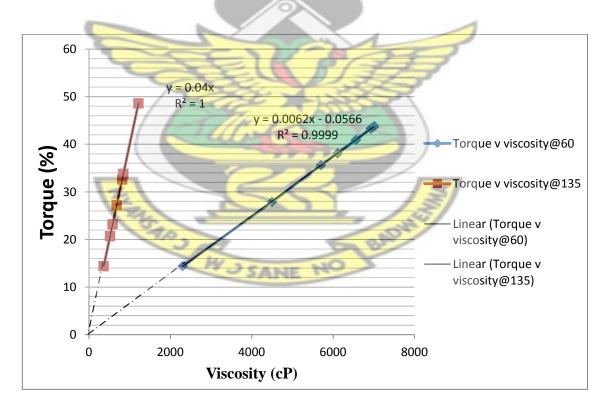


Figure 4.64: Graph of Torque versus viscosity for HDPE-modified bitumen

From the above graphs, the linear relationship of increase in viscosity with applied torque (stress) confirms the overall Newtonian behaviour of bitumen.

#### 4.3 Spectroscopic Analysis

### 4.3.1 Fourier Transform Infra-Red (FTIR) Test

The FTIR test was carried out to detect the functional groups present in the unmodified and polymer modified bitumen. This information will help ascertain whether there is the formation of any possible new bonds via the modification process. Still, the equivalent concentrations prepared for all the different proportions of plastics, will assist in identifying the intensity changes in the peaks of the spectrum. The spectra for the different proportions of both HDPE and PP are shown in Appendix D.

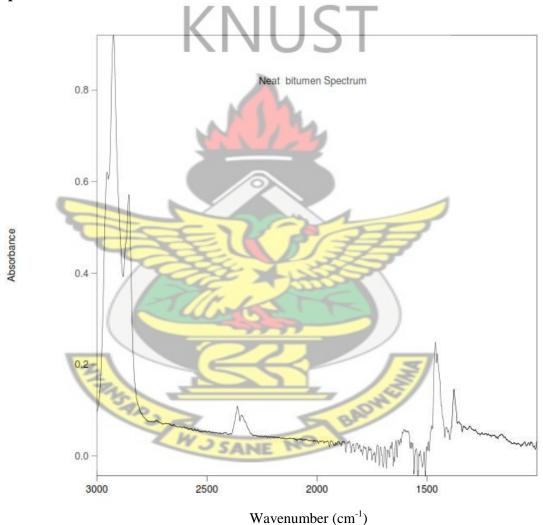
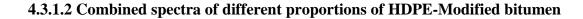




Figure 4.65: FTIR Spectrum of Unmodified Bitumen

Figure 4.65 above, shows the infrared spectroscopy analysis spectrum of the unmodified bitumen tested at room temperature of 27°C. The strongest peak, with an absorbance of 1, can be observed to occur within the 3000-2850cm<sup>-1</sup> IR frequency range. This range is typical of aliphatic –C-H

symmetrical and asymmetrical stretches in alkanes. This confirms within the limitations of the instrument that, the unmodified binder is predominantly composed of aliphatic hydrocarbons. Again, it indicates the presence of high amounts of saturate fractions in the bitumen.  $CH_2$  and  $CH_3$  bends are also observed at the characteristic 1465cm<sup>-1</sup> and 1375cm<sup>-1</sup> respectively. A low intensity peak is propagated within the 2400 cm<sup>-1</sup>-2100cm<sup>-1</sup> range, confirming the presence of a very weak -C=C- or - C=N group with an absorbance of precisely 0.12 (Lu & Isacsson, 2002).



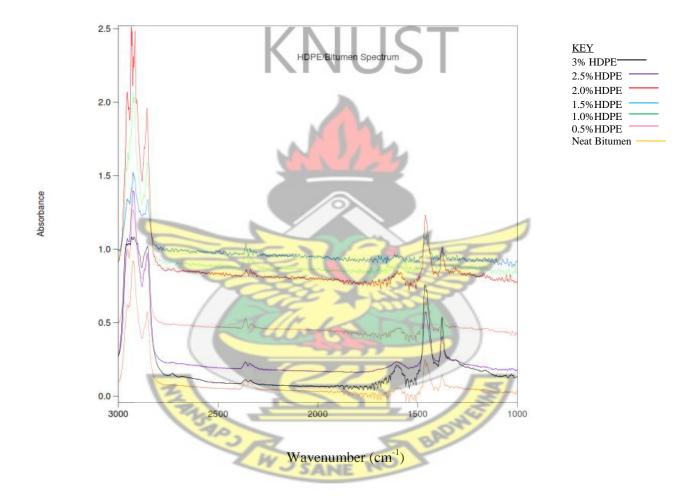


Figure 4.66: Combined FTIR Spectrum of unmodified and various % loadings of HDPE modified Bitumen

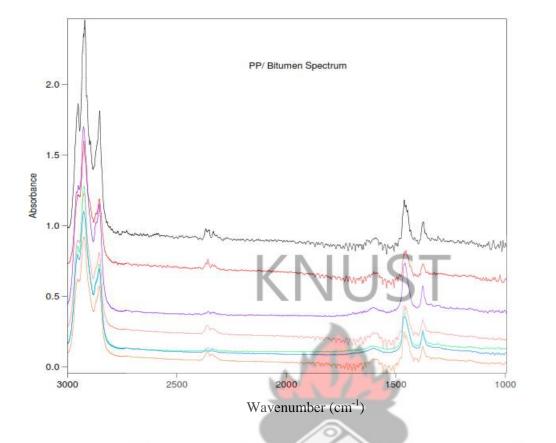
High density polyethylene is primarily aliphatic, composed of only hydrocarbons. The spectrum shown in Figure.4.66 reveals that 0.5% HDPE modification of the unmodified binder yields more than 20% increment in the aliphatic -C-H- group intensity in the binder, the absorbance in the unmodified binder changes from 1.0 to 1.24. The CH<sub>2</sub> and CH<sub>3</sub> bends at 1465cm<sup>-1</sup> and 1375cm<sup>-1</sup>, are

also observed to increase in intensity. A fourfold increment can also be observed in the weak -C=Cor -C=N group as its absorbance becomes 0.5 precisely. Spectra for 1% HDPE and 2% HDPE respectively show profound intensities in the peaks for aliphatic -C-H groups, the CH<sub>2</sub> and CH<sub>3</sub> bends, as well as the triple bond -C=C- or -C=N group. This suggests an active cohesion between the polymer strands and the bitumen fractions. Since no new distinct functional groups are formed, it can be further deduced that the enhanced intensities in the peaks of the original functionalities is the result of a successful blending of the polymer into the binder matrix. Nonetheless, In the spectra for 1.5% HDPE and 2.5% HDPE modified bitumen, it can be observed that, the intensities of the of three prominent peaks are only enhanced slightly as compared to those exhibited by the spectra for 1% and 2% HDPE modified bitumen. This suggests a low shearing of the plastic into the binder.

From the spectrum of 3% HDPE plastic modified bitumen, it can be clearly seen that there is very low influence of this plastic composition on the functional properties of the bitumen. At this maximum polymer ratio, the effect of the high molecular weight plastic becomes very prominent, as the aggregation of unblended polymer strands greatly enhances the peak intensity of the bending  $CH_2$ and  $CH_3$  groups with very little influence on the functional structure of the binder. This further explains the tendency of the composite to gross phase separation under quiescent conditions. HDPE at 3% polymer loading is observed to have the least intense peak. This suggests a poor interaction between the plastic and the bitumen at that percentage of loading. This study reports the most intense peak to occur between 3000 and 2850cm<sup>-1</sup> at 2% HDPE content.

As such the most compatible, stable polymer ratio for HDPE modification under the conditions of this study is 2% HDPE

#### 4.3.1.3 Combined spectra of different proportions of PP-Modified bitumen



KEY
3% HDPE
2.5% HDPE
2.0% HDPE
1.5% HDPE
1.0% HDPE
0.5%HDPE
Neat Bitumen

Figure 4.67: Combined FTIR Spectra of unmodified and various % loadings of PP modified

# Bitumen

From figure.4.67, the prominent peaks in all the different polymer loadings can be observed to occur in the same IR regions as found for the modification with HDPE. Polypropylene plastics can however be observed to have a comparatively reduced influence on the microstructure of the binder at low polymer ratios as compared to HDPE. There is very little increment in the intensity of the prominent peaks as polymer ratio is increased from 0.5% to 1.5%. Between 2% and 3% PP modification, the intensity of the groups absorbing in the aliphatic –C-H IR region become more pronounced. This is indicative of the functional influence the polymer begins to display as its percentage ratio increases. The most intense peak for PP also occurs between 3000 and 2850cm<sup>-1</sup> at 3% PP content. The corresponding trend of increase in peak intensity as polymer ratio increases of the different spectra suggests that the polymer ratio could have been increased beyond 3% for PP modified bitumen.

#### **CHAPTER FIVE**

#### **5.0 CONCLUSION**

The main objectives of this research were to modify and characterize the rheological properties of waste plastic modified bitumen for road construction and repair in Ghana. The use of bitumen modifiers for road making purposes depends on many factors such as cost, construction ability, availability, and expected performance. Bitumen additives have been used to improve bitumen pavement performance as well as to reduce bitumen pavement distresses such as moisture damage, permanent deformation, and thermal fatigue cracking. The performance of modified bitumen concrete pavement is expected to be more stable at warmer temperatures and more flexible at colder temperatures. Polymers have become a permanent part of the highway construction and the degree of modification depends on the polymer property, polymer content and nature of the bitumen.

This study has found the addition of thermoplastic modifiers to conventional bitumen to improve the viscoelastic behaviour of the bitumen and change its rheological properties. Two types of modifiers were used, High density polyethylene (HDPE) and Polypropylene (PP); they were observed to display different amount of influence i.e. or increasing the softening point, decreasing penetration value whilst enhancing the overall dynamic and absolute viscosities of the bitumen.

Spectroscopic analysis carried out by FTIR spectrophotometry did not show new functionalities distinct from the spectrum of the unmodified binder for all the modified bitumen samples. However, the original prominent peaks occurring at the 3000cm<sup>-1</sup>-2850cm<sup>-1</sup> for aliphatic –C-H stretching, 2400 cm<sup>-1</sup>-2100 cm<sup>-1</sup> for triple bond C=C- or -C=N group and 1465cm<sup>-1</sup> and 1375cm<sup>-1</sup> for CH<sub>2</sub> and CH<sub>3</sub> bends are observed to increase in intensity depending on the polymer type and blending ratio. This suggests a successful 'blending-in' in terms of cohesion of the polymer strands into the bitumen matrix.

After conducting laboratory tests on bitumen binder and mixtures with different polymer content and after analyzing the data and comparing the results, the following findings are stated:

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- Polymer-modified bitumen is typically more viscous (thicker) than unmodified bitumen. As thicker binder coatings usually take longer to become brittle, the durability of the pavement can be improved.
- Both modified binders show thixotropic effect at 60°C, that is, the viscosity of the samples decrease with time at a constant shear rate.
- Lower penetration values are accompanied by high viscosities and softening point, vice-versa is also true.
- The most compatible blend for HDPE is achieved at 2% polymer loading.
- The most incompatible blend for HDPE is observed at 3% polymer loading.
- At higher HDPE polymer content (3%) the tendency for gross separation is confirmed by the FTIR spectrum showing scarcely intense peaks when compared with the unmodified binder.
- At all polymer ratios, PP shows good blending behaviour as FTIR spectra show growing peak intensities as the polymer ratio increases.
- The most enhanced compatible blend for PP is achieved at 3% polymer loading.
- Among the two types of thermoplastic modified binders prepared, the mixtures with PP were the most homogenous.
- For all modified binders prepared, the penetration values decrease as polymer ratio increases whilst, softening point values increase as polymer ratio increases.

From the above findings, it is concluded that using waste commodity plastics in binder modification carries the advantage of a cheap, technologically effective means of enhancing conventional binder performance and offers an alternative way to manage plastic waste.

Substantial savings can be made from using plastic waste in bitumen modification. For instance, for a single lane, one layer road that may demand about a ton of bitumen (1000kg, which cost GHC 2,000), modification with 3% of plastic can save 30kg of bitumen (a minimum savings of GHC 60). Again the increased viscosity achieved through polymer modification yields more product when applied as emulsions or cutbacks. This will culminate in substantial savings and cut-down material costs.

### **5.1 RECOMMENDATIONS**

From this study, waste polypropylene modified is recommended for road construction in Ghana, due the relative compatibility and enhancement it provides to conventional bitumen.

The following recommendations briefly describe areas in which further research work is valuable:

- Investigating the mechanical properties (for tensile, compressive strength), flexural strength and morphological properties (using Scanning Electron Microscopy, Tunnelling Electron Microscopy) of plastic modified bitumen.
- Conducting field studies to study the performance of the modified binder versus the conventional binder.
- A life cycle cost analysis of roads constructed using various polymer-modified bitumen binder in comparison to those constructed using conventional binder needs to be performed.
- Evaluating compatibility, chemical reaction, storage stability and effectiveness of other locally available bitumen modifying and filling materials to modify the conventional bitumen.
- Conduct studies on different plastomeric and elastomeric polymers such as LDPE, TPE, natural rubber, crumb rubber, Styrene butadiene Styrene (SBS), Styrene Ethylene Butadiene (SEBS) etc. to evaluate the effect of the polymer types, form and mixing method on the overall quality of the modified binder.

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## APPENDIX

## APPENDIX A

## **ROAD FAILURES FROM OTHER COUNTRIES**

Country in Scope: United States of America (credit: Distress Survey Manual, ODOT)



Figure 2.1A: Moderate severity rutting on Asphalt road Figure 2.2A: High severity rutting on Asphalt road

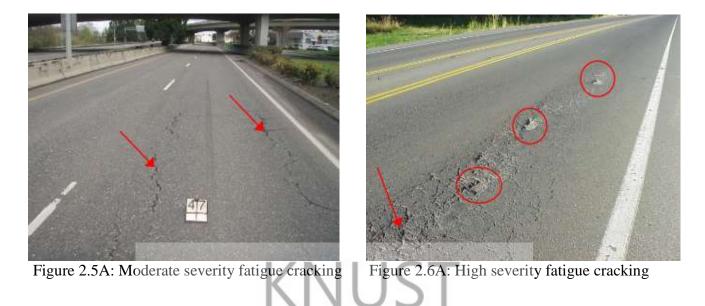


(Credit: Gonçalves et al. 2001)

Figure 2.3A: High severity rutting on Asphalt

Figure 2.4A: High severity rutting on Asphalt road

Country in scope: USA (credit: Distress Survey Manual, Oregon Department of Transportation)



Country in scope: USA (credit: Distress Survey Manual, Oregon Department of Transportation)



Figure 2.7A: Moderate severity Alligator cracking Figure 2.8A: Moderate severity Alligator cracking

Australia (credit: Pavement Maintenance and Rehabilitation, AAPA)



Figure 2.9A: High severity Alligator cracking

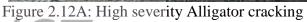


Figure 2.10A: High severity Alligator cracking



Figure 2.11A: High severity Alligator cracking





Country in scope: U.S.A (credit: Distress Survey Manual, Oregon Department of Transportation)



(Credit: Pavement Maintenance and Rehabilitation, AAPA)

Figure 2.15A: Low Severity Block cracking

Figure 2.16A: High Severity Block cracking

Country in scope: U.S.A (credit: Distress Survey Manual, Oregon Department of Transportation)



Figure 2.17A: Medium Severity Longitudinal cracking Figure 2.18A: High Severity Longitudinal cracking

# KNU SPoland



(Credit: Pavement Maintenance and Rehabilitation, AAPA)

Australia

Figure 2.19A: Low Severity Longitudinal cracking Figure 2.20A: High Severity Longitudinal cracking

Country in scope: U.S.A (credit: Distress Survey Manual, Oregon Department of Transportation)



Figure 2.21A: Medium Severity Transverse cracking cracking

Figure 2.22A: High Severity Transverse

## Australia

# Slovakia



(Credit: Pavement Maintenance and Rehabilitation, AAPA)

Figure 2.23A: Medium Severity Transverse cracking Figure 2.24A: High Severity Transverse cracks

USA

Costa Rica



Figure 2.25A: Low Severity Edge cracksFigure 2.26A: High Severity Edge cracks

Country in scope: USA (credit: Distress Survey Manual, Oregon Department of Transportation)



Figure 2.27A: High Severity Ravelling



Figure 2.28A: Medium Severity Ravelling

Country in scope: U.S.A (credit: Distress Survey Manual, Oregon Department of Transportation)



Figure 2.29A: Medium Severity Pothole

Figure 2.30A: High Severity Pothole

Country in scope: USA (credit: Distress Survey Manual, Oregon Department of Transportation)



Figure 2.31A: Moderate Severity Shoving



Figure 2.32A: High Severity Shoving

## **APPENDIX B**

## MISCELLANEOUS TABLES

%HDPE	Mass of polymer(g)	Preparation time/min	<b>Temperature</b> (°C)	Pressure/bar	Speed/rpm
0.5	2	90	170°C - 180°C	6	120
1.0	4	95	170°C - 180°C	6	140
1.5	6	150	170°C - 180°C	6	120
2.0	8	90	180°C - 200°C	6	140
2.5	10	130	180°C - 200°C	6	140
3.0	12	95	180°C - 200°C	6	140
%PP	Mass of	Preparation	Temperature	Pressure/bar	Speed/rpm
	<b>Polymer</b> (g)	time/min	(°C)		-rr
0.5	2	30	160°C - 180°C	6	120
1.0	4	35	160°C - 180°C	6	140
1.5	6	40	160°C - 180°C	6	140
2.0	8	45	160°C - 180°C	6	140
2.5	10	50	160°C - 180°C	6	140
3.0	12	55	160°C - 180°C	6	140

Table 3.1: Preparation conditions for Bitumen-Plastic Composite

Table 3.2A: GHA Specifications for AC-20 Graded Bitumen

Property	Value
Penetration (dmm) at 25 °C, 100g, 5s	-
Softening Point ,°C	48-56
Kinematic Viscosity at 135 °C, cSt, Min.	300
Viscosity at 60 °C, centipoise	2000±400
Specific Gravity	1.01-1.06

# Table 3.2B: Conventional Properties of Unmodified Bitumen

Property	Value
Penetration (dmm) at 25 °C, 100g, 5s	140
Softening Point ,°C	53
Kinematic Viscosity at 135 °C, centistokes	356
Viscosity at 60 °C, centipoise	2300
Specific gravity	1.01

 Table 3.3: HDPE Penetration Test Results-ASTM D5

	Penetration at	25°C, 100g load		
%HDPE	T1	T2	Τ3	Average penetration (dmm)
0	142.1	139.6	139.2	140.3
0.5	88.4	87.1	88.4	88.03
1.0	88.8	89.1	87.2	88.37
1.5	79.6	81.4	82.3	81.10
2.0	79.5	79.3	80.9	79.90
2.5	70.1	71.7	74.4	72.07
3.0	66.5	73.3	70.9	70.20
	12 CM COM	INE NO BA		

%PP	T1	Τ2	T3	Average penetration (dmm)
0	142.1	139.6	139.2	140.3
0.5	135.6	137.6	132.4	135.2
1.0	103.4	104.9	101.8	103.4
1.5	90.4	92.2	91.3	91.3
2.0	87.8	87.5	86.5	87.4
2.5	94.6	76.8	90.8	87.4
3.0	80.7	80.3	81.1	80.7

## Penetration at 25°C, 100g load

 Table 3.4A: Brinell hardness number table for HDPE-modified bitumen

%HDPE	Load, g	t, mm	1/t, mm	D, mm	BHN	Viscosity
0.0	100.25	14.03	0.07	ST.	0.002	2,300
0.5	100.25	8.803	0.11		0.004	4,500
1.0	100.25	8.837	0.11	1/3	0.004	5,700
1.5	100.25	8.11	0.12	BADHER	0.004	6,930
2.0	100.25	7.99	0.13	1	0.004	7,010
2.5	100.25	7.207	0.14	1	0.004	6110
3.0	100.25	7.02	0.14	1	0.005	6560

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%PP	Load, g	t, mm	1/t, mm	D,mm	BHN	Viscosity
0	100.25	14.03	0.07	1	0.002	2,300
0.5	100.25	13.52	0.07	1	0.002	2,130
1	100.25	10.34	0.10	1	0.003	3,900
1.5	100.25	9.13	0.11	1	0.003	4,210
2	100.25	8.74	0.11	1	0.004	4,800
2.5	100.25	8.74	0.11	1	0.004	3,470
3	100.25	8.07	0.12	1	0.004	5,620

Table 3.4A: Brinell hardness number table for PP-modified bitumen

Table 3.5 PP Ring and ball softening point test results

% PP	Softening Temp (°C)
0	53
0.5	50
1.0	55
1.5	54
2.0	55
2.5	54 54
3.0	58 SANE NO BA

_	Softening Temp (°C)	% HDPE
_	53	0
	54	0.5
	56	1.0
	58	1.5
	61	2.0
	63	2.5
		3.0
72	KIN	

Table 3.6 HDPE Ring and ball softening point test results

Table 3.7: PP Brookfield Viscosity test results

%PP		60				170		
	Motor Sp	eed=2.5rpm	Mot	or Speed=100rp	m, Shear	Moto	or Speed=200rpr	n, Shear
	_			Rate=34/s			Rate=68/s	
	Torque	Viscosity	Torque	Torque Shear Strain Viscosity			Shear Strain	Viscosity
	(%)	(cP)	(%)	$(D/cm^2)$	(cSt)	(%)	$(D/cm^2)$	(cP)
0	14.4	2,300	14.4	122.4	357.9	6.8	57.8	85
0.5	13.2	2,130	14.3	122.4	352.1	7.2	61.2	90
1.0	24.4	3,900	16.0	136.0	396.0	10.4	88.4	131
1.5	26.6	4,210	19.0	161.5	471.7	10.9	92.6	136
2.0	30.3	4,800	21.5	182.7	538.5	13.2	112.2	165
2.5	21.7	3,470	20.4	173.4	<u>69</u> 6.7	12.5	106.3	156
3.0	35.3	5,620	24.6	209.1	606.5	19.0	161.5	238

Table 3.8 HDPE Brookfield Viscosity test results

W

Temperature((C))							
%HDPE		60		135			
	Motor Speed=2.5rpm Viscosity Tor		Motor Speed=100rpm, Shear Rate=34/s				
			Torque (%)	Torque (%) Shear strain $(D/cm^2)$			
		( <b>cP</b> )	-		(cSt)		
0	14.4	2,300	14.4	122.4	357.9		
0.5	27.9	4,500	20.7	176	510.9		
1.0	35.6	5,700	23.2	197.2	572.6		
1.5	43.3	6,930	27.2	231.2	672.6		
2.0	43.8	7,010	32.6	277.1	803.7		
2.5	38.1	6110	33.8	287.3	839.1		
3.0	40.9	6560	48.6	413.1	1207.8		

## **Temperature**(°C)

ME

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Table 3.9 Specific Gravity Test Results

Specific Gravity=(C-A)/[(B-A)-(D-C)] A= weight of clean,dry specific gravity bottle and stopper B=weight of Spec. grav. Bottle and freshly boiled distilled water C=weight of Spec. grav. Bottle half-filled with the material D=weight of Spec.grav.Bottle half-filled with material and the other filled with water

	Unmodified Bitumen		
	Test 1	Test 2	Average
A(g)	29.85	29.87	Average
-	59.64	59.65	
B(g)	<b>3</b> 5.34	34.33	
C(g)	59.74	59.68	
D(g) C-A(g)	5.49	4.46	
B-A(g)	29.79	29.78	
D-C(g)	<b>29</b> .79 <b>24</b> .4	25.35	
Specific Gravity	1.018552876	1.006772009	1.013
Specific Gravity	1.010332070	1.000772009	1.013
	0.5% PP-Modifie	ed Bitumen	
A(g)	29.89	29.94	Average
B(g)	59.64	59.64	8-
C(g)	34.29	34.04	
D(g)	59.67	59.66	
C-A(g)	4.4	4.1	
B-A(g)	29.75	29.7	
D-C(g)	25.38	25.62	
Specific Gravity	1.006864989	1.004901961	1.006
	1% PP-Modified	Bitumen	
A(g)	29.9	29.91	Average
B(g)	59.62	59.61	
B(g) C(g) D(c)	34.9	34.08	
D(g)	59.68	59.67	
C-A(g)		4.17	
B-A(g)	29.72	29.7	
D-C(g)	24.78	25.59	
Specific Gravity	1.012145749	1.01459854	1.013
	1.5% PP-Modifie	d Ritumon	
A(g)	29.89	29.92	Average
B(g)	59.65	59.62	11,010,80
C(g)	34.06	35.16	
D(g)	59.72	59.67	
C-A(g)	4.17	5.24	
B-A(g)	29.76	29.7	
D-C(g)	25.66	24.51	
Specific Gravity	1.017073171	1.009633911	1.013
~ v	112		

	2% PP-Modified Bitumen		
A(g)	29.88	29.86	Average
B(g)	59.63	59.65	Ū.
C(g)	34.88	35.21	
D(g)	59.71	59.68	
C-A(g)	5	5.35	
B-A(g)	29.75	29.79	
D-C(g)	24.83	24.47	
Specific Gravity	1.016260163	1.005639098	1.011
	2.5% PP-Modified Bitumen		
A(g)	29.85	29.88	Average
B(g)	59.65	59.66	i i voi ugo
C(g)	35.85	34.72	
D(g)	59.72	59.74	
C-A(g)	6	4.84	
B-A(g)	29.8	29.78	
D-C(g)	23.87	25.02	
Specific Gravity	1.011804384	1.016806723	1.014
Speeme Gravity	1.011001501	1.010000725	1.014
	3% PP-Modified	l Bitumen	
A(g)	29.91	29.9	Average
B(g)	59.63	59.67	U
C(g)	34.45	33.58	
D(g)	59.67	59.69	
C-A(g)	4.54	3.68	
B-A(g)	29.72	29.77	
D-C(g)	25.22	26.11	
<b>Specific Gravity</b>	1.008888889	1.005464481	1.007
-	and the		
	0.5% HDPE Mo	dified Bitumen	
A(g)	29.85	29.89	Average
B(g)	59.63	59.63	-
C(g)	35.35	34.89	
D(g)	35.35 59.68	59.72	
C-A(g)	W 2 SAN 5.5 NO	5	
B-A(g)	29.78	29.74	
D-C(g)	24.33	24.83	
Specific Gravity	1.009174312	1.018329939	1.014
	1% HDPE Mod	ified Ritumen	
A(g)	29.89	29.9	Average
B(g)	59.62	59.62	Tiveluge
C(g)	35.24	35.35	
D(g)	59.68	59.67	
C-A(g)	5.35	5.45	
B-A(g)	29.73	29.72	
D-C(g)	24.44	29.72	
Specific Gravity	1.011342155	1.009259259	1.010
Specific Oravity	1.0113+2135	1.00/20/20/	TOTA

	1.5% HDPE Modified Bitumen		
A(g)	29.92	29.89	Average
B(g)	59.61	59.61	
C(g)	34.92	33.47	
D(g)	59.62	59.65	
C-A(g)	5	3.58	
B-A(g)	29.69	29.72	
D-C(g)	24.7	26.18	
Specific Gravity	1.002004008	1.011299435	1.007
	2% HDPE Modified Bitumen		
A(g)	29.89	29.88	Average
B(g)	59.61	59.63	
C(g)	33.48	33.52	
D(g)	59.61	59.62	
C-A(g)	3.59	3.64	
B-A(g)	29.72	29.75	
D-C(g)	26.13	26.1	
Specific Gravity		0.997260274	0.999
		1.6. 1	
	2.5% HDPE Mo		
A(g)	29.88	29.89	Average
B(g)	59.62	59.61	
C(g)	33.33	34.63	
D(g)	55.55	59.63	
C-A(g)	3.45	4.74	
B-A(g)	29.74	29.72	
D-C(g)	22.22	25	
Specific Gravity	0.458776596	1.004237288	0.732
	3% HDPE Modi	fied Ritumen	
A(g)	29.9	29.86	Average
B(g)	50.61	59.62	Tretuge
C(g)	35.23	33.62	
D(g)	50.62	59.64	
C-A(g)	5.33	3.76	
B-A(g)	29.71	29.76	
D-C(g)	24.39	26.02	
Specific Gravity	1.001879699	1.005347594	1.004

## Table 3.9 (continued)

Polymer Type	Specific Gravity	Density of	Viscosity	Kinematic
		Bitumen/PMB	Reading at 135°C	Viscosity
		(g/cm3)	(cP)	(cSt)
HDPE				
Unmodified	1.006	1.006	360	357
0.5%	1.013	1.013	517.5	510.9
1.0%	1.013	1.013	580	572.6
1.5%	1.011	1.011	680	672.6
2.0%	1.014	1.014	815	803.7
2.5%	1.007	1.007	845	839.1
3.0%	1.006	1.006	1215	1207.8
PP				
0.5%	1.014	1.014	357	352.1
1.0%	1.010	1.010	400	396.0
1.5%	1.007	1.007	475	471.7
2.0%	0.999	0.999	538	538.5
2.5%	0.732	0.732	510	696.7
3.0%	1.014	1.014	615	606.5

Density of Water=1g/cm<sup>3</sup>

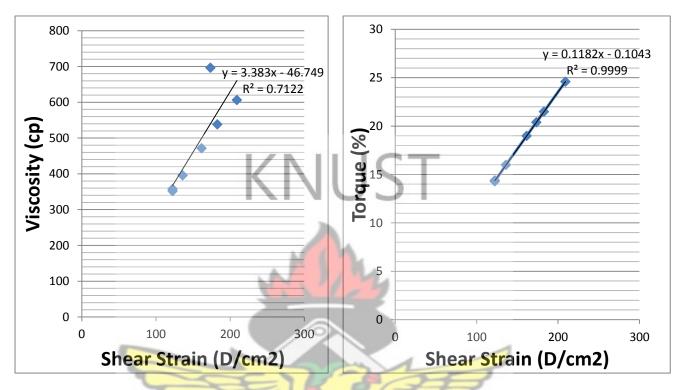
# Table 3.10 Concentrations of bitumen prepared for FTIR Analysis

Volume of n-hexane used 2 ml.

		1 - 1 - I
Sample	Mass (g)	Concentration (g/ml)
Unmodified	0.203	0.102
PP-Modified bitumen	Alle	(STE)
0.5%	0.208	0.104
1%	0.209	0.105
1.5%	0.207	0.104
1.5% 2%	0.206	0.103
2.5%	0.205	NE NO 0.103
3%	0.207	0.104
HDPE-Modified bitumen		
0.5%	0.213	0.107
1%	0.205	0.103
1.5%	0.203	0.102
2%	0.207	0.104
2.5%	0.205	0.103
3%	0.212	0.106

## **Chapter four**

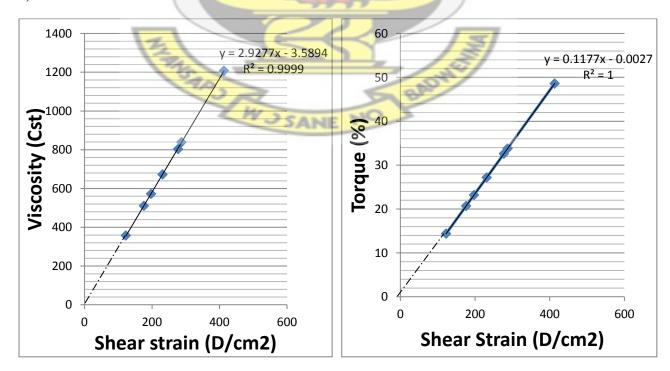
## NEWTONIAN RELATIONSHIPS OF BITUMEN



## I) PP Modified Bitumen at 135°C

Figure 4.1: Viscosity versus Shear strain

Figure 4.2: Torque versus shear strain



## ii) HDPE Modified Bitumen at 135°C

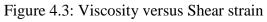
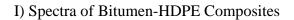
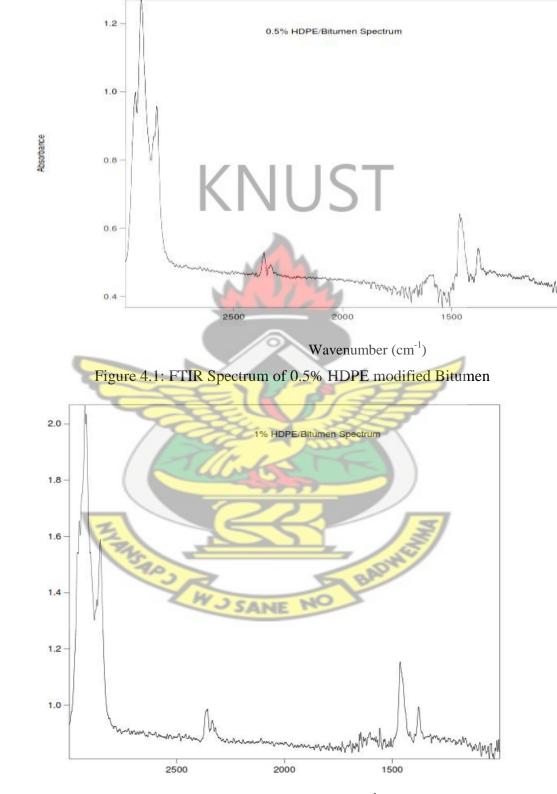


Figure 4.4: Torque versus Shear strain

## FTIR SPECTRA

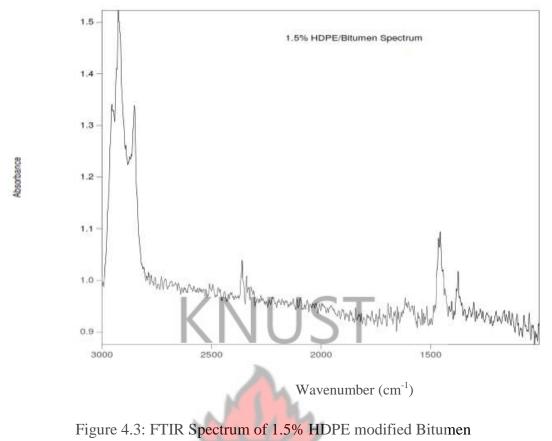
Absorbance



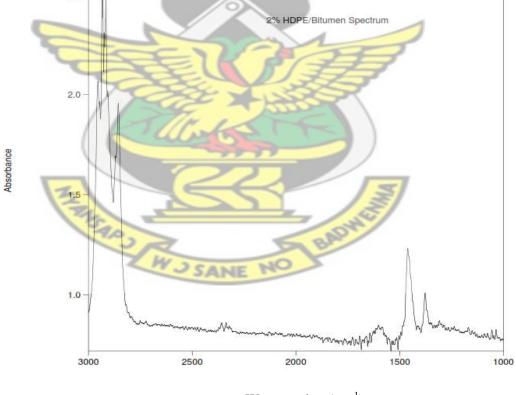


Wavenumber (cm<sup>-1</sup>)

Figure 4.2: FTIR Spectrum of 1.0% HDPE modified Bitumen



2.5 - 2% HDPE/Bitumen Spectrum



Wavenumber (cm<sup>-1</sup>)

Figure 4.4: FTIR Spectrum of 2.0% HDPE modified Bitumen

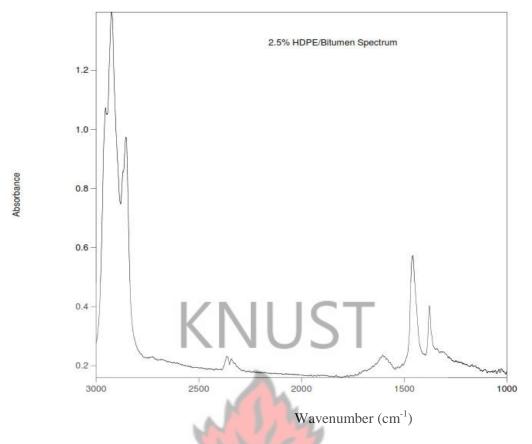


Figure 4.5: FTIR Spectrum of 2.5% HDPE modified Bitumen

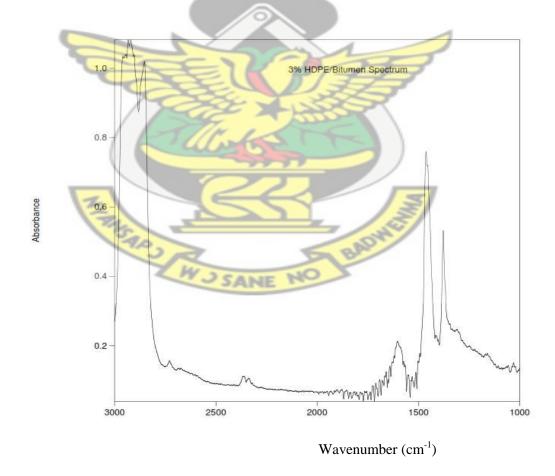


Figure 4.6: FTIR Spectrum of 3.0% HDPE modified Bitumen

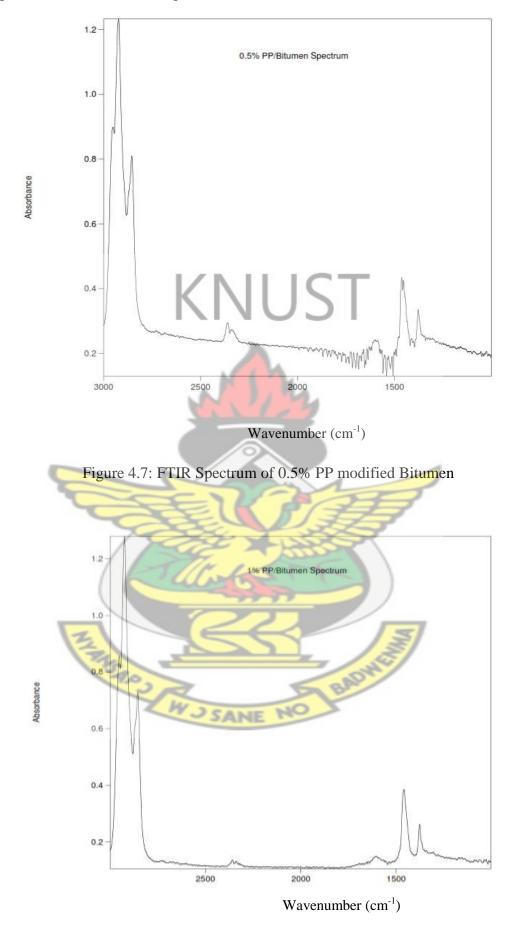


Figure 4.8: FTIR Spectrum of 1% PP modified Bitumen

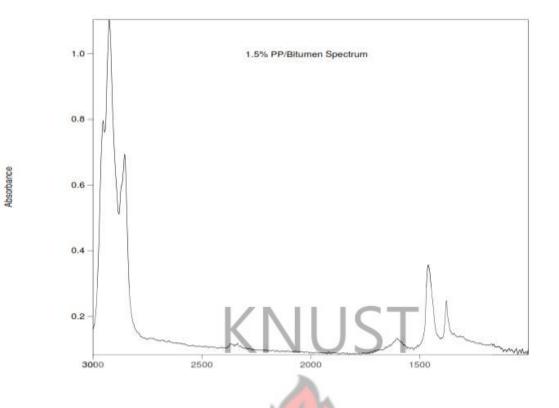
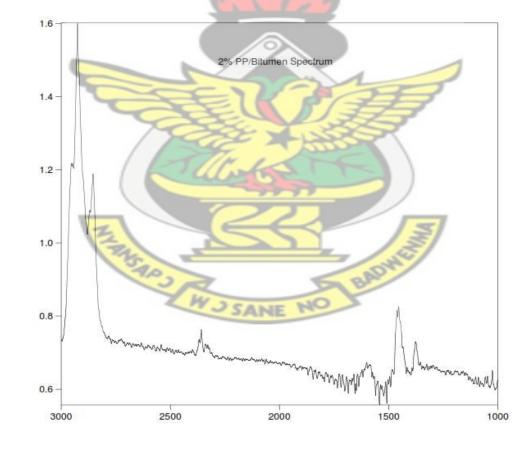


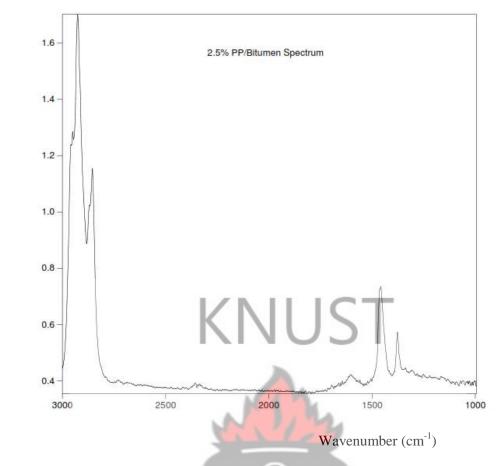
Figure 4.9: FTIR Spectrum of 1.5% PP modified Bitumen



Absorbance

Wavenumber (cm<sup>-1</sup>)

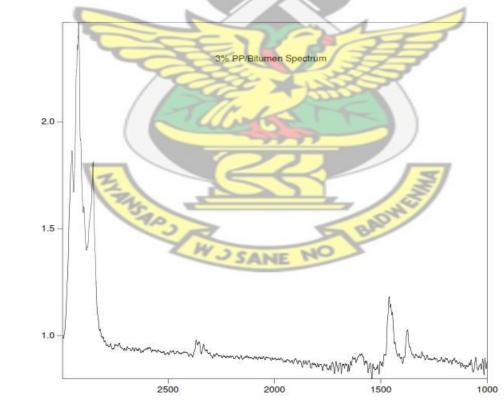
Figure 4.10: FTIR Spectrum of 2% PP modified Bitumen



Absorbance

Absorbance

Figure 4.11: FTIR Spectrum of 2.5% PP modified Bitumen



Wavenumber (cm<sup>-1</sup>)

Figure 4.12: FTIR Spectrum of 3% PP modified Bitumen