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UNIVERSITI TEKNOLOGI PETRONAS

MORPHOLOGY AND RHEOLOGY OF PP AND LLDPE MODIFIED BITUMENS AND THEIR EFFECT ON ASPHALT MIX PROPERTIES

by

NOOR ZAINAB HABIB

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MORPHOLOGY AND RHEOLOGY OF PP AND LLDPE MODIFIED BITUMENS AND THEIR EFFECT ON ASPHALT MIX PROPERTIES

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NOOR ZAINAB HABIB

A Thesis
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DECLARATION OF THESIS

Title of thesis	MORPHOLOGY AND RHEOLOGY OF PP AND LLDPE MODIFIED BITUMENS AND THEIR EFFECT ON ASPHALT MIX PROPERTIES

I NOOR ZAINAB HABIB

hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UTP or other institutions.

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Date :	Date :

DEDICATION

To my beloved family

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ABSTRACT

The deterioration of flexible bound bituminous road layers in the form of creep deformation or fatigue cracking is caused by a number of contributing factors. Of primary importance are the influences of traffic volume, axle loading, mix volumetrics, material properties and environmental conditions. Whenever it is economically viable, polymer modified bitumens (PMBs) have become widely accepted as the binders of choice for the construction of highly durable asphalt mix road surfacings. Although extensive work exists in the literature on characterizing the rheology and chemistry of bitumens and PMBs, there remains the need to better understand the relationships between polymer type, chemistry, morphology and rheology of the resultant PMBs. In this study, 80/100pen grade bitumen was modified with up to 3% polymer content using two polymer types, namely linear low-density polyethylene (LLDPE) and polypropylene (PP). The first part of the research dealt with analysis of virgin and modified bitumens in both unaged and thermally aged states. A number of characterization techniques were employed including: Rheology (penetration, softening point, dynamic shear rheometry), Morphology (Field Emission Electron Microscopy, Atomic Force Microscopy, Transmission Electron Microscopy), Chemical Analysis (SARA fractionation, CHNS Analyzer), Spectroscopic Analysis (FTIR, GC-MS). In the second part of the investigation, asphalt mixtures were manufactured incorporating the aforementioned binders using the Marshall method of mix design to optimize mix proportions. Compacted specimens were subjected to Repeated Load Creep and 4-Point beam fatigue tests. Chemical and morphological analysis indicated that polymer modification led to a disturbance in bitumen colloidal stability as reflected by rheological trends at various polymer contents. Furthermore, polymer/bitumen compatibility as observed with the aid of morphology was in line with rheological and chemical fractionation analysis. Modification also improves rutting and fatigue resistance. More interestingly, PP bitumen modification resulted in superior performance in comparison to LLDPE.

ABSTRAK

Kerosakan yang berlaku pada lapisan-lapisan jalan yang dibuat dari bahan berbitumin dalam bentuk kegagalan deformasi(“creep) dan keretakan(fatigue) adalah disebabkan oleh beberapa faktor. Yang tersohor dianatara factor-faktor tersebut adalah jumlah trafik yang tinggi yang menggunakan jalanraya/lebuhraya, bebanan gandar yang tinggi, sifat bahan yang digunakan dan factor-faktor persekitaran. Bilamana keadaan menunjukkan terdapat keuntungan dari segi ekonomi, penggunaan bitumen yang diubahsuai dengan polimer (polymer modified bitumen) PMB, digunakan secara meluas sebagai binder pilihan untuk tujuan pembinaan permukaan jalanraya yang berdaya lasak. Walaupun terdapat banyak bahan penyelidikan yang mendapati tentang riologi dan hubungan kimia bitumen dalam PMB, masih terdapat keperluan untuk lebih memahami hubung kait jenis polimer, keadaan kimia, morfologi dan riologi bahan PMB yang terus dihasilkan oleh industri pembinaan jalanraya/lebuhraya. Dalam kajian ini, penggunaan bitumen 80/100 telah diubahsuai dengan pencampuran sehingga 3% polimer dalam polythylene (LLDPE) dan polipropilin (PP). Bahagian pertama kajian ini berkisar pada analisis bahan bitumen asal dan yang telah dicampur dengan polimer dalam keadaaan asal dan bahan yang terubah oleh suhu (aged and thermally aged). Beberapa teknik penganalisaan telah digunakan yang termasuk reologi (ujian penetrasi, suhu kelembutan dan ujian dinamik reometri ricih). morfologi (kaedah Field Emission Electron Microscopy, Atomic Force Microscopy, Transmission Electron Microscopy). analisis Kimia (termasuk SARA fractionalization, penganilasaan Karbon/Hidrogen/Nitrogen/Sulfer), analisis spektroskopi (FTIR, GC-MS). Bahagian kedua kajian ini melibatkan penyelidikan tentang sampel campuran berbitumin menggunakan kaedah Marshall untuk memperolehi nilai bahan cecairan (binder) yang optima. Bahan yang telah dipadatkan melalui ujian Bebanan Beban secara Berterusan (Repeated Load Creep) dan Ujian Fatik rasuk di empat titik (4-point beam Fatigue Tests). Analisis kimia dan morfologi menunjukkan bahawa pengubah suaian bitumen dengan polimer menjurus kepada perubahan pada kestabilan koloidal yang boleh menbantu kefahaman tentang tren reologi pada kandungan polimer yang berbeza-beza. Seterusnya, kompatibiliti polimer dan bitumen yang dilihat dengan pertolongan hasil kajian morfologi seiring dengan analisis reologi dan analisis kimia yang kedapatan dari kajian ini. Sebagaimana yang dijangkakan, ketahan deformasi dan fatik bertambah baik dengan adanya penambahan polimer. Lebih teruja, ialah bitumen yang diubahsuai dengan PP memperlihatkan hasil yang lebih baik berbanding LLDPE. Perkara ini lebih terserlah pada ujian fatik (keretakan).

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CHAPTER 1

INTRODUCTION

1.1 Introduction

Bitumen the byproduct of natural depleting resource oil is the most widely used paving material. Its annual production by petroleum industry has now reached to around 100 Mt (metric ton) of which 95% is consumed by paving industry worldwide [1]. According to recent report world demand for bitumen would increase by 2.1 percent annually reaching 108 million metric tons till 2013, which is equivalent to 655 million barrels of bitumen [2]. Demand for China alone would rise to 28% of all world bitumen by 2013 with annual increase of 3.3% through 2013 [2].

With the prevailing scenario and consistent increase in oil prices after the Middle East oil crisis, a price hike in bitumen is unavoidable. Thus with increase in price and global consumption, bitumen industry must now look for alternate solution which can enhance the pavement service life. Although continuous improvements have been made at refinery level by improving the production processes to improve the quality of paving grade bitumen, but the final product from refinery failed to enhance the paving grade quality to protect the pavement from the damages caused by accelerating wear and tear of heavy traffic and harsh climatic conditions which ultimately leads to an increase in the maintenance cost of the pavements. Keeping all these factors in mind modification remains the only alternate choice to enhance the pavement service life and to reduce the cost of maintenance. Polymer modification of bitumen is helping to overcome these challenges since 1975 when French administration played a key role in the innovation of polymer modified bitumen by adding thermoplastic polymer in bitumen [3]. The use of polymer in pavement is at its peak now as according to the Association of Modified Asphalt Producers (AMAP) survey 2009 only in USA 65% of all the roads are modified with polymers to meet the challenge of accelerated traffic growth and deteriorating climatic conditions [4].

1.2 Background of study

Pavements are designed to withstand the stresses applied by moving traffic and to provide smooth riding quality to the road user. In order to achieve the smooth riding quality the pavement must be designed according to the harsh traffic and environmental condition to which it is going to be subjected. The strength and durability of the pavement depends on the bituminous mixture which is mainly composed of binder and aggregate. The binder in bituminous mixture is usually composed of only 5 percent while the rest is composed of aggregate. With this amount of bitumen in the mix the properties of bitumen must be good enough to withstand the increasing wheel load and harsh climatic condition as it is the only deformable component of the bituminous mixture. The study of this deformable component especially in terms of its colloidal structure and viscoelastic characteristics is important to deal with the pavement distresses namely rutting along wheel path at high elevated temperature, fatigue initiating cracks in the pavement due to repeated load action, thermal cracking due to temperature variations, ageing and stripping.

Several studies were conducted to enhance the properties of bitumen of which modification with polymer considered best suited and is being used for a long time as it meets the technical requirement of the modified binder [5]. Thus modification of bitumen with polymer provides an alternate solution to improve the rheological properties of conventional binder enhancing its stiffness and viscoelastic properties that should be sufficient enough to resist pavement distresses.

The two main components of bitumen, asphaltene and maltene are considered dominant factor affecting the properties of the binder. Asphaltene which constitutes only 5 to 25% of the bitumen is dark black coloured component, mainly composed of polar and aromatic material. While maltene is composed of saturates, aromatics and resins. They are also known as dispersing agent for asphaletene [1].

Asphaltene has profound effect on the properties of the binder. It is considered as the major component of bitumen responsible for the colloidal structure of bitumen which particularly depends on the concentration of asphaltene to maltenes. The physical, chemical, rheological and mechanical properties of the bitumen also depends on asphaltene concentration [5].

The research study was conducted in view to understand the enhanced properties of polymer bitumen blend with understanding of interaction between asphaltene and maltene which plays crucial role in deciding its rheological and viscoelastic properties. This would provide an insight to further improve the performance characteristics of the modified binder and thus would develop a better quantitative understanding of the relationship that exists between modified binder characteristics based on rheology, morphology and chemical analysis. To achieve these goals, two polymers namely polyethylene (in the form of Linear Low Density Polyethylene LLDPE and Polypropylene PP) was used as modifier because it is cheap and easily available. Both of these polymers belong to plastomers.

1.3 A Brief Review of Modification of Bitumen with Polymer

Polymers, a long chain of hydrocarbons are extensively used for bitumen modification as it shows better resistance to rutting and thermal induced cracking. Polymer modification also shows decrease in fatigue damage, stripping and temperature susceptibility. Thus polymer modification has been considered as an alternate choice to control excessive wear and tear due to increase in axle wheel load, increase in traffic level, increased tyre pressure and deteriorating climatic conditions. In order to meet the requirement of higher pavement quality demands by the road users, the needs for modification using polymers has become immense. Paving industry is now switching to new modified material in order to meet the technical demand of today. Modification of bitumen with polymer shows improved pavement performance properties at low, medium and high temperature. Modification with polymer shows decrease in thermal susceptibility and permanent deformation (rutting),while enhances the fatigue life of the pavement [6].

Most commonly used polymers in paving industry includes elastomers and plastomers as it shows improved performance properties in terms of rutting and fatigue. Globally 75% of modified binders used by the industry can be classified as elastomers, 15% as plastomers and remaining 10% composed of either rubber or modified material [7].

Among the thermoplastic elastomers Styrene Butadiene Styrene (SBS) copolymers are most commonly used copolymer because of its prominent blending abilities in terms of compatibility but it use increase the cost of the pavement considerably. Thermoplastic plastomers include Ethylene Vinyl Acetate (EVA), Linear Low Density Polyethylene (LLDPE), High Density Polyethylene (HDPE) and Polypropylene (PP) were considered as good modifier which shows promising potential of improving permanent deformation and thermal induced cracking [5].

Although the use of thermoplastic elastomers like SBS is very common in paving industry despite of its higher cost but it still faces the problem of degradation when exposed to atmosphere and higher stress. Thus the use of plastomers belonging to olefinic (like polyethylene) is considered as better choice because it is easily available at a cheaper price but the problem of phase segregation still exist [8].

It is must be remembered that in most of the cases of modification polymer bitumen interaction is just physical one which primarily depends on the polymer architecture [9]. With all the promising improvements with the polymer modification, optimum polymer content, mixing temperature, blending technique, choice of particular polymer for modification and mixing time has profound effect on the end product. Beside these final properties of modified blend, the other related factors such as higher operating temperatures related to mixing, pumping, lay down and compaction must be in accordance with ASSHTO MP1 [10]. Lower polymer content up to 5% is considered as optimum polymer concentration for polymer modified mixes by the paving industry as at this content the achieved viscosity usually remains below 3 Pa s limits as set by ASSHTO MP1 for workable mixes [10].

1.4 Problem Statement

Bituminous binders are considered as complex material as its properties mainly depends on the crude source of the petroleum and refining processes at refinery. Thus the viscoelastic characteristic of bitumen is difficult to define as it varies with the temperature, loading time/condition beside its chemical structure. The incorporation of polymer into bitumen, where as it improves the viscoelastic and performance characteristic of the modified binder but at the same time further increases the complexity of its behavior. Mixing time, temperature and the applied shear rate during blending also affect the rheological, morphological, chemical and thus its mechanical or performance characteristics of the polymer modified binder.

Thermoplastics (polyethylene and polypropylene) although being used because of cost effectiveness but due to problem of least miscibility of polymer with bitumen make its utilization quite difficult, even when used they were usually cross linked or stabilized by grafting any suitable chemical or stabilizing agent.

Thus the focus of this research study was to understand the effect of mixing time (1 hour), slow shear rate (120 rpm) and temperature (160°C) on the complex behavior of thermoplastic modified bitumen on its viscoelastic characteristics which were governed by change in its morphology and chemical structure. The evaluation of the effect of these modified binder properties on the performance characteristic of modified bituminous mixture in terms of rutting and fatigue was the major concern of this research study.

On the basis of the above discussion the current practices of evaluation needs further improvement in order to find the correlation between the rheology, morphology and chemical changes which ultimately affect mechanical characteristics of the modified binder. Thus the need of material characterization in order to study asphaltene – maltene phase in bitumen is considered as vital element of this research to identify the changes in binder due to modification and how it can be related to the performance characteristics of modified binder and thus bituminous mixture.

1.5 Objectives of Study

The objectives of this research study are as follows:

1. To investigate the effect of the polymer modification by using thermoplastic namely linear low density polyethylene and isotactic polypropylene, on the chemical, rheological and morphological properties of virgin 80/100 pen bitumen when blended at slow shear rate at intermediate temperature.

2. To assess the engineering properties of the control and modified bituminous mixtures prepared from virgin 80/100 pen bitumen and polyethylene and polypropylene modified bitumen respectively.

3. To assess the performance properties of control and linear low density polyethylene and polypropylene modified bituminous concrete mix in terms creep and fatigue.

1.6 Scope of Study

This study focuses on the chemical, rheological, morphological and engineering properties of linear low density polyethylene and polypropylene modified bitumen which was blended with virgin bitumen without using any cross linking material or any chemical which can enhance the stability and reduce immiscibility problem of polymer with bitumen. The polymer modified bituminous blend was then analyzed so that it can be related to understand the effect of modification on the rheological, morphological, chemical properties of bituminous blend with its affect on the enhanced engineering and mechanical characteristics (rutting and fatigue) of polymer modified bituminous mixture.

The main elements of study was the preparation of linear low density polyethylene and polypropylene modified bitumen by blending at low shear rate (120 rpm), for 1 hour at 160°C with bitumen All tests were then conducted according to the standard specifications (ASTM, BS or ASSHTO) where as for morphological analysis samples were prepared according to the methods found in literature review used by others researcher.

1.7 Contribution of the study

This research study was conducted in the aspect that complete rheological, chemical analysis and morphological study was adopted to conclude the reason for enhanced mechanical properties of linear low density polyethylene and polypropylene modified bituminous mixture due to modification. The study was conducted with an aim to provide an economical solution to pavement industry by developing mix using existing conventional equipment. For this reason slow shear rate of 120 rpm, mixing temperature as 160°C and mixing time as one hour was being adopted

From the civil engineering aspect this study elaborates the effect of physical dispersion of polymer in bitumen with its affect on the material characteristic of the modified binder and thus its performance characteristics of the bituminous mixture.

1.8 Limitation of Study

This study has following limitations:

- This study limited to modification of only 80/100 penetration grade bitumen with two polymers namely Polypropylene (PP) and Linear low density polyethylene (LLDPE).
- Mixing and blending of polymer was done only at temperature 160°C. Mixing time was kept as 1 hour at speed of 120 rpm. Virgin 80/100 pen bitumen was also subjected to these conditions before use to have uniformity in testing conditions.
- The testing of all performance test specimen were conducted considering the hot climate which exists most of the time in Malaysia was adopted.

- This study was mainly focused on the analysis and testing of modified properties of polymer modified bitumen in view of its chemical, rheological and morphological behavior.

1.9 Organization of Thesis

The research work documented in this thesis is presented in the following chapters:

Chapter 1: presents an introduction and a brief overview of the work conducted.

Chapter 2: presents a comprehensive literature review on the chemistry of the bitumen, the rheological, morphological and performance characteristics of the modified binders. This chapter covers some of the basics adopted for this research study.

Chapter 3: presents the methodology adopted for this research study. The testing methods adopted for aggregate and binders along with performance testing methods are presented. As the main focus of study is on the modified binder characteristics detailed testing methods used to study the chemical, morphological and rheological behavior of the modified binders are presented here.

Chapter 4: presents the results and discussion of the characterization tests conducted on virgin 80/100 pen bitumen, linear low density polyethylene and polypropylene modified binder. This includes the empirical test results (penetration, softening point test and viscosity test), chemical test results (*n* heptane precipitation method and SARA chromatographic technique) and analytical test (FTIR, GC/MS & CHNS analyzer) test results.

Chapter 5: presents the results and discussion of the morphological analysis of the virgin 80/100 pen bitumen and polymer modified binder. This includes the FESEM, AFM and TEM test results.

Chapter 6: presents the results and discussion of the rheological test results of the virgin 80/100 pen bitumen and polymer modified binder. The DSR test results are presented in this chapter.

Chapter 7: presents the results and discussion of the engineering properties of the virgin 80/100 pen bitumen and polymer modified bituminous mixtures. These properties discussed include the workability, density, porosity, Marshall Stability, Marshall Stiffness of the bituminous mixture.

Chapter 8: presents the results and discussion of the fatigue properties of bituminous mixture prepared with virgin 80/100 pen bitumen and from the polymer modified bitumen. The flexural Beam fatigue test results are present in this chapter.

Chapter 9: presents the results and discussion of the creep characteristics of virgin 80/100 pen bitumen and polymer modified bituminous mixtures. Test results obtained from dynamic creep test and wheel tracking test results are presented in this chapter.

Chapter 10: presents the major conclusion drawn from the work presented in previous chapters and recommendations for the future work.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Polymer modified material has been widely used by paving industry to enhance the performance characteristics of the pavement to meet the deteriorating effects of increasing axle wheel load and climatic condition. Polymer modification is considered most suitable solution as it enhances the desired properties required to reduce rutting, decrease thermal and fatigue cracking [11].

Most commonly used modified binder by paving industry belongs to thermoelastic and thermoplastic. Thermoelastic namely styrene butadiene styrene (SBS) and styrene butadiene styrene rubber (SBS-R) are more commonly used because of its promising properties but at a very high cost. Among thermoplastic, Polyethylene (PE) is the most commonly used by paving industry as it is cheaper and easily available but the problem of phase segregation remains there. Despite all the improvements obtained from modification, use of conventional bitumen cannot be replaced because of economic reason. Thus the literature review for this thesis covers all the topics related to conventional bitumen and polymer modified bitumen.

2.2 Bitumen

The use of natural bitumen in road construction started in 1910s with the advent of vacuum distillation process in refinery which made it possible to obtain crude residual in the end as bitumen [12]. From the rheological point of view bitumen is defined as viscoelastic material which is very sensitive to temperature, showing its elastic behavior at low temperature and viscous characteristics at high temperature [6].

Bitumen density at room temperature lies typically between 1.01 and 1.04 g/cm3, depending on the crude source and grade of the bitumen [1]. Depending on the origin of crude, bitumen can be classified as paraffinic, naphthenic or aromatic depending on the presence of saturate, cyclic or aromatic structures. From the various analysis of crude source it was found that bitumen basically contains carbon (82% - 88%), hydrogen (8% - 11%), sulphur (0 – 6%), oxygen (0 – 1.5%) and nitrogen (0 – 1%) [13] This compositional content can vary depending on processing condition during manufacturing or by modification induced by the addition of polymer.

Despite that bitumen is mainly composed of hydrocarbon of different molecular size it also contains heteroatoms (nitrogen, sulfur, oxygen) along with the traces of heavy metals like vanadium and nickel.

2.2.1 Chemistry of Bitumen

The knowledge of bitumen chemistry is essential because of its varying characteristics based on its chemical composition which varies at molecular and intermolecular level. The nature of the bitumen is still not completely known and varies with the origin of crude oil and distillation process used during manufacturing. Generally bitumen is considered as colloidal dispersion of asphaltene in maltene. It is being observed that asphaltene are present in the form of micelles as being first proposed by Nellensteyn in 1924 [14]. According to him the stacked flat sheets of asphaltene are condensed (fused) aromatic rings linked at their edges by chains of aliphatic- aromatic rings in colloidal system, which has the tendency to be attracted towards each other resulting in the formation of agglomeration or colloidal aggregate.

The chemistry of bitumen can be well explained when analyzed in terms of fraction namely saturates, aromatics, resins and aspahltene (SARA) as obtained by chromatographic method, or in term of maltenes (deasphaltenated portion of bitumen) and asphaltene content. Asphaltene are thus defined as non- volatile, high molecular fraction of bitumen which is insoluble or precipitate in light alkanes such as n-heptane and n- pentane.

Masson [15] thus consider SARA fraction as a method to fractionate bitumen in the order of increasing aromacity, hetro atom content and molecular weight which can be presented in order like S< A< R< As. It was being considered by Traxler [16], that bitumen is a complex aggregation of complex molecules which are not all hydrocarbon but include heteroatoms. Thus the physical, rheological and colloidal properties of bitumen depend on its chemical composition, while because of its lower molecular weight regarded as natural polymer whose viscoeastic behavior mainly dependent on its chemical composition [8].

According to Mason [15] bitumen shows three different phases rigid and brittle at low temperature, flexible at room temperature and starts flowing at higher temperature. It is very difficult to explain these properties of bitumen as unlike polymer they could not be related to microstructure, which can be later on related to its viscoelastic characteristic due to unavailability of precise molecular structure and repeat unit for bitumen. Beside this presence of hetero atoms in bitumen make it compatible to polymer forming the reactive groups, thus the interaction of less compatible asphaltenic fraction helps in the formation of primary chemical bond which gave rise to the formation of asphaltic copolymer [9]. Thus in short the chemical composition of bitumen at molecular and intermolecular level plays a vital role in understanding its performance characteristic of the pavement when used as binder [17].

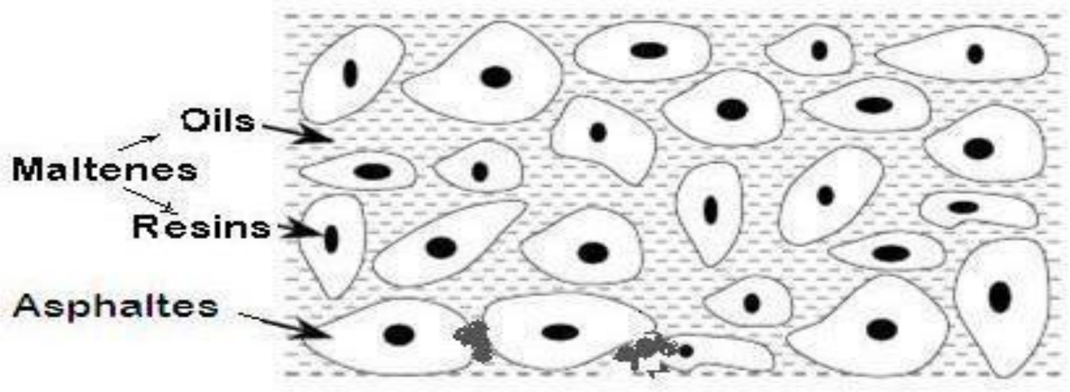

Figure 2.1: Asphaltenes and maltenes [18]

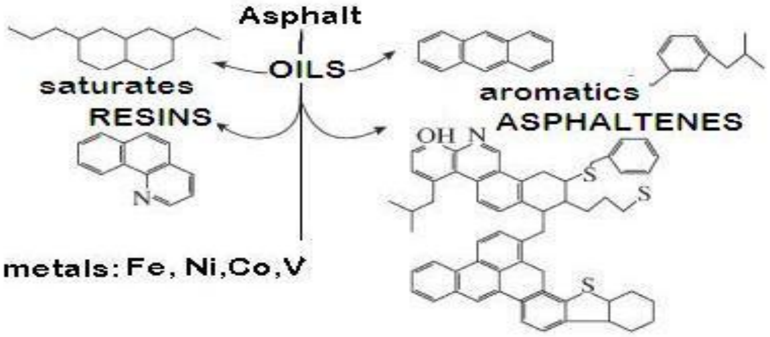

Figure 2.2: Asphalt components [18]

Cheung [19] consider pure bitumen as complex polymeric materials, whose molecular structure can be well explained with the help of colloidal model. The concentration and composition of asphaltene micelle and maltene has great influence on the mechanical behavior of the bitumen. It was being found that there exist two types of bitumen, the first type is similar to disperse system which is characterized by a coagulation structure and the second type resembles the polymer. The difference is because of the content of asphaltene, resinous substances and the nature of hydrocarbon medium [20].

2.2.1.1 Asphaltene

Asphaltenes are characterized as the most polar and most aromatic components in bitumen. Chemically they are defined as the *n*-heptane insoluble, while soluble in toluene. They are fractionated first by SARA from the bitumen through precipitation and filtration. The presence of asphaltene considerably affects the rheological behavior of bitumen. Depending upon the amount of asphaltene they are being characterized as *sol, gel or sol-gel*. It was being considered by Barth [21] that *sol-gel* type of bitumen has asphaltene ranging between 15 to 25%, which are being dispersed by the oily medium. The viscoelastic characteristics of *sol-gel* bitumen increases proportionally with increase in asphaltene micelle concentration and stabilizing phase of maltene. The asphaltene in the bitumen are mainly responsible for its pseudoplastic characteristics.

Rogel [22] consider asphaltenes as the fraction of a crude oil which are insoluble in low boiling alkanes such as n-pentane or n-heptane but shows solubility in toluene or benzene. He also reported that the composition of the asphaltene fraction is not totally understood till today but it is considered to be formed due to the association of polyaromatic sheets with substitutions of different functional groups and alkyl chains on the edges. It is very difficult to completely analyze asphaltene because of its chemical complexity, which is mainly composed of compounds of condensed aromatic structures with alkyl chains with heteroatoms (N, S, and O) & trace metals (e.g. V, Ni, and Fe) [23]. They are also considered as structure formed of high molecular weight hydrocarbon, which are aromatic in character with relatively low content of hydrogen, formed by the hydrogenation and condensation reaction of lower molecular weight aromatic–naphthenic hydrocarbon which has the traces of oxygen, sulfur and nitrogen [24].

Asphaltene get oxidized more readily as observed by Traxler [16], who reported that when bitumen was subjected to oxygen in closed system under atmospheric pressure at 204°C for about three hours, asphaltene get oxidized more readily than oils. The oxidized asphaltene contains approximately 96% carboids, which is insoluble in carbon disulfide. As asphaltene has more condensed aromatic rings and polar groups in comparison to other molecules in bitumen, they do get oxidized. They thus exists as condensed aromatic rings, where planer molecules or stacked sheets are held together by π-π bonding between them [1]. Because of their polar nature they mainly composed of C - C, C - H, C ≡ C (in the form of aromatic rings). Beside this they also exist in the form of porphyrin and non porphyrin structure like C - S, C - O, C - N, S - H and O - H [25].

The solubility parameter has greater effect on the dispersion property of asphaltene It was being observed by Rogel [22], who reported that solubility parameter of asphaltene decreases as the association of the molecules increases. He found that solubility parameter for monomer lies from 14 to 18 $\text{MPa}^{0.5}$ but reduces to 13-14 $\text{MPa}^{0.5}$ for trimer. The aggregation of micelle depends on solubility parameter of solvent, asphaltene content and temperature. Due to this aggregation of asphaltene micelle negative charge arises on the surface and thus asphaltene micelle behave like ions in solution. Because of its behavior as ion in the dispersed phase, it was reported by Petersen [26], that the adhesion of bitumen to aggregates is largely contributed to the presence of negative charge on asphaltene which initiate surface activity and causes the adhesion of bitumen to mineral aggregate.

It is very difficult to get the true concentration of asphaltene, as the asphaltene shows association to each other and to resin, thus initiating the formation of asphaltene micelle. According to Sheu *et al.*[27] the self association of asphaltene leads to the formation of colloids due to greater surface activity. Asphaltene thus exhibit the properties of colloidal system until critical micelle concentration was attained at which these micelle starts to aggregate or start forming floc. The choice of solvent used for the extraction also has important impact on the amount of asphaltene extracted. In most of the cases *n* heptane was used as solvent for precipitation. It was also observed that as the carbon number of extracting solvent increases, the amount of asphaltene obtained by precipitation decreases [25]. It was considered to occur as some of the asphaltene coassociate with resin, where resin get adsorb to asphaltene and form a multilayer structure on the surface of asphaltene [28].

Strausz *et al.* [29] reported that it is very difficult to get the exact amount of asphaltene after precipitation. In order to get correct amount of precipitated asphaltene it should be further extracted by acetone for one week. The asphaltene obtained after this procedure were consider to be pure asphaltene free from all foreign material.

Yousefi [30] reported that polyethylene when blended with bitumen at 160ºC in melt state absorb or adsorb lower molecular weight components of bitumen, which alters the composition of the bitumen, and hence the properties of the existing phase. This, in turn results in a relatively increase in asphaltene content and considered responsible for structural change of bitumen from *sol to gel.*

Thus it can be concluded that asphaltene are the major component of bitumen responsible for the colloidal structure of bitumen, particularly the concentration of asphaltene to maltenes. The physical, chemical, rheological and mechanical properties of the bitumen depend mainly on asphaltene concentration [5].

2.2.1.2 Saturates

Saturate consist of linear chain of n-alkanes which are aliphatic in nature with few polar atoms [1]. They are lightly coloured and easily drained out from the chromatographic column due to their non polar nature.

Lin *et al.* [31] in his study on interaction between asphaltene content and saturate for four different SHRP asphalt using Corbett's fractionate analysis concluded that saturates has significant affect on the viscosity impaired by the formation of asphaltene during oxidation. He reported that as the content of saturate increase with the increase in asphaltene level but a sharp increase in viscosity was observed due to decrease in solvating power of the dispersing phase that is maltene. Thus aggregation of asphaltene micelle was more for maltene phase having higher saturate content. In his another paper he reported that saturate only have function of dilution giving fluidity to the bitumen [32].

The solubility parameter for saturate lies between 15-17MPa [33]. In SHRP report prepared by Harrison [34] he reported that saturate has little or no effect on the thermal behavior of the bitumen. He concluded that crystallite content in saturate (consisting of linear paraffin molecule) are not properly linked thus wouldn't offer any mechanical property in practical application.

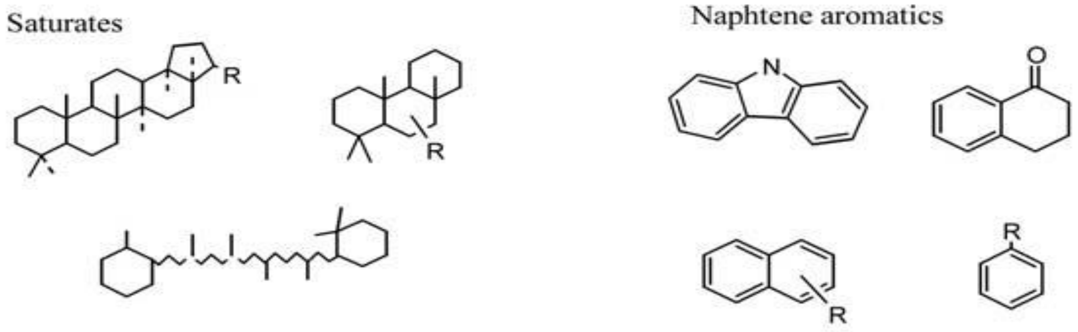

Figure 2.3: Structure of Saturate and Aromatic [35]

2.2.1.3 Aromatics

Aromatics consisting of condensed aromatic rings provide dispersing media for asphaltene. They are slightly polar in nature and provide mobility or acts as dispersing medium for asphaltene present in bitumen. Being slightly polar in nature they are vulnerable to change into resin upon oxidation. They are hydrocarbon having more than one aromatic nuclei which are connected to naphthenic ring or paraffinic side chains [25].

The presence of crystalline linear paraffinic side chain having napthene aromatic ring structure considered major source of crystallization in bitumen and thus would offer increase in hardness and shows better resistance to flow at higher temperature. Thus the adhesive property of aromatics is due to these cross linked chain in bitumen molecule [34].

Mohamad *et al.* [36] in his study on aggregation behavior of fraction in bitumen reported that formation of asphaltenes in bitumen is considered due to the presence of aromatic compounds having π-π interactions would undergo acid-base interactions and self-association through hydrogen bonding. It was also reported by Spiecker *et al.* [37] that solubility parameter of aromatics as nearer to asphaltene was due to low H/C ratio, the π-π bonding interaction and low nitrogen content, which helps in the aggregation of asphaltene resulting in the increases of asphaltene micelle concentration. Thus increase in asphaltene content would leads to ageing. It was also observed on the basis of chemical fractionate composition by Lesurer [1] that ageing starts with first decrease in aromatic content followed by an increase in resin content with the rise in asphaltene content. Lesurer concluded this after extensive literature review that resins is being generated by aromatics which end up with the increase in asphaltene due to conversion of resin to asphaltene.

2.2.1.4 Resins

Resins are semi solid fraction of bitumen which acts as stabilizer for asphaltene. Resin composed of polar aromatic rings with side chain. Yousefi [35] in his study on the bitumen rheology reported that resins constitute of molecules present in polycyclic compounds which can be either saturated, aromatic or heterocyclic (sulfur, nitrogen and oxygen). It may contain some functional groups also like carboxylic and phenolic acids and nitrogen bases. The chemical structure of resins resembles asphaltenes but differ in their molecular weight. Resin are considered responsible for the increase in asphaltene content during ageing process, in which polycyclic compounds of resins undergo polycondensation reactions to form asphaltenes.

Ruan *et al.* [38] in his study reported that resins are mainly responsible for ductility and dispersion of asphaltene in the blend. In view of the colloidal model presented by Traxler [16], the rheology of the bitumen is governed by amount of resin which helps in keeping asphaltene fraction dispersed in maltene. Thus the peptizing effect of resin define it as *sol* type of bitumen exhibiting Newtonian behavior of *gel* type showing non Newtonian behavior or *sol-gel* type of bitumen. It was thus found that resin act as stabilizer for asphaltene. Although the mechanism of stabilization was not clear yet but it has been suggested that the resins get attached to the asphaltenes by providing stabilization, preventing asphaltenes from flocculation. It was also observed that resin get adsorb to asphaltene surface by forming multilayer structure [28].

2.3 Thermoplastic Polymer

Elastomeric modified binders are more common in pavement industry as approximately 75% of the modified binders used by the industry are classified as elastomeric, 15% as plastomeric while the remaining 10% considered either rubber or miscellaneously modified binder [39].

Thermoplastic polymers are characterized as polymer which becomes soft on heating and harden on cooling. They usually come to their original form after cooling and their properties remain unchanged after being reformed. Thermoplastics can be further classified as plastomers and elastomers.

Thermoplastics are basically composed of polyolefins or copolymers of ethylene mainly composed of long chains of covalently bonded carbon atom. Polyolefins includes polyethylene, polypropylene, high density polyethylene (HDPE) and low density polyethylene (LDPE) and linear low density polyethylene (LLDPE). Copolymer of ethylene includes ethyl-vinyl-acetate (EVA) ethyl-methacrylate (EMA) etc. Polyethylene is the most extensively used thermoplastic due to availability of its monomer ethylene, from gas and crude oil [40]. These polymers when blended with bitumen sufficiently enhances the viscosity and stiffness of the bitumen at ambient temperature [41]. Although the plastomers being widely used by the pavement industry the problem of phase segregation upon cooling remains there. Beside this it does not sufficiently enhance the elastic property of modified bitumen [13].

Polacoo *et al* .[42] reported that beside the type of the polymer used, concentration has great impact on the properties of modified bitumen. He concluded that concentration of polymer in bitumen is usually kept between 4 - 6% by weight of bitumen as higher percentage of polymer are considered uneconomical and also becomes a source of material related problems. He also reported that plastomers whenever used as modifier improves the stiffness of the binder and thus would help in reducing load related deformation. Thus increase in stiffness can be related to the modified rheological properties of the binder as being reported by Cristina Fuentes *et al*. [43] who concluded that when recycled polyethylene (RPE) was used as modifier for bitumen shows remarkable improvement in the rheological parameters. RPE when used in low concentration (0 - 5% wt.) increases the storage and loss moduli besides increasing the viscosity. Modification with RPE also enhances the mechanical properties thus impart higher resistance to permanent deformation, thermal and fatigue cracking. These changes were observed due to swelling of polymer by maltenic compounds which alter the microstructure of the modified binder. Heat flow curves for different binder concentration when plotted against varying temperature shows that at 135°C, when polymer concentration exceeds 5% *gel* like characteristics becomes prominent. Thus it was concluded by him that for road paving application lower polymer concentration less than 5% can be beneficial.

The rigid polymer network formation property was also reported by Xiao [44] in his thesis. He reported that plastomers resist deformation of the pavement by their tough and rigid three-dimensional network. The modified bitumen exhibit quick early strength on loading but they are vulnerable to fracture under strain. He concluded that when plastomers are blended with bitumen, the modified binders usually improve the stiffness modulus of HMA pavement. This behavior of polymer by showing high rigidity would thus help in resisting deformation as mentioned by Polacco *et al.* [45] when he used polyolefinic plastomers as modifier. The lower cost and ease in availability makes it more attractive modifier for pavement industry. The two main types of plastomer namely polypropylene PP and polyethylene PE are most commonly used by pavement industry. The high crystalline structure of polyethylene (PP, PE) acts as a barrier prohibiting the interaction of polymer with bitumen. The mixing of polymer at higher temperature greater than melting temperature of PE partially breaks the polymer domains by the applied shear. This partial breakage of polymer is considered responsible for enhanced mechanical properties of modified bitumen as on cooling the interaction of these domains with bitumen would not reverse. Although the interactions offered by plastomeric modified bitumen like polyethylene (PE), ethylene – vinyl acetate (EVA) or ethylene butyl acrylate (EBA) was just physical interaction depending on the structure of particular polymer but sufficient enough to impart rigidity and stiffness to the binder [9]

The addition of waste plastics (which is mainly composed of polyethylene) in bitumen for modification is thus considered as an economical and environmental friendly method where desired properties of modified binder can be attained at cheaper cost [46].

Thus from the above literature review it can be concluded that plastomers are recognized by showing their early strength when stressed but are less flexible than elastomers. The rate of deformation for plastomers is slower than elastomers. The high crystalline structure of plastomer increases the viscosity and also gives them rigidity because of the formation of three dimensional networks. Thus the crystalline network although less flexible but may help in resisting crack propagation when used as modifier for bitumen. Under stress when the molecules of polymers are stretched, more molecules will unfold and start to align, forming areas of crystallinity. With the increase in strain these molecules slide past each other by breaking and reforming weak bonds. Thus with the increase in crystalline structure due to cross linking and rearrangement of these molecules they induces high viscosity in the polymer bitumen blend. Thus the high tensile strength of polymer, due to higher degree of cross linked crystalline structure considered responsible for higher tensile strength and lower elastic property of modified binder. Due to this plastic property of polymer it may help in inhibiting crack propagation in modified pavement. In short the properties of thermoplastic modified bitumen depend on the structure of thermoplastic, which are mainly composed of linear or branched molecule. This structure enable the polymer chains enough freedom of movement to change their form according to variation of temperature [47].

Othman [48] in his thesis on the evaluation of fatigue crack growth behavior in polymer modified asphaltic concrete mixtures, reported that elastomers and plastomer both have its unique property depending on the chemical structure. The elastomers which are derived from diene (two cabon double bond) chemical structure will give toughness to the asphalt and improve its low temperature properties. On the other hand plastomers which are derived from non-diene chemicals improve the high temperature viscoelastic properties of soft grade asphalt and show good low temperature properties.

2.3.1 Linear low density polyethylene (LLDPE)

LLDPE is produced by the copolymerization of ethylene with different alpha olefins like butane or octane in the presence of suitable catalyst. They have less long chain branching than low density polyethylene. The crystalline structure of LLDPE make it rigid and strong [40]. LLDPE has higher tensile strength and impact resistance than LDPE. It has low viscosity at all strain rates during extrusion. This property of LLDPE is due to its short chain branching which slide past each other without entanglement when sheared.

Yousefi [49] used different blends of PE (LDPE, LLDPE and HDPE) with rubber and came to conclusion that polyethylene(PE) alone without rubber modifier show some difficulties as a bitumen modifier because of its extensive phase separation under inactive condition when not being continuously agitated. It failed to offer its desired properties in order to improve low temperature properties of modified binder. These PE blends properties alone also failed to improve the fatigue properties of modified binder because of its inert behavior in the bitumen. The state of dispersion of PE also depends on the crystalline structure of PE which prohibits PE swelling of polymer in bitumen. He also reported that as melt flow index (MFI) for PE increases (i.e., molecular weight decreases) the affinity of the PE towards bitumen constituents increases. This in turn results in an increase in swelling ratio of PE particles. Lower concentration of LLDPE can produce same improvement in the properties of bitumen as produced by HDPE and LDPE.

2.3.2 Polypropylene

Polypropylene polymer belongs to thermoplastic consist of linear chain of ethylene $(CH_2)_n$ with methyl group (CH_3) present after every repeat unit. Commercially produced polypropylene is manufactured using Ziegler Natta catalysis process are isotactic polypropylene. Isotactic polypropylene is recognized by placement of side group (R) along one side of the chain.

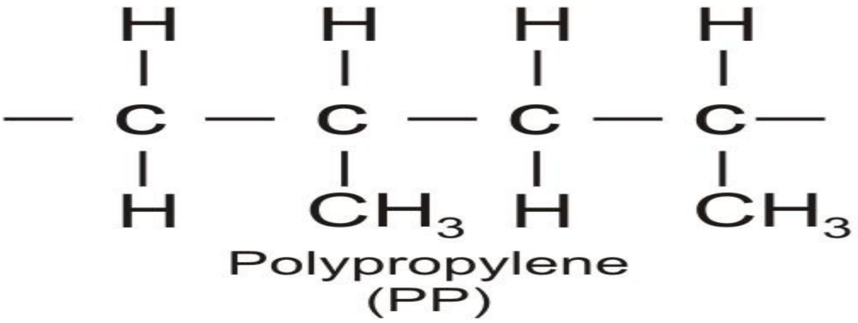

Figure 2.4: Polypropylene [47]

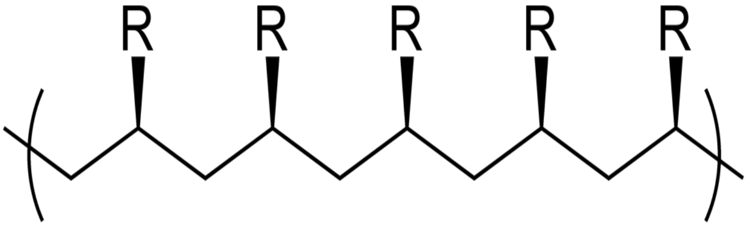

Figure 2.5: Isotactic Polypropylene [47]

The presence of methyl group as shown in Figure 2.4 in the long chain of PP restricts it rotation and thus responsible for less flexible but stronger polymer [47].

Crystallinity in isotactic polypropylene is due to the presence of methyl group which is present on only one side of chain. The macromolecules of the isotactic polypropylene used to form helical shape which aligns these macromolecules in a shape which made them to appear as regularly stacked layer of lamella sheets. The pendent group in isotactic polypropylene is responsible for its helical shape. The molecules are thus held together in their position due to presence of van der Waals forces between them [47]. The crystalline structure of commercially produced polypropylene due to regular arrangement of these side groups makes it tough and flexible. The helical arrangement of the macromolecules thus helps in accommodating large stresses due to slide past of these chains [50].

Yousefi [30] reported that PP when blended with bitumen the solubility parameter of PP which is very close to the solubility parameter of asphalts helps in compatibility. He reported that the amount of propene in polyethylene leads to the formation of longer polypropylene chain. These long chain segments of polypropylene are thus considered responsible for higher compatibility of polymer to asphalt with an increase absorption by polymer particles.

Isotactic polypropylene is considered as a suitable modifier for bitumen because of its crystalline network which consider responsible to inhibit crack propagation when used as bitumen modifier.

Polacco *et al.* [45] reported that Polyethylene (PE) and polypropylene (PP) are immiscible in bitumen to certain extent due to their non polar nature. Because of this non polar nature of plastomer the interfacial tension would be high. It shows little affinity towards water because of its non polar nature.

Among plastomer, polypropylene is consider brittle but due to their plastic property achieved by crystalline network gave them the ability to resist crack propagation systems when used as modifier for bitumen.

2.4 Interaction between Polymer and Bitumen (Compatibility)

According to Isacsson [51] compatibility is defined as “state of dispersion between two dissimilar component” which is governed by bitumen composition, polymer characteristics, polymer content and mixing process. Complete compatibility is difficult to achieve and if though occur it will tremendously increases the viscosity of the blend offering minimum increment in the mechanical properties of the modified bitumen.

Plastomers from thermoplastic group shows little compatibility with the bitumen whether blended at higher temperature or at high shear rate. Difference in densities would be considered as one of the main factor which is responsible for immiscible blend which end up with the phase segregation at storage or even when stirring was discontinued. Compatibility is thus considered as physical and chemical phenomenon which results in the formation of phase segregation. It is thus considered due to higher molecular weight of polymer which increases the viscosity of the polymer modified blend tremendously inducing creaming effect to the blend.

Newman [52] reported that the difference between densities between polymer and bitumen were responsible for incompatibility. This incompatibility between polymer and bitumen leads to the phase segregation which occurs at macro scale with polymer floating at the top of bitumen. Thus the network formation due to this was considered as only due to entanglement of polymer chain that results from physical crosslink as observed by scanned TEM images or by fluorescence microscopy. Although polymer does absorb the aromatic components of the base bitumen and do swell up but unable to form homogenous phase. It always composed of polymer rich phase which occupies 4 - 10 times the volume of the added polymer especially in case of SBS and EVA. For polyethylene modified bitumen, as polyolefin shows lower swelling potential, it occupies less polymer rich phase. Because of this behavior and its partial miscibility and it is very difficult to define the compatibility[1].

Difference in densities between polymer and bitumen leading to creaming is considered as one of the main cause of incompatibility. Beside this coalescence of polymer particles within blend due to molecular diffusion also initiate phase segregation leading to the incompatibility of polymer bitumen blend. This phenomenon becomes more prominent at higher polymer concentration. High melt flow index of polymer also inhibit the production of compatible polymer bitumen blend. The impact of chemical composition on the compatibility of the blend cannot be overlooked as higher asphaltene content leads to incompatible blend. Presence of appropriate aromaticity of the maltenes leads to the compatible blend.[1].

The compatibility for polyethylene was considered only as physical one as also observed by Polacco *et al.* [45] who reported that Polyethylene (PE) and polypropylene (PP) are immiscible due to their non polar nature. The modification of bitumen considered occurs due to the formation of physical network while blending of polymer with bitumen at temperature greater than melting temperature of PE. The swelling of the polymer to a lesser extent is due to absorption of oily content from the bitumen. The compatibility between polymer and bitumen has critical affect on the properties of the modified blend. The difference in molecular weight, polarity and structure of base bitumen and polymer also has critical impact on the compatibility which ultimately leads to the phase segregation which is one of the causes of poor compatibility [51].

Wekumbura *et al.* [53] discussed the changes in the internal structure of the bitumen and concluded that neat bitumen which posses three dimensional association due to interaction between polar molecules which are dispersed in a solution of non polar molecules. The viscoelastic characteristic of the unmodified bitumen is due to the formation and breakdown of this network due to external stresses and changes in temperature. For polymer modified bitumen the network formation is depend on the type of polymer used for modification, concentration and also on the bitumen composition. On the basis of this he concluded that either there is a formation of asphalt rich phase in which polymer is homogenously dispersed in it or polymer rich phase in which asphalt globules are dispersed in it. He concluded that for SBS modified bitumen the polymer absorb oil from the maltene fraction and swells up. The swollen polymer thus form polymer rich phase with these swollen strands of polymer being connected to each other at domains forming three dimensional network which considered responsible for the mechanical strength for polymer modified bitumen.

The amount of aromatics and asphaltene also has significant affect on the compatibility of the blend. Lower aromatic and higher asphaltene content leads to poor compatibility of the blend [51].

Newman [52] reported that most of the polymer failed to form polymer network as they do not reach thermodynamic compatibility and shows phase segregation, a polymer rich phase and bitumen rich phase. He also reported that because of difference in densities phase separation occurs at macro scale leading to complete phase segregation of polymer and bitumen.

Garcı´a *et al.* [10] used modulated differential scanning calorimtry to analyze thermal transition events for different blends of polyethylene (EVA and LDPE). He came to the conclusion that after modification with bitumen change in thermal peak representing melting point of polymer was observed. He considered this change in melting point of polymer occurred due to absorption of some lighter component of bitumen by polymer and changes the crysrtalline fraction of polymer. From this observation he finally concluded that better compatibility can only be achieved when polymer is blended with bitumen, where maltenic fraction of bitumen penetrate into polymer domain resulting in change of cryatalline phase of bitumen.

The compatibility between polymer and bitumen besides being present in all polymer modified blend where there is only physical interaction between polymer and bitumen, polymer do impart some of its properties which considered responsible for the altered favorable rheological properties regardless of incompatibility to certain extent.

2.5 Rheology of Polymer - Bitumen Blend

Behavior of bitumen describe in terms of rheology depend on the applied load and rate of shearing. Temperature is also considered as an important factor in describing the viscoelastic nature of the bitumen.

Strategic highway research program has introduced the characterization of the bituminous material based on rheological testing. The complex modulus (G*) was used to characterize the bituminous binder at different temperature according to specification ASSHTO TP5, 1998 [54].

Cebon 2000 [55] reported that Van der Poel (1954) was the first who introduced the concept of stiffness to describe the mechanical behavior of pure bitumen as function of temperature and loading time. His stiffness concept has disadvantage that the distinction between elastic and inelastic part of the total deformation was not clearly defined.

Van der Poel further extended his model in 1955 by including volume fraction of aggregate beside stiffness of bitumen while considering stiffness of the mix.

According to Mturi [56] bitumen are 20 times more temperature susceptible than any polymeric material. This temperature dependency of material makes its rheological study more important under changing temperature and loading condition. When the deformation and flow behavior of the bitumen was discussed in terms of viscosity, the behavior of bitumen making it Newtonian or non-Newtonian characteristics depends on the composition and source of the crude. Thus viscosity behavior affects its rheological behavior which undergoes remarkable change when being modified with polymer.

Unfortunately standard rheological test for paving grade bitumen such as penetration softening point test when used for polymer modified bitumen failed to give correct rheological properties of the polymer modified binder. It was reported by Oliver and Dickinson [57] that it is difficult to interpret the results of polymer modified bitumen when empirical test methods being used. The difficulty arises as this material is new for which there is a need of new tests which can appropriately handle the fundamental and rheological behavior of the modified binder. This was also previously reported by Isacsson and Lu [41] who found that traditional standardized test methods for road grade bitumen failed to provide a valid description of the improved polymer modified bituminous properties especially in terms of their elastic and tensile properties.

Zaman [58] when conducted his study on the rheological behavior of rubber modified binder, reported that viscosity of modified binders are highly shear rate dependent. They exhibit shear thinning behavior at lower shear rate and shear thickening behavior at higher shear rate. At very low shear rate Newtonian behavior was observed till the viscosity reaches the value of zero shear viscosity but at higher shear rate viscosity highly become shear rate dependent. For polymer modified binder shear stress and shear rate are not linearly related thus exhibit non-Newtonian behavior.

The viscosity behavior of polymer modified blend was further explained by Lu [59] in his study, where he has used SBS modified binder to study the viscosity of the modified binder. He concluded that viscosity of the modified binder was not directly proportional to the polymer content. A drastic increase in viscosity was observed when the concentration of polymer was increased from 3% to 6%. Shear rate dependent behavior was observed for base bitumen and up to 3% SBS modified bitumen while shear thinning behavior was observed for 6 to 9% SBS modified bitumen. He thus concluded that higher the binder modification, the greater would be deviation from Newtonian behavior. Loading and temperature also affect the behavior describing the viscoelastic properties of the material. The internal structure of the base bitumen also play key role. Thus for polymer modified bitumen the non Newtonian behavior of material is because of dependence of viscosity on shear rate and internal structure of bitumen after modification [60].

Bhattacharya [61] in his book on polymer rheology, consider the mixed behavior of the polymeric solution exhibiting the decrease in viscosity with increase in shear rate and again increase in viscosity does not truly represent non-Newtonian behavior but it represent thixotropic effect. The thixotropic behavior of modified bituminous material may be due to reversible breakdown of structure which is commonly found in multiphase system of polymer modified bitumen.

Maharaj [62] reported that rheology is the particular field of science that is used to describe the mechanical properties of different materials under various deformation conditions when they are forced to flow and accumulate recoverable deformation under stress. He also reported that the bulk modulus obtained from the rheological measurement using DSR is an effective way of representing viscoelastic characteristic of the material. Bulk modulus G^* represent stiffness of the material the while phase angle (δ) represent the viscoelastic component of the bituminous material. Higher values of phase angle represent viscous behavior of material while lower values indicate more elastic response. The elastic behavior identified by lower phase angle is offered by material having high stiffness with increased brittleness. The viscous response represented by higher phase angle reflects high ductility and low stiffness. On the basis of this Maharaj concluded that these parameters are helpful in understanding mechanical properties of binder expressed in viscoelastic manner. Blends with relatively lower bulk modulus G* or stiffness and higher phase angles δ are more ductile and flexible resulting behaving as more crack resistant material while the blends with relatively higher value of bulk modulus G* and lower phase angles δ are more elastic and deformation resistant.

Widyatmoko [63] also reported that bitumen rheology can be well explained in terms of two main viscoelastic parameters, namely complex modulus G* and phase angle(δ) which changes with temperature and loading time. Complex modulus represents stiffness, while the viscoelastic characteristic of material is defined by phase angle. A higher value of phase angle indicates more viscous behavior, while lower values indicate more elastic response. He concluded these remarks from the results obtained after modification of bitumen Trindid Lake Asphalt (TLA) and Uintaite with elastomeric and plastomeric modifier. He also concluded that when polymer modified bitumen was used with Trindad Lake asphalt shows improved mechanical properties both at low and high temperature. At lower temperature lower values of complex modulus G* and higher phase angle (δ) represent the ductile and flexible behavior of binder which would be helpful in inhibiting crack propagation. While at higher temperature higher value of complex modulus G* and lower phase angle (δ) reflects an increase in elastic component which would be helpful in resisting deformation or rutting. The chemical structure of the bitumen also helps in explaining the rheological behavior It was being reported by Huang [64] that presence of asphaltene was a major contributing factor in viscosity of the binder. The molecular weight of the asphaltene affects the viscosity leading to non Newtonian behavior. He also studied the effect of shear rate and concluded that shear rate has great influence on the flow behavior of the binder. At low shear rate bitumen behave as Newtonian material and the applied energy is being dissipated by the viscous deformation. At high shearing rate or stresses the non Newtonian and elastic effect becomes dominant observed by change in flow properties which occurred due to breakdown of internal structure of the molecules of the binder. For polymer modified bitumen when they are being sheared the entangled chain of polymer are responsible for the change in flow behavior of the binder. During shearing action or when being stressed, these chains untangle themselves offering minimum resistance to flow. Thus the viscoelastic characteristic of bitumen and polymer modified bitumen depends on the colloidal model which is considered responsible for the formation of elastic network or partially recoverable network.

The influence of the elastic network formation was also reported by Airey [65] who concluded that as bituminous material are viscoelastic in nature thus its characterization is advisable to be confined only to its linear viscoelastic response (small strains) to simplify the mathematical modeling of the material. He concluded that for viscoelastic material defined by complex modulus, phase angle, storage modulus and loss modulus can be well defined under linear viscoelastic (LVE) range. Within this range the rheological measurement the relationship between stress and strain being made is influenced by the temperature and loading time (frequency) and not by the magnitude of the stress or strain.

Although the bitumen is considered as thermorheologically simple material [6] but its whose rheology depends on temperature. The behavior of bitumen because of its temperature sensitivity becomes more complex especially for polymer modified bitumen. Bitumen to be used as binder for road application it must offer adequate viscoelastic response. This could be achieved by acquiring specific feature of binder like viscosity, flexibility, resistance against permanent deformation and cracking, stability and adhesion [5].

Chen *et al*. [66] studied the behavior of styrene- butadiene- styrene copolymer bituminous blend and reported that complex modulus is sensitive to the concentration of polymer in the blend. Increasing polymer content leads to an increase in complex modulus. He related the increase in complex modulus to the formation of polymer network in bitumen. He also reported that the phase angle (tanδ) for polymer modified binder does not increase significantly as observed for pure bitumen at temperature above 30°C. This might have occurred due to the formation of elastic network in SBS modified bitumen. Thus the critical network formed at particular concentration of polymer in bitumen significantly enhances the complex modulus, softening point temperature and toughness of the modified binder.

2.6 Chemical Characterization of Binder

2.6.1 Compositional Measurement

Compositional measurement plays a vital role in understanding the rheology of the binder which depends on composition of binder. Compositional information would give an insight about the behavior of each constituent of the bitumen and the elements which are responsible for its behavior. It can also be used for compatibility of bitumen with polymer so that a compatible binder aggregate system can be developed which would produce a durable long term serviceable mix.

Asphaltene is the most extensively studied component of bitumen which acts as building block controlling the physical and chemical characteristic of binder.

Asphaltene are defined as insoluble component of bitumen in paraffinic solvents (*n* heptanes and *n* pentane) but soluble in aromatic solvent (toluene) [25]. Various techniques were used to know the amount of asphaltene in bitumen of which *n* heptane precipitation method using ASTM D 3279 is the considered as most efficient technique employed to detect the amount of asphaltene in bitumen. The asphaltene obtained from this method are known as C_7 asphaltenes. The amount of asphaltene in bitumen varies from 5% - 25% depending upon crude source. Asphaltene have H/C=1.58 and contains around 14.8 wt% oxygen [1].

Oyekunle [67] reported that the amount of the asphaltene precipitated out from the bitumen depend on the solubility parameter of solvent used. Thus the strength of solvent has key impact on the recovery of asphaltene form the bitumen. He also concluded that asphaltenes in bitumen basically composed of highly polar agglomerated molecules and considered as building block for all structure present in bitumen. The determination of correct amount of asphaltene is important as it has significant effect on the colloidal Index of the bitumen where asphaltene are considered as dominating factor describing the *sol- gel* or *sol* or *gel* behavior of bitumen. It was also found that the amount of asphaltene present in bitumen affects the colloidal stability of the bitumen. In calculating the colloidal instability index "I_c" of the bitumen the important governing factor is asphaltene, where asphaltene were dispersed in dispersing phase. Thus asphaltenes were considered mainly responsible for the viscosity and the colloidal behavior of the blend.[68].

It was also noted by Lesueur [1] that the formation of *sol* type of bitumen occurs when asphaltene were well dispersed among maltene phase. Beside the asphaltene content, other constituent also have the significant on the rheology of the bitumen.

The most commonly used technique SARA also known as Corbett's liquid chromatography procedure as outlined in ASTM D 4124 is widely used standard procedure to fractionate bitumen in to four fractions namely asphaltene, saturate, aromatics and resins (SARA) [1]. The study of SARA fractionate analysis thus provides an insight into the roles that each fraction plays in determining the physical and chemical properties of binder. The interaction between these fractions affects the rheological and morphological properties of binder which ultimately reflected in mechanical properties. It was also reported by Airey [39] in one of his study on the rheological properties of SBS, that study of SARA is helpful in determining the colloidal Index (CI) of the bitumen calculated on the basis of the fractionate composition obtained from SARA analysis. He concluded that thus CI indicates the potential compatibility of bitumen to polymer which in the end affects the rheological behavior of the polymer bitumen blend.

2.6.2 Analytical Measurement

Analytical measurement is widely used in field of organic chemistry. For the analysis of bitumen it was used to provide evidence of compound detected by compositional analysis namely SARA and detection of asphaltene using *n* heptane precipitation method.

Carbon, Hydrogen, Nitrogen and Sulfur (CHNS) analyzer is quick method to detect the elemental composition in bitumen. These elements also known as heteroatom are mainly responsible for the formation of functional groups in bitumen and polymer modified bitumen [25].

Lesueur [1] reported that elemental composition of bitumen mainly depend on crude source and origin. Bitumen mainly consist of 80 - 88 wt% carbon while the remaining composed of hydrogen (8-12 wt %). Bitumen also consists of heteroatoms such as sulphur, nitrogen and oxygen beside the traces of metals like vanadium and nickel. He also reported that sulfur is the most polar atom which appears in the form of sulfides, thiols and sulfoxides (refer Figure 2.6). Oxygen is most commonly occurring as ketones, phenols and as carboxylic acid to a lesser extent while nitrogen is present in the form of pyrrolic and as pyridinic structures. Presences of metals are detected as metalloporphyrins.

Widyatmokyo [63] reported that bitumen with higher percentage of nitrogen content gives better adhesion between binder and aggregate, thus improving stripping and oxidation resistance in the bituminous mix.

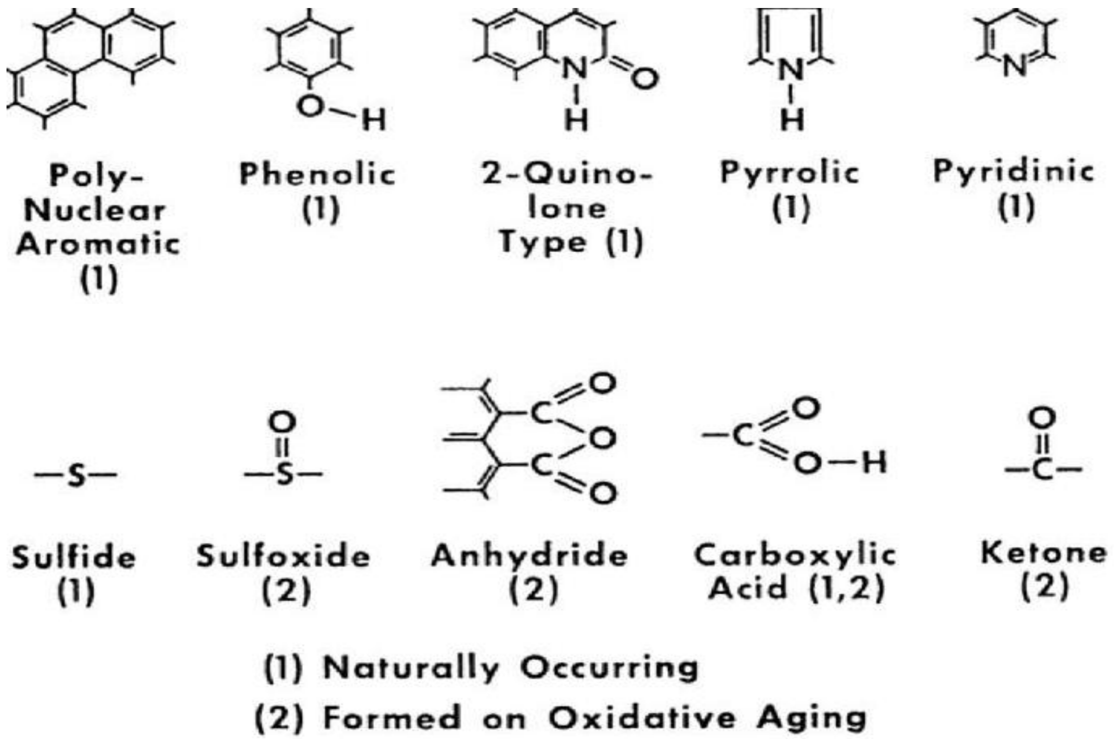

Figure 2.6: Functional groups present in bitumen [1]

From all the heteroatoms sulfur was found to be most polar atom present in bitumen It exists in crude oil in the form of elemental sulfur and hydrogen sulfide (H_2S). Sulfur is considered responsible for initiating oxidation in bitumen [23]. In bitumen it is present in the form of sulfides, thiols and sulfoxides [1]. Presence of sulfur indicates formation of S=O group, which usually get detected by FTIR at absorbance peak around $1030 cm^{-1}$. Since bitumen mainly composed of hydrocarbon but the small percentage of these elements affect the chemical composition of the bitumen and thus also its rheological behavior [16].

Chemical composition of bitumen also affects the physical properties of the binder. Physical properties commonly represented by the consistency commonly represented by viscosity or the penetration grade of the bitumen. A closer look at these physical properties discloses that it is highly dependent on the functional groups present in the bitumen making it polar or non polar. Functional groups which are represented by the presence of heteroatoms like nitrogen, oxygen, sulfur and oxygen beside vanadium, nickel etc are considered responsible for the development of dipole movement. Thus due to the existence of these charged electrochemical behavior of bitumen it shows affinity towards aggregate to form durable mix or get oxidized in the environment initiating the ageing of bitumen. The major cause of agglomeration of bitumen due to variation in asphaltene content also dependent also indirectly depend on the on the presence of these functional groups in the bitumen [1].

Thus Fourier Transform Infrared Spectroscopy (FTIR) in this respect is widely used as tool to detect the presence of heteroatom which is considered responsible for the formation of functional groups in the bitumen. The functional groups are detected using FTIR Spectrometer in the attenuated total reflectance (ATR) mode with zinc selenide prism, used to measure infrared spectra. In ATR technique the sample surface was brought into contact with prism. If the material of sample has infrared absorber compound the total reflection is attenuated in the absorbance frequency regions [69].

Hunter [70] in his book reported that hardening which occur during in service life of the pavement can occur either due to oxidation of binder (loss of hydrogen or gain of oxygen) or volatilization (loss of lighter component) or due to thixotropy (due to change in binder viscous property) or due to polymerization. He also discussed the oxidation process of bituminous material during manufacturing. According to him the rate of oxidation at mixing facility especially at high rate of mixing is practically unavoidable where bitumen is exposed to high volume of oxygen in air at high mixing temperature. He considers that oxidation process of hydrocarbon compound with oxygen can either resulted in a direct union of oxygen with these compounds or with the gain of oxygen or loss of hydrogen. He quoted three reactions (Abraham’s reactions) which commonly can occur during oxidation can be presented as

$$C_xH_y + O \rightarrow C_xH_yO \qquad 2.1$$

$$C_xH_y + O \rightarrow CxHy_{-2} + H_2O \qquad 2.2$$

$$C_xH_y + 2O \rightarrow C_{x-1}H_y + CO_2 \qquad 2.3$$

The first reaction commonly occurs at the exposed surface of the pavement in the presence of ultraviolet rays. It forms a hardened protective outer skin which slowdowns the rate of oxidation of the pavement if not being abraded or washed off.

The oxidation of binder during mixing of polymer and bitumen thus considered as of the main cause of hardening of bitumen, responsible for the deterioration of mechanical properties of the modified binder. The prolong stirring at high temperature brings changes in the chemical composition of binder. This change was considered due to transformation of aromatics to resin and resin to asphaltene also commonly known as primary ageing [6]. In order to determine the functional groups found due to oxidation FTIR is reported as most suitable tool [18]. According to him the change in chemical functionality helps in understanding the extent of intermolecular association which would lead to aging or stripping. The oxidation of bitumen leads to the formation of asphaltene. Increase in asphaltene would alter the behavior of asphalt from *sol* to *gel*. The change in concentration of asphaltene in bitumen might lead to aggregation or phase separation due to agglomeration of these asphaltene. These agglomeration will eventually leads to the hardening which occurs due to oxidation of binder because of the formation of functional groups. According to Petersen [71], the formation of polar groups indicates hardening of binder. These groups mainly composed of polar oxygen resulted due to intermolecular attractive forces, which eventually resulted in the increase of binder viscosity.

Liu *et al.*[72] reported that oxygen content in the binder linearly correlates with the carbonyl content. The carbonyl content can be determined by using FTIR by looking at the absorbance band within wave number from 1820 to 1650 cm^{-1}.The products of oxidation were identified as ketones, carboylic acid and anhydrides. Carboxylic acid present in the bitumen accumulates particularly in the polar fractions or in the resin [73]. Formation of these groups was due to the relationship existing between oxygen, carbonyl and asphaltene content in bitumen. The functional groups observed during IR spectroscopy were presented in Table 2.1.

Table 2.1: FTIR spectrum absorption band for Virgin and Modified bitumen

Wave number (cm^{-1})	Main absorption band
1000 – 600	Finger print region
1060-1030	ν S=O, sulfoxides
1650- 1350	ν C=C, CH_2 presence of aromatics rings
1870- 1650	ν C=O, carbonyl compounds, unsaturated aldehydes or ketones
2400- 2000	C≡N stretch in aliphatic nitriles
2850	ν C-H (CH_2) methylene, C-H stretch in alkane
2920	ν C-H (CH_3), methyl stretch in C-CH_3 compound

"ν" Stretching mode of vibration [74]

It was being reported by Daranga [75] that rate of oxidation of asphaltene decreases with the addition of polymer in bitumen. This finding is consider to be useful as phase segregated polymer layer act as sheath covering the underneath bitumen layer retarding the oxidation of binder due to exposure to ultraviolet rays and moisture, but the compositional changes that occur due to oxidation during mixing at plant or at site gave rise to formation of functional group which were consider being responsible for the change in physical properties of the material [76], which leads to the hardening of binder due to the formation of polar groups. These groups mainly composed of polar oxygen resulted due to intermolecular attractive forces, which eventually resulted in the increase of binder viscosity [71]. These groups mainly composed of polar oxygen resulted due to intermolecular attractive forces, which eventually resulted in the increase of binder viscosity.

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The formation of carbonyl group is linked due to increase in polarity of bitumen which induces the formation of intermolecular hydrogen link. It was reported by Guern *et al.* [77] that the increase in C_7 asphaltene (from *n*- heptanes precipitation method) can be considered due to bitumen oxidation during mixing at plant. This results in the formation of carbonyl group due to increase in polarity of bitumen which induces the formation of intermolecular hydrogen link. The presence of carbonyl area CA (area under the absorbance band of FTIR from 1650 to 1820 cm^{-1}) can also be used as an indicator of oxidation. CA represents the byproducts of oxidation namely ketones, carboxylic acid and anhydrides. The presence of C = O in compounds can be related to viscosity hardening or to the oxidation [38].

Huang [78] studied the infrared spectra to relate it to the ageing properties of bitumen brought by change in chemical composition. He used to report the peak height with the specific wave number for each particular compound. The presence of carbonyl compound was recognized in the region of absorbance band width of 1680 cm^{-1} to 1720 cm^{-1}. Methyl group was recognized in the band from 1370cm^{-1} to 1380cm^{-1}. Sulfoxide was measured in band between 1020 cm^{-1} to 1050cm^{-1}. He concluded that increase in carbonyl content was due to oxidation at mixing. Mixing at higher temperature would increase oxidation rate which may dissociate the aromatic compounds present in bitumen, resulted in enhanced viscosity due to aging of binder. The reliability of FTIR results were confirmed by Lamontagne *et al.* [79] reported that FTIR provides quickly and reliable information regarding aliphaticity, aromaticity and oxygenation rate in the compound. It also gives accurate data on the average distribution aliphatic chains, oxygenation and aromatization of the naphthenic compounds. The usefulness of FTIR in investigating the affect of the formation of polar groups was reported by Hefer [80] in his thesis who reported that Western Research Institute (WRI) in Wyoming used FTIR in ATR mode to investigate the role of polar groups on the formation of interphase layer between bitumen and aggregate. It was found that carboxylic acids moves towards the bitumen aggregate interface surface with time affecting the bonding between aggregate and bitumen.

Gas Chromatography/Mass Spectrometry (GC/MS) is another analytical technique which is used as conformational tool to identify all the compounds which were detected during FTIR analysis. GC/MS is thus considered as powerful tool as it helps in the identification of known or unknown molecule.

Ritchie *et al.* [81] reported that GC/MS is commonly employed analytical technique which can reveal the composition of bitumen using the pyrolysis technique where highly sensitive probe detect the volatile compound present in bitumen. The detected compounds were presented in the form of chromatograph, where retention time depends on mass of molecules and their polarity. Gasthauer *et al.* [82] reported that for bitumen the maximum compound obtained does include linear long chains of saturated hydrocarbons having alkynes from C_{13} to C_{22} or unsaturated and oxidized compounds like C_{12} to C_{15}. Beside these aromatic compounds like mono, bi or tri-cyclic aromatic compounds and sulphur compound like thiophenic were also observed as shown in Figure 2.7.

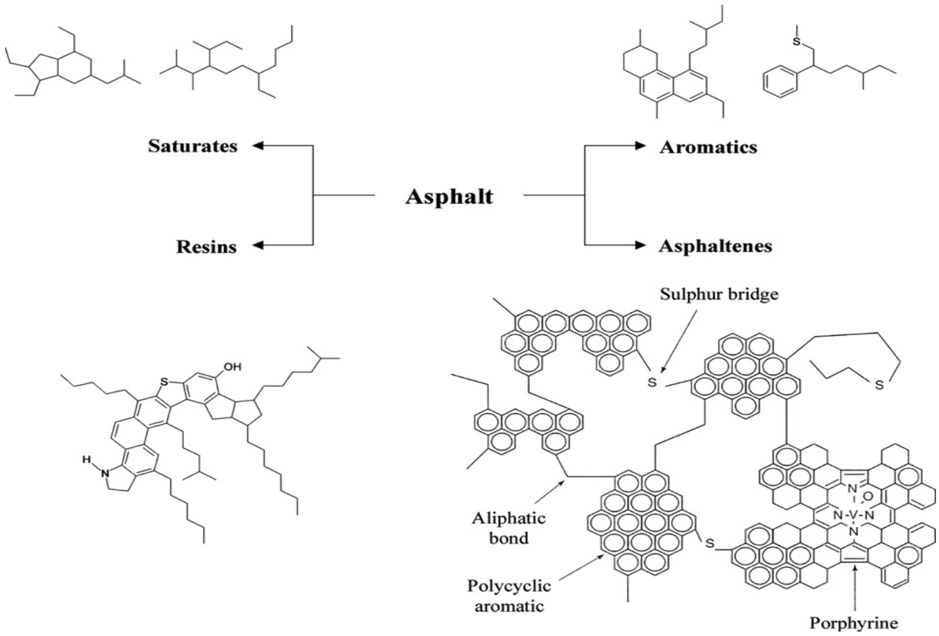

Figure 2.7: Fractionate composition of bitumen [82]

It was also reported by Ritchie *et al.* [81] that the initial peaks of GC/MS observed for bitumen till 2.5 min refer to gas region, where the peaks represent majority of alkanes and alkenes (upto C_8) along with low boiling point aromatics and non condensable gases (CO_2, H_2S, H_2 and CO).

GC/MS was considered as quite good estimation of the compound present in binder [83]. Although the instrument has some limitation in attaining higher temperature greater than 500°C, thus lighter volatile component of binder detected first but the heavier fraction of bitumen may not get detected. Thus there is a chance that non eluted portion may contain larger molecular weight compound with carbon number greater than 36 and higher boiling point which is difficult to get detected under normal condition.

2.6.3 Morphology of Polymer Bitumen Blend

Morphology is the study of microstructure. The use of morphological analysis is becoming very common for the structural analysis with the advent of modern high resolution electron microscope. Thus with the advent of morphological tools it is now possible to analyze the structure of virgin bitumen and polymer modified bituminous blend at nano level and would help in understanding the true morphology of the material which later on can be related to understand the rheological properties of bituminous blends.

The modification of virgin bitumen with the polymer alters the structure of the bituminous whether the interaction considered as only physical interaction or chemical interaction. In both cases the interaction between polymer and bitumen brought changes to the microstructure of the bituminous blend affecting the physio-chemical properties of the PMBs. Whether considering the chemical or only physical interaction the morphology or the structural orientation of the final PMB blend strongly influenced by mixing temperature, technique and time beside the type of the polymer used for modification.

Lesueur [1] defined bitumen as a complex material mainly composed of hydrocarbon produced from the distillation process at high temperature (425ºC) under vacuum with the pressure of around 1-10 kPa (0.01-0.1 bar). The processing conditions used at the refinery and nature of crude source strongly influence the properties of bitumen and thus its chemical structure. Thus in order to understand the complex nature of bitumen study of morphology is considered as vital. It was also reported by Masson *et al.* [84] that bitumen, because of its sticky nature and black color the use of microscopic technique to study morphology was considered quite difficult but with the advent of transmission electron microscopy asphaltene study can be made after dissolving it in proper solvent.

The structural analysis of bitumen was thus considered essential to understand the colloidal model. On the basis of the source of the crude the nature of colloidal model would vary. Bitumen which can be categorized as paraffinic and naphthenic depending on the amount of the chemical composition (saturate, aromatics, asphaltene and resins) in bitumen shows significant affect based on the association among different composition in bitumen. This association leads to the basis of colloidal model [85].

According to Lesueur [1], Nellensteyn [14] was the first person who has suggested the colloidal model based on the assumption that asphaltene are suspended in colloidal form within the maltene phase. This colloidal model was further improved by Pfeiffer [86] suggesting that bitumen colloidal model can further be classified as *"sol", "gel*" or "*sol-gel*" depending on the difference in their rheological properties. Yen [87] further study asphaltene association model based on formation of micelle, explaining the asphaltene agglomeration which is considered as important factor affecting the colloidal stability of the bitumen.

All these earlier concept presented either as colloidal model by Nellensteyn [14] representing asphaltene micelle in maltene phase or by Pfeiffer [88] as *sol, gel* or *sol-gel* model or by Yen [87] based on agglomeration of micelle was proved and further studied in depth with the advent of microscopic techniques as used by Masson *et al.* [84], Rodríguez-Valverde, *et al.* [89] Baginska [90]. It was exposed by these researchers that bitumen is mainly composed of multiphase system, which was concluded after making direct observation of the existing phase.

Rozeveld [91] used environmental scanning electron microscopy (ESEM) to study the network morphology of the bitumen and polymer modified bitumen. He concluded that the rheological properties of the bitumen considerably affected by the network morphology represented by asphaltene in maltene phase. He scanned the sample of both modified and unmodified bitumen, where he found the presence of network fibrils as shown in Figure 2.8 was considered mainly responsible for the ultimate properties of binder. He also reported that the networks revealed by scanned images are different before and after electron beam exposure. The initially flat binder surface appears as random network of fibrils which mainly occurred due to evaporation of lower molecular weight oily constituents from the bitumen while the remaining heavier fraction composed of asphaltene and resin remains over there.

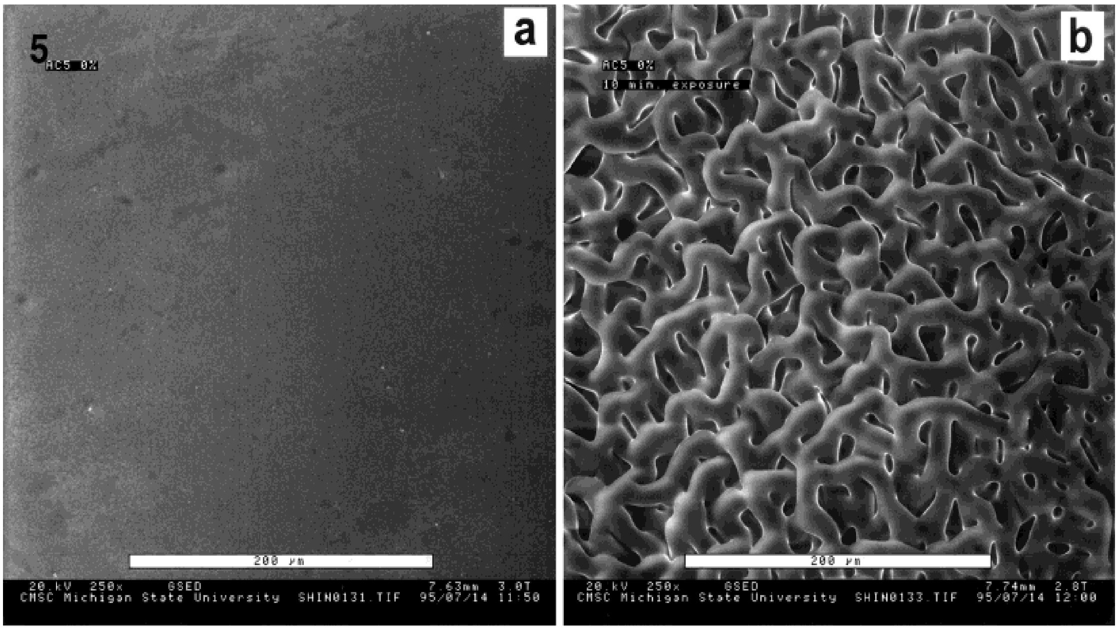

Figure 2.8: ESEM images of unmodified bitumen before (a) and after (b) exposure of electron beam [91]

Atomic force microscopy (AFM) in this regard is considered as most appropriate method because of its non destructive nature and high magnification power which thus preserves the original morphology of the surface of the examined sample making analysis quite easier.

Loeber [92] was the first who made observation of bitumen phase morphology by directly using hot bitumen cast film, there by preserving solid state morpholgy of the bitumen. They have used atomic force microscopy (AFM) and scanning electron microscopy (SEM) to study the bitumen structure. Their AFM results revealed the presence of asphaltene network which they consider it as *gel* asphalt. The images were taken in AFM tapping mode, shows the presence of "bee" structure as shown in Figure 2.9. Loeber suggested the "bee" phase represent asphaltene, which is mostly composed of high molecular weight aromatic compounds.

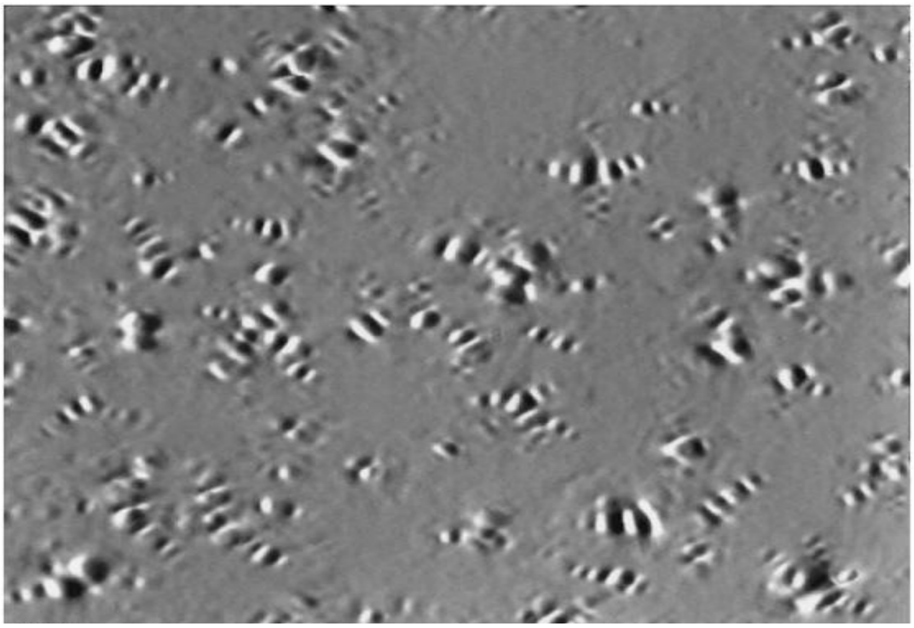

Figure 2.9: AFM image of unmodified bitumen showing bee structure [92]

Masson [84] has used phase detection microscopy to analyze the microstructure of bitumen. After scanning thirteen different kinds of bitumen from different sources he concluded that the morphology of one kind of bitumen differs from another based on the size of domains present varying from 0.1μm - 1μm. These domains have different viscoelastic or stiffness. He figures out that there is a relationship exists between “bee” structure present in bitumen with the traces of vanadium and nickel present in bitumen. The work done by Masson verifies Pfeiffer and Saal works presented in 1940 [86], who presented the colloidal model of bitumen where asphaltene are stabilized by polar aromatics(aromatics) dispersed in medium of naptheine aromatics (resins) and saturated compounds (saturates).

With the advent of atomic force microscopy existence of four bitumen phases were further exposed which were based on chemical composition of the bitumen. The four phases were identified as hard bee phase, hard matrix phase, soft matrix and soft bee phase. It was found that each phase is composed of different component of bitumen which offers different stiffness and elastic characteristic depending upon its chemical composition [93]. The relationship between these phases referred as bee and asphaltene was further elaborated by Masson [94] who discarded the earlier study done by Jager *et al.* [95] who made the correlation between metal content present in bitumen with asphaltene.

The additional use of AFM in phase detection mode (PDM) revealed that bee structure revealed that bee mainly composed of flat structure or flaky domains of 1μ diameter, while the bitumen has at least three phases which are temperature dependent.[95].

Dourado [96] further works on Jager [93] work. He also used atomic force microscopy in indentation mode to relate the variation in bee structure to its stiffness and viscoelastic characteristic. He used nano indentation and come to the conclusion that bee region in maltene matrix is more elastic incomparison to surrounding maltene matrix. His finding confirmed that bitumen is composed of different viscoelastic material depending on concentration of asphaltene in maltene.

Wilson [97], used cryo-scanning electron microscopy which is the combination of SEM and cryo equipment. The conventional SEM has few disadvantages as the surface morphology of the sample is analyzed in vacuum, chances of sample to get destroyed due to exposure of electron beam and charging of sample. With cryo – SEM equipment the rapidly cooled samples of SBS modified samples when scanned at lower magnification between 50 -50000X shows the distribution of polymer nano particles among bitumen phase. The swelling of polymer within bitumen matrix was observed due to presence of domains of honeycomb structure and the chemically reacted polymer shows even distribution among bitumen matrix which is considered as governing factor affecting the workability and mechanical properties of the PMB.

With the use of all the techniques used to understand the morphology of the binder it was concluded that miscibility was the most important governing factor in case of polymer modified bituminous blend. It was revealed by Polcco [8] in one of his studies on different blends of polyethylene and come to the conclusion that due to immiscibility between polymer and bitumen there exists a biphase in matrix, in which polymer form segregated domain as observed by morphological analysis of polyethylene blend. According to his study among different polyethylene studied, linear low density polyethylene (LLDPE) shows compatibility to certain extent although it form separate domains of aggregated polymer among bitumen phase. These segregated domains of polymer preserve its structure and thus its mechanical strength. Beside it polymer network was also there, which was considered responsible for its enhanced properties even at lower polymer content. It was also concluded that the physical network which was observed in LLDPE blend was due to these interconnected polymer chain.

The presence of interfacial tension which exists between two immiscible layers has great effect on the adhesion of binder to aggregate surface. This was revealed by Traxler [16] after studying different asphalts. He found that interfacial tension always exist between two immiscible liquid. He tried to relate the interfacial tension with adhesion between solid and liquid surface. He concluded that the nature of the solid surface has greater effect on adhesion rather than composition of asphalt. The adhesive character of asphalt is due to this interfacial tension and contact angle. Beside dry surface of aggregate, lower contact angle gives better adhesion.

The properties of the polymer and bitumen also have significant effect on the miscibility of the polymer bitumen blend. It was reported by Yousefi [30] who used SEM (scanning electron microscopy) for scanning 1% polyethylene (PE) sample. He concluded that 1% PE sample shows negligible difference in their shape before and after blending with bitumen for 3 hr at 160ºC. The PE at this temperature is in melt state and absorbs some oily constituent from bitumen. He considers that due to absence of Brownian motions among particles the only reason for this breakdown of these particles at high temperatures is creaming, which ends up with coalescence.

It was observed by other researchers also that for polyethylene blends stable phase morphology was observed when the concentration of polymer was kept till 1% concentration [5]. It was also found by R.Maharaj [98] that when polyethylene (LDPE) was blended with bitumen at 140°C with high shear rate mixer, the partially dissolved dispersed polymer in bitumen absorb oil from the maltene fraction of the bitumen producing viscoelastic blend. The dispersion of polymer within the blend depends on maltene composition of the bitumen which in turn depends on the chemical composition (ratio of asphaltene to maltene) of bitumen affecting the compatibility of polymer bitumen blend.

Atomic force microscopy was also used for the determination of different functional groups and modified binder affinity towards water. It was reported by Tarefdar [99] who studied the moisture damage in polymer modified bitumen induced by different functional groups present in bitumen. He conducted his study to know the adhesive or cohesive forces existing between two different polymer modified asphalt (styrene butadiene and styrene butadiene styrene) compared to base bitumen. He used AFM probed tip made up of silicon nitrite (Si_3N_4), carboxyl (–COOH), methyl (–CH_3), and hydroxyl (–OH) representing different functional groups present in asphalt. He concluded that unmodified binder shows more adhesive/cohesive forces in comparison to modified binder when probed with Silicon nitride AFM tip (made up of silica, the most active component present in all aggregate) under dry or wet condition. Functional group doped AFM tips shows less affinity towards polymer modified tip in wet/dry condition in comparison to silicon nitride tip. His work revealed that polymer modified bitumen are less water susceptible in comparison to unmodified base binders.

Thus the use of microscopic techniques to study the morphology of polymer bitumen considered as vital tool especially to understand the compatibility of polymer bitumen blends as polymer bitumen blend are heterogeneous to certain extent showing varying phase morphologies. To understand the relationship between rheological properties of polymer modified bitumen (PMB) and mechanical characteristics, microstructure characterization of the PMB must be made.

2.7 Engineering Properties of Bituminous Mixture

Engineering properties of the modified and neat bituminous mixture depend upon the properties of the binder, physical and chemical characteristics of the aggregate and compatibility of the polymer bitumen blend in case of the modified binder.

Sangita *et al.* [100] in her study on the mechanical properties of the recycled polyethylene bags concluded that improved performance of the modified mixes depends on the processing condition beside the chemical nature and concentration of modifier used. The effect of modifier on the mechanical properties of the mix when evaluated in term of Marshall Stability it was observed that for 6% - 8% modifier in the mix there is an increase in the stability values up to 50%, where as decrease was observed for higher concentration of polymer in the mix. It was thus concluded that at higher concentration of polymer the binder fail to improve the bonding between aggregate and binder due to reduced adhesiveness of the binder. Similar trend for the increases in density and Marshall Quotient was also observed for 8% binder content in the mix indicating resistance to permanent deformation and shearing stress. It was also found that the mechanical properties of the different paving grade bitumen (AC-5, AC-10, AC-20) and SBS modified with AC-10 bitumen in terms of Marshall stability and Marshall quotient was higher in case of polymer modified bitumen than conventional mixes. The cause of the damage that occurred in the asphalt concrete mixes were either due to failure of the binder (cohesive fracture, which occur within the binder) or due to adhesive failure (at the aggregate bonder interface), thus the adhesive bond strength existing between aggregate and binder controls the failure mechanism of Marshall Stability test [101].

Modification of bitumen when analyzed in terms of stability and flow it was observed that for the polymer modified asphalt concrete mix (PMAC) with SBS as modifier higher stability and flow values were observed for PMAC in comparison to AC mix at optimum binder content. The higher stability value for PMAC mix was due to higher viscosity for the modified mix where as high flow values indicate low brittleness of modified binder. The higher flow values were considered positive point as it may reduce the chances of premature cracking. It was also found that air void content for unmodified mix was higher than polymer modified mix, which was considered due to lower bulk density of unmodified mix in comparison to polymer modified mix, while it was also noted that modification also reduces the optimum binder content. [102].

When the effect of the air void content on the properties of hot mix asphalt (HMA) was studied by Kandahl [103], he reported that ageing in HMA increases when the film thickness around aggregate fall below 9 - 10 micron and with the air void content reaching 8% for the compacted mix. It was recommended that for durable HMA, voids in mineral aggregate (VMA) should be 15.6% to accommodate 9 micron film thickness and 4% air void. The durability of the mix and flexible pavement depend upon film thickness. Thicker asphalt binder films are more desirable as with thin binder film induces brittleness and pavement is more subjected to cracking and excessive raveling which destroy the pavement service life.

Beside voids content compaction has significant effect on the service life of the pavement. The degree of compaction is controlled by mix design variables like type of the binder used, gradation, binder content and compaction temperature. Among these mentioned parameters, during compaction gradation and binder content were considered most crucial parameter which has significant effect on the mechanical properties of the mix [104].

When the effect of air void on the strength of mix was evaluated by Pellinen [105] by using triaxial test on mixture strength of dense graded mix (DGM) and stone mastic asphalt (SMA) evaluated the mix stability in the form of shear strength using triaxial test. He concluded that strength of SMA mixes was less affected by the variation of air void content in comparison to DGM. He concluded that DGM shows higher cohesion and unconfined compressive strength below 4% air void content. At higher air void content (12 - 13%) mixture unable to develop shearing resistance due to unavailability of aggregate interlocking action at higher air void content.

When the mechanical properties of polyethylene modified bitumen was studied it was found that the reclaimed polyethylene, in the from linear low density polyethylene (LLDPE) at 2.5% concentration gives better results in terms of Marshall stability, resilient modulus, fatigue life and moisture susceptibility when compared with unmodified bituminous samples.(Panda) [106]. The mechanical strength of the mix also depends on the viscosity, where there is a decrease in binder absorption to aggregate with an increase in viscosity of the binder. The maltene fraction of the bitumen has impact on the absorption capacity of the aggregate which increases with an increase in maltene content [107].

Air void content and voids in mineral aggregate also has significant effect on the durability of the mix. It was noted by Chadbourn [108] the effects of void in mineral aggregate on the durability of asphalt pavement depends on the thickness of the binder film on the aggregate. Adequate voids in mineral aggregate (VMA) allow binder to properly coat the aggregate besides providing sufficient air voids in the compacted pavement structure. He also concluded after studying ten pavement structure of Minnesota that VMA decrease either due to increase in fines due to degradation of aggregate during construction leading to an increases in the surface area of the aggregate blend or higher mixing temperature and long storage time which causes an increase in asphalt absorption into the aggregate in comparison to amount required by mix design, making less asphalt available to coat the aggregate particles. Beside this percentage of air voids in the compacted mixture also depends on the degree of compaction level beside binder content and aggregate packing. It was found that by Ghassan [109] in his that specimen produced by gyratory equipment shows non uniform air void distribution along the diameter and height of the sample. The gyratory compacted sample shows higher air void content at top, bottom and along the wall in comparison to interior portion of the compacted sample. Thus uneven distribution of air void content affects the durability of the mix also.

2.8 Performance Characteristics of Bituminous Mixture

Bituminous pavements are subjected to distress and deterioration because of the increasing wheel load, traffic level and drastic environmental condition. These distresses get aggravated by deficiency in mix design or construction related matter or material or both. Mixture performance in this respect has significant effect on the mechanical strength of the bituminous mixture. Knowledge of these distresses would be helpful in identifying the problems responsible for its initiation. Knowledge of the material especially in case of polymer modified bitumen is helpful in understanding its response to these distresses of which fatigue and rutting is the most commonly encountered problem. Water susceptibility and low temperature cracking also considered as common type of pavement distresses. The literature review over here is confined to fatigue and rutting with an understanding that mostly polymer modified bituminous mixtures are least susceptible to moisture. Low temperature cracking is a problem related to the cold climatic condition where extreme variation in freeze and thaw subject pavement into failure mode. As Malaysia is a tropical country, most encountered distress mode is rutting, fatigue and water susceptibility.

2.8.1 Rutting

Rutting or permanent deformation is the most common type of structural distress that occurs in pavements. Rutting is either caused by the shear flow of bituminous material or densification of material under traffic loads. Plastic deformation of the material also considered as one of the cause which induce shoving and rutting.

Top 50-100 mm layer of pavement material is more vulnerable to rutting. Permanent deformation usually do occur due to consolidation of either underlying base course due to repeated traffic load along the wheel path or due to plastic flow (shear flow of the binder) near the pavement surface [110]. Plastic deformation phenomenon occurs in early life of the pavement, where the aggregate particle moves relative to each other along with the viscous flow of the binder [111]

Youngguk Seo [112] in his study related the effect of air void on permanent deformation concluded that air void and temperature has significant effect on the permanent strain level induced in the material which seems to increase with an increase in air voids and the temperature. Beside this effect of binder type used also has significant effect on the rut performance A study conducted by Hafeez [113] revealed that effect of binder used in the mix had greater impact on rut resistance in comparison to aggregate characteristics. Bituminous mixes prepared with soft grade were less resistant to rutting than mixes prepared from harder grade bitumen or polymer modified binder. Rutting usually occurs at early stage of in service life of the pavement when the binder’s viscosity was quite low. Potential of pavement to rut decreases with an increase in pavement’s life as the binder becomes hard due to ageing leading to an increase in viscosity of the binder.

Densification and shear deformation both occurs in the pavement causing rutting It was revealed by Yang Jun [114] that densification and shear deformation are the two mechanisms commonly considered as cause of rutting. In shear deformation there is a volumetric decrease of asphalt concrete under the wheels which is considered equivalent to the height of the distorted material along the wheel path. He also reported that cohesion of mixture considered as important as gradation where void skeleton plays an important part on the stability of the mixture. Mixture with coarser gradation would offer greater internal friction to resist shearing action while mixture with fines provides higher cohesion.

Widyatmoko [115] used the energy dissipated concept for assessing the resistance to permanent deformation of bituminous mixture. This concept works on the principle that rate of energy which is absorbed by the material during deformation is equal to sum of the rate at which energy is stored and dissipated, expressed as

$$\frac{dw}{dt} = \frac{dwe}{dt} + \frac{dwd}{dt} \qquad \text{equation from [115]}$$

He reported that during cycling loading some part of the work done was done in deforming the upper surface layer of the pavement while the rest of the work is recovered in the form of elastic recovery *(dwe*) due to elastic characteristic of binder. The viscous part of the binder deforms and is considered responsible for the dissipation of energy as heat (*dwd*) by its viscous flow while plastic flow occurs due to the deformation of aggregate, due to reorientation of aggregate which leads to the permanent deformation. It was also revealed by Widyatmoko [116] in his another paper, that air void content has significant affect on the energy dissipation. The higher the air voids in the pavement greater would be the accumulation of irrecoverable strains due plastic flow, leading to a higher level of dissipated energy. It can also be stated that higher value of air void content in bituminous mixture the lower would be the resistance to permanent deformation. He also reported that the mixture prepared with polymer modified bitumen (EVA, SBS & SBR) were less sensitive to air void content than unmodified binder. He concluded that as the achievement of 3% - 5% air voids in field is quite difficult, the use of polymer modified bitumen provides an alternate solution.

It was observed that asphalt content has direct relationship with the behavior of the bituminous mixture. The higher the bitumen content in the bituminous mixture more would be the chances of plastic flow, which would lead to the failure of aggregate bitumen structure. Because of high asphalt content there would be no internal frictional resistance between the aggregate. High plasticity will induce deformation in the pavement as the applied load on the pavement surface were now taken up by the binder itself rather than binder aggregate assembly [117].

2.8.2 Factors Affecting Permanent Deformation

Rutting in bituminous mixtures is mainly affected by the number of variables, among which the mixture composition, degree of compaction and temperature were considered as most influential.

2.8.2.1 Aggregate Type and Gradation

Aggregate gradation has profound effect on the mixture performance. Well graded aggregate gradation offering sufficient amount of coarse aggregate, fine aggregate and filler that would help in the development of proper bonding with binder resisting shearing action of moving traffic loads. Angular aggregates are considered better than rounded one. Similarly aggregates with rough surface texture would offer better internal friction, thereby increasing the resistance to permanent deformation [118].

2.8.2.2 Binder Type and Content

Binder content has significance affect on the mixture performance. Higher binder content would lead to excessive deformation while lower binder content is vulnerable to cracking. Polymer modified binder significantly reduces the rutting in pavements. Polymer modified binder shows better performance in comparison to virgin binders, when designed to satisfy pavement in service conditions [111]. Polymer modified binders due to enhanced viscosity (stiffness) especially at higher temperature resist pavement deformation. Modification improves the temperature susceptibility of the bitumen by increasing binder stiffness at higher service temperature [119]. A study conducted on the rutting performance of HMA concluded that effect of binder used in the mix had greater impact on rut resistance in comparison to aggregate characteristics. Bituminous mixes prepared with soft grade were less resistant to rutting than mixes prepared from harder grade bitumen or polymer modified binder [113].

2.8.2.3 Air Void Content

Air void content defines the percentage of air volume to the total volume of the mix which was being left in the bituminous mixture after proper compaction. Binder type and viscosity of the binder also considered as contributing factor on the amount of air voids present in the bituminous mixture. It was observed that air void content for unmodified mix was higher than polymer modified mix, which was considered due to lower bulk density of unmodified mix in comparison to polymer modified mix. This might be because the polymer modification usually reduces the optimum binder content [102].

Reducing the air void content would lead to the design of bituminous mixtures that will not be prone to excessive hardening due to exposure to air and oxygen. Thus a medium value of 4% is considered as reasonable value for designing air void content in the compacted bituminous mixture as the bituminous mixtures that ultimately consolidate during compaction to less than 3% air voids are vulnerable to rutting and shoving when placed at heavy traffic locations (Asphalt Institute, 2003).[113]. Thus the stiffness of the mix is highly dependent on the air void content [105].

2.8.2.4 Compaction

Beside the air voids content in the bituminous mixture, degree of compaction has significant affect the durability of the mix. Percentage of air voids in the compacted mixture also depends on the degree of compaction level beside binder content and aggregate packing. Poor compaction of the bituminous mixture would result in a mix having lower stiffness and high degree of air voids content which would be susceptible to deformation due to densification of the material under traffic loads [118].

Compaction thus considered as the most significant parameter affecting the service life of the pavement. Degree of compaction was also controlled by mix design variables like type of the binder used, gradation, binder content and compaction temperature. Among these mentioned parameters, during compaction gradation and binder content are considered most crucial parameter which has significant effect on the mechanical properties of the mix [104].

2.8.2.5 Temperature

Stiffness of the mixture is highly dependent on the binder viscosity and flow conditions. These properties of the mixture are governed by the temperature. At higher temperature viscosity of the binder reduces and thus the strength and durability of the mixture. As rutting is considered as high temperature phenomenon, thus pavements which are exposed to high temperature and long time of loading are more vulnerable to rutting. For polymer modified bituminous mixture, it was observed that they were less susceptible to pavement temperature variations in comparison to conventional bituminous mixes [120].

2.9 Fatigue

Cracking in pavement is the major source of distress encountered due to excessive repeated load, insufficient mechanical strength of the mixture or due to lack of durability of the binder. Cracking in pavement that has occurred either because of the material failure or due to accumulation of strain because of the excessive repetition of wheel load can cost a lot in term of maintenance.

Fatigue is considered as most common cause of crack initiation in the pavement. Several studies have been conducted on the fatigue crack origination and propagation in the pavement. Material discrepancy is considered as one of the major factor affecting the fatigue life. Fatigue failure can also occur due to fluctuating stress in the pavement, when the value of developed stress in the pavement exceeds the tensile strength of the material. Fatigue affects the rigidity of the material by constant decrease of the modulus.

Youngguk Seo [112] has conducted a study to develop an air void model which can predict the effect of air void on dynamic modulus and performance of asphalt concrete mixes. He concluded that with an increase in air void decrease in dynamic modulus was observed. He also reported that air void content and temperature has significant affect on the fatigue life of the pavement. The effect of air void on fatigue life is not as significant as it has been observed for the temperature variation for which the resistance to failure at high temperature was quite low.

Polymer modification considered to enhance the fatigue life of the pavement 2 – 3 times as compared to normal bituminous mixture. It was revealed by Panda [106] from his study which was carried out on the use the reclaimed polyethylene from linear low density polyethylene (LDPE). It was observed that at 2.5% concentration of polyethylene when used for modification of bitumen when tested for fatigue life using repeated load indirect tensile test at three different temperature (20°C, 30°C & 40°C) and stress level from 0.045 - 0.25 MPa, the initial strain produced in the sample because of the stress when calculated by using equation reported by Gilmore *et al.*[121], the unmodified bituminous sample longer fatigue life in comparison to PE modified samples (Refer Figure 2.10). He conclude that this behavior was observed as the stiffer mix which was produced by PE modified binder produce much small strain at a particular stress level in comparison to unmodified bituminous samples. Thus the PE modified sample shows 2 to 3 times increased fatigue life in comparison to modified sample.

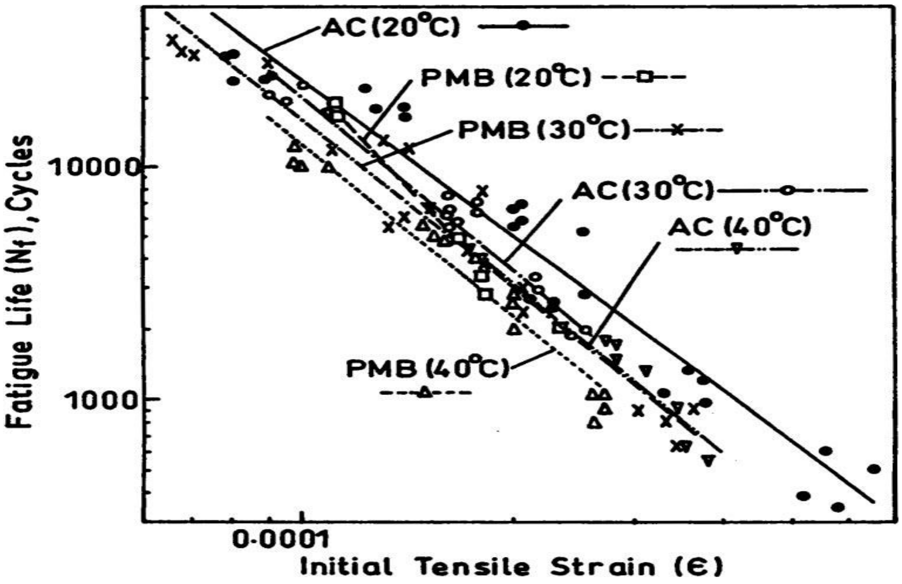

Figure 2.10: Relationship between fatigue life and initial tensile strain [106]

There were different factors which affects the fatigue life some of which were disclosed by Benedetto *et al.* [122] in his paper presented at interlaboratory test campaign by RILEM 182-PEB technical committee, after analyzing 150 fatigue test by using 11 different test equipments. It was reported that fatigue test is very sensitive to the loading conditions and testing procedure and methods used as:

- Small variation in calibration of equipment would affect the test results.
- Variation in test results is unavoidable even for well organized test conditions.
- The fatigue life N_{f50} obtained by using three point bending or four point bending test depend on type of test and mode of loading beside size of the sample used.
- Two phase modes are present during fatigue testing. In the beginning degradation of material occurs, which spread uniformly in the volume of the mix. It is also known as initiation of “micro-crack” which spread in diffuse manner in the material resulting in the decrease of modulus

(rigidity). The second phase occurred due to coalescence of these micro cracks which resulted in “macro-crack” which propagate inside the material. These modes are commonly known as crack initiation and propagation.

Thus the material behavior is considered as important governing factor in fatigue life Shan *et al.* [123] in his one of the paper related the thixotropic characteristic of binder to healing which occurred during rest periods. He reported that fatigue characteristic of asphalt binder can be affected by chemical composition, temperature, stress level etc. He used three stress levels for three different binders (PG 70 - 22). He concluded that thixotropy of the material which occurs due to changes in microstructure of the material due to shearing decreases the viscosity of the binder. During the rest period there is a possibility of the recovery of the damaged micro structure bringing it to its initial viscosity due to Brownian motion of the molecule. He also reported that fatigue behavior of the binder becomes worst under repeated loading. Inclusion of rest period improves binder performance. Longer rest periods always resulted in improved performance although the recovery depends on the material and arrangement of microstructure before rest period.

This behavior of recovery was further investigated by Bhasin [124] who relates it to the self healing characteristic of asphalt binders. He investigated the influence of aging and temperature on the intrinsic healing of asphalt binder. According to him intrinsic healing or strength gain by the binder is composed of instantaneous strength gain due to interfacial cohesion between the surfaces of wetted crack (crack opening) and time dependent strength gain due to reorientation of the molecules at the crack interface responsible for reversal of micro damage (intrinsic healing). Bhasin *et al.* [125] further related the idea of self healing presented by Schapery [126] who consider that healing process in linear viscoelastic material is a combination of wetting and intrinsic healing processes that occur across a crack interface. Bhasin worked on the same line and conclude that like wetting which is considers as mechanical property in which cracked surface comes in contact to each other due to viscoelastic characteristic of material similarly, the initial phase of intrinsic healing can be related to the surface free energy of the asphalt binder. Thus intrinsic changes that occur by the passage of time are due to self diffusion of molecules of asphalt across crack interface. Thus density gradient that occurs across the wetted crack, initiate molecular diffusion which help in regaining the strength of the material at crack interface.

On the basis of the theory and experimental work based on the concept of intrinsic healing and wetting the fatigue test conducted in strain controlled mode of failure seems to give ambiguous results It was reported by F.Perez [127] that flexural fatigue test when run in a strain controlled mode, the failure criterion relating the stress in the bituminous mixture to number of cycles to failure when the stress value in the beam specimen reached half of its initial stiffness value is considered wrong. Thus the failure at half of initial stiffness is considered incorrect especially for the beam specimens prepared with high bitumen content or modified binder. He also reported that as these mixture exhibit viscoplastic characteristic can withstand to the higher level of stress without cracking. He concluded that true fatigue life during these test was seldom achieved especially in the case of beams prepared with polymer modified bituminous mixture.

2.9.1 Factors Affecting Fatigue

There are several factors which affect the fatigue life of the pavement, of which the mode of loading, binder content, compaction method and mixture properties are considered important. The environmental condition especially the variation in pavement surface temperature also considered as an important factor.

2.9.1.1 Mode of Loading

There are two principle mode of loading used in classical beam fatigue analysis.

Constant stress method, where the stress level is kept constant throughout the test while the strain (deformation) increases during the testing.

Constant strain method, where the magnitude of peak cyclic strain is kept constant throughout the testing period by decreasing the stress (load) during the test.

For constant stress method the strain development gradually increases as the specimen becomes weak. The failure of specimen occurs due to rapid propagation of crack. Failure mode in constant stress occurs either at 10% reduction in initial stiffness or when the specimen starts to fracture. In constant stress, failure criteria is quite easy to define as specimen usually undergo relatively short duration of crack propagation [118].

In constant strain mode, strain is being kept constant and reduction in stress is recorded. Since the progressive reduction in stress is very slow thus usually higher numbers of cycles were recorded. Thus at the end of the test, the stress will be reduced to very small value therefore it is most unlikely an evident crack can be seen representing failure of the specimen. For this reason failure criterion for strain controlled mode is limited to 50% reduction of the initial stiffness [127]. At this point a reduction in stress occurs as the crack length increases. The propagation of crack in constant strain mode is comparatively slow in comparison to constant stress mode thus showing longer fatigue life [118]. Constant strain failure mode is being criticized of giving erroneous results especially for the mixtures when prepared with high bitumen content or with modified binders. In such cases mixture tend to behave as visco-plastic material with less stress required to cause strain without cracking. Thus the mixture does not necessarily reach its true fatigue life when the test stops at 50% of its initial flexural stiffness value. For thin layer (surface layer or wearing course), the strain controlled mode is considered more appropriate which flex and moves along with lower structural layer. The lower thick structural layer are subjected to stress control loading system, that’s why considered appropriate to be tested in constant stress mode system [127].

The interpretation of the results obtained either from constant stress or strain can be made by using linear relationship that exist between the log stress σ, or strain ε, and the log of the number of load repetitions to failure N_f as shown in Figure 2.11. A linear part of the plotted line representing initial stage of the accumulated stress and rest almost smooth part of the constant stress values were extrapolated. The stress value corresponding to the intersection of these points as marked by green arrow (↓) is defined as initial stress. The number of cycles to failure was determined in the same way when shape of the plot starts changing.

The failure criteria can be calculated by plotting the graph between

Log stress Vs Log load application.

Log strain Vs Log load application.

This linear relationship can be written in the form

$$\text{Log }(\sigma \text{ or } \varepsilon) = K + n \log N_f \qquad 2.4$$

For stress controlled test, the results are presented in the form:

$$N_f = K\,[1\backslash\sigma]^{\,n} \qquad 2.5$$

While for strain controlled testing, results are presented in the form:

$$N_f = K\,[1\backslash\varepsilon]^{\,n} \qquad 2.6$$

Where, N_f is Number of load applications to failure.

σ is the initial tensile stress or strain amplitude.

K is a material constant

n is a material constant representing the slope of the fatigue line

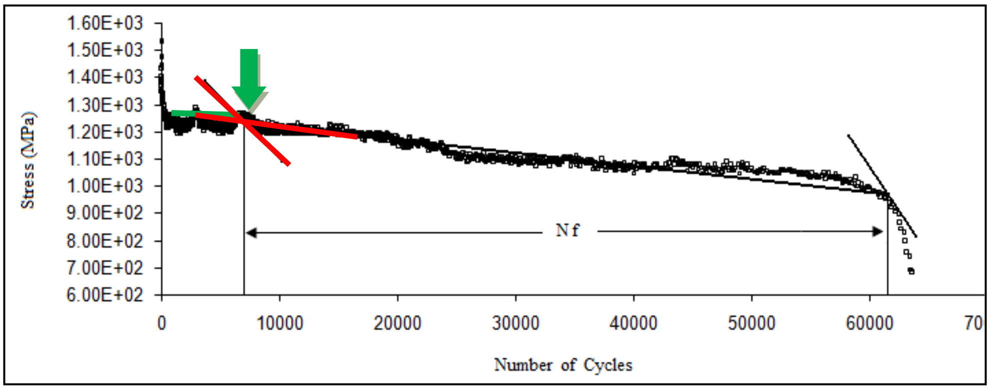

Figure.2.2.11: Determination of initial stress and number of cycles to failure [120]

2.9.1.2 Binder content

Binder content has profound effect on the fatigue life of the pavement. Increasing binder content increases fatigue resistance of the mix [118]. From the study on the effect of binder content on fatigue life revealed that the binder content between 6.0 – 7.0 percent helps in improving the fatigue life. When the effect of the increment of 0.5% binder content on fatigue life was evaluated it was found that it does not impart any significant improvement from the fatigue point of view [128]. Enough quantity of binder provide sufficient coating of bitumen around aggregate, which in turns helps in the development of strong bond among aggregates. It was also observed that 1% reduction in the binder content reduces approximately 70% fatigue life [129].

The type of the binder also has significant effect on the fatigue life. Generally specimen prepared with polymer modified bitumen with high binder content produce stiffer mixes. The resulting specimen with high stiffness shows higher fatigue life in case of stressed controlled mode when tested at particular stress level. Generally the fatigue life of the bituminous mixture can be enhanced by preparing well compacted mixes with viscous and increased binder content [118].

2.9.1.3 Air Void Content, Aggregate and Degree of Compaction

Aggregate and binder content are two important parameters controlling the strength of the bituminous mixtures. A proper well compacted gradation results in maximum theoretical density and would develop a bituminous mix which increases the stability of the mix through interparticle contact area and thus reduces the air void content [130]. Sufficient air voids would allow binder to properly coat the aggregate thereby increasing the durability of the mix. Bituminous mixtures must be prepared with binder content that will produce air void content after densification by traffic to 4%. Pavements designed with less than 4% air void have too much binder which acts as lubricant between aggregate particles induces excessive deformation [131].

The impact of compaction level has profound effect on the fatigue life of bituminous mixtures. The lower the air voids content the higher would be the fatigue life [118]. The fatigue life can be increased by a factor of 9% when the air voids content in the mix was reduced from 8% to 6%. Similarly an increment by a factor of 200 can be achieved when the air voids content reduces to 3% [132]. Although the fatigue life may improved at this lower air voids content but might lead to excessive permanent deformation.

2.10 Summary of the Chapter

This chapter provides a comprehensive literature review made in context with affect of polymer modification on the bitumen characteristics, rheology, morphology, its engineering properties and finally the performance characteristics. The effect of shear rate and blending time adopted has considerable effect on the properties of the modified binder. The concentration of the polymer also has profound effect on the polymer dispersion and compatibility of polymer bitumen blend which ultimately affects the colloidal structure of the bitumen.

Majority of the polymer used for modification belongs to thermo elastics. Reclaimed polyethylene was also used because of its low cost but usually blended by using high shear rate mixer and at higher temperature. The use of thermoplastic was quite rare due to the miscibility problem. Whenever they were used they were cross linked or some additives like chemical modifiers were used in order to increase the elastic property. It was revealed that significant changes in the bitumen structure have profound effect on the characteristics of binder.

Rheology of binder which is governed by the colloidal structure considerably change due to changes in chemical compositional composition. Asphaltene content in the bitumen was thus considered as the most influencing factor affecting the rheology and morphology of the binder. As the interaction of asphaltene with polymer severely affects its flow characteristic and morphology, thus the study of compositional properties using SARA and modern analytical methods were considered essential as it provides an insight of the changes that are responsible for flow characteristic and morphology.

It was also observed from the literature review that in pavement industry SBS and SBS rubber are the most commonly used polymer but for thermoplastic modification by using polyethylene or by reclaimed polyethylene its usage is confined up to 5% as higher concentration leads to phase segregation in the modified bituminous blend. From the literature review on the performance characteristics in terms of rutting and fatigue it was revealed that although performance characteristics being improved by the modification but the significance of aggregate structure cannot be overlooked which normally consist of 95% of the volume of the bituminous mixture. It was revealed by the literature review that creep characteristics were considerably improved by the use of thermo elastics at high pavement temperature. Although the modification improves fatigue properties but the laboratory fatigue test underestimate the actual fatigue life of the pavement as it does not include beneficial aspect of rest period between loadings, where healing phenomenon for the bituminous material during rest periods are now considered as important dominating factor while analyzing the fatigue behavior of the material.

2.11 Research Gap

After an extensive literature review it was concluded, that although a lot of research was being conducted on the rheology, morphology and use of modified binder in improving the performance characteristic of bituminous material was already there, but still there is a need to further study the behavior of thermoplastic modifier. It was found that for the preparation of polymer modified blend usually the mixing was done by high shear rate mixer and at higher temperature. Thus there is a need to investigate in detail the effect of using slow shear rate mixer by using normal mixing temperature that is 160°C. The effect of mixing rate and temperature needs to be evaluated especially for the thermoplastic modifier namely polyethylene blends as majority of the blend preparation was done using high shear rate mixer and at high temperature.

There is a need to address the issue of the effect of slow shear rate mixing on the changes in binder’s rheology and morphology in context with chemical analysis of binder where polymer was just physically dispersed in the bitumen. Thus this study was conducted in view to provide a clear insight of the picture about binder’s rheology and morphology brought about by the chemical interaction of physically dispersed thermoplastic polymer (polyethylene and polypropylene) with bitumen.

From the review on the performance characteristics of bituminous mixture in terms of creep and fatigue revealed that although there is an existence of literature review on the pavement performance characteristic including the rheological behavior of binder especially the effect of thixotropy in fatigue behavior, besides other influencing factors like the effect of stress - strain , aggregate structure, change in climatic conditions etc but still there is a need to further improve the bituminous mixture performance evaluation in context with correlation between binders rheology with reference to polymer bitumen network formation along with chemical alteration due to polymer modification. All these parameters play a significant role in the understanding the reasons for the enhanced stiffness of the material beside the previously mentioned influencing characteristics.

CHAPTER 3

METHODOLOGY

3.1 Introduction

This chapter describes in detail the general scheme of test methods adopted for this research study. As the research topic mainly addresses the rheology, morphology, chemical analysis, engineering properties and performance characteristics the tests were conducted in accordance with standards to describe the methodology adopted to determine the objective of the addressed topics. All tests were carried out in accordance with British Standard (B.S), American Society of Testing and Materials (ASTM) or Jabatan Kerja Raya (JKR) standards.

The first part deals with raw material preparation that consists of material selection and tests conducted to determine its characteristics. The material selection includes selection of granite as coarse aggregate, river sand as fine aggregate and ordinary Portland cement as filler. The binder selection consist of 80/100 pen bitumen along with two types of polymer modified binders. The polymer modified binders includes polypropylene modified bitumen (PP PMB) and linear low density polyethylene modified bitumen (LLDPE PMB).

In order to know the characteristics of coarse and fine aggregates sieve analysis and determination of specific gravity according to JKR specifications was performed. Detailed binder characterization in terms of its chemical, morphology and rheology was performed on both virgin 80/100 pen bitumen and polymer modified bitumen. Polymer modified binder includes polypropylene (PP) modified binders with polymer content varying from 1% - 3% by weight of bitumen and linear low density polyethylene (LLDPE) modified binders with polymer content varying from 1% - 3% by weight of bitumen. All binders were prepared at slow shear rate of 120 rpm at temperature 160°C. All blending of polymer modified binders was done at IKRAM blending facility (Bangi, Malaysia). The tests conducted on binders include characterization tests, morphological tests and rheological tests.

The selected materials were then mixed to get the control mixture obtained from mixing virgin 80/100 pen bitumen with aggregates and six types of polymer modified bituminous mixture. Six types of polymer modified consist of three types of polypropylene bituminous mixture with PP polymer content varying from 1% - 3% by weight of bitumen and three types with LLDPE polymer modified bituminous mixture with polymer content varying from 1% - 3% by weight of bitumen. The modified and control bituminous mixture was then used for the preparation of Marshall Test specimens to calculate the optimum binder content (OBC) for each type of bituminous mixture. The binder content used for the preparation of Marshall Test specimens varies from 4% - 6.5% by weight of the aggregate mix.

Engineering properties of the mixtures were evaluated by preparing Marshall Specimen at evaluated OBC.

The final part of this experimental program includes performance testing. Performance tests carried out on control and modified bituminous mixture includes the wheel tracking test and dynamic creep test to assess the permanent deformation of the bituminous mixture, while beam fatigue test was used to assess the fatigue properties of the bituminous mixture. The mixture engineering properties as obtained from Marshall Test results and mixture performance from permanent deformation and fatigue tests were evaluated and discussed.

Finally the conclusion and recommendations were based on all the facts and results obtained from the entire test discussed above. The flow chart of this study is shown in Figure 3.1.

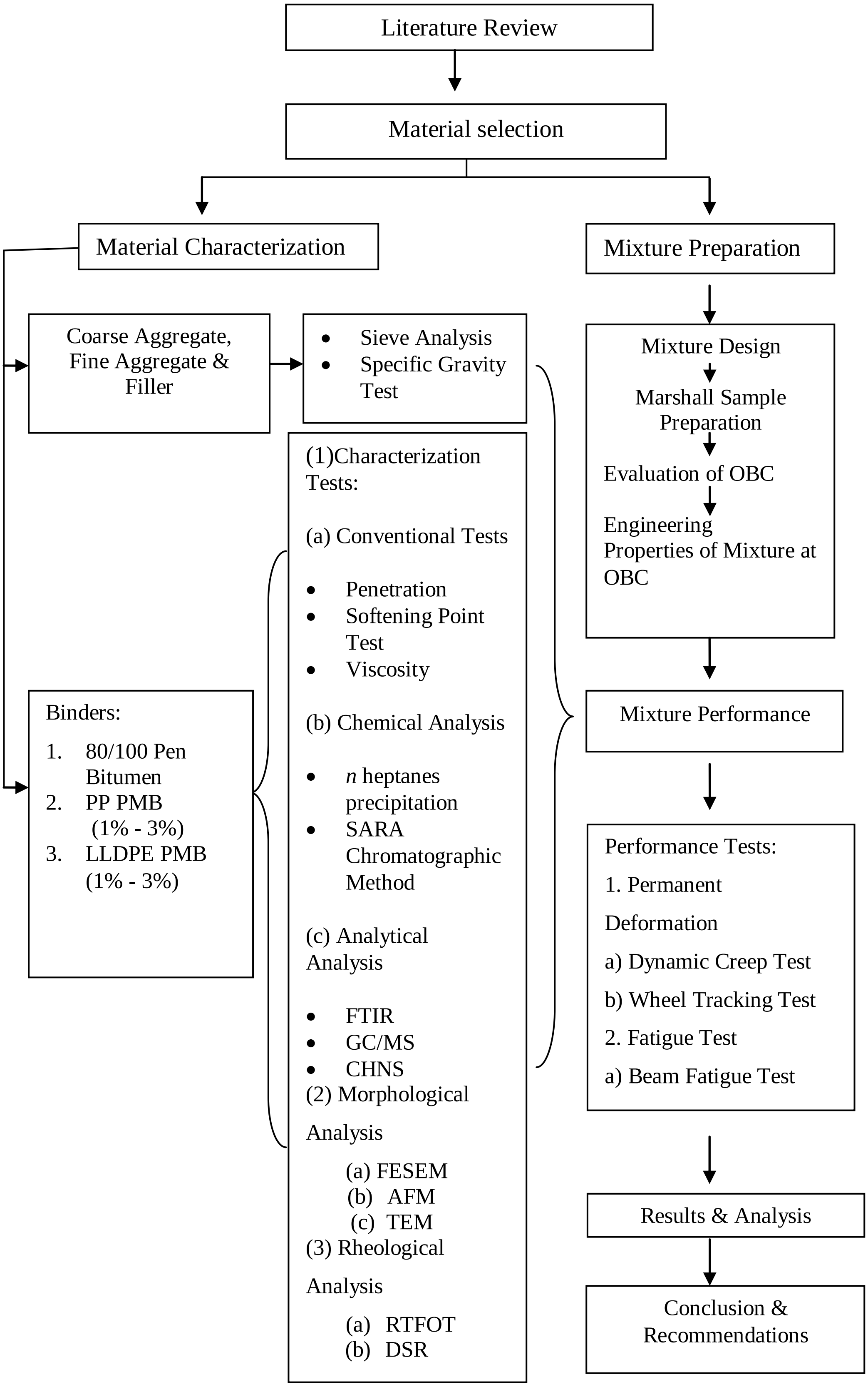

Figure 3.1: Research Flow Chart

3.2 Materials Preparation

Material preparation includes selection of material and determination of its characteristics as discussed in the following sections.

3.2.1 Material Selection

Material selection for the bituminous mix were constitute of selection of binders, coarse aggregate, fine aggregate and filler. The selection of aggregate material and mixture design was done according to the JKR standard (1988).

Three kinds of binders were selected for this study namely 80/100 pen bitumen, polypropylene modified bitumen and linear low density polyethylene modified bitumen.

In this study, asphaltic concrete (AC) mixture designated as ACW 14 was used. The maximum aggregate size used was that retained on sieve size 14 mm and the bitumen content ranged from 4% to 6.5% by weight of the total mix.

The materials selection method includes selection of coarse aggregate, fine aggregate and filler. Preparation of polymer modified bitumen was also discussed in the following sections.

3.2.2 Bitumen and Polymer Modified Bitumen

80/100 pen bitumen was obtained from PETRONAS refinery Melaka, Malaysia. Specific gravity of bitumen was determined according to the procedure mentioned in ASTM D 70-09 test method [133]. Three samples were tested and average density of three test result was used.

Polypropylene in resin form was obtained from the PETRONAS Polypropylene Malaysia, having melt flow index of 8g/10 min and density of 0.8867g/cm^3. The melting point of commercially used isotactic polypropylene ranges from 160 - 170°C [47].

Linear low density polyethylene in pallet form was obtained from POLYETHYLE Malaysia with melt flow index 0.9g/10 min and density of 0.8958g/cm^3. The melting point of LLDPE is 125°C [47].

Mixing of polymer and bitumen was done at slow shear rate of 120 rpm with temperature at 160°C. The concentration of the polymer used for preparation of polymer modified bituminous blend (PMB) was kept between 1 - 3 percent by weight of the bitumen. This was decided after coming to conclusion that polymer content greater than 3 % induce excessive hardening and agglomeration of polymer modified bitumen. The blending was continued for 1 hour. The blended modified bitumen was then covered with aluminum foil and stored in air tight containers. All tests including specific gravity, characterization tests, chemical, morphological and rheological test were carried out on these blended PMB.

Conventional 80/100 pen bitumen was also sheared at 120 rpm at temperature 160°C before testing in order to have uniformity in the testing conditions. Specific gravity of the virgin and polymer modified bitumen was determined using Ultrapycnometer 1000.

3.2.3 Coarse Aggregate

Crushed granite was used as coarse aggregate obtained from quarry in Ipoh, Malaysia. Coarse aggregate was categorized as the material retained on 5 mm B. S sieve size. A well-graded aggregate gradation with a maximum aggregate size equal to 14 mm was used according to the JKR standard (1988) [134].

3.2.4 Fine Aggregate

River sand was used as fine aggregate in this study. Fine aggregate was categorized as material that passes through 5 mm sieve size for well graded bituminous mixture according to JKR standards [134].

3.2.5 Filler

The filler used in this study was ordinary Portland cement with at least 75% of it particle size should pass 0.075 mm sieve size. The Portland cement was obtained from YTL Cement Berhad, Malaysia. It was ensured that filler must be sufficiently dry and essentially free from agglomerations

3.3 Test on Aggregates and Filler

The entire tests discussed were conducted according to the specified standards.

3.3.1 Specific Gravity test

In order to convert the volumetric calculation to mass for mix design procedure, specific gravity of coarse aggregate, fine aggregate and filler was done. For determination of coarse and fine aggregate specific gravity British standard BS 812: Part 107, 1990 was used [135].

Specific gravity or particle size density considered as an important property especially in mixture design procedure. Considering the voids in the aggregate, three relative densities can be evaluated, namely the apparent relative density, relative density on a saturated and surface and relative density on an oven dry. The test also reports the absorption properties of aggregate tested.

The specific gravity test for coarse aggregate was conducted using 1kg of coarse aggregate. The coarse aggregate sample was first washed to remove finer particles and then was immersed in water in the glass vessel at 25°C for 24 hours. The vessel is overfill by adding water and weighted as mass B. Aggregate was dried using cloth until all visible films of water was removed and weighted as mass A. The pycnometer was refilled with water again till the top of cone and the weight was determined as mass C. The aggregate was then dried in the oven for 24 hours and the weight was reported as mass D. Finally the specific gravity and water absorption was determined by using the following equations:

$$\text{RRD} = \frac{D}{A-(B-C)} \qquad 3.1$$

$$\text{RDS} = \frac{A}{A-(B-C)} \qquad 3.2$$

$$\text{ARD} = \frac{D}{D-(B-C)} \qquad 3.3$$

$$\text{WA} = \frac{100\times(A-D)}{D} \qquad 3.4$$

where:

RDD- relative density on an oven-dried basis.

RDS- relative density on a saturated and surface-dried basis.

ARD- apparent relative density.

WA- water absorption (% of dry mass).

For the determination of filler specific gravity Helium Ultrapycnometer was used. Specific gravity of coarse and fine aggregate was also rechecked with helium pycnometer as helium gas can penetrate deeper into pores than water.

3.3.2 Sieve Analysis

Sieve analysis is the process of separating dry aggregate (coarse and fine) into different sizes through a series of sieves arranged in a manner of successively smaller openings in order to determine the particle size distribution Sieve analysis provides the gradation and proportions of the aggregates which can be used for Marshall Mix Design Method. The proportions are determined for coarse, fine aggregate and filler. The aggregates were sieved according to JKR (1988) specification using a series of sieves with different sizes as shown in Table 3.3.

Materials to be sieved were first washed with tap water and then the clean samples were dried in the oven for 24 hours at 100°C. The aggregates were then sieved in sieve shaker for 10 mins. The aggregates after being sieved were put in the separate containers, classified on the basis of their particle size as shown in Figure 3.2.

Figure 3.2: Sieve Shaker along with the bags for storing individual sieve sized aggregate

As only one JKR gradation specification ACW -14 was used for this study, each aggregate particle size was then weighed according to the aggregate gradation proportion which was already being selected for preparation of mixture specimens. The amount of the filler (OPC) used for mix design was kept at 5% of the weight of total mix. The total percentage of the aggregate and filler weight must be 100%. All bituminous mixture used in this study were prepared with this fixed aggregate gradation proportion. Since the study was focused on behaviour of the polymer modified binder and its effect on the mixture performance, the same aggregate type and gradation was used throughout the study.

3.4 Test on Binders

Characterization test on binders virgin 80/100 pen bitumen, PP modified and LLDPE modified bitumen were categorized as conventional test on binders, chemical test on binders, analytical analysis of binder, morphological analysis of binder and rheological analysis of binder.

All tests were conducted on binder already prepared as mentioned in section 3.2.2. The detailed procedure and standard used are discussed in following section.

3.4.1 Conventional Test on Binders

Standard conventional tests were used to investigate the consistency of the 80/100 penetration grade bitumen and polymer modified binders. The test was carried on all PMB blend with the polymer content varying from 1% - 3% by weight of the bitumen. The test methods used are explained in the following section.

3.4.1.1 Penetration Test

Penetration test was performed according to ASTM D5-97 [136]. In this method penetration needle was allowed to penetrate the standard needle for 5 seconds under 100 gm load into the bitumen which was already maintained at temperature of 25°C. The distance travelled by the penetration needle was recorded as penetration expressed in decimillimeter (dmm). For each binder three values were taken and average of three values were recorded to nearest whole unit as penetration for that specific binder.

3.4.1.2 Softening Point (Ring & Ball) Test

Ring and Ball softening test was performed according to ASTM D 36-97 [137]. To find the softening point 3.5gm steel ball were placed on the surface of the bitumen surface which was already poured into the brass rings. The brass rings were then placed in a glass assembly filled with distilled water. The whole assembly was then heated at a uniform rate of 5°C/ min until the trapped bitumen in the brass ring start to deform due decreasing viscosity. The temperature at which deformed bitumen touches the base plate which was 25mm apart from the ring was recorded as softening point temperature. Three test run was made in order to know the correct softening temperature.

3.4.1.3 Viscosity Test

Viscosity measurements were made according to ASTM D 4402-06 [138]. Viscosity test was conducted using Brookfield viscometer (model CAP 2000+). It is designed to rotate cone spindle over a temperature controlled shearing plate, which can be subjected to varying speed ranging from 5 to 1000 RPM. The analyzed material viscosity was thus obtained as a function of shear rate and temperature.

All the viscosity measurements were taken at 135°C. A small quantity of sample was placed on the plate and selected spindle was lowered to the point so that it touches the base plate. The sample was then allowed to attain the test temperature. After the temperature was being stabilized, it was subjected to shearing by applying torque. If the applied torque value was within the full scale range (FSR) range it will display value. The shear rate was then increased in progressive manner and viscosity measurements were made within FSR measureable range. The viscosity of the material with the increasing shear rate was recorded in Pa s. The viscosity results were then plotted against shear rate at that particular temperature. For each binder three test runs were made.

3.4.2 Chemical Analysis

In order to understand the fractionate composition of bitumen chemical analysis is the ultimate answer. The chemical analysis of the binder helps in understanding the effect of bitumen constituent on rheology and morphology of the binder. It also provides an insight about polymer- bitumen compatibility. The most widely used test method includes *n* heptanes precipitation method and SARA chromatographic method.

3.4.2.1 n heptane Precipitation Method

For the determination of asphaltene content in bitumen and polymer modified bitumen standard ASTM D 3279-07 [139] was used. Figure 3.4 and 3.5 show the method followed for the determination of the mass percent of asphaltene in *n* heptane solution of reagent grade. For paving grade bitumen a small quantity varying between (0.7 - 0.8 gm) was dissolved in *n* heptanes in ratio of 100 ml of solvent per 1gm of sample. The sample along with solvent in Erlenmeyer flask was gently heated on hot plate with proper reflux condenser. The magnetic stirrer in the flask will gently make the stirring homogenous. Stirring was continued under reflux for 15 - 20 min. The flask was then allowed to cool down over night in a dark place. This would allow the precipitated asphaltene to settle down. The asphlatene solution was then filter through glass fibre filter pad placed in Gooch crucible by applying suction. The crucible with trapped asphaltene on filter pad was transferred to oven maintain at 107°C for 15min. The heated crucible was then cooled in desiccator and weighed. Percent asphaltene in bitumen was calculated as

Mass percent insoluble asphaltene % = A/B %

Where: A= total mass of insoluble B= total mass of sample

Figure 3.3: (a) Bitumen sample in Erlenmeyer flask (b) Erlenmeyer flask on hot plate with reflux condenser

Figure 3.4: (a) Filtering *n* heptane solution (b) Weighing collected precipitated asphaltene on glass fibre filter pad

3.4.2.2 SARA Chromatographic Method

The standard ASTM D 4124-01 [140] for the separation of bitumen into four fractions namely saturates, aromatic, resin and asphaltene was used to determine the amount of the fractionate composition. Chromatographic method separates the bitumen by elution adsorption method where calcined alumina of chromatographic grade CG-20 present in chromatographic column act as filter bed.

The deasphaltened bitumen portion obtained after *n*-heptane precipitation (ASTM D-3279) called "petrolenes" or maltenes, was further fractionated into saturate, aromatics and resin after passing through chromatographic column. As maltene solution was passed through the *n* heptane pre wet column it gets adsorbed to aluminum oxide bed (chromatographic grade) and elute under gravity when flushed with appropriate solvent of increasing polarity and aromaticity to remove the increasing polar molecules. Saturates are eluted first followed by aromatics and resins. Reagents used in this study was 99 minimum mol% (pure grade) obtained from Merck chemicals. The reagent used for separation of bitumen includes:

- *n* heptane to flush saturates, saturates are collected as colorless liquid. The cut off point for saturate was decided on appearance of yellow color ring in column.

- Toluene was used for elution of aromatics. Aromatics were collected as dark orange or yellow to red color elute. The cut off point for the aromatic was decided as the black ring in column reached the aluminum bed.

- Methanol/toluene (50/50) solution followed by trichloroethylene was used for elution of resin. Resin was collected as black color liquid.

The solvent from the three collected elute was removed by using rotavapor. The concentrated fraction was then dried under nitrogen environment in separate glass vials on dry bath heater in order to get the weight percent of each fraction. The detailed procedure adopted for column chromatography is shown in Figure 3.5 to 3.10.

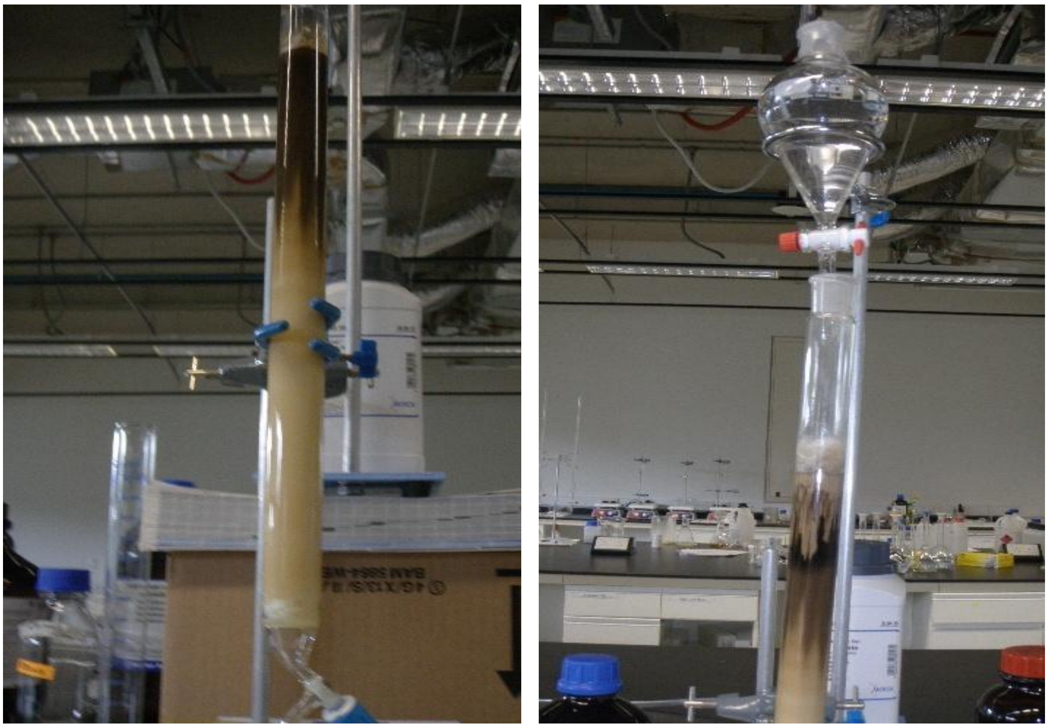

Figure 3.5: (a) Maltene in aluminium column bed (b) Addition of *n* heptane through equal pressure funnel into the column

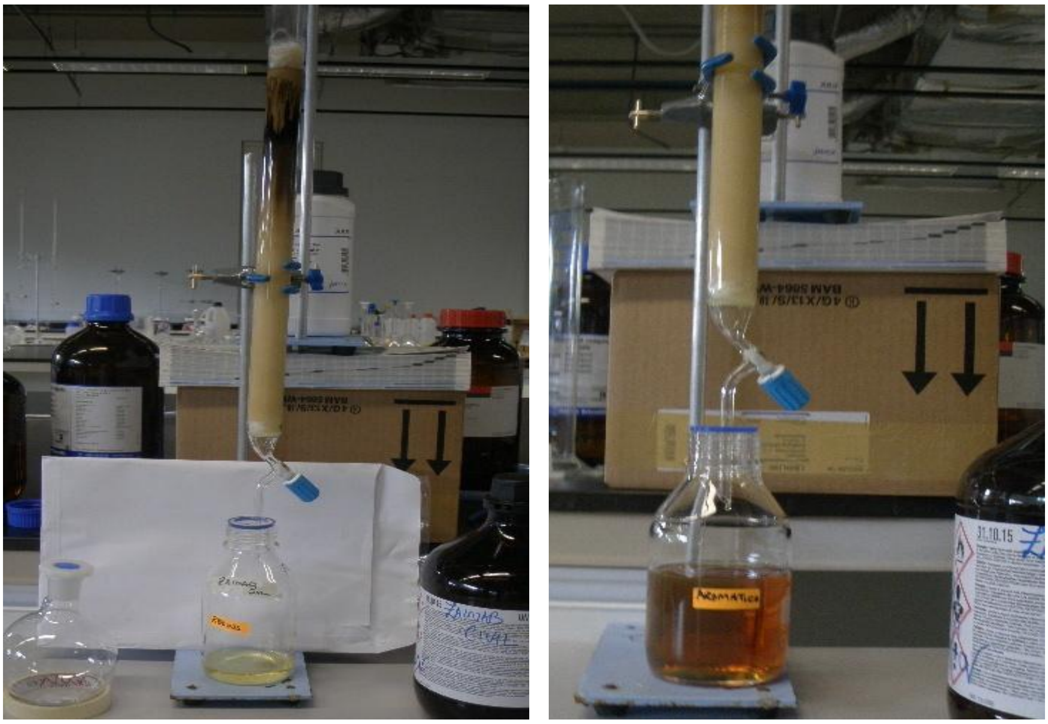

Figure 3.6: (a) Collection of saturates (b) Collection of aromatics

Figure 3.7: Collection of resin

Figure 3.8: Removal of solvent using rotavapor

Figure 3.9: Left over bitumen fraction after solvent removal by rotavapor

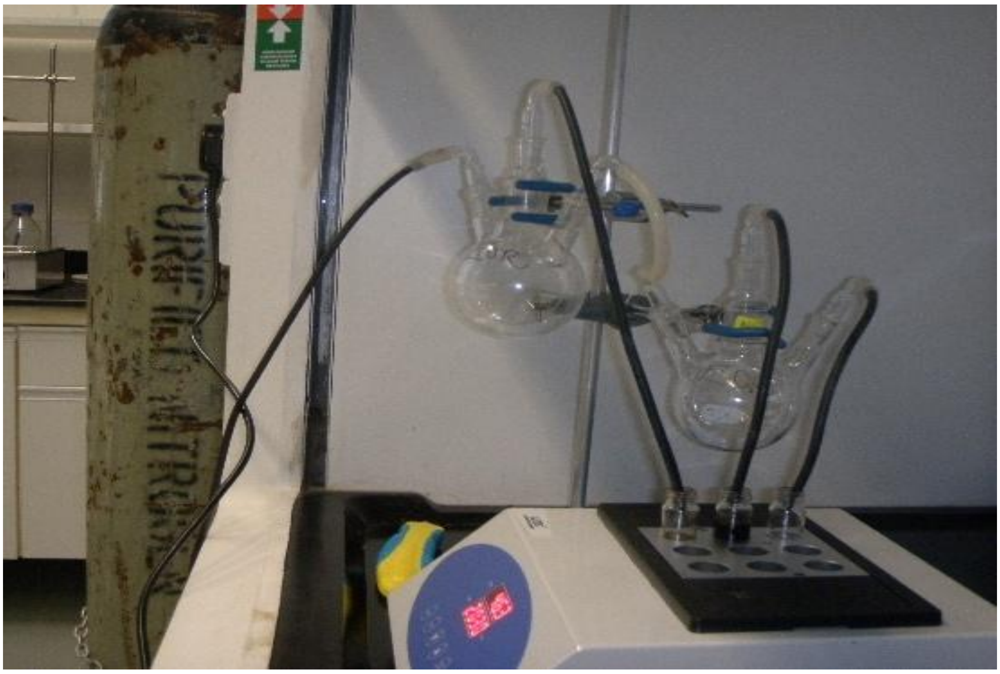

Figure 3.10: Drying of eluted fraction in glass vials under nitrogen environment on dry bath heater

3.4.3 Analytical Analysis

The chemical characterization, both quantitative and qualitative was done using GC/MS, CHNS Analyzer and FTIR Spectroscopy using ATR Mode. Analytical techniques are considered as quick method to study the changes in bituminous binder due to oxidation process. To study the compositional changes GC/MS can be used. For the information about polar component in bituminous binder FTIR can be used. For the determination of elemental composition CHNS analyzer can be used.

3.4.3.1 Gas Chromatography/Mass spectrometry (GC/MS)

GC / MS was done using Agilent GC / MS 5975C. Identification and quantification of volatile and semi volatile organic compounds in a mixture can be obtained by pyrolysis a small quantity of sample at high temperature. The pyrolysis probe consists of platinum coil into which a small quantity of sample around few milligrams was inserted in 30 m long stainless steel column packed with 5% Phenyl Polysilphenylene –siloxane (BPX-5). The GC/MS was performed with the oven temperature 300°C (held for 5mins) and was then raised at rate of 10°C/ min till 500°C.The carrier gas was nitrogen flowing at rate of 1.0 ml/ min.

As soon as the samples of virgin or polymer modified bitumen (LLDPE & PP PMB) was inserted they were subjected to pyrolysis. The different chemical composition of molecules in a mixture will get separated along the length of the column. The molecules take different amounts of time (called the retention time) to come out of (elute) from the gas chromatograph and this allows the mass spectrometer to capture, ionize, accelerate, deflect, and detect the ionized molecules separately. The results are presented in form of chromatograph where each peak in the chromatogram represents a distinct chemical compound, or a mixture of compounds with identical retention times. The retention times in the chromatogram provide the first indication of the sample constituents. The retention times of chromatograph was then related to the built in library which helps in the identification of the particular compound present in the mixture.

3.4.3.2 Fourier Transform Infrared Spectroscopy FTIR

SHIMADZU 8400S Spectrometer in attenuated total reflection (ATR) mode was used for structural characterization of both virgin and polymer modified bitumen. Equipment was equipped with Zinic Selenide prism (wave length 10000 – 500 cm^{-1} & transmittance 65% T). The equipment was first calibrated using PET (polyethylene terephthalate) film before use. Measurements were taken with ZnSe prism (refractive index 2.4) using resolution of 2 cm^{-1} and 40 scans.

In ATR mode a small quantity of sample was pressed against prism, tight adhesion between the sample and the prism was maintained by applying pressure. The infrared ray was then allowed to penetrate through the sample which was the refracted by ZnSe prism. The diffracted rays were then recorded and produced in forms of peak. The spectra of the samples were analyzed in the range of 600 - 4000 cm^{1}.

3.4.3.3 CHNS Analyzer

Elemental analysis (C, H, N, S and 0) was carried out on both virgin and polymer modified bitumen (LLDPE & PP PMB) samples using LECO CHNS – 932 analyzer. For elemental analysis a small quantity of sample (1 - 3 mg) in tin capsule under goes oxidative decomposition in pure oxygen environment at very high temperature at 1000°C. Analyzer detects the percent composition of Carbon, Hydrogen, Nitrogen, and Sulfur in sample while Oxygen content was determined by difference.

3.5 Morphological Analysis

Morphological analysis was done to study the evolution of structure brought by chemical changes in the virgin and polymer modified bitumen. The analysis was done using Field Emission Scanning Electron Microscopy (FESEM), Atomic Force microscopy (AFM) and Transmission Electron microscopy (TEM). All analysis was performed at ambient room temperature.

3.5.1 Field Emission Scanning Electron Microscopy (FESEM)

SUPRA 55VP by Carl Zeiss AG, Germany was used for FESEM analysis. The ultra high resolution imaging technique can analyze the surface morphology at nano scale.

Slides were prepared by applying a thin film of specimen on aluminum sheet which were then coated with ultra thin film of gold to make the sample conductive. The sample was then subjected to well define electron beam which impinge on the specimen and leads to the generation of secondary electron beam, scattered electron beam and absorbed electron beam. These electrons beam can be detected by suitable detector and give information about the surface structure and morphology of the specimen.

3.5.2 Atomic Force Microscopy (AFM)

Topographical and surface information was obtained by using AFM model SII NANO NAVI (E- Sweep). Scanning was performed in phase detection mode (PDM) of dynamic force mode (DFM).

The samples were prepared by applying hot bitumen film on silicon wafer. The film was gently heated to obtain uniform thickness and was then cooled to ambient temperature. All AFM measurements were made on these prepared slides.

The samples were scanned using silicon tip SI – DF 20, with resonance frequency f = 149 kHz and spring constant C= 16 N/m. The surface characteristics were made in phase mode. AFM measurement was made in tapping mode while maintaining the distance between the probe AFM tip and the sample. All the images were taken at room temperature and at normal atmospheric pressure.

In tapping mode when the surface characteristics of sample are different the effects of interaction between the probe and sample were detected by the phase change. Images were obtained by the deflection of cantilever tip which scan the sample surface by detecting the forces between cantilever tip and sample surface change. The cantilever of AFM was excited to oscillate close to its resonant frequency. Thus the tip of AFM which was only in intermittent contact with the sample surface records the changes of the effective (vertical) forces acting on the tip caused by the alteration in the oscillation amplitude and phase. Thus images were taken by monitoring the difference between the oscillation signal sent to AFM cantilever and its actual oscillation which corresponds to the interaction of cantilever tip and sample interaction.

3.5.3 Transmission Electron Microscopy

The morphology of the modified bitumen was observed using TEM model ZEISS LIBRA 200 FE. The samples were prepared by dissolving bitumen and polymer modified bitumen in toluene (reagent grade). One drop of bitumen was dissolved in approximately 10 drops of toluene. The sample was then sonicated in digital ultrasonic sonicator Pro’sKIT SS-802 as shown in Figure 3.12. Each sample was sonicated till eight times, where each sonincation process continued for about 480 secs. The purpose of sonication was to disintegrate the agglomerated material, so that well dispersed specimen would be available for final sample preparation. After sonication sample were left in glass vials for about one hour before transferring it to copper grid. The copper grid was then coated with Formvar. The solvent was allowed to evaporate before final scanning.

Figure 3.11: Ultrasonic Sonicator

A high voltage electron beam (220 kV) was allowed to pass through a condenser lens by producing parallel rays. These rays impinge the sample and subsequently produce bright field image, which were captured by camera during scanning. The scanning of sample can be performed till 0.14 nm resolution. The magnification of nano scaled sample can be done up to 1000000 X. As each sample morphology differs from sample to sample thus to capture good images the magnification level used in this study differs.

3.6 Rheological Test on Binders

3.6.1 Rolling Thin Film Oven Test (RTFOT)

Standard test method ASTM D 2872-04 [141] was used to find the effect of air and heat on the moving film of semi solid asphaltic material. This test simulates the ageing condition which the bituminous mixes would encounter during mixing with the aggregate in mixing facility. A pre weighed material in glass containers were subjected to air and heat for 85 min at 163°C. The residue of the test sample was then used for DSR testing.

3.6.2 Dynamic Shear Rheometer (DSR) Test

Dynamic measurements were made on the residue obtained from RTFOT according to ASSHTO TP5- 1994 [142]. HAAKE Rheo Stress 6000 was used for dynamic measurement. Dynamic measurements were made in controlled strain mode with sinusoidal oscillatory frequency of 1.59 Hz (10 rad/sec), which represents the shearing action corresponding to vehicle speed of about 100 km/ h (SHRP REPORT 379) [143]. Temperature sweep was used in order to cover the range of temperatures that may encounter during service life of the pavement. Measurements were taken at temperatures varying from 46°C - 82°C, with an increment of 6°C.

In AASHTO TP5 standard test method a thin bitumen specimen was sandwiched between two parallel metal plates held in a constant temperature medium. One of the plates remains fixed while the other oscillates, at an angular frequency of 10 radians per second for 10 cycles, with respect to the other. The dynamic shear rheometer evaluates the specimen's response to the sinusoidal stresses and calculates the specimen complex modulus (G*) and phase angle (δ) with computer software equipped with rheometer.

3.7 Mixture Design

A total of seven different mixtures comprising of control mix prepared from virgin 80/100 pen bitumen and polymer modified bituminous mix prepared from LLDPE and PP modified binder varying from (1% - 3%). These mixes were used for the preparation of Marshall Mix specimen and for performance tests. The performance tests conducted in this study includes the dynamic creep test and wheel tracking test (to determine the deformation characteristics of the mix) and the beam fatigue test (to determine the fatigue or cracking properties of the mix).

3.7.1 Marshall Mixture Specimen

A total of 24×7 test specimen's were prepared for the Marshall test was conducted to get the optimum bitumen content for control and six types of polymer modified bituminous mixes. The optimum bitumen content obtained from the Marshall test was used for the preparation of the performance test specimens. A detailed description about specimen preparation is given in the following sections.

3.7.1.1 Marshall Test Method

All Marshall Samples were prepared according to ASTM D1559 [144]. Standard size 101.6 mm (4 in) diameter and 60 -65 mm (2½ in) high samples were prepared by using Gyratory compactor as shown in Figure 3.12 -3.13. Gyratory compactor was adjusted at an angle of gyration of 1.25°, normal pressure of 600 kPa and number of gyration was kept at 200 according to ASSHTO 2001 specification. For Marshall Sample preparation, 1200gms of well graded aggregate according to JKR specification for ACW – 14 was blended with bitumen at varying bitumen percentage between 4 - 6.5%, in order to get the optimum bitumen content (OBC) for a mix. Three different types of Marshall Samples were prepared namely control mix prepared with virgin bitumen, PP and LLDPE polymer modified. Marshall Samples using modified bitumen was also prepared with polymer concentration varying from 1% – 3% by weight of bitumen to calculate the OBC. The Marshall specimen were then tested for stability and flow after immersing the specimens in water bath at 60ºC for 30 min and loaded to failure by applying the compressive force at constant rate of 51mm/min. Density measurements were made before soaking the specimen for the calculation of voids properties. The Marshall Stability value (in kN) is the maximum force that the specimen could withstand until it fails, while the flow (in mm) is the deformation at that force. The values of stability, flow, air voids, density, voids filled with bitumen and voids in mineral aggregate for each binder was obtained by averaging three calculated values. All of these parameters were plotted against the binder content. The optimum binder content was calculated as the average of binder contents that meet the maximum stability, maximum density, maximum Marshall Quotient and 4% air voids.

The equations used to calculate the density, stiffness, air voids, voids in mineral aggregate and voids filled with the bitumen are given below:

$$\text{Density} = \frac{Wair}{Wair - Wwater} \tag{3.1}$$

$$\text{VMA} = (Vair\ + Vbitumen) \times 100\% \tag{3.2}$$

$$\text{VFB} = \frac{Vbitumen}{(Vair\ + Vbitumen\ )} \times\ 100\% \tag{3.3}$$

$$\text{Air Voids} = [1 - (Vaggregate\ + Vbitumen)] \times 100\% \tag{3.4}$$

$$\text{Marshall Quotient} = \frac{Stability}{Flow} \tag{3.5}$$

Figure 3.12: (a) Electric Mixer (b) Gyratory Compactor

Figure 3.13: (a) Marshall Specimen (b) Marshall Testing Machine

3.8 Performance Tests

To assess the mechanical characteristic of virgin and polymer modified bituminous mixtures for performance prediction, three main tests were used namely dynamic creep test, wheel and beam fatigue test. Dynamic creep and wheel tracking test was used to evaluate the rutting performance of the mix while the beam fatigue test was used to evaluate the fatigue properties of the mix.

3.8.1 Dynamic Creep Test

To measure the permanent deformation resistance of bituminous mixes dynamic creep test was used. Test was conducted on triplicate Marshall Specimen already prepared at optimum binder content.

The dynamic creep test was performed according to British Standard DD 226 [145], using Universal Testing Machine (UTM) 4-19, to find out the accumulated strains and creep modulus in the specimen by Linear Variable Displacement Transducers (LVDTs). The creep deformation of standard Marshall Specimens prepared at optimum bitumen content for virgin and polymer modified mix as shown in Figure 3.14 was measured as a function of pulse counts or rather time. The load used on the specimens was uniaxial and dynamic, which was representing the repeated application of axle loads on the pavement structure. The Marshall specimen prepared at OBC were placed in chamber for 1hr at 40°C before loading to attain uniform temperature, as estimated by transducers inserted in dummy specimen located near test specimen in chamber. The specimen was preloaded with 12 kPa stress for two minutes before being subjected to 100 kPa stress for 1 hr (Figure 3.15). The 1800 load duration was applied includes 1000 ms pulse width and 1000 ms rest period. The results obtained were used to develop the relationship between mixture stiffness to the binder stiffness as obtained by Van der Poel nomograph to predict mechanical performance of mix.

Figure 3.14: Marshall Creep Specimen

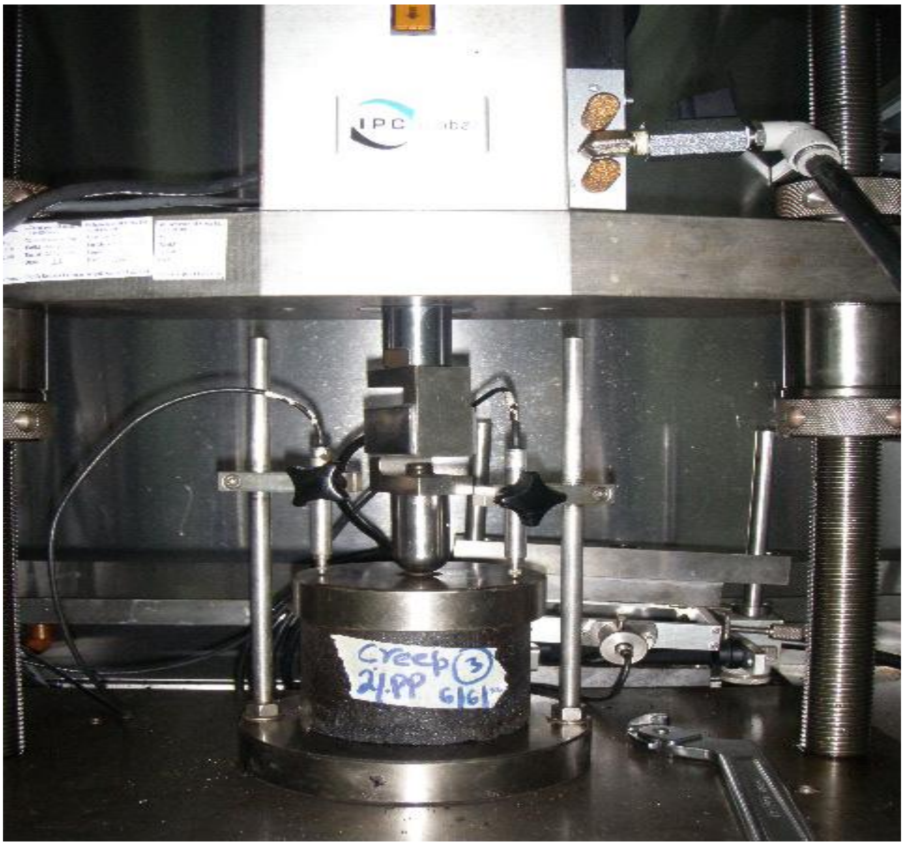

Figure 3.15: Dynamic Creep Test Assembly

3.8.2 Wheel Tracking Test

The wheel tracking test was performed according to British Standard BS 598-110 [146] using Wessex wheel tracker machine, to determine permanent deformation characteristics of the mixtures. The wheel tracking specimens were prepared by mixing 10Kg of aggregates with binder (modified and virgin) at OBC obtained by Marshall test results. The material was mixed at 160°C in a mixer and was then compacted with compactor in a mould of size 305 mm×305 mm×50 mm as shown in Figure 3.16 (a). An actual wheel of 200 mm diameter and 50 mm width applies 520 N load, which runs backward and forward direction across a bituminous sample at a frequency of 42 wheel passes/minute as shown in Figure 3.16 (b). The test was carried out at 40°C and Wessex software records the total rut depth for number of wheel passes for 45 minute loading period

Figure 3.16: (a) Wheel Tracking Sample Preparation (b) Inside View of Wheel Tracking Machine

3.8.3 Beam Fatigue Test

In all 63 rectangular beam specimens were prepared using rectangular metal mould at optimum binder concentration along with 0.5 percent above and below the optimum binder concentration for beam fatigue testing. The mass of material used in the mixture was approximately 7600 g to prepare a beam with dimension of 100 mm x 100 mm x 500 mm. The materials used consisted of coarse aggregate, fine aggregate and filler was first heated and then mixed with binder at the different OBC at 160°C using the electric mixer. Grease was applied on the inner sides of the rectangular metal mould before the mixture was poured, for easy removal of the solidified specimen. The specimen was then compacted in two layers using the electric hand compactor shown in Figure 3.17. The beams were allowed to cool for 24 hrs and then removed from the mould as shown in Figure 3.18. Three beams were prepared for each mixture variation (- 0.5% OBC, at OBC and + 0.5% OBC) as shown in Figure 3.19.

A diamond saw cutter was used to cut the beam specimen into two with the dimension of approximately 50 mm x 65 mm x 380 mm as shown in Figure 3.20.

Fatigue test was performed using Universal Testing Machine (UTM 4-21) according to ASSHTO TP 8-94 [147]. All the specimens were kept at 20°C for 2 hours before testing. The beam fatigue test was conducted by applying a repeated flexural bending to a bituminous beam specimen in constant strain mode. For constant strain mode of testing failure criterion as defined by conventional approach considered achieved when the specimen reaches 50% reduction in the initial stiffness modulus. This criterion does not seem reasonable especially for the beam specimen prepared with polymer modified bitumen [127].

Thus for the determination of the fatigue behavior of the bituminous mixes, all beam were tested in this study under constant strain mode were flexed till the level when the micro crack starts initiating. The number of failure registered was thus the accumulation of number of cycles till failure either due to prominent advent of micro cracks or complete beam failure.

Three strain levels 100, 300 and 500 µm were used to determine the relationship between stress and the number of application of load to failure. The beams were compacted with same compaction effort and checked for the porosity in order to maintain the air voids content in the compacted beam between 3% - 5%. The applied force and the resulting beam deflection were measured using an on-specimen Linear Variable Displacement Transducers (LVDTs). Figure 3.21 shows the beam fatigue apparatus. The parameters used in beam fatigue test are as follow:

1. Default Poisson ratio: 0.4

2. Loading conditions:

    - Control mode: sinusoidal strain
    - Pulse width: 200 ms
    - Frequency: 5 Hz
    - Peak to peak: 100 micro strain
    - Conditioning: 50 cycles

3. Termination conditions:

    - Termination stiffness: 50% of the initial stiffness or
    - Stop test after 1,000,000 cycles

The tabulated test data of the load and deformation was updated at every 10th cycle by the corresponding UTM 4-21 software of the apparatus. These results were utilized to develop relationship between different strain level and number of load applications to failure, which provides information about material response to particular strain level.

Figure 3.17: Beam Fatigue Specimen Compaction

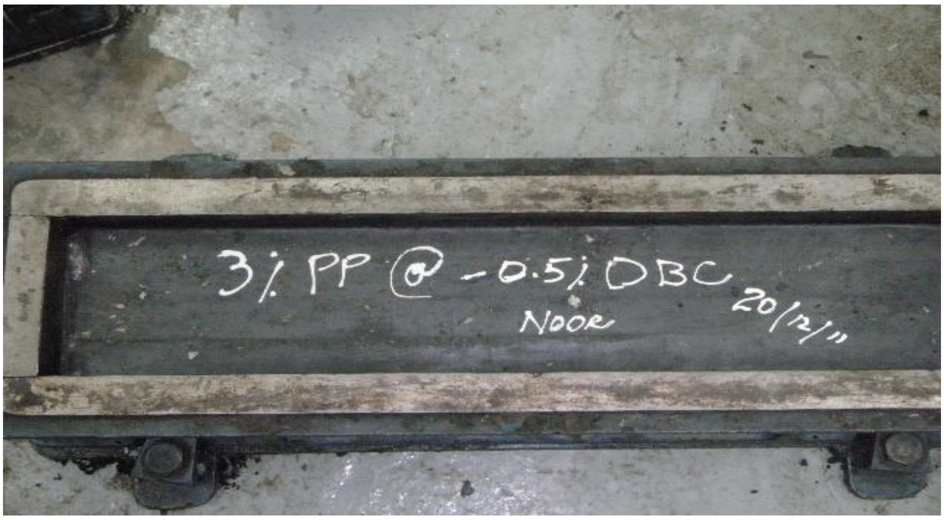

Figure 3.18: Compacted Beam Fatigue Specimen in mould

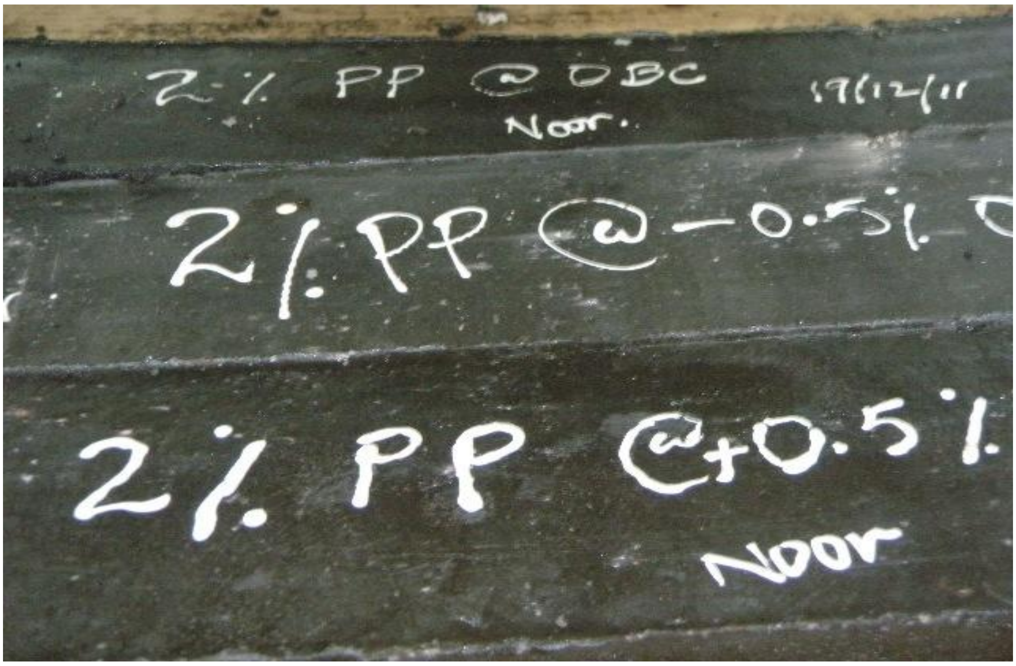

Figure 3.19: Prepared Beam Fatigue Specimen at different OBC

Figure 3.20: Saw cutter used for cutting of beams

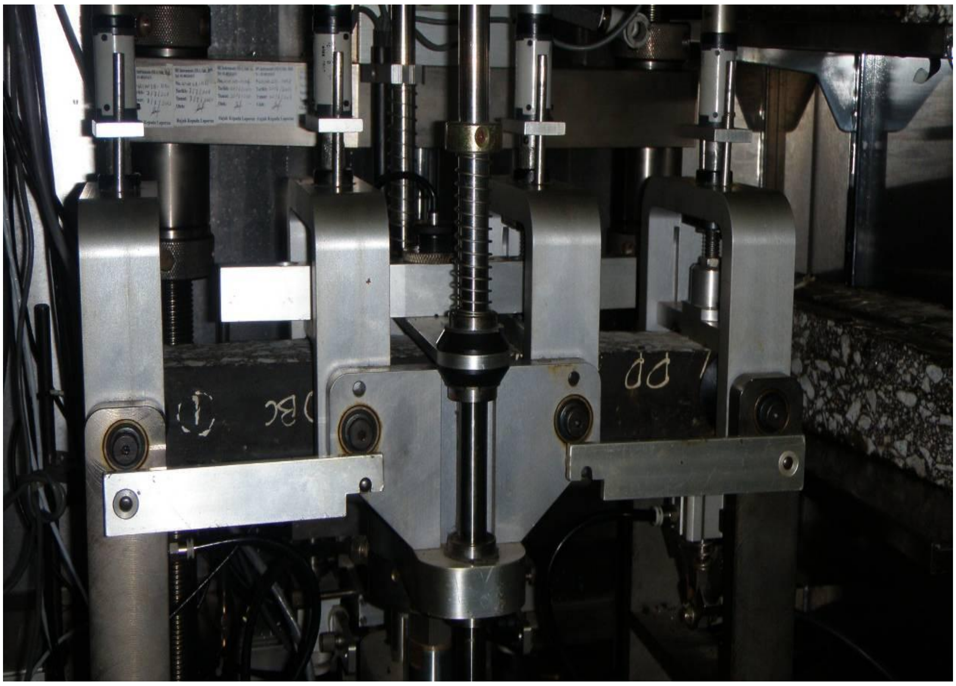

Figure 3.21: Beam Fatigue Testing Device

CHAPTER 4

CHARACTERIZATION TEST RESULTS

4.1 Introduction

Characterization of the binder is considered as most important tool as it relates the properties of binder whether modified or unmodified to its performance characteristics. In order to understand the fundamental properties of binder and the changes that occur due to polymer modification, compositional analysis is considered best suited technique.

The rheological and mechanical properties of binder especially the viscosity and stiffness particularly depend on chemical composition. The study of characterization was thus consider essential in order to understand the key role played by polymer in altering the rheological properties and the way these properties get affected due to environmental condition especially due to oxidation.

Thus the role of this chapter is to discuss the test results in following manner

- The results of conventional test carried out on the binders which include penetration, softening point and viscosity test methods.
- The results obtained from chemical characterization test, which were conducted using compositional measurement and analytical measurements on polymer modified and virgin bitumen.

The test results of all above mentioned tests were used to develop a relationship that exists between binder properties with respect to change in rheology which later can be related to morphology.

The virgin base binder 80/100 pen grade when blended with Polypropylene (PP) and Linear low density polyethylene (LLDPE) at low shear rate of 120rpm for 1 hour at temperature 160ºC induces some changes which alter the chemical structure of the virgin bitumen.

The change in properties due to oxidation is considered as most important factor which cannot be overlooked, although it also does occur during bitumen manufacturing process at refinery [148]. The absorption of oily component of bitumen by polymer while blending [30] also alter the chemical composition of the virgin bitumen, affecting its rheology and morphology.

Thus the objective of work presented in this chapter is to determine the impact of the change in chemical composition/ characteristics on the rheological characteristics which later on related to morphological changes and mechanical characteristics of binder evaluated by performance test on virgin and polymer modified bituminous mixes.

The characterization test results discussed in this chapter includes

1. **Conventional Test on binders**

- Penetration (ASTM D - 5)
- Softening Point Test (ASTM D - 36)
- Viscosity (ASTM D - 4402)

2. **Compositional measurement using**

- Precipitated asphaltene content (ASTM D - 3279) by using *n*-heptane.
- SARA chromatographic method (ASTM D - 4124)

3. Analytical Measurements

Analytical techniques were used to provide definite evidence of the extent of polymer modification of the binders. Analytical techniques used include:

- Chemical composition of binder using modern analytical technique

  GC/MS.
- Infrared measurement using FTIR to determine the carbonyl compound, which indicates binder oxidation.
- Elemental composition using CHNS analyzer.

4.2 Conventional Test Results on Binders

4.2.1 Penetration Test Results

From Table 4.1 it was observed that there is a sharp decrease in the penetration value for all polymer modified bituminous blend in comparison to 80/100 penetration grade base bitumen. For control 80/100 pen bitumen a sharp decrease in penetration from 84dmm to 34dmm & 35 dmm for 1% PP PMB and LLDPE PMB respectively was observed. This trend of decrease in penetration value was observed for all polymer concentration in the blend. It reflects that increase in the hardness of the PMB is associated with polymer loading. The use of the high molecular weight PP and LLDPE having a melt flow index of 8g/10min and 0.9g/10 min respectively increases the viscosity of the PMB with the increase in polymer content. It is obvious from the results that PP and LLDPE belonging to thermoplastics family influences more on the penetration with the increase in the viscosity of the bitumen [13]. Although PP has a melting temperature between 160 - 166°C, it does not completely dissolved into the bitumen but it absorbs some oil and release low molecular weight fractions into the bitumen which increases the viscosity of the PMB [30]. Similarly for LLDPE at melting temperature of 122ºC, the crystalline polymer would break into smaller pieces during blending which tremendously increases the viscosity and thus hardness of the modified PMB blend. As complete compatible polymer bitumen blend could not be achieved during one hour mixing at a temperature of 160ºC, thus partially miscible polymer bitumen blend was achieved at the end of mixing.

Table 4.1: Properties of Virgin and Polymer Modified Binders

Binder Type	80/100 Pen Bitumen	LLDPE PMB				PP PMB			
% Polymer	-	1%	2%	3%	5%	1%	2%	3%	5%
Penetration (dmm)	84	35	30	25	13	34	30	28	15
Softening Point ºC	53	53	53	60	67	54	55	55	59
Viscosity at 135ºC (Pa s)	0.44	0.63	0.76	1.43	1.87	0.78	0.81	0.83	1.25

When this partially miscible polymer bitumen blend was allowed to cool, it would form two segregated layer. The top layer composed of floating immiscible polymer, while the lower one composed of partially miscible polymer bitumen blend. The phase segregated polymer layer at top for the PP and LDPE PMB would thus act as a sheath against the penetration needle, where the stiffness of the top separated layer increases with the increase in polymer concentration.

Thus the hardening effect induced by the modification can be considered beneficial as it would increase the stiffness of the material. This would in turn increase the load spreading capabilities of the structure but also can lead to fretting or cracking [13].

4.2.2 Softening Point Test Results

The results obtained from the softening point test are shown in Table 4.1. It shows that no significant difference in the softening temperature for PMBs up to 2% concentration of polymer in blend was observed as compared to virgin 80/100 pen bitumen. This behavior of PMB reflects the properties of thermoplastics, where modification does not significantly affect the softening point as compared to the penetration [13].

One hour mixing time at temperature 160ºC was considered insufficient to chemically break isotactic polypropylene or linear branched low density polyethylene. Formation of thermodynamically stable internal structure might also be considered as the cause of stable softening temperature at lower polymer concentration. As the concentration of polymer increases LLDPE shows rapid increase in softening point in comparison to PP.

The insignificant difference in softening temperature of 80/100 pen bitumen and PP PMB was due to the phase segregated layer in the brass ring. The lower phase segregated layer consisting of bitumen portion with minimum amount of partially dispersed polymer will deform at slightly higher temperature than the softening temperature of virgin bitumen while the upper segregated polymer layer stays there. Thus lower phase segregated layer with partially dispersed polymer was considered to be responsible for minimum increase in softening temperature till 5% polymer concentration in PP PMB.

For LLDPE PMB as the melting temperature of LLDPE was lower, thus chances of polymer melting during one hour mixing was more. Although phase segregation was still there but the concentration of miscible polymer within polymer bitumen blend in the lower layer would be high. Thus increase in temperature with an increase in polymer concentration was observed, as higher temperature would be required to soften the LLDPE PMB at higher polymer concentration. This was confirmed by 3% and 5% LLDPE PMB which shows higher softening temperatures. The softening test results of PP and LLDPE modified binders were considered as highly favourable, as least variation in softening temperature of polymer modified bitumen would thus benefit in resisting shear flow of material at higher pavement temperature.

4.2.3 Viscosity Test Results

The flow behavior of the material described in terms of viscosity, has considerable influence on internal friction thus on shearing behavior of mixture. Binder with a higher viscosity gives better aggregates interlocking with higher internal friction angle of modified asphalt mixture [114]. Temperature and loading also affect the behavior describing the viscoelastic properties of the material. The internal structure of the base bitumen also play key role affecting the flow characteristics of the binder [60] . Whether mixing was achieved by mechanical or chemical method, the differences in molecular weight and polarity of base bitumen and polymer has critical affect on compatibility [149] and thus on the viscosity of the final blend. Thus the viscosity of the binder was considered as influencing factor relating the rheological behavior of the binder to its morphological evolution.

Viscosity test results discussed over here includes LLDPE and PP PMB results with respect to viscosity 80/100 penetration grade bitumen. To meet the requirements of ASSHTO MP1 (Specification for Performance Graded Asphalt Binders) viscosity measurements were made at 135ºC, using Brookfield viscometer.

In order to compare the results obtained from viscosity test results, Bitumen Test Data Chart (BTDC) developed by Heukelom (1960) and Asphalt institute 2001 was used as reference.

BTDC provides the range of viscosity for mixing and compaction. According to BTDC for mixing at temperature between 135 - 160ºC, ideal viscosity was considered between 0.2 – 2 Pa s. At this viscosity the binder can coat the aggregate properly. For compaction the viscosity range at 135ºC was defined in between 2 Pa s to 20 Pa s, considering the workability of the mix [13]. AASHTO MP1 put maximum viscosity limit of 3 Pa·s when tested at 135ºC to ensure sufficient workability of the mixture.

Mixing and compaction viscosities for Superpave mix design as revealed by Asphalt institute 2001 recommends 0.17 ± 0.02 Pa s at mixing temperature and 0.28 ± 0.03 Pa s at compaction. The manual also put the note that these viscosities are not valid for modified asphalt binders [150].

From the above mentioned discussion it was noted that there is no specification available to determine the viscosity of the modified binder. Determination of viscosity by using viscometer considered the only choice to determine the viscosity range of the modified binder at specific polymer content.

Figure 4.1 and 4.2 presents the viscosity test results of LLDPE modified binder and PP modified binder respectively. From Figure 4.1 the viscosity profile of 80/100 penetration grade bitumen shows minimum fluctuation in the viscosity against increasing shear rate. Thus for 80/100 pen bitumen, almost 0.44 Pa s viscosity was observed at all shear rate. This behavior of bitumen represents Newtonian characteristics. Thus it can be safely concluded that virgin 80/100 pen bitumen offers some sort of *sol* - *gel* characteristics.

From Figure 4.1 it was also observed that there was an increase in viscosity with the addition of polymer in bitumen except for 1% LLDPE concentration where decrease in viscosity with respect to virgin bitumen was observed. This unusual behavior of 1% LLDPE PMB exhibits shear-thinning behavior or pseudoplasticity, where linear branched low density polyethylene molecule disassociates or break with increasing shear rate. The lower concentration of polymer in blend does show weak interaction between polymer and bitumen [59] which was being confirmed by scanned images of LLDPE PMB (presented in chapter on morphological analysis) where distinct phase separated domains of polymer and bitumen were visible. This non- Newtonian characteristic for LLDPE PMB was observed with the decrease in viscosity with the increase in shear rate for all concentration of polymer in blend expect for 2% LLDPE PMB where the change in viscosity with respect to shearing was quite insignificant. Thus it can be concluded that viscosity of polymeric solutions are shear rate dependent, as shear rate influences the internal structure of the PMB [60]. This behaviour of modified bitumen can also be attributed due to reversible breakdown of structure which is commonly found in multiphase system of polymer modified bitumen [151]. As LLDPE although have melting temperature of 122ºC, was not fully dispersed in bitumen because of higher molecular weight, exhibit both thixotropy and viscoelasticity at all concentration of polymer in the blend. 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 later on end up with creaming [5].

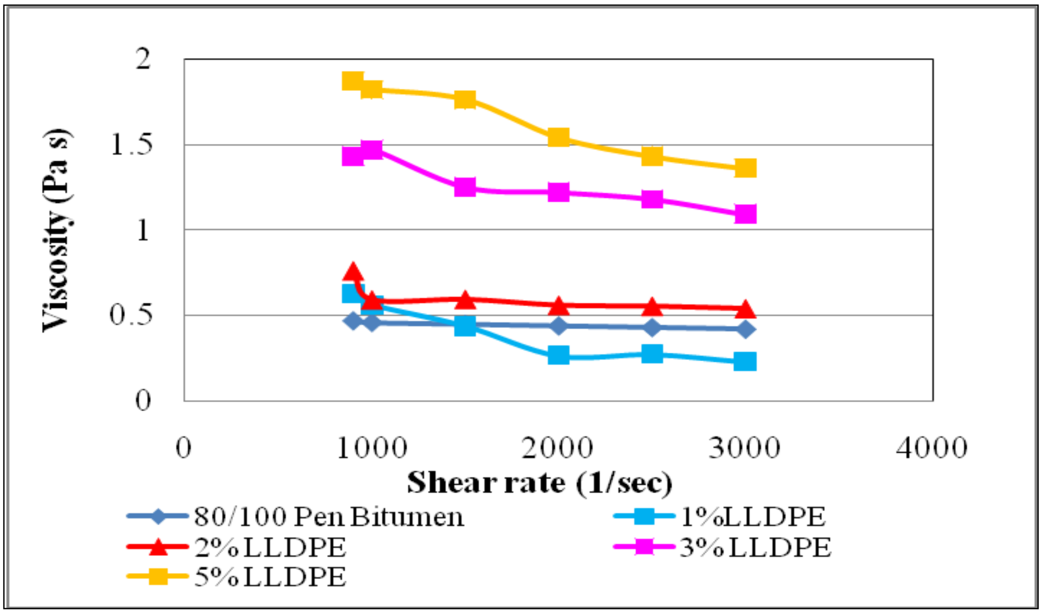

Figure 4.1: Viscosity of Virgin 80/100 Bitumen & LLDPE PMB at 135ºC

From Figure 4.2 it was observed that there is an increase in viscosity with an increase in polymer concentration. PP PMB also offers less fluctuation at all concentration of polymer in the blend. It is very difficult to say that polymer modified bitumen purely exhibit shear thinning phenomenon with the decrease in viscosity with the increase in shear rate as very mild shear thickening phenomenon was also observed at 5% LLDPE and PP PMB. This pseudo plastic behaviour of PMB may be attributed due to breakdown of structure, or polymer particles existing in equilibrium state being more aligned offering lesser resistance to flow. With the increase in shear rate these particles would offer higher resistance due to agglomeration, aggregation or flocculation of particle in multiphase system as the inter particle forces like Brownian, van der Walls forces become prominent [151].

Although thermoplastic does not swell well when blended with bitumen but increases the viscosity. Even this minor volumetric change in the blend was because of the structural change in the PMB blend enhancing the mechanical properties of the blend. The improved viscous property of modified binder would be considered as one of additional factor increasing the cohesion and internal friction angle of mixture offering higher shear strength reducing the chances of rutting in the pavement. From the viscosity test results as presented in Table 4.1 it was observed that the values of viscosity for all polymer concentration are well below 3Pa s, as mentioned by ASSHTO MP1 for workable bituminous mix [43].

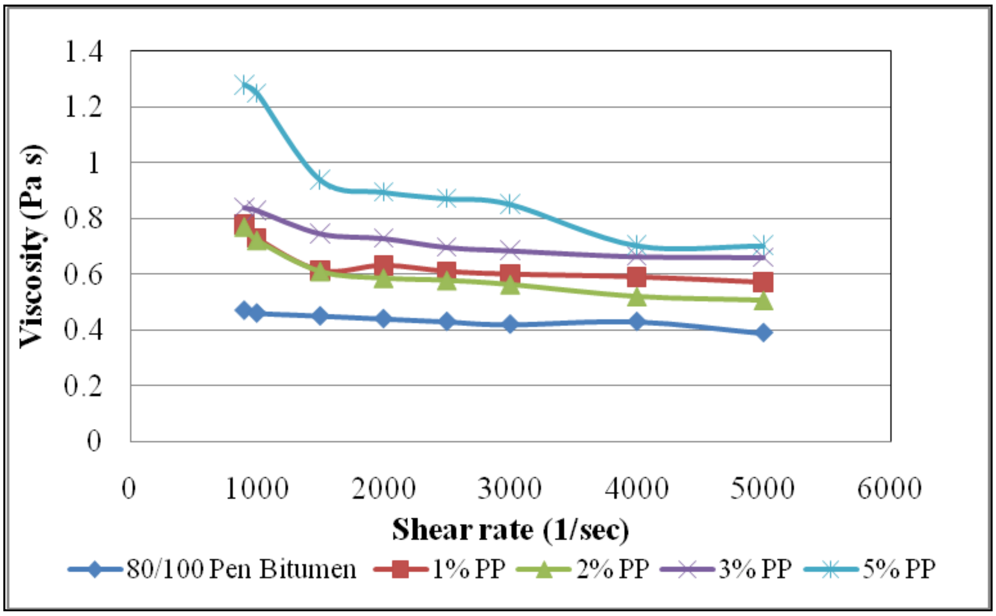

Figure 4.2: Viscosity of Virgin 80/100 Bitumen & PP PMB at 135ºC

4.3 Compositional Measurements Results

4.3.1 *n*-heptane Precipitation Results

Precipitated asphaltene contents were determined by using n-heptane precipitation method. The type of asphaltene determined by this method is known as C_7 asphaltenes. The amount of asphaltene in bitumen varies from 5% - 25% depending upon crude source. Asphaltene have H/C = 1.58 and contains around 14.8 wt% oxygen [1]. The amount of the asphaltene precipitated out from the solution depend on the solubility parameter of solvent used [67]. Thus the amount of asphaltene extracted from bitumen would depend on the strength of the solvent.

The asphaltene content of both virgin and polymer modified bitumen were determined using the above mentioned method are shown in Figure 4.3. Asphaltenes in bitumen basically composed of highly polar agglomerated molecules and considered to be the building block for all structure present in bitumen [67]. The amount of asphaltene present affects the colloidal stability of the bitumen. In calculating the colloidal instability index “CI” of the bitumen the important governing factor is asphaltene, where asphaltene were dispersed in dispersing phase. Asphaltenes are mainly responsible for the viscosity and the colloidal behavior of the blend [68].

From the Figure 4.3, an increase in asphaltene content was observed with the addition of polypropylene (PP) polymer and linear low density polyethylene (LLDPE) into virgin 80/100 pen bitumen.

This variation in asphaltene composition with the addition of polymer indicates that there exists some slight chemical reactivity in the blend although both polypropylene and linear low density polyethylene were non - polar in nature. The mixing and shearing of polymer at temperature between 160ºC may form some free radicals which would react later with the tertiary carbon atom in polymer chain and induces some polymer degradation [8]. Thus the macromolecule which was produced due to degradation, having free radical may undergo to chain scission or cross linking with another chain or molecule and thus helps in the formation of new molecule. Thus it can be safely concluded that an increase in asphaltene content in the blend might have occurred because of this phenomenon. The formation of asphaltene can also be considered due to the oxygen uptake by the reactive part of bitumen [68] mainly considered as heteroatoms.

The increase in asphaltene can also be related to the oxidation of the bitumen during mixing at higher temperature, where the binder get oxidized by the formation of carbonyl groups ($C = O$), which increases the polarity of the bitumen and thus it shows more association to other polar compound or asphaltene [152] which are less soluble and can be easily separated upon precipitation.

Polypropylene (PP) and polyethylene in the form of LLDPE which belongs to plastomeric group of polymer when blended with bitumen were partially immiscible due to their non-polar nature. During blending at temperature 160ºC, there is a chance of thermal degradation which might have occurred with the discharge of free radical which then interact with the tertiary carbon atom in long chain of polymer forming crosslinking [8].

This behavior of Polypropylene (PP) can also be well explained by looking at its structure. Polypropylene (PP) which is basically non-polar in nature mainly composed of carbon and hydrogen beside methyl pedant group. When PP is added to virgin 80/100 pen bitumen some of the branch segment of PP get detached because of weak London dispersive forces and get oxidized forming more stabilized oxidized compound mainly composed of asphaltene. Thus a linear increase in asphaltene content was observed with the increase in polymer content. The same phenomenon can be considered applicable for linear low density polyethylene which is also nonpolar in nature. For LLDPE the trend in the increase of asphaltene with the increase in concentration of polymer in the blend was quite consistent or rather insignificant with the marginal increment of asphaltene. Thus it can be safely concluded that short branched chain structure of LLDPE shows little affinity to get oxidized during mixing at 160ºC. As asphaltene content is considered as byproduct of oxidation, thus LLDPE was considered to be less oxidized during blending because of its nonpolar nature showing marginal increment of asphaltene with the increase in concentration of polymer in the blend.

Although the formation of asphaltene is still not clear till today, but it has been suggested by the researchers that number of forces like Van der Waals, dipole-dipole interaction, hydrogen bonding or due to π - π bonding between aromatics considered as one of the cause of formation of asphaltene [25].

Thus the change in asphaltene concentration for both LLDPE and PP polymer modified bitumen were confirmed by the penetration and viscosity test results where there was a decrease in penetration and increase in viscosity of all polymer modified blend in comparison to virgin bitumen was observed.

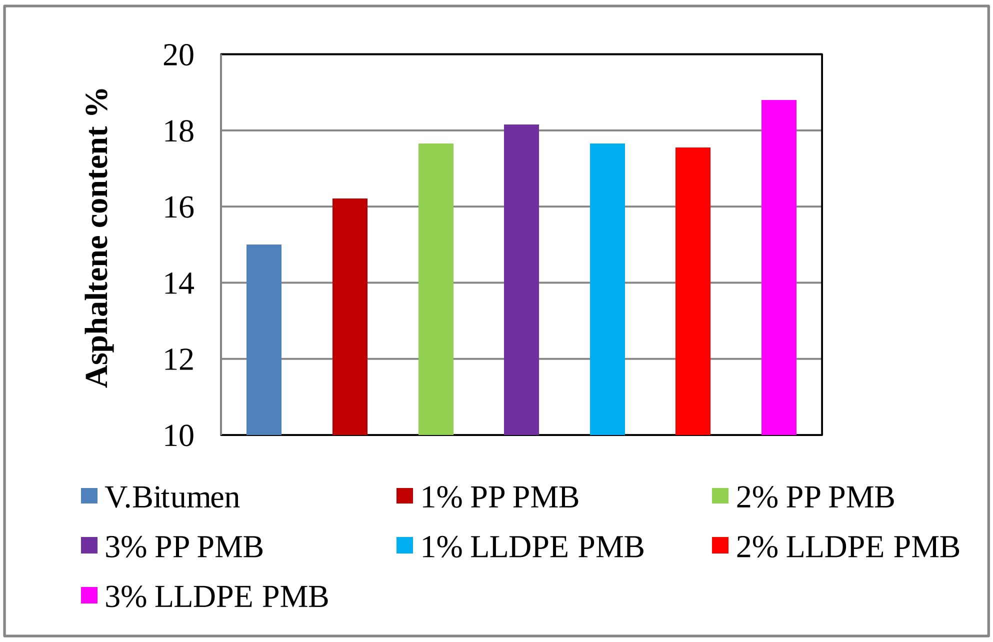

Figure 4.3: Asphaltene content in Virgin & Polymer modified bitumen

4.3.2 SARA Chromatographic Results

The study of SARA fractionate analysis provides an insight into the roles that each fraction plays in determining the physical and chemical properties of binder. The interaction between these fractions affects the rheological and morphological properties of binder which ultimately reflected in mechanical properties.

From the SARA test results presented in Table 4.2, it was being observed that modification of bitumen by the inclusion of PP changes the composition of different fraction of virgin bitumen. There was an increase in asphaltene content at the expense of aromatics were observed for all PP modified bitumen. Thus the possibility of aging due this chemical change confirmed by the decrease in aromatic content with the increase in resin content along with asphaltene [1]. The generation of resin can be attributed due to decrease in aromatics leading to the generation of asphaltene [13].

Table 4.2: Compositional Analysis of Virgin Bitumen and Polymer Modified Bitumen

	Asphaltene (5 - 25)wt%	Saturate (5 - 15)wt%	Aromatics (30 - 45)wt%	Resins (30-45)wt%	Colloidal Index CI
V.Bitumen	15	12	41	31	0.38
1%PP PMB	16.2	6.77	39.63	36.8	0.30
2%PP PMB	17.65	7.52	38.28	40.66	0.31
3% PP PMB	18.15	8.09	25.45	46.10	0.37
1%LLDPE PMB	17.65	19.74	34.44	27.33	0.6
2%LLDPE PMB	17.56	18.25	37.54	25.52	0.57
3%LLDPE PMB	18.8	17.33	41.85	21	0.57

$$\text{Colloidal Index CI} = \frac{(\text{Asphaltene} \quad +\text{Saturate})}{(\text{Aromatics} \quad +\text{Resin})}$$

Saturate are the lighter fraction of bitumen consisting of linear chain of n- alkanes. They lack polar functional group thus doesn’t get adsorbed on the column bed and eluted first. The decrease in saturate was also observed for all percentage of PP modification.

Decrease in saturate for all PP modified blends indicates that these linear chain of low molecular weight might have been absorbed by the polymer while the rest get eluted from the chromatographic column when flushed with *n* heptane. This causes polymer to swell due to absorption of oily component of bitumen by polymer. Saturate are responsible for the fluidity or responsible for dilution effect [32] helping dispersion of asphaltene in oily medium.

The decrease in aromatics for PP was observed with the corresponding increase in resin content. This decrease can be attributed due to oxidation of aromatics to resin and resin to asphaltene [6, 77].

SARA results was used to further understand the colloidal stability of the system by calculating colloidal index (CI), which is ratio of dispersed medium (Asphaltene + Saturate) to dispersing medium (Aromatic + Resin). It was observed that values of CI increase with the increase in concentration of polymer in the blend. The lower value of CI indicates that asphaltene micelles were well dispersed in the dispersing medium (aromatics & resins). As the CI increases the stability of the blend decreases [67]. Increase in resin content considered beneficial to polymer modified as increases the adhesive properties of binder beside increasing its ductility [67]. Another reason for the increase in resin content with the increase in concentration of polymer might be because of certain amount of un precipitated asphaltene which were remain trapped in *n*- heptane solvent may not have washed out when treated with trichloroethylene solvent. As the structure of resin chemically resembles the structure of asphaltene which is mainly composed of nitrogen, sulfur, oxygen with traces of metal beside carbon hydrogen [67] thus consider responsible for the increase in asphaltene content.

In short it can be concluded that the PP modified blends shows better colloidal stability because of the lower CI observed for all concentration of polymer in bitumen. The SARA results for PP polymer modified bitumen revealed the truth about viscoelastic behavior as observed by viscosity test result. The enhanced viscosity and non Newtonian characteristic of PP modified bitumen was due to increase in colloids formed due to modification. As the concentration of PP increases a slight change in viscosity was being observed while sheared apart at increasing shear rate. This behavior may be attributed due to increase in asphaltene which were formed during mixing process which increases the polarity of the blend. The increases in the molecular mass and decrease in the content of aromatics hydrocarbons, thus contribute to the formation of *gel* type of bitumen behaving more or less like polymeric solution [20].

From Table 4.2 it was observed that there was an increase in saturates and a decrease in aromatics and resins were observed for all LLDPE modified binder. The increase in saturate content for LLDPE indicates the inert behavior of LLDPE during mixing. The decrease in aromatics and resin indicates the hardening of binder due to oxidation [153]. Decrease in resin indicates an instability of the blend, as resin acts as stabilizer to the asphaltene [28] reported that resin might get adsorb to asphaltene forming a multilayer structure on the surface of asphaltene.

This behavior attribute to the formation of harden binder where there is a decrease in maltene or dispersing medium. The LLDPE modified binder thus behaves more like *gel* solution with the decrease in elasticity due to increase in viscosity of the binder. The hardening of the binder was also confirmed by the increase in colloidal index, with the increase in percentage of polymer in bitumen.

The increase in saturate content also has impact on the increase in viscosity of the binder with the corresponding increase in asphaltene content [31]. This is due to low solvating potential of the maltene phase which fails to disperse the asphaltene thus enhancing the agglomeration of asphaltene micelle enhancing the viscosity of the blend.

Since the lower value of colloidal index (CI) indicates a well connected network structure, while higher value of CI values indicates higher agglomerated asphaltene micelle in bitumen leading to the formation of gel type structure [154] thus it can be safely concluded that PP modified bitumen would offer better compatibility behaving more or less like *sol- gel* type bitumen while higher CI values for LLDPE modified bitumen indicating the *gel* behavior of binder.

The results obtained by SARA fractionate would thus helped in understanding the viscosity results for both PP and LLDPE modified bitumen where puesdoplastic behavior and enhanced viscosity at higher polymer concentration would be considered rendered by the increase in asphaltene content. Although the SARA analysis provide information about the fractionate composition of binder but the chemistry of multi phase (asphaltene rich phase and polymer rich phase) is still unclear as the multiphase system of polymer bitumen blend not only depends on polymer and bitumen constituent but also on the mixing temperature and time. Significance of SARA results in binder characterization is considered as most important as it would further helps in understanding the properties of modified binder in view of its rheology and morphology which can be later on related to the mechanical strength of the PP and LLDPE modified bituminous mixture.

4.4 Analytical Measurements Results

4.4.1 Gas Chromatography/Mass spectrometry (GC/MS) Results

The chromatograph representing detected compounds obtained from GC/MS are attached in Appendix. From the retention time observed for each chromatograph it was observed that chromatograph of virgin and polymer modified bitumen represent almost the same compound as observed for crude oil when compared with the built in library of the equipment.

For virgin 80/100 Pen bitumen the maximum compound obtained at retention time of 1.218 min, indicates presence of propene C_3H_6 in abundance, followed by hexene, heptene etc as shown in Table 4.3. All these compound observed in GC/MS analysis are product of olefins, an unsaturated chemical compound mostly produced during the production of crude oil. Bitumen being by product of crude oil shows similarity with crude oil composition as revealed by GC/MS results. The chromatograph signals for 18 min retention time shows maximum unsaturated olefins.

The GC/MS results obtained from PP PMB shows maximum content of propene with greater retention time, revealing the abundance of propene which is the major constituent of polypropylene polymer. Presence of esters compounds, like methyl propyl ester shows the presence of oxidized compounds, outcome of oxidation as also being confirmed by FTIR and CHNS results.

The GC/MS result for LLDPE PMB shows that at all polymer concentration, the presence of oxidised compounds like aromatics cycles with paraffinic and naphtenic carbons. Presence of polycyclic aromatic hydrocarbons containing sulphur element (like thiophenic compound) also indicate presence of oxidized compounds. Thus GC/MS results thus confirms the SARA chromatographic test result where presence of saturates in bitumen detected as paraffinic compound (saturated chains) and napthenic cycles of lower polarity and molecular mass. Aromatic are found in bitumen as aromatic cycles having paraffinic alkanes (C_n+H_{2n}) and napthenic hydrocarbon (cycloalkanes). Sulfur also exists with aromatics [82] detected as thiophenic compond.

Table 4.3: Compound detected in GC/MS

Compounds detected in V.Bitumen and Polymer Modified Bitumen	**Detected compound represents**
80/100 pen Bitumen: 1) Propene 2) Hexene, Heptene, Octene, Nonene, Decene, Tridecene & Tetradecene. 3) Benzenesulfonic acid, Ethyl ester, 4-methyl ester. 4) Benzenedicarboxylic acid, 2-methylpropyl ester.	1) Major component of crude oil, detected in bitumen. 2) Representing all unsaturated hydrocarbon having double bonds(C=C) usually alkenes. 3) Compound representing presence of sulfoxide compound(S=O). Sulfur content always present with asphaltene. 4) Compound representing presence of oxidized compound(C=O) having benzene ring.
1% PP modified bitumen: 1) Butene, 1-propene, Heptene, Nonene, Tridecene, octadecene. 2) Sulfurous acid, butyl tridecyl ester, 2-propyl tridecyl ester.	1) Unsaturated hydrocarbons. 2) Indicates presence of sulfoxide compound and hydroxyl group.
2% PP modified bitumen: 1) Butene, 1-propene, Heptene, Nonene, Tridecene, octadecene. 2) Benzene, 2- dimethyl ester, cyclohexane, 3- dimethyl benzene, benzo thiophene, dibenzothiophene. 3) 2- propyl tridecyl ester, sulfurous acid, oxalic acid, cyclo hexane, cyclohexanecarboxylic acid.	1) Unsaturated hydrocarbons. 2) Presence of aromatics cycles with paraffinic and naphtenic carbons containing sulphur element (like thiophenic compound). 3) Indicate presence of oxidized compound in bitumen.
3% PP modified bitumen: 1)Propene,nonene,decene,decane. 2) Benzene, cyclohexane, cyclopentane,cyclopropane, benzothiophene,hexadecane. 3) Sulfurous acid, 2-propyl ester, cyclopropanecarboxylic acid, cyclohexanecarboxylic acid, 2-propyl tridecyl ester.	1) Unsaturated hydrocarbons. 2) Presence of aromatics cycles with paraffinic and naphtenic carbons containing sulphur element (like thiophenic compound). 3) Indicate presence of oxidized compound in bitumen.

Compounds detected in Polymer Modified Bitumen	Detected compound represents
1% LLDPE modified bitumen: 1) Pentene, heptane,Decane, cyclohexane, undecene. 2) Benzene, tetra methyl, 5-methylene, napthalene. 3)Sulfurous acid, 2-pentyl ester,cyclododecane, cyclohexane, cyclopropane, benzothiophene. 4)isobutyl heptadecyl ester, oxalic acid,ethanol.	1) Unsaturated hydrocarbons. 2) Presence of aromatics cycles with paraffinic and naphtenic carbons. 3) Presence of polycyclic aromatic hydrocarbons,containing sulphur element (like thiophenic compound). 4) Indicate presence of oxidized compound in bitumen.
2% LLDPE modified bitumen: 1)1-Propene, 2-Butene, 1-Nonene. 2) Cyclopentane, benzene, cycloheptane, cyclododecane, cyclopropane, benzothiophene, 2-methylbenzaldehyde, naphthalene. 3) Benzothiophene, ethanol, oxalic acid, isobutyl heptadecyl ester, sulfurous acid, 2-propyl tridecyl ester.	1) Unsaturated hydrocarbons. 2) Presence of aromatics cycles with paraffinic and naphtenic carbons. 3) Presence of polycyclic aromatic hydrocarbons,containing sulphur element (like thiophenic compound).Indicates presence of oxidized compound.
3% LLDPE modified bitumen: 1) Cyclooctane, undecene, dodecene. 2) Benzene, naphthalene, 2-ethenyl trimethyl naphthalene, Cyclopropane, benzothiophene. 3) Sulfurous acid, oxalic acid, ethanol, octadecyl 2-propyl ester.	1) Unsaturated hydrocarbons. 2) Presence of aromatics cycles with paraffinic and naphtenic carbons. 3) Presence of polycyclic aromatic hydrocarbons,containing sulphur element (like thiophenic compound).Indicates presence of oxidized compound.

4.4.2 Fourier Transform Infrared (FTIR) Spectroscopy Results

FTIR was used in order to study the functional groups present in the virgin bitumen and polymer modified bitumen.

It is well understood that modification of bitumen with polymer brings in the compositional changes as observed by the SARA results. These changes that occur due to oxidation during mixing at plant or at site gave rise to formation of functional group which then consider being responsible for the change in physical properties of the material [76]. Thus FTIR helps in the determination of the changes in chemical composition of binder due to oxidation both at mixing at plant or due to ageing at site which ultimately will ends up hardening or deterioration of binder properties. The deterioration may occur in the form of loss of adhesion between binder and aggregate or loss of cohesion in the form of bitumen phase separation [18].

The FTIR spectra for virgin and modified bitumen are shown in Figure 4.4 to 4.12. From the spectra observed for unmodified virgin bitumen and polymerized bitumen shows that there was a slight change in the spectra for PP and LLDPE modified bitumen. From these spectra it can be safely concluded that addition of polymer might have reduced the rate of oxidation of asphaltene in bitumen [75].

From the spectra shown in Figure 4.4 to 4.10, a small number of sulfoxide groups were noted at band frequency of 1030 cm^{-1} due to (S = O) stretching. This might have produced due to oxidation of sulfur compounds which almost remain consistent with the increase in polymer concentration of bitumen indicating modification does not induces oxidative aging which usually occurs in the early part mixing. Strong peaks of aromatics C - H stretching and methylene vibration was observed at band frequency of 2850 cm^{-1} and 2920 cm^{-1}. The FTIR spectra for the PP and LLDPE modified bitumen indicates that although the mixing was done with slow shear rate mixture and at 160°C, but the interaction of polymer with bitumen sufficiently changes the chemical structure of the modified binder as it was observed by SARA chromatographic test results. The change in maltene composition of the polymer modified bitumen was thus confirmed by the FTIR test results.

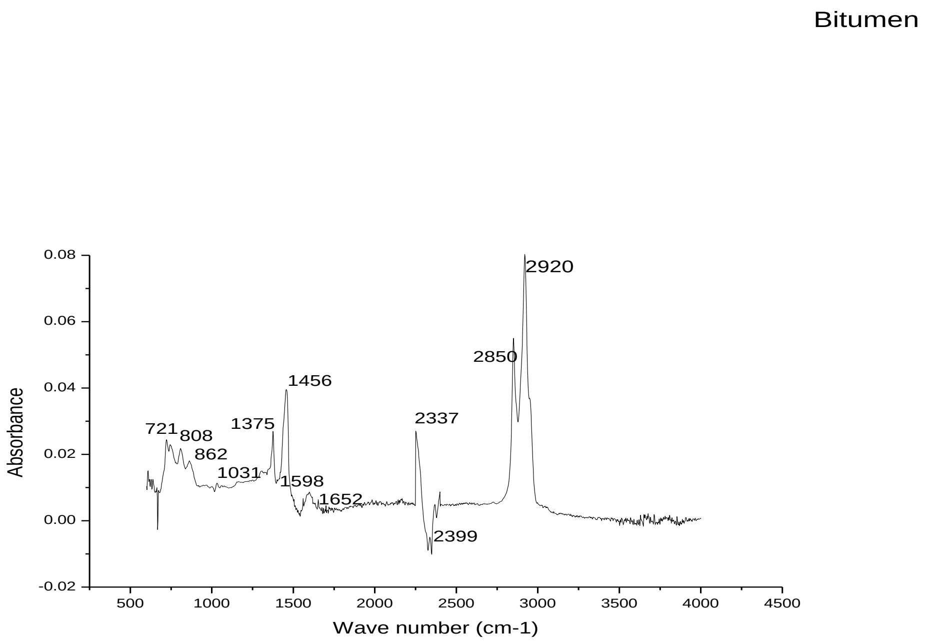

Figure 4.4: FTIR Spectra of Virgin Bitumen

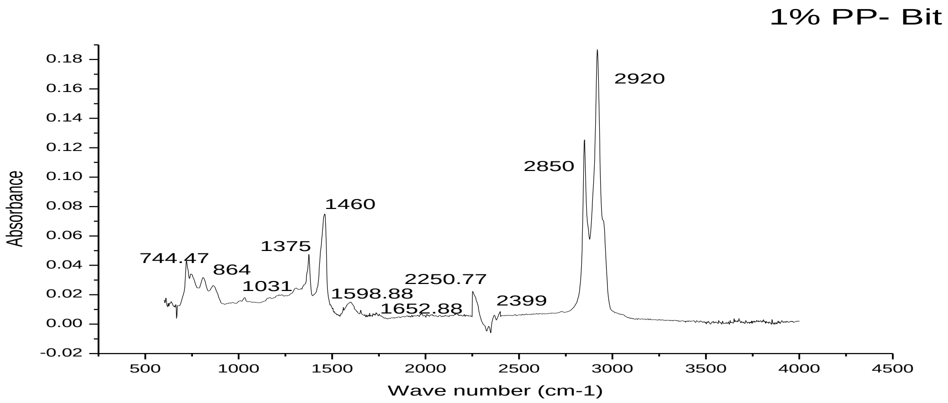

Figure 4.5: 1% PP –Bitumen FTIR Spectra

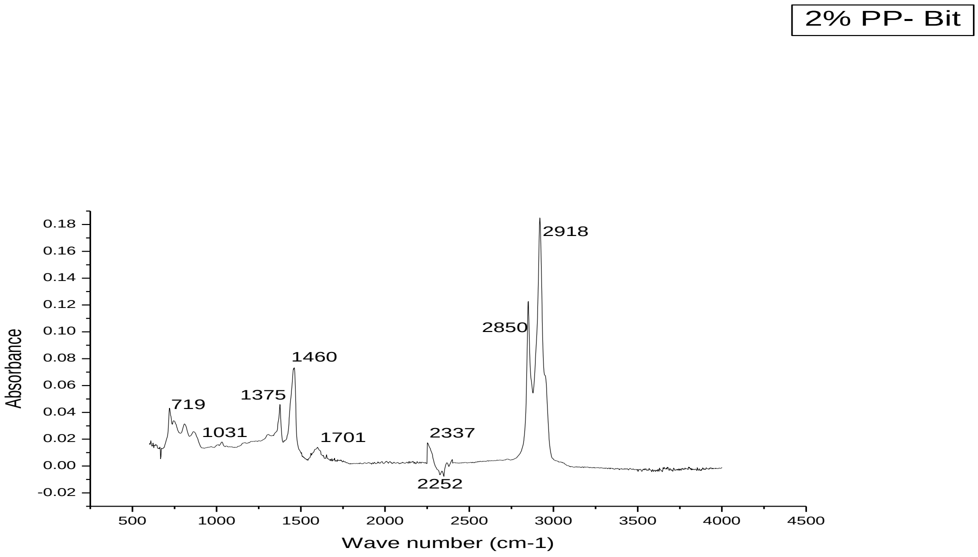

Figure 4.6: 2% PP –Bitumen FTIR Spectra

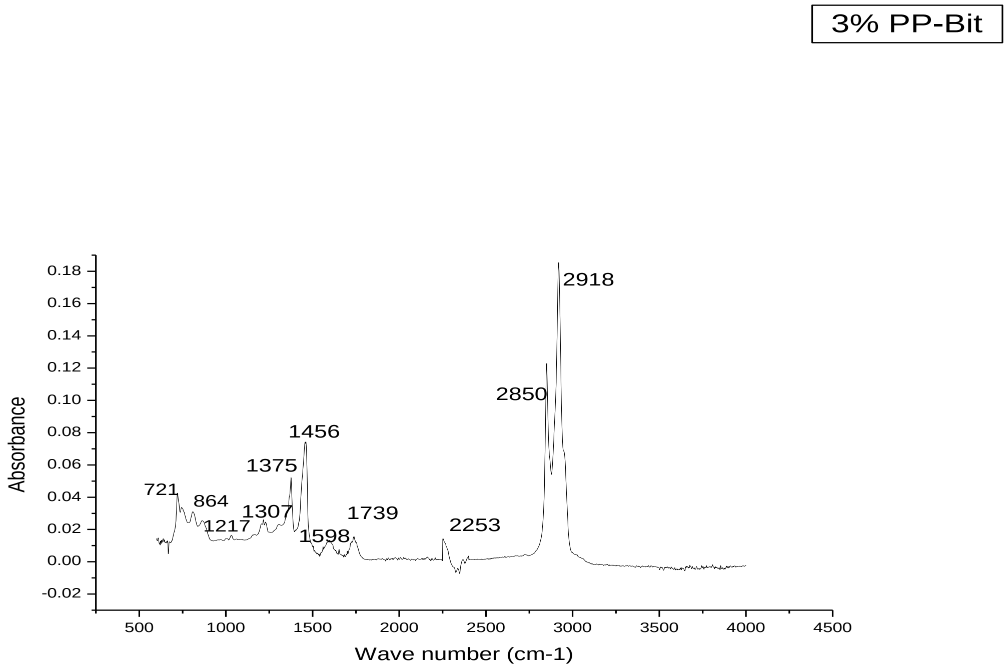

Figure 4.7: 3% PP –Bitumen FTIR Spectra

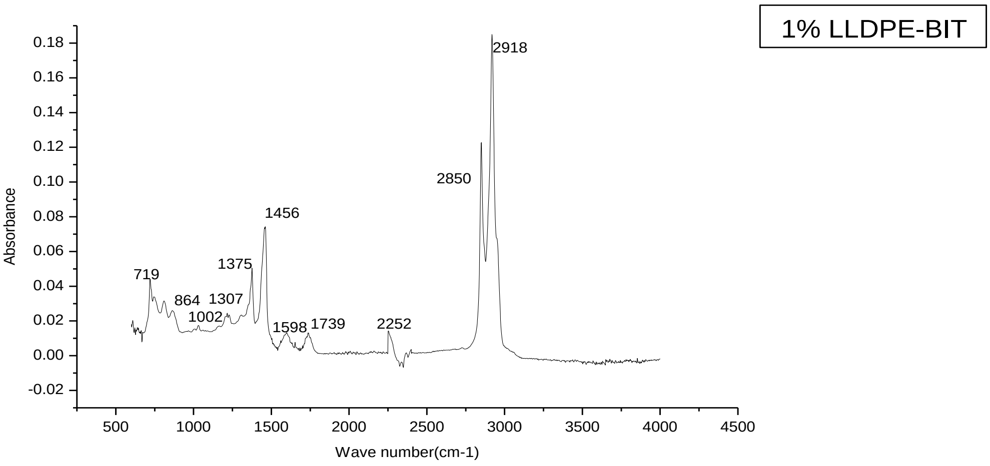

Figure 4.8: 1% LLDPE –Bitumen FTIR Spectra

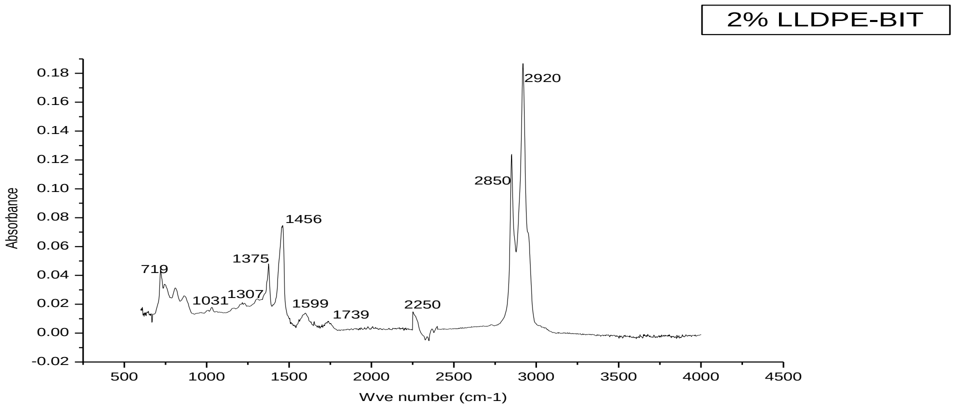

Figure 4.9: 2% LLDPE –Bitumen FTIR Spectra

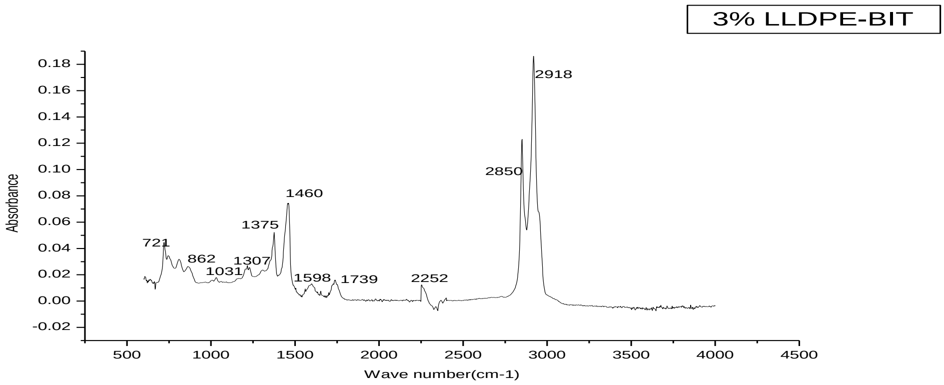

Figure 4.10: 3% LLDPE –Bitumen FTIR Spectra

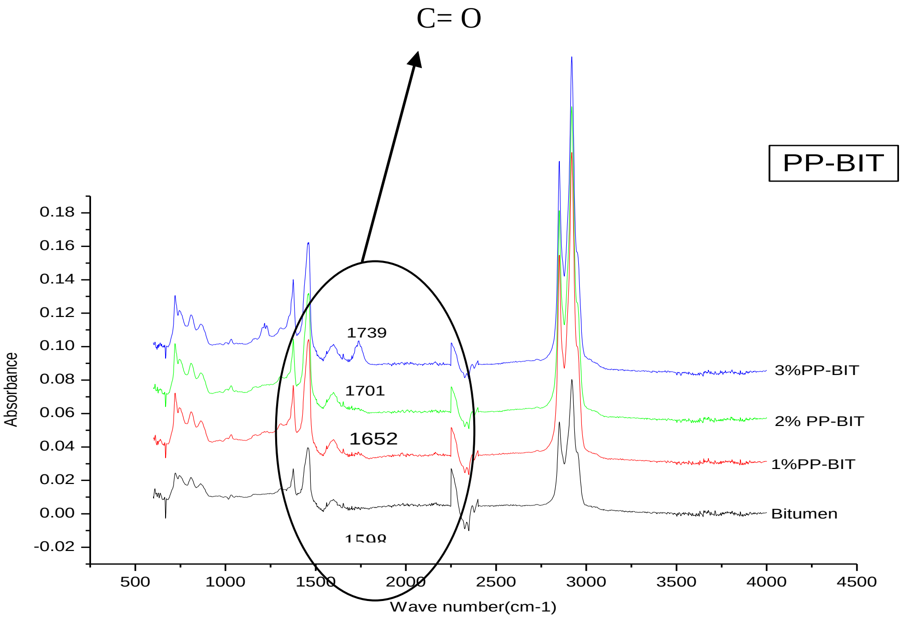

Figure 4.11: Combine FTIR spectra of Virgin Bitumen and PP modified bitumen

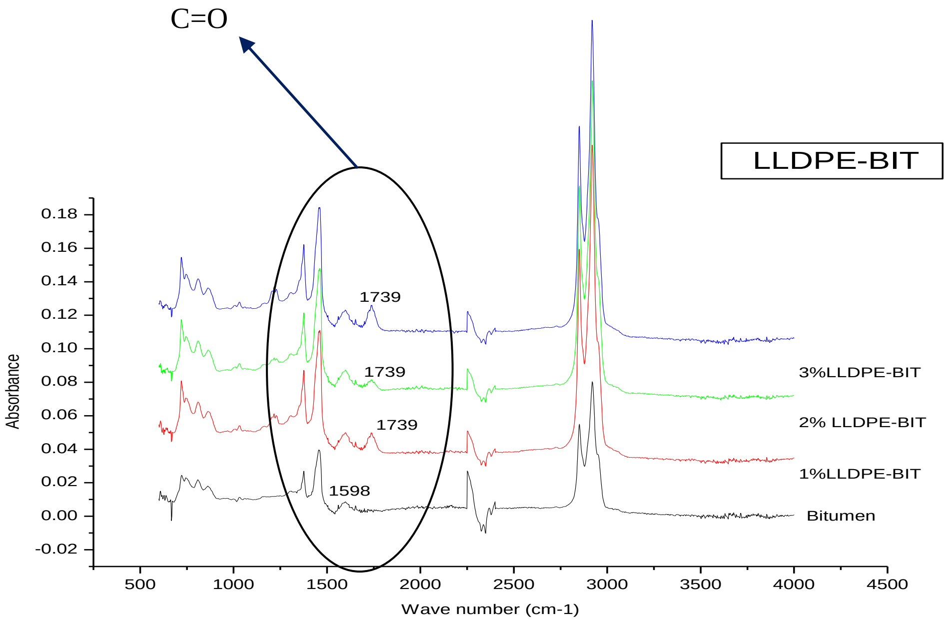

Figure 4.12: Combine FTIR spectra of Virgin Bitumen and LLDPE modified bitumen

Clear peaks around band frequency of 1375 cm^{-1} and 1465 cm^{-1} was observed representing either C - O bands or aromatic carboxylic acid. The carbonyl group was observed at absorption frequency of 1598 cm^{-1} for virgin bitumen which increases with the addition of polymer in bitumen till 1739 cm^{-1} (refer Figure 4.11) indicating presence of unsaturated or aromatic carboxylic acid formed due to stretching of C=O. The functional groups that are formed during oxidation include carboxylic acid, ketones and aldehydes.

Functional group composition variation effect the physical properties of the material as these group represent the presence of asphaltene and resin fraction [76]. For PP modified bitumen the growth of oxidative compounds increases linearly with the concentration of polymer indicating increase in polarity of the blend. The inert behavior of LLDPE modified binder was also confirmed by FTIR results where for LLDPE modified bitumen the increase in polymer concentration doesn't enhances the oxidation rate or in other words formation of polar compound does not increase with the increase in polymer concentration as being observed by 1739 cm^{-1} peak for all concentration of LLDPE in bitumen (refer Figure 4.12).

The results of FTIR verifies the result of SARA for PP and LLDPE modified bitumen which shows increase in asphaltene content for PP modified bitumen but insignificant increase in asphaltene content for LLDPE modified bitumen as observed from the FTIR spectra shown in Figure 4.11 & Figure 4.12 for PP and LLDPE modified bitumen. Thus the increase in C_7 asphaltene can be considered due to bitumen oxidation during mixing at plant which results in the formation of carbonyl group due to increase in polarity of bitumen which induces the formation of intermolecular hydrogen link [77]. The increase in polarity due presence of polar compounds also consider as a factor helping affinity of binder adhesion to mineral aggregates in mix.

Thus information about functional group composition helps in understanding asphaltene and resin fraction. Thus presence of heteroatom along with functional group affects the physical properties of the material due to chemical interactions, which resulted due to changes in the colloidal properties of the bitumen [76].

4.4.3 CHNS Analyzer Test Results

Elemental composition analyzer is a quick method used to detect the presence of carbon, hydrogen, nitrogen and sulfur in organic matter where as oxygen is calculated from difference. The amount of heteroatom in the bitumen gives an indication about the type of functional groups present in the material. The content of heteroatom present in bitumen depends on origin of crude oil.

From CHNS results as presented in Table 4.4 it was observed that there is no change observed in sulfur content with modification but weak peak around frequency 1030 cm^{-1} indicating presence of sulfoxide (S = O) which considered as the product of oxidation of bitumen was observed in FTIR spectra for all modified sample. Thus the chances of oxidation due to sulfur cannot be over looked as existence of sulfur containing compounds provokes oxidation process. Sulfur is always present with asphaltene.

Table 4.4: Elemental Analysis using CHNS analyzer

Fraction	C (82-88%)	H (8-11%)	N (0-1%)	S (0-6%)	O^d (0-1.5%)
Pure Bitumen	87.01%	9.50%	0.401%	3.86%	0%
1% PP –Bit	84.95%	9.29%	0.529%	3.13%	2.10%
2% PP –Bit	84.31%	9.54%	0.413%	3.58%	2.15%
3% PP –Bit	83.36%	8.52%	0.345%	3.55%	4.21%
1% LLDPE- Bit	81.28%	9.99%	0.859%	3.305%	3.93%
2% LLDPE-Bit	78.51%	9.69%	1.06%	3.393%	7.3%
3% LLDPE –Bit	77.55%	9.51%	0.949%	3.379%	8.6%

O^d Oxygen is determined by difference

Oxygen being the polar component of bitumen also increases with the modification for all concentration of polymer in the blend. The increase in polarity was due to formation of ketones, phenols and carboxylic acid [1]. The FTIR spectra of PP and LLDPE modified bitumen verifies the increase in polarity of the binder with the formation of carboxylic acid at band frequency of 1739cm^{-1}. For virgin bitumen the traces of oxygen was almost negligible as being detected by CHNS analyzer but modification induces oxidation resulting in the formation of carbonyl (C - O) or hydroxyl (O - H) or carboxylic acid (C = O). The increase in oxygen content for 2% and 3% LLDPE modified bitumen also confirms the results of SARA where an increase in asphaltene and aromatic content was observed for LLDPE modified bitumen as also observed from the SARA chromatographic test results as presented in Table 4.2.

From the CHNS results as presented in Table 4.4, it was observed that there was a an increase in oxygen for all percentages of PP and LLDPE modified bitumen in comparison to virgin bitumen which does not show any traces of oxygen in the sample. For PP modified bitumen the highest percentage was observed for 3% PP and for 3% LLDPE modified bitumen. Thus the presence of oxygen indicates formation of ketones, phenols or carboxylic acid. The concentration of these polar atom acts as initiator for the formation of most functional groups which was already being detected during FTIR analysis. The presence of these compounds may lead to deterioration of pavement by ageing.

Although the amount of carbon, nitrogen, hydrogen and sulphur detected by CHNS analyzer was small but presence of these elements in small percentage has significant impact on the chemical composition of bitumen [16] which affect the rheological behavior of the binder.

Thus it can be safely concluded that an increase in viscosity can be related to an increase in oxygen content which is the basic source of formation of hydroxyl, carbonyl and ester groups. The formation of ester groups are of importance as it links two different molecule and thus contribute to the formation of higher molecular weight material. The increase in asphaltene content was related to this change which affect the colloidal stability and rheological properties of bitumen [16].

4.5 Summary of the Results

From the above discussed results it was revealed that modification of the bitumen with linear low density polyethylene and polypropylene has significant effect on the physical and chemical properties of the binder. Although the mixing of polymer with bitumen was done by slow shear rate mixer at 160°C, but one hour mixing significantly affected the chemical and rheological behavior of the modified bitumen. For PP modified binder the changes were reflected by the compatibility of polymer with bitumen as being observed by lower CI values in comparison to LLDPE modified bitumen. This compatibility was reflected by the increase in hardness and increase in binder’s viscosity. The softening temperature almost remained same but it was observed it increases with an increase in polymer loading as also being reflected by the increase in viscosity especially for LLDPE modified binder. The increase in viscosity was found to be well correlated with an increase in asphaltene content, well detected by the presence of carbonyl group which was confirmed by the formation of aldehyde, ketones and phenol. The compounds detected either by GC/MS or by FTIR or by CHNS analyzer proved the existence of chemical activity which was attained by only physical dispersion of the polymer in the bitumen.

From the conventional test results it was revealed that for modification of bitumen by LLDPE or PP, polymer concentration up to 3% seems more effective as higher concentration would lead to excessive increase in viscosity of the modified binder.

CHAPTER 5

MORPHOLOGICAL ANALYSIS OF VIRGIN AND POLYMER MODIFIED BITUMEN

5.1 Introduction

Morphology is the study of microstructure. Understanding of chemistry and microstructure is essential to properly define the compatibility of the bitumen and polymer modified bitumen. As the polymer is blended with the bitumen chemical structure and morphology changes, which ultimately influence the rheological and mechanical properties of binder [155].

The morphological analysis was used in this study to have an insight of polymer – bitumen interaction and how it is going to affect the rheological and mechanical properties of the final blend. The modification of virgin bitumen with the polymer alters the structure of the bituminous bend whether the interaction considered as only physical interaction or chemical interaction. In both cases the interaction between polymer and bitumen brought changes to the microstructure of the bituminous blend affecting the physio-chemical properties of the PMBs. Thus, in short the morphology or the structural orientation of the final PMB blend is strongly influenced by mixing temperature, technique and time beside the type of the polymer used for modification.

In this research morphological analysis was carried out with view that it can be later related to rheological changes that occurs due to modification. The morphological phases that evolved after mixing also influence the mechanical characteristics of the binder or in short the performance characteristic of the modified bituminous mixture.

The morphological analysis for this research was conducted using Field Emission Electron Microscopy (FESEM), Atomic Force Microscopy (AFM) and Transmission Electron Microscopy (TEM).

5.2 Analysis of Field Emission Electron Microscopy Scanned Images

FESEM images gives information about phase describing the extent of compatibility of the blend. The analyzed samples describe the extent of the continuous phase in the blend and compatibility of the polymer with bitumen within the blend. The compatibility of the bitumen with the polymer depend on molecular weight, as higher molecular weight polymer are incompatible with lower molecular weight bitumen [1].

For all scanned images two phenomenon's flocculation and creaming was very prominent. Creaming is caused due gravitational effect, due to difference in density between dispersed phase and continuous phase. The difference in particle size, particle size concentration and distribution of particle to dispersing phase also considered as controlling factor for the stability of the colloidal system. Instability in the system can lead to gravity induced flocculation and creaming side by side [156, 157].

Although there is slight difference between densities of polymer (LLDPE = 0.918 g/cm^3 & PP = 0.95 g/cm^3) and bitumen (1.01 g/cm^3) creaming due to gravitational affect do occur. Thus instable colloidal system which occurs due to difference in densities would simultaneously undergo gravity induced flocculation and creaming side by side as observed for all scanned images of PP and LLDPE polymer modified bitumen samples.

The FESEM scanned sample of virgin 80/100 penetration bitumen as shown in Figure 5.1 does not show any morphological behavior of bitumen due to low resolution power of FESEM. When the same virgin bitumen blended with polymer (PP or LLDPE) a change in morphology was observed even at this low resolution.

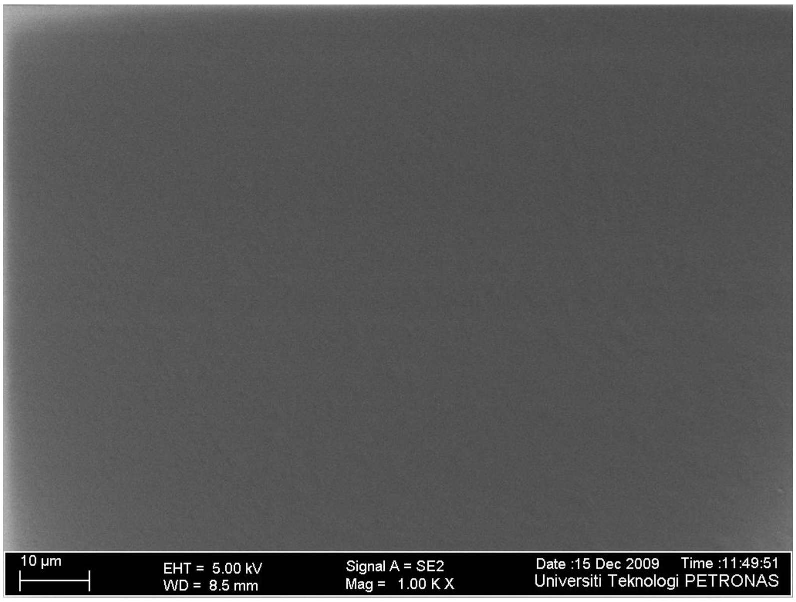

Figure 5.1: FESEM Scanned image of Virgin Bitumen

From Figure 5.2 (a) till 5.2 (c) LLDPE modified scanned images were presented. LLDPE which was used in pallet form seems to remain undissolved to certain extent although the melting point of LLDPE is 125ºC. The partial breakage of periphery of the pallet remains suspended in bitumen as observed for all LLDPE concentration of polymer. As the concentration of polymer increases more creaming of blend was observed which was also confirmed by the viscosity test results which shows increase in viscosity with the increase in concentration of polymer in the blend.

For LLDPE, when polymer was blended at 160°C it releases some lower molecular weight fraction in bitumen which increases the viscosity of the blend. The flocculation among particles was due to absence of Brownian motions among particles and the only reason for the breakdown of these particles at high temperature was creaming, which ends up with coalescence [30].

The FESEM scanned images confirm the results of SARA analysis where an increase in colloidal index (CI) with value 0.6 was observed for 1% LLDPE PMB sample. This increase can be attributed due to the change in chemical composition with the addition of polymer in bitumen.

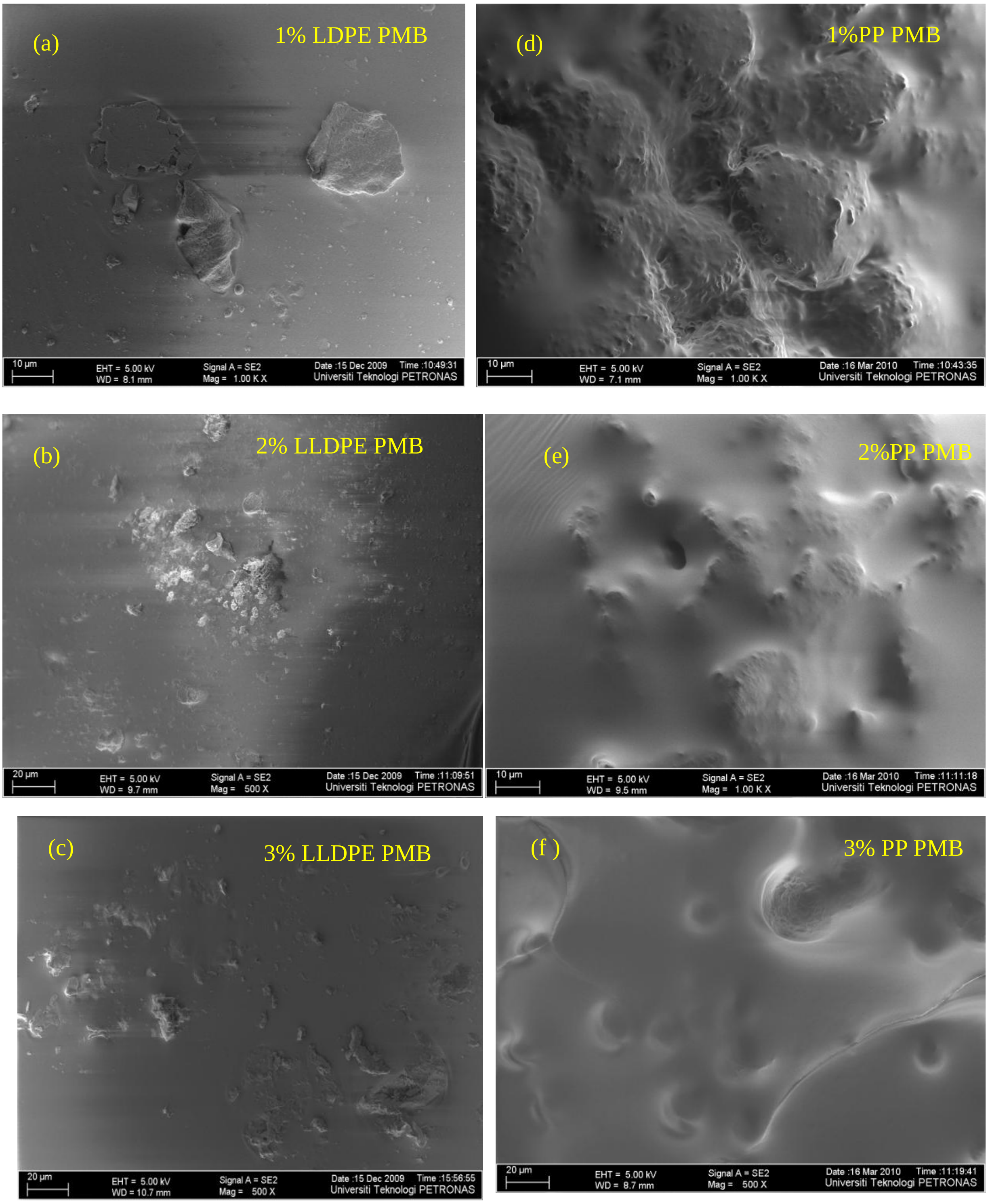

Figure 5.2: FESEM scanned images of LLDPE and PP modified bitumen

Although mixing for 1 hr at 160°C unable to completely dissolve the pallet of LLDPE but increases the viscosity due to breakage of short side branched chain or due to chain scission (breaking of a molecular bond causing the loss of side group or shortening of overall chain). No swollen polymer was observed even at lower concentration of polymer as LLDPE belongs to polyolefin group which shows lower tendency of swelling when blended with bitumen [8].

It was also observed from Figure 5.2 (b) and (c) that for 2% and 3% LLDPE PMB, insignificant variation in morphology was observed indicating that as the concentration of polymer increase more suspended undissolved particles were there which increases the viscosity of the final blend. From SARA with CI of 0.57 for both concentrations it is confirmed that compatibility of polymer with bitumen decreases as the concentration of polymer increases. Thus the incompatibility of LLDPE with bitumen, which was earlier reported by chemical analysis using SARA chromatographic method, is now being confirmed by FESEM scanned images.

From the scanned images of polymer PP modified bitumen as shown in Figure 5.2 (d) – 5.2 (f) swollen PP was observed in scanned samples till 2% polymer concentration. As the concentration was increased from 2% more creaming effect was observed which was due to the agglomeration of partially dissolved polymer. The main cause of phase separation of PMB was due to Brownanian coalescence followed by gravitational flocculation and later on end up with creaming [5].

At higher temperature of mixing, partially dispersed fine particles which are present among large polymer particles coalesce after meeting each other it causes splitting of the bitumen film inducing phase separation. The movement of these tiny particles due to Brownian motion increases the volume of the resulting particle due to agglomeration. Agglomeration cause an increase in the buoyancy force acting on the resulting large particle which when moves upward, it captures other slow upward moving particles in its way to the surface of the blend [158]. Thus the mechanism of this phase separation in PMB is also defined as coalescence followed by creaming which was observed more for 3% PP in blend.

The solvency of polymer PP was better in comparison to LLDPE as being observed with FESEM scanned images. This may be due to reduced size of PP as reduced particle size will decrease the buoyancy forces on the particles, which results in the stability of modified binder [30]. The maltene or oily component of bitumen shows better compatibility with polymer. PP which absorbs the oily component of bitumen swell up to certain extent as observed in figure 5.2 (d) for 1% PP PMB sample. This behavior of polymer PP was also confirmed from SARA test results where there was a decrease in saturate content by modification. For 2% & 3% PP PMB the creaming affects due to flocculation becomes more pronounced. Thus the flocculation affect for polymer PP in PMB blend was observed for all concentration of polymer in bitumen as observed by FESEM scanned samples which increases with the increase in concentration of polymer in the blend.

The results of PP modified FESEM scanned images are well supported by SARA results which explained the compatibility of blend in terms of colloidal index (CI). The lower values of CI varying between 0.3 - 0.37 for all PP modified samples shows that polypropylene offer better compatibility in comparison to LLDPE modified samples.

5.3 Analysis of Atomic Force Microscopy Scanned Images

In AFM the scanning was performed in phase detection mode (PDM) of dynamic force mode (DFM). The surface characteristics were made in phase mode. AFM measurement were made in phase detection microscopy (PDM) mode, conducted in tapping mode while maintaining the distance between the probe AFM tip and the sample. All the images presented here were taken at room temperature and at normal atmospheric pressure.

In tapping mode when the surface characteristics of sample are different the effects of interaction between the probe and sample were detected by the phase change. Images were obtained by the deflection of cantilever tip which scan the sample surface by detecting the forces between cantilever tip and sample surface change. The cantilever of AFM is excited to oscillate close to its resonant frequency.

Thus the tip of AFM which is only in intermittent contact with the sample surface records the changes of the effective (vertical) forces acting on the tip caused by the alteration in the oscillation amplitude and phase.

Thus PDM images which were taken by monitoring the difference between the oscillation signal sent to AFM cantilever and its actual oscillation corresponds to the interaction of cantilever tip and sample interaction [84]. The detected phase lag (δ) in output signal is considered analogous to rheological parameter used in bituminous material study tan δ which occur due to difference in stress and strain (tan δ= loss modulus/storage modulus or viscous component/elastic component) [84]. By recording the phase angle difference between the excitation force and the tip response of AFM it is possible to image compositional variations in heterogeneous samples [159]. The simultaneous recording of the topography and the phase shift by the oscillation of the cantilever relative to the driving signal as reference allows mapping of interaction properties of a heterogeneous sample. This phase imaging thus help to explore material properties like adhesion and viscoelastic properties [160].

5.3.1 AFM Analysis of Virgin Bitumen

AFM images were taken in tapping mode, which provides information in three dimensional topography and phase shift, as shown in the images of virgin bitumen in Figure 5.3 - 5.5. Phase shift contrast in tapping mode of AFM reveals different surface compositions on a surface.

Figure 5.3 & 5.4 shows a two dimensional phase image of virgin bitumen in which “bee” structure can be observed, which was believed to be asphaltene micelles [1, 92]. The three dimensional phase image of the same bee structure is shown in Figure 5.4, in which protruding tubers from the surface of maltene fraction can be observed. Within this protruding structure two different phases can be observed with alternating dark and bright regions [96].

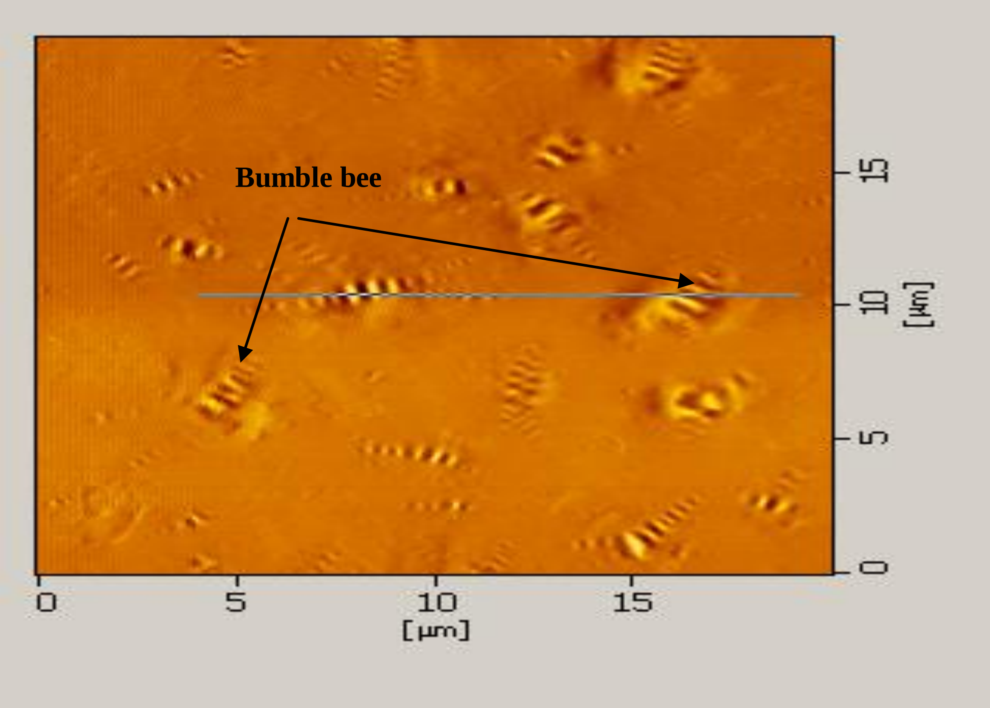

Figure 5.3: 2D Phase image of Virgin Bitumen

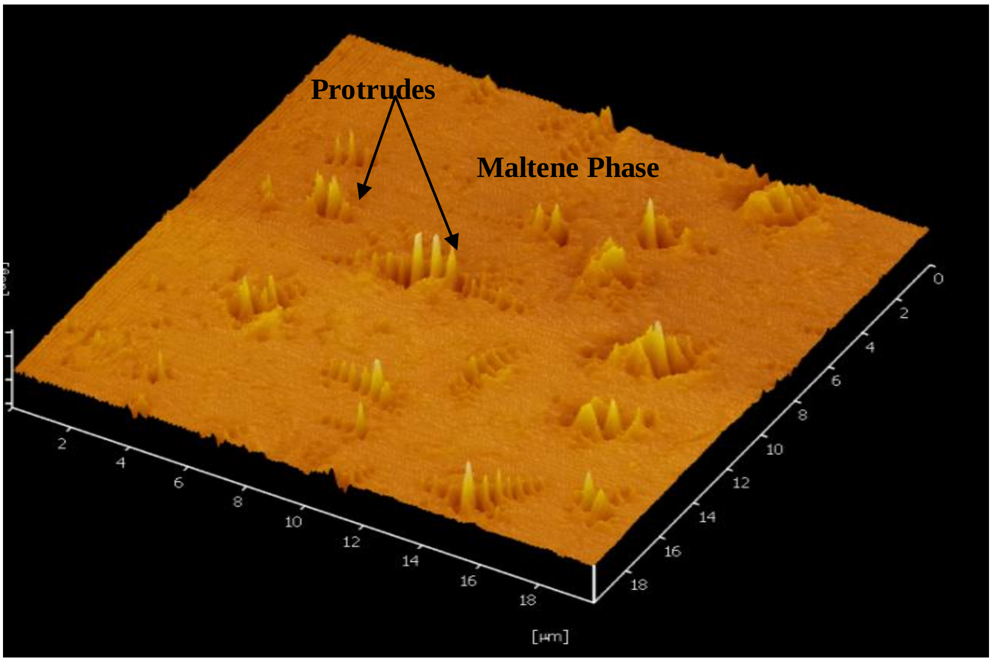

Figure 5.4: 3D Phase image of Virgin Bitumen

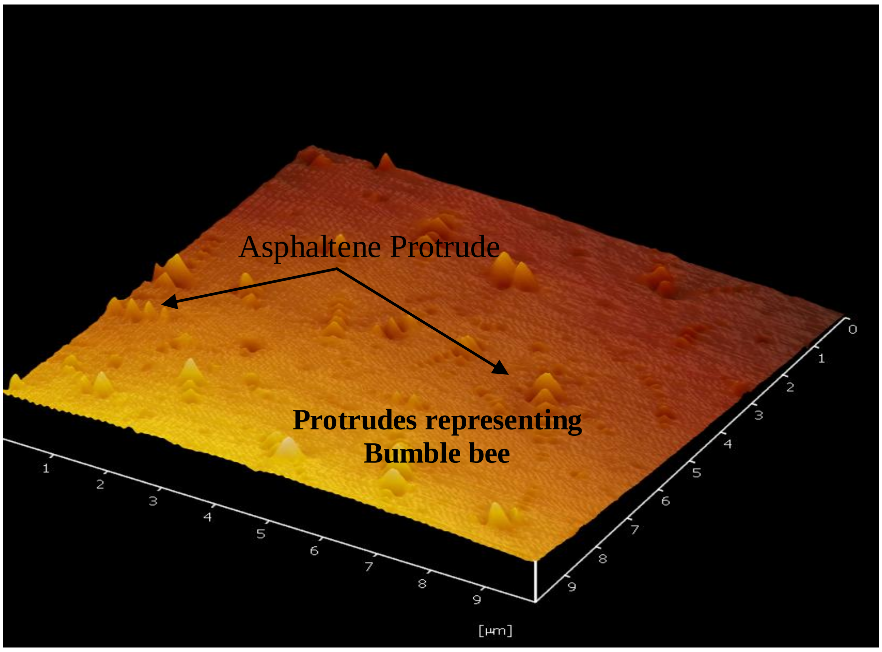

Figure 5.5: Topographic image of Virgin Bitumen

These alternating light and dark regions in bee represents portion of different relative stiffness (different viscoelastic properties) having contrasting mechanical properties. According to Loeber *et al* [92], catanaphase or bee can be assigned to the most polar fraction of the bitumen which is asphaltene, where the surrounding phase around bee structure formed by lighter or less polar fraction maltene composed mainly of resin and aromatics. The surrounding flat surface may be concluded as non polar saturates or alkanes. The phases observed within protruding structure has varying stiffness offering different mechanical properties depending upon the amount of protruds, commonly considered as asphaltene [93], the most aromatic structure composed of fused aromatic rings stacked together forming heaviest molecular weight fraction of the bitumen.

Bitumen comprising mostly of hydrocarbon also has traces of metals like Nickle, Vanadium or Iron which occurs in the form of oxides or porphyrine [13] or in the form of chelates (Ni2+ or VO2+) surrounded with asphaltene. Thus it can be suggested that *catana* or bee phase in bitumen consist of stacked layers of asphaltene or fused aromatic rings which were held together with considerable amount of Ni2+ and VO2+, chelated to form porphyrins [84] . Thus the dark and light protruding tubers emerging from the base as observed in the topographic image (Figure 5.5) needs further investigation although it is being confirmed that it has varying viscoelastic properties.

The greatest advantage of using AFM is in the calculation of phase lag (δ), which gives information about the viscoelastic characteristic of scanned images. The delay in phase lag represented by higher phase degree, represents that tip is in contact with higher viscoelastic part of the sample. The tip takes longer time to retract as being observed by higher phase lag.

For the bumble bee portion which is considered as asphaltene the phase lag values from peak to valley varies from 2.9° - 4.4°, showing highly viscoelastic character of asphaltene. For the well dispersed maltene phase the phase lag varies from 0.41° - 0.64°. From the above mentioned phase lag values it can be safely concluded that virgin bitumen necessarily composed of two phase, a well dispersed maltene phase in which highly viscoelastic asphaltene were present. Thus *gel* to *sol- gel* characteristic of bitumen as revealed from colloidal index value was confirmed by AFM phase images.

5.3.2 **AFM Analysis of Polypropylene Modified Bitumen**

The evolution of phase changes with the addition of PP in bitumen is shown in Figure 5.6 – 5.8. Phase evolution was observed with the formation of phase segregated polymer layer on the surface of bitumen whose thickness seems to be increasing with concentration of polymer in blend as higher molecular weight polymer seems to be incompatible with the lower molecular weight bitumen thus causing the phase segregation [1].

The 3D phase images of PP modified bitumen shows variation in surface roughness which decreases with the increase in polymer concentration in the blend. From Figure 5.6, 1% PP PMB phase image shows phase segreagted polymer layer almost totally covering the underneath bitumen layer, as evidenced by the disappearance of the “bee” structures.

It was also noted from Figure 5.6 that the phase image of 1% PP PMB is very rough, indicating that the surface is a micro-mixture of two materials having different viscoelastic properties. Thus it is possible to interpret from this image that PP segregated to the sample surface but has not covered it completely, and forming a surface that is a micro-mixture of bitumen and PP.

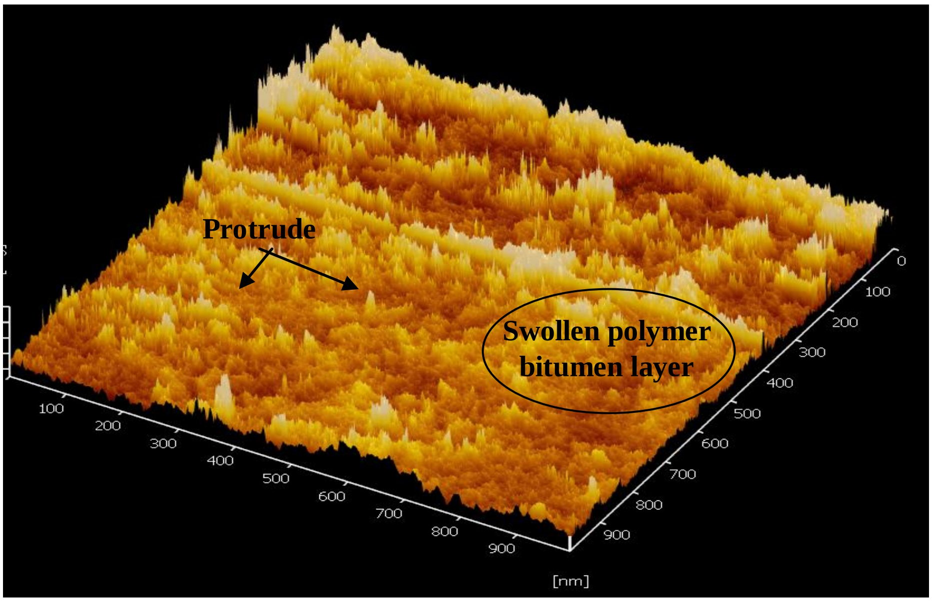

Figure 5.6: Phase image of 1% PP modified bitumen

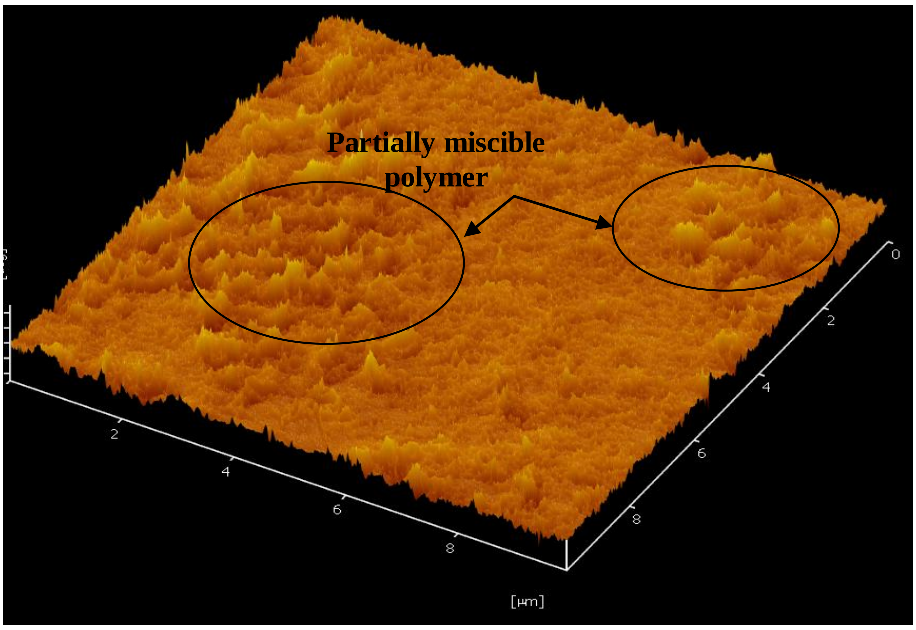

Figure 5.7: Phase image of 2% PP modified bitumen

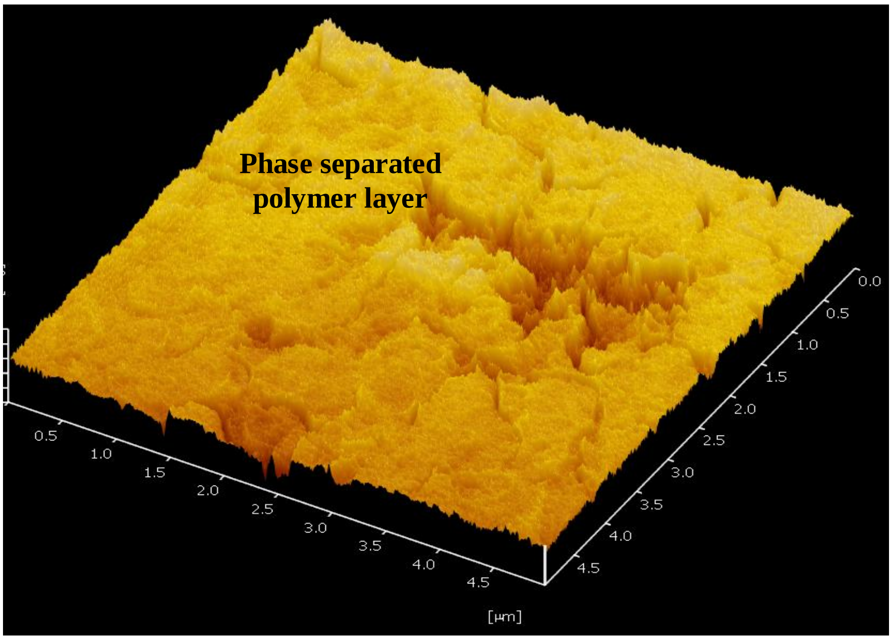

Figure 5.8: Phase image of 3% PP modified bitumen

Figure 5.7 of 2% PP PMB also shows surface roughness, but to much less degree as compared to 1% PP PMB, indicating that the cover-up of the surface by segregated PP is more complete when PP concentration is increased to 2% & 3% PP PMB (Figure 5.7 & 5.8) phase image expose a complete flat phase segregated layer of polymer above the bitumen.

These AFM phase images unfold the surface evolution by the segregated polymer is the phenomenon, which was observed for all polypropylene blends. The compatibility of polymer and bitumen are the two most important factors controlling the rheological behavior of the modified bituminous blend. The mechanical properties of the modified bituminous blend thus also depend on the extent of the compatibility and the concentration of polymer within the blend.

From all scanned images it was being confirmed that polypropylene which belongs to thermoplastic polyethylene group has the tendency of phase segregation which increases with the increase in polymer concentration in the bituminous blend.

The above images when analyzed in context with phase lag (δ) which is analogous to the rheological parameter tanδ (loss modulus/storage modulus) [84], helps in understanding the viscoelastic characteristic of modified binder. From analysis it was revealed that the viscoelastic characteristic of phase segregated polymer bitumen shows variation in phase lag values due to variation in viscoelastic characteristics induced by the inclusion of polymer in the bitumen blend as already being observed by scanned images.

For 1% PP PMB the phase segregated polymer bitumen layer shows the phase lag (δ) of 0.822°, indicating that the segregated surface composed mixture of two different materials which has higher viscoelastic characteristic due to the inclusion of polymer PP in comparison to virgin bitumen. Although inclusion of polymer affect the compatibility of virgin bitumen but lower value of colloidal index CI as observed by SARA test results i.e. 0.31 for 1% PP indicates that at lower concentration of polymer it does not completely change the chemical structure of bitumen but rather enhances its viscoelastic structure as being observed by phase lag for the 1% PP PMB blend.

For 2% PP, compatibility of polymer bitumen blend was confirmed with the lower value of CI as 0.31, which is rather a marginal increment in comparison to 1% PP, but increase in phase lag δ was observed from AFM which was found to be 1.006°. This increase in phase lag again refers to increase in viscoelastic component due to phase segregated polymer bitumen layer of 2% PP PMB.

For 3 % PP in bitumen production of instable and incompatible blend was observed which was also confirmed by increase in CI i.e. 0.37. The phase lag (δ), for 3% PP PMB found to be 0.865° indicating that blend was composed of highly viscous material but also composed of totally phase segregated polymer layer as observed by AFM scanned image. The segregated layer would thus consider unable to enhance the viscoelastic component of PMB which was obtained by the micro mixture composition of polymer and bitumen.

5.3.3 AFM Analysis of Linear Low Density Polyethylene modified bitumen

The compatibility and evolution of phase change due to modification for linear low density polypropylene (LLDPE) polymer modified bitumen are presented in Figure 5.9 - 5.14.

LLDPE pallet was used for blending with bitumen. The concentration of pallet was kept as 1%, 2% and 3% by weight of bitumen. LLDPE which has melting temperature around 125ºC [47], when mixed at 160ºC, the molecules of LLDPE starts moving and as the polymer melt it expand and get stretched, which ultimately breaks the Van Der Waals bond existing among long chain of polymer molecule beside strong covalent bond. Thus some part of side branch chain of LLDPE break and move around freely in the bitumen medium but remains entangled as the rate of mixing is quite low i.e. 120 rpm. By the time blending process completed and it was allowed to cool, the randomly entangled polymer chain starts to realign themselves or in other words may arrange themselves as neatly packed layer or stacked sheets which were observed as phase segregated well dispersed polymer layer and separate polymer domains in the scanned images.

Thus the morphological analysis of LLDPE PMB blend was studied in order to relate the above mentioned behavior of polymer in bitumen and how it is going to influence the rheological and mechanical properties of PMB as observed by changes in morphological properties. High molecular weight LLDPE seems to be incompatible with bitumen as the phase segregation because of the agglomeration of polymer was prominent in all scanned images of AFM.

From Figure 5.9 scanned phase images of AFM for 1% LLDPE which was taken in tapping mode, polymer seems to cover the underneath bitumen layer completely as the protruding tuber previously seen in virgin bitumen scanned image was no more visible in 1% LLDPE phase image.

The scanned phase images also revealed that it consist of two distinctive phases one showing the agglomerated polymer domain light in color indicates swollen polymer, was formed due to absorption of oily content of bitumen (maltene) by the polymer LLDPE and swells up [43], which is being confirmed by SARA test results for 1% LLDPE PMB, which shows that there is a decrease in aromatic contents with the inclusion of polymer in the blend.

Another phase observed in 1% LLDPE was composed of well dispersed polymer bitumen network. It can be concluded that at lower rate of mixing chances of agglomeration on cooling was more. The LLDPE starts to get separated from the bitumen because of it lower density (0.915 - 0.97 g/cc) in comparison to bitumen (1.01 g/cc) and thus tends to float and do agglomerate. The domains of agglomerated polymer can be well observed by light color patches in the Figure 5.9 & 5.10 in well dispersed dark color polymer bitumen blend.

From phase images it was found that these two different phases in LLDPE PMB blend have different viscoelastic characteristics as the phase shift observed for these were different. Phase shift which is considered analogous to phase lag (δ) representing ratio of viscous to elastic component of bitumen [84]. For well dispersed polymer bitumen surface phase shift varies from 0.51° - 0.8° while for the agglomerated phase separated polymer domains the phase shift was found to be 1.09°. The higher value of phase lag for swollen polymer domain represents adhesive character of swollen polymer. Thus the different viscoelastic characteristics would offer different adhesive properties when the modified binder would come in contact with aggregate in the matrix.

Thus it can be safely concluded that at the lower concentration of polymer, the well dispersed network of the polymer in the blend can be observed which was found due to melting of LLDPE but reprecipitate and agglomerate to form separate domains which mainly composed of segregated polymer and well dispersed polymer bitumen network, having different viscoelastic characteristic as observed by difference in observed phase shift. The scanned images also revealed that the compatibility of polymer even at lower concentration is rather low as observed by phase segregated layer of polymer above bitumen layer.

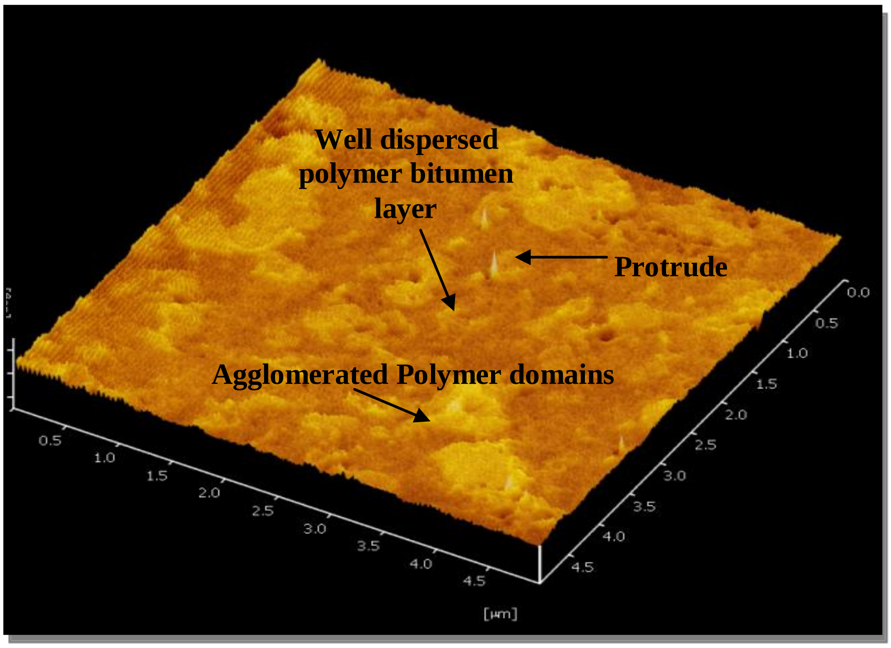

Figure 5.9: Phase image of 1% LLDPE modified bitumen

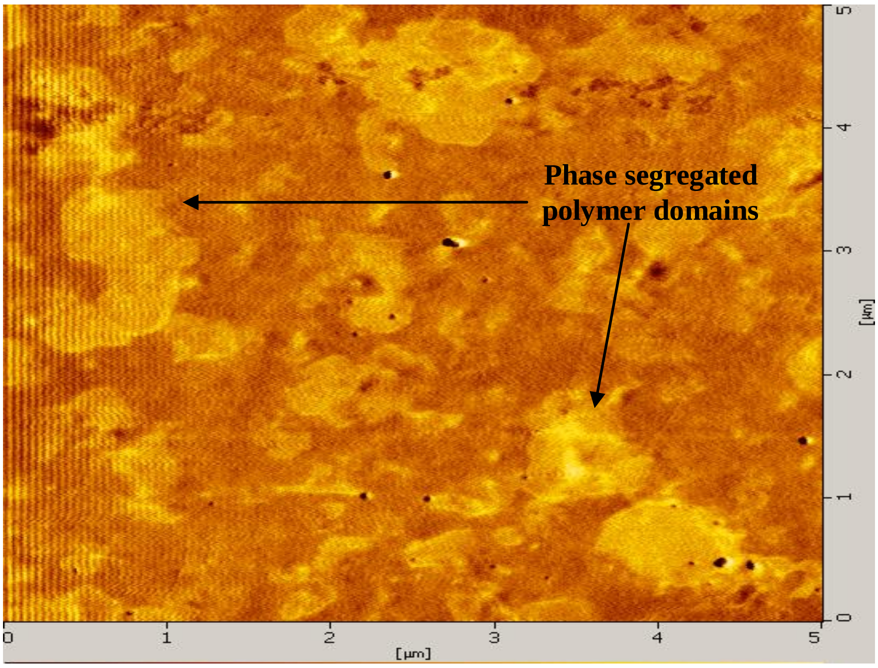

Figure 5.10: Phase image (Top View) of 1% LLDPE modified bitumen

For 2% LLDPE AFM scanned images as shown in Figure 5.11 & 5.12, it was observed that as the concentration of polymer increases, the segregated swollen polymer domains in matrix can be observed. The phase shift for these separate agglomerated domains varies from 0.5º - 0.7º. Beside these segregated domains, the protrude which were previously identified as asphaltene were found emerging from the base. The shape of these protrude differs from virgin bitumen protrudes which mainly composed of stacked sheets of fused aromatic rings as suggested by most of the researchers [1, 84].

The phase shift for these single asphaltene protrudes varies from 1.09º - 1.14º which previously for virgin bitumen found to be 2.9° - 4.4°. This change in structural appearance of protrudes identify the changes in chemical composition of bitumen when blended with polymer. By the addition of polymer in bitumen, the polymer layer intervenes between the fused aromatic rings or chemically interacts with bitumen and thus able to break the bonding existing between these fused stacked aromatic rings. This finding in the change in morphological character of blended PMB must be investigated that how it does affect the rheological and mechanical properties of 2% LLDPE PMB blend.

The evenly well dispersed polymer - bitumen layer have different viscoelastic characteristic from the rest of the blend where the phase shift varies from 0.38º - 0.45º. Thus it can be concluded after examining 2% LLDPE PMB scanned images that the three phases observed have different viscoelastic characteristic and would affect the rheology and mechanical properties of the modified binder.

From 3% LLDPE scanned images it was observed that as the percentage of polymer increases, the compatibility between the polymer and bitumen decreases. The agglomerated polymer forms separate domain and seems to be floating within the bitumen matrix. These protrude representing asphaltene can be observed clearly from the phase image of the 3% LLDPE PMB blend.

From Figure 5.13 & 5.14, the surface morphology revealed that there exist four phases. The agglomerated segregated phase formed due to incompatibility of polymer bitumen blends as observed by light color domains where change of phase varies from 0.7º - 1.28º. The phase shift indicates the viscoelastic characteristic associated with agglomerated polymer domains. The second phase observed composed of well dispersed polymer bitumen on the base, with phase shift varies from 0.38º - 0.45º.

With the increase in polymer concentration the phase shift for well dispersed polymer bitumen remains same indicating that addition of concentration of polymer fails to change the viscoelastic characteristic of the PMB blend.

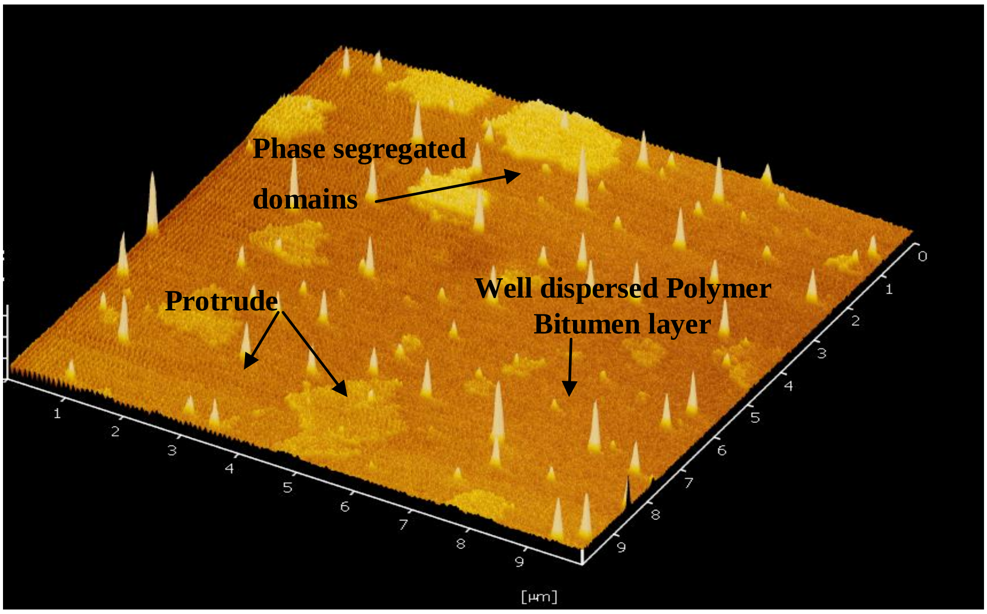

Figure 5.11: Phase image of 2% LLDPE modified bitumen

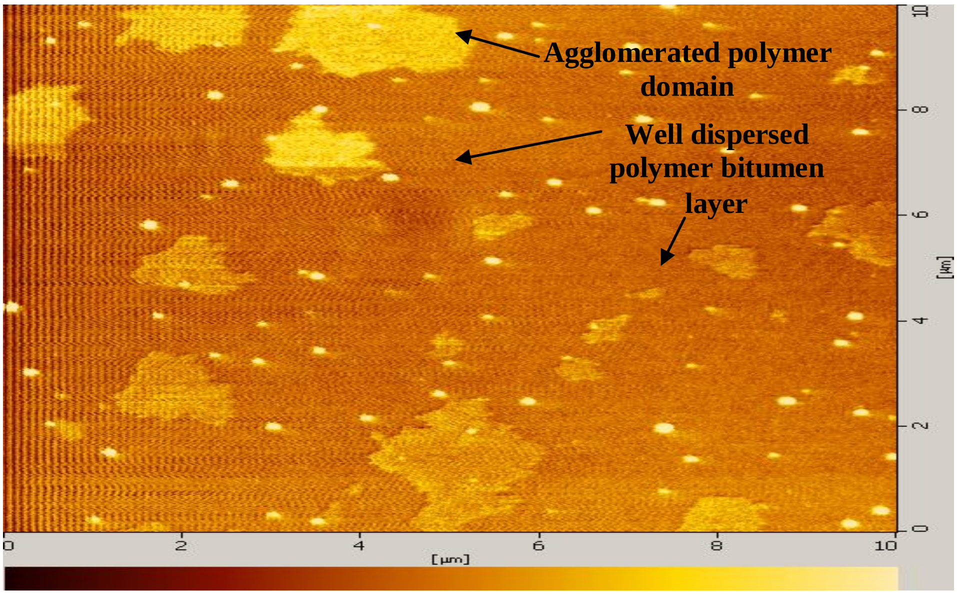

Figure 5.12: Phase image (Top View) of 2% LLDPE modified bitumen

This behavior of 3% LLDPE resembles behavior of 2% LLDPE PMB blend where phase shift for well dispersed polymer layer was found to be varying between

0.38° - 0.45°. This behavior can also be explained in terms of colloidal index CI calculated from SARA analysis. The CI value for 2% and 3% LLDPE were same.

The dispersion of polymer with the increase in polymer content seems to form network although the segregation was also observed. From the phase image of 3% LLDPE, the protrude which was previously defined as “bumble bee” for virgin bitumen phase image can be observed in phase image of 3% LLDPE scanned image, where the phase shift for these protrude goes up to 3°. An increase in phase shift for these protrude indicates that the chemical structure of bitumen was altered by inclusion of polymer. Protruding tubers from the base after modification were due to different viscoelastic characteristics incorporated by polymer concentration in the PMB blend which might have occurred due to increase in the asphaltene content for 3% LLDPE blend in comparison to 2% LLDPE blend.

The dark patch observed in Figure 5.11 (a) & (b) only indicates that 3% LLDPE unable to completely blended with bitumen. Thus it can be safely concluded that the 3% LLDPE PMB offers modified bitumen properties along with the viscoelastic characteristic of virgin bitumen as observed by the presence of protrude besides segregated polymer domains.

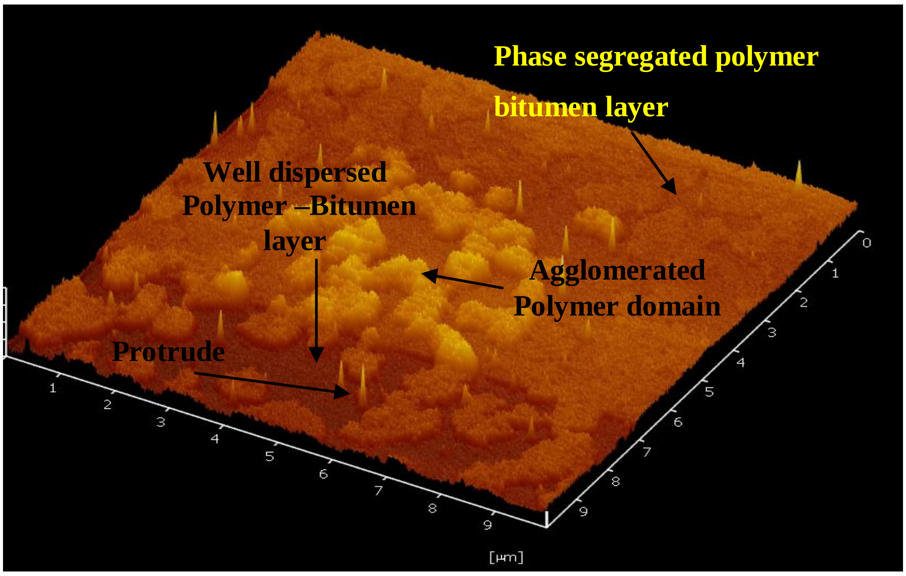

Figure 5.13: Phase image of 3% LLDPE modified bitumen

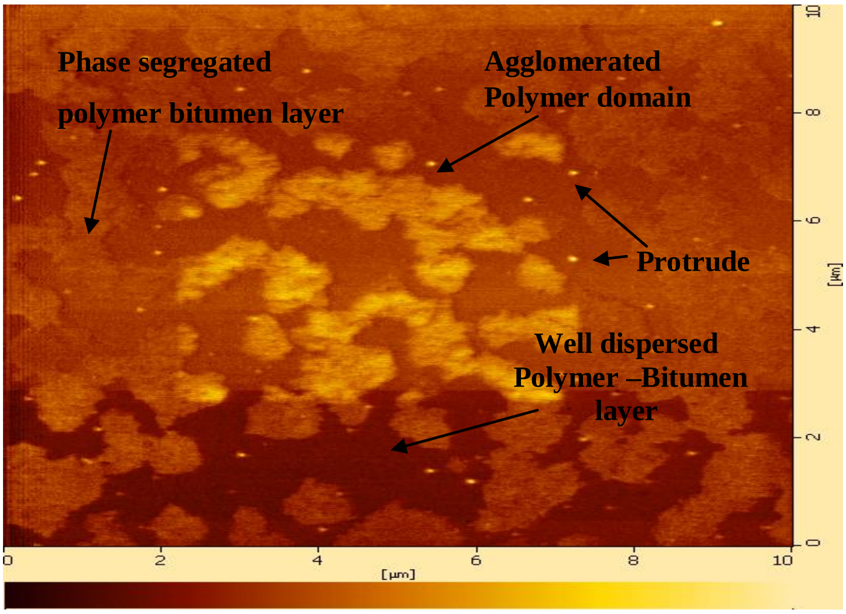

Figure 5.14: Phase image (Top View) of 3% LLDPE modified bitumen

5.4 Analysis of Transmission Electron Microscopy Scanned Images

Morphological analysis using TEM makes the study of bitumen possible after precipitating it in proper solvent. The use of TEM technique helps to understand the morphology of polymer bitumen blend. The compatibility of polymer bitumen blends which is considered as heterogeneous to certain extent showing varying phase morphologies as was confirmed from TEM scanned images.

5.4.1 TEM Analysis of Virgin Bitumen

Figure 5.15 shows the TEM image of virgin bitumen. The bumble bee which was previously detected in AFM scanned images was also observed over there. The noticeable part during scanning was the disappearance of bumble bee due to prolong exposure to electron beam. Thus it can be safely concluded that protruding bee on the maltene surface might have composed of wax or any other material which is sensitive to beam exposure. This needs further investigation as the bumble bee which was considered as asphaltene might compose of other material beside stacked sheets of polar aromatics.

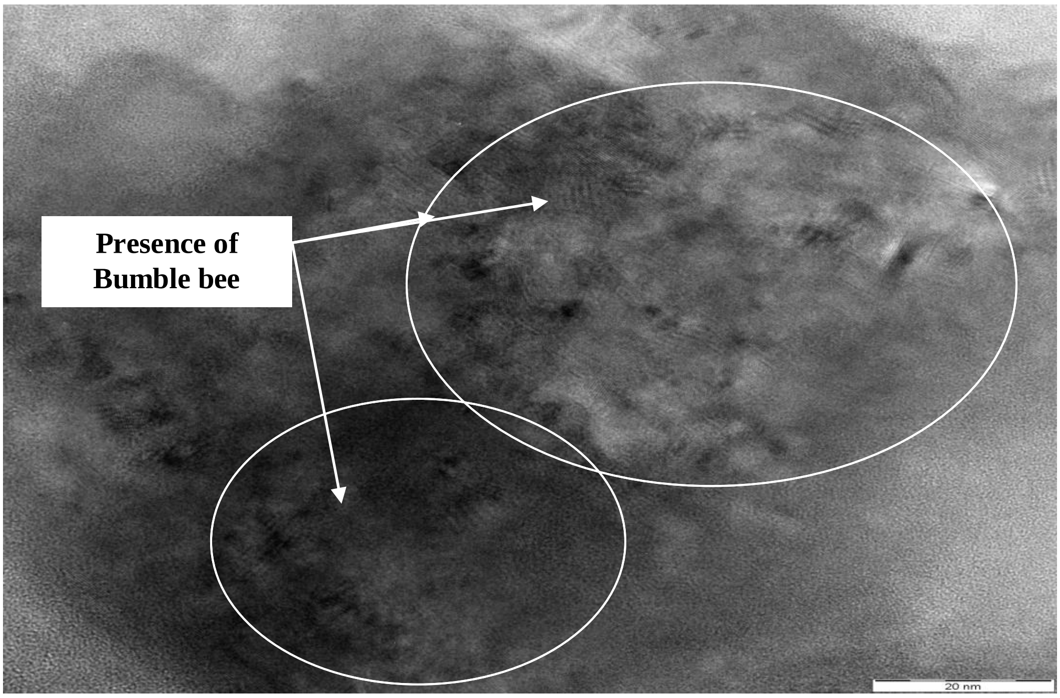

Figure 5.15: TEM image of Virgin Bitumen

5.4.2 TEM Analysis of Polypropylene modified bitumen

The TEM images for 1% - 3% PP PMB shows the presence of polymer PP in the helical form confirming that polymer shows better compatibility with bitumen with the formation of helical network as observed by TEM images as shown in Figure 5.16 - 5.18.

The noticeable part of these images are the entanglement of polymer PP lamella forming network which was considered responsible for the strength imparting factor to the modified blend. The stiffening effect induced by PP to the modified bituminous blend was due to the formation of this well dispersed network. These entangled chains of polymer would thus help in accommodating larger stresses by sliding pass each other under stress or reorienting themselves.

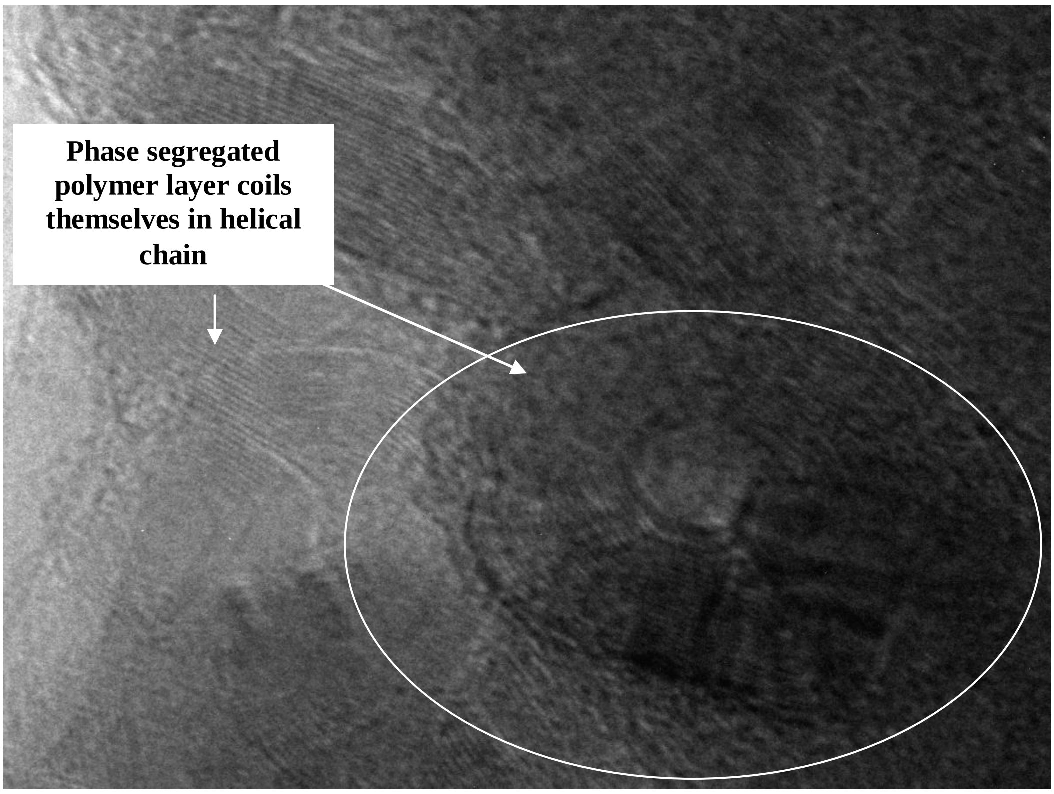

Figure 5.16:TEM image of 1% PP Modified Bitumen

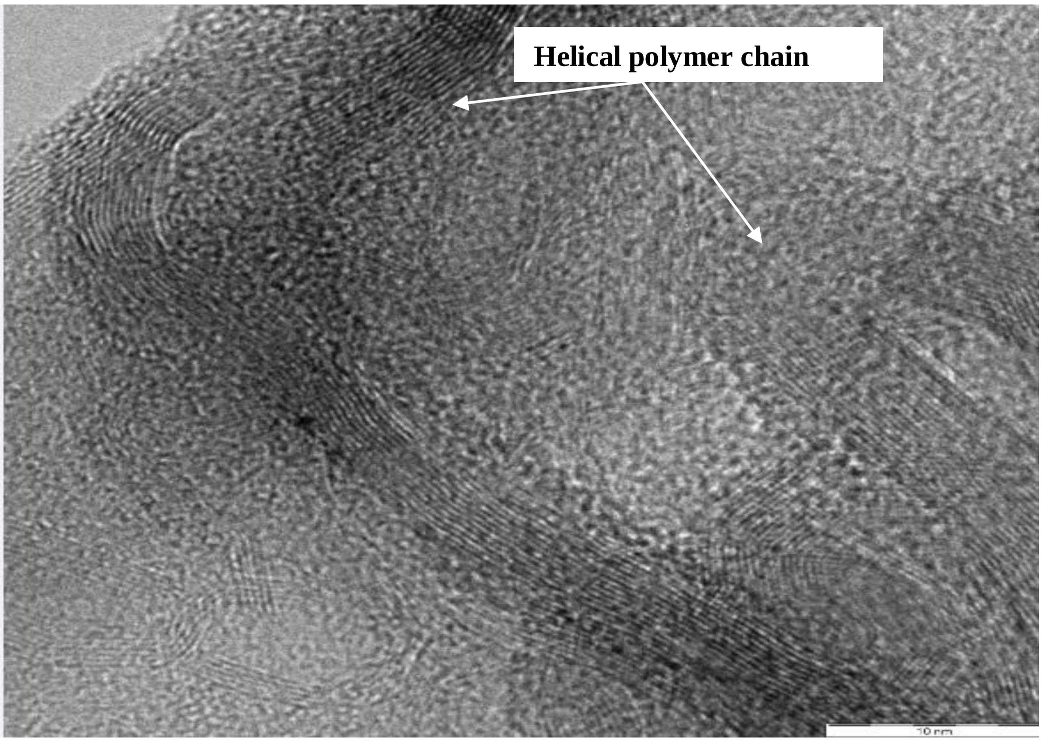

Figure 5.17: TEM image of 2% PP Modified Bitumen

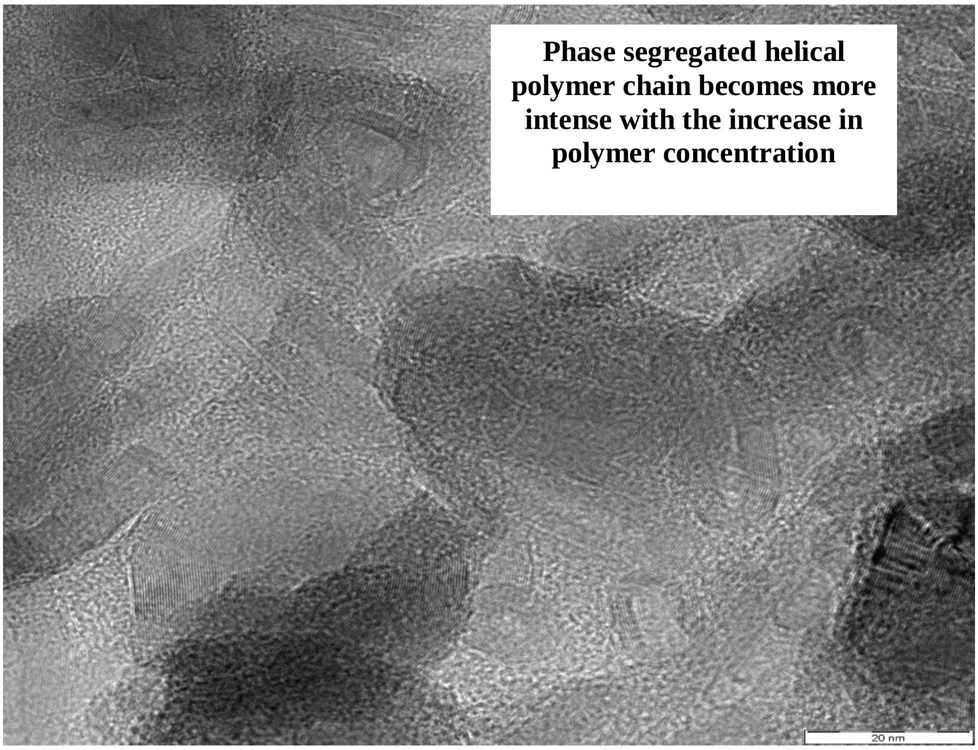

Figure 5.18: TEM image of 3% PP Modified Bitumen

From all the above shown scanned images it is noticeable that thickness and orientation of this polymer lamella depends on the concentration of polymer in the blend. At lower concentration of polymer these lamella seems to be dispersed well in bitumen phase while with the increase in concentration of polymer the polymer phase becomes prominent with the formation of intense polymer network as observed by 3% PP TEM scanned images. Thus it can be safely concluded the orientation and distribution of lamella in bitumen base is better and well dispersed forming a polymer bitumen network at lower polymer concentration. The strength and stiffness obtained due to modification was due to the formation this polymer bitumen network.

5.4.3 TEM Analysis of Linear Low Density Polyethylene modified bitumen

Linear low density polyethylene because of its lower miscibility in bitumen fails to form a proper network as observed by all scanned TEM images. The formation of segregated polymer domains which is considered as distinctive identity of polyethylene modified bituminous blend was also observed in TEM scanned images.

Scanned images for LLDPE are shown in Figure 5.19 - 5.20. For 1% LLDPE scanned image partially miscible polymer was observed by the formation of irregularly dispersed segregated polymer domains. These domains failed to form proper network which is considered responsible as strength imparting factor for modified bituminous blend.

For 2% LLDPE modified bituminous blend, scanned image revealed that with the increase in polymer concentration in bitumen, a slight increase in network formation was observed with the presence of stacked lamella. The lamellas were observed as dispersed domains, not properly connected to form a network. Thus after observing the scanned images it can be safely concluded that 2% polymer concentration in the bitumen was not well enough to form proper polymer bitumen network.

For 3% LLDPE modified bitumen blend proper polymer bitumen network can be observed with the formation of entangled polymer lamella in bitumen phase. Thus this entangled polymer bitumen network would thus offer the desired property of polymer modified bitumen which was considered responsible for enhanced mechanical properties of polymer modified bituminous blend.

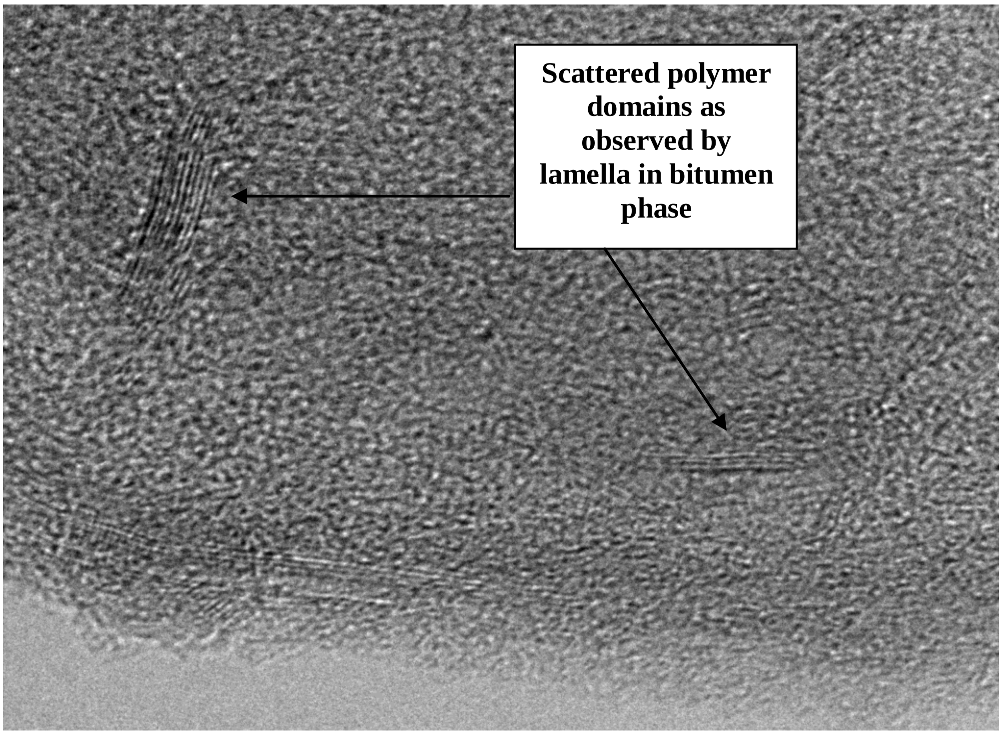

Figure 5.19: TEM image of 1% LLDPE Modified Bitumen

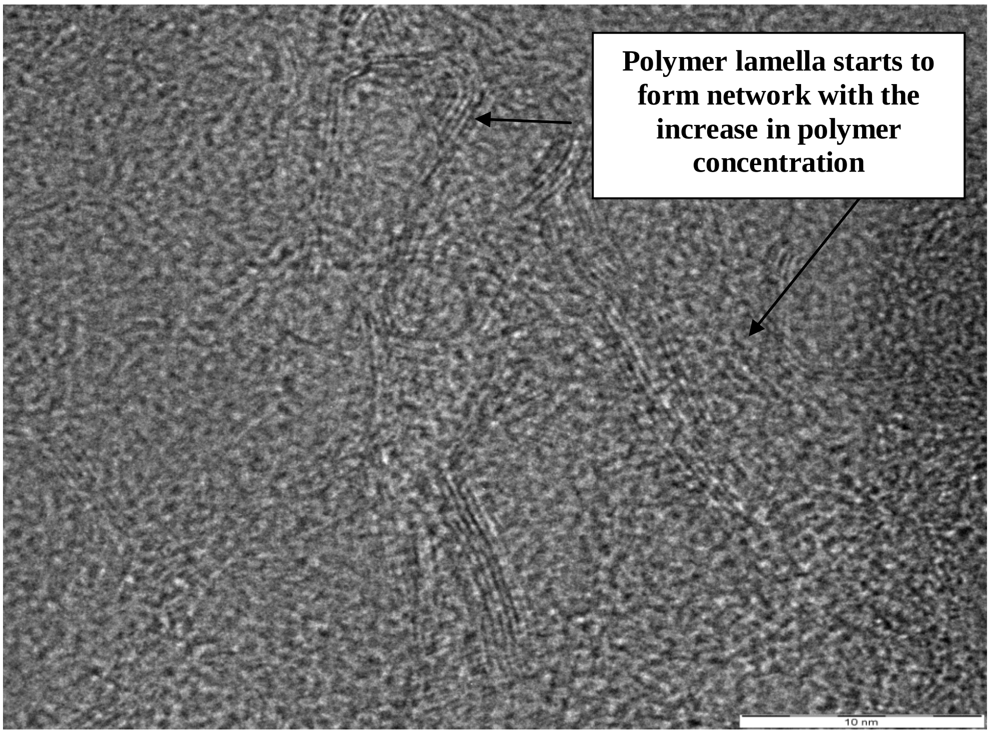

Figure 5.20: TEM image of 2% LLDPE Modified Bitumen

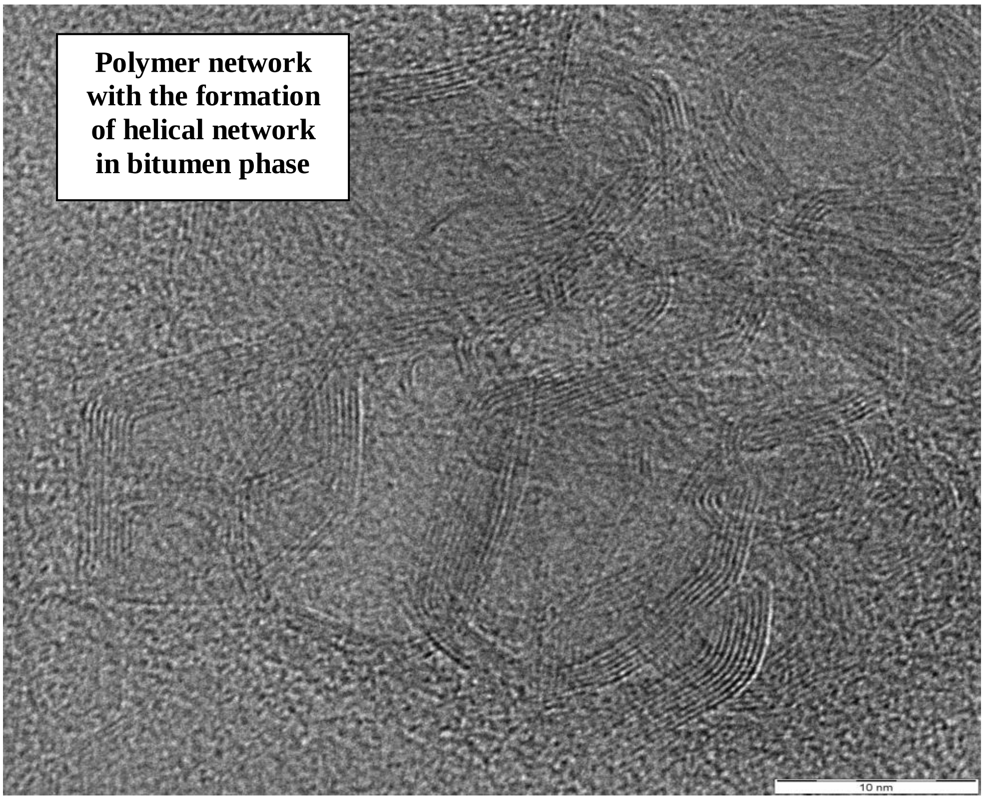

Figure 5.21: TEM image of 3% LLDPE Modified Bitumen

5.5 Summary of Morphological Analysis

The morphological analysis which was used as tool to understand the behavior of polymer in bitumen affecting the rheological and mechanical properties revealed that the miscibility of the polymer within bitumen was the influencing factor in network formation. Beside the polymer concentration, the mixing time, rate of shearing and mixing temperature has profound effect on the compatibility of polymer bitumen blend.

From the FESEM scanned images it was confirmed that there was an enhancement of viscosity and agglomeration with the increase in polymer concentration. The effect was found more pronounced and clearly visible in images taken for PP modified bituminous blend. As the compatibility of PP with bitumen was found to be more than LLDPE , it was disclosed by 1% PP AFM scanned images that phase segregated layer was composed of micro mixture of two different material which offer different viscoelastic characteristics. With the increase in polymer concentration the thickness of segregated layer increases. This phase segregated layer was considered responsible for the decrease in penetration value. The enhanced viscoelastic characteristic for 1% PP PMB was confirmed by presence of protrude at lower polymer concentration and phase lag value which decreases with the increase in polymer content as observed by 0.86° for 3% PP PMB.

AFM analysis of LLDPE PMB shows that protrude emerged after modification has different appearance and structural behavior as observed by phase lag. For these protrude which were recognized as asphaltene has phase lag value varying from 1.09º - 1.14º. Similarly lower phase lag value was observed for dispersed polymer bitumen phase.

Thus the formation of helical polymer network as exposed by TEM scanned images confirmed the existence of polymer bitumen compatibility as was observed by for PP modified bitumen, while scattered polymer domains for LDPE modified bitumen confirms the incompatibility of polymer with bitumen. The morphological results thus confirm the results of SARA analysis which on the basis of colloidal index revealed that PP offers better compatibility in comparison to LLDPE modified bitumen.

CHAPTER 6

RHEOLOGICAL ANALYSIS

6.1 Introduction

Many materials whenever stressed will exhibit both elastic and viscous response or in short would exhibit viscoelastic property. The study of such material behavior is considered essential as it affect the flow and deformation characteristic of material or its mechanical properties. Thus the part of science which deals with flow and deformation characteristics of material under the influence of an applied stress is defined as rheology [61]. Rheological analysis gives information about the mechanical properties of different materials under different deformation condition when being stressed and flow [98]. For the study of bituminous material, rheology can be defined as fundamental measurement which is associated with bitumen's flow and deformation behavior when being stressed or sheared [161]. Bitumen being viscoelastic in nature would offer both elastic and viscous properties depending on loading conditions and temperature. Modification by using polymer definitely alters the rheological properties of the modified bitumen. In order to understand the altered properties rheological study of polymer modified binders is considered helpful in understanding the response of modified binder to varying loading times, temperatures and environmental conditions [162].

Rheology of the polymer modified bitumen differs from that of pure bitumen, as the rheological properties of modified binder depend on polymer structure and base bitumen properties, thus the flow behavior of material while being stressed varies depending on the composition of material [61]. The phase morphology of the binder also effect the rheological properties of the modified binders [163].

Thus for polymer modified binders, concentration of polymer, polymer structure, dispersion phase and temperature has significant effect on binder’s rheology. The conventional test based on penetration and softening point considered incapable of describing the true rheological behavior of polymer modified binders. Thus the rheological study of the bituminous binders is considered helpful in understanding the pavement performance.

6.2 Rheological Parameters

Rheological parameter considered for the study includes complex modulus (G*) and phase angle (δ). Since bitumen usually considered as thermo-rheologicaly simple material which undergo changes with temperature variations, the testing was carried out over a wide range of temperature using the dynamic shear rheometer (DSR). DSR testing considered as replacement of old conventional tests like penetration and softening point which do not consider the effect of time of loading and temperature on binder’s performance [30].

The rheological parameters are often defined in terms of complex modulus (G*) and phase angle (δ). Complex modulus G* is defined as the ratio of maximum (shear) stress to maximum strain. It is the measurement of the total resistance to deformation when the bitumen is subjected to shear loading. Complex modulus is composed of storage modulus (G') and the loss modulus (G'').The storage modulus (G') is the elastic or recoverable part of the material. The loss modulus (G'') is the viscous or non recoverable part of the material [151].

The phase angle (δ) is defined as the phase difference between stress and strain in an oscillatory mode, which measures the viscoelastic behavior of the material. When phase angle δ equals to 90º, then the bituminous material can be considered as purely viscous in nature, while δ equals to 0º corresponds to purely elastic behavior. Between these two extremes the material exhibit viscoelastic characteristics which is a combination of viscous and elastic responses [39]. Increase in phase angle correspond to decrease in elastic response [7]. The viscoelastic behaviour of the modified binder was due to change in flow behaviour under applied stress. While stressed, the molecules of the polymer bitumen blend deform under shear force but will realign and try to return to their original position on the removal of stress. Thus the viscoelastic property of the polymer modified blend was due to the presence of this phenomenon [61].Complex modulus G* along with the phase angle δ, represent the resistance of the material to deformation within viscoelastic region [164].

6.3 Results and Discussion

In the following sections the rheological parameters for aged and unaged binders are presented separately in order to have a better understanding of rheological characteristics of binders used for the study. Both aged and unaged PP PMB and LLDPE PMB with concentration varying between (1 - 3%) along with virgin 80/100 pen bitumen were analyzed. For the analysis of results two test temperature 58°C and 70°C were used which is considered nearer to maximum pavement temperature that might encountered during pavement life time.

6.3.1 Results for Polypropylene Modified Bituminous Blend

6.3.1.1 Relationship between Rutting Parameter (G/sinδ) and Temperature*

The rutting performance of the modified binder can be better presented by G*/sinδ as function of temperature. The rutting parameter or shear modulus (G*/sinδ) is considered as binder stiffness to deformation under load at certain specified temperature [164]. As rutting is considered as phenomenon related to high pavement service temperature, therefore it was considered best to test the binder after short term aging in rolling thin film oven test (RTFOT) as it represent the binder properties at early stage of pavement [165]. The reason for choosing G*/sinδ as rutting parameter was due to controlled testing conditions. During testing the binders do experience the same conditions, which truly represent the actual binder condition in service life. According to SHRP-A-410 report, for unaged binders the temperature at which G*/sinδ=1 kPa considered as maximum temperature that would offer good viscoelastic characteristic when used as binder for pavement [5]. For aged binders after RTFOT, SHRP put the limitation of G*/sinδ values at 2.2 kPa to consider the maximum temperature that would offer good viscoelastic characteristics [166]. For analysis of results for rutting parameter two temperatures, 58°C and 70°C was considered significant as at these temperatures the pavements are more prone to rutting.

Figure 6.1, presents the plot between G*/sinδ versus temperature, which represents a measure of the high temperature stiffness or rutting resistance of the aged base and PP PMB binders. Table 6.1 presents the rheological parameters of binders at 58°C and 70°C, which are considered as highest in service pavement temperatures.

From Table 6.1, it was observed that modification significantly enhances the stiffness as observed by increase in complex modulus (G*) for all PP modified binders. Decrease in phase angle δ, after short term aging in RTFOT, indicates that modification enhances the elastic component of the binder. 1% and 3% PP exhibit slightly higher elastic behaviour at 58°C in comparison to 80/100 pen bitumen. 1% PP PMB offer higher shear modulus at both 58°C and 70°C, indicating deformation resistance at higher in-service pavement temperature. From Figure 6.1 and Table 6.1 it was also observed that there is a reduction in G*/sinδ values as it reaches higher temperature. For 2% PP PMB highest reduction in G*/sinδ was observed at 58°C, where it almost approaches the value of 80/100 base bitumen at that temperature. This attitude of 2% PP PMB shows an indication that it would offer higher resistance to rutting, by showing improved viscoelastic response [113, 167].

From Figure 6.1, it was also observed that SHRP limitation of 2.2 kPa value of shear modulus was achieved by PP PMBs at temperature above 76°C, where binder would offer viscoelastic characteristics.

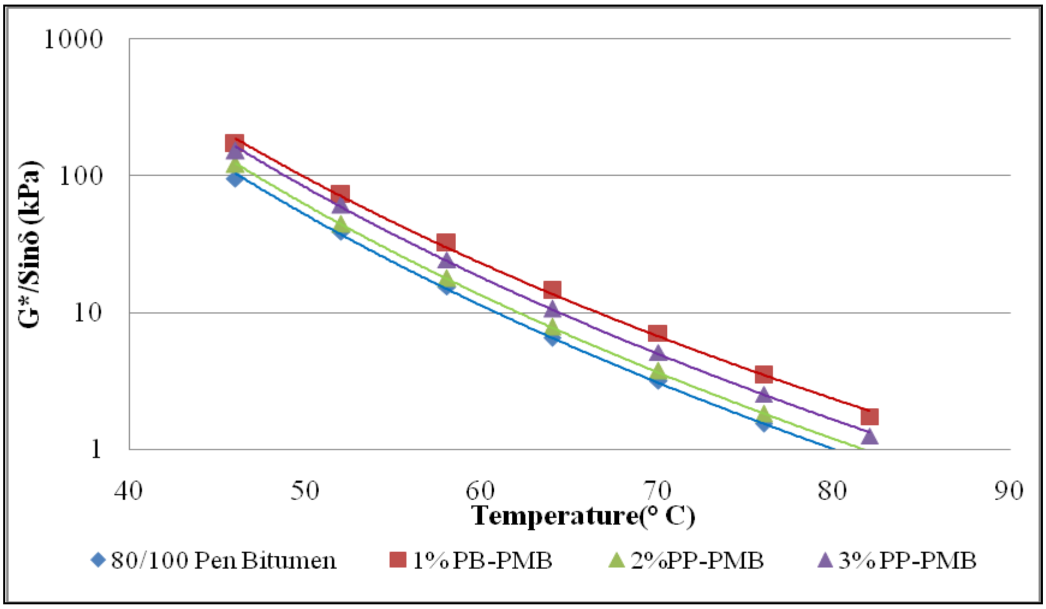

Figure 6.1: G*/sinδ Vs Temperature for PP PMB & 80/100 Pen Bitumen

Table 6.1: Rheological Properties of PP PMB & 80/100 Pen Bitumen after RTFOT

Bituminous Binder	Temp °C	Loss Modulus *G″* (kPa)	Storage Modulus *G*'(kPa)	Complex Modulus G*(kPa)	Phase Angle δ(°)	Rutting Parameter (G*/sinδ)kPa
80/100 Pen Bitumen	58 70	15.07 3.17	2.443 0.1745	15.30 3.18	80.59 86.86	15.51 3.18
1% PP PMB	58 70	30.56 6.99	7.04 0.917	31.36 7.06	77.01 82.53	32.18 7.11
2% PP PMB	58 70	17.30 3.70	3.15 0.385	17.61 3.72	79.73 84.05	17.90 3.74
3% PP PMB	58 70	23.15 5.08	5.27 0.562	23.78 5.12	77.12 83.68	24.39 5.15

6.3.1.2 Relationship between Complex Modulus G and Phase Angle δ*

Stiffness of the binders can be well presented by the complex modulus and phase angle. When the rheological parameter G* is plotted against phase angle (δ), it gives information about the viscoelastic characteristic of the binder. The diagram has advantage that rheological characteristics measured at different temperature can be plotted on single graph which are independent of temperature and frequency. Such diagrams are commonly known as "Black diagram"[56]. As Black diagrams can be plotted without any manipulation of rheological data prior to presentation, thus they provides a simple way to assess the effect of polymer modification and oxidative ageing on the rheological properties of bituminous binders [168]. In rheological study of binders, Black diagrams has great significance as they are known be very sensitive to the morphology of the binder [53].

Figure 6.2 presents the Black Diagram, where the combine plot between G* and δ for unaged and aged binders is presented. For clarity, firm solid filled icons were used for unaged binders, while unfilled hatched icons of the same colour were used for aged binders. The diagram was generated with temperature sweep varying between 46°C - 82°C at 10 rad/sec. From the Figure 6.2, it was observed that G* smoothly decreases with an increase in the temperature, confirming the behaviour of polymer modified binder from viscoelastic to almost complete viscous liquid as the phase angle (δ) approaches 90° value. At high temperature range (58°C - 70°C), the binder does exhibit its visoelastic characteristic beside increasing stiffness as observed by the corresponding higher value of G*. Thus shift of curve towards left (lower phase angle) after short term ageing indicates enhancement of viscoelastic characteristic of modified binders along with enhanced stiffness which was considered as an indicator of existence of polymer bitumen network.

Thus from the Figure 6.2 it can be safely concluded that although one hour mixing at temperature 160°C which was considered insufficient for producing complete homogenous blend, found to be sufficient enough to alter the stiffness and viscoelastic characteristics of the modified binder. It was also observed that up to 3% polymer concentration (by weight) in bitumen, the behaviour of the modified binder remains close to the 80/100 base bitumen

This observation was also confirmed by the insignificant difference of colloidal Index (CI) values observed by SARA test results for PP PMB. Thus the rheological parameter of the modified binder is governed by their continuous phase where sufficient polymer network exists in polymer bitumen blend [169].

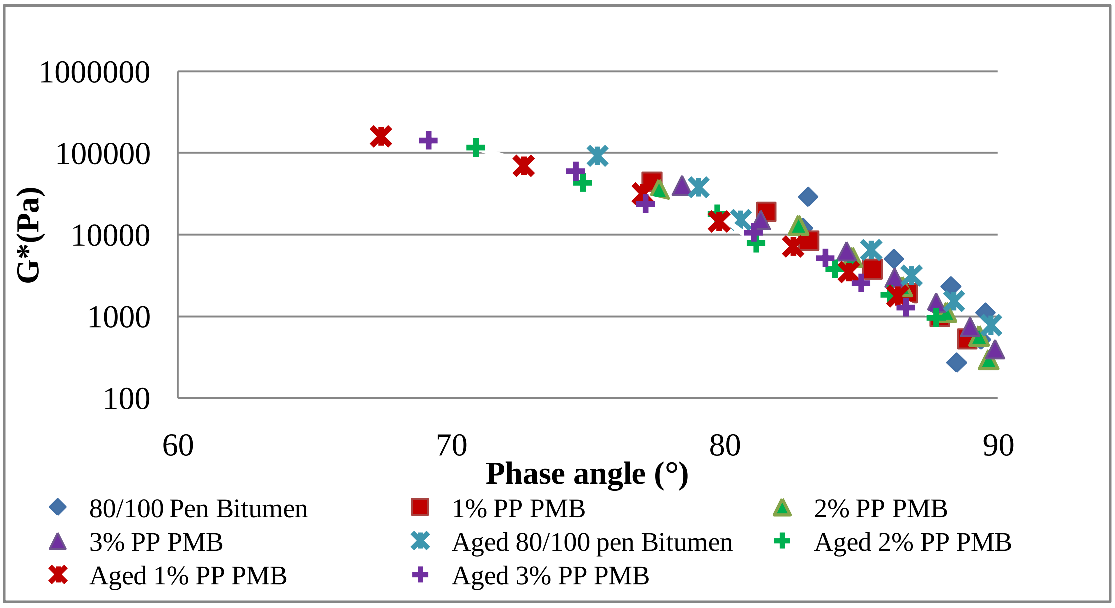

Figure 6.2: Black Diagram, G* Vs δ for PP PMB & 80/100 Pen Bitumen

6.3.1.3 Relationship of Loss Modulus and Storage Modulus with Temperature

The other linear viscoelastic characteristic that can be obtained from the test includes the storage modulus (*G'*), or the loss modulus (*G"*).

The loss shear modulus or viscous, *G*" is the out of phase component of the complex modulus. It represents the viscous component of the complex modulus that measures the energy lost or dissipated during a loading cycle. The storage shear modulus or elastic, *G'* is the in phase component of the complex modulus. It represents the elastic component of the complex modulus that measures the energy stored during a loading cycle.

In actual the elastic component of the response only represents a part of the storage shear modulus *G*' while viscous response represents only a part of the loss modulus *G*″. Both these parameters reflect a part of the delayed elastic response, which in case of viscoelastic material is time dependent but completely recoverable [56].

In general when *G*″ > *G*', the solution / liquid character of the material becomes prominent, where material shows sufficient increase in viscosity. The viscous behaviour dominates the elastic phase and material exhibit characteristics of liquid in linear viscoelastic range [56].

Although from the Table 6.1 it was observed that *G*″ > *G*', but PP modified binders shows improved value of storage modulus (*G*') in comparison to 80/100 pen bitumen. This behaviour indicates that short term aged modified binder has enhanced the elastic component to certain extent. The higher value of *G*' indicates improved resistance to deformation, as *G*' measures the elasticity of the binder [164]. As storage modulus is the in phase component of the complex modulus, where phase angle δ considered sensitive to the chemical structure of binder, thus decrease in phase angle represent improved elastic network (entanglements) and also improved storage modulus in comparison to 80/100 pen bitumen.

From Table 6.1 it was observed that at 58°C significant increment in storage modulus for 1% PP PMB was observed followed by 3% PP PMB. This behaviour of PP PMB indicates that compatibility of polymer with bitumen as confirmed by SARA test results. Partially dispersed PP even at lower polymer concentration was sufficient enough to form the elastic network responsible for the improved elastic property of the binder. At higher temperature around 70°C as observed from Table 6.1 sufficient decrease in storage modulus was observed for all concentration of PP PMB. This behaviour indicates that viscous component of the binder becomes dominant thus reducing the elastic component. Such behaviour would be considered as favourable, as decrease in elasticity indicates the loss in dissipated energy which would reduce the cracking potential due to dissipation of absorbed energy.

From Table 6.1, it was also observed that modification significantly enhances the viscous or the loss modulus (*G″*) in comparison to 80/100 pen bitumen. At higher temperature 70°C viscous modulus was found to be higher than the base bitumen. Such behaviour of PP PMB indicates predominantly viscous behaviour of the blend due to modification. Higher viscous modulus was observed for 1% PP PMB followed by 3% PP PMB. The enhanced viscous behaviour can be attributed to asphaltene, which were formed during mixing process, which considerably increases the polarity of the blend. From SARA results it was also observed that there was an increase in the asphaltene content and decrease in the aromatic content due to modification. This attitude would thus contribute to the formation of *gel* type of bitumen behaving more or less like polymeric solution [20] which offer delayed elastic response (time dependent and completely recoverable) because of enhanced viscous component.

In short the PP modified binder shows a predominant viscous behavior over whole range of test temperature (46°C- 82°C).

6.3.1.4 Relationship between Complex modulus G and Temperature*

The behaviour of the modified binder in term of enhanced stiffness or resistance to deformation over the wide range of temperature can be well presented by the plot between complex modulus and temperature. It was observed from the Figure 6.3, that there was sufficient increase in complex modulus G*, after short term aging. More pronounced effect was observed at lower testing temperature range. With the increase in temperature decrease in modulus was observed.

From the Figure 6.3, it was observed that at lower temperature sufficient difference in complex modulus was observed between unaged and aged binders. As the temperature increases less difference in complex modulus was observed. As complex modulus represents the resistance to deformation that modified binder would offer, better rutting resistance between temperatures ranges of 46°C - 70°C was observed. 1% PP PMB shows highest modulus value indicating the compatibility of polymer with bitumen was more effective due proper dispersion of polymer and formation of well connected polymer bitumen network.

It was also observed that 2% PP modification shows decrease in complex modulus after it was subjected to short term ageing in rolling thin film oven test (RTFOT). This change in rheological behaviour of 2% PP PMB can be attributed to the degradation (rearrangement) of polymer into lower molecular weight fraction, where rheological characteristics of 2% PP PMB resembles to certain extent to virgin 80/100 base bitumen properties.

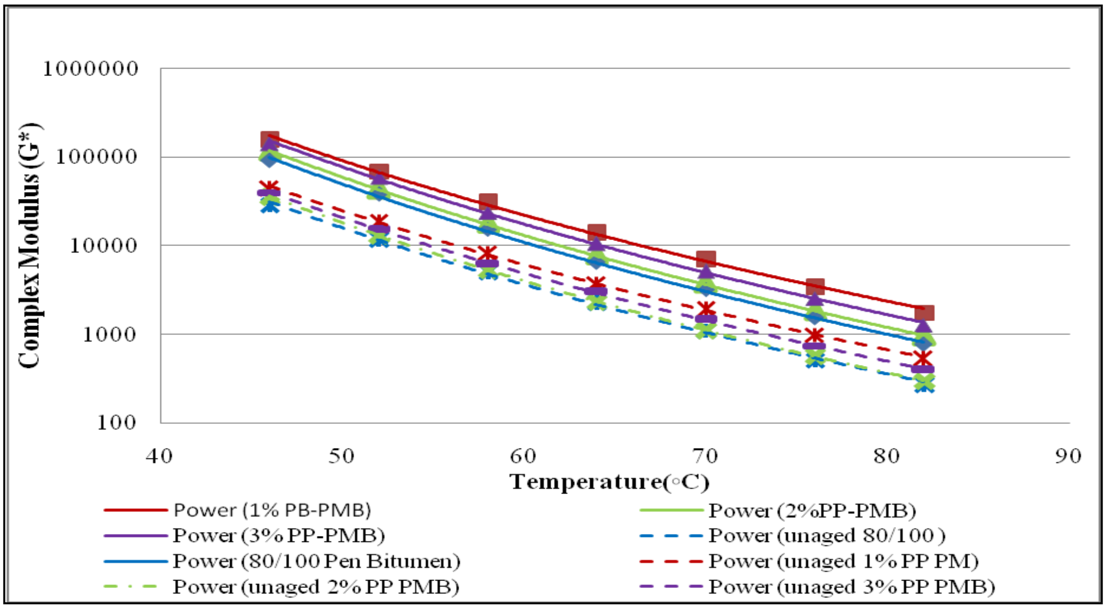

Figure 6.3: Complex Modulus Vs Temperature for PP PMB & 80/100 Pen Bitumen

6.3.1.5 Relationship between Phase Angle δ and Temperature

Figure 6.4, presents the graph plotted between phase angle δ and temperature. It was observed from the plot that after short term ageing, PP modified binder shows an increases in the elastic response at medium to high temperature (between 46° - 64°C), where the value of phase angle varies from 60°-70°. More viscous response was observed by higher phase angle, reaching up to 90°. This behavior was due to change in chemical composition due to temperature as phase angel δ is considered more sensitive to the chemical structure of the binder [39].

The reduction of phase angle for modified binder with respect to the base bitumen represents that modification brought some changes into the structure of the base bitumen by the inclusion of polymer network. Thus elastic network due to presence of entangled polymer considered responsible for viscoelastic properties. With the increase in temperature reduced elastic and enhanced viscous response of binder was observed which represent that the polymer bitumen becomes more mobile due to transition of polymer from solid to liquid state [151] thus helping in the formation of polymer bitumen network.

From the results discussed above it was observed that modification of bitumen with polymer leads to the formation of complex system, as observed by the change in morphological and rheological behavior. The concentration and type of the polymer used also has profound effect on the rheological behavior. The degree of dispersion also has profound effect as it affect the compatibility of polymer bitumen blend. The effect of polymer as observed even at lower polymer concentration, thus use of higher concentration of polymer for modification might not be beneficial as excessive increase in complex modulus would bring brittleness, thus because of this reason the higher concentration of polymer was considered economically less viable by the pavement industry [149].

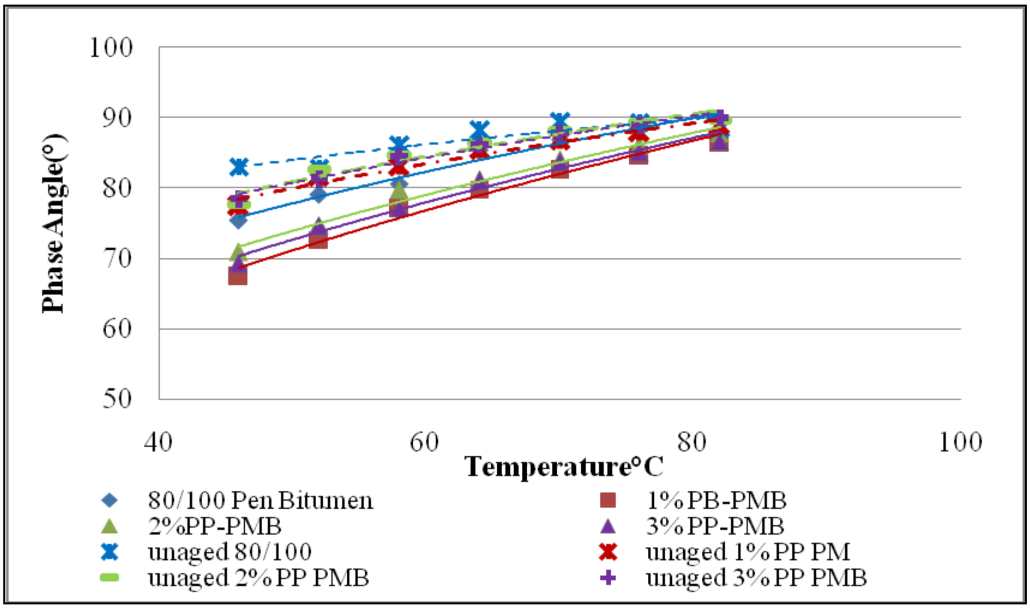

Figure 6.4: Phase Angle Vs Temperature for PP PMB & 80/100 Pen Bitumen

6.3.2 Results for Linear Low Density Polyethylene Modified Bituminous Blend

In the following section the rheological properties of aged and unaged binders would be presented. As LLDPE was in pallet form, thus the compatibility of polymer bitumen has significant effect on the rheology of the modified binder.

6.3.2.1 Relationship between Rutting Parameter (G/sinδ) and Temperature*

The SHRP rutting parameter G*/sinδ when plotted against temperature (refer Figure 6.5) it was observed that significantly high values of shear modulus (G*/sinδ) was observed in comparison to base bitumen indicating that modification has improved the rutting performance. 1% and 2% LLDPE PMB shows almost same amount of increment in shear modulus value. This rheological behavior of 1% and 2% LLDPE PMB confirms the results of SARA, where same amount of asphaltene content, indicates that enhancement in stiffening effect would be same for the both modified binders. From Table 6.2 it was observed that 3% LLDPE PMB shows 6 times enhancement in complex modulus with respect to 80/100 base bitumen at 58°C. Even at lower temperature such as at 46°C drastic increment in modulus was observed. This behavior indicates that stiffening effect may lead to embrittlement. With the increase in temperature (70°C above) the modulus value suddenly drops to very lower side as observed in Figure 6.5. Such behavior of 3% LLDPE PMB indicates that at higher temperature degradation of binder might have occurred and which does even make binder susceptible to temperature variation.

Very high values of rutting parameter (G*/sinδ) was observed at both 58℃ and 70°C for all concentration of PMB. The significant increase in complex modulus due to significant increase in binder viscosity which might increase its stiffness property but at the lost of elastic property as observed from the values of phase angle at higher testing temperature. Such behavior of the binder would not be considered beneficial as higher stiffening effect might lead to binder embrittlement when subjected to loading.

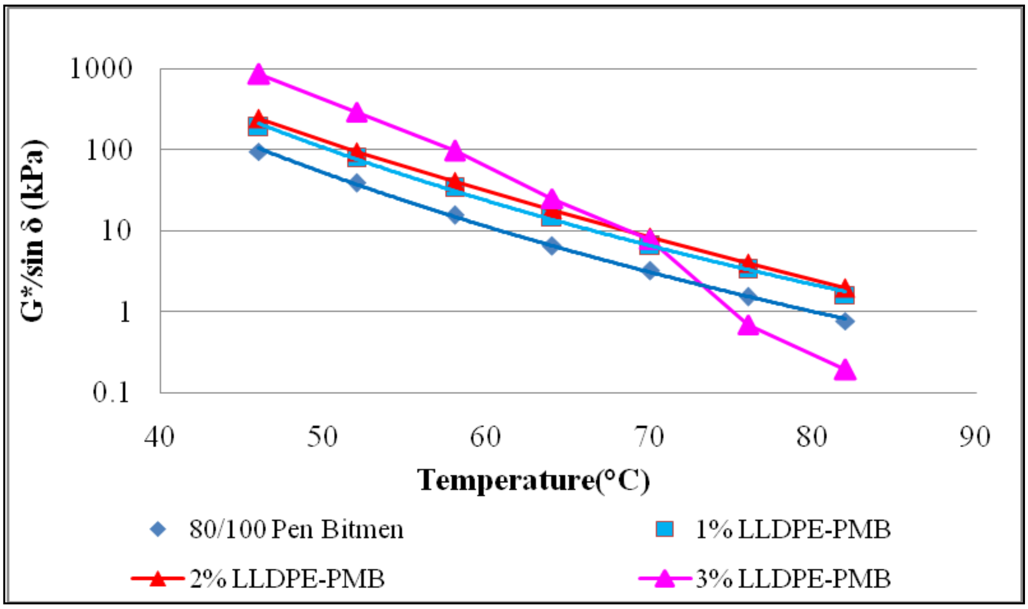

Figure 6.5: G*/sinδ Vs Temperature for LLDPE PMB & 80/100 Pen Bitumen

Table 6.2: Rheological Properties of LLDPE PMB & 80/100 Pen Bitumen after RTFOT

Bituminous Binder	Temp °C	Loss Modulus G'' (kPa)	Storage Modulus G' (kPa)	Complex Modulus G* (kPa)	Phase Angle δ(°)	Rutting Parameter (G*/sinδ)kPa
80/100 Pen Bitumen	58 70	15.07 3.17	2.443 0.1745	15.30 3.18	80.59 86.86	15.51 3.18
1% LLDPE PMB	58 70	31.81 6.40	7.45 2.37	32.68 6.46	76.81 82.89	33.75 6.5
2% LLDPE PMB	58 70	37.47 8.23	9.64 0.932	38.85 8.28	75.79 83.54	40.08 8.343
3% LLDPE PMB	58 70	87.75 7.80	29.90 0.311	92.73 7.81	71.54 88.14	97.72 7.882

6.3.2.2 Relationship between Complex Modulus G and Phase Angle δ*

The phase morphology that was observed during morphological analysis of LLDPE PMB, was well observed in Black diagram too (refer Figure 6.6). The curve was plotted between complex modulus G* and phase angle δ, generated with temperature sweep varying between 46°C - 82°C at 10 rad/sec.

From the Figure 6.6 it was observed that 80/100 pen bitumen shows smooth transition with the increase in complex modulus and phase angle after subjected to short term aging in rolling thin film oven. At 1% and 2% concentration of LLDPE, significant increase in complex modulus and decrease in phase angle was observed after short term ageing. This shift of complex modulus to higher side and phase angle to lower side indicates hardening of the binder due to ageing [39]. This behavior of binder seems identical with the test results of penetration observed for LLDPE modified binder.

For 3% LLDPE PMB such scenario was not observed where tremendous increase in complex modulus was observed up to 64°C and then decrease in complex modulus was observed. This behavior of 3% LLDPE PMB can be attributed due to lack of compatibility that exists between LLDPE and base bitumen. The incompatibility of the polymer bitumen blend was also observed during AFM analysis and from colloidal Index values calculated from SARA results. The increase in asphaltene and decrease in maltene has led to an incompatible blend where polymer and bitumen instead of behaving as homogenous phase, resulted in incompatible separated phases as observed by rheological parameter G* and δ. This incompatibility might be because of the insufficient time for mixing or due to inert chemical nature of polyethylene, resulting in the incomplete reaction where polymer failed to chemically interact with the bitumen, resulting in limited absorption of bitumen molecules [98].

From the Figure 6.6 it was also observed that phase angle (δ) shifted towards left indicating substantial increase in the viscoelastic component of the binder at 1% and 2% polymer concentration. Increase in phase angle with the increase in temperature was also observed indicating increase in viscous component of the binder. For 3% LLDPE fluctuation in behavior with the increase in temperature can also well observed by Black diagrams, as these diagrams are more sensitive to variation in the morphology and chemical structure of the binder [53].

From the above discussion it can be safely concluded that LLDPE PMB shows an increase in the viscoelastic component at 1% and 2% LLDPE PMB to certain extent. Increase in complex modulus with increase in polymer concentration indicates excessive hardening induced in the binder which might be subjected to embrittlement under loading conditions.

The results observed from CHNS analyzer also revealed that 3% LLDPE shows higher percentage of oxygen in comparison to the rest. Such behavior of 3% LLDPE PMB indicates that even during blending of polymer with bitumen, the blend get oxidized sufficiently. The deficiency of proper polymer bitumen network for LLDPE PMB as being observed from the FESEM, AFM and TEM scanned images resulted in the formation of the blend where bitumen and polymer individually imparts their characteristics rather than as one homogenous blend.

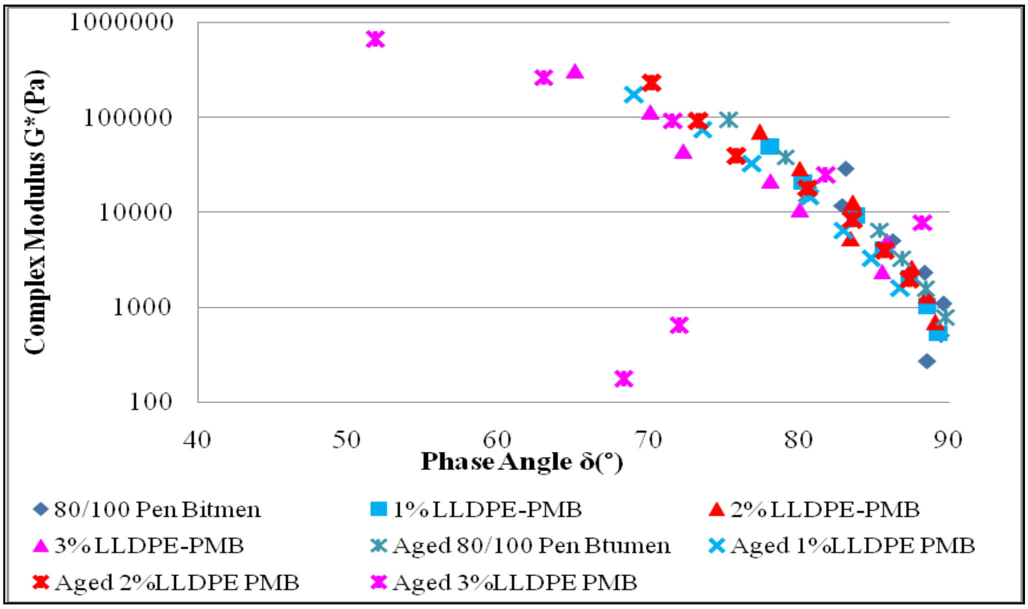

Figure 6.6: Black Diagram, G* Vs δ for LLDPE PMB & 80/100 Pen Bitumen

6.3.2.3 Relationship of Loss Modulus and Storage Modulus with Temperature

From the Table 6.2 it was observed that loss modulus values (*G″*) was greater than storage modulus (*G*') for all LLDPE modified binders. Sufficient increment in loss modulus values was observed for 1% & 2% polymer concentration. Such behavior of LLDPE modified bitumen when accompanied with the elastic component of the binder indicates that at higher temperature above 70°C polymer modification would be beneficial as it will resist deformation due to increment in elastic component and would avoid cracking due to loss of dissipated energy by viscous component of the complex modulus.

3 % LLDPE PMB shows tremendous increment in *G″* indicating enhancement of the viscous part of the complex modulus at both upper and lower end of temperature.

From Table 6.2 it was also observed for 3 % LLDPE at 58°C, sufficient increment in elastic and viscous component was observed. This behaviour might improve the rutting performance at this temperature but vulnerable to embrittlement due to excessive increment in loss modulus. For 3% LLDPE PMB further increase in temperature (above 64°C) shows deviation from usual behaviour, where decrease in storage and loss modulus was observed. Such behaviour of 3% LLDPE PMB confirmed the incompatibility of polymer bitumen blend as also observed by morphological test results.

6.3.2.4 Relationship between Complex modulus G and Temperature*

Figure 6.7 present the plot of complex modulus G* and temperature. From the figure it was observed that short term aging sufficiently enhances the complex modulus of the binders. Sufficient increase in complex modulus was observed at 1% LLDPE polymer concentration, while no remarkable increment in complex modulus was observed after short term aging for 2 % LLDPE PMB in comparison to 1% LLDPE PMB. This behavior was also confirmed by SARA results which showed marginal difference in asphaltene content for 1% LLDPE and 2% LLDPE modified binders. Asphaltene are basically considered responsible for the rigidity of the binder. For 3%

LLDPE a sharp increase in complex modulus followed by sharp decrease of complex modulus indicates that at medium to high temperature range the polymer sufficiently enhances the elastic and viscous component of the binder. Further increase in temperature leads to the degraded polymer bitumen blend which failed to offer any of its characteristics.

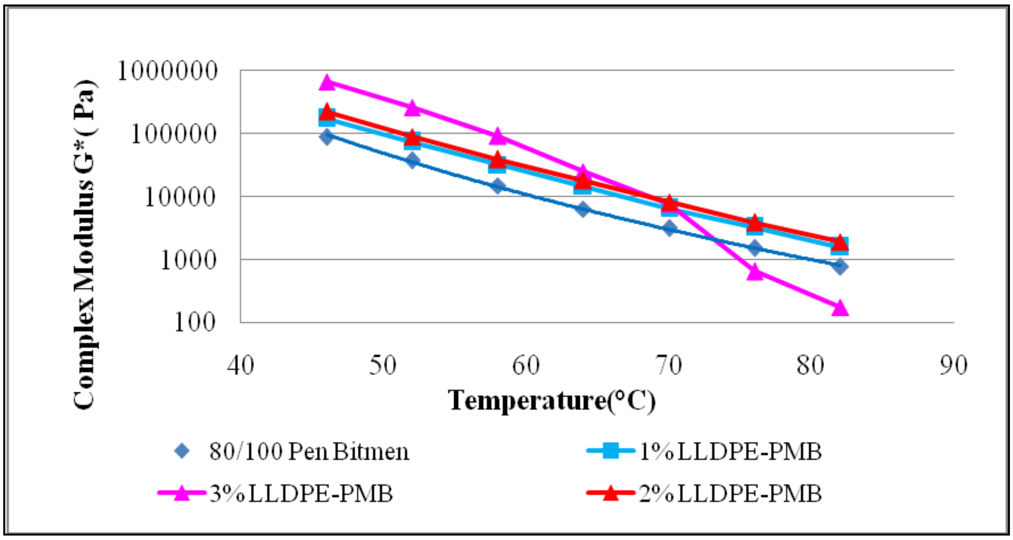

Figure 6.7: Complex Modulus Vs Temperature for LLDPE PMB & 80/100 Pen Bitumen

6.3.2.5 Relationship between Phase Angle δ and Temperature

Figure 6.8 presents the rheological behavior of the binder when plotted between phase angle and temperature. Significant decrease in phase angle with respect to base bitumen was observed for 1 % and 2 % LLDPE PMB after short term aging till 58°C. This behavior represents an increase in the elastic component of the binder up to 58°C. For 3% LLDPE PMB unusual behavior was observed with the tremendous decrease in phase angle up to 60°C, followed by an increase in phase angle and then sudden drastic decrease. Such behavior of 3% LLDPE PMB indicates that there was absence of any structure in the polymer bitumen blend. At higher concentration of polymer it does not possess any property of compatible polymer bitumen blend. Such behavior might also have occurred as polymer pallet at higher concentration do agglomerate and thus failed to form a proper polymer bitumen blend.

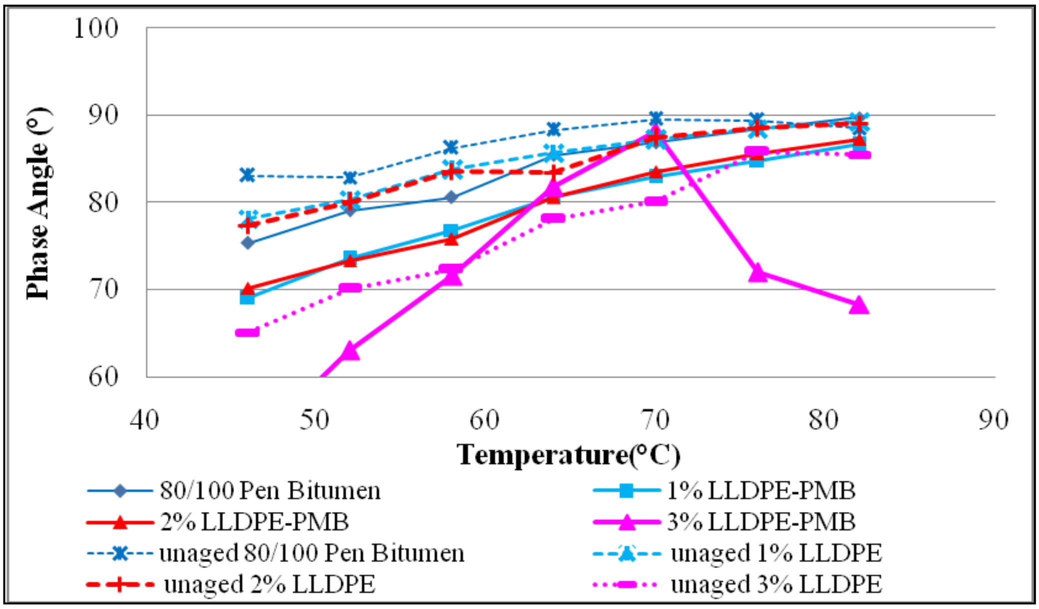

Figure 6.8: Phase Angle Vs Temperature for LLDPE PMB & 80/100 Pen Bitumen

6.4 Summary of the Results

The rheological test data obtained from DSR results considered as reliable test in comparison to old conventional rheological tests (Penetration and softening pointy) as it consider the variation of temperatures and loading times. The decrease in phase angle at medium to higher temperature for PP PMB indicates the formation of polymer bitumen network as observed by TEM and lower colloidal Index values. Because of compatibility of polymer PP with bitumen it will offer higher rutting resistance in medium to high temperature range. This behavior of the PP PMB can be attributed to enhancement in viscoelastic characteristic of modified binder as observed from the lower phase angle values for the PP modified binder.

For LLDPE modified binder sufficient increase in stiffness was observed even at lower concentration of polymer LLDPE in bitumen. Increase in viscous component for LLDPE modified binder was more in comparison to PP modified binder. Although unusual behavior was observed for 3% LLDPE modified binder but it can also be deduced from the plotted graphs between shearing resistance and temperature that at 3% the behavior would be closer to the binder which would offer enhanced viscoelastic characteristic by showing resistance to deformation. Thus 3% LLDPE would offer good rutting resistance at higher pavement temperature above 76°C.

CHAPTER 7

ENGINEERING PROPERTIES OF BITUMINOUS MIXTURES

7.1 Introduction

Strength of bituminous mix defined in terms of the mechanical strength not only depends on the properties of the binder but also on the aggregates. In the matrix of bitumen and aggregates where bitumen plays the main role as binder, aggregate also has significant effect on the composite properties. Proper aggregate skeleton with sufficient air void content along with binder has significant effect on the mechanical properties of the end product. The binder’s rheology and chemical structure of the binder also shows its dominance on the altering the engineering properties especially in case of polymer modified bituminous mixture.

As the main research objective of this study was to use the thermoplastic polymer as bitumen modifier for 80/100 pen bitumen, thus the engineering properties calculated from standard laboratory procedure would be discussed with focus on binder characteristics rather than aggregates and filler used. The parameter discussed over here provides a preliminary prediction of the mixture’s performance for both modified and control mixes. The gyratory method of compaction was adopted in order to subject the mixture to actual compaction level encountered during construction process and in service life of the pavement.

Engineering properties of the mix strongly depends on the aggregate properties. In order to calculate the engineering properties the specific gravity of the binder and aggregate was calculated using standard test procedures as explained earlier. The values obtained for specific gravity of the binder is presented in Table 7.1. The aggregate properties are presented in Table 7.2.

Table 7.1: **Specific gravity of Binders**

Type of Binder	Specific Gravity [a]
Bitumen	1.01
1% PP PMB	0.984
2% PP PMB	0.996
3% PP PMB	0.996
1% LLDPE PMB	1.03
2% LLDPE PMB	1.04
3% LLDPE PMB	1.04

[a] Average of three evaluation

Table 7.2: Properties of Aggregate and Filler

Material	Property	Value	Ultrapycnometer
Coarse Aggregate	Bulk Specific Gravity	2.57	2.632
	Specific Gravity on SSD	2.48	
	Water Absorption (%)	0.55	
Fine Aggregate	Bulk Specific Gravity	2.62	2.645
	Specific Gravity on SSD	2.54	
	Water Absorption (%)	3.5	
Filler	Specific Gravity	_	3.266

(SSD = Saturated Surface Dry)

Since ACW-14 gradation was used for the research study, thus the preparation of Marshall Specimen sample, the aggregates were weighed according the calculated weighed amount shown in the Table 7.3. The plotted gradation curve as shown in Figure 7.1, shows that the chosen gradation lies within specified gradation limit as specified by JKR for ACW-14.

Table 7.3: Aggregate Gradation (JKR Standards: 1988)

B.S Sieve	% Passing by weight		% Retained	Weight Retained (gram)
	Gradation Limit	Gradation Used		
20.0mm	100	100	0	0
14.0mm	80-95	87	13	156
10.0mm	68-90	77	10	120
5.0mm	50-72	60	17	204
3.35mm	45-62	52	8	96
1.18mm	30-45	36	16	192
425μm	17-30	22	14	168
150 μm	7-16	10	12	144
75 μm	4-10	5	5	60

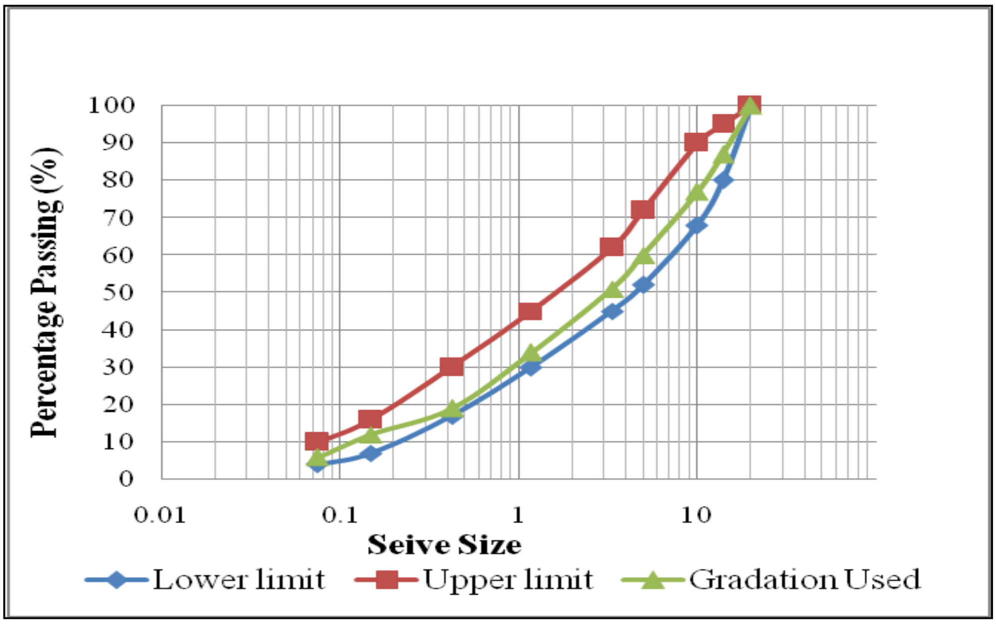

Figure 7.1: Gradation limit and design curve for ACW-14

7.2 Results & Discussion of Engineering Parameters Calculated from Marshall Mix Design

Marshall Mix design method according to ASTM D 1559 was used to study the effect of polymer modification on the engineering properties of polymer modified bituminous mixed samples. Polypropylene and Linear low density polyethylene used for modification of bitumen were mixed in proportion of 1%, 2% & 3% by weight of bitumen. Crushed granite was used as coarse aggregate, river sand as fine aggregate while ordinary Portland cement was used as filler. Only one gradation (ACW-14) was used throughout the experimental work following the standard JKR specification.

The properties of modified mixtures were compared with control mix prepared from virgin 80/100 pen bitumen. The parameters considered for the discussion of engineering properties results includes:

- Workability
- Density
- Voids in mixed aggregate
- Voids filled with bitumen
- Porosity
- Marshall Stability
- Marshall Flow
- Marshall Stiffness/ Quotient

7.2.1 Workability

Workability can be defined as a mix property that describes the ease with which bituminous mixture can be placed and compacted. Workability of the bituminous mixture is highly dependent on the composition of the mixture like grade of the binder, amount of binder used, aggregate type and gradation used for the design mix. Beside these external parameter such as type of equipment used for the compaction and temperature of compaction also has profound effect on the workability of the mix [170]. Workability thus considered as significant parameter in HMA design which confirms the relative ease or movement of aggregate particles during compaction having profound effect on the density of the compacted mix. Sufficient workability in the mix helps to construct the pavement with desired smoothness and density. In optimization of mix design by selecting appropriate binder content, workability of the mix can also be used as an effective indicator. Workability of mix at selected binder content and compaction level would represent the achievable density at particular amount of air void for that particular binder content.

In this study three types mixes namely control mix made from 80/100 pen bitumen and two polymer modified mixes incorporating polypropylene (PP) and linear low density polyethylene (LLDPE) were used. For polymer modified specimens, modified PP and modified LLDPE specimens were prepared with 1%, 2% & 3% polymer concentration by weight of the bitumen were used. The mix was prepared at 160ºC and compacted at 135ºC using the Servopac gyratory compactor. The number of gyration was set at 200 (from ASSHTO 2001) after considering anticipated traffic level over a period of 20- year with traffic loading ≥ 30 millions of ESALs. A 1.25° angle of gyration and normal pressure of 600 kPa(87psi) was adopted. For each type of mix, three specimens were prepared at binder content varying from 4%- 6.5%. The behavior of the control and modified bituminous mix during compaction was evaluated by registering the number of revolution at every 25, 50, 75, 100, 125, 150, 175 and 200 revolution of the gyratory compactor to decrease in height of the specimen. The graph plotted between the decrease in porosity as represented by the decrease in height of the specimen against number of cycle/ revolution, which is later on related to workability index (WI). WI indirectly represents the ease with which the bituminous mix can be laid and compacted during construction as a good workable mix was also considered responsible for the mechanical stability of the bituminous mix.

To understand the behavior of individual mix, a graph which was plotted between porosity and logarithm number of revolutions was used to develop a linear relationship by using expression

$Y= A- Bx$

Where: Y= porosity of the mix

x= log number of gyratory revolution

A= intercept and B= slope of line

When the porosity of the mix was plotted against gyratory revolution in logarithm scale it was observed that for all modified mixes and control mix, the lines plotted between porosity and number of revolution were parallel indicating that the porosity of the specimen decreases linearly with the number of revolutions, while the position of each line for particular bitumen content indicates its workability and the slope of the line represents the sensitivity of the mixture at that particular bitumen content.

Workability Index (WI) is the term which can effectively define the workability of the mix [171]. Workability Index was represented as inverse of mixture's porosity value or inverse of intercept "A" on zero revolution multiplied by 100, where as the mixtures having workability index less than 6, considered to offer difficulties during compaction in the field.

Workability Index $WI = 100/A$

Where W= Workability Index

A= the intercept of the line and y – axis

It was observed that polymer modified bituminous mix shows difficulty in compaction due to increased binder viscosity thus the binder would offer resistance against compaction as observed by the decrease in workability index.

It was observed that the workability index for all PP PMB modified bituminous mixture was still above minimum limiting value of 6.0. One the reason for this was due to increase in resin content beside increase in asphaltene content as observed by SARA test results. The resin which acts as stabilizer for asphaltene helps in the formation of a *sol - gel* kind of modified binder which was considered as the one of the helpful parameter in achieving better workability level for the mix up to 3% polymer content. The binder in the mix thus does coat the aggregate properly enhancing the strength of the mix but at the same time gives enough fluidity to the mix to be compacted properly. The entangle chain of polymer in the binder when being stressed during shearing action would untangle themselves and realign accordingly to the direction of applied shear stress [64]. This property of the binder would be held responsible for the better workability for the PP modified mixes.

For the LLDPE modified mix the agglomeration of particle due to addition of polymer was more for 2% and 3% polymer in the blend as observed by FESEM scanned images and SARA results for LLDPE PMB. The increase in asphaltene was also observed with the polymer loading for all LLDPE PMB. Partially dispersed LLDPE which was unable to form polymer network thus induce agglomeration in the blend. Due to this agglomeration although an increase in the viscosity of the blend was observed but at the same time it failed to properly coat the aggregate to offer desired adhesive properties required for a compatible bituminous mix. Thus due to in availability of proper bitumen polymer network and agglomerated polymer domains as observed by the AFM scanned images, the polymer bitumen network failed to offer enough fluidity to the blend but rather due to agglomeration offer resistance against shearing action of gyratory compactor.

Even at lower concentration of LLDPE polymer in the blend a sufficient increase in viscosity was observed. Thus enhanced viscous component of binder considered responsible for better aggregate coating providing sufficient fluidity, as also observed with an increase in WI values with the increase in binder content in the mix. For higher concentration of polymer (3%) in bitumen which would lead to a drastic increase in viscosity as also observed by coalesce and creaming effect in FESEM scanned images would be held responsible for failure in development of proper bonding between aggregate and modified binder. Thus due do insignificant fluidity in bituminous mixture it would offer resistance against shearing action of the gyratory compactor as observed by decrease in WI values even with an increase in binder content as shown in Table 7.4. In general the trend observed for workability index is that there is an increase in WI with an increase in binder content (refer Figure 7.2 & 7.3).

The workability index for the polymer modified binder doesn’t truly represent the shearing resistance of these binders. The shearing stress offered by gyratory compactor was by means of compaction where as modified binders offers shear thinning or pseudoplasticity when sheared apart [150]. Thus WI for modified binders cannot be considered as a true indicator of effectiveness and durability for polymer modified binder when represented in terms of workability.

In context with the above discussion it can be safely concluded that WI for the polymer modified bituminous mixes is very difficult to quantify. The other means like viscosity function calculated at 135°C was also considered as another method of looking at the workability of the mix. These viscosity measurements done at 135°C provides a better insight to the polymer modified bitumen behavior especially at handling, lay-down and compaction [172].

One of the reasons for these workable mixes obtained in this study was due to the lower concentration of binder used for the modification (up to 3%) as all the viscosity measurement in this study conducted at 135°C fall below the target 3Pa.s maximum viscosity parameter which was laid by ASSHTO MP1 for workable mix. At lower concentration of polymer in the mix the behavior of PMB was more or less like an emulsion where polymer rich phase found floating among asphalt rich phase [1]. Since complete compatible polymer bitumen mixture was not achieved, the blend thus offers the characteristic of polymer beside the properties of bitumen.

The pavement industry thus purposely restrict the use of polymer to lower concentration as higher concentration of polymer would lead to the formation of incompatible system which shows difficulties at handling, lay down and compaction because of segregation of aggregate from binder under wheels of roller during compaction.

Void in mineral aggregate (VMA) also has significant effect on the workability of the mix. The PP PMB mixes shows greater VMA than LLDPE PMB mix as shown in Table 7.5 for mix properties at optimum bitumen content. Decrease in VMA was observed at optimum binder content for LLDPE modified mix samples. It indicates that sufficient voids were unavailable to allow binder to properly coat the aggregate. Thus inadequate film thickness was also considered as one of the cause of the decrease in WI at optimum bitumen content. The Asphalt Institute 1990 recommends that for mix containing 14mm maximum size aggregate must have at least 15% VMA for durable mix.

From the calculated values of WI as presented in Table 7.4 & 7.5 it can be safely concluded that polymer modified binder up to 3% polymer content in the mixture was able to produce the modified mixture having sufficient properties of spread ability and compatibility which could be evenly distributed during laying process and would exhibit compact mixture behavior by rearranging the aggregate particles when later compacted at site by roller.

Table 7.4: Workability Index for PMB and Control Mix

Binder content %	Control Mix	1%PP PMB Mix	2%PP PMB Mix	3%PP PP PMB Mix	1% LLDPE PMB Mix	2% LLDPE PMB Mix	3% LLDPE PMB Mix
4	6.36	6.42	6.57	6.46	6.0	5.88	6.13
4.5	7.51	7.37	6.39	7	7.13	6.10	6.98
5	9.41	7.71	7.77	8.27	7.90	6.50	7.37
5.5	9.32	9.23	7.85	7.14	9.94	6.88	9.01
6	10.13	13.44	13.29	10.64	9.95	11.51	11.27
6.5	15.12	10.38	12.44	19.57	10.94	12.21	11.78

Table 7.5: VMA at OBC for different mixes

	Control Mix	1% PP PMB	2% PP PMB	3% PP PMB	1% LLDPE PMB	2% LLDPE PMB	3% LLDPE PMB
OBC%	5	5	5.2	5.2	5.2	5.4	4.7
VMA %	15	15.55	15.1	14.8	14.12	14.67	14.11
W.I	9.41	7.47	7.77	8.28	7.13	6.1	6.46

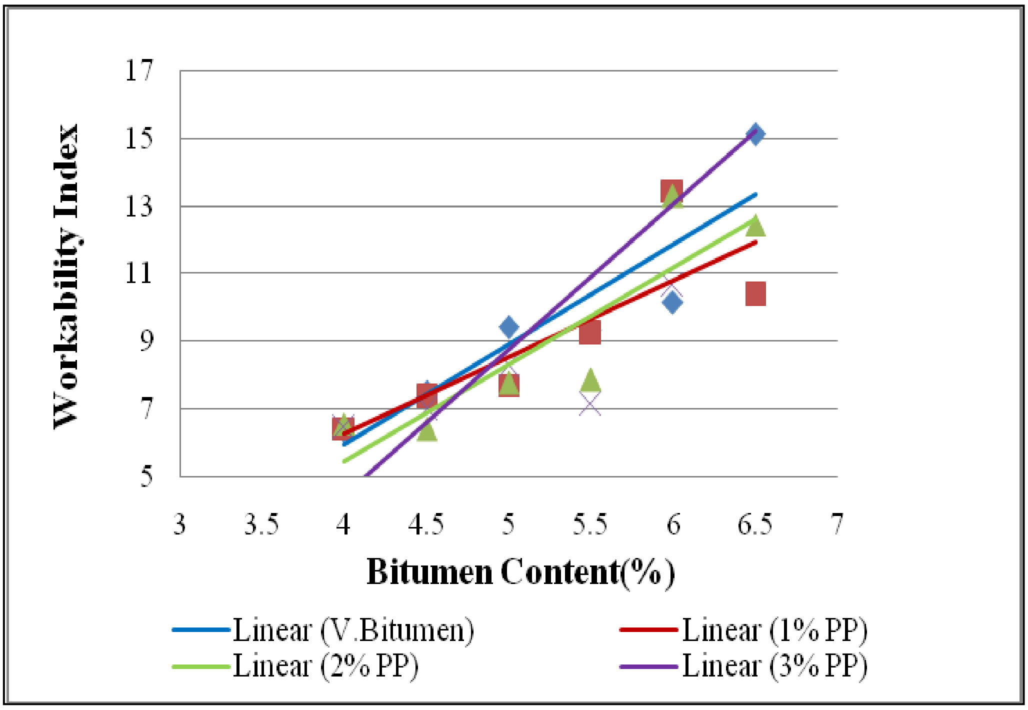

Figure 7.2: Workability Index Vs Bitumen Content for PP Modified Bitumen

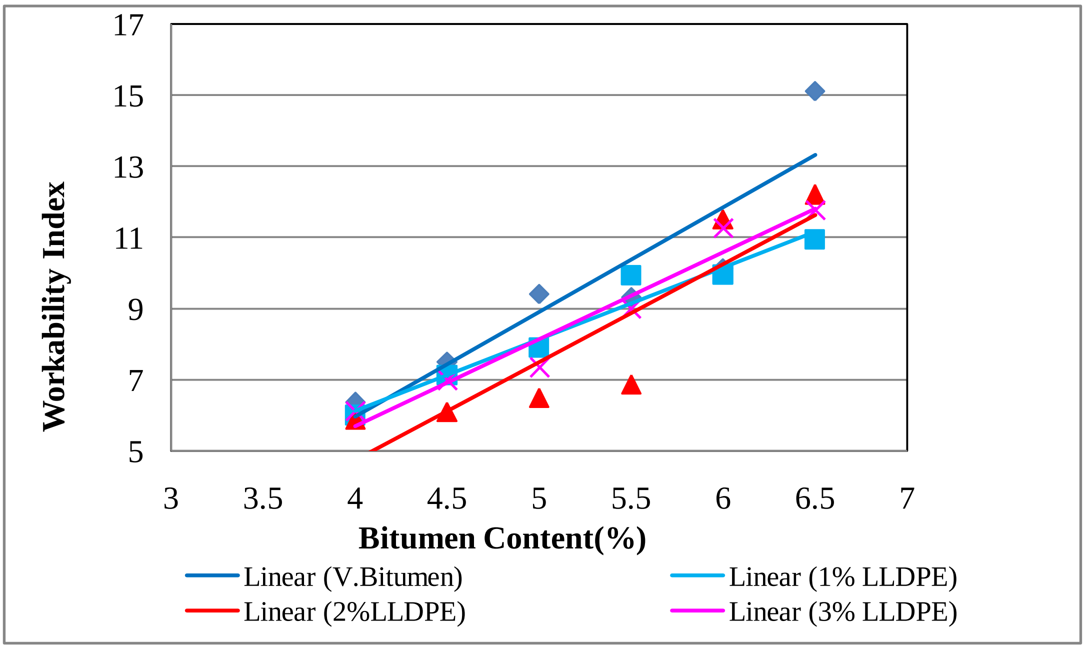

Figure 7.3: Workability Index Vs Bitumen Content for LLDPE Modified Bitumen

7.2.2 Density

Density is one of the most important factors in the construction of the HMA pavements which affects the service life of the pavement. The density of the mix also gets affected by the type of the binder, aggregate gradation and size. Use of appropriate mixing and compaction temperature helps in proper coating of aggregate with binder thus also affect the density of the HMA mixtures [111]. Density is also rather used as an indicator of pavement behavior in service when constructed at desired compaction level indicating the anticipated traffic level to be encountered in future.

Density for the polypropylene modified sample and linear low density polyethylene modified sample are shown in Figure 7.4 & 7.5. In general the density of the bituminous mixture shows increment with the increase in binder content until it reaches a peak value after which it decreases. This trend was observed due to the binder's viscosity which coats the aggregate and acts as a lubricant allowing the aggregate to slide past each other when being compacted. Maximum density was observed when all the voids were filled with binder. After the optimum value had been reached the binder failed to enhance the cohesiveness among aggregate and thus only act as medium to displace the aggregate.

From the graph for the density Vs bitumen content for polypropylene modified mix as shown in Figure 7.4, it was observed that 2% PP modified bituminous mixture exhibit a 1.3% increase in density value in comparison to other concentration of polymer in the blend. Highest peak in density for control and modified sample was observed at 5.5% binder content. An increase in density can be related to the better compatibility of PP with bitumen as observed by the colloidal Index which represents the compatibility of polymer bitumen blend. Thus with better compatible polymer bituminous blend with least variation in CI values were reflected in density of both PP modified and control mix bituminous mixture. Thus compatible polymer bitumen blend as observed during morphological study of the blend would impart viscoelastic characteristics beside the polymer characteristics. Thus the modified binder with enhanced viscosity and stiffness results in the development of binder which besides properly coating the aggregate gives mechanical strength to the bituminous mixture.

The most noted point for all PP modified binder was the higher density values in comparison to control mix at lowest binder content i.e. at 4% binder content. This attitude of the modified binder can be attributed to the lower specific gravity of PP modified binder (0.964) which had the ability to fill voids thus enhancing the density of the mixture.

Viscosity of the modified binder also considered as contributing factor by forming a firm film around the aggregate which also enhances the density of the bituminous mixture. Lower polymer content like 1% PP in bitumen would be considered insufficient to impart the properties of modifier in comparison to 2% and 3% polymer content in bitumen.

Figure 7.5 shows the graph plotted for density Vs binder content for LLDPE modified mix specimen. The same trend of increases in density with the increase in binder content till 5% was observed. Decrease in density was observed with further increase in binder content. Density of LLDPE modified mix specimen shows 1.3% increase in density in comparison to control mix. 2% and 3% LLDPE modified specimen shows higher densities in comparison to control mix. The higher density at the same compaction effort can be attributed to proper coating of binder around aggregate leaving less unfilled voids in the mix. The specific gravity of LLDPE modified binder (1.04) slightly higher than specific gravity of bitumen (1.01) properly coats the aggregate and thus shows an increase in density and decrease in unfilled voids in the mixture.

In view of above discussion it can be safely concluded that both LLDPE and PP modified specimen shows an increase in density of the mix at 3% polymer concentration in the blend. For both modified mix specimen this increase was 1.3% higher than control mix specimen. Highest density was achieved for all mixes around 5 - 5.5% binder content which gradually decreases with the increase e in binder content.

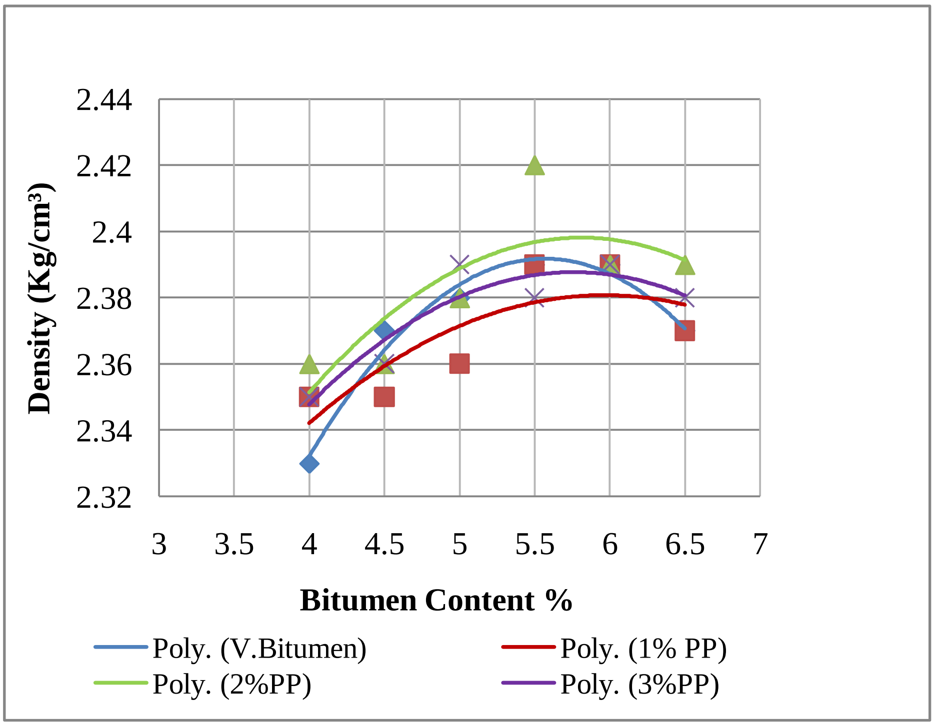

Figure 7.4: Density Vs Bitumen Content Graph for PP modified and Control Mix

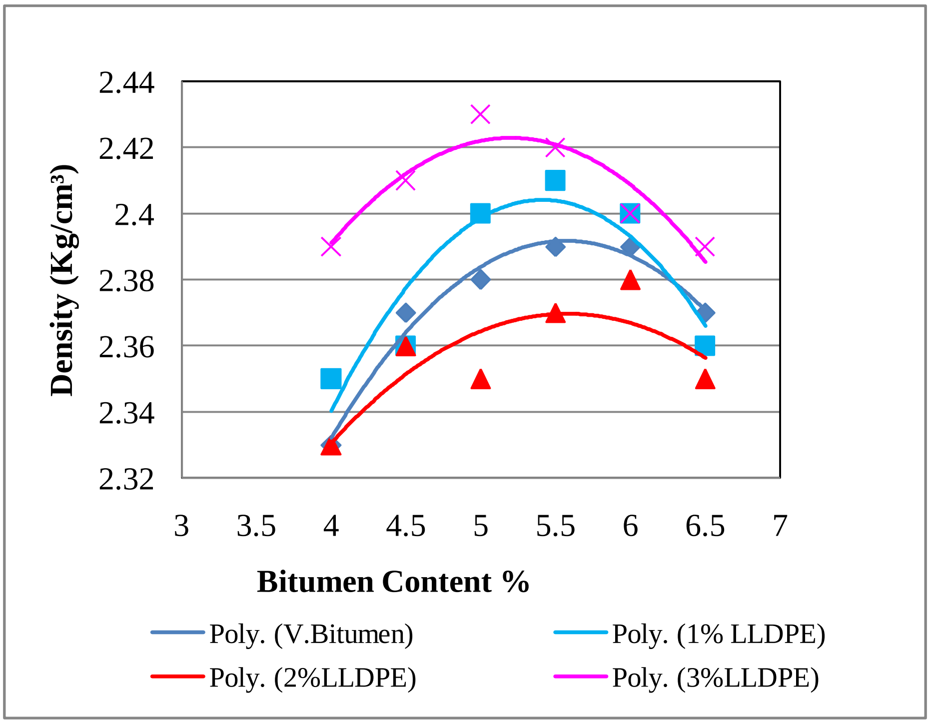

Figure 7.5: Density Vs Bitumen Content Graph for LLDPE modified and Control Mix

7.2.3 Voids in Mineral Aggregate (VMA)

Voids in mineral aggregate expressed as percentage, refers to the volume occupied by air voids and the amount of binder not absorbed by aggregate. VMA is considered as the most important parameter which affects the durability of bituminous mixture. Adequate amount of voids provide enough space for the binder to properly coat the aggregates along with sufficient space available for the leftover binder which was not being absorbed by the aggregate. Proper coating of binder along with adequate VMA would leads to a durable mix which would not offer stability problem during in service life of the pavement [108].

The importance of VMA in designing of bituminous mixture cannot be neglected as it gives an idea about the voids which were left among aggregates after compaction. Too little VMA would not allow binder to coat the aggregate properly, resulting in thin film of binder around aggregate. Insufficient coating of aggregate by binder results in bituminous mixture which would be vulnerable to either stripping due to existence of weak bond between binder and aggregate or leads to the oxidation of the binder where entrapped air easily hardens the bitumen.

As there is no limitation being specified by Jabatan Kerja Raya (JKR) Malaysia standards for VMA, thus Asphalt Institute design criterion 1990 [173] for roads specification was used. According to this standard for maximum stone size of 14 mm which was used in this study, the minimum VMA must not be less than 15%.

From Figure 7.6 it can be observed that there was a decrease in VMA till 5% binder content for control and PP modified specimen followed by an increase in VMA. Increase in VMA was observed as the binder content increases. The minimum 15% VMA content criteria was satisfied by control, 1% and 3% PP modified specimen but 2% PP modified specimen shows slightly lower than 15% at 5% binder content.

The VMA characteristics when considered in view of packing characteristics of aggregate and binder properties it was revealed that PP modified bituminous blend with lower colloidal index (CI) helps in providing proper coating of aggregate beside giving strength to the mixture. The development of strong bond between aggregates would thus resist further densification as observed by the availability of the desired amount of VMA in the mix after 200 gyrations. Thus it can be safely concluded that for PP modified bituminous specimen, proper coating of aggregate with binder helps in the formation of well developed aggregate bitumen structure imparting mechanical strength to the mix making it more durable. Thus decrease in VMA till 5% binder content for 2% and 3% PP PMB modified specimen indicates that it will increase the mixture strength and stability.

From Figure 7.7, for LLDPE modified specimen decrease in VMA was observed at the higher concentration of the polymer in the blend. This behavior might have occurred due to incompatibility of the polymer bitumen blend which increases with increase in modifier in the bitumen. An increase in colloidal index (CI) value was observed for LLDPE modified bitumen indicating the incompatibility of the polymer bitumen blend.

This incompatibility was due to the formation of segregated polymer domains as being observed in AFM images for LLDPE modified bituminous blend. Thus enhanced viscosity of LLDPE PMB offer hindrance in binder absorption to aggregate [107] which was more pronounced for 3% LLDPE modified specimen.

2% LLDPE shows greater percentage of VMA in comparison to 1% and 3% LLDPE modified specimen indicating that enough VMA being available which can accommodate the variation in large stresses due to deformation of viscous component of the binder or reduction of air voids due to further densification of the material during in service life of the pavement.

This behavior of LLDPE modified doesn’t necessarily represent the true aggregate structure in the mixture responsible for VMA but rather represent a complex behavior of modified binder which can only be justified by the performance test for the bituminous mixture.

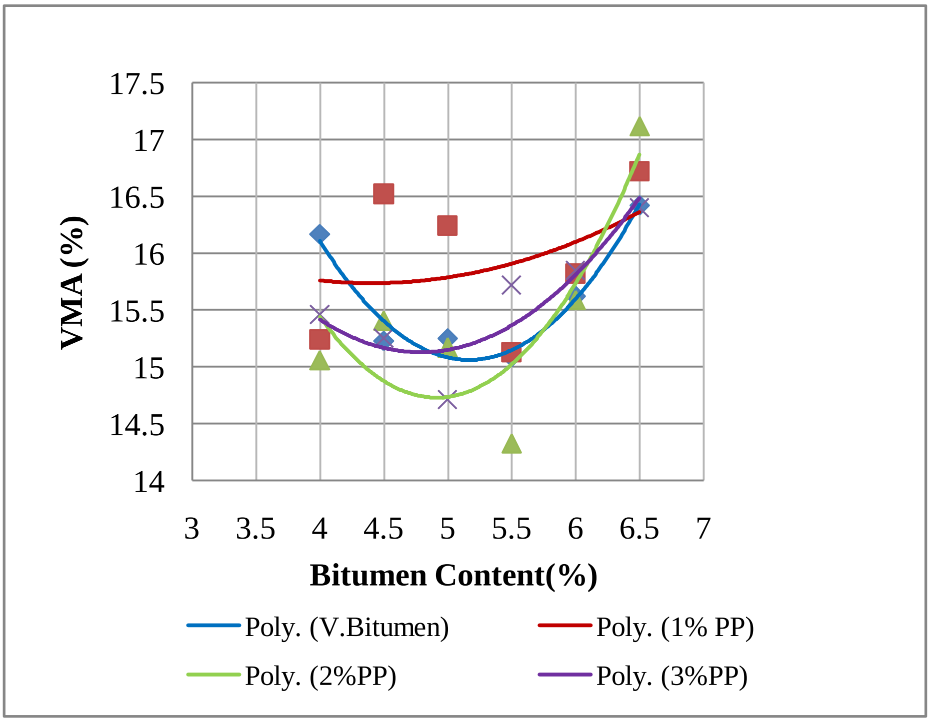

Figure 7.6: VMA Vs Bitumen Content Graph for PP modified and Control Mix

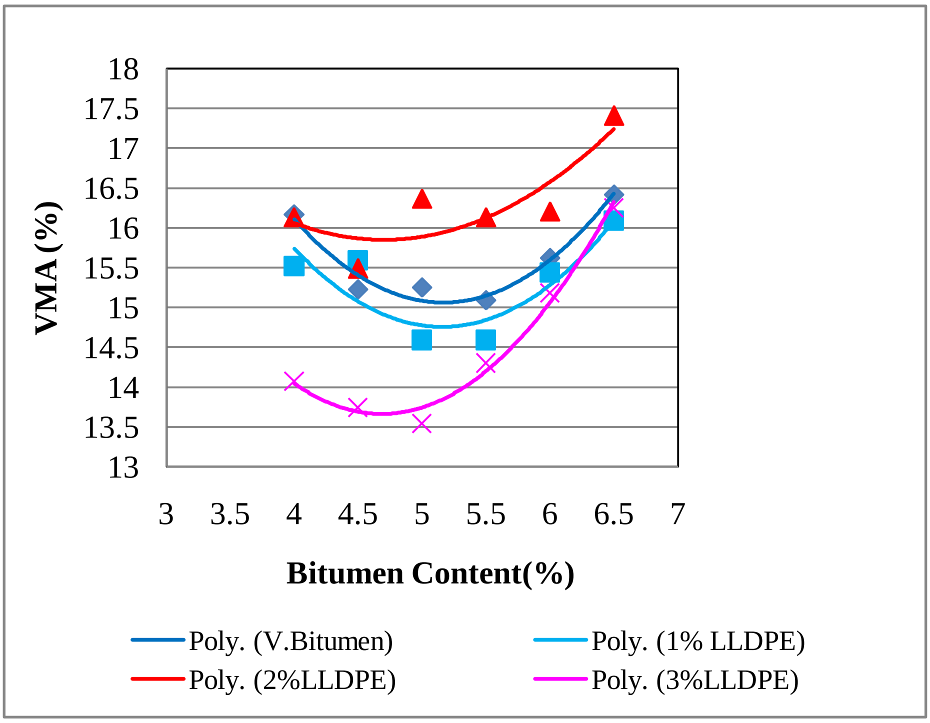

Figure 7.7: VMA Vs Bitumen Content Graph for LLDPE modified and Control Mix

7.2.4 Voids Filled with Bitumen

According to the JKR standard the requirement for void filled with bitumen in the bituminous mix ranges from 70 - 80%. The VFB results for all mixtures are presented in Figures 7.7 and 7.8. It can be observed that in all the mixes (control & modified mixes) the requirement of JKR was met after 5% binder content in the mix which keeps on increasing with increase in binder content for all mixtures.

From Figure 7.8 it was also observed that trend observed for VFB was almost same for all bituminous mixes. 2% PP PMB modified specimen shows a greater percentage of VFB in comparison to other above 5% bitumen content. This behavior can be attributed due to existence of compatible polymer bitumen blend for 2% PMB modified specimen where modified binder because of it enhance viscosity and compatibility properly coat the aggregates thus properly fill the gaps or voids among ggregate particle. An increase in VFB by 18% was observed for 5.5% binder content for 2% PP modified specimen indicating the compatibility of modified binder with aggregate. Similar trend was observed for both control mix and modified binder after 5% binder content in the bituminous mix. Thus it can be safely concluded after 5.5% binder further increase would be of no use as it would not be useful in strength enhancing factor for bituminous mixture by the development of strong bond between binders and aggregate.

From Figure 7.9, for LLDPE modified specimen it was observed that as the bitumen content increases the VFB also increases. The trend observed for 3% LLDPE modified specimen was different which meets the requirement of JKR at 4.5 % binder content in comparison to other mixes where up to 80% VFB criteria met at 5.5% binder content. This behavior may be attributed to the enhanced viscosity and incompatible polymer bitumen blend which makes 3% LLDPE modified binder remain unabsorbed in the pores of aggregate thus producing greater percentage of VFB in the bituminous mixture. For 2% LLDPE modified specimen, VFB trend indicates that although the viscosity of modified binder was increased but does get absorbed by the aggregate leaving appropriate amount of voids in the mix or VMA.

In general, for both control and modified mix specimen VFB content after 5% binder content increases significantly indicating that less air voids would be left in the compacted specimen.

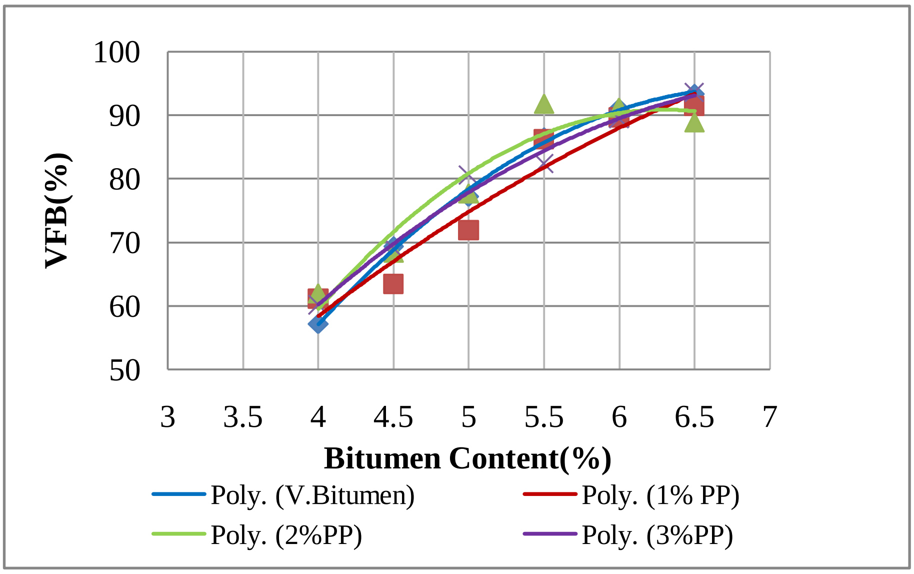

Figure 7.8: VFB Vs Bitumen Content Graph for PP modified and Control Mix

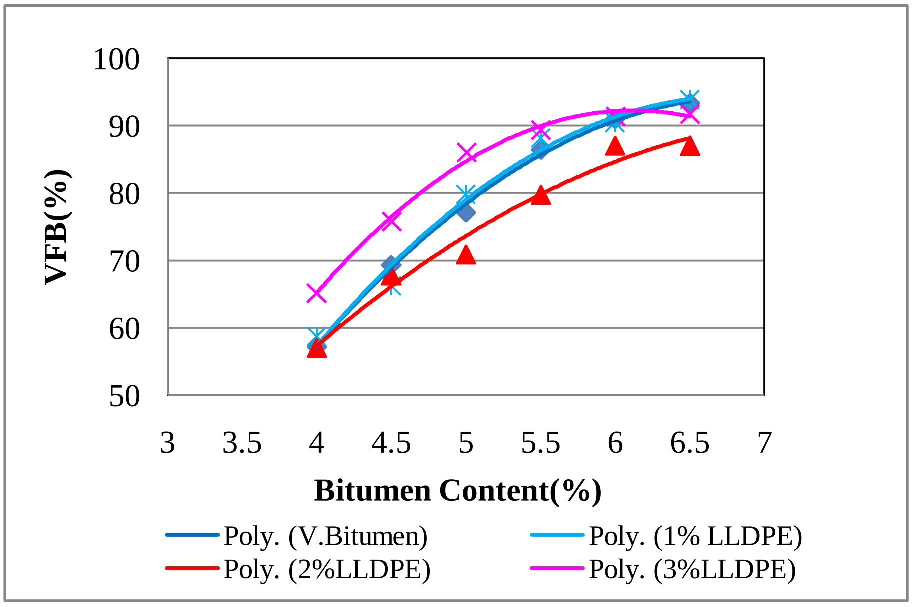

Figure 7.9: VFB Vs Bitumen Content Graph for LLDPE modified and Control Mix

7.2.5 Air Voids (AV)

Air voids (AV) is the percentage of air volume to the total volume of compacted asphalt mixtures. It expresses the percentage of small air pockets between the coated aggregate particles in the compacted bituminous mixture. The required air voids as specified by JKR standard is 3% up to 5%. A medium value of 4% is considered as reasonable value for designing air void content in the compacted bituminous mixture as the bituminous mixtures that ultimately consolidate during compaction to less than 3% air voids are vulnerable to rutting and shoving when placed at heavy traffic locations [113].

Pellinen 2004 [105] reported that stiffness of the mix is highly dependent on the air void content. Percent air void in the mix is considered a critical issue from the durability point of view. Greater the air void content, the more easily air and water can access the binder leaving a weak aggregate binder bond [120]. Air void content in the mixture also depends on the voids in mineral aggregate (VMA).

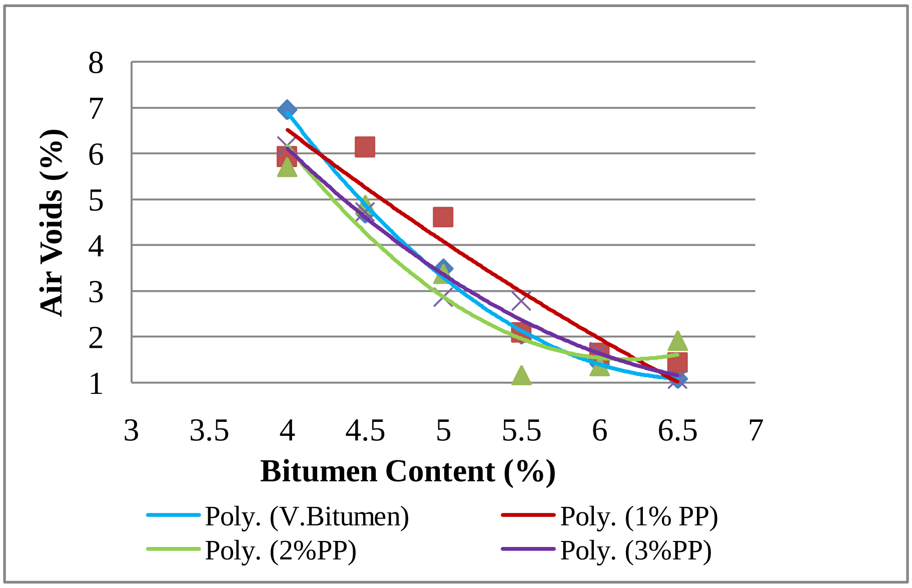

Figure 7.10: Air Voids Vs Bitumen Content Graph for PP modified and Control Mix

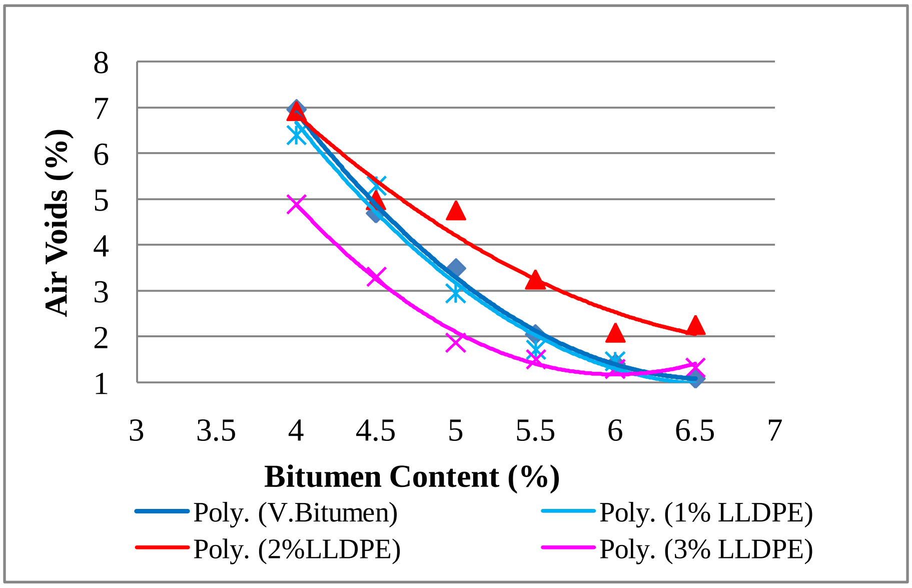

Figure 7.11: Air Voids Vs Bitumen Content Graph for LLDPE modified and Control Mix

From the Figure 7.10 & 7.11 it is observed that there was a decrease in air voids content with the increase in binder content for both polymers modified and control mix.

For PP modified specimen from the trend of curves it was observed that 1% PP PMB specimen shows a slightly higher void content in comparison to 2% and 3% PP PMB specimen. This behavior can be attributed to the viscous behavior of PMB which make it less incompressible. Beside viscosity, compaction manner also has great impact on the void content in the resulting compacted mixture.

The dispersion of polymer PP within the bitumen also has profound effect on the viscosity enhancement of the binder and its ability to fill in the gaps between aggregate. PP PMB with lower specific gravity (0. 964) penetrates easily among the gaps present between the aggregates. Air void content indirectly represents the compaction effort or the density of the mixture. Thus lower air void content for PP PMB specimen indicates that under shearing action of the gyratory compactor the shear thinning behavior of the binder makes the mixture more compressible leaving less air voids with the increase in binder content.

For LLDPE modified specimen as shown in Figure 7.11, 1% LLDPE modified specimen follows the same trend as control mix indicating that the modification at lower concentration of polymer failed to impart any significant affect on the mixture properties. For 2 % LLDPE modified specimen higher air void content at low binder content was observed. For 2 % LLDPE modified specimen it varies from 6.9% - 2.66% in comparison to 3% LLDPE modified specimen which varies from 4.9% - 1.33%. The higher viscosity and greater specific gravity (1.048) for 2% LLDPE PMB failed to properly coat the aggregate and ingress among the voids present in aggregate as also observed by higher VMA values.

For 3% LLDPE modified specimen, the higher viscosity value induces agglomeration affect as observed by the FESEM scanned images and higher colloidal index responsible for this behavior. The modified binder failed to be absorbed into the pores of the aggregate and remain as it is even at binder content below 5%.

Thus it can be safely concluded that 2% LLDPE modified specimen would produce stiff durable mix with air void content criteria meeting the standard specification requirement till 5% binder content.

7.2.6 Marshall Stability

Evaluation of mix stability using Marshall Stability method is widely used as an indicator of mix stiffness. JKR specification recommends a minimum stability value higher than 8kN for heavy traffic loading. Figure 7.12 & 7.13 shows the graphs of Marshall Stability versus binder content. The general trend observed for both modified PP & LLDPE specimen indicates an increase in stability values in comparison to control mix.

For PP modified specimen as shown in Figure 7.12, all PP modified specimen shows an increase in stability values. Slightly higher stability values were observed for all PP PMB modified specimen. This behavior can be attributed to the high rigid polymer structure of polypropylene resin. Blending of polymer with bitumen where as increases binder's viscosity, it also imparts rigidity to the binder. An increment of 12.5% in stability value was observed for 1%PP modified specimen in comparison to control mix at 5% binder content. For 2% and 3% PP modified specimen an increase of 11.7% in stability value was observed. This shows that variation in polymer concentration brings marginal increase in stability values.

It was also observed from the stability values for 2% and 3% PP PMB modified specimen that increase in binder content after achieving the peak value doesn't necessarily decrease stability of the mix drastically. This attitude of PP PMB modified specimen was due enhanced viscosity of modified binder which was considered sufficient enough to properly coat the aggregate developing a strong bond between aggregate.

For LLDPE modified specimen as shown in Figure 7.13 increase in stability values were observed at all concentration of polymer. Highest stability value was observed for 3% LLDPE modified specimen which shows an increment of 85.6% in comparison to control mix. For 1% and 2% LLDPE modified specimen an increase of 13.6% and 24.5% respectively was observed at 5% binder content.

This drastic increment in stability values that occurred at 3% polymer concentration considered to be brought due to take over of bitumen phase by polymer phase. Thus the polymer phase becomes dominant imparting the high rigidity property of polyethylene. This behavior was previously detected during chemical characterization of binder where value of colloidal index (CI) indicates the incompatibility of polymer bitumen blend.

From Figure 7.13 it was also observed that decrease in stability values were observed with increase in binder content for all LLDPE modified specimen. This indicates that stability of the mix is sensitive to certain optimum binder content after which further increment in binder content failed to enhances the mechanical strength of the modified specimen.

Thus it can be safely concluded that for polymer modified specimens density doesn’t necessarily represent as reflective indicator for stability as it merely depend on the degree of compaction. The stability values of the modified mixes reflect the viscous behavior of the modified binder beside the individual polymer properties as observed by the compatibility of the polymer bitumen blend.

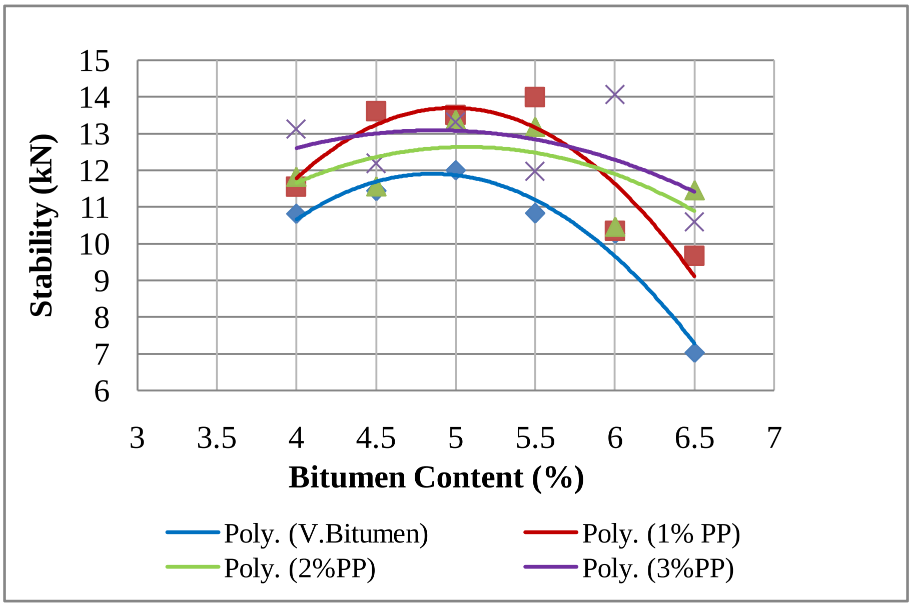

Figure 7.12: Stability Vs Bitumen Content for PP modified and Control Mix

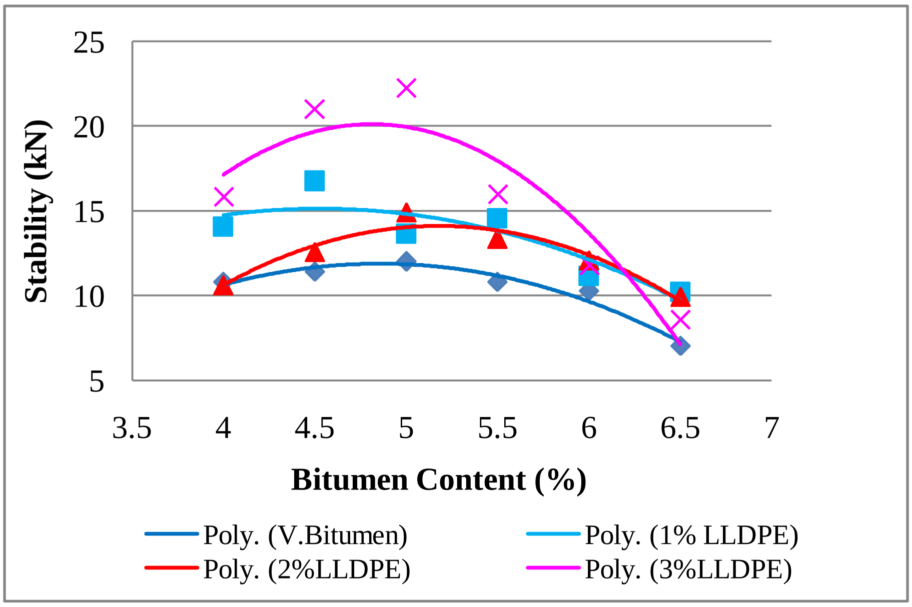

Figure 7.13: Stability Vs Bitumen Content for LLDPE modified and Control Mix

7.2.7 Marshall Flow

Flow characteristic of bituminous mixture gives an indication of the deformation of bituminous specimen that takes place in Marshall Test at failure. Flow values do not necessarily represents actual permanent deformation of the mix, rather it is considered analogous to the deformation mechanism. JKR standard defines flow values from the Marshall test from 2 – 4 mm.

Figure 7.14 & 7.15 presents the graph of flow for PP and LLDPE modified binder versus binder content. Generally the flow value increase with the increase in binder content indicating that addition of bitumen will reduce the frictional resistance among the aggregate particles, permitting it to deform under load.

Lower flow values were observed for 2% and 3% PP modified specimen in comparison to control mix indicating that modified binder helps in enhancing the strength of bituminous mixture by the formation of strong bonding between binder and aggregate. 1% PP modified specimen shows slightly higher flow values in comparison to control mix indicating that modified binder might unable to strengthen the modified mixture sufficiently. However all the values of flow for PP modified mixture and control mix are within permissible limit as specified in JKR standard.

From Figure 7.15 higher flow were observed for LLDPE modified specimen in comparison to PP modified mixtures and control mix. 3% LLDPE modified specimen exhibit slightly higher flow in comparison to control and 1% and 2% LLDPE modified specimen.

Marshall Flow although being used as indicator for deformation but does not necessarily represents the true picture especially for polymer modified binder where effect the effect of thixotropy cannot be over looked.

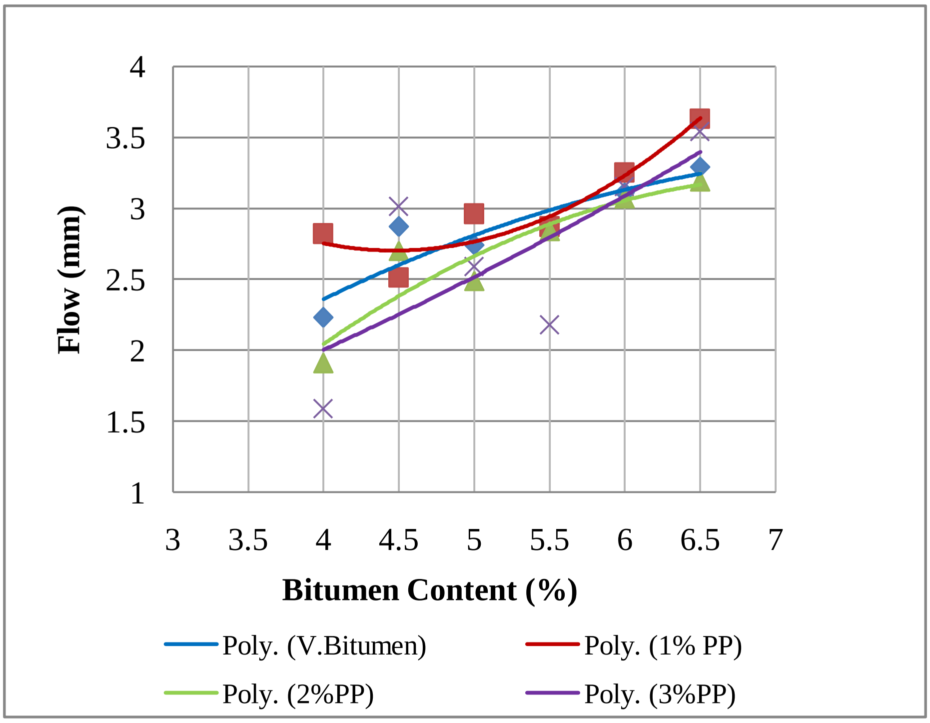

Figure 7.14: Flow Vs Bitumen Content for PP modified and Control Mix

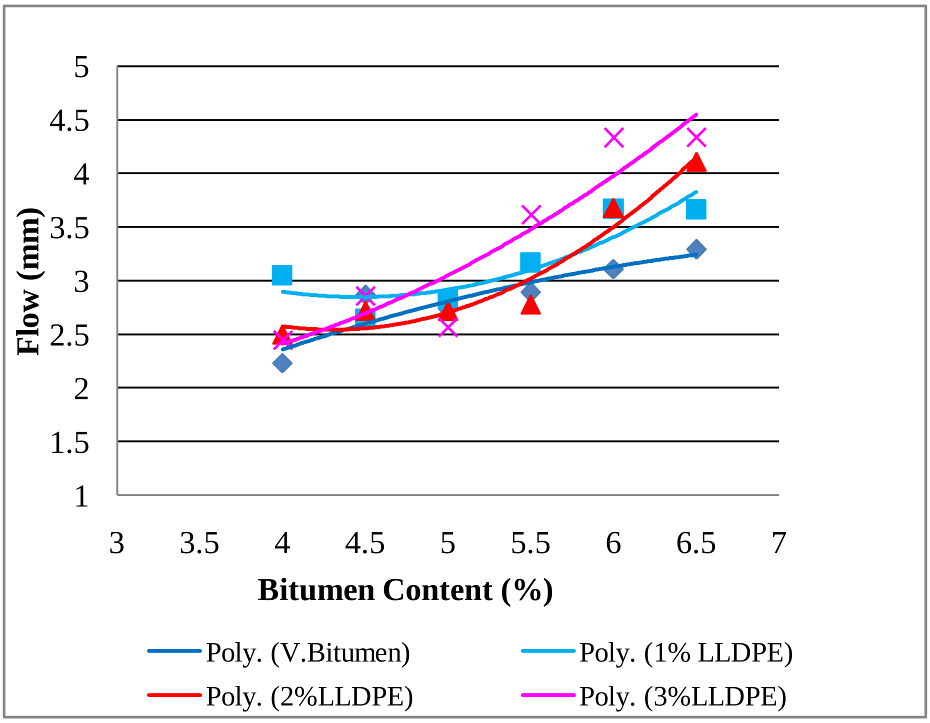

Figure 7.15: Flow Vs Bitumen Content for LLDPE modified and Control Mix

7.2.8 Marshall Quotient

Marshall Quotient is the parameter used to represent the stiffness of the Marshall specimen against deformation due to constant applied load. Calculated as the ratio of stability to flow, is considered as a better indicator of the resistance of bituminous mixture to deformation rather than just stability or flow alone.

Haddadi *et al.*,[174] considered the Marshall Quotient as an indicator of the resistance to the shear stress or permanent deformation. High values of Marshall Quotient values represent high stiffness of mix and therefore offer greater ability of the mixture to resist failure by cracking.

Figure 7.16 shows the Marshall quotient (MQ) for PP modified specimen versus binder content. For 1% PP modified specimen there is an increase in MQ values was observed to a maximum value with the increase in binder content. Further increase in binder content reduces the MQ value. This behavior of 1% PP modified specimen can be attributed due to the enhanced viscosity and compatibility of polymer bitumen blend which helped in proper coating of aggregate. Thus better interlocking among aggregate and binder due to increased cohesion was reflected as increased MQ value of modified mixes in comparison to control mix up to certain polymer content. Further increment acts as lubricant without enhancing the cohesiveness responsible for increased MQ value for 1% PP modified specimen.

For 2% PP and 3% PP modified specimen as shown in Figure 7.16, higher MQ values were observed at lower binder content which decreases progressively with the increase in binder content as shown by flatter curve. An increment of 27% for 2% PP and 49% for 3% PP was observed at 4.5% binder content. This behavior indicates that lower binder content was sufficient enough for bond development between aggregate and binder. The increased concentration of the polymer was considered as an additional strength enhancing factor, where polymer imparts its own rigidity due to its isotactic chain structure which sufficiently increases the MQ value at the same binder content. Further increase in binder content failed to increase MQ values as observed by high flow values with increase in binder content.

From Figure 7.17 it was observed that all LLDPE modified specimen shows increase in MQ at lower binder content which reduces with the increase in binder content. A drastic increase of MQ value was observed for 3% LLDPE modified specimen indicating the stiffening effect induced by the immiscible polymer resin which imparts its individual rigid characteristic of polymer. 2% and 3% LLDPE modified specimen also shows enhancement in the stiffness characteristic of modified binder. For all LLDPE modified specimen one thing was clear that higher binder content failed to develop strong bonding between binder and aggregate which thus acts only as lubricant, which can be easily compressed under same degree of compaction.

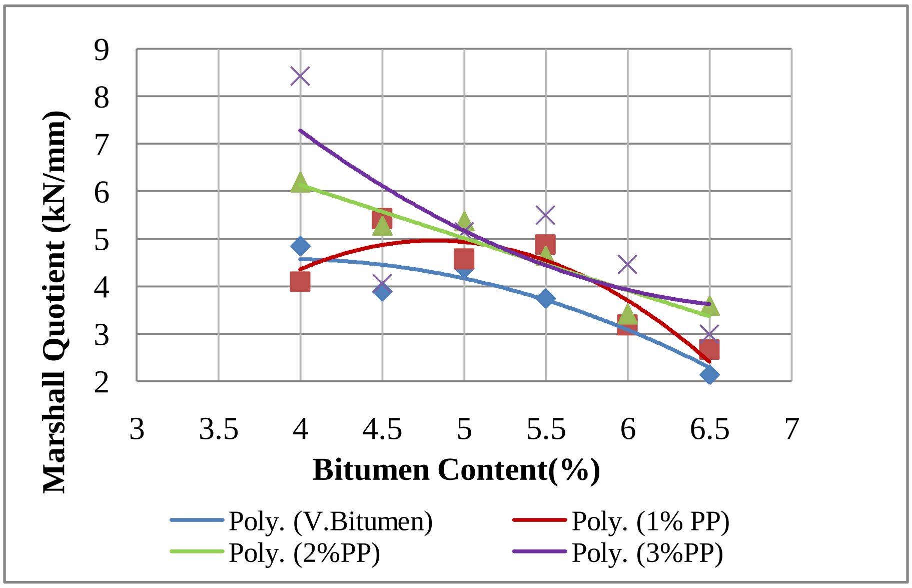

Figure 7.16: Marshall Quotient Vs Bitumen Content for PP modified and Control Mix

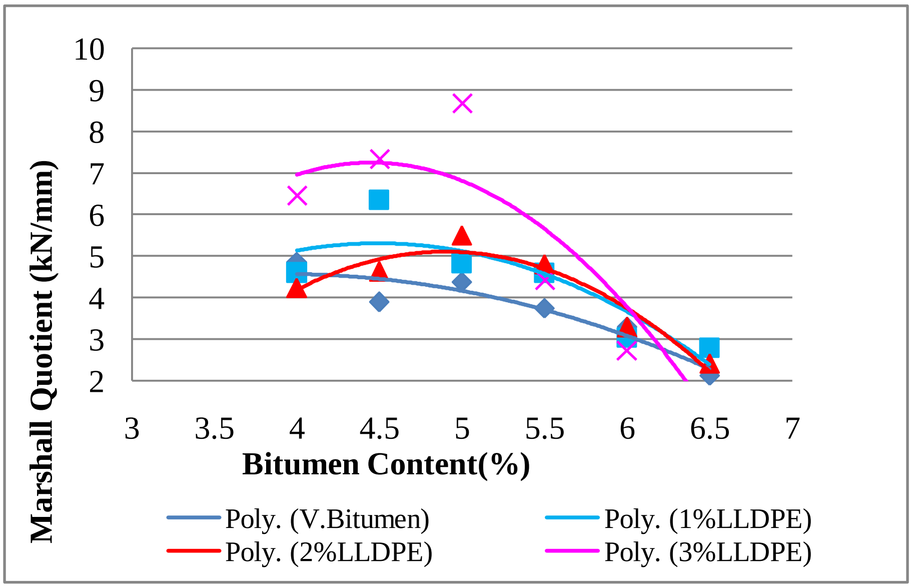

Figure 7.17: Marshall Quotient Vs Bitumen Content for LLDPE modified and Control Mix

7.2.9 Optimum Binder Content (OBC)

Optimum binder contents calculated as the average of binder contents corresponding to maximum stability, maximum unit weight (density), maximum stiffness (Marshall

Quotient) and 4% air voids were determined for different binders and are presented in Table 7.6. Marshall properties at optimum binder contents are also shown in the Table 7.6.

Many factors influence the behavior and performance of the bituminous mixture of which binder content has most significant place. A mix designed with this binder content must have sufficient stability to meet the demand of traffic, shows enough workability to be properly laid and compacted at site without segregation of aggregate from binder. Thus workable mix designed at OBC shows sufficient air voids, required ensuring the stability and durability of the designed pavement.

The calculated optimum bitumen content (OBC) for control and polymer modified mixes are shown in Figure 7.18. OBC value for control mix was found to be 5%. For 1% PP modified mixtures no variation in binder content was observed. A slightly higher binder content of 5.2% was observed for 2% and 3% PP modified mixtures.

For LLDPE modified mixtures a mixed trend was observed. With the addition of polymer an increase in binder content was observed from 5.2% for 1% LLDPE modified mixture to 5.4% for 2% LLDPE modified mixture. A decrease in OBC value was observed for 3% LLDPE modified mixture.

It is evident from the above mentioned OBC values for PP modified mixes that when PP PMB was used as binder there was insignificant increase in demand by the aggregate to provide an appropriate coating to produce durable mix. This attitude can be attributed to viscosity function of binder at mixing and compaction temperature. The enhanced viscosity of PP PMB was sufficient enough to properly coat the aggregate and when compressed under gyratory action of compactor, PP resin plays it part imparting physical and chemical characteristic rather than bitumen. Thus for the lower concentration of polymer like 1% PP no increment was observed. With the increase in polymer concentration a slight increment of 0.2% was observed. This minor increment can be attributed to increase desire of the mixture to provide sufficient fluidity to the mixture in order to get properly compacted during shearing action of gyratory compactor.

For LLDPE modified mixture the viscous part of the modifier along with immiscible polymer in the blend failed to coat the aggregate properly. With insufficient fluidity of binder, requirement of binder content increases as being observed by the 5.2% to 5.4% with just 1% polymer increment in the blend.

With the addition of 3% polymer drastic increase in the viscosity was observed which might have created problems during coating of aggregates with binder. Thus demand of binder by aggregate decreases due to increased agglomerated highly viscous nature of partially miscible 3% LLDPE modified binder.

7.3 Properties of Bituminous Mixture at Optimum Binder Content

The properties of control and modified mixes at their optimum bitumen content (OBC) are presented in Table 7.6. These values presented in Table 7.6 are compared with limiting criteria set by Jabatan Kerja Raya (JKR) Malaysia standards [134] as shown in Table 7.7. However as there is no limitation being specified by JKR for VMA, thus Asphalt Institute design criterion 1990 [173] for roads specification was used. According to this standard for maximum stone size of 14mm which is used in this study, the minimum VMA must not be less than 15%.

7.3.1 Properties of Control Mixture at Optimum Binder Content

Analysis of the results presented in Table 7.6 for control mixture it was observed that all the observed values stability, flow, VMA and stiffness at OBC are well above the limiting criterion held by JKR. The higher stability value and stiffness can be attributed to the selected coarse aggregate and gradation used in the mixture beside the excellent binding properties of 80/100 pen grade bitumen. The air voids values were towards the lower side of limiting criteria. This behavior may be due to usage of OPC as filler having larger surface area which fill in the voids left between the aggregates. The proper coating of aggregate with binder also considered as influential factor by producing dense mixture having lower air void content. This behavior of the mix is also confirmed by VMA which also meets the limiting criteria. Thus bituminous mixture prepared with 5% bitumen content might be vulnerable to deformation as in sufficient air voids content in the mix would not be able to accommodate further densification which would occur during in service life time of the pavement. Thus it is better to evaluate the performance of the mix at OBC – 0.5% and OBC + 0.5% binder content.

7.3.2 Properties of PP Modified Mixture at Optimum Binder Content

From the properties presented in Table 7.6 for PP modified mixture it is observed that modification increases the stiffness of the mix substantially. The formation of compatible polymer bitumen network as observed by the low colloidal index values and in scanned images of modified binder considered responsible for enhanced properties of modified mixture.

For 1% PP concentration sufficiently enhanced viscosity of the binder develop strong bond between binder and aggregate. The lower specific gravity of the modified binder penetrates well into the pores of the aggregate as observed by the amount of VMA left in the mix. Thus 1% PP modified mixture exhibit higher stability, lower flow values hence higher stiffness of the mix. The effect of the viscosity was reflected on the workability of mixture but still the value of workability index is above indicating it can be properly laid and compacted. For 2% and 3% PP modified mixture although the binder content was same but a slight difference in density and flow values were observed. A slightly lower value of density for 3% PP modified mixture represent the enhanced viscous component of the binder which offer resistance against densification during gyratory action of compactor. The lower flow values also support this behavior of modified binder showing resistance to deformation.

From the above analysis it can be safely concluded that PP modified binder sufficiently enhances the properties of binder even at lower concentration of the polymer in the bitumen. As the air void content in the mix for 2% PP and 3% PP were found to be at lower side of limiting value thus it is suggested that true behavior of the binder must be evaluated by using OBC – 0.5% and OBC + 0.5% binder content.

7.3.3 Properties of LLDPE Modified Mixture at Optimum Binder Content

From the properties presented in Table 7.6 it was observed that stability, flow, VFB and stiffness all meet the criteria set by JKR standard except for air voids and VMA which were found to be at lower side of specified limit. The enhanced viscosity of the LLDPE modified binder significantly enhances the stability of the mix. An increment of 70 % in stability value was observed for 3 % LLDPE modified mix specimen. Such a significant increment in stability with the correspondingly lower flow value definitely indicates stiffening effect induced by the polymer. The immiscible partially dispersed separate domains of LLDPE as observed in AFM scanned images considered responsible for this behavior. Polymer domains would impart its physical and chemical characteristic which polyethylene is well known for.

This behavior of LLDPE must be dealt with care as such drastic changes brought even at lower concentration of bitumen content may lead to brittle failure of pavement structure under load as the viscoelastic component of bitumen was overtaken by polymer itself. Thus it is suggested that properties of modified LLDPE bituminous mixture can only be evaluated by performance test where as Marshall test provide only crude information about performance behavior especially in case of polymer modified bituminous mixtures.

7.4 Summary of the Results

It was observed that polymer modification does not significantly enhance the optimum bitumen content for all modified mixes except for 3% LLDPE modified bitumen where there was a decrease in OBC was observed. Such behavior of 3% LLDPE represents that increase in viscosity of the binder decreases the amount of the binder required for coating. The higher viscosity of 3% LLDPE decreases the desire of aggregate to absorb the binder. Promising behavior in terms of increase in Marshall stability, density and Marshall Quotient was observed for both PP and LLDPE modified binder.

Since sufficient increment in viscosity was there due to polymer modification it affected the void content in the mix, which found to be at the lower side of the specified limit. Although it was known that polymer modification sufficiently increases the viscosity of the blend but the mixture produced from these showed sufficient workability as all the workability index values for PP modified bituminous mixture were well above limiting value of 6.0. For LLDPE modified bituminous mixture these values found to be at little bit lower but still above the limiting value of 6.0 thus can be compacted and lay down with ease.

Table 7.6: Engineering properties of Control & Modified Mixes at OBC

	Control Mix	1%PP PMB	2%PP PMB	3%PP PMB	1%LLDPE PMB	2%LLDPE PMB	3%LLDPE PMB
OBC %	5	5	5.2	5.2	5.2	5.4	4.7
Density (g/cm3)	2.38	2.37	2.41	2.39	2.46	2.4	2.4
Air void %	3.5	4.2	3.1	2.55	3.0	3.5	3.26
VMA %	15	15.55	15.1	14.8	15.39	14.67	14.11
VFB %	77	69	79	78	78.65	79.45	77.2
Stability (kN)	11.3	14.2	13.3	13.4	15.75	15.4	19.18
Flow (mm)	2.74	2.65	2.6	2.3	3.25	3.46	2.43
Stiffness kN/mm	5.15	5.6	5.3	5.4	4.85	4.45	7.88
W.I	9.41	7.47	7.77	8.28	7.13	6.1	6.46

Table 7.7: Asphaltic Concrete Mixture Requirements (JKR, 1988)

Parameter	**Wearing Course**
Stability (S)	> 8000 N
Flow (F)	2.0-4.0 mm
Stiffness (S/F)	> 2000 N/mm
Air void in mix	3-5 %
Void in aggregate filled with bitumen	70-80 %

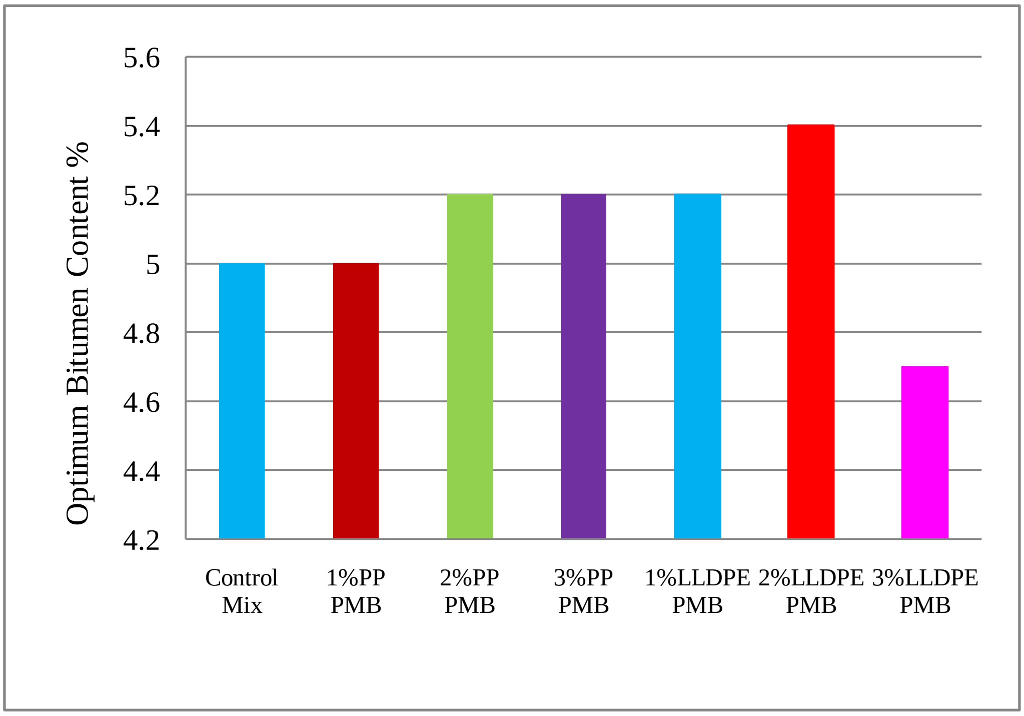

Figure 7.18: Optimum Bitumen Content for the Control & Polymer Modified Mixes

CHAPTER 8

FATIGUE CHARACTERISTICS OF BITUMINOUS MIXTURES

8.1 Introduction

Fatigue is a fracture phenomenon observed under repeated or fluctuating stress whose maximum value is less than the tensile strength of the material [13]. Highway pavements are subjected to continuous repeated wheel loading resulting in the accumulation of stresses as reflected by the loss of stiffness which ultimately leads to the fatigue cracking. Repeated loads cause the pavement to flex, thereby inducing tensile stresses at the base of the bituminous layer. When these stresses exceeds the tensile strength of the mix, will cause the crack to propagate upwards towards the road surface as shown in Figure 8.1 [175]. This occurs because there is a progressive weakening of these layers which in turn increases the level of stress transmitted to the lower layers and sub grade to a level that brings about excessive deformation. Thus with the repeated loading action of traffic the pavement starts to fatigue with the development of micro cracks.

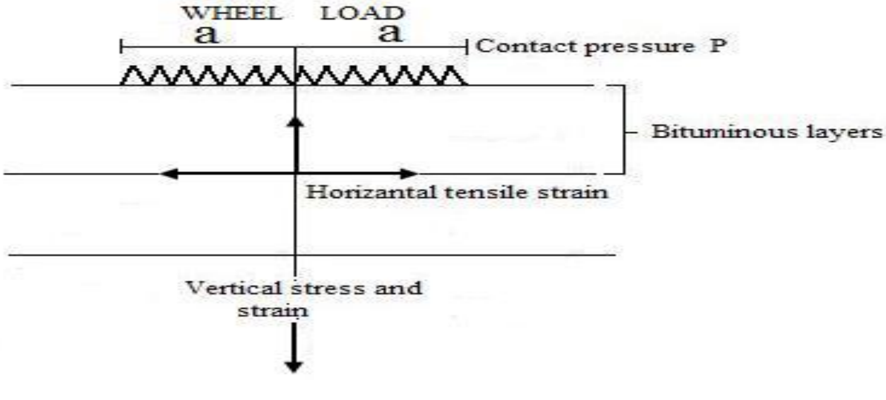

Figure 8.1: Location of stress and strain in the pavement layers [175]

Thus the development of tensile strain in the bound layer with the passage of each wheel load is considered responsible for fatigue besides repetitive loading which initiates the crack in the bound layer where the tensile stresses are higher than the structural strength of the pavement and by the time the crack becomes apparent, the damage was already there [176]. Pavement life because of fatigue decrease as the strain increases. Since for fatigue analysis the top wearing course (50mm) is more vulnerable to distress induced by moving traffic and harsh environmental conditions. Thus the stiffness of top layer is considered important which later on transmit stresses to the bound layer due to shear and tensile stresses.

8.2 Discussion of Beam Fatigue Test Results

Beam fatigue is one of the fundamental tests used for the performance characterization of the bituminous mixture widely used for the design of flexible pavements. The test is highly sensitive to the different parameters, among which temperature and mode of loading used for testing considered significant.

Beam fatigue test results for control and polymer modified mixes were presented in the following sections. All the beams were tested in constant strain mode of testing. Three strain levels 100, 300 and 500 micro strain were used to determine the relationship between stress and the number of application of load to failure. The beams were compacted with same compaction effort and checked for the porosity in order to maintain the air voids content in the compacted beam between 3%- 5%. These beams were then later tested and results were utilized to develop relationship between different strain level and number of load applications to failure, which provides information about material response to particular strain level.

For constant strain mode of testing failure criterion as defined by conventional approach considered achieved when the specimen reaches 50% reduction in the initial stiffness modulus. This criterion does not seem reasonable especially for the beam specimen prepared with polymer modified bitumen. Thus for the determination of the fatigue behavior of the bituminous mixes, all beam were tested in this study under constant strain mode. The beams were flexed till the level when the micro crack starts initiating. The number of failure registered was thus the accumulation of number of cycles till failure either due to prominent advent of micro cracks or complete beam failure. Summary of the fatigue results is attached in Appendix.

8.2.1 Test Results of Polypropylene Modified Bituminous Mixtures

Figure 8.2 presents the fatigue lines plotted at different concentration of polypropylene modified mixes compared to control mix at optimum binder content (OBC). All the beams were prepared with polypropylene modified bitumen (PP PMB) at concentration of 1%, 2% and 3%. Binder content used for the preparation of beams were OBC – O.5%, OBC and OBC + O.5% , in order to check the effect of binder content on the fatigue life of the bituminous mixtures.

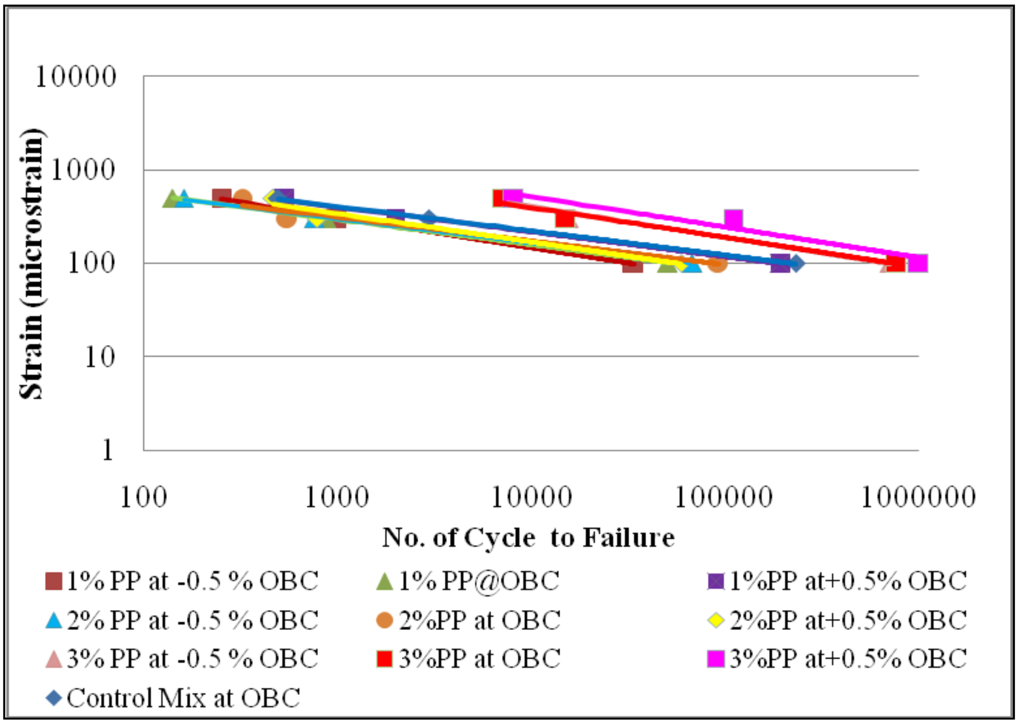

Figure 8.2: Fatigue Life N_f Vs Initial Strain for PP PMB & Control Mix

The regression analysis of the fatigue data was performed using power law. The format for the power law equation used was

$$\varepsilon = K\, N_f^{\,n} \tag{8.1}$$

Where: ε is the initial strain

K is the material constant which determines the position of line.

n is also material constant representing slope of line. The regression parameter depends on the material properties mixture.

The trend line obtained from different concentration of polymer at different binder content indicates that no significant improvement in fatigue life was observed for 1% and 2% PP PMB bituminous mixture in comparison to control mix. Only 3% PP PMB at (OBC – 0.5%), OBC and (OBC + O.5%) binder content shows significant improvement in the fatigue life of the bituminous mixture.

The effect of the binder content on fatigue life was as such is difficult to interpret as the binder's rheology and morphology also play an important part on the achieved fatigue life of the polymer modified bituminous mixtures. Obvious increase in fatigue life with an increase in binder content was also only observed for 3% PP (OBC+0.5%). For rest of the specimens such interpretation could not be made.

Although it was generally assumed that increase in stiffness of the mixture decreases the fatigue life in constant strain mode but for polymer modified mixes the binder's rheology does affect the behavior of the binder.

As fatigue is a low temperature phenomenon, thus the rheological data obtained from DSR results at temperature between 40ºC - 80ºC cannot be used as reference as an indicator of binder behavior in term of complex modulus (G*).

Morphological analysis as observed by AFM results conducted in non contact mode can be used as better explanation for fatigue test results. The phase lag (δ) which is considered analogous to rheological parameter tan (δ) = loss modulus/ storage modulus, indicates that an increase in phase lag with respect to virgin bitumen was observed. For virgin 80/100pen bitumen, the value of phase lag varies from 0.41º- 0.64º. With the addition of PP an increase in phase lag (δ) of 0.882º was observed for 1% PP and 1.006º for 2% PP. For 3% PP phase lag of 0.865º was observed. These values indicate that sufficient increase in viscosity was considered responsible for these values. Higher values of phase lag indicates that longer time period being required to retract the AFM tip from contact material. In other words the binder might also have the property of the viscoelasticity. From the DSR test results on aged samples also confirms the increase in viscoelastic component with the polymer modification. These findings of AFM morphological analysis and DSR results were confirmed, as 3%PP offer higher fatigue life in comparison to all polypropylene modified mixes. The formation of proper polymer bitumen network considered responsible for this altered rheological properties of the modified binder which enhances the viscoelastic component of the modified binder thus bituminous mixes.

The complete phase segregated polymer layer of 3% PP PMB was also considered responsible for improved fatigue life. AFM analysis for 3% PP PMB confirmed that it is composed of two segregated layers of different stiffness. Top layer composed of higher stiffness polymer PP while the lower stiffness partially miscible polymer bitumen layer at the bottom. This lower layer would thus flex under repeated load action, thus help in inhibiting crack propagation enhancing the fatigue life of 3% PP PMB mixture specimen in comparison to control mix [177] as shown in Figure 8.7. This interpretation of the AFM analysis was also confirmed by the beam fatigue test results for 3% PP PMB specimen when tested at high strain level, where higher fatigue life cycles was even observed at 500 micro strain level in comparison to all mixtures as shown in Figure 8.5. The network formation as observed by TEM images also support the behavior of 3% PP where entangle polymer chain align themselves against themselves against the repeated loading action.

The equations of fatigue line shown in Figure 8.2 are presented below

Control Mix at OBC $N_f = 2453\ (1/\varepsilon)^{-0.26}$

1% PP at OBC – 0.5% $N_f = 2921\ (1/\varepsilon)^{-0.32}$

1% PP at OBC $N_f = 1918\ (1/\varepsilon)^{-0.27}$

1% PP at OBC + 0.5% $N_f = 2442\ (1/\varepsilon)^{-0.26}$

2% PP at OBC – 0.5% $N_f = 1802\ (1/\varepsilon)^{-0.26}$

2% PP at OBC $N_f = 1831\ (1/\varepsilon)^{-0.25}$

2% PP at OBC + 0.5% $N_f = 2686\ (1/\varepsilon)^{-0.30}$

3% PP at OBC – 0.5% $N_f = 8539\ (1/\varepsilon)^{-0.33}$

3% PP at OBC $N_f = 7652\ (1/\varepsilon)^{-0.32}$

3% PP at OBC + 0.5% $Nf = 10901\ (1/\varepsilon)^{-0.33}$

Figures 8.3, 8.4 and 8.5 show the fatigue life of each mix at different strain level. From these figures it was observed that only 3% PP PMB shows improved fatigue life at all strain level in comparison to other mixes. This behavior of modified mixtures indicates that although partially miscible polymer increases the stiffness modulus of the mixture for 1% PP and 2% PP but failed to withstand against repeated loading action. Only 3% PP modified bituminous mixture shows better performance. As the strain level being increased reduction in stress was achieved quite quickly as observed by the reduction in number of cycles to failure (N_f) for control, 1% PP and 2% PP modified bituminous mixture.

Control mixture prepared from virgin bitumen shows improved fatigue life in comparison to 1% PP and 2% PP modified bituminous mixture. This unusual behavior of the control mix can be attributed due to viscoelastic characteristic of 80/100 virgin bitumen. For the 1% PP and 2% PP although the stiffness of the binder was increased but the phase segregated polymer bitumen layer was neither stiff nor flexible enough to accommodate the repeated loading action. Thus it can be safely concluded that for PP modified bituminous mixture, at 3% polymer content modified bituminous mixture gives better result in terms of fatigue thus it would offer higher fatigue life at 3% polymer content and might also shows better performance at higher content when tested. When the fatigue life of the PP modified bituminous mixture was compared with the endurance limit criteria defined in NCHRP report 646 [178], it was observed that for high volume traffic lane the endurance limit found to be 65 micro strain which is well below 100 micro strain test level. Thus the performance of 3% PP modified bituminous mixture at 100 micro strain level found to be well above that level thus can effectively be used for high volume traffic lanes. The different fatigue crack patterns observed for PP modified beam at different polymer content are shown in attached Appendix.

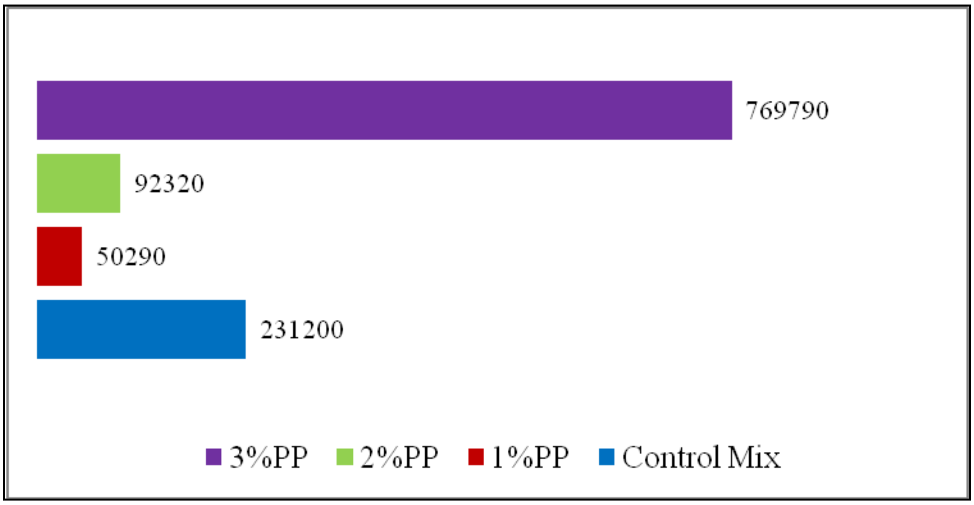

Figure 8.3: Fatigue Life at 100 με level for PP PMB & Control Mix Beam Specimen

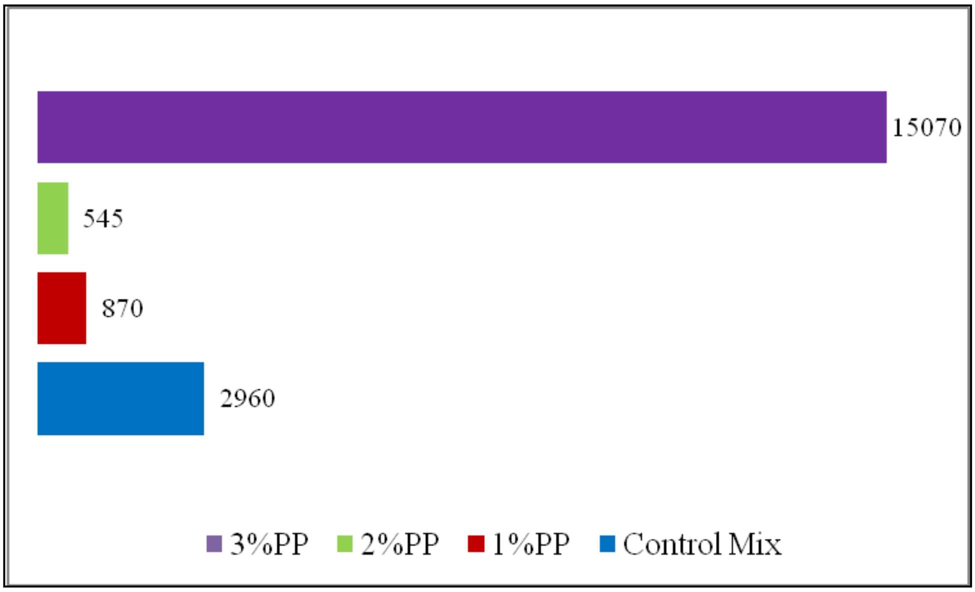

Figure 8.4: Fatigue Life at 300με level for PP PMB & Control Mix Beam Specimen

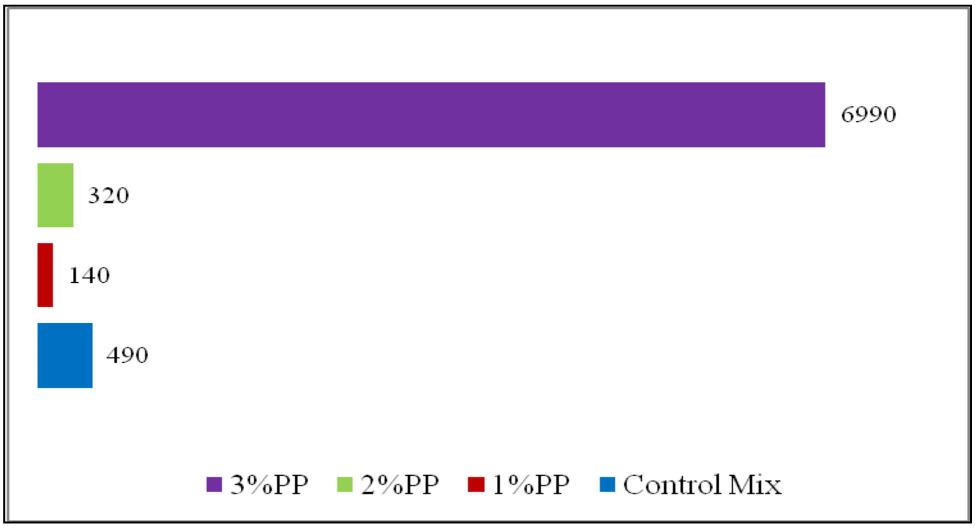

Figure 8.5: Fatigue Life at 500 με level for PP PMB & Control Mix Beam Specimen

Evaluation of tensile strain at the bottom of the pavement also provides information about mixture resistance to fatigue. Thus when the tensile strain (ε) developed due to fatigue resistance of bituminous mixture with the reference to one million (1,000,000) number of load repetition was calculated, it was found that the 3% PP at (OBC + 0.5%) shows the highest value of 114 μm/m. Beside this it was also noted from the results presented in Table 8.1, that all bituminous specimens prepared with 3% PP PMB at all binder content offer significant fatigue resistance.

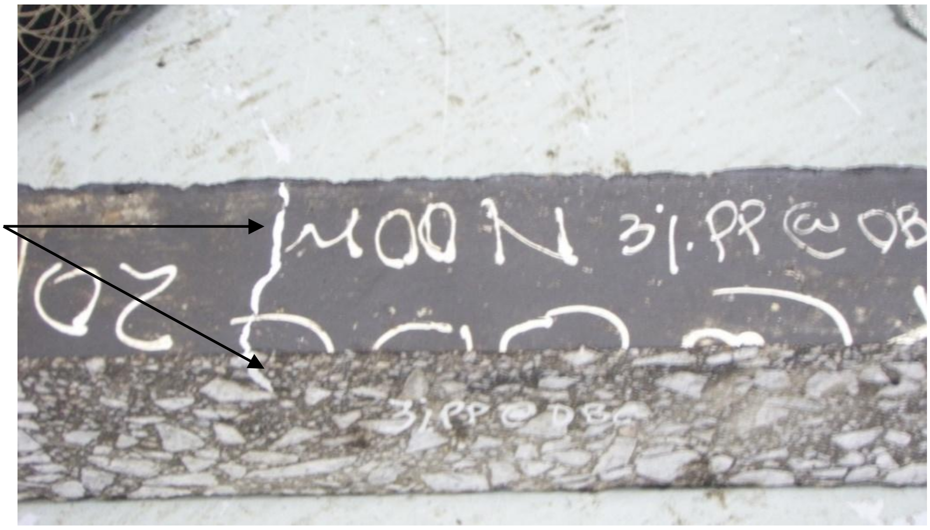
Crack
Propagation

Figure 8.6: Fatigue Crack pattern observed for 3% PP at OBC at failure

Table 8.1: Tensile Strain (ε) using Fatigue line regression coefficient

Mixture	k	n	$\varepsilon = K\,N_f^{\,n}$ µm/m	R^2
Control Mix	2453	-0.26	68	0.999
1%PP (0BC -0.5%)	2921	-0.32	35	0.998
1%PP (0BC)	1918	-0.27	46	0.989
1%PP (0BC +0.5%)	2442	-0.26	67	0.989
2%PP (0BC -0.5%)	1802	-0.26	50	0.995
2%PP (0BC	1831	-0.25	58	0.947
2%PP (0BC+-0.5%)	2686	-0.30	59	0.953
3%PP (0BC -0.5%)	8539	-0.33	89	0.972
3%PP (0BC)	7652	-0.32	92	0.973
3%PP (0BC +0.5%)	1091	-0.33	114	0.936

8.2.2 Test Results of LLDPE Modified Bituminous Mixtures

The trend line obtained by plotting the fatigue life for different concentration of polymer at different binder content indicates that no significant improvement was observed for LLDPE modified bituminous mixture in comparison to control mix. All sample prepared with 3% LLDPE PMB failed immediately on loading.

The equations of fatigue line shown in Figure 8.7 are presented below

Control Mix at OBC $N_f = 2453\,(1/\varepsilon)^{-0.26}$

1% LLDPE at OBC – 0.5% $N_f = 3899\,(1/\varepsilon)^{-0.34}$

1% LLDPE at OBC $N_f = 3326\,(1/\varepsilon)^{-0.32}$

1% LLDPE at OBC + 0.5% $N_f = 2356\ (1/\varepsilon)^{-0.27}$

2% LLDPE at OBC – 0.5% $N_f = 2416\ (1/\varepsilon)^{-0.28}$

2% LLDPE at OBC $N_f = 3041\ (1/\varepsilon)^{-0.29}$

2% LLDPE at OBC + 0.5% $N_f = 2731\ (1/\varepsilon)^{-0.27}$

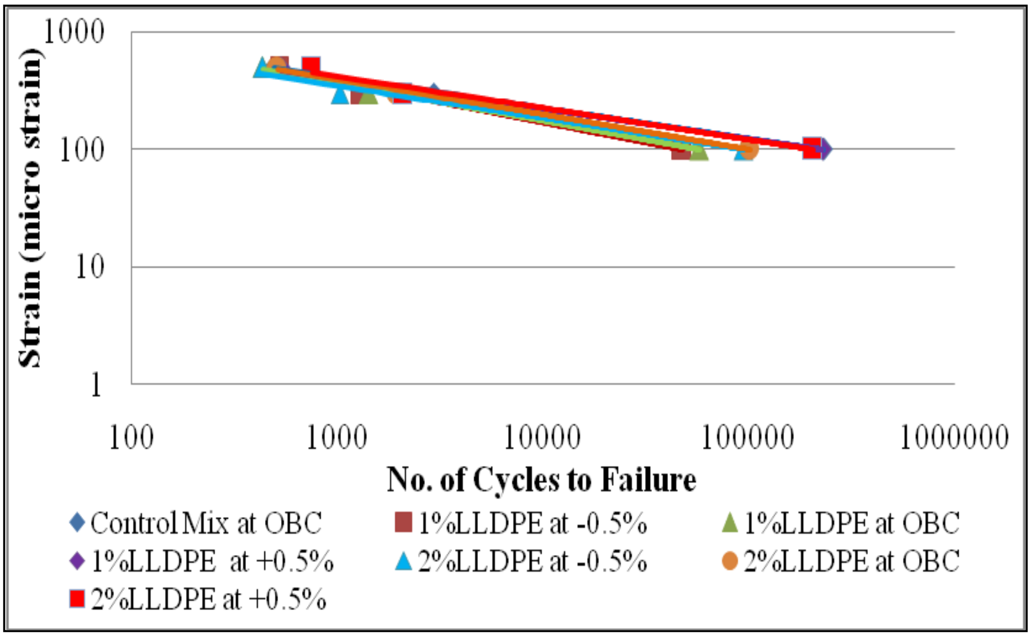

Figure 8.7: Fatigue Life N_f Vs Initial Strain for LLDPE PMB & Control Mix

As from Figure 8.7, it is very difficult to compare the performance of mixture in terms of fatigue life thus Figure 8.8, 8.9 and 8.10 were plotted in form of histogram. From these figure it was observed that specimen of control mix shows improved fatigue life at 100 and 300 micro strain levels in comparison to polymer modified mixes. At 500 micro strain level 2% LLDPE shows improved performance in term of higher fatigue life. This behavior was thus considered to occur due to the presence of compatible polymer bitumen phase segregated layer which was being observed during AFM scanned images. The upper well dispersed polymer bitumen layer thus has sufficient elasticity and stiffness which makes to sustain higher stress for longer time period. Thus the improved fatigue behavior of 2% LLDPE modified bituminous mix might have occurred due to slight formation of polymer bitumen network as observed by AFM and TEM scanned images, which to certain extent considered responsible for enhancing the stiffness beside the viscoelastic component in comparison to 1% LLDPE.

For 3% LLDPE, increase in the viscosity and the formation of well connected network induce sufficient stiffness as being observed by the drastic increase in Marshall stability and Marshall quotient values for 3% LLDPE modified bituminous mixture. The drastic increase in stiffness of the bituminous mixture thus makes the beam difficult to flex under load, resulting in the immediate failure of the beam. The general pattern of crack propagation observed for LLDPE modified bituminous mixture is shown in Figure 8.11 while the rest are provided in attached Appendix.

From the fatigue results it can be safely concluded that the segregated immiscible polymer domains were responsible for increased stiffness of the bituminous mix while the bitumen offer its viscoelastic characteristic to certain extent. As the blending was continued for only one hour at 160°C thus sufficient time was not available to completely impart its properties. The blend which was formed was heterogeneous mixture which composed of partially dissolved polymer bitumen which sufficiently enhances the viscosity of the blend beside immiscible polymer particles. Thus this behavior where polymer and bitumen retains its own individuality occurred due to short blending time resulted in the formation of polymer bitumen blend where polymer besides imparting its viscoelastic characteristics properties to certain extent, also affects its rheological and morphological behavior, thus considered responsible for the extended fatigue life for 2% LLDPE modified bituminous mixture at higher strain level.

For 3% LLDPE modified mixture specimens the immediate failure of specimens have occurred due to the presence of separate domains of high stiffness polymer and low stiffness base bitumen that would not undergo flexing together as an entity but rather failed immediately due to increased rigidity of the beam.

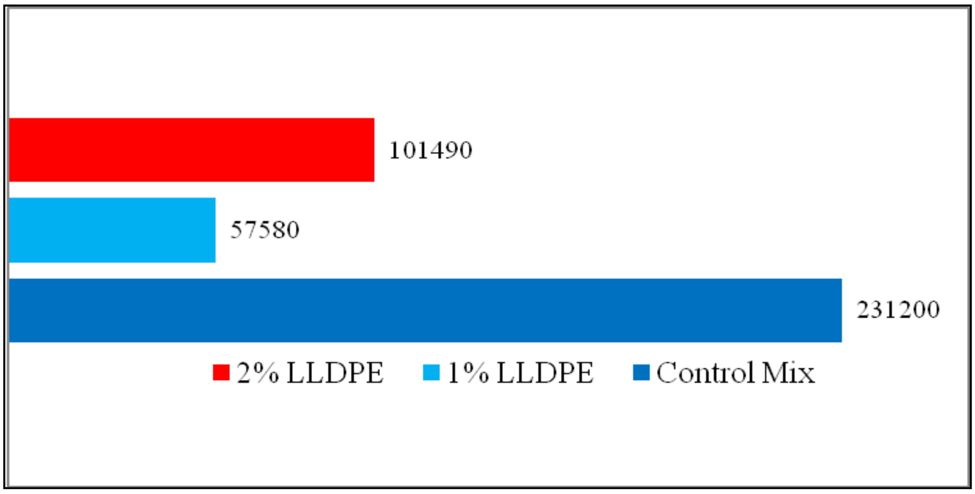

Figure 8.8: Fatigue Life at 100με for LLDPE PMB & Control Mix Beam Specimen

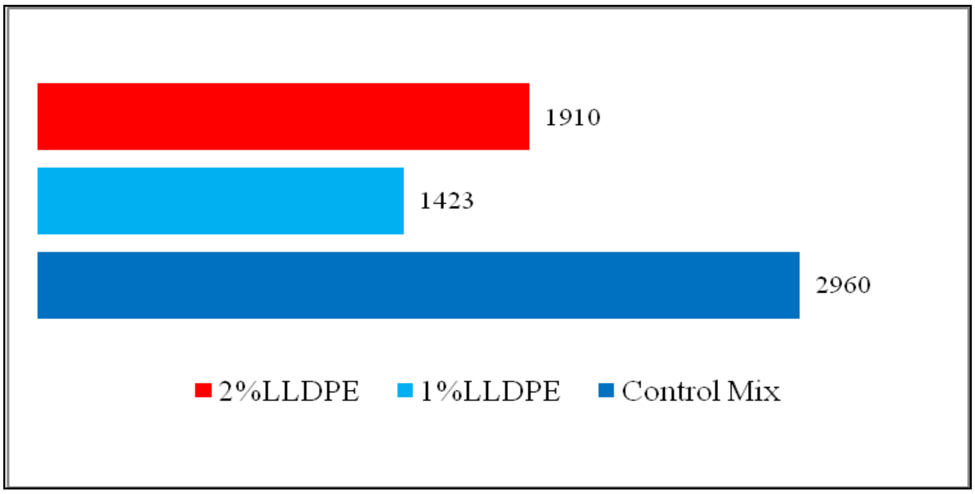

Figure 8.9: Fatigue Life at 300με for LLDPE PMB & Control Mix Beam Specimen

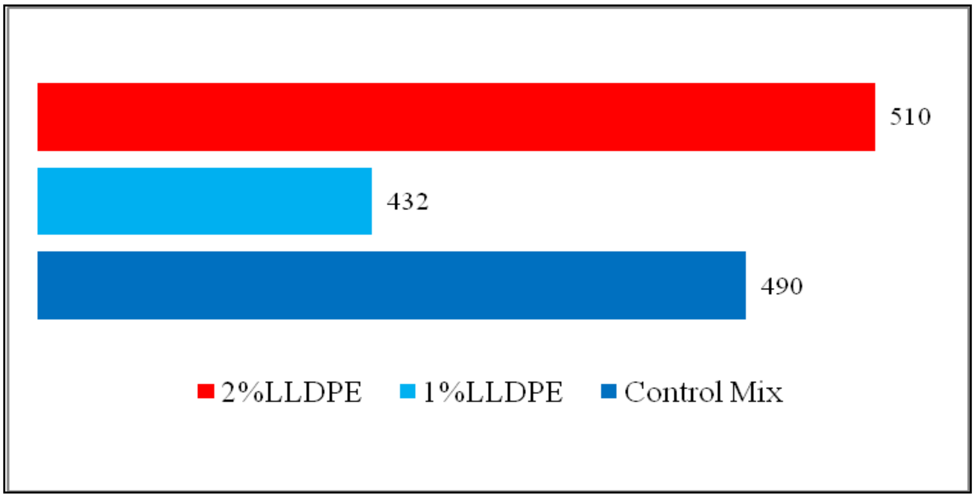

Figure 8.10: Fatigue Life at 500με for LLDPE PMB & Control Mix Beam Specimen

When the development of tensile strain in the specimen were calculated with reference to one million (1,000,000) load repetition, using the regression coefficient obtained from plotted fatigue line it was found that 2% LLDPE (OBC + 0.5%) shows higher tensile strain value (Refer Table 8.2) in comparison to all mixes. The increase in binder content would thus result in the longer fatigue life. Thus it can be safely concluded that mixture prepared with 2% LLDPE (OBC + 0.5%) would offer higher fatigue life in comparison to the rest.

Figure 8.11: Fatigue crack pattern observed for LLDPE Specimen

Table 8.2: Tensile Strain (ε) using Fatigue line regression coefficient

Mixture	k	n	$\varepsilon = K N_f^{\,n}$ µm/m	R^2
Control Mix	2453	-0.26	68	0.999
1%LLDPE (0BC -0.5%)	3899	-0.34	36	0.985
1% LLDPE (0BC)	3326	-0.30	53	0.993
1% LLDPE (0BC +0.5%)	2356	-0.27	57	0.987
2% LLDPE (0BC -0.5%)	2416	-0.28	50	0.972
2% LLDPE (0BC	3041	-0.29	55	0.994
2% LLDPE (0BC+-0.5%)	2731	-0.26	75	0.979

8.2.3 Ranking of Bituminous Mixture

From the above discussion it was observed that polypropylene modified mixture shows improved fatigue life in comparison to control and LLDPE modified bituminous mixes. In order to rank the bituminous mixture in terms of their improved fatigue life it was observed that 3% PP modified mixtures at all strain level showed superior performance in comparison to the rest of the mixes. The compatibility of PP with bitumen helps in the formation of well connected polymer bitumen network which sufficiently enhances the stiffness of the mix beside its viscoelastic characteristics.

From the obtained fatigue life at all strain level when plotted for all bituminous mixture (modified and control) as shown in Figure 8.12 – 8.14, ranks 3% PP modified bituminous mixture as best beside 2% LLDPE modified bituminous mixture at 500 micro strain only.

From the combine plotted fatigue life of different mixes it was observed that 3% PP modified mixture showed better performance in terms of fatigue with respect to others at all strain level. The general trend that was observed from plotted fatigue life is that even for PP modified bituminous mixture improved fatigue life starts from 3% polymer content. Thus it can be safely concluded that for PP modified bituminous mixture, higher fatigue life starts from 3% polymer content while for LLDPE modified specimen addition of LLDPE without any cross linking material or chemical modifier would lead to the brittleness because of the excessive increase in stiffness without sufficient increase in visco elastic component.

This behavior of the material was also confirmed by the higher fatigue life for control bituminous mixture where the binder because of it viscoelastic component shows better behavior in comparison to 1%, 2% LLDPE and PP modified bituminous mixtures when tested at 20°C.

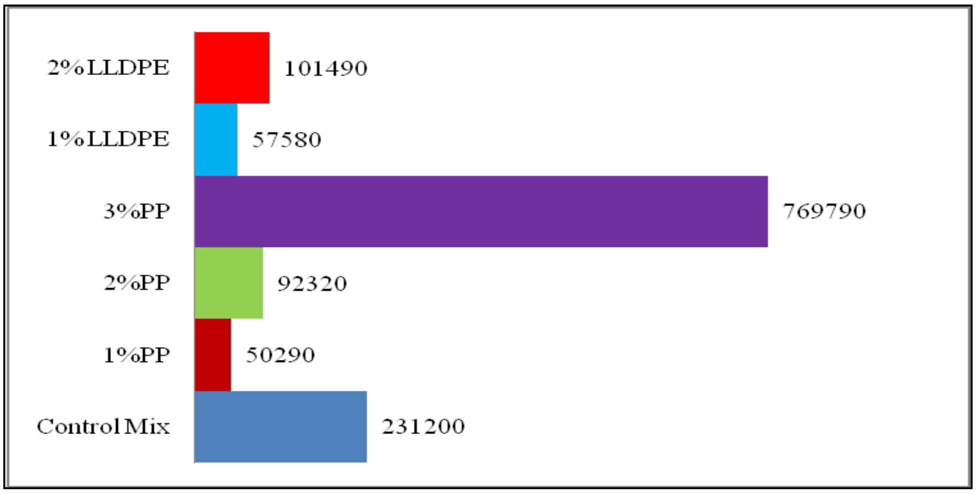

Figure 8.12: : Fatigue Life at 100 micro strain level for all Bituminous Mixture

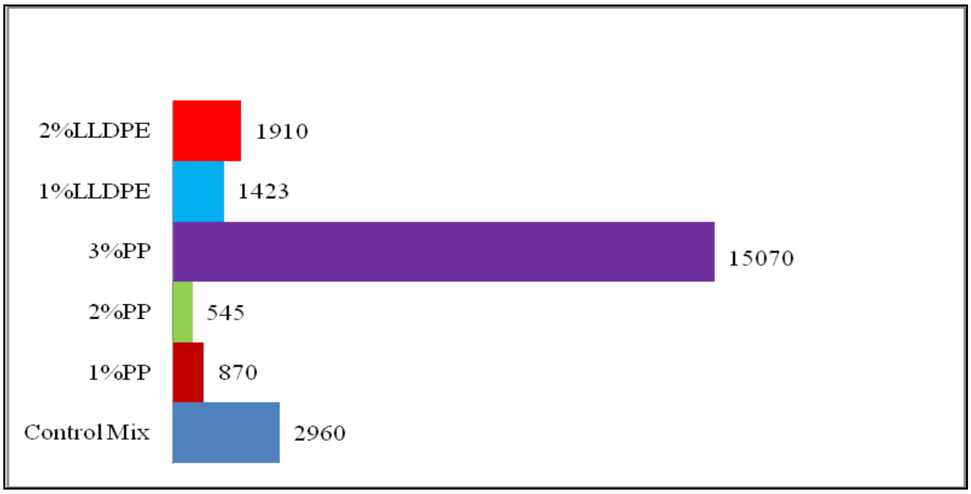

Figure 8.13: Fatigue Life at 300 micro strain level for all Bituminous Mixture

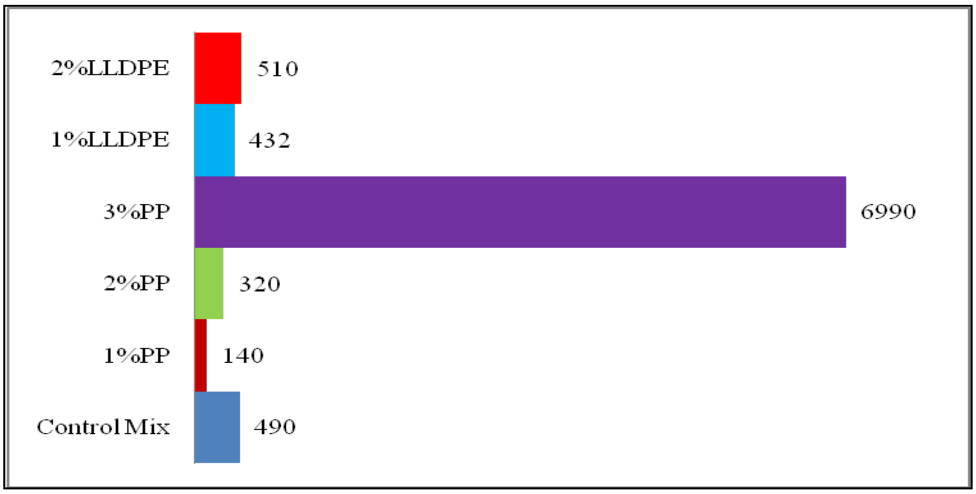

Figure 8.14: Fatigue Life at 500 micro strain level for all Bituminous Mixture

8.3 Summary of the Results

From the fatigue results it was observed that modification of the bitumen with polymer only without use of any cross linking material or any chemical modifier would not result in higher fatigue when tested at 20°C as observed by the lower fatigue life in comparison to virgin/control bituminous mixture. Polypropylene shows some promising behavior in comparison to rest but true conclusion can be made only when it would be tested further at higher polymer concentration exceeding 3% polymer concentration.

From the observed fatigue behavior it can be safely concluded that 3% PP modified mixture at 100 micro strain shows highest fatigue life i.e. for OBC + 0.5 % modified bituminous mixture fatigue life reaches up to one million. Thus 3% PP can be safely used for high volume traffic lanes, climbing lanes at traffic signals as it was found well above the endurance limit of 65 micro strain. For low volume roads where the endurance limit was set at 300 micro strain, 3% PP modified bituminous mixture would show better performance.

LLDPE modified bituminous mixture failed to show any improved performance because of its brittleness due to enhanced stiffness without sufficient flexibility.

CHAPTER 9

CREEP CHARACTERISTICS OF BITUMINOUS MIXTURES

9.1 Introduction

One of the distresses that commonly occurred in flexible pavement at high pavement temperature is rutting due to accumulation of permanent deformation of each layer of the pavement structure under repetitive traffic loading action. Rutting in flexible pavements usually occurs within the depth of the pavement. Rutting would eventually leads to serious problem of hydroplaning and reduction in service life of the pavement mainly for heavily trafficked bituminous roads [120].

Rutting can also occur due to loss of the viscoelastic component of the binder when being sheared apart under extreme cases. Huang [64] reported that under extreme shearing conditions, the molecules of the bitumen may untangled completely and get aligned, offering minimum resistance to flow. Further increase in shearing stress will eventually leads to the breakage of main chain of bond leading to permanent deformation or rutting. Whatever be the cause of the rutting, it significantly reduces both structural and functional performance of the pavement.

In this study mixture resistance to permanent deformation or rutting was evaluated using dynamic creep test and the verified by wheel tracking test on mixtures prepared with both virgin 80/100 Pen bitumen and polymer modified bitumen. The polymer modified binders used for testing includes polypropylene and linear low density polyethylene in concentration of 1%- 3% by the weight of the bitumen. The detailed procedure of testing was documented in the chapter of methodology.

9.2 Results and Discussion

In order to investigate permanent deformation properties of the bituminous mixture dynamic creep test was conducted on both modified and conventional 80/100 pen bituminous mixture specimens. Wheel tracking test was also conducted in order to verify the trends observed by dynamic creep test. The result obtained from dynamic creep test was used to correlate the mixture resistance to permanent deformation by the estimated rut depths observed by wheel tracking test.

As both dynamic creep and wheel tracking test were performed at 40°C, rutting behavior at higher temperature (60°C and above) would be discussed in view of the results obtained by rheological test parameter shear modulus ($G^*/\sin\delta$) presented in chapter 6.

9.2.1 Dynamic Creep Results for Polypropylene and Linear Low Density Polyethylene Modified Bituminous Mixture

Creep modulus obtained from the dynamic creep test indicates the mixture resistance to permanent deformation [110]. Creep results can be used to analyze the stiffness of the mixture to stiffness of bitumen in order to develop the relationship between two. Similarly they can be used to correlate the trend observed for different bituminous mixes by the estimated rut depths from creep modulus.

9.2.2 Relationship between mixture stiffness with bitumen stiffness

Dynamic creep test was performed according to British Standard DD226 by preparing triplicate samples at optimum bitumen content obtained by Marshall The results obtained are presented in the form of creep stiffness. The average mix stiffness modulus (S_{mix}) obtained from the creep modulus of three prepared mix specimen at optimum binder content for particular bituminous mix is plotted in double logarithmic scale against stiffness modulus of bituminous binder (S_{bit}), evaluated by using Van der Poel’s nomograph as shown in Figure 9.1& 9.2 for PP and LLDPE modified bituminous mixture respectively. The $S_{bit + polymer}$ was also determined using Van der Poel’s nomograph (attached in Appendix) considering their penetration, softening point and penetration Index(PI) as presented in Table 9.1.

The resistance to permanent deformation from the creep test was determined by analyzing the slope of the line obtained from the log-log relationship of mixture stiffness versus binder stiffness, where mixture stiffness corresponds to a fixed loading time or the time to reach a critical strain level. This manner of characterization in the mixture behaviour was based on the fact that more resistant mixtures have stiffness that would be greater and decrease less rapidly with increasing time. Stiffness of mixes containing control and both PP and LLDPE polymer modified bitumen are shown in Figures 9.1 to 9.3 at any particular time of loading. Table 9.2 present the coefficient of the equation of the line plotted in logarithmic scale relating the stiffness of the mix to the stiffness of the bitumen.

The equation of the stiffness of the mix to the stiffness of bitumen are presented in the form of

$$S_{mix} = a \times (S_{bit})^{b} \text{ ......} \qquad 9.1$$

The equations of the line when plotted in log scale would be obtained in the form of

$$Y= a X^{b} \qquad 9.2$$

Where a = the interception of the line with Y axis

b= the slope of the line

Y= stiffness of the mix (MPa)

X= stiffness of the bitumen (MPa)

In the above equation, the coefficient “*a*” and “*b*” represents mixture stiffness and slope or sensitivity of the mixture to loading time. Mixture exhibiting higher value of coefficient “*a”* and lower value of slope “*b*” would offer higher resistance to permanent deformation [120].

It was observed from Figure 9.1 that 1% PP and 2%PP modified bituminous mixture shows better performance in comparison to 3% PP and control 80/100 pen bituminous mixture. From Figure 9.2 it was observed that 3% LLDPE modified mixture shows better performance in comparison to 1% & 2% LLDPE bituminous mixture.

Figure 9.3 shows the combine mix stiffness of all the mixtures. It was observed that 1% PP, 2% PP and 3% LLDPE modified mixture remarkable improved performance in comparison to the rest of the mixture.

Since the slope of the S_{mix} to S_{bit} relationship indicates mixture susceptibility to time of loading, it was observed from Table 9.2, 1% PP has lower slope indicating less susceptible to creep deformation. The trend observed by slopes of the individual mixes indicates that 1% PP, 2%PP and 3% LLDPE were more resistant to permanent deformation. The slope of the line of the log-log relationship of mixture stiffness versus binder stiffness of the creep test for each particular mix indicates sensitivity of the mix to loading time and hence bitumen stiffness [118].

It was also observed from Table 9.2 that 2% PP offer highest mixture stiffness in comparison to the rest of the mixes. This behavior of 2% PP bituminous mixture indicates that although the mixture stiffness was sufficiently enhanced by increase in polymer concentration, but the chances of brittleness of the binder cannot be overlooked making it more susceptible to permanent deformation.

For LLDPE modified bituminous mixes it was observed from Table 9.2, that only 3% LLDPE bituminous mix offered increased mixture stiffness in comparison to 1% LLDPE and 2% LLDPE bituminous mixes. At higher concentration of polymer (3%) the increase in viscosity makes the binder rather incompressible while the partially immiscible polymer induces the stiffening affect. The behavior of the LLDPE at lower polymer concentration could be attributed by the failure of formation of proper polymer bitumen network as observed by the higher colloidal index values for LLDPE modified binder and by AFM scanned images.

As the creep test was conducted at 40°C, the binder performance at higher temperature was observed by DSR test, considering rutting parameter.

The same trend observed from the creep performance at 40°C was verified by the behavior of the binders when tested by dynamic shear rheometer at higher testing temperature of 58°C and 70°C. From the results presented in Table 6.1(refer chapter 6), the values of rutting parameter $G^*/\sin\delta$, shows that 1% PP PMB, 3% PP PMB & 3% LLDPE PMB shows higher shear modulus which is an indicator of rutting resistance in comparison to control and other modified binder when tested at higher temperatures. As rutting is a phenomenon that occurs at high pavement temperature, it can be safely concluded that these polymer modified binders would show better performance even at higher pavement temperatures.

It was observed that 1% & 2% PP bituminous mixture shows better performance at 40°C in comparison to 3% PP modified bituminous mixture. The shear modulus($G^*/\sin\delta$) observed at 58°C and 70°C for 3% PP was better than 2% PP PMB. Such behavior of the binder at higher temperature can be attributed to the polymer network which becomes more intense by creating helical coils at 3% PP concentration as observed from TEM scanned results. The higher polymer concentration would increase the viscous component of the complex modulus (G^*), which would increase the viscosity of the binder beside elastic modulus at higher temperature.

The higher molecular weight of polymer also effect the creep behavior, as higher molecular weight increases the secondary bonding between polymer chains making it more creep resistant. The well dispersed PP in bitumen blend as being observed by AFM and TEM scanned images was considered responsible for the enhanced stiffness of the bituminous mixtures. The 3D network that was observed for all concentration of PP in bitumen also plays its major role in enhancing the stiffening effect.

For LLDPE modified binder at higher temperatures highest values of rutting parameter ($G^*/\sin\delta$) was observed for 3% LLDPE PMB, followed by 2 % and 1% LLDPE PMB as presented in Table 6.2. From these results it can be safely concluded that LLDPE modified mixes might give better performance at higher temperature.

Table 9.1: Properties of 80/100 Pen Bitumen & Polymer Modified Bitumen

	Penetration (dmm)	Softening Pt °C	Viscosity (Pa s)	Penetration Index P.I
80/100 Pen Bitumen	84	53	0.44	0.5
1% PP PMB	34	54	0.78	-1.5
2% PP PMB	30	55	0.81	-1.25
3% PP PMB	28	55	0.83	-1.5
1% LLDPE PMB	35	53	0.63	-1.5
2% LLDPE PMB	30	53	0.76	-1.85
3% LLDPE PMB	25	60	1.43	-0.7

Table 9.2: Creep Results in Terms of S_{mix} Vs S_{bit}

Binder Type	Mixture Stiffness “a”	Sensitivity of Mixture “b”	r- square
80/100pen Bitumen	549.7	0.421	0.945
1% PP	1446	0.290	0.958
2% PP	1783	0.346	0.958
3% PP	426.3	0.349	0.929
1% LLDPE	323.3	0.380	0.953
2% LLDPE	369.7	0.373	0.958
3% LLDPE	1268	0.342	0.976

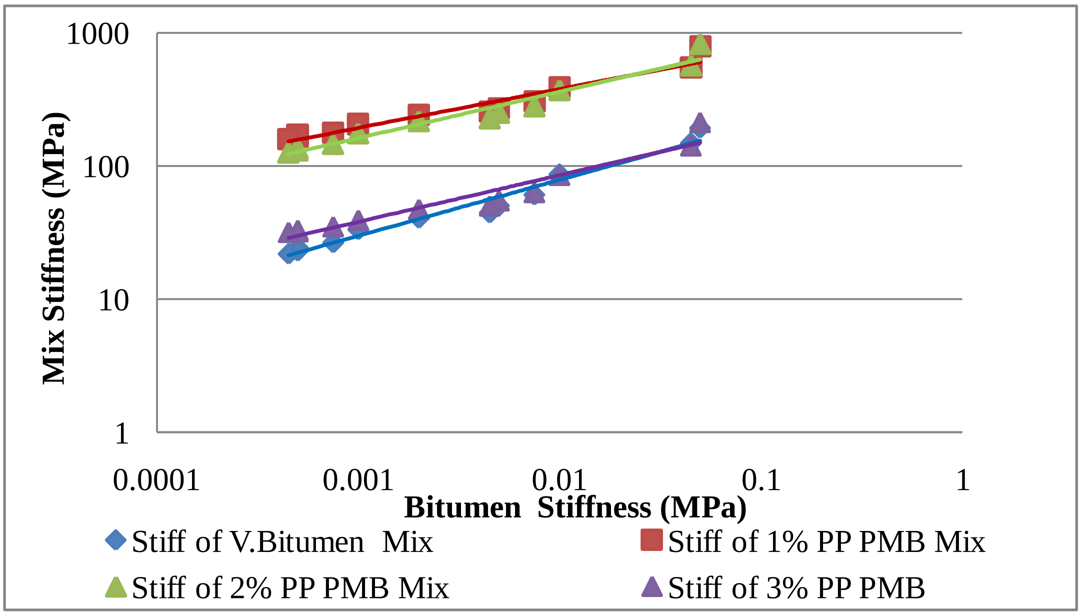

Figure 9.1: Relationship between PP Mix Stiffness and Bitumen Stiffness

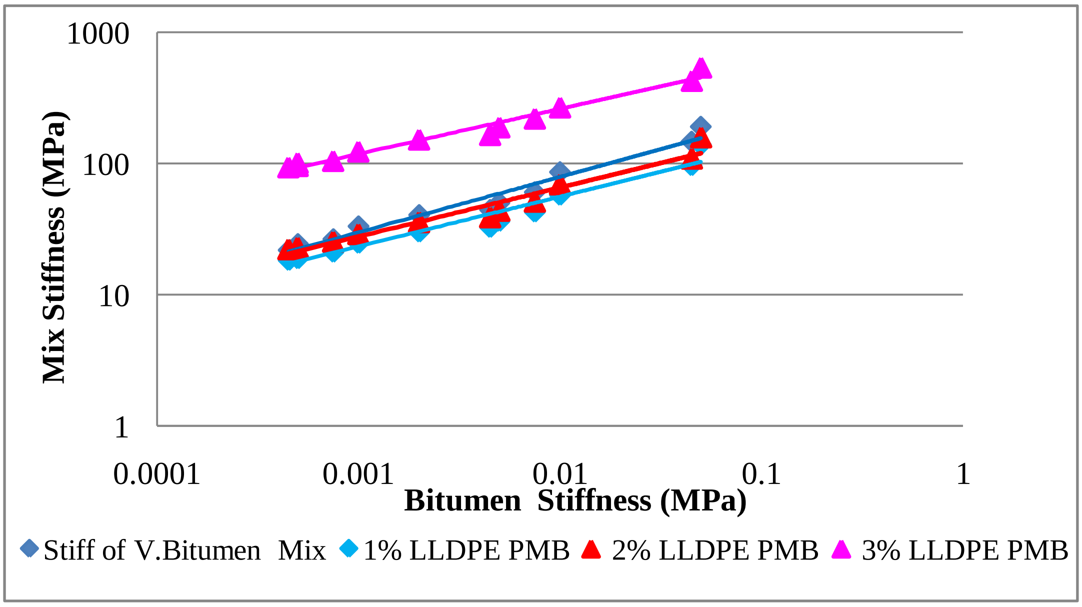

Figure 9.2: Relationship between LLDPE Mix stiffness and Bitumen Stiffness

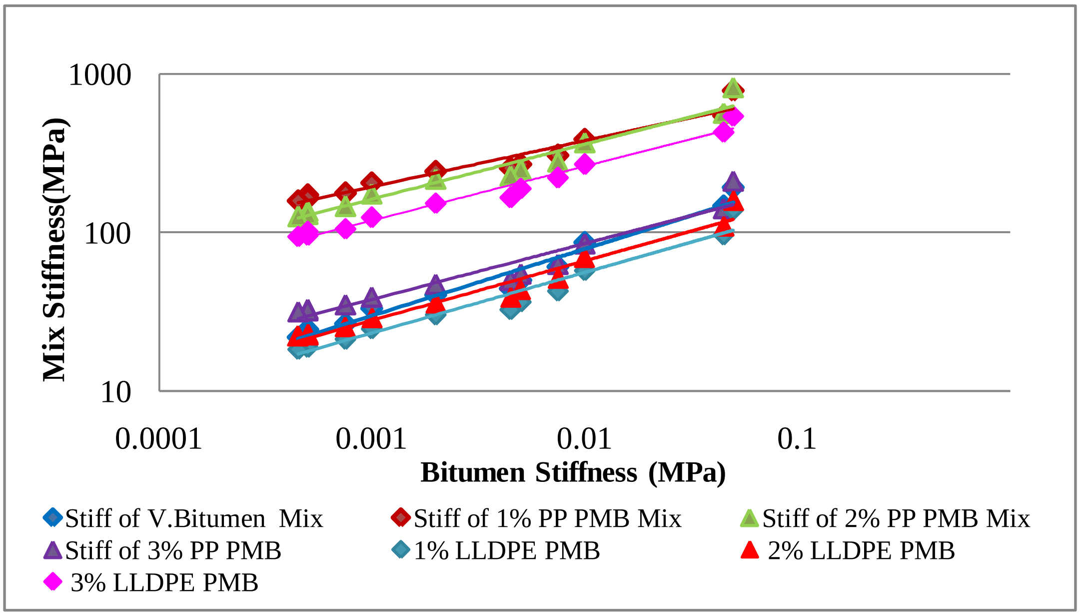

Figure 9.3: Combine Mix Stiffness and Bitumen Stiffness for PP & LLDPE Mixtures

9.2.3 Relationship between Accumulated Strain and Time of Loading for Control and Modified Bituminous Mixtures

Figure 9.4 shows the relationship between logarithm of accumulated strain and logarithm of loading cycles. For the analysis first 100 cycles were not considered as being regarded as data obtained during preconditioning pulse. From the rest of the plot it was observed that initially the slope of the line (primary slope) was steep followed by stable plateau (secondary slope). The slope of the line represents sensitivity of mixture to resistance against deformation. The slope of the lines for 1% PP, 2% PP and 3% LLDPE were rather flat in comparison to virgin bitumen representing mixture resistance against deformation. The primary slope of the line when compared to the secondary slope it represent sensitivity of mixture against resistance to deformation. From the plotted lines it can be safely concluded that resistance to deformation for 1% PP, 2% PP and 3% LLDPE was higher where the amount of accumulated strain (deformation) was lower in comparison to control, 3% PP, 1% LLDPE and 2% LLDPE modified bituminous mixture.

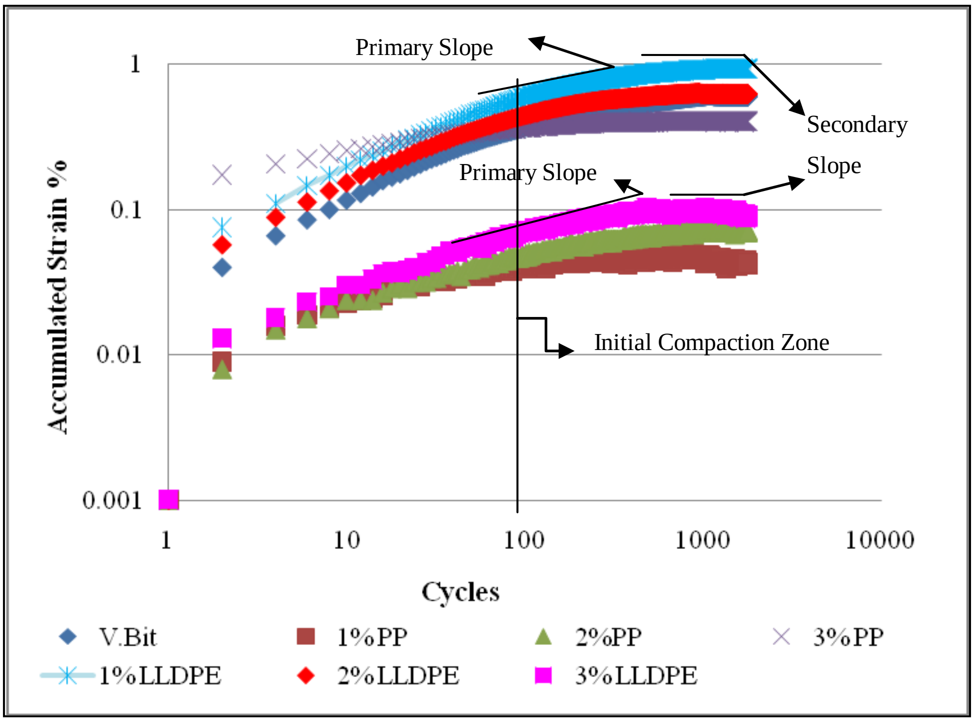

Figure 9.4: Log Accumulated Strain Vs Log No of Cycles

9.2.4 Ranking of Bituminous mixture

Creep results can also be used to rank the bituminous mixture in term of their stiffness maintained till end of the test. From the test results it was observed that there was an increase in stiffness of modified the bituminous mixture in comparison to control mix. It was also observed that modification enhances the creep stiffness by 25 times, 13 times and 8 times for 1% PP, 2% PP and 3% LLDPE modified bituminous mixture respectively when compared to control bituminous mixture. for 3% PP modified bituminous mixture 3 times increment in creep stiffness was observed, while 1% LLDPE and 2% LLDPE modified samples failed to show any improved performance as observed from the results presented in Table 9.3.

LLDPE was unable to perform well in comparison to PP as the localized separate domains of polymer as observed from AFM and TEM images failed to form dispersed polymer bitumen network. The well connected work was thus considered as strength enhancing factor for modified bituminous mixtures, thus PP modified bituminous mixtures performed better than LLDPE modified bituminous mixtures.

Table 9.3: Mix Stiffness at Start & End of Dynamic Creep Test

Mix Type	Stiffness at Start (MPa)	Stiffness at End (MPa)	Increment expressed in times w.r.t control mix
80/100 Bitumen Control Mix	192.05	18.98	
1% PP PMB	788.88	111.06	25
2% PP PMB	822.7	66.02	13
3% PP PMB	212.3	29.89	3
1% LLDPE PMB	139.33	12.53	-
2% LLDPE PMB	159.59	16.835	-
3% LLDPE PMB	540.66	48.09	8

9.2.5 Estimation of Rut Depth

Creep results can also be used to estimate structural rut depths caused by the repeated traffic loads as it shows good correlation with the behavior of the specimens used in laboratory creep test results [120].

Bitumen being viscoelastic material when subjected to continuous loading would deform under continued loading but get recovered upon removal of loading. Recovery of the material depends upon the viscous component of the binder which in turn depends on loading time and temperature. As stiffness of the bituminous material also depends on the temperature and loading time, therefore it can be concluded that permanent deformation also depends on the viscous component of the modulus $(S_{bit})^v$[120].

Hills[179] suggested the following equation for determining the stiffness modulus of bitumen corresponding to its viscous part:

$$(S_{bit})^v = 3\eta / N.T_W$$

Where: $(S_{bit})^{v-}$ viscous component of the stiffness modulus of the bitumen.

ŋ- viscosity of the binder as a function of PI, and ring and ball temperature and it was obtained from Figure 9.5.

N- number of wheel passes in standard axles.

Tw - time of loading for one wheel pass (0.02 sec corresponding to vehicle speed of 50km/hr)

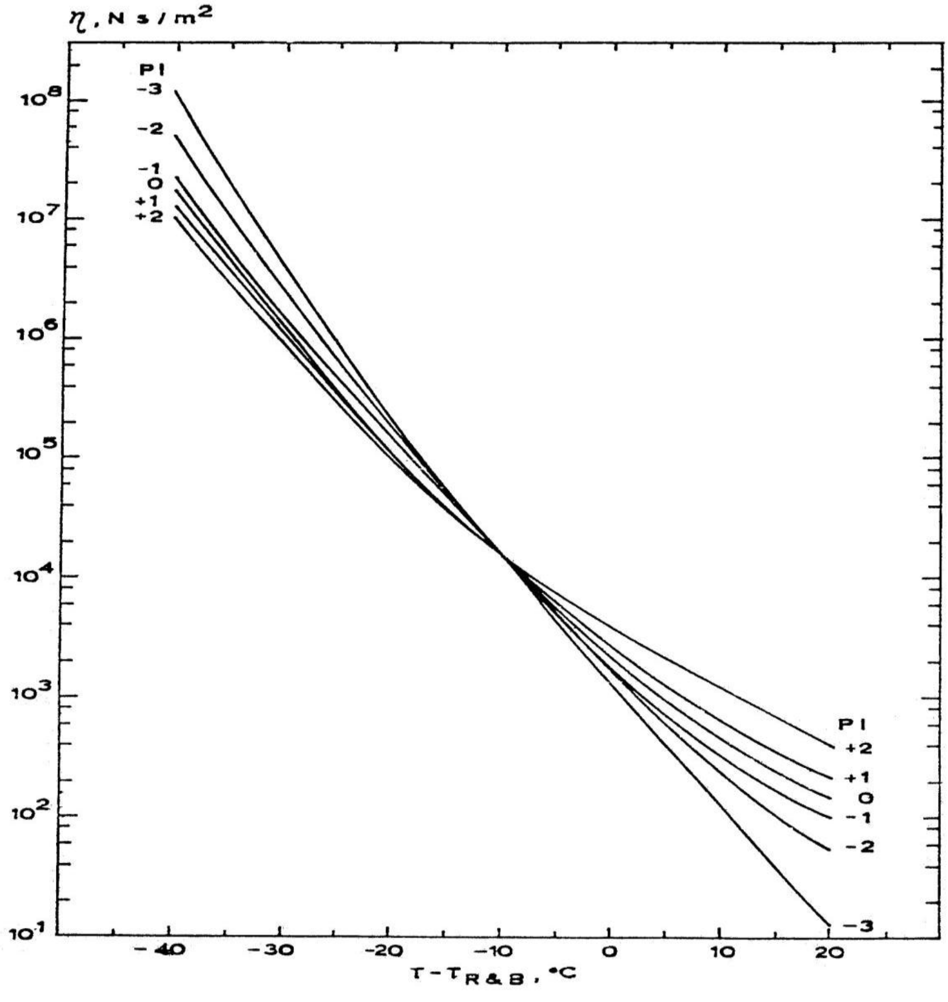

Figure 9.5: Viscosity of bitumen as a function of (T-T $_{R\&B}$°C) and PI obtained from Van der pool's nomograph

The rut depths can be calculated from creep results by using the equation proposed by Van der Loo [180] which relates rut depth (R_d) with the stiffness of mix using following equation

$R_d = C_m \times H \times (\sigma_{av} / S_{mix})$ ---------9.1

Where,

R_d calculated rut depth of the pavement,

C_m correlation factor for dynamic effect, varying between 1.0- 2.0 (average1.5 is taken)

H Pavement layer thickness (taken as 50mm for wearing course)

σ_{av} Average stress in the pavement related to wheel loading and stress distribution.(0.25 MPa)

S_{mix} Stiffness of design mixture derived from creep test at a certain value of stiffness related to the viscous part of bitumen.

The above relationship was used to find the rut depths using dynamic creep results. Results of the estimated rut depth calculated from creep results are shown in Figure 9.6 and Figure 9.7 relating rut depth to the number for standard axle repetitions. The red vertical line marked in Figure 9.6 shows the rut depth of different bituminous mixture corresponding to one million standard axle load repetitions.

The lowest rut depth was observed for bituminous mixture modified by 1% PP followed by 2% PP and 3% LLDPE bituminous mixture. The enhanced stiffening effect and well developed polymer bitumen network was considered responsible for such behavior.

2% LLDPE bituminous mixture offer the highest rut depth in comparison to all modified and control mixes. Such behavior of mix exhibits that either polymer degradation occurred during mixing or due to Newtonian viscosity behavior of 2% LLDPE binder which was observed when being sheared at 135°C. The Newtonian behavior of 2% LLDPE makes it more compressible under loading as observed by higher rut depth in comparison to the rest of the mixes.

From Figure 9.6 the results of the rut depth estimation show significant correlation with the number of standard axle repetition. Table 9.4 presents the effect of polymer modifier on resisting pavement rutting. All the results were presented with regression coefficient “a” and “b”, which is mainly, intercepts coefficient and slope coefficient respectively. The mixture performance to loading was determined by the value of the slope “b”. All the mixes shows good co relationship as observed by coefficient of linear regression (R^2) greater than 0.98.

From the Figure 9.7, it was observed that 1%PP, 2% PP, 3%PP and 3% LLDPE modified bituminous mixtures shows lower rut depth in comparison to control mix. The presence of methyl group in PP makes it more resistant to deformation. For one million standard axle wheel repetitions 1% PP, 2% PP and 3% LLDPE modified bituminous mix shows lowest rut depth of 0.66 mm, 1.13 mm, 3.65 mm and 1.14 mm respectively in comparison to control mix which shows 10.57 mm rut depth. Thus with the addition of PP decrease in rut depths of 93 %,89 % and 65 % was observed for 1% ,2% and 3% PP respectively. Addition of 3% LLDPE decreases rut depth up to 89% when compared to control mix rut depth. The 1% & 2% LLDPE failed to show any improvement in rut resistance. The presence of shear thinning behavior as observed for 1% and 2% LLDPE modified bitumen considered responsible during repeated loading action where slippage of the molecular chain of the modified binder failed to get recovered during repeated loading action.

The pattern of estimated rut depth can be explained in context with the viscosity function with respect to aggregate coating also. Although enhanced viscosity of binder increases stiffness in bituminous mix but doesn’t necessarily reduces the rut depth as it also depend on aggregate cohesion in mix, binder content, degree of compaction and porosity in mix. The LLDPE PMB mix unable to show better performance as branched polymer usually shows high degree of shear thinning, where irreversible bulk deformation of polymer which is associated with irreversible slippage of molecular chains doesn’t exists sufficiently to overcome the strains induced due to repeated load action. As LLDPE belongs to thermoplastics group it shows creep behavior under load where deformation increases with time [47]. PP although belong to thermoplastic group but presence of methyl group (–CH3) restrict the rotation of PP chain and thus produce stronger polymer having good chemical, moisture resistance and high stability[47].

From Table 9.4 it was observed that lowest slope “b” was observed by PP modified bituminous mixture followed by 3 % LLDPE modified bituminous mixture. It was also observed from the Table 9.4 that slope “b” of the regression line for 3% PP was lower than 2% PP bituminous mixture line. Thus 3% PP would offer better resistance to permanent deformation in comparison to 2% PP bituminous mixture.

The behavior of mixture when analyzed with results of rheological parameter (refer Table 6.1), the complex modulus (G*), which is an indicator of resistance to permanent deformation shows higher value for 3% PP in comparison to 2% PP when tested at 58°C. For 3% LLDPE significant enhancement of complex modulus (refer Table 6.2) was considered responsible for lower anticipated rut depth value as observed by lower value of slope “b” at one million axle repetition of loading.

Therefore the use of PP modified binders seems to be more promising in resisting permanent deformation of the bituminous pavement. 3% LLDPE shows better performance in comparison to 1% and 2% LLDPE modified bituminous mixes.

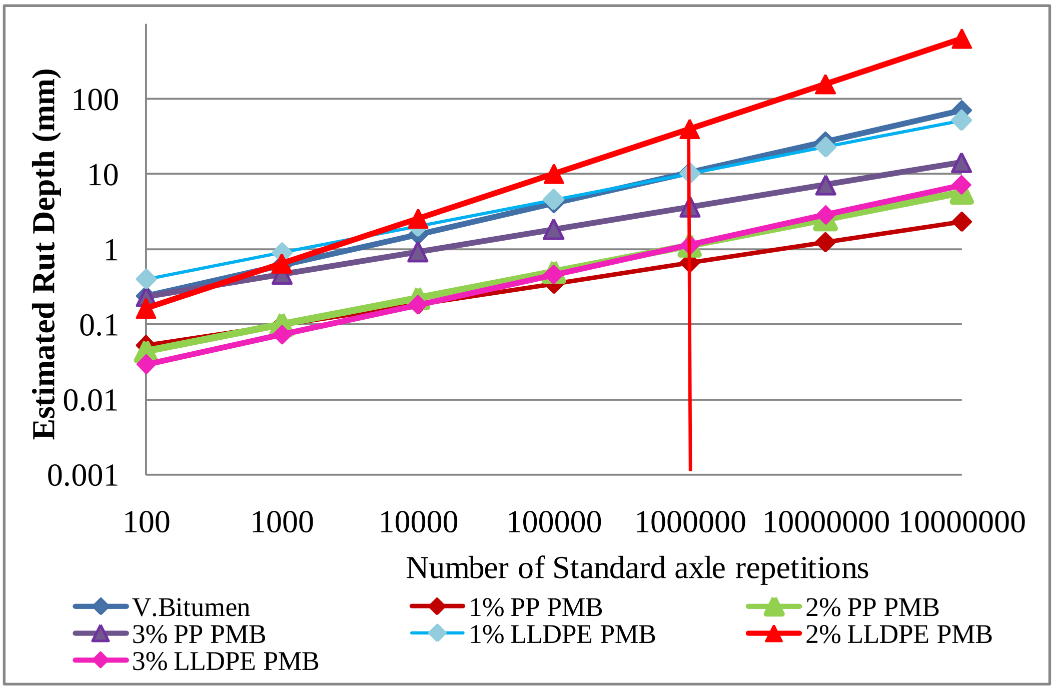

Figure 9.6: Estimated rut depths at 40°C based on creep behavior of mixes

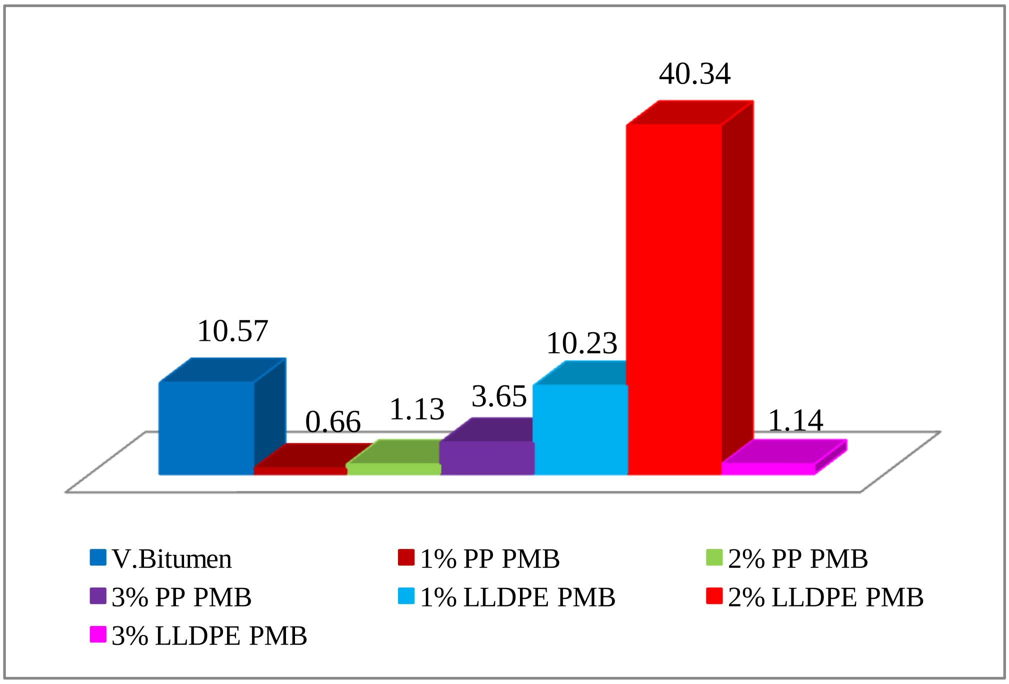

Figure 9.7: Bar chart representation of estimated Rut Depth values (mm) from Dynamic Creep Results for 1 million standard axle repetitions

Table 9.4: Coefficient of regression line for estimated rut depths from creep test results

Binder Type	“a”	“b”
80/100 pen Bitumen	0.035	0.412
1% PP	0.14	0.275
2% PP	0.008	0.351
3% PP	0.059	0.298
1% LLDPE	0.078	0.352
2% LLDPE	0.010	0.598
3% LLDPE	0.004	0.398

“a” Intercept Coefficient

“b” Slope Coefficient

9.2.6 Wheel Tracking Test Results for Polypropylene and Linear Low Density Polyethylene Modified Bituminous Mixture

Wheel tracking test was used to analyze the ability of pavement material to resistance against permanent deformation. Wheel tracking test provides a qualitative evidence of mixture resistance against flow of material during rutting [117], thus considered as important performance based test. The deformation trend observed during 45 minutes wheel tracking test are presented in Figure 9.8, which follows the same trend as observed for percentage accumulated strain observed during dynamic creep test results. 1%, 2% PP and 3% LLDPE modified bituminous mixture performs well when compared with control 80/100 pen bituminous mixture and rest of the modified mixes.

Among LLDPE modified bituminous mixture, 3% LLDPE mixture shows better performance in comparison to the rest of the bituminous mixture prepared with 1% and 2% polymer concentration.

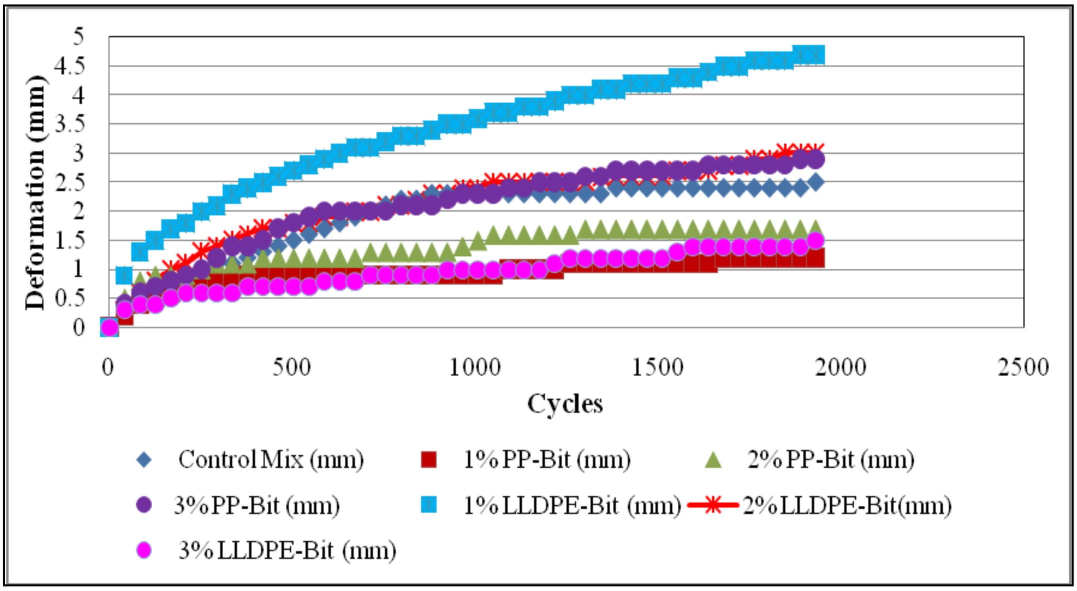

Figure 9.8: Combine Wheel Tracking Test Result for Control and Modified bituminous mixture

Beside the binder viscosity which contributes to adhesion ability to resist deformation, aggregate packing due to interlocking offering frictional resistance considered as major factor influencing the deformation behavior of the mix. The phase separated layer as observed by the AFM scanned images for PP PMB can be considered as positive factor resisting material deformation against back and forth action of wheel during test. The helical structure which was observed during TEM scanned images considered as major supporting factor for resistance against permanent deformation.

The improper distribution of LLDPE polymer in the blend as observed by both AFM and TEM scanned images unable to form proper network even at lower concentration of polymer in the blend. 3% LLDPE shows better performance, which might have occurred due to the formation of polymer network by the side chains of polyethylene beside bitumen which imparts it viscoelastic characteristics as confirmed by the presence of protruding asphaltene observed in the AFM scanned image of 3% LLDPE blend. SARA results also confirmed the presence of asphaltene by the increase in asphaltene content for 3% LLDPE PMB.

Although the mixing of polymer–bitumen was considered as physical blending but change in chemical composition due to partial breakage of side chain of polymer cannot be overlooked which was considered as one of the causes in bringing in the structural or in short mechanical characteristics of the blend.

The difference in rut depths obtained from dynamic creep and wheel tracking was due to the difference in confinement condition for dynamic creep results and wheel tracking test. In dynamic creep viscoelastic response of material due to unconfined condition of sample leads to higher Poisson’s ratio thus energy dissipation was considered more revealing to less stress- strain ratio while the confining condition for wheel tracking test results in lower Poisson’s ratio revealing higher stresses or higher deformation [116]. In actual rutting is a three dimensional phenomenon in which vertical compression and lateral flow of material contributes to the total observed rutting [181].

Another way to assess the performance of bituminous mixture in the wheel tracking test by analyzing wheel tracking rut depth rate for 45 minutes [182]. By looking at the deformation rate as shown in Table 9.5, lower deformation rate was observed for 1% PP and 3% LLDPE modified bituminous mixture followed by 2% PP, 3% PP and 2% LLDPE bituminous mixture.

The formation of well connected polymer bitumen network at higher concentration was considered responsible for the superior behavior. 1% PP modified blend with lower specific gravity (0.996) provides better coating of aggregate, resulting in the formation of well connected aggregate bitumen structure thus more resistant to deformation. Beside this the phase segregated polymer bitumen layer as also exposed by AFM scanned images would thus provide resistance to deformation. Highest deformation rate was observed for 1% LLDPE modified bituminous mixture where incompatibility of polymer with bitumen failed to form proper polymer bitumen network and thus failed to enhance the stiffness of the mix resulting in failure of mixture to resistance to deformation. Thus the trend observed from the deformation rate after neglecting initial deformation that occurs due to densification of material follows the same the trend observed for accumulated strain vs cycle observed from the dynamic creep test at 40°C.

Table 9.5: Wheel Tracking rate (mm/hr)

Control Mix	1% PP	2% PP	3% PP	1% LLDPE	2% LLDPE	3% LLDPE
2.32	1.05	1.58	2.52	3.99	2.56	1.17

9.3 Summary of the Results

From the dynamic creep test results it was revealed that better compatibility of polymer with bitumen resulted in the formation of proper polymer bitumen network which enhances the strength of the mix as being observed by the resistance to deformation.

When the polypropylene modified bituminous mixture was assessed it was found that at 1% and 2% polymer content significant increase in stiffness beside viscoelastic component resulted in resistance to deformation as observed lower slope values and enhanced stiffness. For 3% PP higher concentration of polymer leads to the formation of highly viscous blend which unable to coat the aggregates properly, while the phase segregated polymer bitumen sufficiently increases the stiffness of the mix which induces the embrittlement in the mix.

LLDPE modified mixes failed to perform well in terms of resistance to deformation due to absence of polymer bitumen network up to 2% polymer concentration. 3% LLDPE modified bituminous mixture shows resistance to deformation because of the existence of the polymer bitumen network which imparts viscoelasticity besides stiffening effect.

Thus the results obtained from dynamic creep test found to be well correlated with the results obtained from rheological and morphological analysis.

The wheel tracking rates for these mixes shows lower tracking rates for 1% PP, 2% PP and 3% LLDPE bituminous mixes in comparison to the rest. Similar trend was observed for trend of deformation by wheel tracking test as observed for dynamic creep test.

CHAPTER 10

CONCLUSIONS AND RECOMMENDATIONS

10.1 Conclusions

This research study evaluated rheological, morphological and engineering properties of polymer modified bitumen with its effect on pavement performance characteristics. A number of tests were conducted on both virgin 80/100 pen bitumen and polymer modified binders (LLDPE & PP) having polymer concentration between 1% - 3%.

Based on empirical test results conducted on virgin80/100 pen bitumen and polymer modified bitumen (1% - 5%) polymer concentration it was concluded that modification of 80/100 pen bitumen with polymer PP and LLDPE significantly decreases the penetration values. Decrease in penetration indicates the hardening effect induced as being observed by higher stability values and higher stiffness for the modified mixes.

Since thermoplastics were least affected by temperature variation as confirmed by minimal difference in softening temperature thus considered as positive point as the binder would least affected by change in pavement temperature.

Change in rheological behavior of the modified binder is due to the change in Newtonian behavior of virgin 80/100 pen bitumen to non- Newtonian behavior due to polymer modification. One hour mixing time at 120 rpm and at temperature 160°C, sufficiently alter the rheological properties of the modified binder as observed by enhanced viscosity test results. The altered rheological property of polymer modified binders shows shear thinning behavior for both PP and LLDPE modified binders.

Viscosities of the modified binders at all polymer concentration were within the limit of 3 Pa s at 135°C as proposed by ASSHTP MP1 for workable mixes.

Compatibility of polymer bitumen blend considered responsible for enhanced viscosity and altered rheological properties. The compatibility of polymer bitumen blend which was evaluated in terms of the colloidal index (CI) were well correlated with morphological results where proper compatibility as observed by lower colloidal index was observed for PP modified bituminous mixes as also confirmed by the presence of proper compatible bitumen as revealed by scanned images. Similarly of LLDPE incompatiblty of polymer with bitumen as observed by higher CI values obtained from SARA was confirmed by scanned images. Thus the SARA result shows well correlation with the scanned images taken by FESEM or by AFM or by TEM. The presence of helical polymer bitumen network confirms the existence of compatibility between polymer and bitumen as being revealed by SARA test results also.

The presence of oxidized compound as detected by GC/MS, by FTIR and CHNS analyzer revealed the reason for enhanced viscosity for the polymer modified bituminous mixture. The presence of asphaltene as revealed by *n* heptane precipitation results was also confirmed by the enhanced viscosity and by the evidence of agglomeration and creaming effect as exposed by FESEM scanned images. These results were found well correlated with the increase in carbonyl group formed due to increase in asphaltene content with the increase in polymer content in the binder. Thus the presence of chemical activity during blending was confirmed although the mixing time was kept to one hour, while slow shear rate mixing was adopted. It was also confirmed that although the slow shear rate was adapted just to physically disperse the polymer within bitumen but would results in the initiation of chemical activity as being observed by enhanced viscosity, increase in stiffness and viscoelasticity for PP and LLDPE modified bituminous mixture.

Increase in binder stiffness as revealed by DSR results was confirmed by the dynamic creep test results. The enhancement of complex modulus G* was confirmed by the increased stiffness while higher rutting resistance as revealed by G*/sin δ values was confirmed by dynamic creep results. Thus a good correlation was observed by DSR results and dynamic creep results.

The results for the engineering properties reveled that there was an insignificant variation in optimum binder content (OBC) for the virgin, PP and LLDPE modified bitumen. The OBC value for control mix prepared from virgin bitumen was 5.0% which increases till 5.2% for PP modified bituminous mixture while for LLDPE modified bituminous mixture OBC was increased till 5.4%. For 3% LLDPE modified bituminous mixture a decrease in OBC was observed. The insignificant increase in demand of modified binder by aggregate mixture indicates that although the viscosity of the binder was good enough to properly coat the aggregate but due to enhanced viscosity slightly greater amount of modified binder would be required to coat the aggregates properly. Since the same gradation was used for preparation of all bituminous mixtures thus the available surface area of coarse and fine aggregate to be coated would remain same. Insignificant difference in density was also observed as the binder content for all the bituminous mixtures were almost same. For 3% LLDPE although the reduced binder content was observed but the agglomerated polymer domains would help in resistance to compaction at the same energy level thus maintains the density. This stiffening effect as observed for 3% LLDPE was also confirmed by lower rut depth as observed by the wheel tracking test and higher stiffness of mix as observed during creep test.

Enhancement in stiffness was also confirmed for the modified bituminous mixtures, where for PP modified bituminous mixture an increase in stiffness from 5% - 9% was observed while for LLDPE modified bituminous mixture only 3% LLDPE shows significantly enhanced stiffness of 53% when compared to control bituminous mixture stiffness. LLDPE modified bituminous mixture failed to show enhanced stiffness property at 1% and 2% LLDPE. This behavior of the bituminous mixture was due to the formation of polymer bitumen network as observed by morphological analysis. The drastic increase in stiffness can be attributed due to presence of crystalline separate domains in 3% LLDPE PMB which significantly enhances the binder viscosity and stiffness of the bituminous mixture.

The behavior of modified bituminous mixture during laying and compaction was observed by workability index. For PP modified bituminous mixture WI was found well above the minimum limiting value of 6, while lower values were observed for 2% and 3% LLDPE modified bituminous mixture indicating that it will offer difficulty during laying and compaction. This behavior also confirms the viscosity test results where drastic increase in viscosity was observed for 3% LLDPE modified binder in comparison to the rest of the mix.

The performance test finally gave an idea about the effect of binder's properties on the bituminous mixture performance. Dynamic creep results for PP modified bituminous mixture shows improved stiffness modulus at all polymer concentration. Only 3% LLDPE shows improved stiffness modulus values in comparison to rest of the LLDPE modified bituminous mixture while 1% PP, 2% PP modified mixture shows higher mixture stiffness indicating the resistance to permanent deformation. The trend observed by the dynamic creep test was found well correlated with wheel tracking test results. Thus the binder behavior as revealed by the rheological, morphological and chemical analysis shows well correlation with the results obtained from mixture performance.

Fatigue test results obtained for constant strain mode showed higher and improved fatigue life for 3%PP modified mixtures at all strain levels. 3%PP modified specimen at (OBC + 0.5%) showed higher tensile strain (114µm/m) with respect to one million load repetition in comparison to 2% LLDPE (OBC + 0.5%) which showed only 75µm/m while control mix showed only 68µm/m. At low strain levels (100 micro strain) 1% and 2%PP modified beam specimen shows inferior behavior as compared to control mix, while for 3%PP showed 4 fold enhancement in fatigue life in comparison to control mix. The proper well connected network polymer network which significantly increases the stiffness of the beams was considered responsible. Same observation was observed at the higher strain level.

Thus PP modified bituminous mixture would perform well in fatigue as the max tolerable strain level set as endurance limit for large traffic volume and long life asphalt pavement as reported in NCHRP report 646 [178] is 65 micro strain.

LLDPE failed to show improved performance in fatigue behavior. The behavior of 1% and 2% LLDPE even at 100 and 300 micro strain was lower than control mixture. 2% LLDPE modified bituminous mixture showed improved performance at 500 micro strain level. The highly crystalline branched structure of LLDPE considered responsible for the lower fatigue life, which significantly enhances the viscous component without enhancing the elastic component. The incompatible polymer bitumen network as observed by AFM scanned images and from CI value for LLDPE PMB blend confirmed this behavior.

Thus it was concluded that plastomer especially the polyethylene without any cross linking or chemical modifier significantly enhances the complex modulus but failed to offer good result in fatigue as observed by the results.

From the above discussion it can be safely concluded that polypropylene (PP) modification of the bitumen showed superior performance in resistance to deformation (rutting) as observed by the1% PP and 2% PP dynamic creep and DSR rutting parameter results thus can effectively be used for high volume traffic lane, roundabout, at traffic signals, climbing lanes etc.

3 % PP showed better performance in terms of fatigue at 100 micro strains which is well above the fatigue endurance limit of 65 micro strain for long life asphalt pavements and for large traffic volumes. 3%PP can effectively be used for low volume roads where strain levels of 300 micro-strains are usually considered as upper limit. 2% LLDPE modified bituminous mixture at high strain level 500 micro strain showed improved fatigue life thus also can be used for low volume roads.

In view of the above discussion, Polypropylene modified bitumen has emerged as a promising modifier in comparison to virgin bitumen and PE modified bitumen, while material characterization provides definite evidence for the enhanced mechanical properties of the modified binder.

10.2 Recommendations

In view of the findings and conclusions drawn from this study, author suggests the following recommendations:

1. Since compatibility of polymer with the bitumen is the most important parameter for polymer modification thus it is recommended to characterize polymer in terms of molecular weight, structure, molecular weight distribution and degree of crystallinity before using it as modifier.

2. Use of softer grade bitumen (200 pen grade) is recommended for use with the PP and LLDPE polymer.

3. It is recommended that physio chemical analysis of the modified binder using DSC (differential scanning calorimetry) and T_m (melt temperature) must be done in order to have idea about the physical characteristics of the binder which affects the chemical characteristics and thus stability of polymer bitumen blend.

4. Cross linking of polymer, either using vulcanized rubber or addition of aromatic oil or use of copolymer is recommended in order to improve the viscoelastic character of PP or LLDPE modified binders.

5. As the morphological study was conducted only at room temperature, the author recommends to be conducted at varying temperature to have better understanding of polymer bitumen interaction.

6. It is suggested that all chemical test must be performed on aged binders obtained after RTFOT (rolling thin film oven test) in order to have idea about oxidation which is considered responsible for ageing.

7. SARA chromatography must also be conducted on aged binder in order to know change in asphaltene and maltene content due to ageing, which is considered responsible for the hardening of the binder.

8. It is recommended to perform fatigue testing by including the rest periods during loading in order to utilize the concept of intrinsic healing and wetting which consider that there is a chance of healing of micro cracks at higher pavement temperature during rest periods.

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LIST OF PUBLICATIONS

Book Chapter

Ibrahim Kamaruddin, **N. Z. Habib**, Isa Mohd Tan, Masaharu Komiyama and Madzlan Napiah, "Effect of Polymer Dispersion on the Rheology and Morphology of Polymer Modified Bituminous Blend," in 7th RILEM International Conference on Cracking in Pavements. vol. 4, ed: Springer Netherlands, 2012, pp. 859-868.

Journal Publications / Proceedings

1. I. Kamaruddin, **N.Z.Habib**, I. Tan, M.Napiah & Y. Komiyama (2012) "Effect *of Polymer Dispersion on the Rheology and Morphology of Polymer Modified Bituminous Blend*", 7th RILEM International Conference on Cracking in Pavements 2012, Delft, Netherlands published in the Proceedings of the 7th RILEM International Conference on Cracking in Pavements

2. **N.Z.Habib**, I.Kamaruddin, M.Napiah & I. Tan (2011) "*Effect of Mixing Process on Polypropylene Modified Bituminous Concrete Mix Properties*" International conference on Civil and Environmental Engineering ICCEE 2011, October 26 - 28, Bali, Indonesia. Published in journal of World Academy of Science, Engineering and Technology. Vol.58, pp 830-835, 2011.

3. **N.Z.Habib,** I.Kamaruddin, M.Napiah & I.Tan (2010) "*Rheological Properties of Polyethylene and Polypropylene Modified Bitumen*" presented at International Conference on Civil and Environmental Engineering, Singapore 2010, published in International Journal of Civil and Environmental Engineering 3:2.

4. **N.Z.Habib,** I.Kamaruddin, I.Tan & Napiah (2010) "*Effect of Thermoplastic Copolymers on microstructure and Viscoelastic behaviour of Bitumen*". Proceeding of Malaysian Universities Transportation Research Forum and

Conferences 2010 (MUTRFC 2010), 21 December 2010, Universiti Tenaga Nasional. ISBN XXX-XXX-XXXXX-X-X

Conferences

1. **N. Z. Habib,** I.Kamaruddin, M.Napiah & I.Tan (2010) "*Rheological and Morphological Analysis of Polymer Modified Bitumen*" International Conference on Sustainable Building and Infrastructure Conference ICSBI 2010 Kuala Lumpur, Malaysia.

2. **N.Z.Habib**, I.Kamaruddin, I.Tan & M. Napiah (2010) "*Effect of Thermoplastic Copolymers on microstructure and Viscoelastic behaviour of Bitumen*". Malaysian Universities Transportation Research Forum and Conferences 2010 (MUTRFC 2010), 21 December 2010, Universiti Tenaga Nasional. ISBN XXX-XXX-XXXXX-X-X

3. **N.Z.Habib**, I.Kamaruddin, M.Napiah & I.Tan (2010) "*Rheological Properties of Polyethylene and Polypropylene Modified Bitumen*" presented at International Conference on Civil and Environmental Engineering, Singapore 2010.

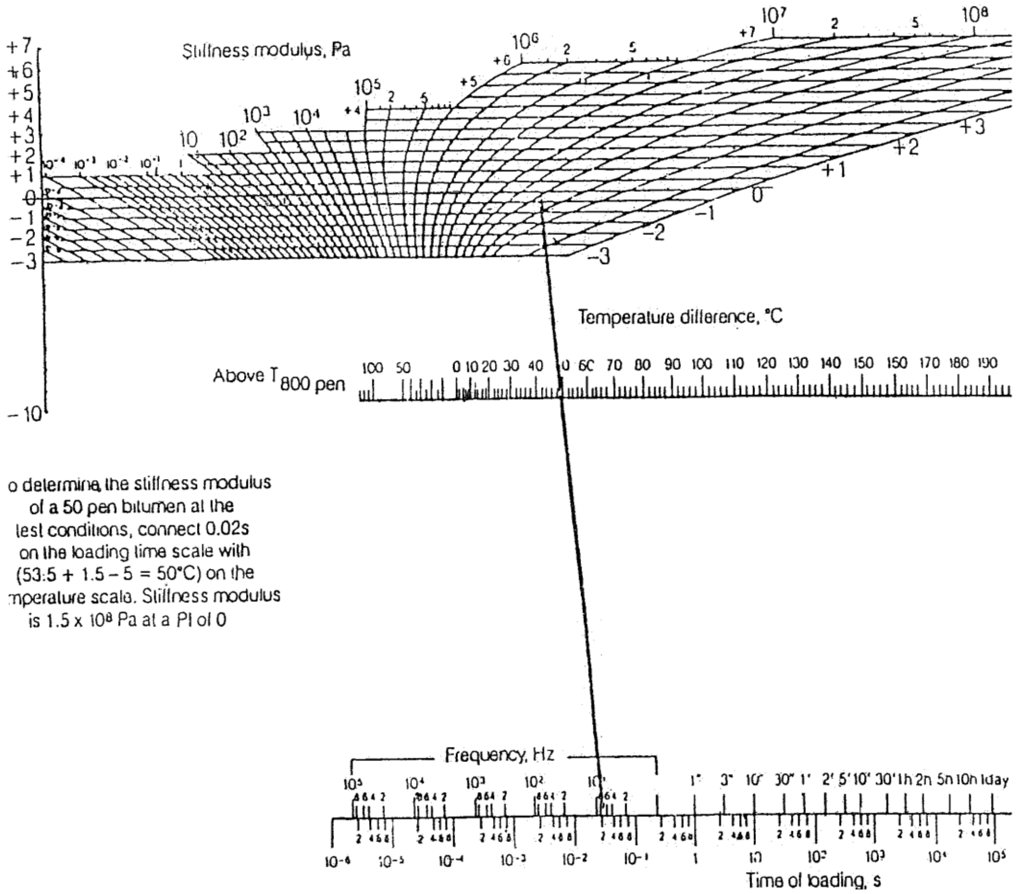
4. **N.Z.Habib**, I.Kamaruddin, I.Tan & M.Napiah (2011) "*The Application of Modern Analytical Techniques to study Rheology and Morphology of Polymer Modified Bitumen*", presented at National Post graduate Conference held in Uinversiti Teknologi PETRONAS Sept.19-20, 2011.

5. *N.Z.Habib*, I.Kamaruddin, M.Napiah & I. Tan (2011) "*Effect of Mixing Process on Polypropylene Modified Bituminous Concrete Mix Properties*" International conference on Civil and Environmental Engineering ICCEE 2011, October 26 - 28, Bali, Indonesia.

6. I.Kamaruddin, **N.Z.Habib**, I.M. Tan, Y.Komiyama & M.Napiah (2012) "*Effect of Polymer Dispersion on the Rheology and Morphology of Polymer Modified Bituminous Blend*", 7th RILEM International Conference on Cracking in Pavements 2012, Delft, Netherlands.

7. **N.Z.Habib**, I.Kamaruddin, M.Napiah & I.M.Tan (2012) "*Evaluation of Deformation behavior of Virgin and Polypropylene Modified Bituminous Mixture using Dynamic Creep Test*" International Conference of Civil, Environmental and Offshore Engineering ICCOEE 2012,June12-14, Kuala Lumpur, Malaysia.

APPENDIX



o determine the stiffness modulus of a 50 pen bitumen at the test conditions, connect 0.02s on the loading time scale with (53.5 + 1.5 – 5 = 50°C) on the mperature scale. Stiffness modulus is 1.5 x 10^8 Pa at a PI of 0

Figure 1: Van der Pool nomograph for S_{bit} determination [183]

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Instrument :   GCMS1
Sample Name:
Misc Info :
Vial Number: 0

Virgin Bitumen

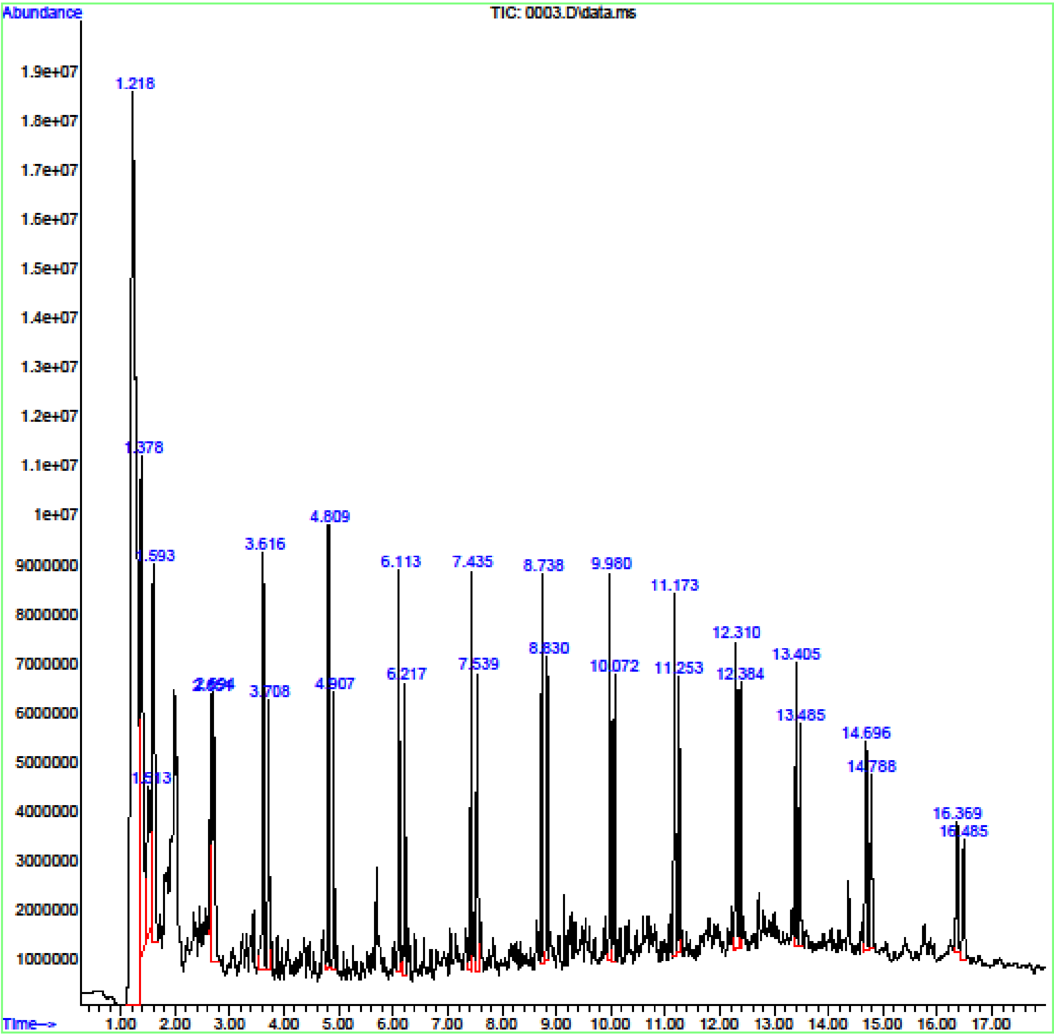

Figure 2: GC/MS Chromatograph of Virgin 80/100 Pen Bitumen

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Instrument : gcms1
Sample Name: 1% PP - Bit
Misc Info : pyrolized @ 500 C
Vial Number: 1

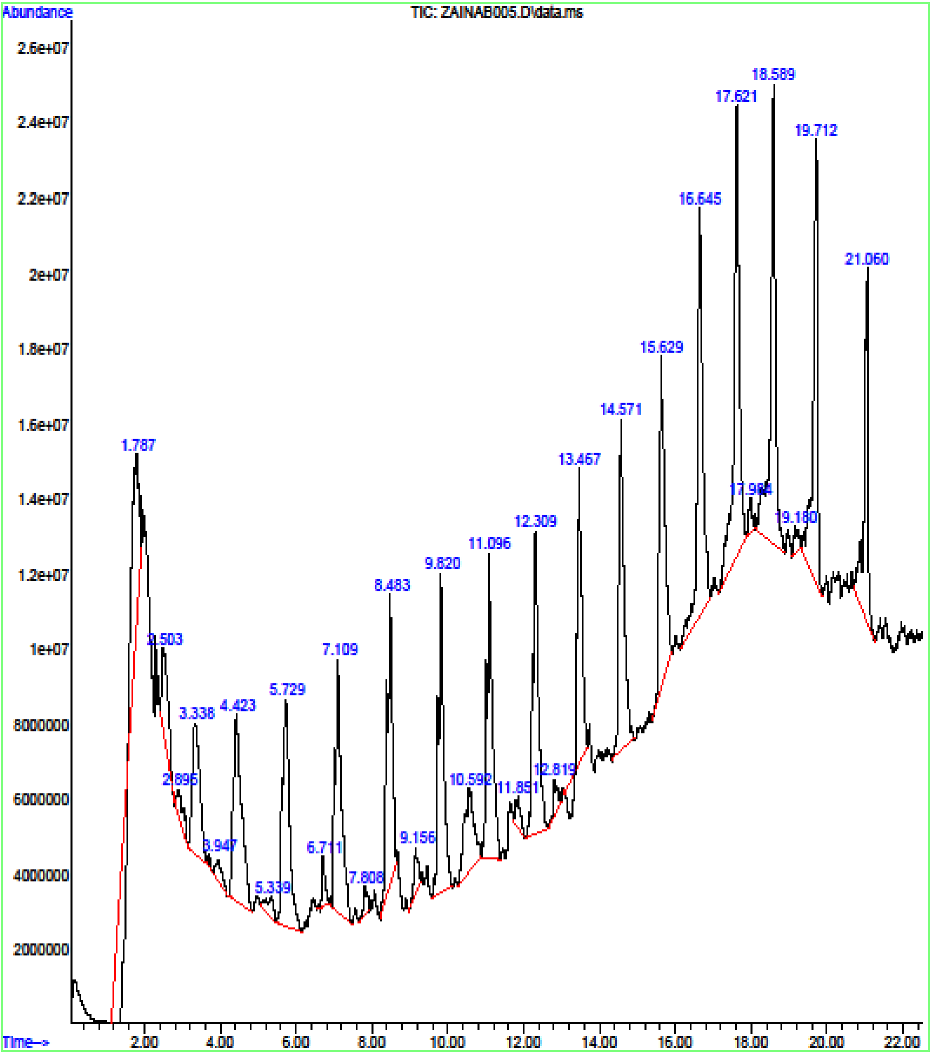

Figure 3: GC/MS Chromatograph of 1% PP Modified Bitumen

File :C:\msdchem\CAL 2010\DATA\2011\zainab\ZAINAB003.D
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Misc Info : pyrolized @ 500 C
Vial Number: 1

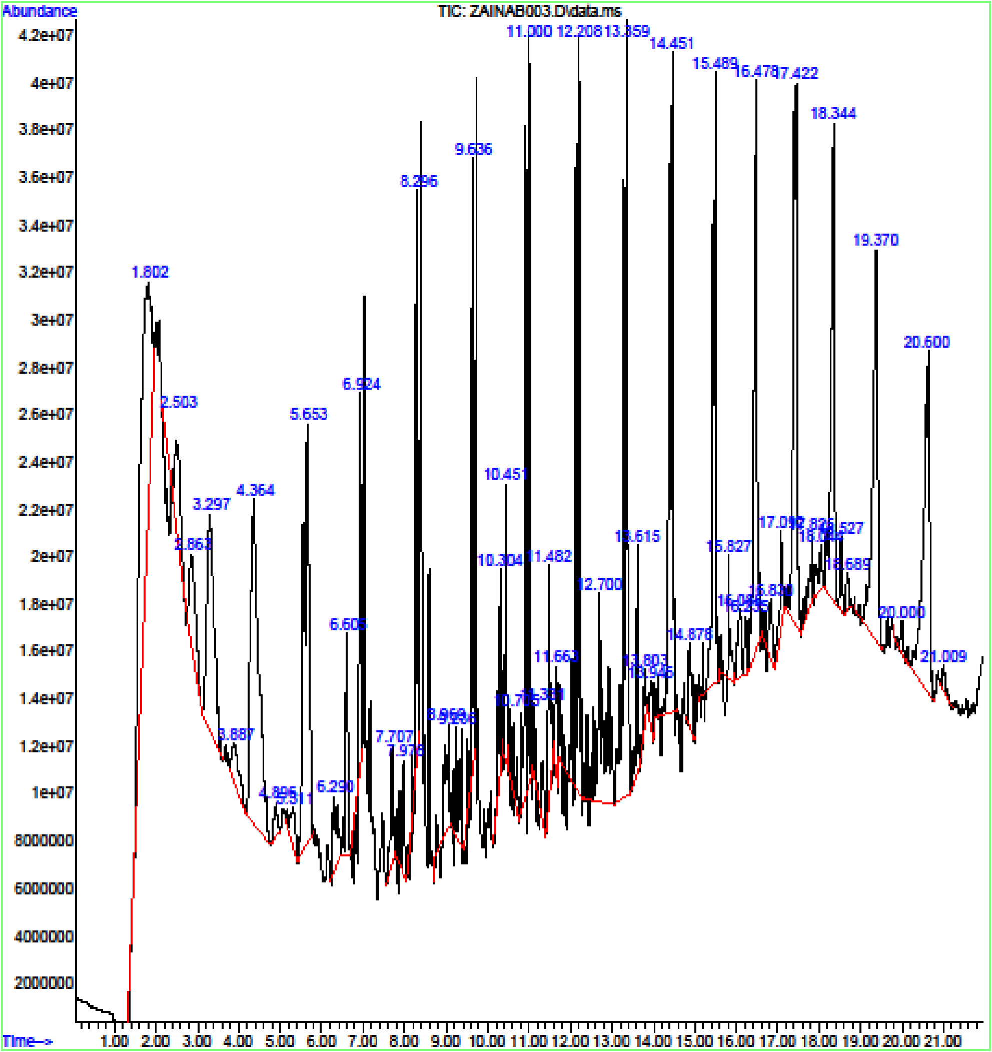

Figure 4: GC/MS Chromatograph of 2% PP Modified Bitumen

File   :C:\msdchem\CAL 2010\DATA\2011\zainab\ZAINAB004.D
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Vial Number: 1

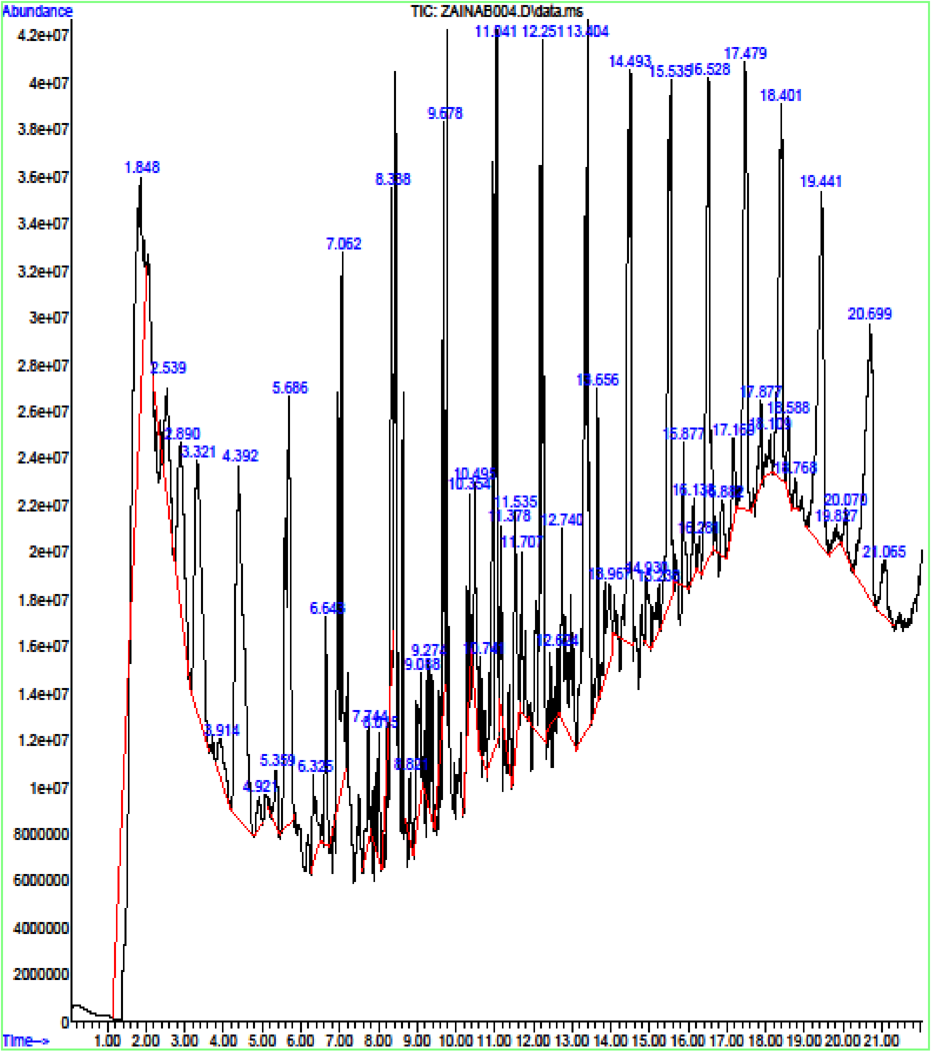

Figure 5: GC/MS Chromatograph of 3% PP Modified Bitumen

File :C:\msdchem\CAL 2010\DATA\2011\zainab\ZAINAB009.D
Operator : mohdfab
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Instrument : gcms1
Sample Name: 1% LLDPE - Bit
Misc Info : pyrolized @ 500 C
Vial Number: 1

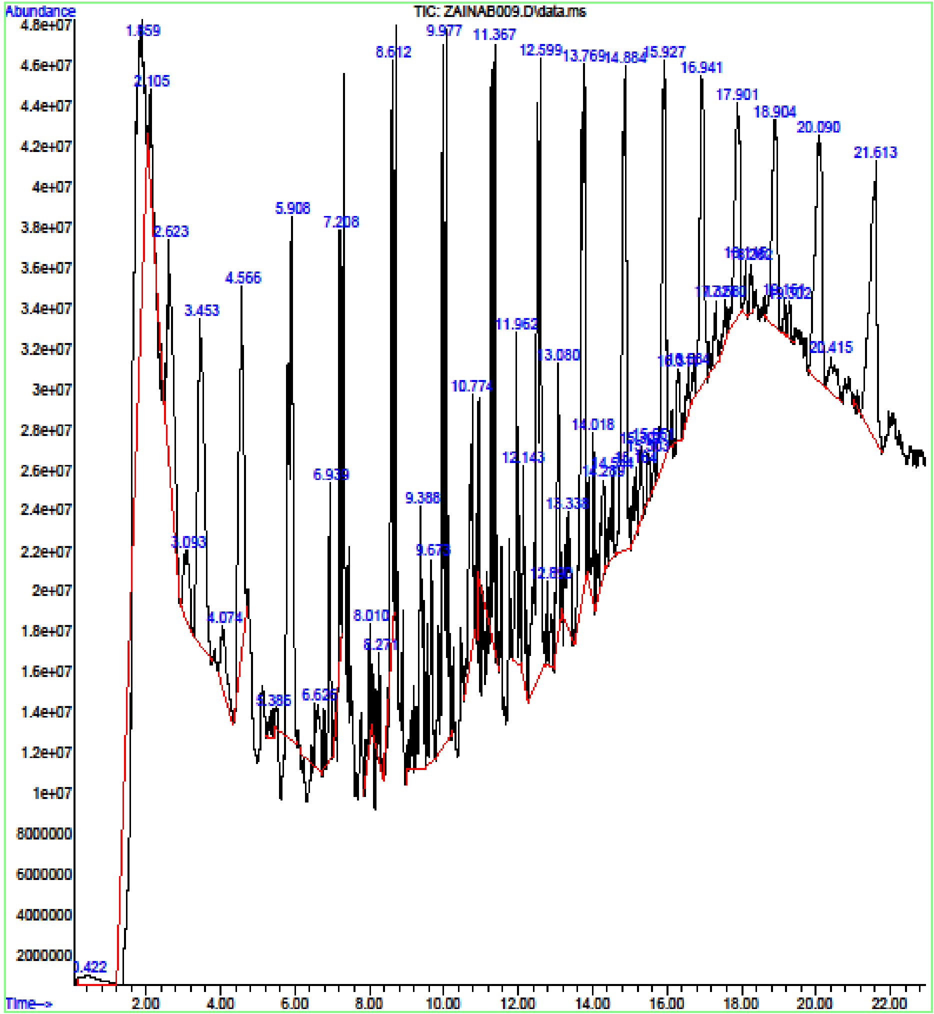

Figure 6: GC/MS Chromatograph of 1% LLDPE Modified Bitumen

File :C:\msdchem\CAL 2010\DATA\2011\zainab\ZAINAB010.D
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Vial Number: 1

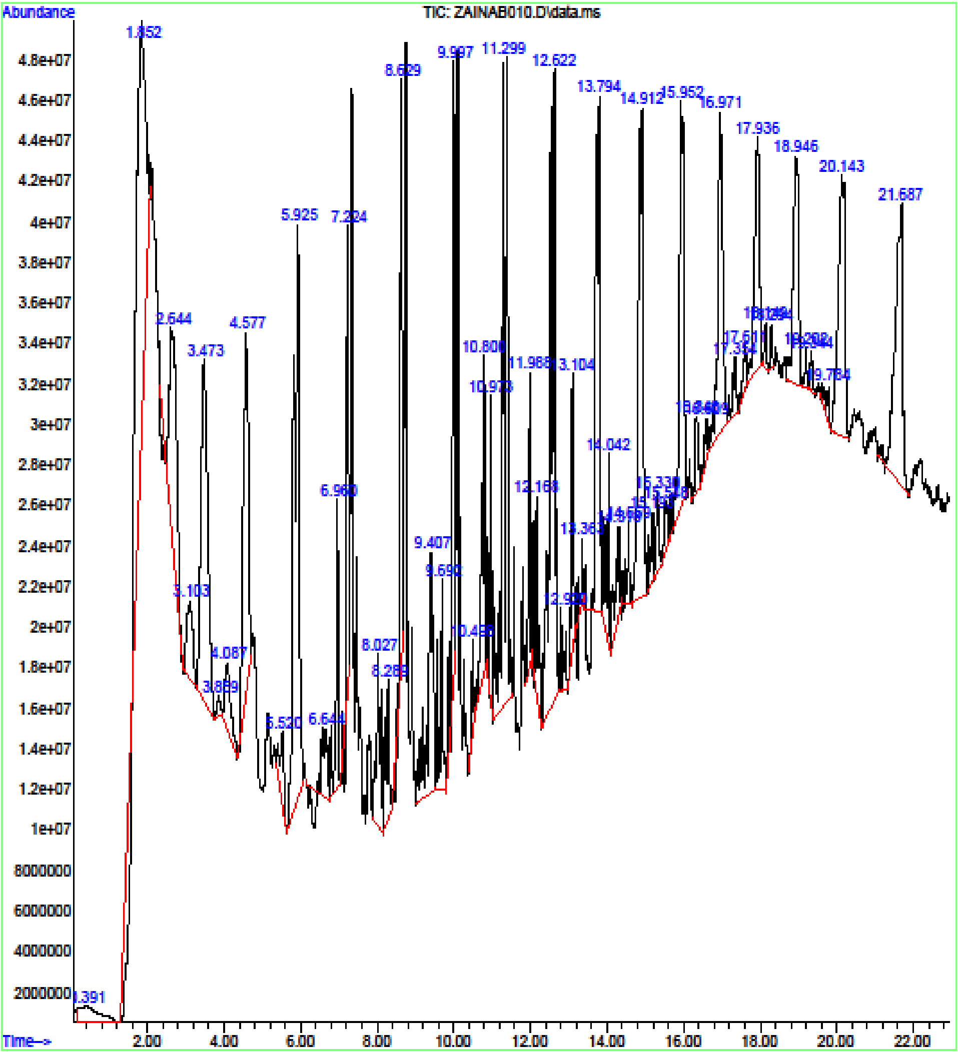

Figure 7: GC/MS Chromatograph of 2% LLDPE Modified Bitumen

File   :C:\msdchem\CAL 2010\DATA\2011\zainab\ZAINAB011.D
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Misc Info : pyrolized @ 500 C
Vial Number: 1

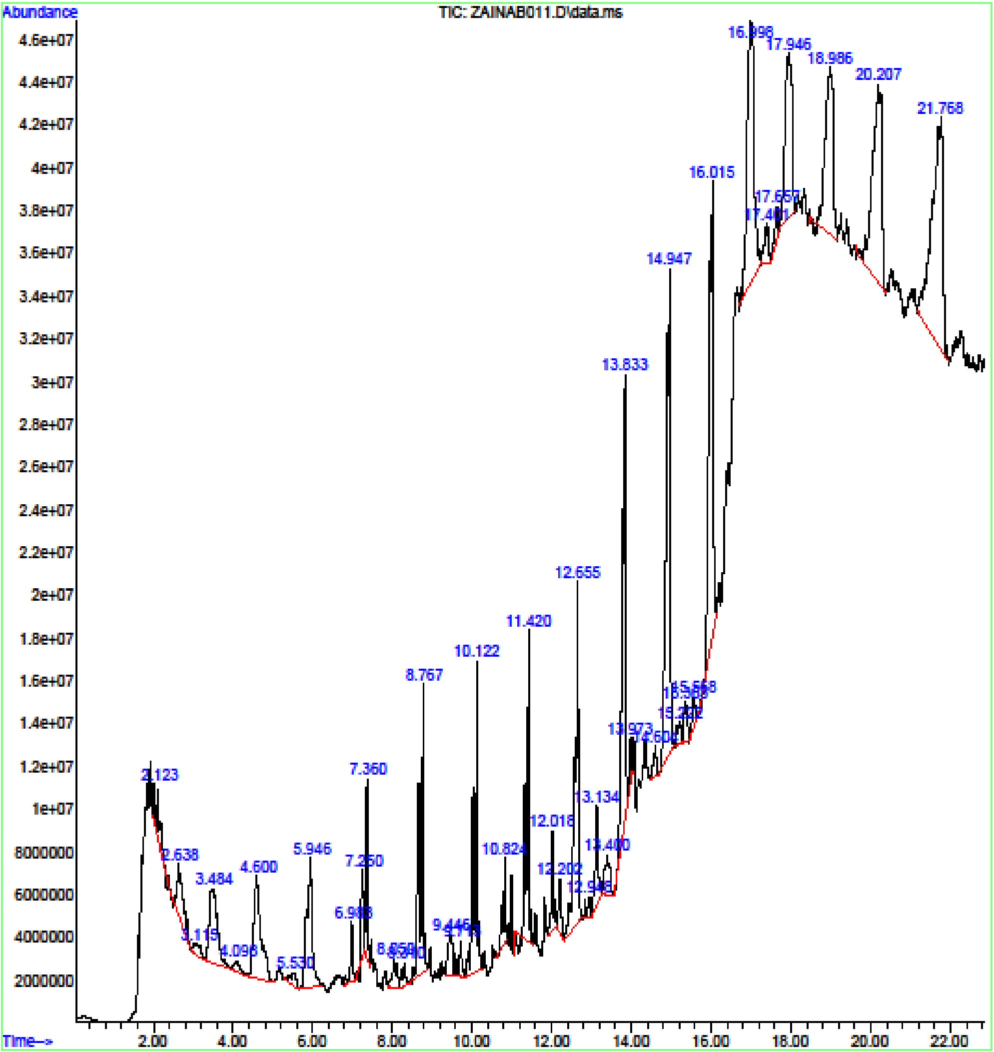

Figure 8: GC/MS Chromatograph of 3% LLDPE Modified Bitumen

Table 1: Rheological Test Data for Aged 80/100 Pen Bitumen

T (°C)	G* (Pa)	G' (Pa)	G" (Pa)	delta(δ)	G*/1000 (kPa)	G*/Sinδ
46	92083	23291	89047	75.341	92.083	95.18607
52	38065	7201	37366	79.054	38.065	38.77063
58	15302	2443	15078	80.595	15.302	15.5114
64	6471.6	516.349	6444.2	85.378	6.4716	6.493027
70	3181	174.56	3176.2	86.855	3.181	3.186098
76	1536.9	43.202	1536.1	88.388	1.5369	1.537515
82	765.93	3.3873	765.93	89.747	0.76593	0.766007

Table 2: Rheological Test Data for Aged 1% PP PMB

T (°C)	G* (Pa)	G' (Pa)	G" (Pa)	delta(δ)	G*/1000 (kPa)	G*/Sinδ
46	158420	60193	146240	67.436	158.42	171.5616
52	69194	20488	66025	72.666	69.194	72.4924
58	31361	7043.5	30560	77.019	31.361	32.18361
64	14200	2513.6	13977	79.821	14.2	14.42796
70	7056.6	917.55	6996.4	82.531	7.0566	7.117095
76	3454.1	327.12	3438.7	84.565	3.4541	3.469714
82	1743.3	110.95	1740.1	86.351	1.7433	1.746969

Table 3: Rheological Test Data for Aged 2% PP PMB

T (°C)	G* (Pa)	G' (Pa)	G" (Pa)	delta (δ)	G*/1000 (kPa)	G*/Sinδ
46	114980	37637	108550	70.904	114.98	121.6848
52	42970	11249	41471	74.825	42.97	44.52388
58	17615	3154.44	17305	79.735	17.615	17.90324
64	7799	1199.8	7704.8	81.162	7.799	7.892926
70	3725.7	385.96	3705.5	84.054	3.7257	3.745928
76	1822.3	125.27	1818.2	86.059	1.8223	1.826684
82	947.12	37.045	946.4	87.758	0.94712	0.947878

Table 4: Rheological Test Data for Aged 3% PP PMB

T (°C)	G* (Pa)	G' (Pa)	G" (Pa)	delta(δ)	G*/1000(kPa)	G*/Sinδ
46	142440	50733	133030	69.184	142.44	152.3911
52	58915	15582	56772	74.56	58.915	61.12149
58	23783	5270.8	23155	77.126	23.783	24.39783
64	10554.9	1642.54	10418.7	81.063	10.5549	10.68526
70	5120.9	562.68	5087.8	83.689	5.1209	5.152329
76	2532.3	220.77	2522.8	84.999	2.5323	2.541959
82	1261.8	73.824	1259.6	86.644	1.2618	1.264075

Table 5: Rheological Test Data for Aged 1% LLDPE PMB

T (°C)	G* (Pa)	G' (Pa)	G" (Pa)	delta (δ)	G*/1000(kPa)	G*⁄sinδ
46	175040	62985	163070	68.968	175.04	187.5496
52	74821	21418.8	71533	73.555	74.821	78.01981
58	32684	7450.7	31810	76.817	32.684	33.57025
64	14639	2372.396	14426	80.676	14.639	14.83632
70	6464.9	806.01	6406.4	82.892	6.4649	6.515066
76	3296.1	302.79	3282.2	84.73	3.2961	3.310334
82	1599.3	93.164	1596.7	86.661	1.5993	1.602023

Table 6: Rheological Test Data for Aged 2% LLDPE PMB

T (°C)	G* (Pa)	G' (Pa)	G" (Pa)	delta (δ)	G*/1000(kPa)	G*⁄sinδ
46	228330	77587	214170	70.133	228.33	242.8009
52	90021	25460	86201	73.32	90.021	93.97745
58	38852	9648.6	37479	75.779	38.852	40.08253
64	18039	2948.9	17796	80.591	18.039	18.28586
70	8289.8	932.22	8236.5	83.549	8.2898	8.343196
76	3924.2	298.77	3913	85.633	3.9242	3.936008
82	1940.6	91.954	1938.1	87.284	1.9406	1.942932

Table 7: Rheological Test Data for Aged 3% LLDPE PMB

T (°C)	G* (Pa)	G' (Pa)	G" (Pa)	delta(δ)	G*/1000(kPa)	G*⁄sinδ
46	674490	416760	529520	51.782	674.49	858.5667
52	263410	119760	234570	62.991	263.41	295.6673
58	92737	29901	87758	71.542	92.737	97.77227
64	24894	3790.8	24588	81.744	24.894	25.15562
70	7817.4	311.648	7807.8	88.148	7.8174	7.822093
76	657.08	65.808	646.18	71.985	0.65708	0.691009
82	177.99	63.47	165.46	68.303	0.17799	0.191572

Table 8: Rheological Test Data for Unaged 80/100 Pen bitumen

T (°C)	G* (Pa)	G' (Pa)	G" (Pa)	delta (δ)
46	28815	3443.011	28573	83.06
52	11825	1431.4	11681.6	82.874
58	5046.8	332.529	5026.9	86.201
64	2304.4	68.506	2303.3	88.295
70	1095.2	8.7607	1095.2	89.542
76	511.63	5.4265	511.6	89.391
82	270.4	7.06	270.31	88.504

Table 9: Rheological Test Data for unaged 1% PP PMB

T (°C)	G* (Pa)	G' (Pa)	G" (Pa)	delta (δ)
46	43517	9477.2	42437	77.362
52	18826	2780.1	18618	81.533
58	8259.5	1004.168	8169.4	83.097
64	3723.1	296.91	3711.1	85.426
70	1888.9	108.08	1885.9	86.72
76	978.87	36.06	978.22	87.888
82	519.51	10.0365	519.41	88.893

Table 10: Rheological Test Data for unaged 2% PP PMB

T (°C)	G* (Pa)	G' (Pa)	G" (Pa)	delta (δ)
46	36077	7813.7	35168	77.608
52	13079	1717.7	12906	82.705
58	5307.6	492.56	5283.9	84.67
64	2320.2	141.2	2316.1	86.51
70	1113.3	36.601	1112.9	88.118
76	568.8	6.8025	568.74	89.315
82	295.77	1.7782	295.77	89.656

Table 11: Rheological Test Data for unaged 3% PP PMB

T (°C)	G* (Pa)	G' (Pa)	G" (Pa)	delta (δ)
46	39591	7926.6	38783	78.462
52	15144	2315.93	14935	81.321
58	6192.7	592.34	6162.5	84.478
64	2987.3	196.64	2980.8	86.226
70	1459	57.32	1458	87.747
76	741.92	13.213	741.82	88.981
82	390.78	0.656	390.78	89.904

Table 12: Rheological Test Data for unaged 1% LLDPE PMB

T (°C)	G* (Pa)	G' (Pa)	G" (Pa)	delta (δ)
46	48622	10059.6	47561	78.088
52	20906	3459.66	20499	80.285
58	9052.2	969.43	8996.1	83.823
64	4129.1	310.37	4117.3	85.689
70	2000.6	95.184	1998.3	87.273
76	1020.2	27.441	1019.8	88.457
82	535.6	6.7657	535.56	89.276

Table 13: Rheological Test Data for unaged 2% LLDPE PMB

T (°C)	G* (Pa)	G' (Pa)	G" (Pa)	delta (δ)
46	70042	15415	68250	77.353
52	29151	5103.8	28597	79.996
58	12602	1399.55	12493	83.557
64	5346.9	614.48	5292.4	83.423
70	2657.3	116.24	2655.1	87.493
76	1324.3	34.344	1323.8	88.514
82	693.3	11.295	693.2	89.066

Table 14: Rheological Test Data for unaged 3% LLDPE PMB

T (°C)	G* (Pa)	G' (Pa)	G" (Pa)	delta (δ)
46	311610	130799	281800	65.085
52	114500	38905	107676	70.107
58	44472	13110	42271	72.3
64	21495	4436	21033	78.093
70	10749.8	1842.6	10580.7	80.066
76	5050.6	368.953	5032.7	85.798
82	2406.1	188.98	2398.8	85.496

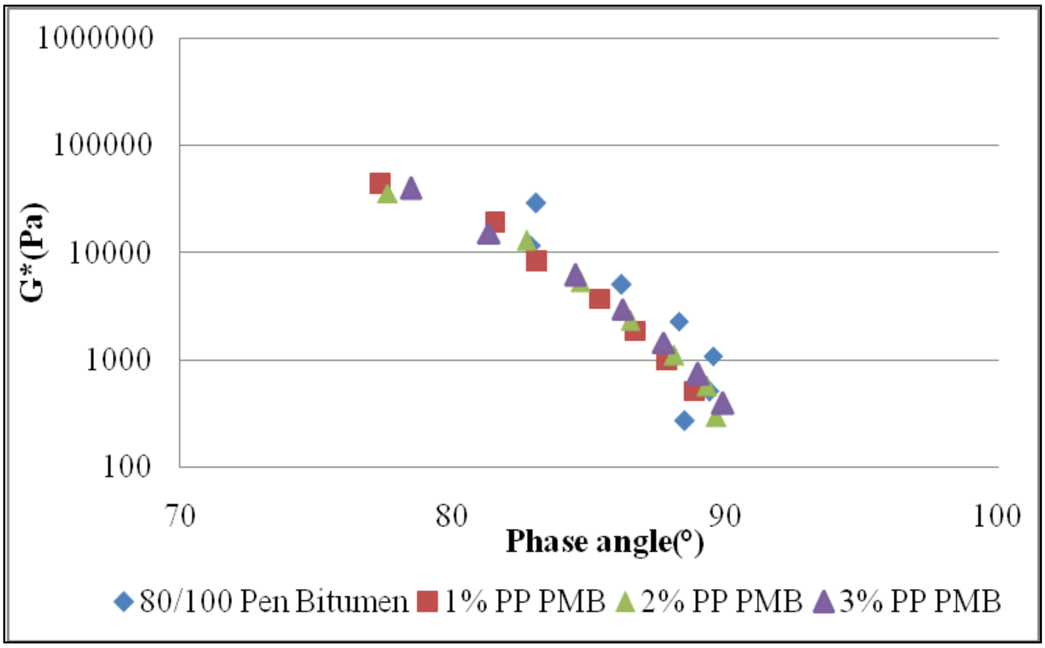

Figure 9: Complex Modulus Vs Phase angle for unaged PP PMB & 80/100 Bitumen

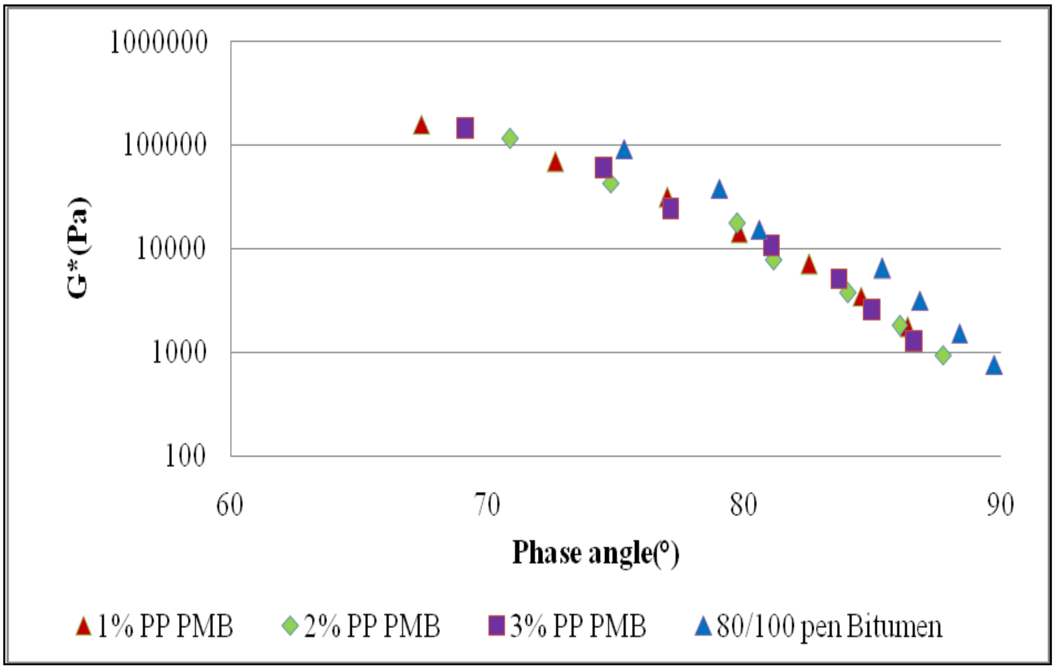

Figure 10: Complex Modulus Vs Phase angle for aged PP PMB & 80/100 Bitumen

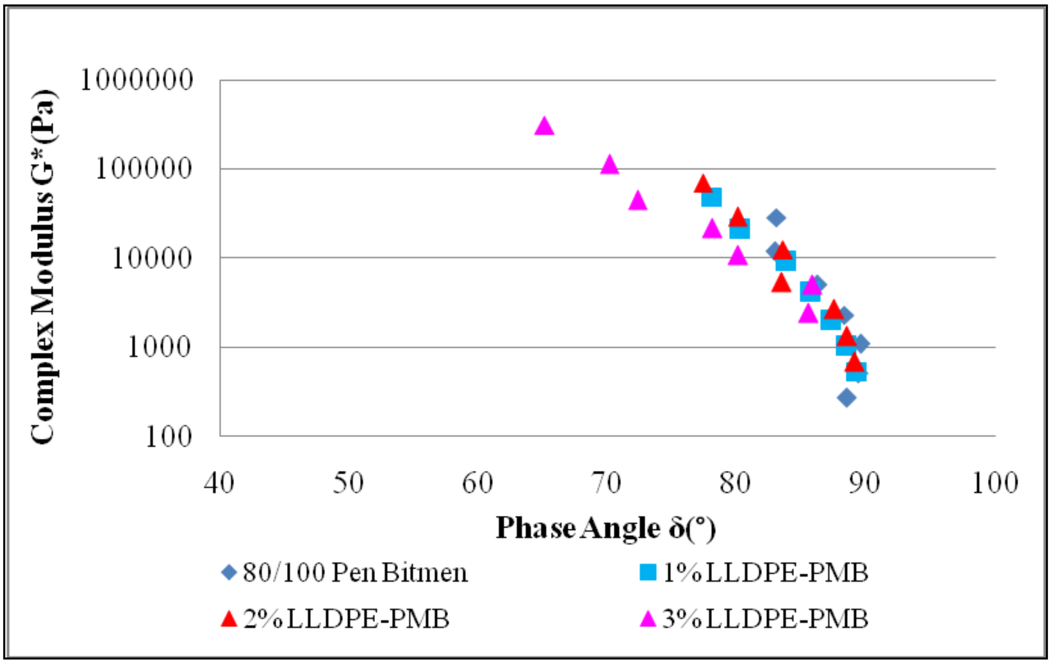

Figure 11: Complex Modulus G* Vs Phase angle δ for unaged LLDPE PMB & 80/100 Bitumen

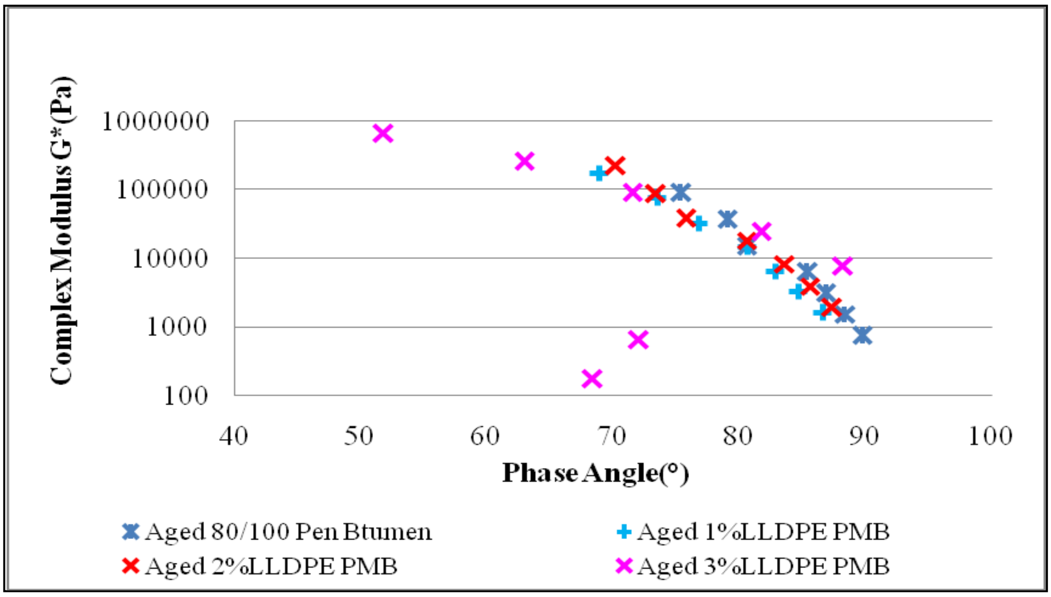

Figure 12: Complex Modulus g* Vs Phase angle δ for aged LLDPE PMB & 80/100 Bitumen

Table 15: Fatigue Test Results

Binder Content	Strain micro strain	Stress kPa	Stiffness GPa	Porosity %	Fatigue Life N_f
Control Mix (OBC – 0.5%)	100 300 500	812 1213 2220	8.12 4.04 4.44	4.58	102645 980 310
Control Mix OBC%	100 300 500	828 1670 3050	8.82 5.57 6.1	5.8	231200 2960 490
Control Mix (OBC + 0.5%)	100 300 500	908 1921 4160	9.08 6.40 8.32	4.6	173730 3020 130
1% PP PMB (OBC – 0.5%)	100 300 500	638 1312 1790	6.38 4.37 3.58	3.7	33730 984 250
1% PP PMB (OBC %)	100 300 500	948 1213 1580	9.48 4.04 3.16	3.2	50290 870 140
1% PP PMB (OBC + 0.5%)	100 300 500	865 1585 1890	8.65 5.28 3.78	3.46	193440 1980 530
2% PP PMB (OBC – 0.5%)	100 300 500	369 770 1202	3.69 2.57 2.40	5.0	67260 745 160
2% PP PMB (OBC %)	100 300 500	757 1706 2670	7.57 5.69 5.34	3.87	92320 545 320
2% PP PMB (OBC + 0.5)	100 300 500	1040 1838 2270	10.4 6.13 4.54	3.09	59280 780 460
3% PP PMB (OBC – 0.5%)	100 300 500	1380 2160 3500	13.8 7.2 7.0	4.90	710610 15530 7510
3% PP PMB (OBC)	100 300 500	1841 3140 3078	18.41 10.47 6.156	5.05	769790 15070 6990

Binder Content	Strain micro strain	Stress kPa	Stiffness GPa	Porosity %	Fatigue Life N_f
3% PP PMB (OBC + 0.5%)	100	778	7.78	3.49	999950
	300	2236	7.45		109720
	500	5753	11.506		8110
1% LLDPE (OBC – 0.5%)	100	854	8.54	4.9	47560
	300	2127	7.09		1310
	500	2753	5.51		520
1% LLDPE (OBC)	100	823	8.23	3.5	57580
	300	1698	5.66		1423
	500	2045	4.09		432
1% LLDPE (OBC + 0.5%)	100	847	8.47	4.5	227260
	300	1150	3.83		2110
	500	1893	3.78		532
2% LLDPE (OBC – 0.5%)	100	1080	10.8	4.8	94800
	300	1360	4.53		1024
	500	2020	4.04		430
2% LLDPE (OBC)	100	549	5.49	4.5	101490
	300	1574	5.25		1910
	500	2035	4.07		510
2% LLDPE (0BC + 0.5%)	100	1310	13.1	3.9	205690
	300	2470	8.23		2089
	500	3875	7.75		750

Figure 13: Crack Pattern observed for 80/100 pen Bituminous mixture beam

Figure 14: Crack Pattern observed for 1%PP PMB Bituminous mixture beam

Figure 15: Crack Pattern observed for 2%PP PMB Bituminous mixture beam

Figure 16: Crack Pattern observed for 3%PP PMB Bituminous mixture beam

Figure 16: Crack Pattern observed for 1% LLDPE PMB Bituminous mixture beam

Figure 17: Crack Pattern observed for 2% LLDPE PMB Bituminous mixture beam

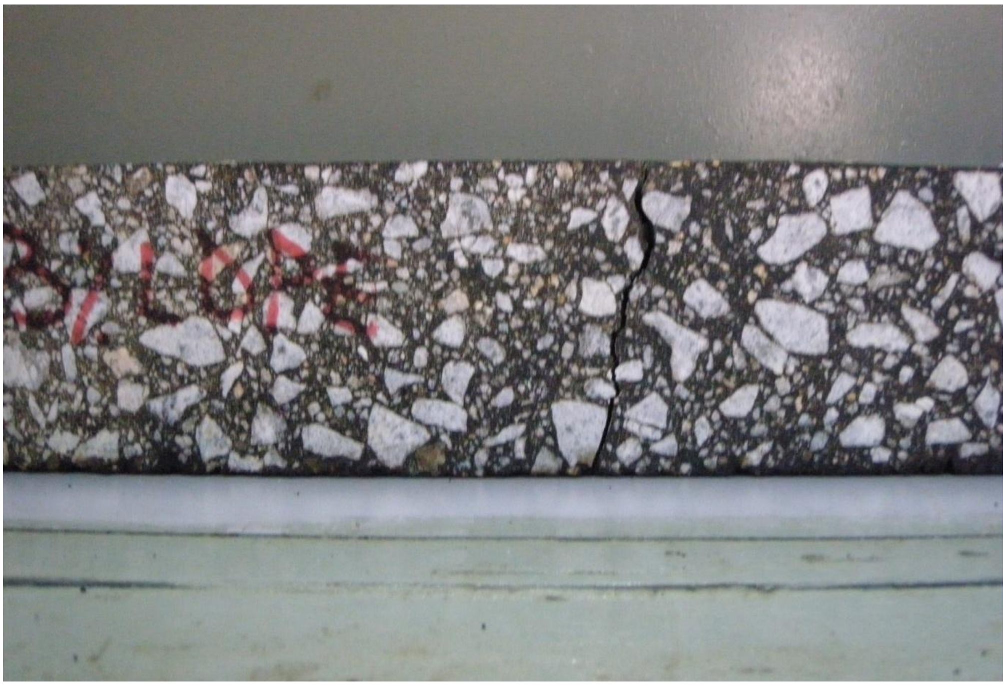

Figure 18: Crack Pattern observed for 3% LLDPE PMB Bituminous mixture beam