Improving the Aging Resistance of Asphalt by Addition of Polyethylene and Sulphur

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A thesis submitted in partial fulfillment of
the requirements for the degree of

Master of Science

in

Transportation Engineering

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School of Civil and Environmental Engineering (SCEE)
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Islamabad, Pakistan

(November, 2019)

THESIS ACCEPTANCE CERTIFICATE

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Dedication

Dedicated to my exceptional parents and adored siblings whose tremendous support and cooperation led me to this wonderful accomplishment.

ACKNOWLEDGEMENT

I am very thankful to ALLAH (S.W.T), whom blessing helped me to complete my research.
I would like to extend much appreciation and gratitude to my advisor Dr. Arshad Hussain whose countless inspiration and guidance made it possible to complete my research work. In addition, Dr Kamran Ahmad and Engr. Kamran Mushtaq in the capacity of committee member, gave me guidance and feedback throughout the thesis process. I would like to pay gratitude to the NIT lab staff including Syed Iftikhar Ali Shah, Hidayat Ullah and Mahmood Hussain.

(Engr. Maria Iqbal)

ABSTRACT

The demand for bituminous pavement is increasing with the increase in traffic volume. Pavement distresses are the main cause that affect the service life of bituminous pavement. Failures in asphalt pavement are not only due to the increased traffic load but also due to the extreme climate conditions. One of the main cause of early deterioration of pavement is the aging of asphalt binder. Aging can be defined as the hardening of asphalt binder due to oxidation and volatilization of light components in the asphalt binder materials during construction and service phase. The phenomena of aging significantly affect the chemical and rheological properties of asphalt binder. The structural changes as well as the permanent hardening occurring as a result of aging may cause significant loss in the bituminous binder's elasticity and therefore induce effects such as rutting, fatigue cracking, thermal cracking and moisture sensitivity. As a result, this reduces the estimated service life and comfort associated with the pavement. Therefore to extend the service life span of an asphalt pavement, it is necessary to improve its anti-aging performance characteristics. There are many modifiers available that have proven to improve the aging characteristics of asphalt binder. This research focuses on the use of one polymeric additive Polyethylene (PE) and one non polymeric additive Sulphur (S) to enhance the aging resistance of asphalt. These modifiers were evaluated for their effect on the aging mechanism in comparison with the unmodified base binder. Aging of the original and modified asphalt binder will be realized by the RTFO and PAV. Physical properties of the aged and unaged asphalt binder are evaluated through empirical testing like Penetration test, Softening point test and Ductility test. Optimum content of the modifiers is obtained by comparing the results of conventional properties before and after aging. Fourier transformed infrared spectroscopy (FTIR) and scanning electron microscope (SEM) are performed to bring out the chemical and morphological changes in the modified binder. Rheological properties of modified asphalts are studied using a Dynamic Shear Rheometer (DSR). Results indicate improvement in the physical properties of the modified asphalt even after the aging. Penetration index increased which shows less temperature susceptibility of the modified binders. Carbonyl and sulfoxide index are used as aging indicators which shows reduction in case of modified samples. Decrease in the sulfoxide and carbonyl index indicate better oxidation resistance of the modified samples. Morphological analysis proves good compatibility of the modifiers with asphalt binder. DSR results indicate improved visco-elastic properties of the modified binders.

Contents

LIST OF ABBREVIATIONS

ASTM	American Society of Testing Materials
PE	Polyethylene
S	Sulphur
HMA	Hot Mix Asphalt
SBS	Styrene Butadiene Styrene
FTIR	Fourier Transformed Infrared Spectroscopy
SEM	Scanning Electron Microscope
CPEC	China Pakistan Economic Corridor
TRB	Transportation Research Board
SHRP	Strategic Highway Research Program
FHWA	Federal Highway Administration
PG	Performance Grade
UV	Ultraviolet
DMA	Dynamic Mechanical Analysis
G*	Shear Modulus
δ	Phase Angle
G*/Sin δ	Complex Modulus
PARCO	Pak Arab Refinery Ltd
PAV	Pressure Aging Vessel
DSR	Dynamic Shear RheometeR
HP-GPC	High Penetration Gel Permeation Chromatography
RTFO	Rolling Thin Film Oven

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CHAPTER 1

INTRODUCTION

1.1 Background

Asphalt binder has been used for centuries. Asphalt binder existed in natural seepages around the world and was used for construction and Water proofing long before refining was even invented. The first known use of asphalt binder was located in Mesopotamia, the cradle of civilization, located in modern Iraq. In these ancient times asphalt binder was taken directly from natural fields or lakes. Traces of early use of asphalt binder have been found on every continent around the world. All ancient civilization used natural asphalt binder for various applications. The first use of asphalt binder as a construction material for road pavement appeared in Europe in 1830s, simultaneously in France and England. Asphalt binder then widely began to use in pavements and roofs.

In Pakistan, roads and highways are the major source of transportation. Almost 95% of the population and freight movement are served by its major highways (Division, 2018). Now with the development of CPEC, the importance of road infrastructures has also increased. This massive usage of highways in Pakistan makes it the backbone of the country’s economy. For improved economy we need efficient and sustainable methods and techniques (R. West).

The kilometer-age of paved roads existing in a country is often used as an index to assess the extent of its development (Aldagheiri, 2009). Hence it is important to invest into the extension and development of road transport infrastructure. With the increase in transportation through roads, the demand for bituminous pavement has also been increased as flexible pavements are more economical and provide smooth riding quality; therefore pavements are failing before reaching the end of their design life. Mix rutting is one of the major failure encountered on such roads. Traditional pavement materials are unable to meet the practical demands for current and future traffic loadings. Thus, higher quality, more safe, more reliable and more environment friendly pavement materials are urgently demanded (R. Li, Xiao, Amirkhanian, You, & Huang, 2017). In recent years, different types of polymers and modifiers have been used in asphalt to improve the performance and life of the pavement. Asphalt binder modification has been in practice for decades. There are several modifiers available that are believed to enhance the physical as well as rheological characteristics of asphalt binder. The use of Polymer Modified Asphalts

(PMAs) increase pavements life and help in reduction of maintenance costs (Hasan*et al.,* 2012). Various types of polymers like Styrene-Butadiene- Styrene (SBS) (Larsen *et al.,*2009), polyethylene (Al-Hadidi,2009), polypropylene (Al-Hadidi,2009) etc., have been used in asphalt pavements previously. Studies show that these polymer modifiers bring significant improvements in the rheological, physical and mechanical properties of the asphalt binder. They enhance the resistivity of asphalt binder against different distresses and pre-mature failures.

Asphalt binder is produced by petroleum refineries. It is a viscoelastic material which behaves like a viscous and elastic material at the same time. Performance of asphaltic mixture mainly depends upon three factors; Aging effects, temperature susceptibility and viscoelasticity. One of the main causes of early deterioration of pavement is the aging of asphalt binder. Aging is defined as the oxidation of light components which causes hardening of asphalt binder during construction and service phase. The primary cause of asphalt aging during service life time is the atmospheric oxidation of molecules which results in the formation of highly polar and strongly interacting functional groups containing oxygen(Sirin, Paul, & Kassem, 2018).

As we know that at low temperature asphalt binder has stiff nature(Ragni, Ferrotti, Lu, & Canestrari, 2018). This is the reason that a specified test of temperature is essential and results can never be interpreted without this. Depending upon the temperature, different grades of asphalt binder have been specified and these grades behave in different manners according to the temperature susceptibility. Such as at low temperature the asphalt mixture will be brittle and stresses increases beyond the strength which leads towards the development of transverse crack on the pavement surface. Loading time also effect the behavior of asphalt, usually under short loading interval asphalt act as a stiffer material. These two factors; temperature and load duration can be used interchangeably due to the dependence of asphalt binder behavior on them.

The phenomena of aging greatly affect the rheological and chemical properties of asphalt binder. This may reduce the elasticity of asphalt binder and thus causing distresses like thermal cracking, rutting, and fatigue and moisture damage. This results in the reduced service life of pavement.

Asphalt binder modification has been in practice for decades. There are several modifiers available that are believed to enhance the physical as well as rheological characteristics of asphalt binder. Among many tried and tested methods, polymer modification has always been the most popular approach(Selvavathi, Sekar, Sriram, & Sairam, 2002).

Asphalt binder is also characterized by its viscoelastic property as this property exhibit simultaneously both elastic and viscous nature of the asphalt binder. Viscoelastic behavior is interrelated with the thermo-mechanical nature of the asphalt binder and then it governs mechanical properties of HMA mixes by controlling its time-temperature dependence. When the temperature is high or more than 100°C, asphalt binder behaves entirely as a viscous fluid and its consistency becomes equal to that of a lubricant. Similarly, at lower temperatures or less than 0°C asphalt binder changes its behavior and acts most likely as an elastic solid, it returns to its original shape when loaded and unloaded, this property characterized its linear viscoelastic behavior. In most of the pavement systems asphalt binder exhibits both the properties of viscous fluid and an elastic solid at the intermediate temperature.

1.2 Problem Statement

As flexible pavements have some advantages over rigid pavements such as, stage construction, economical smooth riding quality etc., hence majority of the roads in our country are of flexible pavements type. Despite of the lower construction cost, the life cycle cost of the bituminous pavement is higher than the rigid pavements due to their higher maintenance cost. In flexible pavements, mostly, failure of the highway occurs due to the non-structural rutting or different types of cracking. Non-structural rutting occurs due to the poor asphalt mixture properties, heavy traffic loads, or due to high temperatures. Softening point of grade 60/70 asphalt binder in Pakistan ranges from 46°C to 52°C. There is much difference between pavement and air temperature; pavements are approximately 15°C hotter than air. Most of the time during summers, the temperature exceeds much as it crosses the temperature limit of softening of asphalt binder. Deterioration of pavement mainly depends upon the age of asphalt binder. Rheological and chemical properties of asphalt binder are altered by aging. This lessens the estimated service life and comfort linked with the bituminous pavement. Therefore there is a need to improve the characteristics that contribute to anti-aging performance of asphalt pavement to increase its life span.

1.3 Research Objectives

- To improve the aging properties of asphalt binder with the addition of polyethylene and Sulphur.
- To evaluate the physical properties of asphalt binder in un-aged and aged conditions.

- To determine the effect of modifiers on morphology and chemical composition of asphalt by conducting Fourier Transformed Infrared Spectroscopy (FTIR) and Scanning Electron Microscope (SEM).
- To analyze rheological characteristics of modified binder using Dynamic Shear Rheometer (DSR).

1.4 Scope of Study

Present study focuses on the use of locally available polymeric and non-polymeric additives that add up to the anti-aging performance of asphalt binder. Aging of asphalt binder is observed with RTFO and PAV in laboratory. Optimum percentages of modifiers were determined. Physical and performance testing was then conducted for different samples of aged and unaged asphalt binder. Chemical and morphological analysis was also carried out with SEM and FTIR techniques.

Table 1 Test Matrix

Type of Sample	**Polyethylene (%)**	**Sulphur (%)**	**Penetration Test**	**Softening Point Test**	**Ductility Test**	**RTFO**	**PAV**	**SEM**	**FTIR**	**DSR**	**Total samples**
Virgin Asphalt binder (60/70)	-	-	3	3	3	3	3	3	3	3	24
Virgin Asphalt binder + Polyethylene	2	-	3	3	3	3	3	3	3	-	21
	3	-	3	3	3	3	3	3	3	3	24
	5	-	3	3	3	3	3	3	3	-	21
Virgin Asphalt binder + Sulphur	-	2	3	3	3	3	3	3	3	3	24
	-	3	3	3	3	3	3	3	3	-	21
	-	5	3	3	3	3	3	3	3	-	21
Total			21	21	21	21	21	21	21	9	156

1.5 Thesis Outline

Chapter 1: This chapter depicts brief background and motivation for the research related to aging susceptibility of asphalt binder. It also provides an approach to the statement of problem, hypothesis as well as objectives of the research.

Chapter 2: This chapter provides an overview of the previous researches already carried out on the proposed topic. Moreover it also includes an overview of the mechanism of aging mechanism of asphalt binder, how to modify it and what are the effects of various modifiers on rheological and physical properties of asphalt binder.

Chapter 3: This chapter includes the details about the materials used in this research and the research methodology. The primary materials include 60/70 penetration grade asphalt binder, an elastomer Polyethylene and chemical Sulphur. The testing approach includes both the physical properties and the viscoelastic parameters to be evaluated.

Chapter 4: Explained the results obtained from laboratory testing. All the analysis done in finding the results.

Chapter 5: It is comprised of the conclusive comments based on the research finding as well as recommendations and suggestions for future research studies.

CHAPTER 2

LITERATURE REVIEW

2.1 Background

Economic Development of a country mainly depends upon presence of a healthy road transport network. Development of a country is often calculated by the kilometer-age of its paved roads (Aldagheiri, 2009). Hence it is important to invest into the extension and development of road transport infrastructure. For a long time, asphalt is used for the building of pavements while asphalt binder is the main constituent of asphalt. Now a day, pavements are failing before reaching the end of their design life, due to rapid increase in the traffic loading and number of vehicles. Mix rutting is one of the major failure encountered on such roads. Demands of current and future traffic loadings cannot be fulfilled by traditional pavement materials. Therefore there is an urgent need of good quality, environment friendly safe and reliable pavement materials (R. Li *et al.,* 2017). Various types of modifiers and polymers are added in asphalt to improve its life and performance. Mechanical properties of asphalt are improved by the addition of crumb rubber. Moreover addition of polymer in asphalt increase pavements life and help in reduction of maintenance costs (Hasan et al., 2012). Various types of polymers like Styrene-Butadiene- Styrene (SBS) (Larsen *et al.,*2009), polyethylene (Al-Hadidi,2009), polypropylene (Al-Hadidi,2009) etc., have been used in asphalt pavements previously. Studies show that mechanical, physical and rheological characteristics of the asphalt binder are enhanced by the addition of these polymer modifiers. They enhance the resistivity of asphalt binder against different distresses and pre-mature failures.

2.2 Asphalt Binder History

Asphalt binder/Asphalt binder is produced by petroleum refineries. It is used to make a dense mass by binding the aggregate particles together. Aging effects, temperature susceptibility and visco-elasticity are the three major properties of the asphalt binder that play a very important role in the performance of asphalt mixture. Aging of asphalt binder is considered one of the main causes of early deterioration of pavement. Aging is defined as the oxidation of light components which causes hardening of asphalt binder during construction and service phase. Atmospheric oxidation of molecules causing the formation of highly polar and strongly interacting functional groups containing oxygen is the primary cause of asphalt aging during service life time.

Asphalt binder is also characterized by its viscous and elastic nature and this property of asphalt binder is termed as viscoelastic property. Viscoelastic behavior is interrelated with the thermo-mechanical nature of the asphalt binder and then it governs mechanical properties of HMA mixes by controlling its time-temperature dependence. When the temperature is high or more than 100°C, asphalt binder behaves entirely as a viscous fluid and its consistency becomes equal to the motor oil or some other lubricant. Similarly, asphalt binder changes its behavior and acts most likely as an elastic solid at very low temperatures hence maintain its original shape when loaded and unloaded, this property characterized its linear viscoelastic behavior. At the intermediate temperature, in most of the pavement systems asphalt binder exhibits both the properties of elastic solid and viscous fluid.

2.3 Asphalt Binder Composition

In the European specifications, asphalt binder is defined as “virtually in volatile, adhesive and waterproofing material derived from crude petroleum, or present in natural asphalt, which is completely or nearly completely soluble in toluene, and very viscous or nearly solid at ambient temperatures”.

Asphalt binder is a combination of very complex molecules that are the result of millions of years of intense heat, radiation and pressure acting on dead decaying plant, animal and fish life. This process breaks down and indeed reforms very complex molecules to form this mixture of hydrocarbons that we call crude oil. The crude oil is then refined into its component parts, the heaviest and the most complex molecule of which are called asphalt binder.

2.3.1 Elemental Composition

Asphalt binder is a nitrogen compound showing a highly complex constitution. Many different chemicals present in the asphalt binder structure make its chemistry complex. To resume asphalt binder, many of the chemicals consist in carbon and hydrogen atoms. Moreover, atoms, such as nitrogen, sulphur and oxygen are usually present. Some traces of metal have also been found. The most frequent being vanadium and nickel.

Table 2 Elemental composition of asphalt binder ("Bitumen components- composition of bitumen- Bitumen Characterization," n.d.)

Carbon	80-84 wt.%
Hydrogen	8-12 wt.%
Sulphur	0-9 wt.%
Nitrogen	0-2 wt.%
Oxygen	0-2 wt.%
Vanadium, Nickel, Iron, Aluminum, Silicon	traces

2.3.2 Chemical Composition

The chemistry of asphalt binder is often simplified into four generic groups, often referred to as SARA, which help to define the behavior of asphalt binder. These are as follow, firstly the saturates, these are colorless, nonpolar oils. Secondly the aromatics, these tend to be dark brown, nonpolar viscous liquids. Thirdly, resins, these are dark brown, polar semisolid or solid. Finally the asphaltenes, these are dark brown or black very polar solids. The relative proportion of these SARA components dictates the physical behavior of the asphalt binder. For example, asphaltenes contribute significantly to the solid nature of the asphalt binder. The resins to the addivity of the asphalt binder and the aromatics dictate how well dispersed the asphaltenes are and so will also influence the solid liquid balance of the asphalt binder. Therefore the balance of the SARA is the fundamentally important in how the asphalt binder behaves in service.("1- Bitumen: Origins,

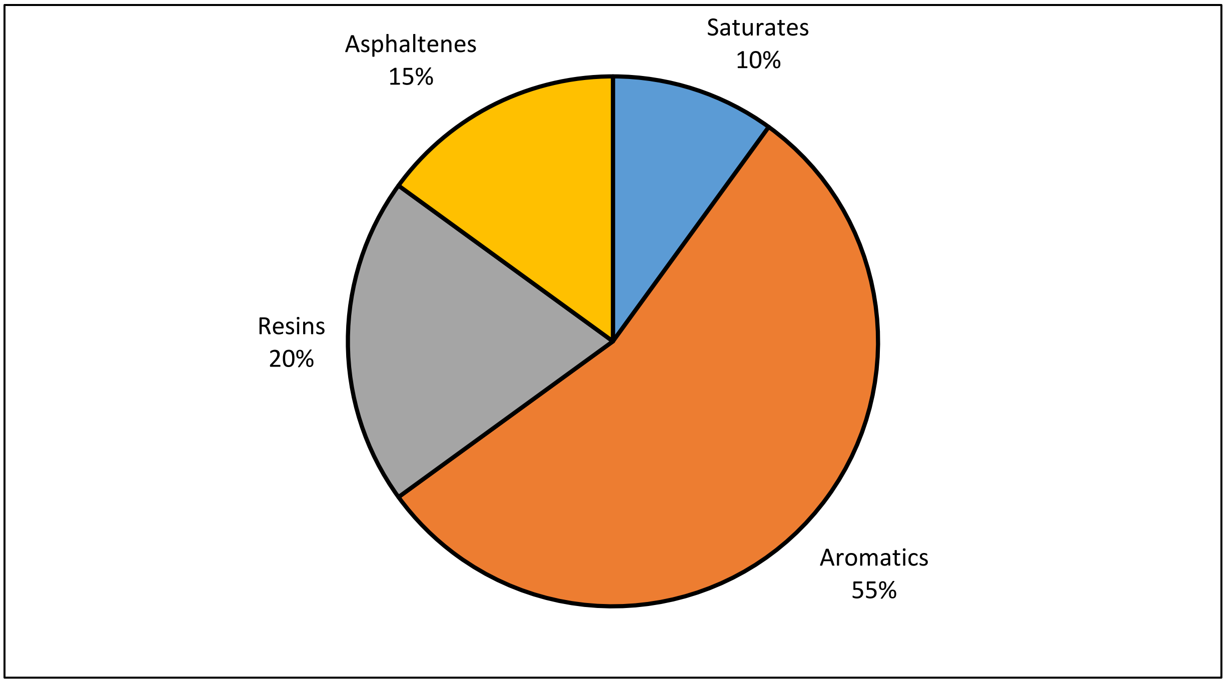


Figure 1 Chemical Composition of Asphalt

(history, definition, terminology - Bitumen market, generalities, the manufacture of bitumen, transport, uses of bitumen, main developments and alternatives | Coursera," n.d.)

2.4 Super Pave Grading System

The Super pave is a complete package which includes tests methodology, specifications and best engineering practice that enable engineers to select suitasble material and guideline for mixing the material properly to meet the heavy traffic and extreme climatic condition for particular highway project.

In 1984 transportation research board (TRB) published a report title as "Transportation special report 202" with emphasize on six research areas with long term pavement performance program as one of key research area. Accelerating the search for innovation, the need for publishing such report was to find a solution premature failure of flexible pavement which was matter of concern for the US government as large amount of tax payer money was spent on it. This report paved the way for US congress to sanction 50 million dollar for the Federal Highway Administration (FHWA) (transportation, 2017-2018).It started an agenda which is known as (SHRP).This report provided certain recommendation to (AASHTO) which made a start for inclusion of new testing methodology, new and improved tools and improved method of mix design of asphalt in a new edition of AASHTO. The strategic highway program which was started in 1987 ended in 1993 which primary focus on pavement deteriorations like rutting phenomenon, cracks due to fatigue and low temperature cracking which were the major causes for the premature failure of asphalt pavement. In order to curb pavement distresses new testing methods and tools were developed which simulate field condition in lab better three main area of research of strategic highway research program is mentioned as below:

- Specifications of Performance Graded (PG) Asphalt Binder
- Mix Design (Volumetric)
- Prediction of Mix Analysis Performance

The important breakthrough of SHRP was to make a technique to classify the binder which was termed as performance graded asphalt binder specification. This approach helps engineers to classify the asphalt binder based on maximum average seven days pavement temperature. For example, 76-16 means that this asphalt binder can be used in a locality where the maximum seven days temperature is 76°C while the lowest seven days pavement temperature is -16°C. It is important to mention that maximum seven days pavement temperature can be calculated my measuring Seven-day hottest day of the year and taking average of it similarly average lowest temperature can be measured and taking average of it this temperature data can obtained from metrological department of Pakistan. There are different approaches to convert maximum air temperature to maximum seven-day pavement temperature, the most prominent is model developed by strategic highway research program.

Tpav = (Tair - 0.00618 Lat2+0.2289 Lat +42.4) 0.9545 - 17.78 (Mampearachchi*et al.*, 2012)
Where:
Tpav= High pavement temperature at 20 mm which is lower than atmospheric temperature (Celsius)
Tair= air temperature (high)

Lat=Latitude of the section, degrees

Table 3 AASHTO Specification for minimum values of complex modulus (Fini, 2016)

Material	Value	Specification	HMA Distress Concern
Un aged binder	$G*/sin\delta$	≥ 1.0 KPa	Prone to Rutting
RTFO aged	$G*/sin\delta$	≥ 2.2 KPa	Prone to Rutting
PAV aged	$G*.sin\delta$	≤ 5000 KPa	Prone to Fatigue

2.5 Asphalt Binder Aging

Aging is about the changing chemistry of asphalt binder which occur as a result of exposure to heat, air or UV etc. The process of aging occur either in the storage chamber where the temperature is much higher or in the mixing chamber where asphalt binder is open to heat and air or indeed during the service phase on a road where it is in direct contact with air and UV radiations for longer period of time. Main impact of these factors is the oxidative reactions occurring to these complex asphalt binder molecules. The key changes occurring in asphalt binder is the shifting in SARA analysis, the most noticeable of which is the rise in asphaltenes, considerable reduction in resins and aromatics level and some rise in the saturates. Most important factor affecting the service life and causing the failure of bituminous pavement is the phenomena of aging(Gawel*et al.*, 2016).

Asphalt aging affects the pavement flexibility negatively after many years of service life in field(Fernández-Gómez*et al.*, 2013). The process of aging is greatly dependent on the chemical composition of bituminous mixture(Tauste, 2018).

Siddiqui and Ali, 1999 from their experimental studies stated that aging of the asphalt binder decreases the ductility and penetration values of binder while increases the softening point ignition temperature, which ultimately increases the binders viscosity making it more stiffer(Siddiqui and Ali, 1999).

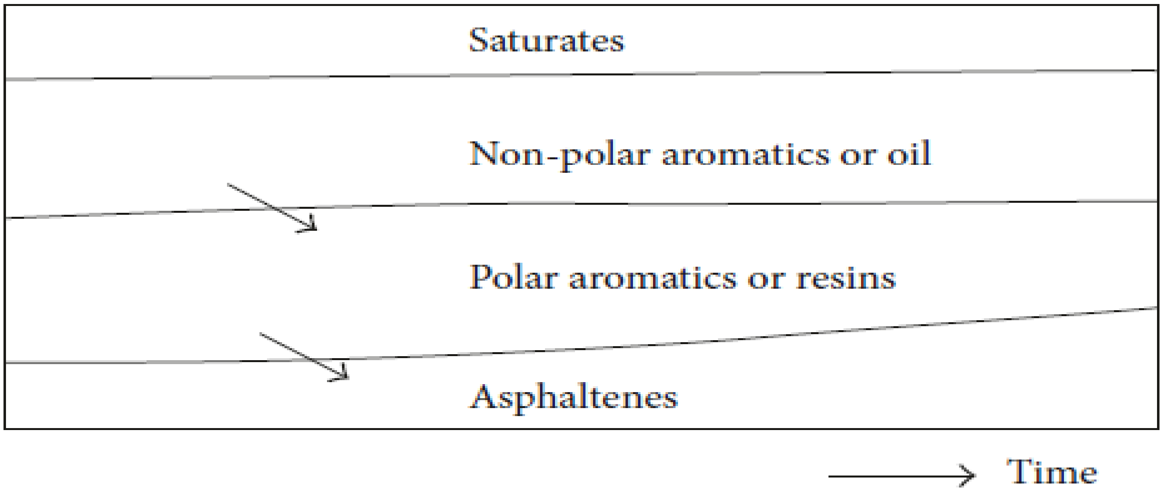


Figure 2 Effect of aging on chemical composition of asphalt binder

(Sirin, Paul, and Kassem, 2018)

Chemical composition of asphalt binder affected by aging is shown in the figure. Researchers indicate that the ratio of asphaltenes/maltenes changes due to aging which causes the increase in viscosity and make asphalt binder more hard and brittle (Lesueur, 2009).

Siddiqui and Ali, 1999studied the aging behavior of Arabian asphalt and found that the percent weight of oxygen and sulphur as carbonyl and sulfoxide groups respectively increased in asphaltenes after the aging phenomena. (Siddiqui and Ali, 1999)

Hence the steps in the process of oxidation effect in asphalt binder structure can be grouped as dehydrogenation, formation of sulfoxide from oxidation of alkyl sulfurs, formation of ketones from oxidation of benzyl carbons and formation of carboxylic acids from oxidation of the latter with the subsequent dicarboxylic anhydrides(Tauste, 2018)(Tauste, 2018)(Tauste, 2018)(Tauste, 2018)(Petersen, 2009).

Different factors affecting the aging process of asphalt binder includes type of binder, mixture compaction and its impact on proportion of voids, binder content, chemical composition of the material, origin of asphalt binder, environmental condition, polarity of molecules and exposure to UV radiations(Tauste, 2018).

Gawel et al considered the asphaltenes ratio as a parameter to understand the aging behavior of asphalt pavements in India. (Gawel *et al.,* 2016)

2.5.1 Short Term Aging

This phenomena take place when the asphalt binder material is mixed, transported, stored and compacted in the field(Tauste, 2018). Short term aging comprises almost 70% of total aging (Çalışıcı*et al.,* 2018). Rolling Thin Film Oven (RTFO) is used to stimulate it in laboratory conditions. Short-term aging temperature and added chemical type affect the recovery behavior of asphalt binder (Ragni*et al.,* 2018). Aging occurring within 2 to 3 years after the application of asphalt mixture in field also fall in the short term aging category.

2.5.2 Long Term Aging

Long term aging occur throughout the service life of asphalt pavement due to exposure to sun and UV radiations(Tauste, 2018). Long term aging is a reversible process in which chemical composition of asphalt are changed while rheological properties remain unchanged (Santagata*et al.,* 2014).

Pressure Aging Vessel (PAV) is used in laboratories to simulate the effect of long term aging. The asphalt binder is exposed to increased temperature and high pressure for 20 hours.

Wang *et al.* 2019 analyzed the aging behavior of samples taken from different bituminous pavement structures. GPS, FTIR, DSR and fluorescence microscope (FM) were used as analytical tools to characterize the aging mechanism of different samples. It was found that degree of aging in the upper most layer of the pavement are more prominent, weak in the medium layer and weakest in the bottom layers. That's why proper treatment of the pavement structures should be done considering the different impact of aging on different layers*(Wang et al.,* 2019).

Effect of aging on asphalt binder can be studied by using following techniques i.e. Dynamic Shear Rheometer (DSR), Brookfield or rotational viscosity test, Softening Point Test, High pressure gel permeation chromatography (HP-GPC), Thin Layer Chromatography with Flame Ionization Detection (TLC_FID), Scanning Electron Microscopy (SEM), Fourier Transformed Infrared Spectroscopy (FTIR), Atomic Force Microscopy (AFM) and Penetration Test (Tauste, 2018)

2.6 Viscoelastic Behavior of Asphalt

Dynamic mechanical analysis (DMA) is usually conducted to investigate the rheology of asphalt binders. Asphalt binders exhibit a visco-elastic behavior which means, elastic at low temperature and viscous at high temperature. Similarly, loading time and aging conditions also affects their response. Their visco-elastic behavior ultimately directs the field performance of asphalt mixture. Visco-elastic behavior of asphalt binder is studied by Dynamic Shear Rheometer (DSR) by measuring the phase angle (δ) and complex shear modulus (G*) at required loading frequency and temperature. From this data, the visco-elastic response of asphalt binder is predicted(Kumbargeri & Biligiri, 2016). Complex shear module express the material's total resistant against deformation subjected to recurring shearing stress. Loss modulus (G") and storage (G') are two main components complex shear module. First one is the elastic component while the second one is the viscous component. Vector representation of G* is shown in Fig. 3. Component along the vertical axis is 'viscous' while elastic component is shown along the horizontal axis. G* is the resultant vector, actually. The angle made by G* with the horizontal axis is termed as 'Phase Angle (δ)' and it gives a measure of the amount of temporary and permanent deformation. In Fig 20 complex shear moduli of two visco-elastic materials are shown(Sun, Huang, Chen, Jia, & Ding, 2016). First one has higher shear strength but is less elastic as it has a higher phase angle value. Although material two has low shear strength but is more elastic than material one.

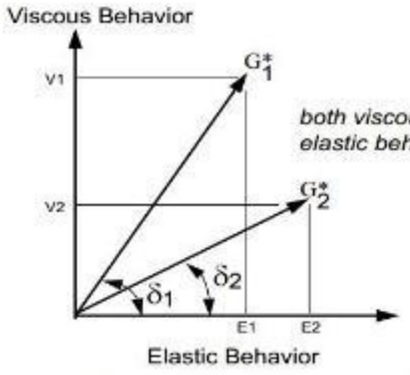


Figure 3 Viscoelastic Behavior of Asphalt binder in terms of G* and δ

(North Carolina Department of Transportation, 2016)

2.7 Asphalt Binder Modification

Polymer modification is the polymer integration in asphalt binder either by chemical action or mechanical means. (Ragni *et al.,* 2018). Various amendment to asphalt are being explored owing to increasing demand for higher performance(Selvavathi et al., 2002).

Porto *et al.*conducted a thorough literature review of the latest research papers regarding the asphalt binder chemistry and its modification. They concluded that, in the modification of asphalt, chemical composition of base asphalt binder is an important factor. Many modifiers improve the performance characteristics of asphalt binder to some extent but they can also cause some compatibility issues in the production and storage. In this regard the importance of waxes to solve the compatibility problems of polymers in asphalt binder was admitted(Porto *et al.,* 2019).

Since 1970s, several number of research articles have been published on the subject of polymer modification of asphalt binder. Effects of several polymers such as styrene ethylene/ butylene-styrene, styrene-isoprene-styrene, thermoplastic elastomers, ethylene-butyl acrylate, polyethylene, ethylene-vinyl acetate and plastomers are studied in these articles(Zhu, Birgisson, & Kringos, 2014). The results showed considerable improvement in the asphalt binder performance characteristics like better rutting resistance, high stiffness at high temperatures, improved low temperature cracking, moisture resistance and improved fatigue life (Alataş & Yilmaz, 2013).

Ragni et al. studied the short term aging performance of polymer modified asphalt binder for warm mix asphalt under the effect of varying chemical additives and temperature and find out that short term aging effect on binders performance is reduced by chemical additives. They also found that the type of chemical additive and the aging temperature considerably affect the recovery behavior of asphalt binder(Ragni *et al.,* 2018).

Chemical and physical properties of straight run asphalt binder affected by phosphorous compounds were studied by using RTFO and concluded that the aging resistance of the binder was greatly improved (De Filippis*et al.,* 1995).

Modification of asphalt binder can be done by adding different percentages of elastomers up to 7%. Soft modifications contain a polymer content of up to 3% while medium modifications have polymer content of about 4.2%. Hard modifications have polymer content higher than 5%(Porto *et al.,* 2019).

Gawel *et al.* 2016 tested naturally obtained oleic imidazoline as anti-oxidant to asphalt binder. Asphalt binder was analyzed before and after RTFO aging. Amount of oxygen uptake was set as criteria to determine the effects of aging on the neat and modified binder. Imidazoline reduced the oxygen uptake of asphalt binder after aging. It improved the colloidal stability of asphalt binder and acted as dispersing agent and anti-oxidant. Hence imidazoline can be used as an ageing inhibitor to asphalt binder which is environmental friendly as well (Gawel *et al.,* 2016).

Chen *et al.* 2016 used organic expanded vermiculite (OVEMT) and inorganic nanoparticles as asphalt binder modifier to examine the asphalt binder's rheological properties. RTFO, PAV and UV aging was done to the samples. XRD was used to examine the microstructure of modifiers. DSR results revealed good improvement with regard to complex module and phase angle which indicates good thermal and UV resistance of the modifiers.(Chen, Zhang, Zhu, and Zhao, 2015)
Li et al. studied the effects of adding polymer (elastomer, plastomer), oil and polymer plus oil into the base asphalt binder to assess its aging susceptibility. Different levels of aging were achieved using PAV and RTFO. Rheological properties of binder were measured with DSR and BBR, and chemical properties were determined using FTIR and GPC. It was observed that the aging susceptibility of asphalt binder was reduced by polymer modificationwhile aging resistance was enhanced by the modification with hybrid (elastomer + plastomer). Aging properties of the binder were not significantly improved by oil modification alone. Therefore it might be concluded that the aging behavior of asphalt depends upon the type and complexity of modification as well as interaction between the two modifiers (oil and polymer) (Y. Li*et al.,* 2016).

Rek *et al.*2005 used two asphalt binder from different sources and SBS as modifier to estimate the aging properties of polymer modified binder. Short term aging effects on the binder was stimulated by using RTFO. After aging, chemical and rheological changes in asphalt binder structure were analyzed by using FTIR, dynamic shear rheometer (DSR) and rotational viscometer (RV) tests. Viscosity of asphalt binder from both sources increased after the addition of SBS and after aging. Moreover it was also concluded that source/origin of asphalt binder also influence the effect of modifier on aging properties of asphalt binder. However for the assessment of aging behavior of PMB, both chemical and rheological methods are required(Rek*et al.,* 2005).

2.7.1 Polyethylene Modified Binder

Kumar and Satyanarayana, compared the effect of adding polyethylene (PE) and styrene-butadiene-styrene (SBS) into base asphalt binder. Engineering properties of the modified asphalt binder were determined using conventional testing. It was found that both modifiers PE and SBS improve the engineering properties of base binder while SBS modified binder shows more promising results than PE modified asphalt binder(U. A. Kumar and Satyanarayana, 2015).

Napiah *et al.* 2014 determined the creep behavior of a neat 80/100 Pen asphalt binder concrete mixture and a linear low density polyethylene (LLDPE) modified bituminous concrete. To study the deformation behavior of the asphaltic concrete samples, dynamic creep test was used. 3% of LLDPE observed to be the optimum content at which the mix gave better results as compared to 1% and 2% of LLDPE. 3% LLDPE improved the mixture stiffness at 40°C as well as the rut depth was also improved measured by wheel tracking test(Napiah*et al.,* 2014).

To tackle the problem of phase separation and storage stability, Padhan and Sreeram incorporated some cross-linking additives and specific reactive polymers into the PE modified asphalt binder. Conventional tests, storage stability test and super pave performance tests were performed. Results indicate better improvement in the stability and phase separation issues. Fluorescence microscope showed better dispersion of the modifier resulting in better overall performance of the modified binder.(Padhan and Sreeram, 2018)

Diab *et al.*2019 carried out a series of tests to explore the aging effect on the engineering properties of polymer modified asphalt binder. Added polymers include SBS, polycarbonate (PC), polypropylene (PP), high density polyethylene (HDPE) and styrene-acrylonitrile (SAN). Findings of this study revealed that the aging resulted in more carbon component in all modified samples while the increase in sulphur, nitrogen and hydrogen was not obvious for any polymer modification. Overall properties of asphalt binder were improved by polymer modification(Diab*et al.,* 2019).

Brożynaa Kowalski studied the effect of polyethylene type polymers on asphalt modification. Linear low density polyethylene (LLDPE), low density polyethylene (LDPE), high density polyethylene (HDPE), copolymer EBA and terpolymer EBM were used as modifiers. Asphalt binder properties before and after RTFO were determined and more softening point and less penetration value was observed. No improvement in elastic recovery was observed except for terpolymer EBM(Brożynaa and Kowalski, 2016).

Ghuzlan suggested 3% polyethylene content to be the optimum content. Polyethylene content of 5% or more was regarded as not applicable because the polyethylene modified binder became unworkable at these percentages due to the high values of rotational viscosity(Ghuzlan, 2015).

Punith and Amirthalingam, 2007 added different percentages of polethylene (PE) to an 80/100 paving grade asphalt. Hamburg wheel track test, indirect tensile test, dynamic creep test, resilient modulus test were performed on the PE modified concrete mixture. The analysis showed that the PE modified blends gave better performance results than the conventional asphalt mixtures. Temperature susceptibility and rutting resistance was improved. The authors suggested a PE content of 5% to be used for better performance of asphalt mixtures(S. Punith and Amirthalingam, 2007)

2.7.2 Sulphur Modified Binder

Use of sulfur in modification of asphalt has been in practice since 1970s. Sulphur was used as an extender as it replaces the asphalt binder, such asphalts were called sulphur extended asphalt (SEA). Sulfur extended asphalt was discouraged due to the higher cost of sulphur and health and environment concerns. But later with the advancement in technology, the use of pelletized sulphur became popular due to less handling and storage issues and also due to huge production of sulphur made it more economical to use it as a modifier(Saboo, 2014).

Storage stability of tire rubber modified asphalt binder affected by sulphur was studied by Ghaly. Tire rubber (TR) proved to enhance the performance characteristics of asphalt but there are some compatibility issues and storage stability issues that limit the use of TR. To overcome this deficiency, SBS and sulfur were used to enhance the storage stability of TR modified asphalt binder. 60/70 pen grade asphalt binder was modified with various proportions of TR, SBS and S. Physical tests, Marshall stability test, wheel tracking test and flow test were performed to measure the change in physical and performance characteristics. Results suggested that the penetration temperature susceptibility (PTS) of modified asphalt binder was largely decreased. Storage stability improved to higher extent and the Marshall stability and plastic deformation resistance was enhanced with the addition of sulfur.(Ghaly, 2008)

Rezvani studied the preparation method and characteristics of sulfur extended asphalt (SEA). Direct addition of sulfur into the asphalt mixing plant was opted due to its advantage of less emission. Sulfur in different percentages from 0 to 45% was added to a 60/70 grade asphalt binder. Physical properties prior to and subsequent to RTFO were studied. It was found that the adding up sulfur reduced the binder's viscosity, increased the penetration and improved the ductility to greater extent. Lower viscosity will lead to decreased mixing and compaction temperature making it more economical and energy efficient. Increase in penetration was more obvious for S content of up to 5% by weight of asphalt binder (Rezvani, 2015).

Reddy and Pavani cconducted a series of experiments to find the proper mixing temperature, time and content of sulfur that will result in the best modification of VG30 asphalt and studied the rheological characteristics of sulfur modified asphalt through DSR. Results indicate the mixing of 2% sulfur by weight of asphalt binder at 140°C mixed for 30 minutes results in the best homogenous modification of VG30 binder. Rheological and physical properties of 2% S modified asphalt binder were improved prior to and subsequent to RTFO (Reddy and Pavani, 2017).

Prolongo et al. investigated the thermal behavior of sulphur modified asphalt by adding 0-35% of S at 130 and 140°C temperature, by means of differential scanning calorimetry (DSC). Moreover, high temperature emissions were also estimated through loss in weight measurements(Prolongo, Paez, & Ayala, n.d.).

Due to increased number of petroleum and oil refineries in the Gulf region the production of huge amount of sulfur has become a challenging issue. To discover new technologies for the use of sulphur in asphalt pavements has become a challenge for many civil engineers. In this regard, Al mehthel et al. carried out a collaborative study to investigate the feasibility of sulfur as a potential substitute in road construction. The research provided different aspects of using sulphur in asphalt pavements as well as field trials and a four years monitoring program that dealt with the different distresses of pavement. The research indicated that the performance of optimum replacement of 30% S resulted in the superior viscoelastic properties of pavement than the conventional asphalt pavement in terms of rutting. Fume emissions of sulphur at mixing temperature below 145 were well below the permissible limits(Al-mehthel*et al.,* 2010).

Das and Panda investigated the rheological characteristics of sulfur modified asphalt binder (SMB) and found the optimum content of sulfur. SHRP rutting and fatigue criteria, master curves and multiple stress creep recovery test were used to study high and low temperature properties of SMB. Aging index of 2% SMB increased which indicate decrease in aging susceptibility of asphalt binder. Hence 2% SMB resulted in superior performance characteristics in terms of rutting, fatigue, storage stability and aging resistance(Das and Panda, 2017).

Elkholy et al. conducted laboratory study on the sulphur modified samples in proportion of 40/60 S/A , 30/70 S/A and20/80 S/A mixtures. Conventional and rheological test were performed using ring and ball apparatus, penetrometer, rotational viscometer and dynamic mechanical analyzer (DMA). Physical test showed that penetration of modified binder was decreased while softening point was increased by adding 20-40% sulphur. Increase in penetration index from -0.7 to 0.9 of 40/60 sulfur asphalt mixture was also recorded which show better rutting at high pavement temperatures and better resistance against thermal cracking at low temperature. The performance grade of the modified samples using DMA was also increased from 52C for base asphalt to 58C for 20/80 S/A, 64C for 30/70 S/A and 70C for 40/60 S/A mixture(Elkholy *et al.,* 2018).

By addition of 2% sulfur at 160C, he obtained a more gel like structure due to the chemical bonding of sulfur with asphalt binder. Plastification of the material decreased the dynamic mechanical properties of the modified binder(Fritschy, Papirer, & Chambu, 1981).

P. Kumar and Khandetermined the optimum percentage of sulfur and evaluated the physical properties of sulfur and found its resistance to aging. 3% S was found to be the optimum percentage based on the physical test results. Addition of sulphur increased softening point and decrease penetration of binder. The aging results of the modified binder were within the permissible limits.(P. Kumar and Khan, 2013)

High temperature viscosity of the asphalt binder is generally decreased by the addition of sulphur which makes it more workable at high temperatures and improves its resistance to deformation at low temperatures. A sulphur content of 4-6% is required for its application in road construction. (Ehinola*et al.,* 2012)

Gedik andLav investigated asphalt binder of 50/70 grade asphalt binder by varying proportion of sulphur (S) up to 50%. Samples were aged using RTFO and PAV. Morphological, Analytical and rheological behavior of aged and unaged samples was tested and results indicated that all the sulphur extended asphalts (SEBs) possessed lower viscosity grade irrespective of the amount of granular sulphur and temperature which indicate high resistance against cracking. Compaction and mixing temperature reduction was also observed which make it more energy efficient. Rheological aging index was greater than 1 for all the SEBs except for 30% S which depicts the hardening effect of sulphur modified binder after RTFO and PAV aging. Morphology results indicate good compatibility of GS with the asphalt binder.(Gedik and Lav, 2 016)

Sulphur addition below 10% made 60/90 paving asphalt binder more plastic and higher percentages of S made the asphalt binder more stiff as compared to neat asphalt binder. SEBs possessed better mechanical properties and durability as compared to original asphalt binder(Syroezhko*et al.*, 2003).

2.8 Literature related to FTIR and SEM

Weigel & Stephan predicted the properties of asphalt binder with the help of Fourier transformed infrared spectroscopy (FTIR). 32 samples of different refineries and different viscosities and aging conditions were used to evaluate the physical and chemical properties based on FTIR results. It was concluded that the FTIR help in differentiating the source of binder. It also help in describing the chemical parameters. Rheological and conventional parameters including softening point, content of asphaltenes, log of penetration and log of phase angle and complex shear modulus at different aging levels.(Weigel & Stephan, 2017)

Reena & Verinder used FTIR and SEM to characterize the asphalt binder modified with e-plastic waste. FTIR spectra of modified binder showed the appearance of some new peaks while some peaks disappeared which were much stronger in the base binder’s spectra. This indicated the structural changes which occurred due to the addition of e-plastic. These changes add in the high performance of the e-PMB. SEM results showed the improved physical and engineering properties of the plastic waste modified binder as the results showed good homogeneity of the modifier in binder.(Reena & Verinder, 2012)

Fourier Transformed Infrared (FTIR) spectroscopy and high pressure gel permeation chromatography (HP-GPC) were used to evaluate the aging properties of zinc dialkyldithiophosphate modified asphalt by Ouyang et al. An increase in carbonyl group and molecular weight of asphalt was observed as a result of oxidative aging of base binder while the ZDDP modified binder after aging showed no change in molecular weight and restricted the formation of carbonyl group which indicate that ZDDP is a good modifier to improve the aging properties of asphalt binder(Ouyang*et al.*, 2006a).

Improvements in aging properties of asphalt binder were studied by using SBS and highly reclaimed (HRR). Physical characters, aging behavior of SBS modified asphalt (SBSMA), type and content of HRR were investigated. FTIR was used to determine major functional group of SBSMA before and after UV and thermal aging. Content of HRR affected the aging of SBSMA. It was found that HRR improved the physical properties and short term aging resistance of SBS modified asphalt. Morphological analysis done by SEM showed good compatibility between SBS and HRR(Rasool*et al.,* 2017).

Ouyang*et al.* 2006 bused oil, zinc dibutyldithiocarbamate (ZDBC) and zinc dialkyldithiophosphate (ZDDP) to improve the aging resistance of base and SBS tri-block copolymer modified asphalt (PMA). FTIR was used to characterize the oxidation rates of asphalt binder. IR spectra showed a raise in carbonyl group in case of PMA after aging while the addition of antioxidants ZDDO or ZDBC in the PMA reduced the formation of carbonyls which indicate good aging resistance of the additives(Ouyang*et al.*, 2006b)

Lu *et al.*2008 compared the rheological and physical properties of laboratory aged and field aged samples of asphalt binder using DSR and FTIR. Laboratory aged samples produced a high amount of carbonyl group and low amount of sulfoxides while the formation of sulfoxides was much higher for the field aged asphalt binder samples. This might be owing to the fact that higher temperatures in laboratory aging produces higher level of carbonyls while longer duration in field generates sulfoxides. Such differences in the properties of aged binder suggest that the aging mechanism of the asphalt binder in the field might not be as same as done in the laboratory aging tests(Lu*et al.*, 2008).

Improvement in short term aging resistance by using newly synthesized diethylene glycol based polyboron compound (DEGPB) was studies by Mustafa *et al.* 2018 Oxidation rates of the modified binder were examined through FTIR. DEGPB improved the physical characteristicsin addition to short term aging resistance of the asphalt. Marshal stability of the bituminous mix was also improved(Çalışıcı *et al.*, 2018).

2.9 Summary

This chapter includes a brief introduction about the history of the pavements and different distresses associated with them which are more common in Pakistan. A brief history of asphalt binder, its chemical and elemental composition is discussed. Mechanism of aging and different methods for simulating aging effect in the laboratory has been discussed. SHRP Super pave criteria for different distresses i.e. rutting, fatigue is mentioned. And finally the methods for improving the aging properties of asphalt binder by its modification with polymers and other chemical additives has been discussed in the light of recent researches carried out on the same topic.

CHAPTER 3

METHODOLOGY

3.1 Introduction

Methodology adopted to perform different tests to achieve the required research objectives are discussed in this chapter. Sulphur (S) and polyethylene (PE) has been used to modify the asphalt and their effect on physical, rheological and aging characters of asphalt binder are studied. Different test procedures were adopted to check the behavior of virgin asphalt binder and modified asphalt binder under similar conditions.

3.2 Materials

The objective of this research is to improve the binder aging properties with other material so for this purpose selection of modified alternative binder material is very crucial step. Material are selected as per the availability and cost efficiency of the material. Following mixture of material were used for preparation of samples for different experimentation.

- 60/70 Asphalt binder
- Polyethylene (PE)
- Sulphur (S)

3.2.1 Asphalt binder

60/70 pen grade asphalt binder supplied by PARCO sales office Rawalpindi was used as a base binder. Table 4 shows the basic properties of base binder. The purpose of selecting grade 60/70 is that it is typically used in Pakistan and is appropriate for colder to Intermediate temperature regions. According to the standards and specifications all the necessary tests were performed on acquired bitumen.

Table 4 Physical properties of base binder

Properties	Value	Standard
Penetration Value (0.1mm)	64	ASTM D5
Softening Point (°C)	49	ASTM D36
Ductility mm (25°C)	>100	ASTM D113

3.2.2 Modifiers

Polyethylene and sulphur were purchased from a local vendor in Rawalpindi. Polyethylene used in this research is in liquid form while sulphur is used in powder form. Material are selected as per the availability and cost efficiency of the material. Physical properties of polyethylene (PE) are mentioned in table 5.

Table 5 Physical properties of polyethylene

Properties	Result
Chemical Formula	$(C_2H_4)_n$
Melting Point	115-135 °C
Density	0.88–0.96 g/cm^3

Sulphur can be found in be found in both free and combined states. Sulphur is a nonmetal with symbol S and atomic number 16. Sulphur is obtained from natural gas and petroleum. Use of sulfur in modification of asphalt has been in practice since 1970s. Sulphur was used as an extender as it replaces the asphalt binder, such asphalts were called sulphur extended asphalt (SEA). Sulfur extended asphalt was discouraged due to the higher cost of sulphur and health and environment concerns. But later with the advancement in technology, the use of pelletized sulphur became popular due to less handling and storage issues and also due to huge production of sulphur made it more economical to use it as a modifier(Saboo, 2014).

Table 6 Physical properties of sulphur

Properties	Result
Appearance	Yellow Crystalline Solid
Specific Gravity	1.92
Melting Point	120°C

3.3 Modification of Asphalt

Manual mixing method were adopted in which asphalt binder were heated at 140°C and were stirred continuously for over 30 minutes. The stirring were done with glass rod gently so that P.E and S can be completely dissolved in asphalt binder.

3.4 Aging

3.4.1 Short Term Aging

After short term aging of asphalt binder, evaluation of its rheological properties is very important to assess quality of asphalt binder. Mixing, spreading, storage and compaction of asphalt binder cause its short term aging. In laboratory, the effect of short term aging was stimulated by RTFO. Asphalt in RTFO is aged by heating and blowing of hot air at 163ºC for 80 minutes. Short term aging is loss of volatile in an asphalt binder when it is heated at asphalt plant and subsequently laid at site. This procedure is described by ASTM D2872.

Apparatus include the following

- Glass bottles
- Balance
- Back for bottles.
- Oven equipped with carousal which exhibit circular motion and a nozzle for hot air.

Figure 4 RTFO

Figure 5 Rolling Thin Film Oven (RTFO)

3.4.2. Long Term Aging

Exposure to heat and UV radiation during its life span cause long term aging of asphalt pavement. In laboratory, Pressure Aging Vessel (PAV) was used to simulate the effect of long term aging. To simulate the effect of in-service aging of asphalt binder, the binder was exposed to high temperature and pressure for 20 hours. This procedure is described by ASTM D6521.

Apparatus includes the following.

- Sample Pan/trays
- PAV
- Vacuum oven

Figure 6 Pressure Aging Vessel

Figure 7 PAV Samples

3.5. Material Testing

Physical and Performance testing were performed on virgin aged and un-aged and modified aged and unaged asphalt binder. Modified asphalt binder was obtained through extensive physical testing by determining an optimum content of Polyethylene and Sulphur. Physical and performance test results, which includes low temperature cracking, rutting resistance and Fatigue resistance of virgin and modified asphalt binder were compared.

3.5.1. Physical Testing

3.5.1.1.Penetration

To measure the consistency of asphalt binder at room temperature, penetration test is used. In this test, a standard loaded needle is vertically penetrated in the sample of asphalt binder under standard condition and its penetration depth is measure up to tenths of a millimeter. Softer binder gives greater values of penetration. According to AASHTO T49-03 temperature used was 25°C, load of 100 grams, while time for the test equal 5 seconds, until unless the situations are not explicitly stated. Using PARCO 60/70 specimen, three values from each specimen were taken after performing penetration tests. All values obtained fulfilled the required criteria of penetration test as per specification.

Following are the apparatus that is use in penetration test.

- Penetrometer
- Digital timer
- Water bath
- Penetration cup

Figure 8 Penetrometer

Figure 9 Samples for Penetration

3.5.1.2. Softening Point

It is the mean temperature at which the asphalt binder in the rings becomes soft and fall to a distance measuring 25mm because of the mass of a steel ball lying upon asphalt binder. Test was performed according to ASTM D36.

3.5.1.2.1. Procedure

- The asphalt binder sample was heated until it becomes sufficiently fluid.
- The sample is then poured into the rings as shown in Fig 11.
- Samples were allowed to cool at room temperature for 30 minutes and the access asphalt binder was cut away.
- The apparatus was assembled and filled the glass vessel with water up to 105mm depth. The balls were placed on brass rings and heat the vessel at uniform rate of 5 ^{o}C/min as shown in Fig 10.
- The temperature for each ball at which the asphalt binder surrounding the ball touch the bottom plate was noted down and that temperature is the softening point of the asphalt binder.

Figure 10 Ring and Ball Apparatus

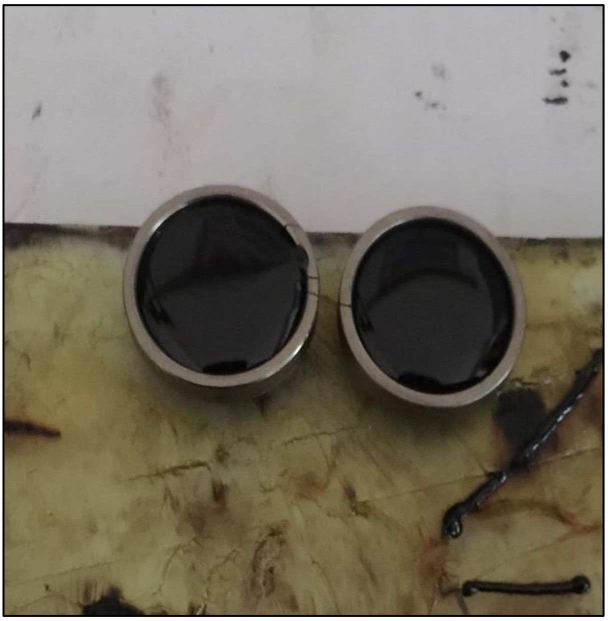


Figure 11 Samples for Softening Point

3.5.1.3.Penetration index

Penetration index is the quantitative measure of the asphalt binder response to the variation in temperature as described by Pfeiffer and Van Doormaal (Ehinola et al., 2012). By means of PI the behavior of asphalt binder in an application can be predicted. Moreover the type of binder can be described based on the deviation of its behavior from Newtonian to non-Newtonian. The value of PI ranges from about -3 for highly temperature susceptible asphalt binder to around +7 for low temperature susceptible asphalt binder and highly blown asphalt binder. Generally for road construction, asphalt binder have PI between -2 to +2. Asphalt binder having PI values smaller than-2 shows Newtonian behavior with brittleness at lower value and those greater than +2 are less brittle, exhibiting high elastic properties under higher strains.

From Penetration value and SP, variation in the thermal sensitivity of asphalt binder can be calculated by using Penetration Index. Penetration Index (PI) can be calculated using following equation.(Ehinola et al., 2012)

$$PI = \frac{1952 - 500 \log pen - 20 \text{ softening point}}{50 \log pen - \text{softening point} - 120}$$

Where:

Pen= penetration at 25°C

Table 7 Penetration index for different types of asphalt binder

Asphalt binder Type	PI
Blown asphalt binder	>2
Conventional paving asphalt binder	-2 to +2
Temperature susceptible asphalt binder (Tars)	<-2

It is generally known that a high value of PI indicate lower temperature susceptibility. The binder is considered high susceptible to temperature if it has Penetration Index value smaller than -2. The binder will behave more brittle at lower ranges of temperature and it will undergo transverse cracking in colder regions.

3.5.1.4. Ductility

Ductility depicts material's ability to withstand tensile stresses. The ductility of a bituminous material is measured by the distance in "cm" to which it will elongate before breaking when a standard briquette specimen of the material is pulled apart at a specified speed and a specified temperature. Test was performed according to ASTM D113-17.

3.5.1.4.1. Procedure

- To perform the test first molds were assembled on a brass plate and filled with bituminous sample (Fig 13).
- Then the samples were kept at room temperature for 30-40 minutes.

- The samples were then placed in water bath for 30 minutes and cut off extra asphalt binder.
- Side briquettes were removed and the samples were placed in duclilometer by clamping the samples on both sides.
- The samples were pulled at speed of 5cm/min until sample ruptures while keeping the temperature constant at 25°C.
- Distance at which the asphalt binder sample break was measured in centimeters.
- That distance represents the ductility value of the asphalt binder sample.

Figure 12 Ductilometer

Figure 13 Ductility test sample

3.5.1.5 Aging Index:

To evaluate the temperature sensitivity of the bituminous binder, different physical/rheological aging indices are used. Aging index is defined as the ratio of physical/rheological property of aged asphalt binder to that property of unaged asphalt binder. Physical aging index used in this research are penetration aging ratio (PAR), softening point increment (SPI) and ductility retained ratio (DRR). These index are calculated by formulas given below:

$$\text{Penetration Aging Ration (PAR)} = \frac{\text{Aged Penetration Value}}{\text{Unaged Penetration Value}} \times 100$$

$$\text{Softening Point Increment (SPI)} \ = \frac{\text{Aged Softening Point}}{\text{Unaged Softening Point}} \times 100$$

$$\text{Ductility Retained Ration (DRR)} = \frac{\text{Aged Ductility Value}}{\text{Unaged Ductility Value}} \times 100$$

3.5.2. Rheological Analysis

3.5.2.1. Dynamic Shear Rheometer

Asphalt binder is a viscoelastic material which means it acts as elastic and viscous material at the same time. DSR is an instrument that is used to measure the viscoelastic behavior of asphalt binder. Dynamic shear rheometer measures the asphalt binder properties at different service temperatures, mostly from intermediate to high. The output of DSR test is in the form of the complex shear modulus (G*) and the phase angle of asphalt binder. DSR is also used to calculate the performance grade of asphalt binder. The DSR may be admitted as the most convincing and composite instrument for classification of the asphalt binder flow properties.

DSR used in this research to find the rheological properties of modified and unmodified asphalt binder was made of Anton Paar model 101(Fig 14). 25mm and 8mm DSR plate geometries were used for this study as shown in the Fig 15. Gap between two plates was kep1 1mm and 2mm for 25mm and 8mm sample respectively (Fig 15).

Figure 14 Dynamic Shear Rheometer

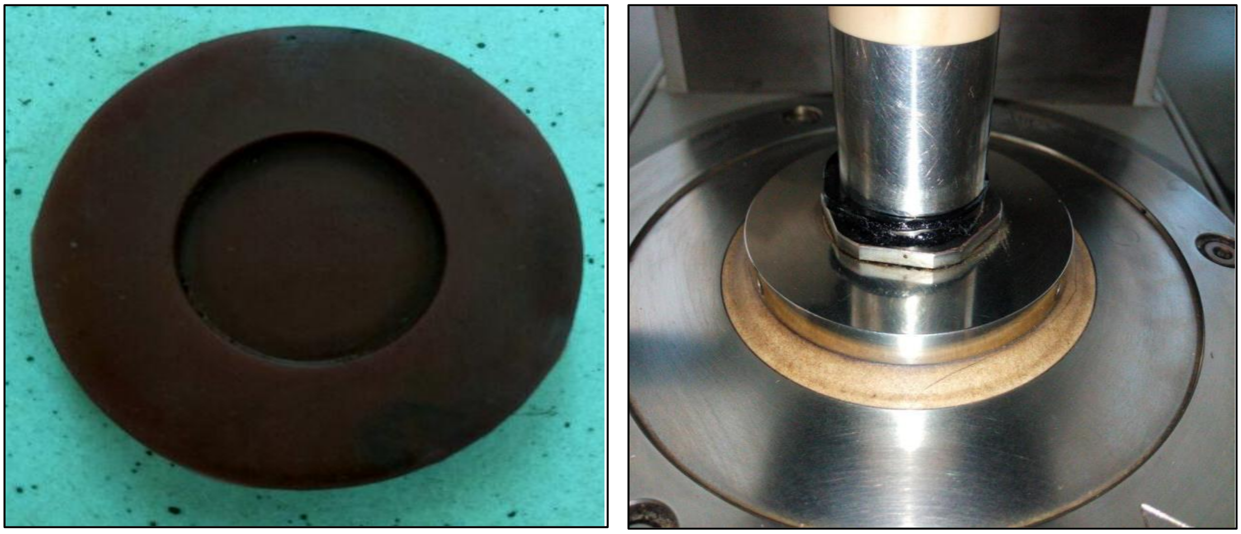


Figure 15 Sample preparation

3.5.3. Rheological Aging Indices

Aging susceptibility of asphalt binder can be evaluated by means of aging index. It is defined as the ratio of rheological property of aged asphalt binder to unaged asphalt binder. Rheological index which are used in this research are complex modulus aging index (CMAI) and phase angle aging index (PAAI) and they are calculated as given below:

$$\text{Phase angle aging index} = \frac{Aged\ Phase\ Angle}{Unaged\ Phase\ Angle}$$

$$\text{Complex modulus aging index} = \frac{Aged\ Complex\ Modulus}{Unaged\ Complex\ Modulus}$$

3.5.4. Fourier Transformed Infrared Spectroscopy

FTIR spectroscopy is a simple analytical technique used to study the structural modification of different samples and determining the influence of aging on modified asphalt binder. In infrared spectroscopy, IR radiations are passed through the sample. The wavelength ranges from 4000 cm^{-1} to 400cm^{-1}. Some of the infrared radiations are absorbed by the sample and some of it passed through (transmitted). The resulting spectrum represents the molecular absorption and transmission, creating a molecular finger print of the sample. This makes FTIR a good tool for chemical identification.

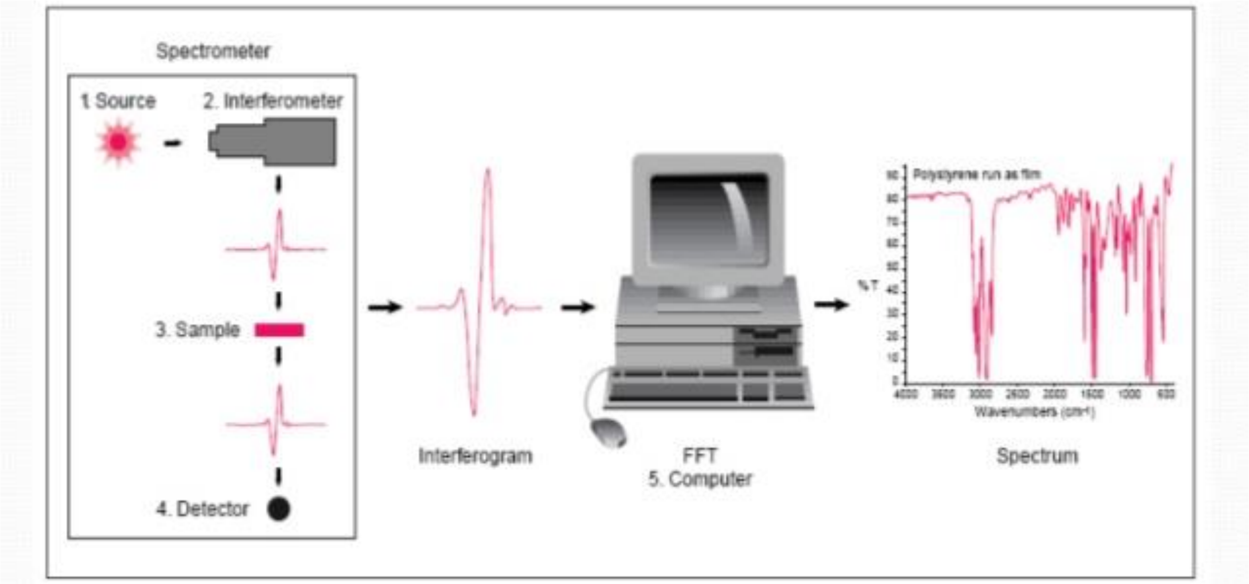


Figure 16 Fourier Transformed Infrared Spectroscopy Mechanism

Figure 17 Fourier Transformed Infrared Spectroscopy

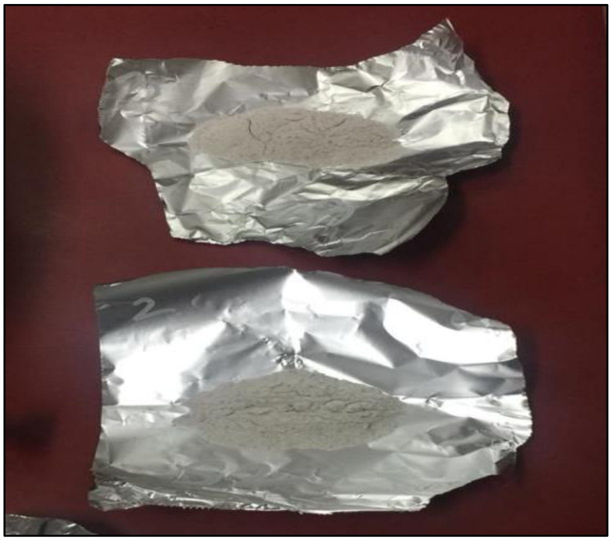


Figure 18 FTIR Samples

3.6. Morphological Analysis

Scanning Electron Microscope

“Morphology is a branch of science to study the intermolecular structural form of a material using advanced microscope instrument especially scanning electron microscope (SEM) for a very high zoom”. In Scanning Electron Microscopy (SEM) an electron beam is subjected on the sample with high intensity and then the image of the surface of sample is taken with the help of reflected beam of electrons. In this research this technique was used to observe the homogeneity of the modifiers in the asphalt binder after its modification.

Samples for the SEM were prepared by putting a drop of PE modified and S modified asphalt binder on glass slide and then spreading that asphalt binder uniformly on the surface of the slide in the form of thin layer to study the dispersion of the modifiers in asphalt binder as shown in the Fig 20.

After preparing the samples, scanning electron microscope (SEM) was used to check the dispersion of modifiers in asphalt binder. Asphalt binder is a petroleum compound and contain volatile components in it. When bituminous samples are subjected to focus electron beam the volatile components of asphalt binder evaporate which contaminate the chamber of Scanning Electron Microscopy. To overcome this problem the samples of the asphalt binder are first coated with a thin film of gold palladium. This process of placing thin film of gold palladium is called sputtering. After preparing the samples and sputtering of samples SEM images were taken at different magnifications. It analyzed that whether modifiers were uniformly dispersed in asphalt binder or not.

Figure 19 Scanning Electron Microscope

Figure 20 SEM Samples

3.7. Summary

This chapter focused on the adopted methodology for the research study. Selection of material used in this research and their basic properties are mentioned. Conventional testing is done on the neat and modified samples which includes penetration test, softening point test and ductility test. Testing is done on the samples before aging and after RTFO and PAV aging and the results before and after aging are compared. Optimum percentage of the modified samples is determined based on the conventional test results. Optimum samples were then tested for their rheological, chemical and morphological properties. SEM, FTIR and DSR are adopted to evaluate the changes in the properties of modified binders before and after aging.

CHAPTER 4

RESULTS AND DISCUSSION

4.1. Introduction

In this section all the results are presented in the form of tables and graph. Consistency analysis is done based on the results of penetration and softening point and penetration index (PI) is determined. Results before and after RTFO are compared to obtain the best possible blend of modifier and asphalt binder. Chemical and morphological analysis is done using FTIR and SEM. Functional groups are assigned to relative peaks from IR spectra. Morphological an

4.2. Normal Temperature Fluidity (Penetration)

Penetration results for neat asphalt binder and asphalt binder modified with Polyethylene and Sulphur are presented in table 8 and 9 respectively. Penetration value represents the stiffness and hardening of asphalt binder at normal temperature. Lower penetration value indicates that binder has become stiff. From table 8, it can be observed that with the increase in Polyethylene content from 1% to 5%, the penetration value of asphalt binder decreased which is an indicative of decrease in fluency and increase in the consistency of asphalt binder at normal temperature.

Table 8 Penetration result for P.E

	Penetration		
Additive rate %	**Unaged**	**RTFO aged**	**PAV aged**
0%	66	54	40
2%	54	43	35
3%	50	37	30
5%	42	31	22

Figure 21 represents the results of PAR for unmodified and PE modified binder after short and long term aging. It is evident that the penetration of unmodified and modified asphalt binder decreased after the two different aging. Moreover, higher the PE content lower the value of penetration aging ratio which leads to reducing the degree of aging of PE modified binder. Therefore polyethylene addition improves the binder's resistance to oxidative aging.

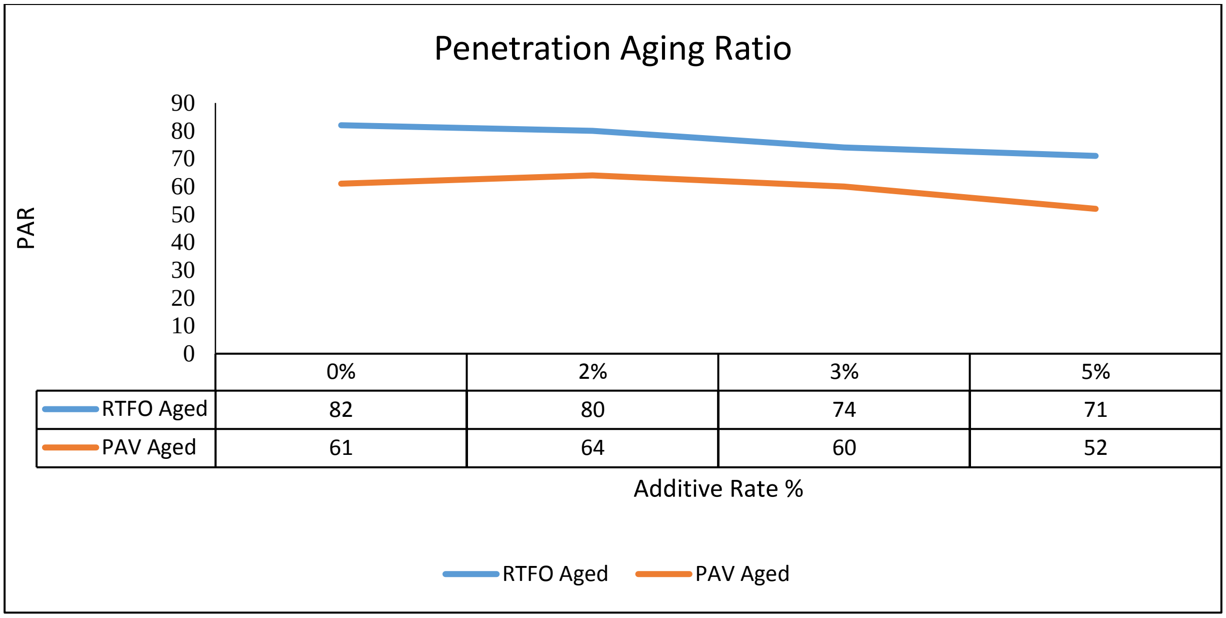


Figure 21 PAR graph for P.E modified asphalt binder

By addition of 2% to 5% sulphur into the base binder the penetration value increases significantly. It indicates that sulphur has a plasticizing effect on asphalt binder and it has more resistance against thermal cracking especially at low temperatures. This result is in correspondence with the findings of (Elkholy et al., 2018) for the sulphur modification. The results after the short term and long term aging are presented in the form of PAR in figure 22. The trend observed after aging is quite different from the unaged binder. Sulphur modified binder becomes stiff after the aging and the stiffness increases as the percentage of S increase.

Table 9 Penetration values for S modified asphalt binder

	Penetration		
Additive rate %	**Unaged**	**RTFO aged**	**PAV aged**
0%	66	54	40
2%	80	45	39
3%	88	40	35
5%	97	30	25

PAR of the sulphur modified binder as shown in figure 22 reduced significantly which indicates that the modified binder is more resistant to aging susceptibility than the virgin asphalt binder.

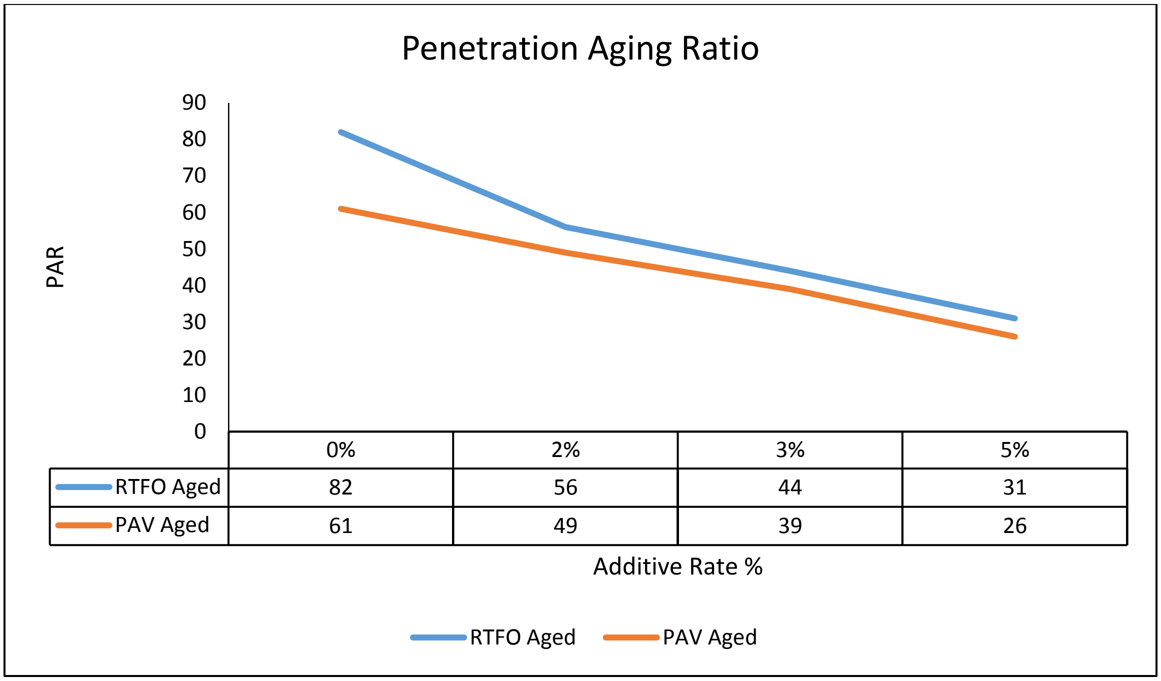


Figure 22 PAR for S modified asphalt binder

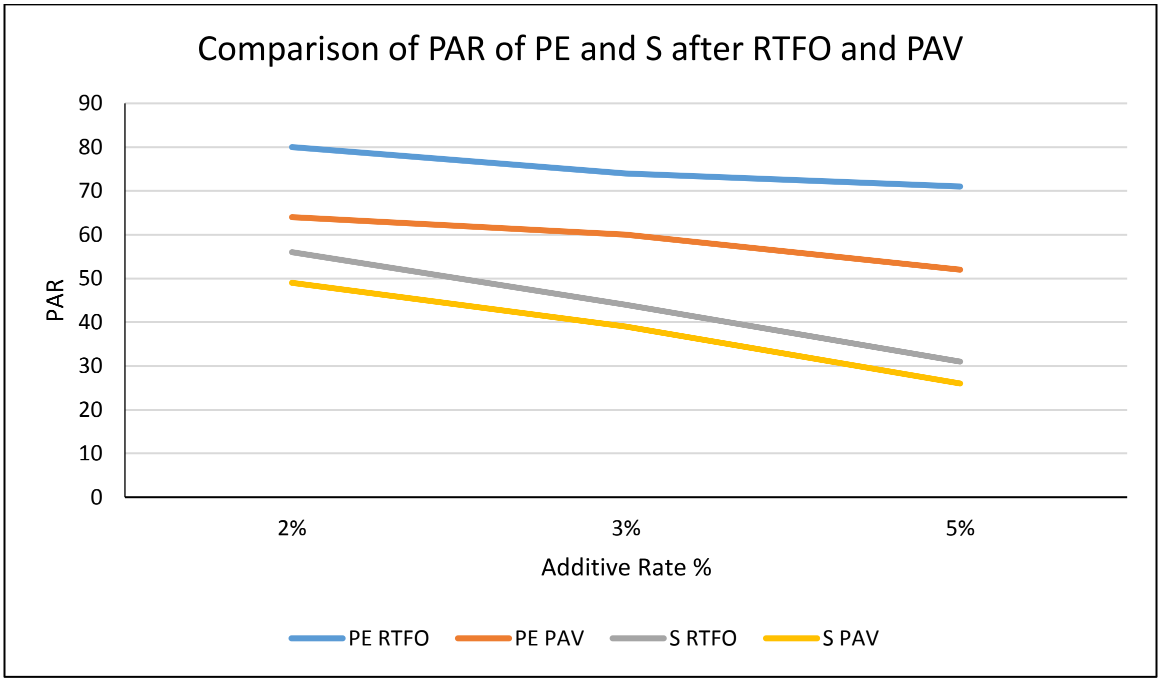


Figure 23 Comparison of PAR of PE and S after RTFO and PAV

4.3. High Temperature Fluidity (Softening Point)

Softening point test is generally used to describe an approximate limit between viscous and viscoelastic behavior of asphalt binder, and it represents the degree of resistance of asphalt binder against permanent deformation. By adding 2% to 5% of polyethylene into the base binder, softening point of the modified asphalt binder increased. 2% addition of PE resulted in 3% increase in softening point. Even after the aging phase, with the increase in the modifier content the high temperature stability of the binder is improved constantly. The impact of aging on the neat and modified binder can be seen in the form of softening point increment in figure 24 and 25. It is generally concluded that the addition of PE made the asphalt binder more stable against flowing when subjected to high temperatures, which means that the PE modified asphalt binder has a better high temperature rutting resistance.

Table 10 Softening point results for P.E modified asphalt binder

	Softening Point		
Additive rate	**Unaged**	**RTFO aged**	**PAV aged**
0%	45	49	51.1
2%	47	50	53
3%	49	51.5	55
5%	50	53	56

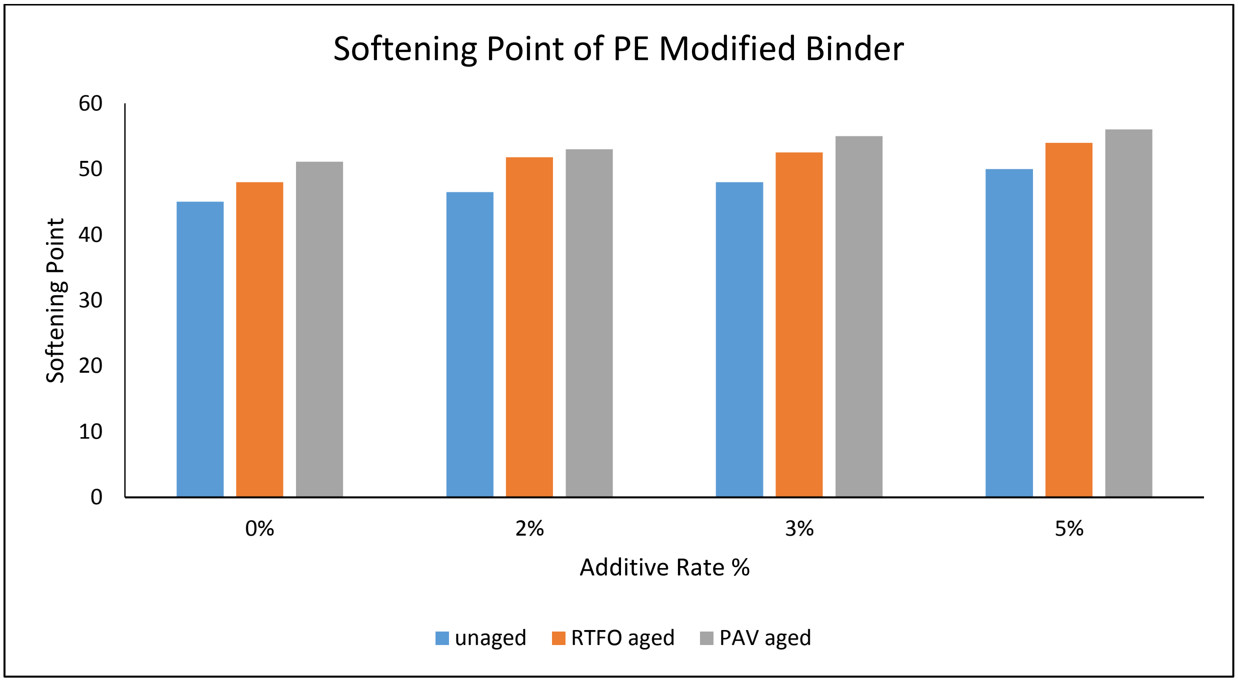


Figure 24 Softening Point of PE modified Asphalt binder

Similar trends are obtained for the softening point temperature of Sulphur modified asphalt as that of penetration test result for SMB. It is generally known that a higher softening point indicates a lower temperature susceptibility. For unaged condition, sulphur modified asphalt samples showed a consistent decrease in the softening point which back the previous findings made on the basis of penetration result that asphalt binder becomes softer on the addition of sulphur. But after the short and long term aging the hardening level of modified asphalt binder kept on increasing. This can be observed by the increase in softening temperature after the two aging. A higher softening point asphalt cement is mostly preferred in hot regions.

Table 11 Softening point result for S modified asphalt binder

	Softening Point		
Additive rate %	**Unaged**	**RTFO aged**	**PAV aged**
0%	45	49	53
2%	44.5	54	55.8
3%	44	57	57
5%	43.5	59	58

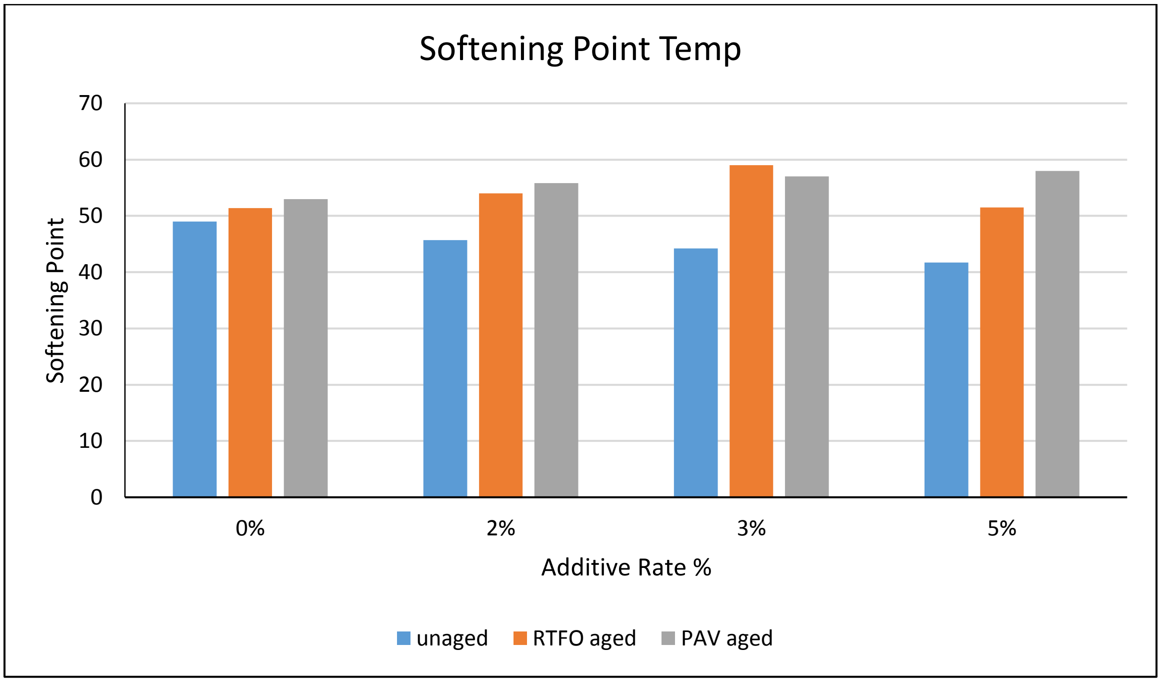


Figure 25 Softening point result of Sulphur modified asphalt binder

4.4. Penetration Index

It is generally known that a high value of PI indicate lower temperature susceptibility. The binder is considered high susceptible to temperature if it has Penetration Index value smaller than -2. The binder will behave more brittle at lower ranges of temperature and it will undergo transverse cracking in colder regions.

All the PI values obtained in our case are within the normal range of -2 to +2 for road paving application and shown in table 12 and 13. The value for neat binder is more towards down side of the criteria i.e. -2 which means the binder is more susceptible to temperature variations. But with the addition of polyethylene and sulphur the PI value increased which indicated the lower temperature susceptibility of the modified binders. With the increasing percentages of PE and S i.e. 2%, 3%, and 5%, the PI value also increased indicating the better aging resistance of modified binders. The results obtained after long term and short term aging showed more improvement in temperature susceptibility as the PI values moved towards the upper side. Higher PI values indicate higher temperature resistance. (Ali, Mashaan, & Karim, 2013)

At 3% addition of PE into base asphalt binder, PI increased by 10% with respect to base binder and the addition of 2% S by weight of asphalt binder resulted in 36% increase in the penetration index. This increase in the PI will result in better resistance against thermal cracking of the pavement at low temperatures, and lower permanent (plastic) deformation at high temperatures.

Table 12 Penetration index for Polyethylene

	Penetration Index		
Additive rate %	**Unaged**	**RTFO aged**	**PAV aged**
0%	-1.92	-1.54	-1.42
2%	-1.81	-1.10	-1.25
3%	-145	-1.25	-1.12
5%	-1.58	-1.27	-1.59

Table 13 Penetration index for Sulphur

	Penetration Index		
Additive rate %	**Unaged**	**RTFO aged**	**PAV aged**
0%	-1.92	-1.28	-1.42
2%	-1.59	-0.50	-0.42
3%	-1.49	-0.11	-0.40
5%	-1.38	-0.31	-0.86

Moreover, when we compare the PI results of polyethylene (PE) and sulphur (S) as shown in figure 26, sulphur modified binder showed higher values of PI which means higher resistance to thermal susceptibility, lower brittleness and better elastic properties under higher strains.

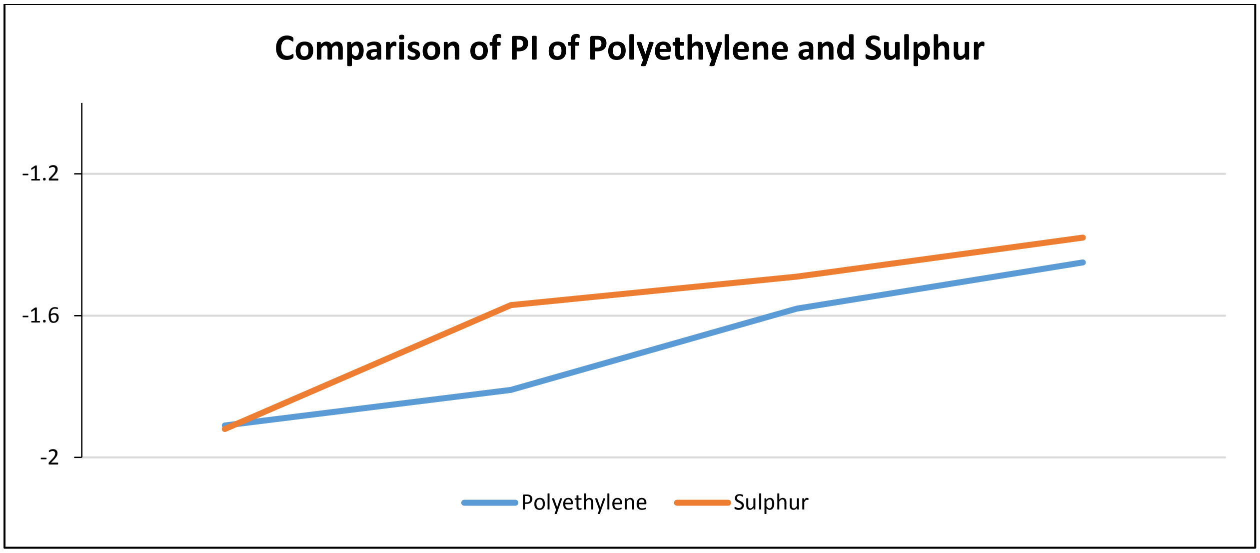


Figure 26 Comparison of Penetration Index of Polyethylene and Sulphur

4.5. Low Temperature Fluidity (Ductility)

Table 14 and 15 shows the ductility test results of PE and S modified asphalt binder respectively. Decrease in ductility was observed in case of Polyethylene modified asphalt binder. At 3% addition of PE the ductility value reduced from 100 to 83 causing a decrease of 25% with respect to base binder. This reduction in ductility indicate the stiffening effect of asphalt binder after the addition of PE. While for Sulphur modified binder, the reduction in ductility was not significant. In fact, addition of S enhanced the ductility of unaged binder at all added percentages. These results are in consistent with the previous findings that sulphur modified binder acts more like a plastic material rather than a viscous material. However the results after short term and long term aging showed a constant decrease in the ductility indicating that aging makes the binder stiffer.

Table 14 Ductility values for PE modified binder

	Ductility		
Additive rate %	**Unaged**	**RTFO aged**	**PAV aged**
0%	110	100	90
2%	89	85	80
3%	85	83	79
5%	72	68	65

The ductility value is decreasing with the increase in percentage of PE and S but the DRR is increasing which represented that the addition of PE and S can reduce deterioration in ductility of asphalt during aging.

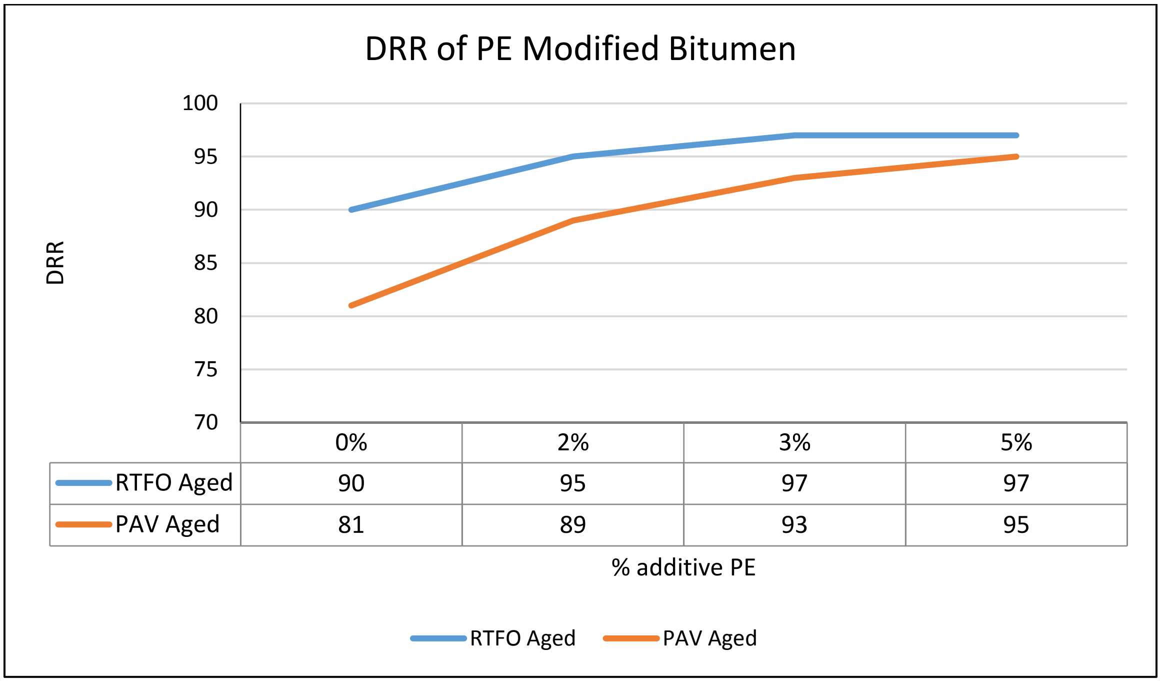


Figure 27 variation in Ductility Retained Ratio for Polyethylene

Table 15 Ductility results for Sulphur modified binder

	Ductility		
Additive rate %	**Unaged**	**RTFO aged**	**PAV Aged**
2	+120	100,80	90,72
3	+100	90,83	80,76
5	+100	73, 87	65,78

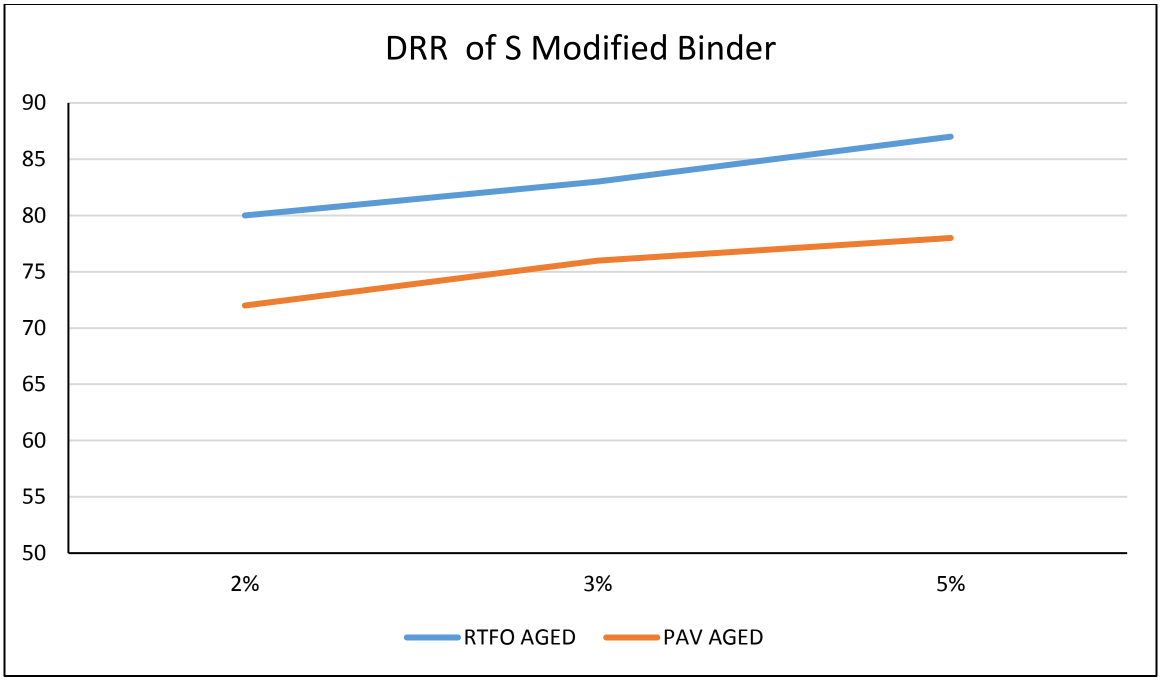


Figure 28 Ductility retained ratio of Sulphur modified binder

4.6. FTIR Results

Figure 28 and 29 shows the IR spectra of neat asphalt binder and asphalt binder modified with Polyethylene and Sulphur. While looking at the spectra of neat asphalt binder we observe the peak in the region of 3200 to 3600 which indicates that OH stretching of alcohol group. Peaks at 2917 and 2846 corresponds to the C-H aliphatic stretching of alkanes while peak at 1617 refers to C=C aromatic stretching. Peaks in the region of 1720-1750 represents the C=O carbonyl functional group. Peak at 1453 and 1102 corresponds to C-H bending of alkane group and C-O stretching of secondary alcohol group respectively. The region between 1070-1030 represents the strong S=O stretching of sulfoxide group. Peaks at 887 and 817 refer to C=C bending of alkene group and peak at 773 indicates C-S or C-H bending. When we look at the IR spectra of Polyethylene and sulphur modified asphalt binder, very little or no considerable change of peaks is observed. The intensity of peaks may vary but the range of functional groups more or less remains the same. It confirms that the modification of asphalt binder with polyethylene and sulphur is purely physical in nature as it does not change its chemical composition.

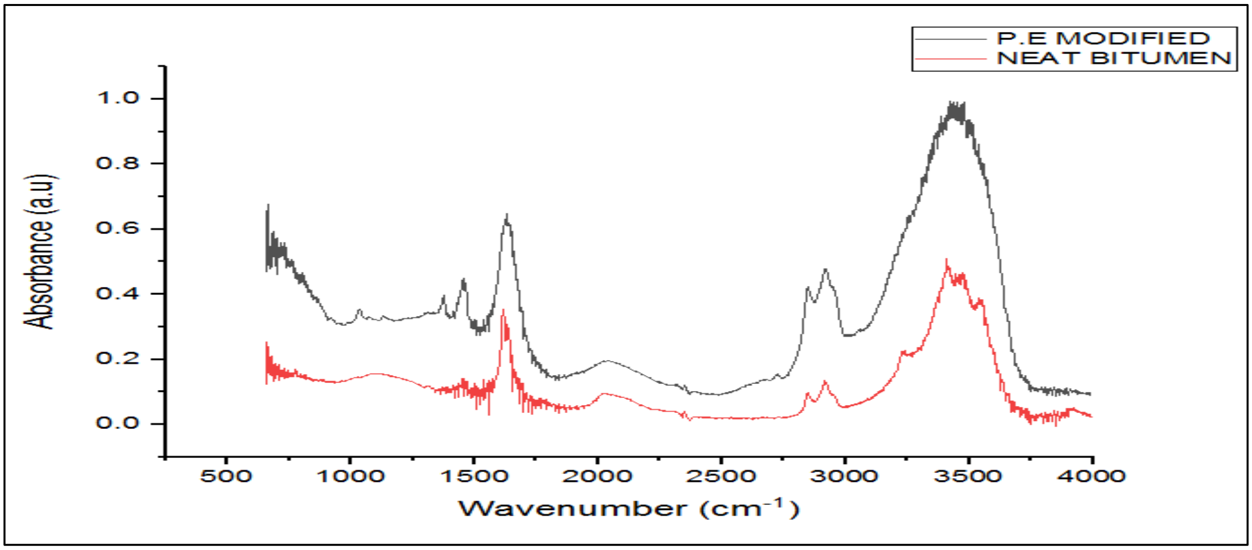


Figure 29 IR Spectra of Neat and Polyethylene modified Asphalt binder

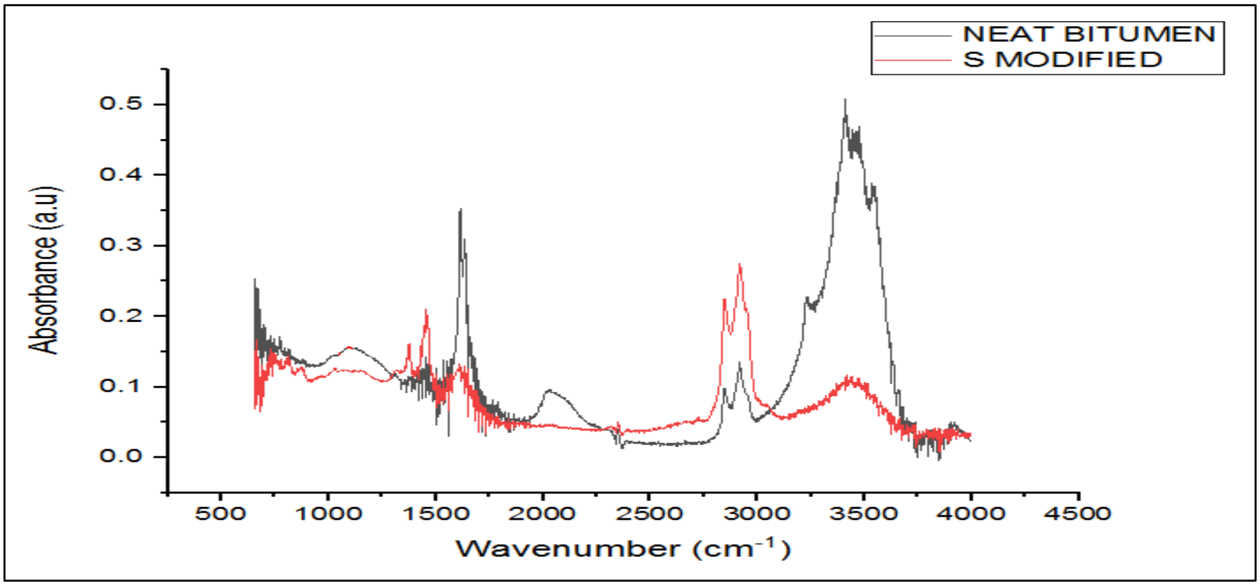


Figure 30 IR Spectra of Neat and Sulphur Modified Asphalt binder

Now when we compare the spectrum of neat and modified asphalt binder after aging, we can clearly see that the addition of polyethylene and sulphur hinders the oxidation rate which can be seen as the reduction in carbonyl and sulfoxide areas of two modified binders with respect to original binders in figure 30. It is generalized from the previous literature view that S=O and C=O are the two functional groups that are responsible for asphalt binder hardening. From the results obtained in the FTIR spectroscopy of modified binders it is concluded that the polyethylene and sulphur are good additives to improve the anti-aging properties of asphalt binder.

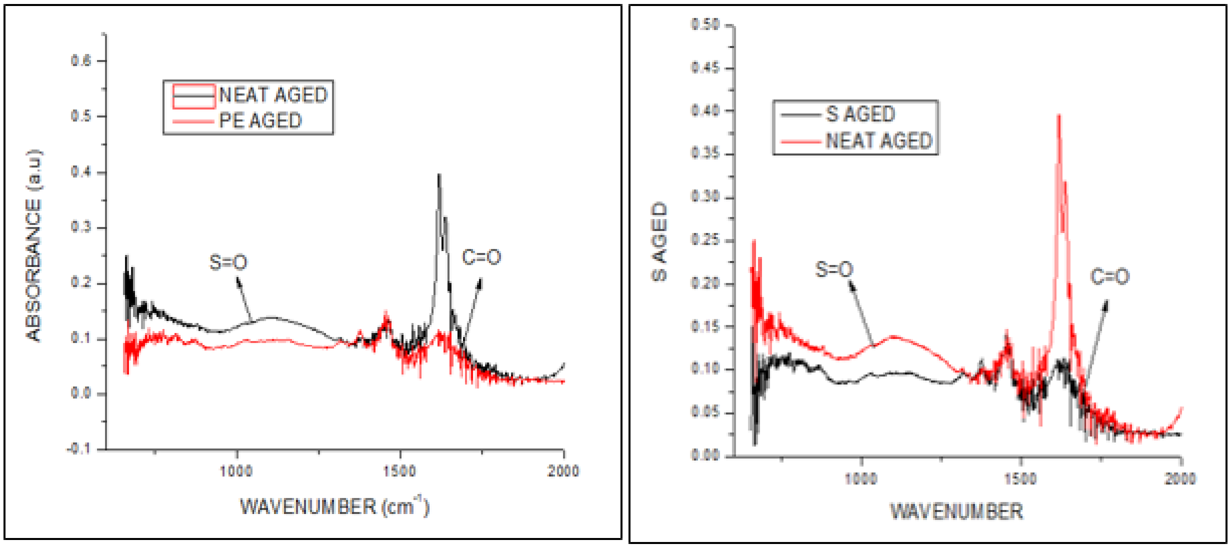


Figure 30 IR Spectra of Neat and Modified Asphalt binder after RTFO

(Lamontagne et al. 2001) computed structural index by numerical integrating peak of target functional group and then dividing it by entire area between 600 cm-1 to 2000 cm-1. Carbonyl and sulfoxide can be calculated by numerical integrating the peak of carbonyl and sulfoxide functional groups at 1750 and 1030 respectively and dividing it by the sum of specific areas.

$$\text{Carbonyl Index} = \frac{A_{1750}}{\sum A}$$

$$\text{Sulfoxide Index} = \frac{A_{1030}}{\sum A}$$

Structural index after the RTFO aging are presented in table 16 and figure 31. Carbonyl and sulfoxide index of the modified binders decreased with respect to neat binder. Carbonyl index decreased by 17% in case of 3% PE modification while it decreased by 23% by addition of 2% S. Similarly, sulfoxide index decreased by 33% and 42% in case of PE and S respectively. This decrease in the structural index indicate the greater capability of the modifiers to resist oxidation in asphalt.

Table 16 Structural Index after RTFO aging

	Structural Index	
Sample	**Carbonyl Index**	**Sulfoxide Index**
Virgin 60/70	0.051	0.056
Virgin + 3% PE	0.042	0.037
Virgin + 2% S	0.039	0.032

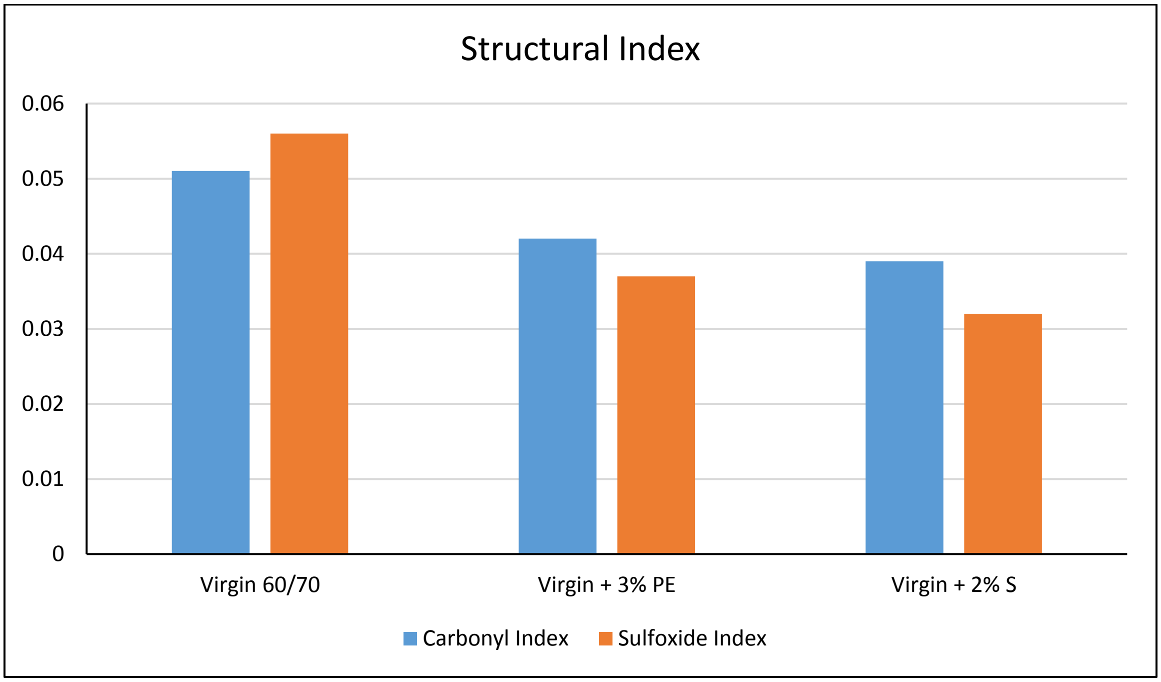
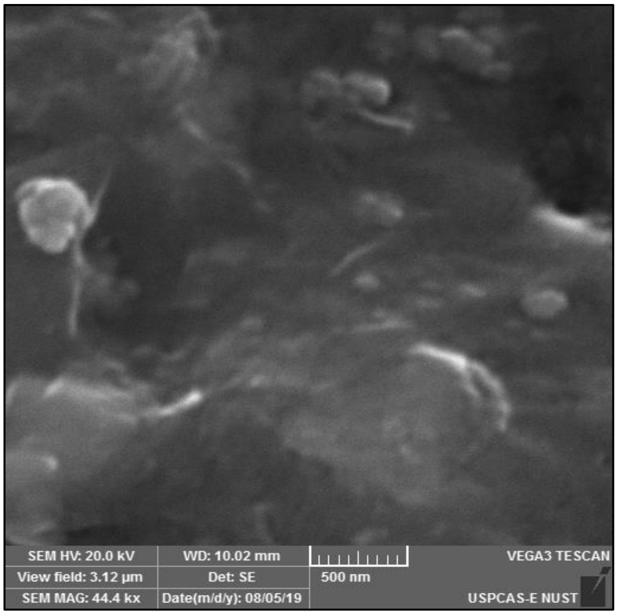


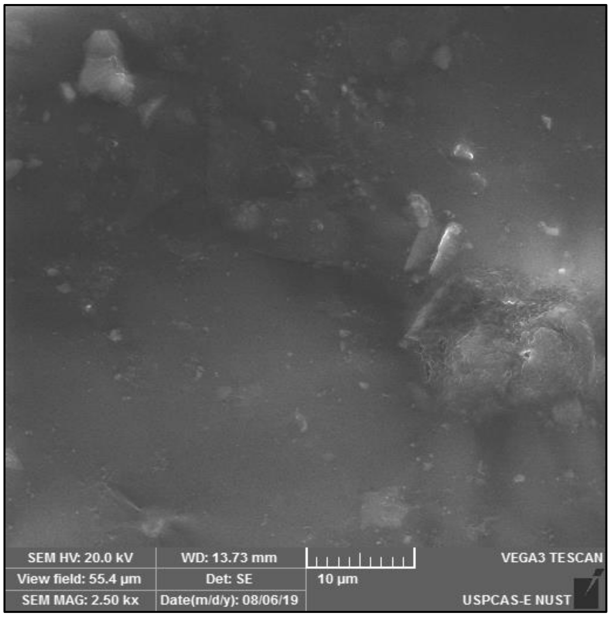
Figure 31 Structural index of neat and modified binders after RTFO

4.7. SEM Results

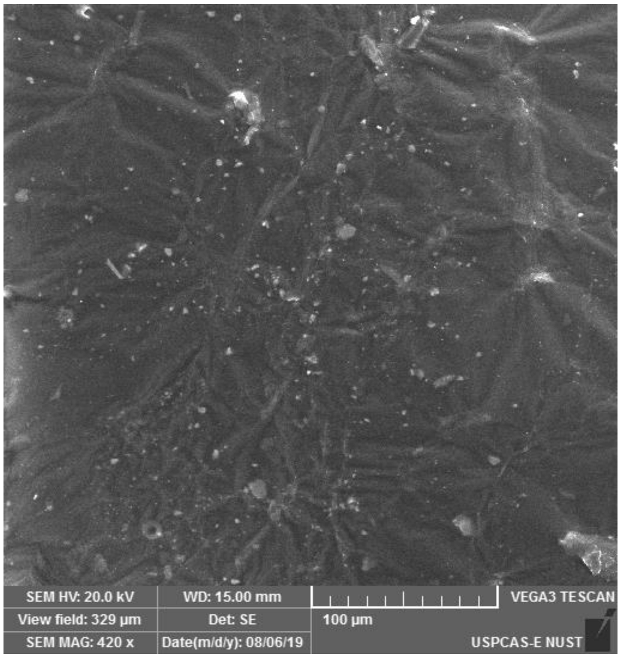
SEM was performed to check the changes in chemical structure and homogenous dispersion of modifiers in asphalt binder. As polyethylene is a non-polar polymer, its dispersion in asphalt binder is purely physical in nature. Asphalt binder itself is in black color while white patches shows the presence of modifiers i.e. PE and S. it is clear from the SEM images in figure 32 that with the increase in percentages of added polyethylene and sulphur, the white area is increasing



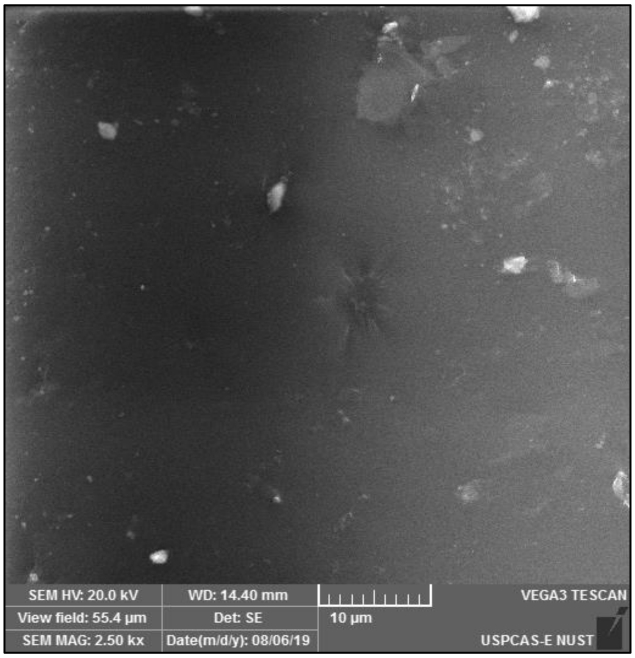
(a) 2% S unaged



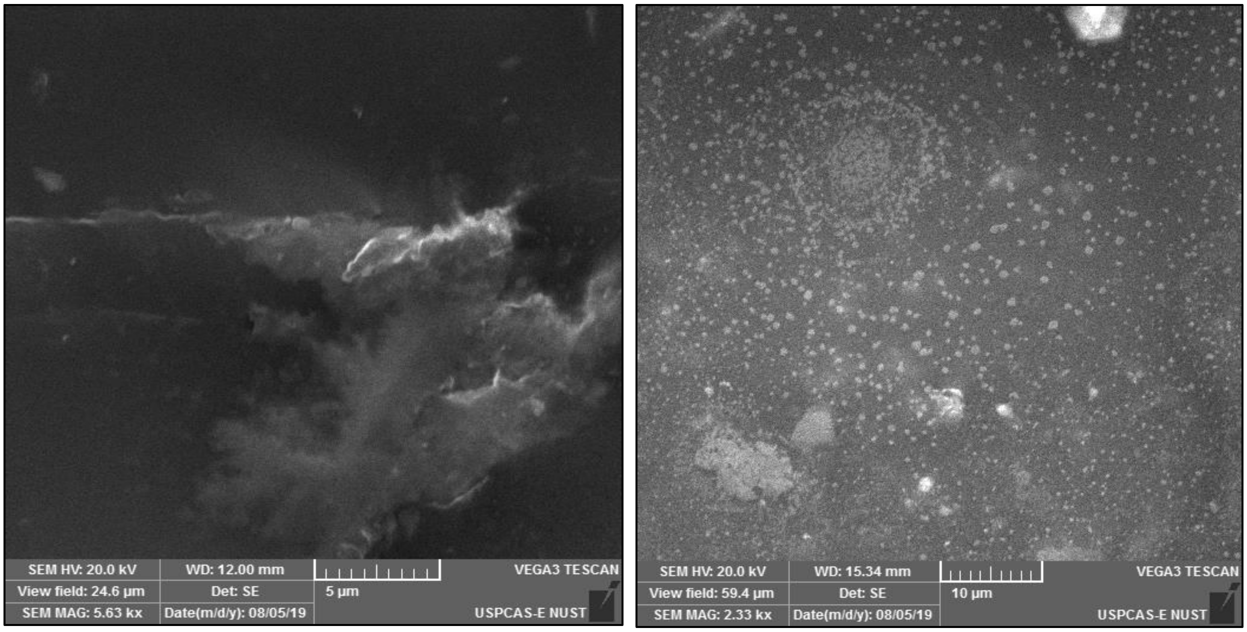
(b) 2% S Aged



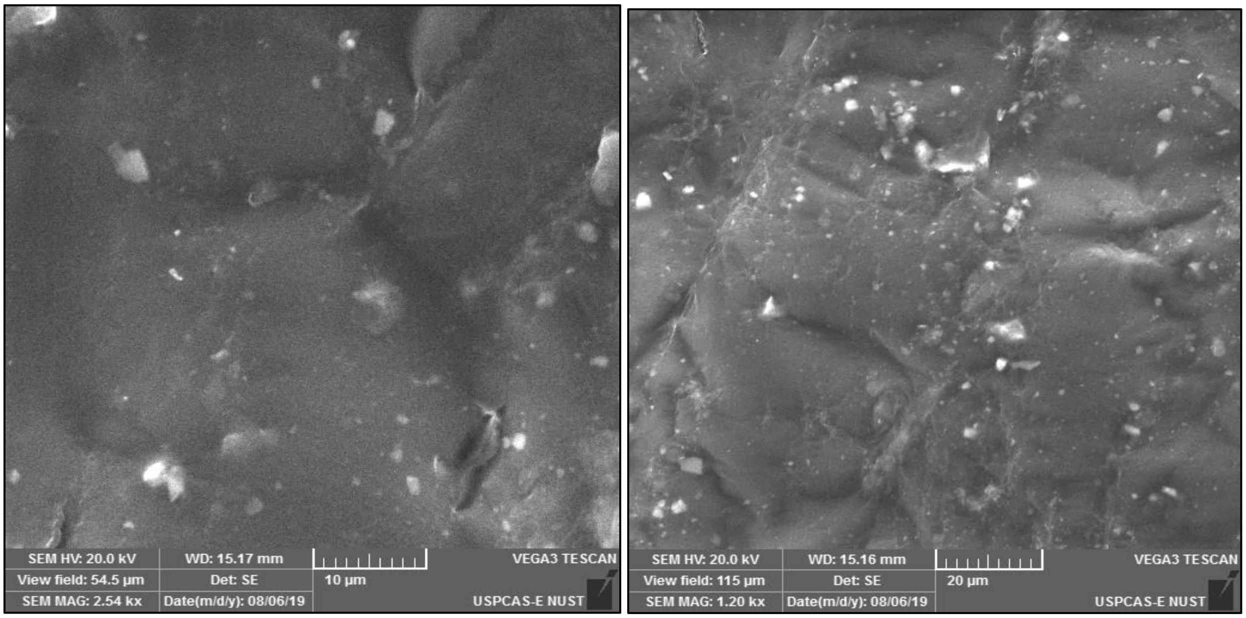
(c) 3% P.E Unaged



(d) 3% PE RTFO



(e) 3% S **(f) 5% S**



(g) 2% PE **(h) 5 % PE**

Figure 32 SEM images (a) 2% S unaged, (b) 2% S aged, (c) 3% PE unaged, (d) 3% PE aged, (e) 3% S, (f) 5% S, (g) 3% PE, (h) 5% PE

As compared with neat asphalt binder the roughness of surface of sulphar modified asphalt binder was more and it is increased as the percentage of sulphur in asphalt binder was increased from 2% to 5%. Tiny particles of sulphur either swollen or dispersed inside the base asphalt binder can be seen in SEM images of 2%, 3% and 5% sulphur by weight of asphalt binder. These images also show that asphalt binder is homogenized thus it represents the compatibility of modifier with asphalt binder.

At the same rate of additives, normally the surface area of sulphur modified asphalt binder was rougher than PE modified asphalt binder. This figure shows that particle size of PE was smaller than S and during blending the particles of PE remained in liquid form and stick together while in case of S the particles of S remain in powder form and were separate from each other hence offer more surface area to interact with asphalt binder. In SEM images of 2%, 3% and 5% PE by weight of asphalt binder, the PE additive were able to be found. According to Airey, 2003, most of the small polymers that are compatible with some part of neat asphalt binder are easily swollen by them if the additive rate of polymer is less than 5% by weight in the modified asphalt binder. Hence it might be the reason that only little additive could be seen in SEM image.

4.8. Dynamic Shear Rheometer Analysis

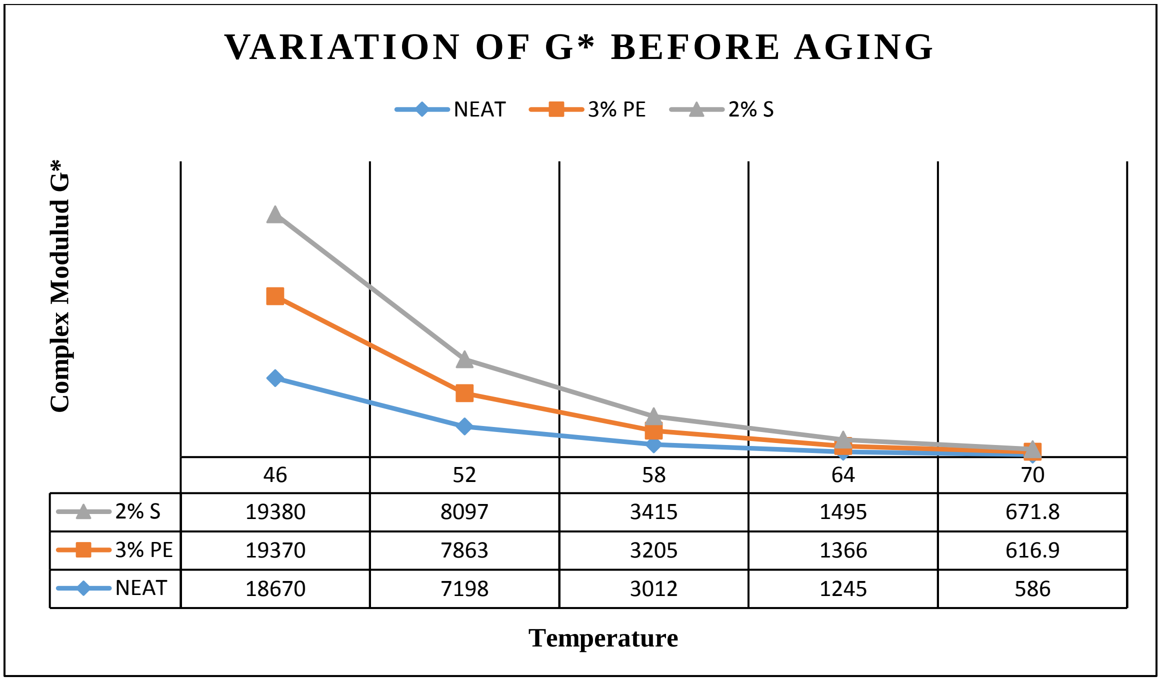
DSR test was conducted to check the rheological properties of asphalt binder at intermediate to high temperatures of 45, 52, 58, 64, 70, 76, and 82. Original, modified aged and unaged sample were tested. Complex modulus and phase angle were obtained as a result to evaluate the viscoelastic behavior of different asphalt samples.

4.9. Behavior of Original Asphalt Binder

Complex modulus and phase angle represents the behavior of the original asphalt binder on increasing temperature range. The G* value of binder decreased with the increase in temperature showing increase in asphalt binder’s stiffness, while phase angle increased which shows raise in asphalt viscous portion over elastic portion.

4.10. Effect of Modifiers

The effect of modification on the asphalt binder was obvious. Binder stiffness was increased and phase angle was decreased by adding polyethylene and sulphur into base binder. It means addition of polyethylene and sulphur into asphalt resulted in improved elastic behavior of asphalt.



	46	52	58	64	70
▲ 2% S	19380	8097	3415	1495	671.8
■ 3% PE	19370	7863	3205	1366	616.9
◆ NEAT	18670	7198	3012	1245	586

Figure 33 Variation of Complex Modulus of Neat and Modified Binder

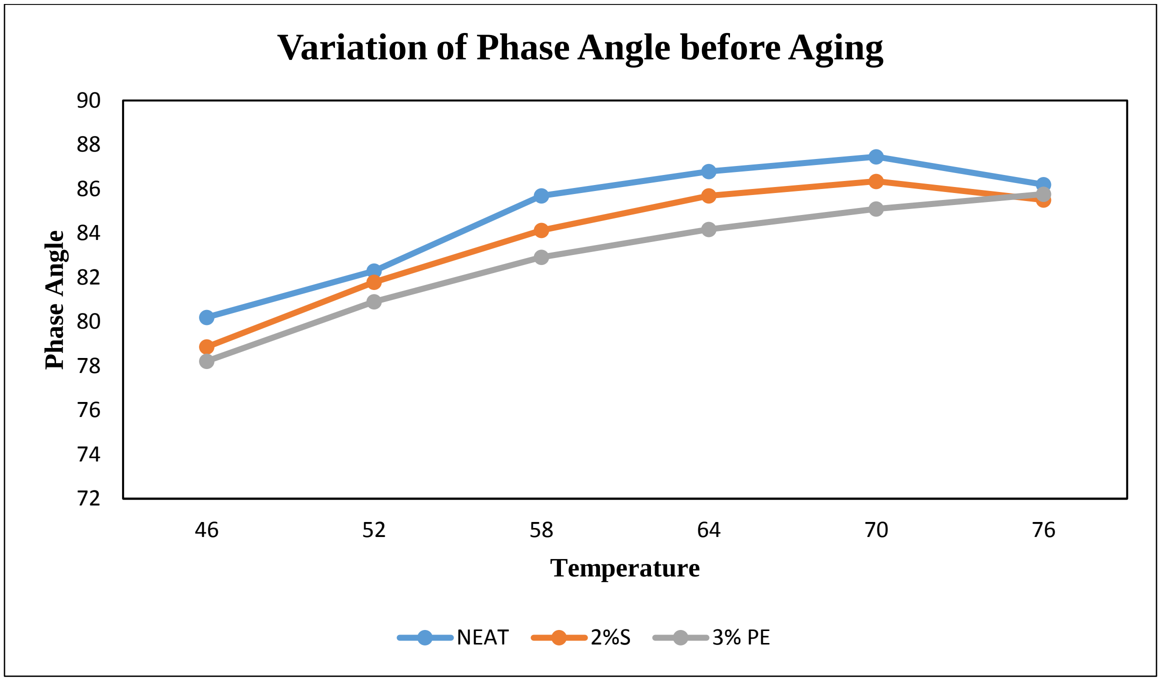


Figure 34 Variation of Phase Angle of Neat and Modified Binder

4.11. Intermediate and High Temperature Performance Characteristics

Influence of aging on the rheological behavior of neat and modified binder was evaluated in terms of rheological aging indices. Complex modulus aging index (CMAI) and phase angle aging index (PAAI) were used to evaluate the aging properties of asphalt binder.

$$\text{Phase Angle Aging Index (PAAI)} = \frac{Aged\ Phase\ Angle}{Unaged\ Phase\ Angle}$$

$$\text{Complex Modulus Aging Index (CMAI)} = \frac{Aged\ Complex\ Modulus}{Unaged\ Complex\ Modulus}$$

4.11.1 Complex Modulus Aging Index (CMAI)

The results of CMAI of neat and modified asphalt binder are presented in figure 35. G* value indicate the binder’s total resistance to permanent deformation. Generally lower value of CMAI indicate higher resistance to aging(Wu, Li, Yu, Xu, & Xie, 2016). Figure 35 shows that the CMAI of both modified binder is less than the CMAI of neat binder which means that the PE modified and S modified binder offer higher resistance to oxidative aging, hence improving the rutting potential of asphalt.

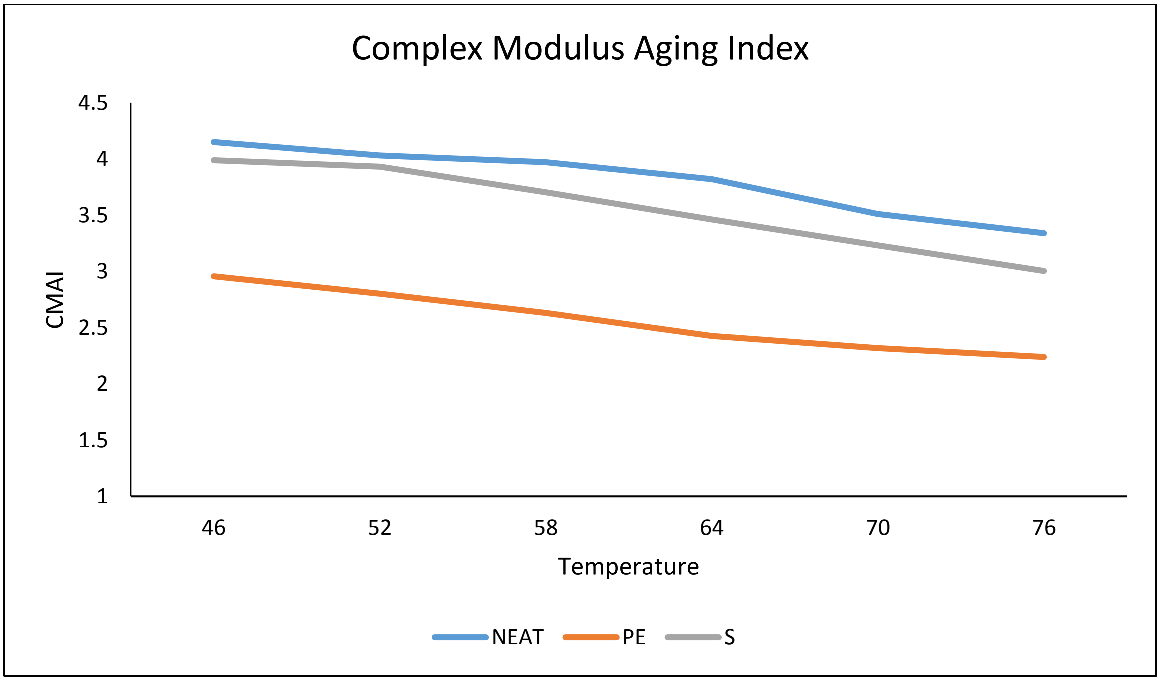


Figure 35 Complex Modulus Aging Index of Neat and Modified Binders

4.11.2 Phase angle aging index (PAAI)

Phase angle aging index was used to understand the effect of temperature on the behavior of phase angle. Phase angle present the viscous behavior of asphalt. As the resistance of asphalt against low temperature cracking increases the value of phase angle also increases (Panda *et al.*, 2016). It can be seen in the figure 36 that at all temperatures, the phase angle aging index for PE and S modified binder is always greater than the neat binder. It represents that, after aging the modified asphalt had indicate improved viscous behavior and improved low temperature cracking resistance.

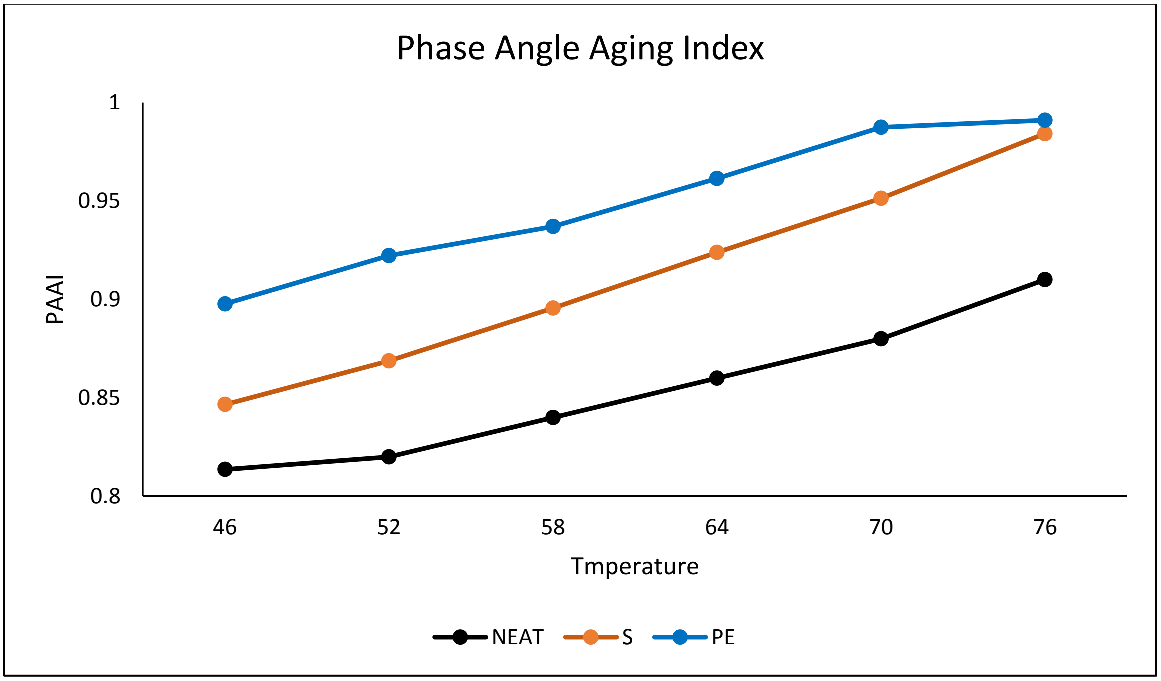


Figure 36 Phase Angle Aging Index of Neat and Modified Binders

4.11.3 Determination of Failure Temperature

To determine the failure temperature of neat and modified asphalt binder, temperature sweep test was performed. SHRP rutting factor parameter was considered as the failure criteria when it gets below 1 kPa for unaged and 2.2 kPa for RTFO aged samples. Failing temperature of the unaged binder improved from 64ºC to 70ºC and 71.5ºC for PE modified and S modified binder respectively. While after the RTFO, the failure temperature increased to 73.5ºC for polyethylene modified binder and 75ºC for sulphur modified binder. This improvement in the failure temperature indicate the improved rutting resistance of modified binders. Performance grade of the binder increased from PG64 to PG70 in case of polyethylene and sulphur.

Table 17 Failure temperature of neat and modified asphalt binder

	Failure Temperature	
Sample	**Unaged**	**RTFO aged**
Virgin 60/70	64	67
Virgin +3% PE	70	73.5
Virgin + 2% S	71.5	75

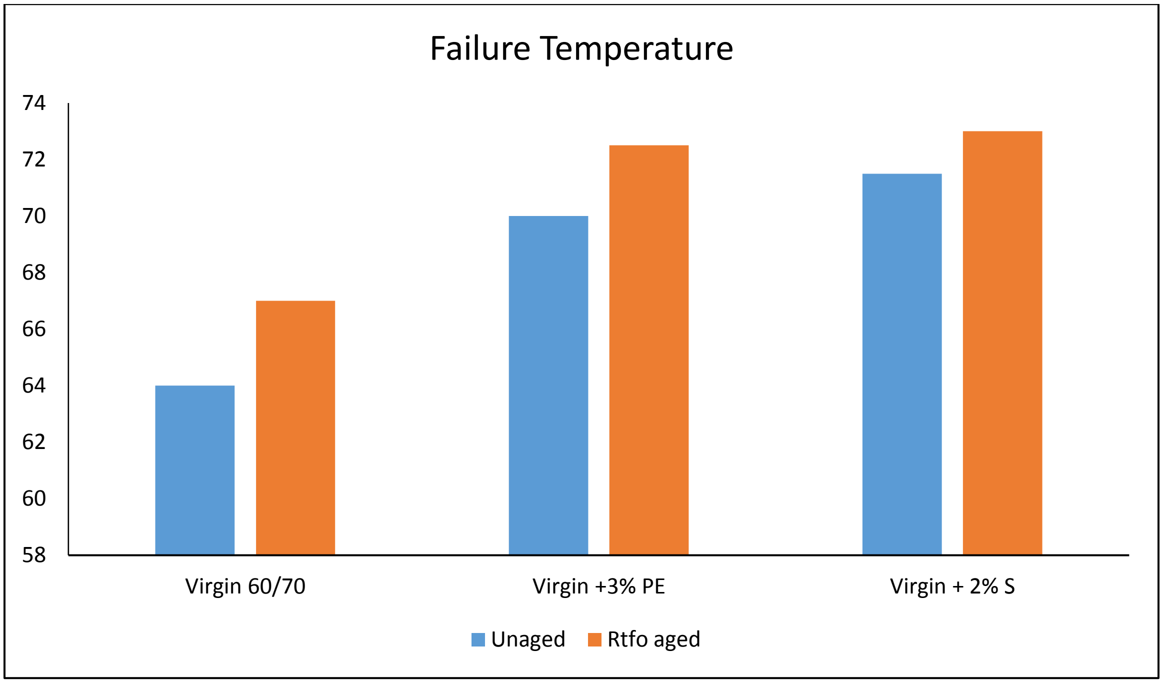


Figure 37 Failure Temperature of Neat and Modified Binders

4.12. Summary

This chapter is comprised of results of the study presented in the form of table and figures. Consistency analysis is done based on the results of penetration and softening point and penetration index (PI) is determined. Results before and after RTFO are compared to obtain the best possible blend of modifier and asphalt binder. Chemical and morphological analysis is done using FTIR and SEM. Functional groups are assigned to relative peaks from IR spectra. Morphological analysis shows good compatibility of modifiers with asphalt binder. DSR results indicate improvement in the performance grade of asphalt binder from PG64 to PG70.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1. Summary

Present study was conducted to determine polyethylene and sulphur effect on the aging properties of PARCO 60/70 grade asphalt binder. Increase in the performance related properties of Asphalt binder increases the service life of roads. To observe the effect of modifiers on the Performance Grade of Asphalt binder, performance testing of modified and unmodified asphalt binder were carried out. The key findings based on the performed laboratory testing are concluded in this chapter.

5.2. Conclusion

After successful completion of extensive lab testing, carried out in an effort to obtain the targeted objectives of this research work, following conclusions can be drawn based on lab test result and logical observations.

- Results indicate that the addition of polyethylene and sulphur improved the physical properties of binder for both unaged and aged conditions.
- Penetration value of the polyethylene modified binder decreased and softening point increased which indicate high resistance of the modified binder against rutting.
- Sulphur modified binder showed a considerable increase in the penetration value and decrease in the softening point. This depicts the plastic behavior of modified asphalt. However after the aging, the binder behaved more like a stiffer material in comparison with the neat binder and hence high temperature cracking resistance of the sulphur modified binder increased.
- Penetration aging ration decreased by 10% for polyethylene and 30% for sulphur after the short term aging which indicate binders improved resistance to oxidative aging.
- Penetration index of all modified binder before and after aging is within the permissible limit of -2 to +2 for road paving applications. Moreover, PI of all modified binder is greater than the neat asphalt binder which indicate improved temperature susceptibility of the modified binders.

- FTIR results show that the addition of polyethylene and sulphur into neat binder is physical in nature.
- Results indicate decrease in carbonyl and sulfoxide index with respect to neat binder after the RTFO which indicate improvement in aging resistance.
- Morphological analysis carried out by SEM shows the compatibility of the modifiers with the neat asphalt binder.
- Polyethylene and sulphur improved the viscoelastic properties and other rheological characteristics of the neat binder in terms of phase angle and complex modulus.
- Increase in the failure temperature of modified binders proved their better rutting performance.

5.3. Recommendations

This research focused on improving the short term aging resistance of asphalt. Intermediate and high temperature viscoelastic characteristics of the neat and modified binder were determined. Further research should be carried out on the following areas:

- Effect on the low temperature performance and effect on Fatigue properties of asphalt binder and asphalt should be studied before the implementing PE and S modified asphalt binder in cold areas.
- More work should be done in carrying out performance testing such as Rutting, Fatigue, Marshall Stability, flow test.

References

Bitumen: Origins, history, definition, terminology - Bitumen market, generalities, the manufacture of bitumen, transport, uses of bitumen, main developments and alternatives | Coursera. (n.d.). Retrieved October 8, 2019, from https://www.coursera.org/lecture/mastering-bitumen/1-bitumen-origins-history-definition-terminology-oFsmS

Al-mehthel, M., Wahhab, H. I. A., Al-idi, S. H., & Baig, M. G. (2010). Sulfur extended asphalt as a major outlet for Sulfur. *Sulphur World Symposium*, 1–16.

Alataş, T., & Yilmaz, M. (2013). Effects of different polymers on mechanical properties of bituminous binders and hot mixtures. *Construction and Building Materials*, *42*, 161–167. https://doi.org/10.1016/j.conbuildmat.2013.01.027

Aldagheiri, M. (2009). The role of the transport road network in the economic development of Saudi Arabia. In *WIT Transactions on the Built Environment* (Vol. 107). https://doi.org/10.2495/UT090251

Ali, A. H., Mashaan, N. S., & Karim, M. R. (2013). Investigations of physical and rheological properties of aged rubberised bitumen. *Advances in Materials Science and Engineering*, *2013*, 1–8. https://doi.org/10.1155/2013/239036

Bitumen components- composition of bitumen- Bitumen Characterization. (n.d.). Retrieved October 8, 2019, from http://rahabitumen.com/bitumen-components/

Brożynaa, D., & Kowalski, K. J. (2016). Modification of asphalt binders by polyethylene-type polymers. *Journal of Building Chemistry*, *1*(May), 37–41.

Çalışıcı, M., Gürü, M., Çubuk, M. K., & Cansız, Ö. F. (2018). Improving the aging resistance of bitumen by addition of polymer based diethylene glycol. *Construction and Building Materials*, *169*, 283–288. https://doi.org/10.1016/j.conbuildmat.2018.03.018

Chen, Z., Zhang, H., Zhu, C., & Zhao, B. (2015). Rheological examination of aging in bitumen with inorganic nanoparticles and organic expanded vermiculite. *CONSTRUCTION & BUILDING MATERIALS*, *101*, 884–891. https://doi.org/10.1016/j.conbuildmat.2015.10.153

Das, A. K., & Panda, M. (2017). Investigation on rheological performance of sulphur modified bitumen (SMB) binders. *Construction and Building Materials, 149*, 724–732. https://doi.org/10.1016/j.conbuildmat.2017.05.198

De Filippis, P., Giavarini, C., & Scarsella, M. (1995). Improving the ageing resistance of straight-run bitumens by addition of phosphorus compounds. *Fuel*, *74*(6), 836–841. https://doi.org/10.1016/0016-2361(95)00015-W

Diab, A., Enieb, M., & Singh, D. (2019). Influence of aging on properties of polymer-modified asphalt. *Construction and Building Materials, 196*, 54–65. https://doi.org/10.1016/j.conbuildmat.2018.11.105

Division, S. (2018). *National Health Accounts Pakistan 2015-16*. 1–99.

Ehinola, O. A., Felode, O. A., & Jonathan, G. (2012). Softening point and Penetration Index of bitumen from parts of Southwestern Nigeria. *Nafta*, *63*(9–10), 319–323. Retrieved from http://hrcak.srce.hr/index.php?show=clanak&id_clanak_jezik=136086

Elkholy, S. A., Abd El-Rahman, A. M. M., El-Shafie, M., & Abo-Shanab, Z. L. (2018). Physical and rheological properties of modified sulfur asphalt binder. *International Journal of Pavement Research and Technology*. https://doi.org/10.1016/j.ijprt.2018.07.005

Fernández-Gómez, W. D., Quintana, H. R., & Reyes Lizcano, F. (2013). *A review of asphalt and asphalt mixture aging El fenómeno de envejecimiento en asfaltos y mezclas asfálticas. Una revisión*. *33*(1), 5–12.

Fini, E. H. (2016). *Producing a Sustainable , Bio-Based Alternative to Petroleum-Based Asphalt Binder Final Report for Innovations Deserving Exploratory Analysis (IDEA) Programs Managed by the Transportation Research Board*. (April).

Fritschy, G., Papirer, E., & Chambu, C. (1981). Sulfur modified bitumen: A new binder. *Rheologica Acta - RHEOL ACTA, 20,* 78–84. https://doi.org/10.1007/BF01517475

Gawel, I., Czechowski, F., & Kosno, J. (2016). An environmental friendly anti-ageing additive to bitumen. *Construction and Building Materials, 110,* 42–47. https://doi.org/10.1016/j.conbuildmat.2016.02.004

Gedik, A., & Lav, A. H. (2016). Analytical, morphological, and rheological behavior of sulphur-extended-binder. *Canadian Journal of Civil Engineering*, *43*(6), 532–541. https://doi.org/10.1139/cjce-2015-0409

Ghaly, N. F. (2008). *Effect of Sulfur on the Storage Stability of Tire Rubber Modified Asphalt*. *3*(2), 42–50.

Ghuzlan, B. K. A. (2015). *Rheological Properties of Polyethylene-Modified Asphalt Binder*. (June), 75–88.

Hasan, Z., Kamran, R., Mohammad, F., Ahmad, G., & Hosein, F. (2012). Evaluation of Different Conditions on The Mixing Bitumen and Carbon Nano-Tubes. *International Journal of Civil & Environmental Engineering IJCEE-IJENS*, *12*(6), 53–59.

Kumar, P., & Khan, T. (2013). *Evaluation of Physical Properties of Sulphur Modified Bitumen and its Resistance to Ageing*. 13104–13107.

Kumar, U. A., & Satyanarayana, P. V. . (2015). Comparison of the Polyethylene and SBS Polymer Modified Bitumen's Effect – A Case Study. *International Journal of Engineering Trends and Technology*, *22*(7), 325–330. https://doi.org/10.14445/22315381/ijett-v22p268

Kumbargeri, Y. S., & Biligiri, K. P. (2016). Rational performance indicators to evaluate asphalt materials' aging characteristics. *Journal of Materials in Civil Engineering*, *28*(12), 1–9. https://doi.org/10.1061/(ASCE)MT.1943-5533.0001681

Lesueur, D. (2009). The colloidal structure of bitumen: Consequences on the rheology and on the mechanisms of bitumen modification. *Advances in Colloid and Interface Science*, *145*(1–2), 42–82. https://doi.org/10.1016/j.cis.2008.08.011

Li, R., Xiao, F., Amirkhanian, S., You, Z., & Huang, J. (2017). Developments of nano materials and technologies on asphalt materials – A review. *Construction and Building Materials*, *143*, 633–648. https://doi.org/10.1016/j.conbuildmat.2017.03.158

Li, Y., Moraes, R., Lyngdal, E., & Bahia, H. (2016). Effect of polymer and oil modification on the aging susceptibility of asphalt binders. *Transportation Research Record*, *2574*(January), 28–37. https://doi.org/10.3141/2574-03

Lu, X., Talon, Y., & Redelius, P. (2008). Aging of bituminous binders – laboratory tests and field data. *The 4th Eurasphalt & Eurobitume Congress*, 1–12.

Mampearachchi, W. K., Mihirani, G. S., Binduhewa, B. W. P., & Lalithya, G. D. D. (2012). Review of asphalt binder grading systems for hot mix asphalt pavements in Sri Lanka. *Journal of the National Science Foundation of Sri Lanka*, *40*(4), 311–320. https://doi.org/10.4038/jnsfsr.v40i4.5045

Napiah, M., Habib, N. Z., & Kamaruddin, I. (2014). Creep Behavior of Polyethylene Modified Bituminous Mixture. *APCBEE Procedia*, *9*(Icbee 2013), 202–206. https://doi.org/10.1016/j.apcbee.2014.01.036

North Carolina Department of Transportation. (2016). *Asphalt quality Management System*.

Ouyang, C., Wang, S., Zhang, Y., & Zhang, Y. (2006a). Improving the aging resistance of asphalt by addition of Zinc dialkyldithiophosphate. *Fuel*, *85*(7–8), 1060–1066. https://doi.org/10.1016/j.fuel.2005.08.023

Ouyang, C., Wang, S., Zhang, Y., & Zhang, Y. (2006b). Improving the aging resistance of styrene-butadiene-styrene tri-block copolymer modified asphalt by addition of antioxidants. *Polymer Degradation and Stability*, *91*(4), 795–804. https://doi.org/10.1016/j.polymdegradstab.2005.06.009

Padhan, R. K., & Sreeram, A. (2018). Enhancement of storage stability and rheological properties of polyethylene (PE) modified asphalt using cross linking and reactive polymer based additives. *Construction and Building Materials*, *188*, 772–780. https://doi.org/10.1016/j.conbuildmat.2018.08.155

Panda, M., Ojha, J., & Purohit, S. (2016). Development and evaluation of sulphur modified bitumen binder. *8th International Conference on Maintenance and Rehabilitation of Pavements, MAIREPAV 2016*, 774–783. https://doi.org/10.3850/978-981-11-0449-7-137-cd

Petersen, J. C. (2009). A review of the fundamentals of asphalt oxidation: chemical, physicochemical, physical property, and durability relationships. *Transportation Research Circular*, (E-C140).

Porto, M., Caputo, P., Loise, V., Eskandarsefat, S., Teltayev, B., & Rossi, C. O. (2019). Bitumen and bitumen modification: A review on latest advances. *Applied Sciences (Switzerland)*, *9*(4). https://doi.org/10.3390/app9040742

Prolongo, M. G., Paez, A., & Ayala, M. (n.d.). *Thermal behaviour of bitumen modified by sulphur addition*. (June 2012), 13–15.

Ragni, D., Ferrotti, G., Lu, X., & Canestrari, F. (2018). Effect of temperature and chemical additives on the short-term ageing of polymer modi fi ed bitumen for WMA. *Materials & Design*, *160*, 514–526. https://doi.org/10.1016/j.matdes.2018.09.042

Reddy, S. R., & Pavani, G. S. (2017). *ENGINEERING CHARACTERIZATION AND EVALUTION OF SULPHUR MODIFIED BITUMINOUS BINDERS M . Tech (Transportation Engineering), Department of Civil Engineering , Viswabarathi college of ABSTRACT :* *6*(2), 235–244.

Reena, G., & Verinder, K. (2012). Characterization of bitumen and modified bitumen (e-pmb) using FT-IR, thermal and SEM techniques. *Research Journal of Chemical Sciences*, *2*(8), 2231–2606.

Rek, V., Vranjeś, N., & Barjaktaroví, Z. M. (2005). Evaluation Of Ageing Properties Of Polymer Modified Bitumen. *Materials Research Innovations*, *9*(4), 113. https://doi.org/10.1080/14328917.2005.11784917

Rezvani, V. (2015). Characteristics and Preparation Method of Sulfur Extended Asphalt Mixtures. *American Journal of Civil Engineering*, *3*(2), 69. https://doi.org/10.11648/j.ajce.s.2015030202.24

S. Punith, V., & Amirthalingam, V. (2007). Behavior of Asphalt Concrete Mixtures with Reclaimed Polyethylene as Additive. *Journal of Materials in Civil Engineering - J MATER CIVIL ENG*, *19*. https://doi.org/10.1061/(ASCE)0899-1561(2007)19:6(500)

Saboo, N. (2014). *Rheological Investigations of Sulfur Modified Bitumen*. (October 2014), 703–713.

Santagata, E., Baglieri, O., Dalmazzo, D., & Tsantilis, L. (2014). 8th International RILEM Symposium on Testing and Characterization of Sustainable and Innovative Bituminous Materials, SIB 2015. *International Journal of Pavement Research and Technology*, *7*(1). https://doi.org/10.1007/978-94-017-7342-3

Selvavathi, V., Sekar, V. A., Sriram, V., & Sairam, B. (2002). MODIFICATIONS OF BITUMEN BY ELASTOMER AND REACTIVE POLYMER—A COMPARATIVE STUDY. *Petroleum Science and Technology*, *20*(5–6), 535–547. https://doi.org/10.1081/LFT-120003577

Siddiqui, M. N., & Ali, M. F. (1999). Studies on the aging behavior of the Arabian asphalts. *Fuel*, *78*(9), 1005–1015. https://doi.org/10.1016/S0016-2361(99)00018-6

Sirin, O., Paul, D. K., & Kassem, E. (2018). State of the Art Study on Aging of Asphalt Mixtures and Use of Antioxidant Additives. *Advances in Civil Engineering*, *2018*. https://doi.org/10.1155/2018/3428961

Sun, Y., Huang, B., Chen, J., Jia, X., & Ding, Y. (2016). Characterizing rheological behavior of asphalt binder over a complete range of pavement service loading frequency and temperature. *Construction and Building Materials*, *123*, 661–672. https://doi.org/10.1016/j.conbuildmat.2016.07.047

Syroezhko, A. M., Begak, O. Y., Fedorov, V. V, & Gusarova, E. N. (2003). *Modification of Paving Asphalts with Sulfur*. *76*(3), 491–496.

Tauste, R. (2018). Understanding the bitumen ageing phenomenon : A review. *Construction and Building Materials*, *192*, 593–609. https://doi.org/10.1016/j.conbuildmat.2018.10.169

tur Rasool, R., Wang, S., Zhang, Y., Li, Y., & Zhang, G. (2017). Improving the aging resistance of SBS modified asphalt with the addition of highly reclaimed rubber. *Construction and Building Materials*, *145*, 126–134. https://doi.org/10.1016/j.conbuildmat.2017.03.242

Wang, X., Guo, H., Yang, B., Chang, X., Wan, C., & Wang, Z. (2019). Aging characteristics of bitumen from different bituminous pavement structures in service. *Materials*, *12*(3). https://doi.org/10.3390/ma12030530

Weigel, S., & Stephan, D. (2017). The prediction of bitumen properties based on FTIR and multivariate analysis methods. *Fuel*, *208*, 655–661. https://doi.org/10.1016/j.fuel.2017.07.048

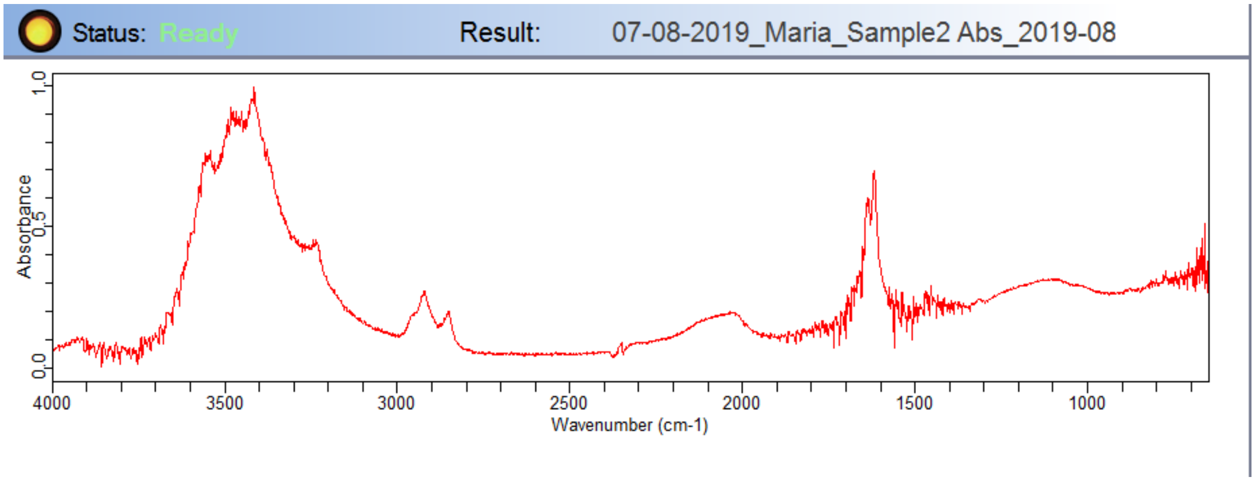
Wu, H., Li, L., Yu, J., Xu, S., & Xie, D. (2016). Effect of layered double hydroxides on ultraviolet aging properties of different bitumens. *Construction and Building Materials*, *111*, 565–570.

https://doi.org/10.1016/j.conbuildmat.2016.02.140

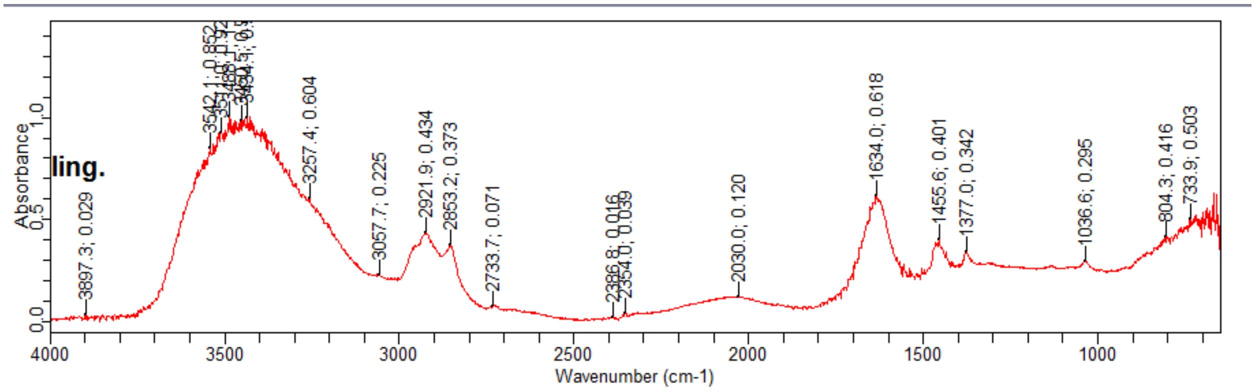
Zhu, J., Birgisson, B., & Kringos, N. (2014). Polymer modification of bitumen: Advances and challenges. *European Polymer Journal*, *54*(1), 18–38. https://doi.org/10.1016/j.eurpolymj.2014.02.005

APPENDICES

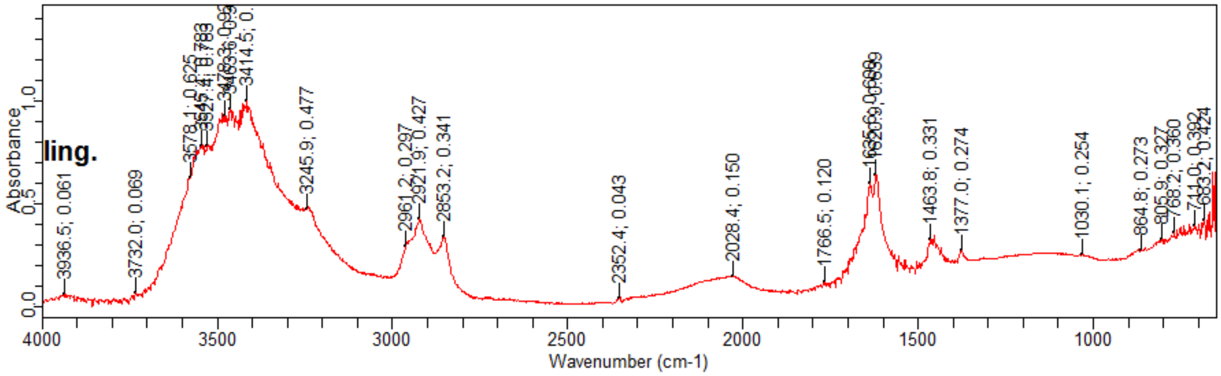
APPENDICES I FTIR REPORTS



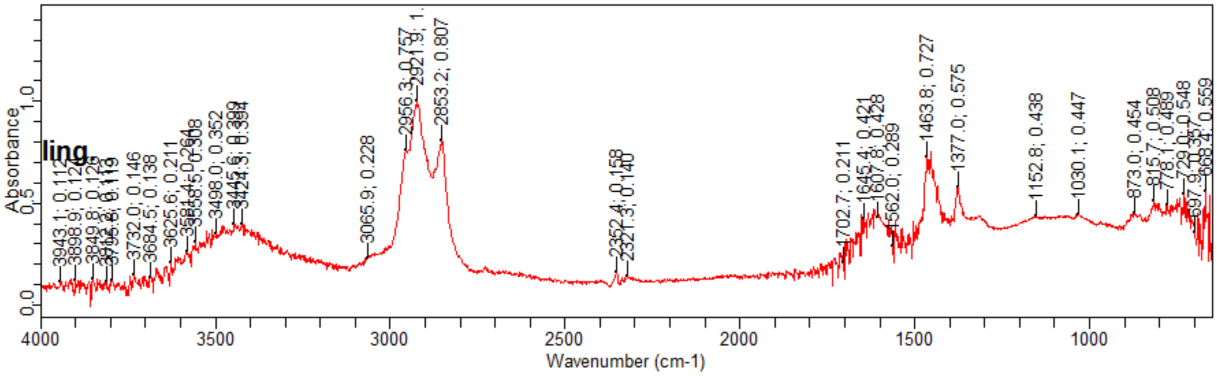
NEAT BINDER



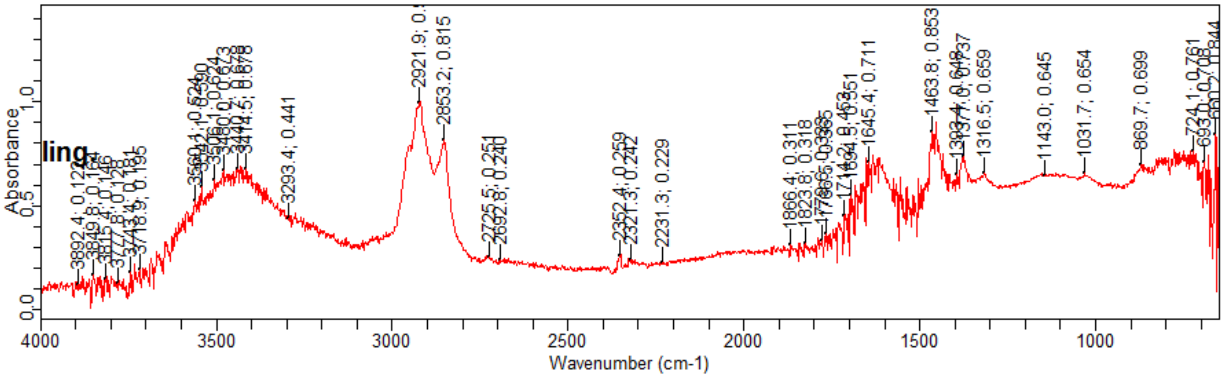
NEAT BINDER AFTER AGING



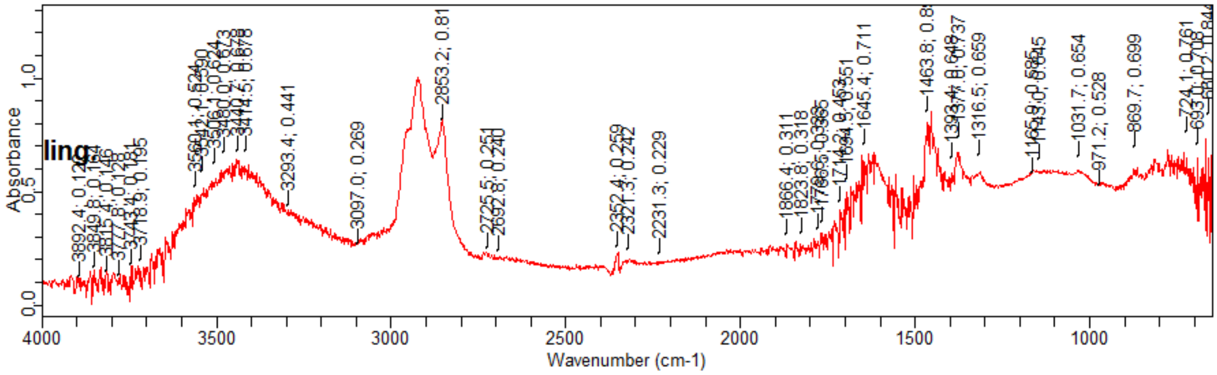
S MODIFIED BINDER BEFORE AGING



S MODIFIED BINDER AFTER AGING

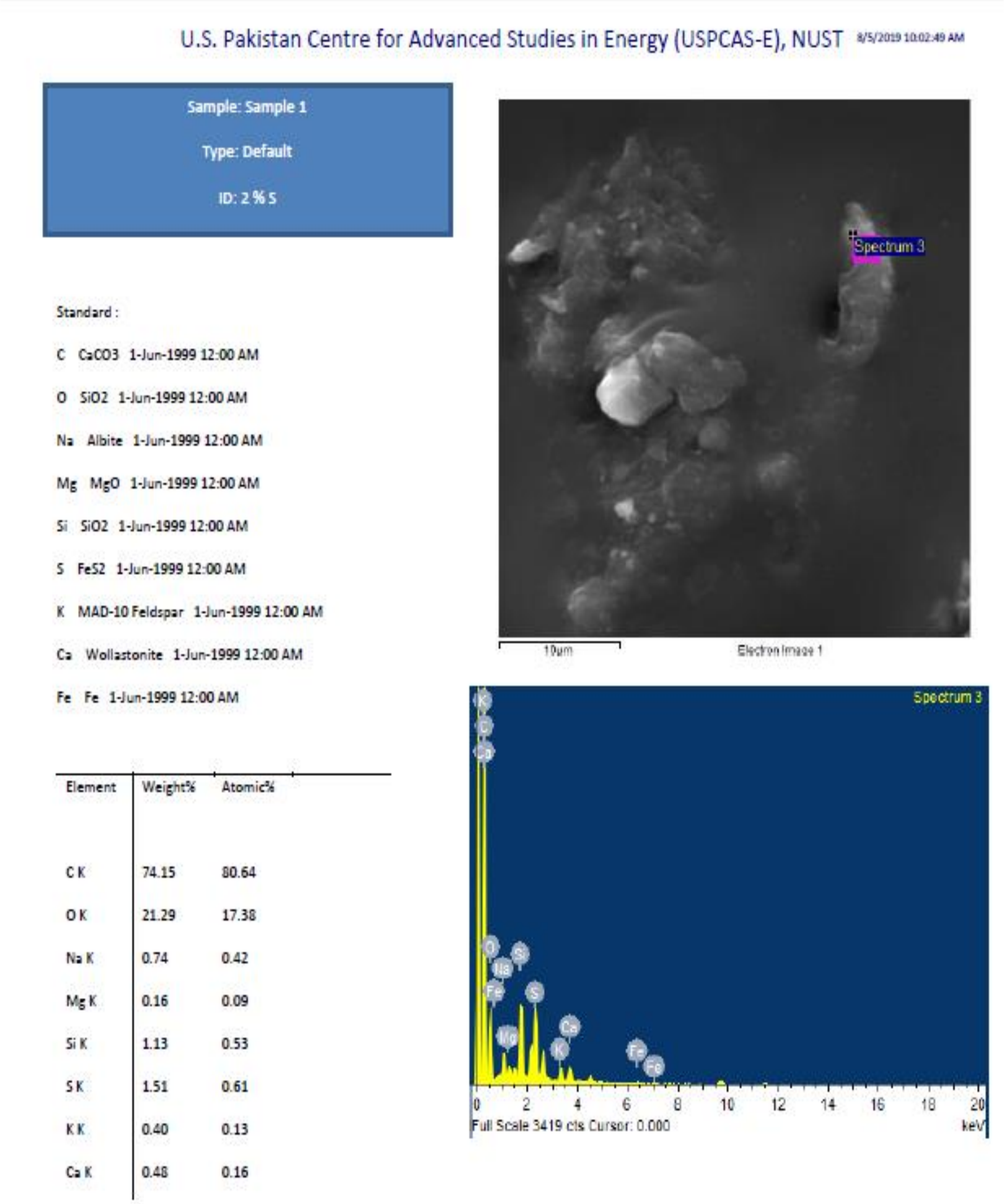


PE MODIFIED BINDER BEFORE AGING



PE MODIFIED BINDER AFTER AGING

APPENDICES II SEM REPORTS



U.S. Pakistan Centre for Advanced Studies in Energy (USPCAS-E), NUST 8/5/2019 10:02:49 AM

Sample: Sample 1

Type: Default

ID: 2 % S

Standard :

C CaCO3 1-Jun-1999 12:00 AM

O SiO2 1-Jun-1999 12:00 AM

Na Albite 1-Jun-1999 12:00 AM

Mg MgO 1-Jun-1999 12:00 AM

Si SiO2 1-Jun-1999 12:00 AM

S FeS2 1-Jun-1999 12:00 AM

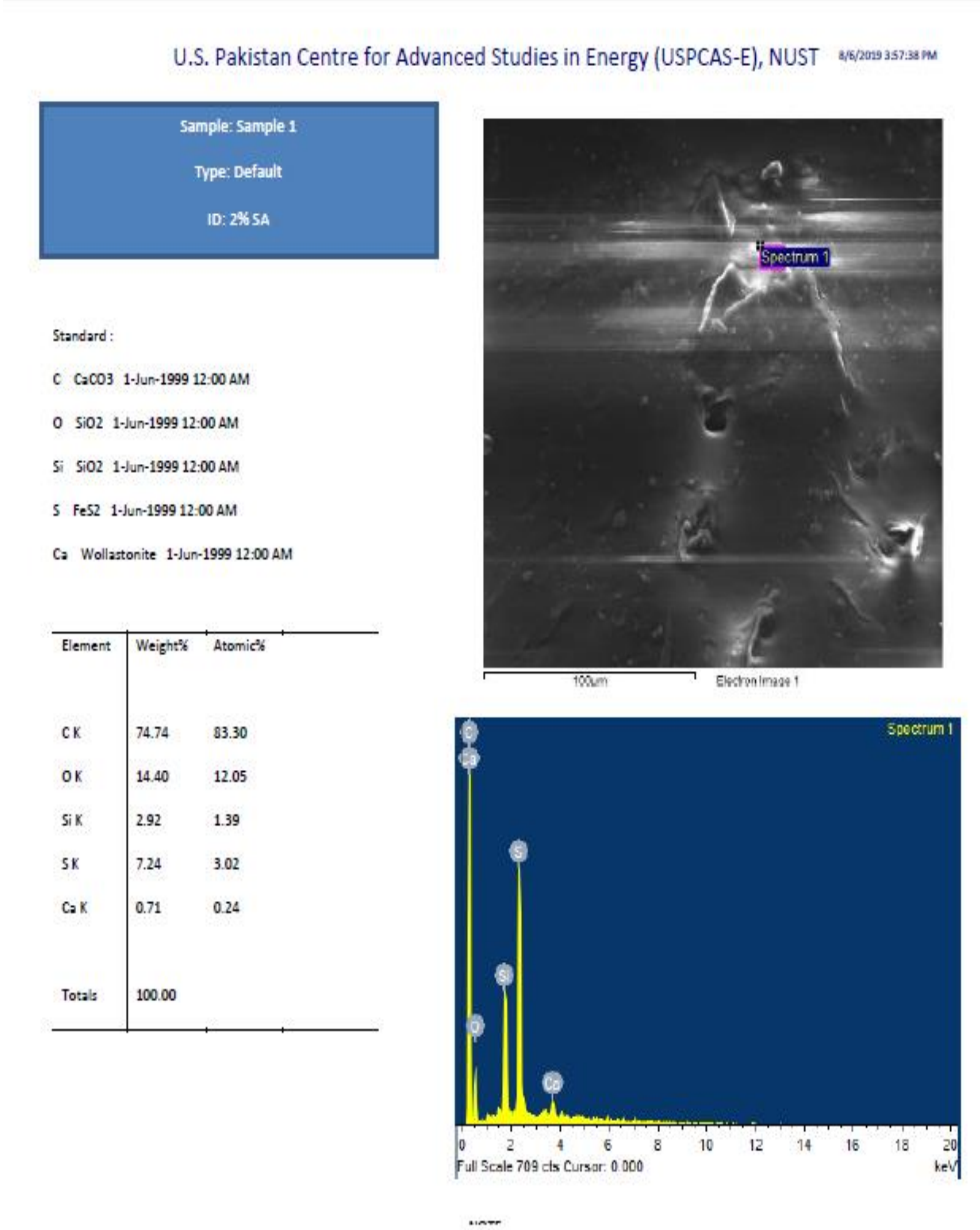
K MAD-10 Feldspar 1-Jun-1999 12:00 AM

Ca Wollastonite 1-Jun-1999 12:00 AM

Fe Fe 1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
C K	74.15	80.64
O K	21.29	17.38
Na K	0.74	0.42
Mg K	0.16	0.09
Si K	1.13	0.53
S K	1.51	0.61
K K	0.40	0.13
Ca K	0.48	0.16

2% S UNAGED



U.S. Pakistan Centre for Advanced Studies in Energy (USPCAS-E), NUST 8/6/2019 3:57:38 PM

Sample: Sample 1

Type: Default

ID: 2% SA

Standard :

C CaCO3 1-Jun-1999 12:00 AM

O SiO2 1-Jun-1999 12:00 AM

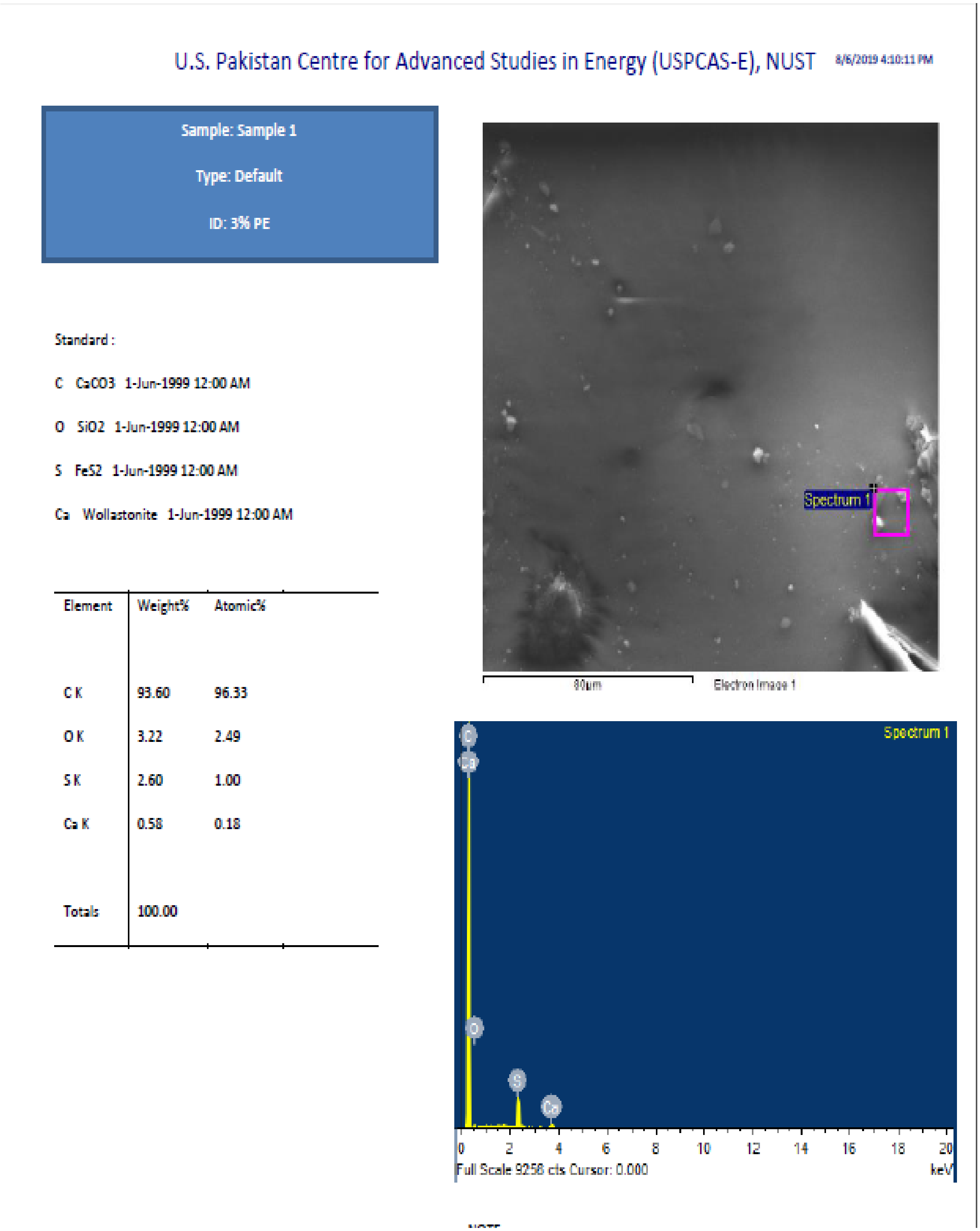
Si SiO2 1-Jun-1999 12:00 AM

S FeS2 1-Jun-1999 12:00 AM

Ca Wollastonite 1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
C K	74.74	83.30
O K	14.40	12.05
Si K	2.92	1.39
S K	7.24	3.02
Ca K	0.71	0.24
Totals	100.00	

2% S AGED



U.S. Pakistan Centre for Advanced Studies in Energy (USPCAS-E), NUST 8/6/2019 4:10:11 PM

Sample: Sample 1

Type: Default

ID: 3% PE

Standard :

C CaCO3 1-Jun-1999 12:00 AM

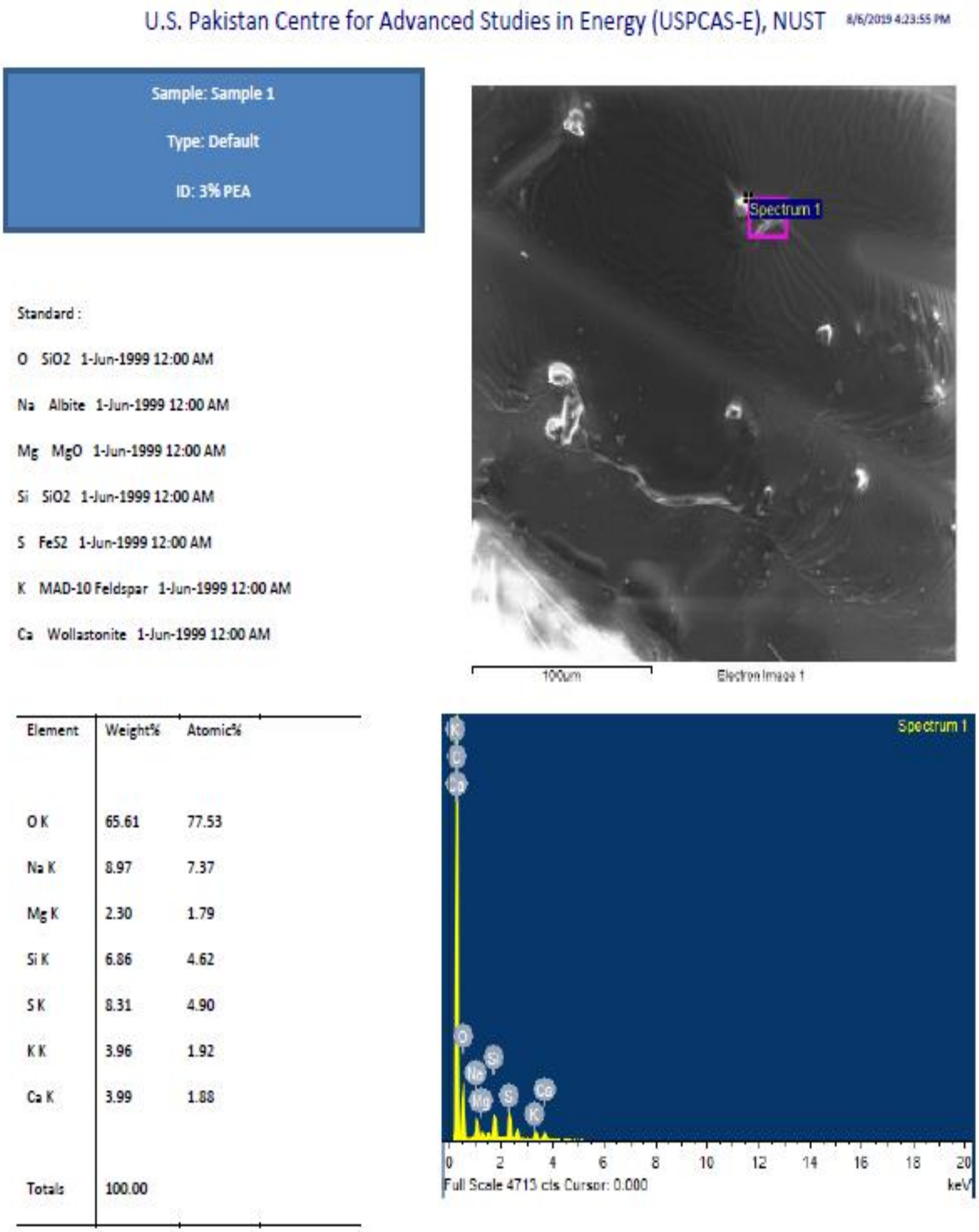
O SiO2 1-Jun-1999 12:00 AM

S FeS2 1-Jun-1999 12:00 AM

Ca Wollastonite 1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
C K	93.60	96.33
O K	3.22	2.49
S K	2.60	1.00
Ca K	0.58	0.18
Totals	100.00	

3% PE UNAGED



U.S. Pakistan Centre for Advanced Studies in Energy (USPCAS-E), NUST 8/6/2019 4:23:55 PM

Sample: Sample 1

Type: Default

ID: 3% PEA

Standard :

O SiO2 1-Jun-1999 12:00 AM

Na Albite 1-Jun-1999 12:00 AM

Mg MgO 1-Jun-1999 12:00 AM

Si SiO2 1-Jun-1999 12:00 AM

S FeS2 1-Jun-1999 12:00 AM

K MAD-10 Feldspar 1-Jun-1999 12:00 AM

Ca Wollastonite 1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
O K	65.61	77.53
Na K	8.97	7.37
Mg K	2.30	1.79
Si K	6.86	4.62
S K	8.31	4.90
K K	3.96	1.92
Ca K	3.99	1.88
Totals	100.00	

Full Scale 4713 cts Cursor: 0.000

3% PE AGED