

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

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### Abstract

With the increase in demand of flexible pavements, due to their various advantages over rigid pavements, there is a need to improve the aging properties of the bitumen in order to enhance its resistance against different types of distresses such as rutting, fatigue cracking. This research focus 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 are evaluated for their effect on the aging mechanism in comparison with the unmodified bitumen. Aging of the original and modified bitumen is realized by the Rolling Thin Film Oven (RTFO) and Pressure Aging Vessel (PAV). Physical properties of the aged and unaged asphalt binders are evaluated through empirical testing like penetration, ductility and softening point 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 asphalt are evaluated with the help of a Dynamic Shear Rheometer (DSR). Results indicate improvement in 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 indicates better oxidation resistance of the modified samples. Morphological analysis proves good compatibility of the modifiers with asphalt binders. DSR results indicate improved viscoelastic properties of the modified binders. Hence it can be concluded that Polyethylene and Sulphur are good options to improve the aging resistance of asphalt in terms of their cost effectiveness and environment friendly nature.

*Keywords:* Bitumen Modification; Aging; Binder Aging; Polyethylene; Sulphur.

### 1. Introduction

Pakistan is a developing country where roads and highways are major source of transportation. Almost 95% of the population and freight movement is served by its major highway [1]. Due to rapid increase in transportation through roads, demand for bituminous pavement has also been increased as flexible pavements are more economical and provide smooth riding quality [2, 3]. Despite the lower construction cost, the life cycle cost of the flexible pavement is higher than the rigid pavement due to its higher maintenance and rehabilitation cost [3].

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

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temperatures. Aging is one of the prime causes of early failure of asphalt pavement [4-6]. Aging is defined as the oxidation of light components which causes the stiffening of bitumen during construction and service phase [5, 7]. It affects the chemical and rheological properties of bitumen, causing it to fail before the estimated service life. Asphalt aging affects the pavement flexibility negatively after many years of service life in field [8]. The process of aging is greatly dependent on the chemical composition of bituminous mixture [4]

A lot of research has been carried out to enhance the aging resistance of bitumen. Various types of polymers like Styrene Butadiene Styrene (SBS) [9], polyethylene [9], polypropylene [9] etc., have been used in asphalt pavements previously. Studies show that these polymer modifiers bring significant improvements in the mechanical, rheological and physical properties of the bitumen. They also found that the type of chemical additive and the aging temperature considerably affect the recovery behavior of asphalt binder [10].

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% [11]. 3% LLDPE improved the mixture stiffness at 40°C as well as the rut depth was also improved measured by wheel tracking test [12]. PE modified bitumen is also tested to tackle the problem of phase separation and storage stability [13]. 3% polyethylene content was suggested to be the optimum content. Polyethylene content of 5% or more was regarded as not applicable because the polyethylene modified bitumen became unworkable at these percentages due to the high values of rotational viscosity [14]. Hamburg wheel track test, resilient modulus, dynamic creep and indirect tensile test were conducted 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 [15].

SBS and sulfur were tested to enhance the storage stability of TR modified bitumen. Results suggested that the Penetration Temperature Susceptibility (PTS) of bitumen was largely decreased. Storage stability improved to higher extent and the Marshall stability and plastic deformation resistance was also enhanced with the addition of sulphur [16]. Addition of Sulphur decreases the viscosity of bitumen. Lower viscosity will lead to decreased mixing and compaction temperature making it more economical and energy efficient [17]. 2% sulfur by weight of asphalt binder at 140°C mixed for 30 minutes results in the best homogenous modification of VG30 binder [18].

Calculation of aging index is one of the most realistic approaches to observe the impact of aging on various characteristics of bitumen. Aging index of asphalt can be defined as the ratio of some property of asphalt after aging to the same property of asphalt before aging as given in Equation 1 [19].

$$\text{Aging index} = \frac{\text{binder property after aging}}{\text{same property before aging}} \quad (1)$$

The aim of this study is to improve the rheological properties of asphalt in terms of aging by using cheap and environment friendly modifiers. Polyethylene which is the main source of plastic is left undisposed, causing the huge waste pollution. Similarly, now days, almost all elemental Sulphur obtained is the by-product of gas and petroleum. Therefore the incorporation of abundantly existing materials into pavement industry is a technique which is both cost effective and environment friendly. Moreover, the addition of the modifiers reduces the cost of the pavement as well as increases the service life of flexible pavements by decreasing the amount of distresses whose major cause is the phenomena of aging in asphalt.

## 2. Research Methodology

Methodology adopted in conducting this research is summarized in the chart below;

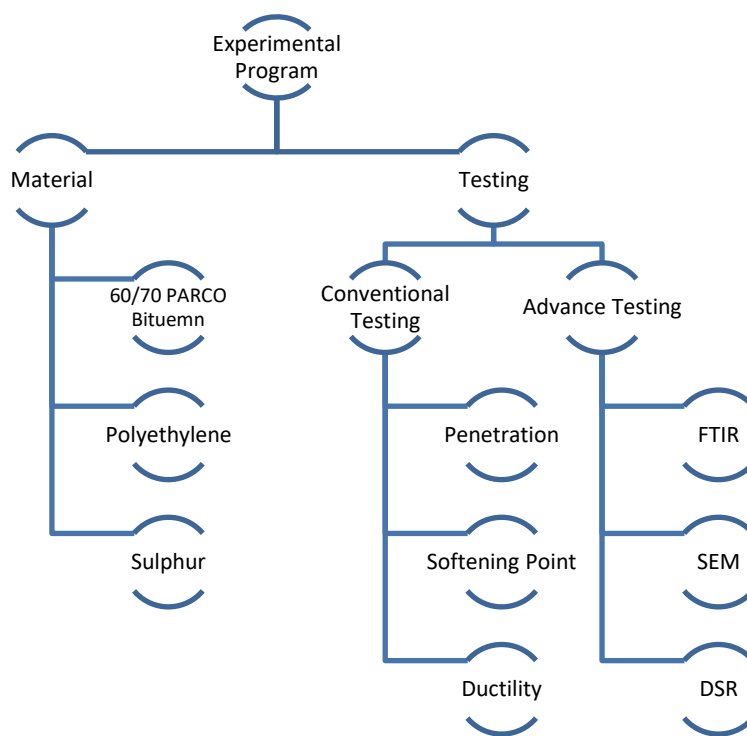


Figure 1. Flow chart of experimental work

2.1. Material Selection

Penetration grade of 60/70 bitumen supplied by PARCO sales office Rawalpindi was used as base bitumen. Table 1 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. Polyethylene (PE) and Sulphur (S) were used as modifiers. 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 and Sulphur are listed in Tables 2 and 3 respectively.

Table 1. Physical properties of 60/70 asphalt

Property	AASHTO Designation	Result	AASHTO Specification
Penetration	T49	66	60-70
Softening Point	T53	49	49/56
Ductility	T51	117	100 cm
Specific Gravity		1.02	1.04 Max
Viscosity at 135.5°C	T316	450cP	≤3 Pa.s

Table 2. Physical properties of polyethylene

Properties	Result
Chemical Formula	(C <sub>2</sub> H <sub>4</sub> ) <sub>n</sub>
Melting Point	115-135 °C
Density	0.88–0.96 g/cm <sup>3</sup>

Table 3. Physical properties of sulphur

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

## 2.2. Preparation of Modified Binder

Samples were prepared by adding three percentages 2, 3 and 5% by weight of polyethylene (PE) and Sulphur (S) into 60/70 base binder. 500g of bitumen for each percentage of each modifier was heated until it turned into liquid. High rate shear mixer was used for the mixing of modifiers into base bitumen at 140°C and 1200rpm. The mixing was continued for about 30 minutes so that P.E and S can be completely dissolved in asphalt binder.

## 2.3. Aging of the Bitumen

Rolling thin film oven (RTFO) was used to feign the effect of short term aging on neat and modified binders. Asphalt in RTFO is aged by heating and blowing of hot air at 163°C for 80 minutes. PAV was used to observe the effect of in-service aging of bitumen i.e. long term aging. The binder was exposed to high temperature of 100°C and a pressure of 2.1 MPa for 20 hours in pressure aging vessel.



Figure 2. Pressure Aging Vessel (PAV)



Figure 3. Rolling Thin Film Oven (RTFO)

## 2.4. Conventional and Rheological Testing

Penetration, ductility and softening point test were performed on neat and modified binders before and after aging. To amount the consistency of bitumen at room temperature, penetration test was performed according to AASHTO specification T49. Softening point of all test samples was determined using Ring and Ball apparatus according to ASTM D36 and ductility test was performed according to ASTM D 113-17.

Rheological characteristics of neat and modified binders were determined using Dynamic Shear Rheometer (DSR). Dynamic shear rheometer measures the bitumen 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 ( $\delta$ ) of bitumen. DSR is also used to calculate the performance grade of bitumen. DSR used in this research was made of Anton Paar model 101.25 mm and 8 mm DSR plate geometries were used for this study. Gap between two plates was kept 1 mm and 2 mm for 25 mm and 8 mm sample respectively. Test was performed at temperature ranges of 45, 52, 58, 64, 70, 76, and 82 and at a constant frequency of 1.59 Hz.



Figure 4. Dynamic Shear Rheometer (DSR)

## 2.5. Chemical and Morphological Analysis

Fourier transformed infrared spectroscopy was used to examine the chemical and structural modification of different samples and to evaluate the influence of aging on modified bitumen. IR radiations were passed through the sample. The wavelength ranges from 4000 to 400  $\text{cm}^{-1}$ . The resulting spectrum represents the molecular transmission and absorption of the sample. Morphological analysis of the modified binders before and after aging was carried out by Scanning Electron Microscope. 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 bitumen uniformly on the surface of the slide in the form of thin layer to study the dispersion of the modifiers in asphalt binder. The samples were first coated with a thin gold palladium film and after sputtering, SEM images were taken at different magnifications.



Figure 5. Fourier Transformed Infrared Spectroscopy



Figure 6. Scanning Electron Microscope

## 3. Results and Discussion

In this research, different physical and rheological aging index were used to observe the impact of aging on various characteristics of neat and modified bitumen. Aging index can be described as the ratio of given property of aged asphalt binder to the same property of unaged bitumen. Aging index used in this research are Penetration Aging Ratio (PAR), Softening Point Increment (SPI), Ductility Retained Ratio (DRR), Phase Angle Aging Index (PAAI) and Complex Modulus Aging Index (CMAI) which can be calculated by the given formulas:

$$\text{Penetration Aging Ratio (PAR)} = \frac{\text{Aged Penetration Value}}{\text{Unaged Penetration Value}} \times 100 \quad (2)$$

$$\text{Softening Point Increment (SPI)} = \text{Aged Softening Point} - \text{Unaged Softening Point} \quad (3)$$

$$\text{Ductility Retained Ratio (DRR)} = \frac{\text{Aged Ductility Value}}{\text{Unaged Ductility Value}} \times 100 \quad (4)$$

$$\text{Phase Angle Aging Index (PAAI)} = \frac{\text{Aged Phase Angle}}{\text{Unaged Phase Angle}} \quad (5)$$

$$\text{Complex Modulus Aging Index (CMAI)} = \frac{\text{Aged Complex Modulus}}{\text{Unaged Complex Modulus}} \quad (6)$$

### 3.1. Penetration Test Results

Penetration value represents the stiffness and hardening of asphalt binder at normal temperature. Lower the value of penetration higher the stiffness of bitumen. From Figure 7(a), it can be perceived that with the rise in polyethylene content from 1 to 5%, the penetration value of bitumen decreased which is an indicative of decrease in fluency and increase in the consistency of asphalt binder at normal temperature. By addition of 2 to 5% sulphur into the base binder, the penetration value increases significantly as shown in Figure 7(b) [20]. It indicates that sulphur has a plasticizing effect on asphalt binder and it has more resistance against thermal cracking especially at low temperatures [21].

The penetration results after the short term aging and long term aging of the modified bitumen are presented in the form of PAR in Figures 8(a) and 8(b). PAR of the sulphur modified binder and polyethylene modified binder as shown

in figures reduced significantly which indicate that the modified bitumen is more resistant to oxidative aging than the virgin bitumen.

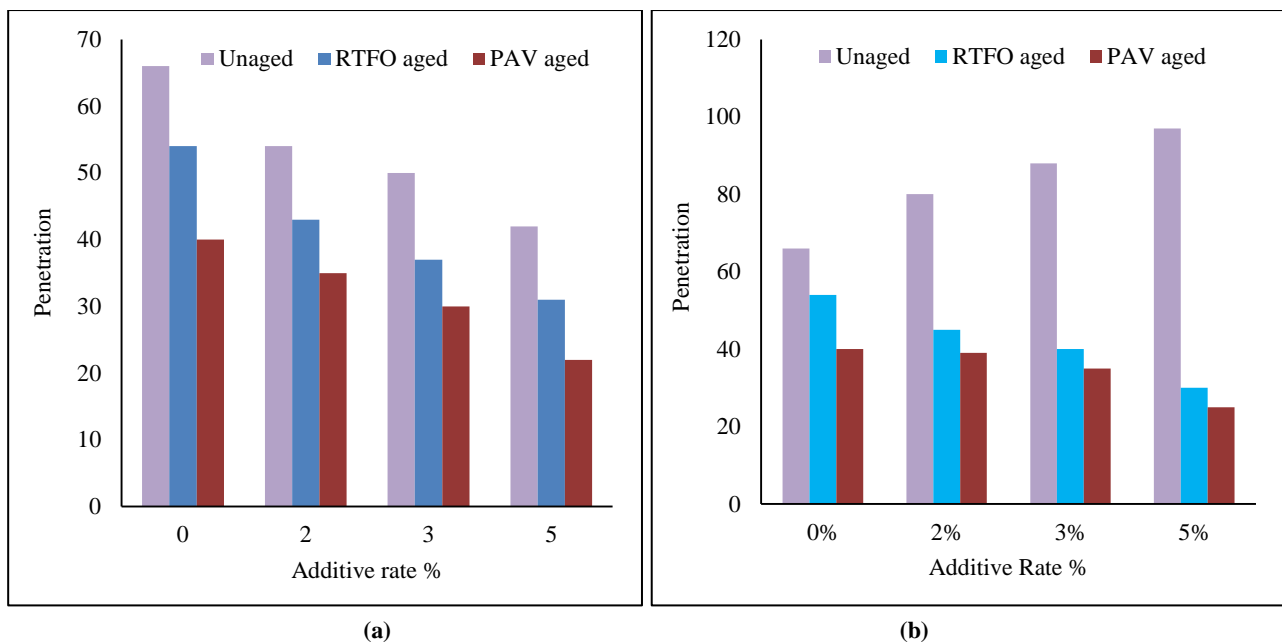


Figure 7. Penetration value of (a) Polyethylene modified bitumen and (b) Sulphur modified bitumen

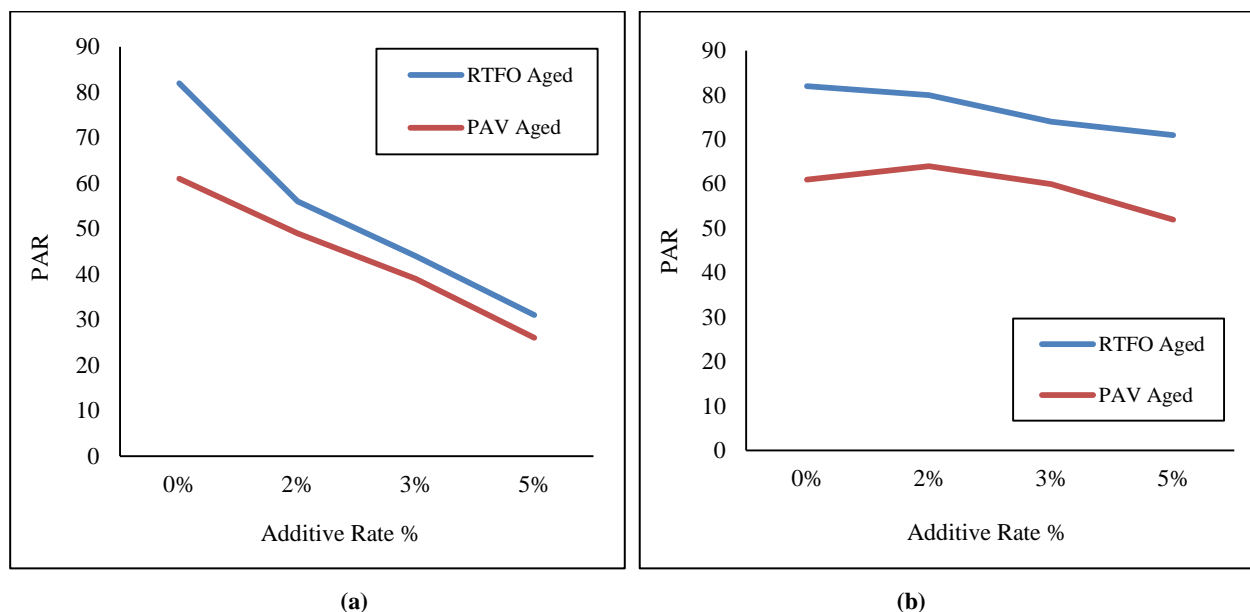


Figure 8. PAR graph of (a) Polyethylene modified bitumen and (b) Sulphur modified bitumen

### 3.2. Softening Point Test Result

By adding 2% to 5% of polyethylene into the base binder, softening point of the 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 Figures 9(a) and 9(b). It is generally concluded that the addition of PE improved the high temperature flowing properties of bitumen and made it more stable against flowing. It means that the PE modified bitumen has a better high temperature rutting resistance.

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 aging, the hardening level of modified bitumen binder kept on increasing. This can be observed by the increase in softening temperature after the two aging. Higher softening point asphalt cement is mostly preferred in hot regions.

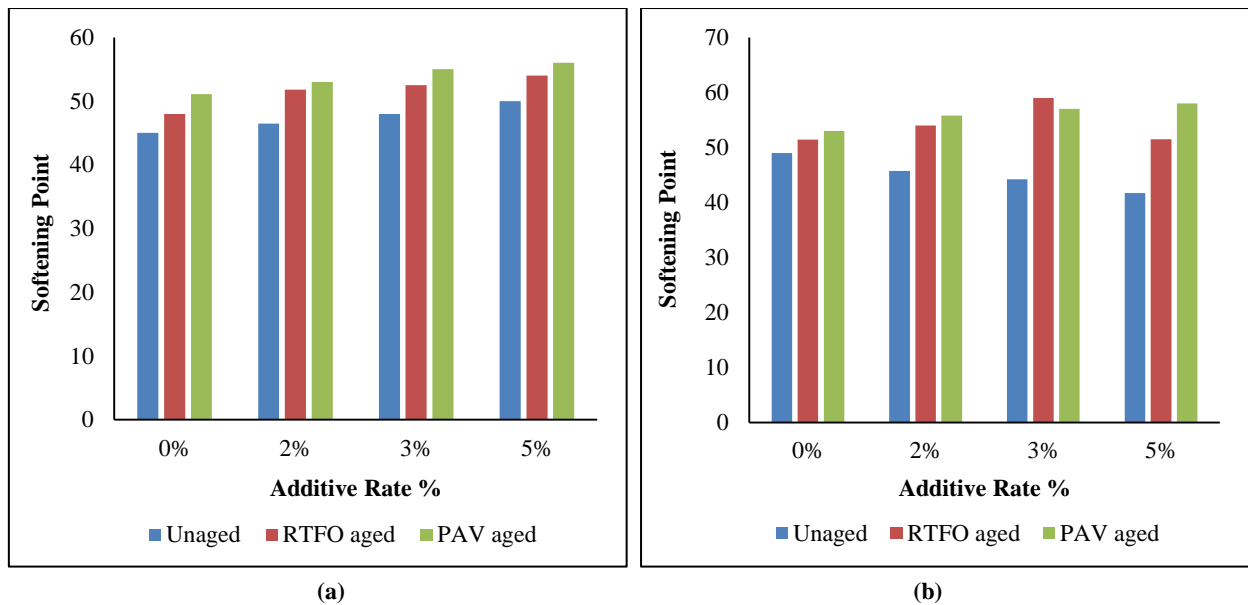


Figure 9. Softening Point of (a) Polyethylene modified bitumen and (b) Sulphur modified bitumen

### 3.3. Penetration Index

It is a quantitative measure of the response of bitumen to the variations in temperature as described by Pfeiffer and V Doormaal [22]. The type of binder can be identified by its penetration index. Its value generally lies between -3 and +7. (-3) for highly temperature prone bitumen and (+7) for less temperature prone or highly blown bitumen. Higher PI values indicate higher temperature resistance. [19]. Generally for road construction, asphalt binder has PI between -2 to +2. Penetration Index (PI) is calculated by following Equation 7 [22].

$$PI = \frac{1952 - 500\log(\text{pen}) - 200SP}{50\log(\text{pen}) - SP - 120} \tag{7}$$

Where;

Pen = Penetration

SP = Softening Point

All the PI values obtained in our case are within the normal range of -2 to +2 for road paving application and shown in Figure 10. The upsurge in PI values indicated the lower temperature vulnerability of modified bitumen.

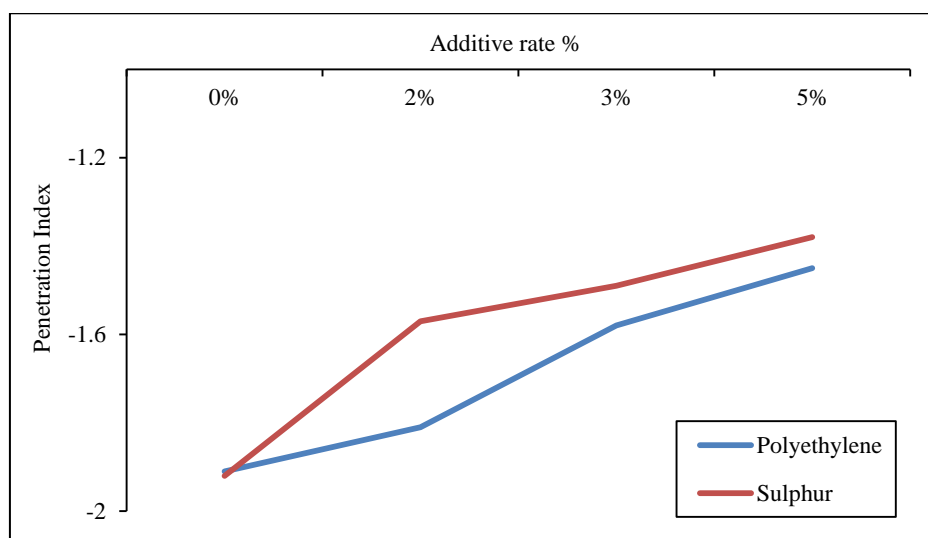


Figure 10. Comparison of Penetration Index of Polyethylene and Sulphur

### 3.4. Ductility Test Results

Ductility retained ratio (DRR) is another way of evaluating the impact of aging on the ductile characteristics of

bitumen. DRR of polyethylene and Sulphur modified binder is displayed in Figures 11(a) and 11(b) respectively. DRR in both cases is increasing which represented that the addition of PE and S can reduce deterioration in ductility of asphalt during aging. At 3% addition of PE the ductility value reduced from 100 to 83 causing a decrease of 25% with respect to base binder.

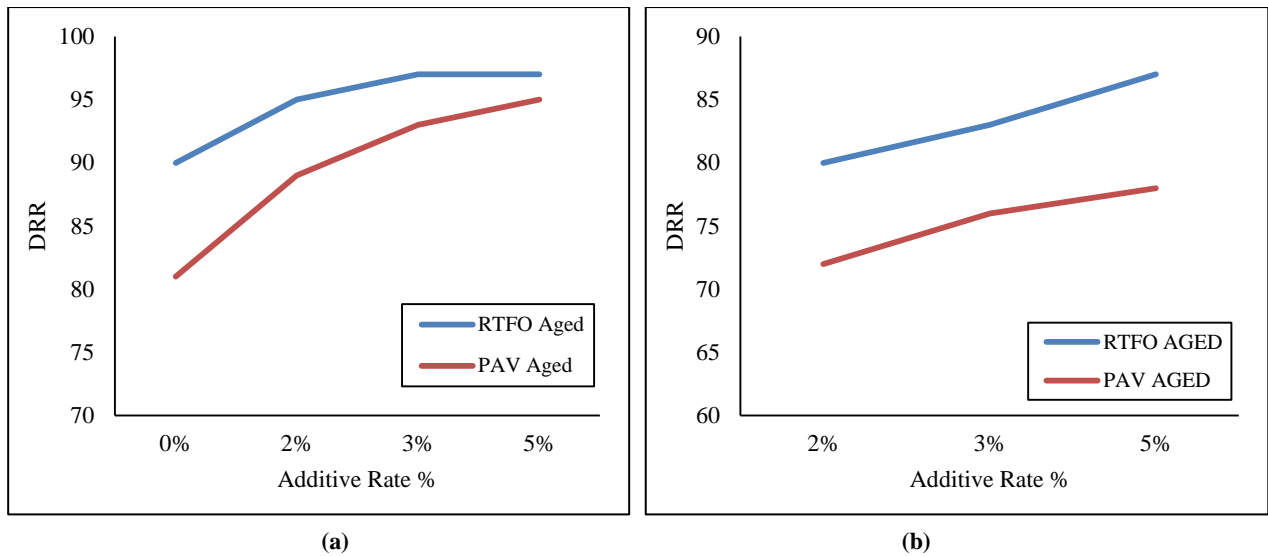


Figure 11. Ductility Retained Ratio for (a) Polyethylene modified bitumen and (b) Sulphur modified bitumen

### 3.5. FTIR Results

Figures 12(a) and 12(b) demonstrate the IR spectra of neat asphalt binder and 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.

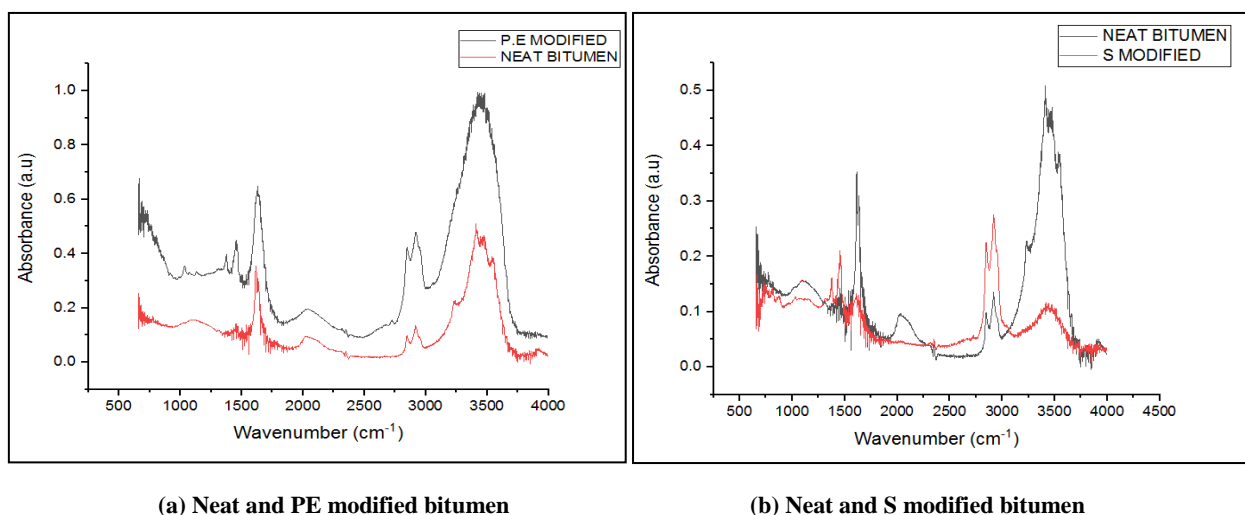


Figure 12. IR Spectra of Neat and modified bitumen

IR spectra of neat and modified bitumen after short term aging are shown in Figure 13. 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 [23]. Structural index was computed by numerical integrating peak of target functional group and then dividing it by entire area between 600 cm<sup>-1</sup> to 2000 cm<sup>-1</sup> [24]. Carbonyl index and sulfoxide index can be calculated by

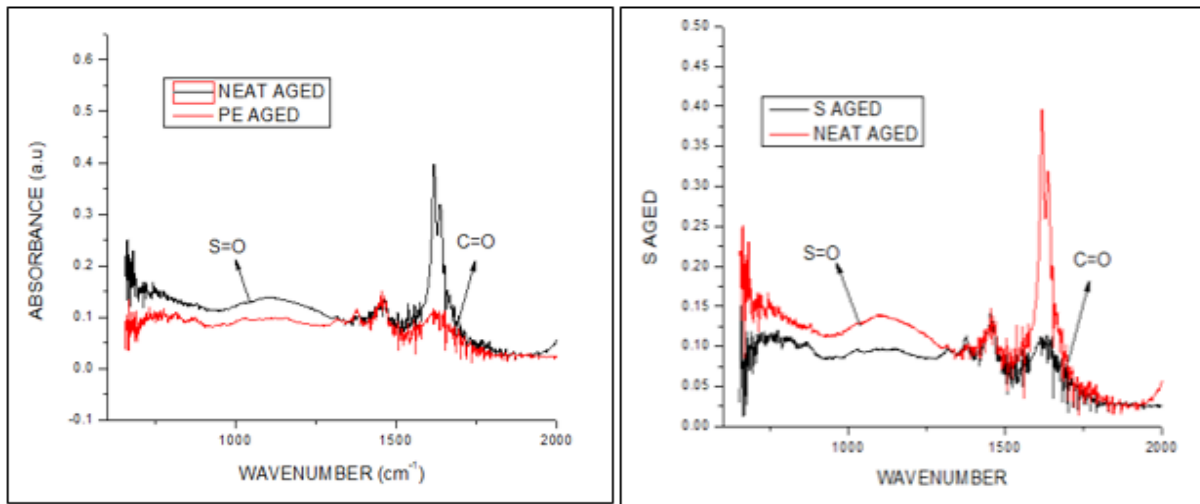


numerically integrating the peak of carbonyl and sulfoxide functional groups at 1750 and 1030 respectively and dividing it by the sum of specific areas as given in Equations 8 and 9.

$$\text{Carbonyl Index} = \frac{A_{1750}}{\sum A} \tag{8}$$

$$\text{Sulfoxide Index} = \frac{A_{1030}}{\sum A} \tag{9}$$

Carbonyl and sulfoxide index of the modified binders decreased with respect to neat binder as presented in Figure 14. 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 indicates the greater capability of the modifiers to resist oxidation in asphalt.



(a) Neat and PE modified bitumen

(b) Neat and S modified bitumen

Figure 13. IR spectra of bitumen after aging

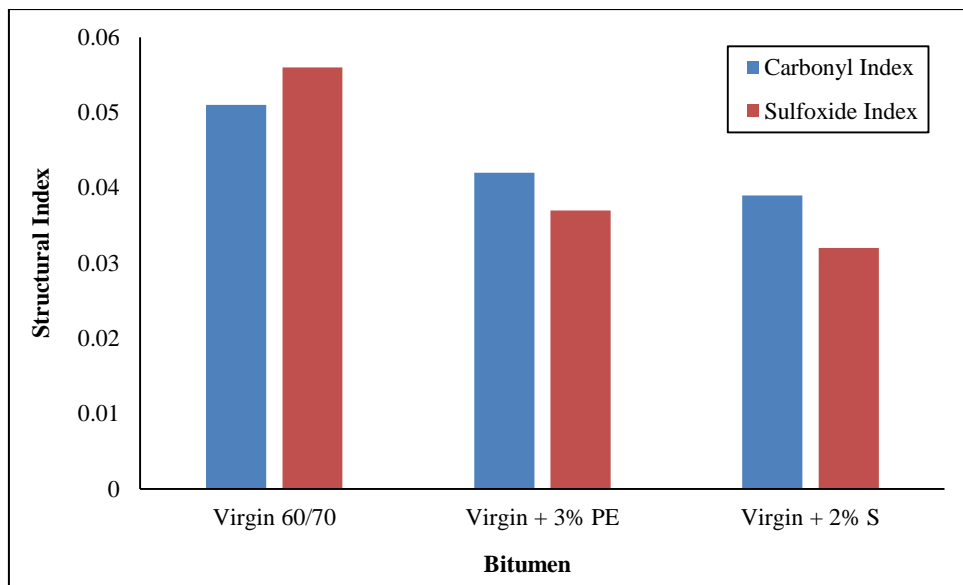


Figure 14. Structural index of neat and modified binders after RTFO

### 3.6. SEM Results

Scanning electron microscope test was performed to determine the compatibility and homogeneous dispersion of modifiers in base bitumen. SEM images of modified binders are shown in Figure 15. Asphalt binder itself is in black color while white patches shows the presence of modifiers i.e. PE and S. As compared with neat bitumen the roughness of surface of sulphur modified bitumen was more and it is increased as the percentage of sulphur in bitumen was increased from 2 to 5%. Tiny particles of sulphur either swollen or dispersed inside the base bitumen can be seen

in SEM images of 2, 3 and 5% sulphur by weight of bitumen. These images also show that bitumen is homogenized thus it represents the compatibility of modifier with bitumen.

SEM images before and after aging shows good compatibility of modifiers with base binder. Even after the aging, no phase separation was observed and the surface area was smooth with small irregularities. Therefore it can be concluded that the modifiers are compatible with the base bitumen and their dispersion is homogenous.

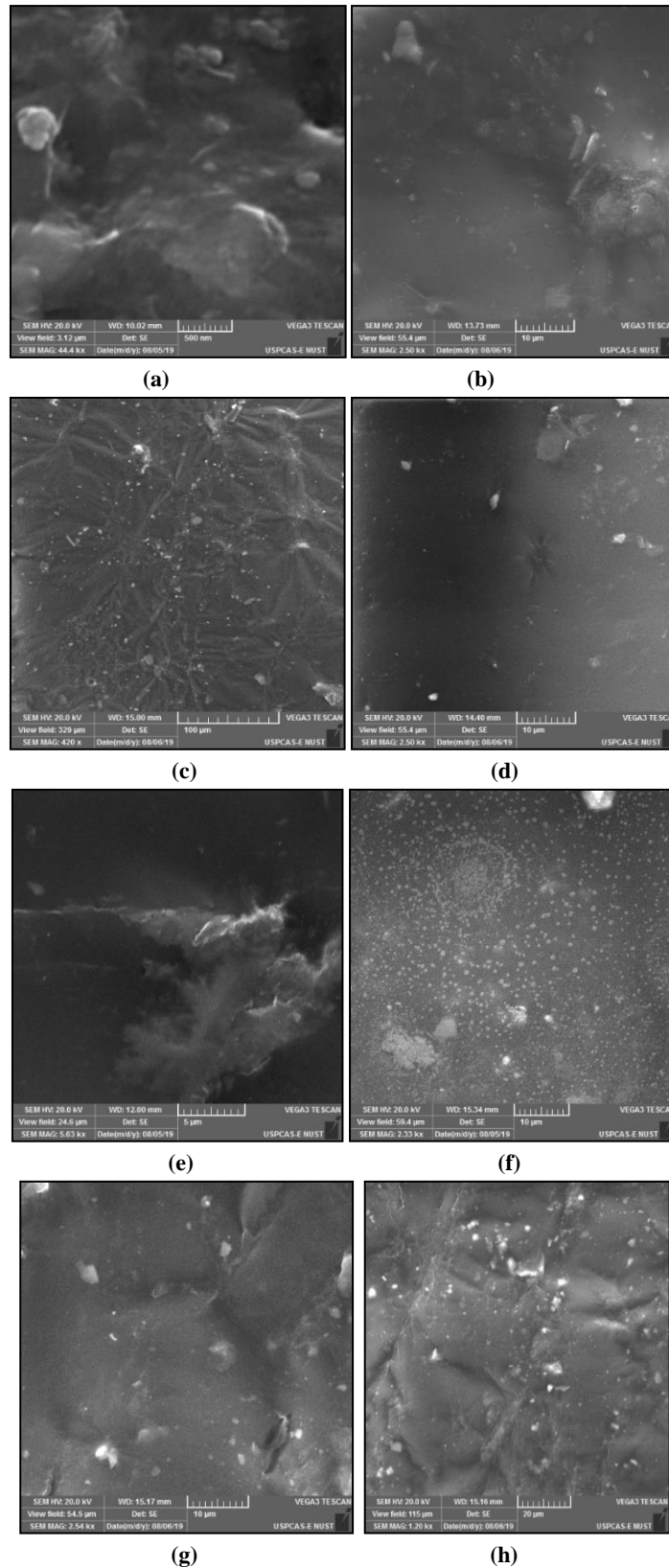


Figure 15. SEM images (a) 2% S unaged, (b) 2% S aged, (c) 3% PE unaged, (d) 3% PE aged, (e) 3% S, (f) 5% S, (g) 3% PE, (h) 5% PE

### 3.7. Dynamic Shear Rheometer Analysis

DSR test was performed to check the rheological characteristics of bitumen at intermediate to high temperatures of 45, 52, 58, 64, 70, 76, and 82. Original, modified aged and unaged sample were tested. Complex modulus  $G^*$  and phase angle  $\delta$  were obtained as a result to assess the viscoelastic behavior of different asphalt samples.

### 3.8. Behavior of Original Bitumen

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

### 3.9. Effect of Modifiers

The effect of modification on the bitumen was obvious as shown in Figure 16. 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.

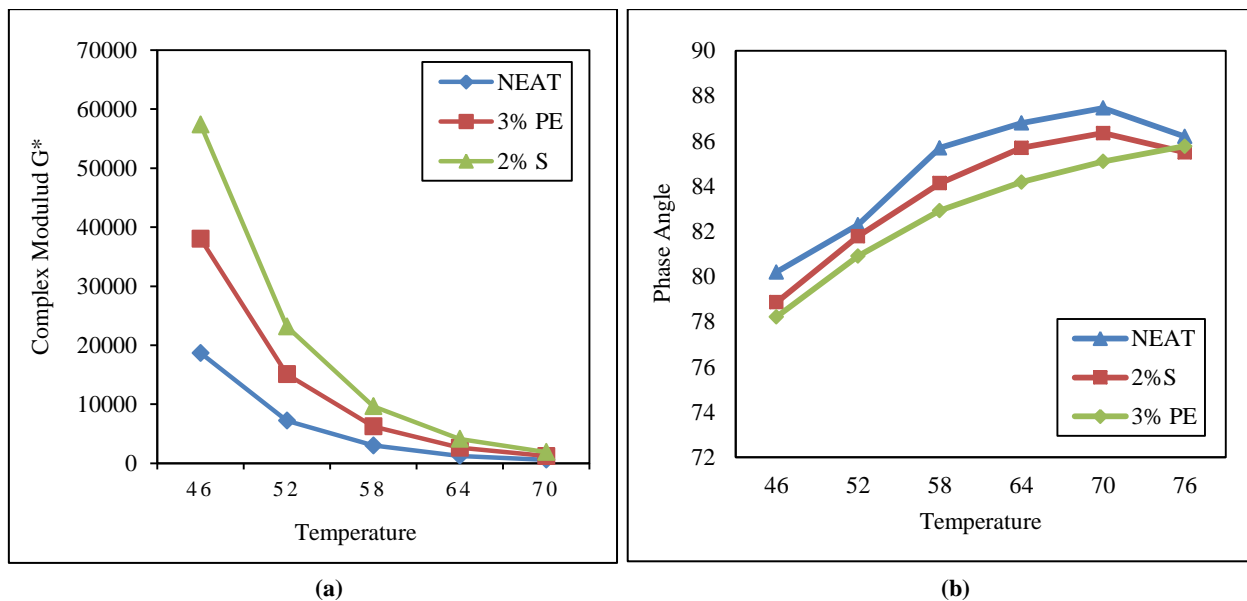


Figure 16. Variation of (a) Complex Modulus and (b) Phase angle of Neat and Modified bitumen before aging

### 3.10. Intermediate and High Temperature Performance Characteristics

Impact of aging on the rheological performance of neat and modified bitumen was evaluated in terms of rheological aging indices. Complex modulus aging index (CMAI) from Equation 10 and phase angle aging index (PAAI) from Equation 11 were used to assess the aging properties of asphalt binder.

$$\text{Phase Angle Aging Index (PAAI)} = \frac{\text{Aged Phase Angle}}{\text{Unaged Phase Angle}} \tag{10}$$

$$\text{Complex Modulus Aging Index (CMAI)} = \frac{\text{Aged Complex Modulus}}{\text{Unaged Complex Modulus}} \tag{11}$$

### 3.11. Complex Modulus Aging Index (CMAI)

The results of CMAI of neat and modified bitumen are presented in Figure 17(a).  $G^*$  value indicate the bitumen's total resistance to permanent deformation. Generally lower value of CMAI indicate higher resistance to aging [25]. Figure 17(a) shows that the CMAI of both modified bitumen 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.

### 3.12. 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 [26]. It can be seen in the Figure 17 (b) 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.

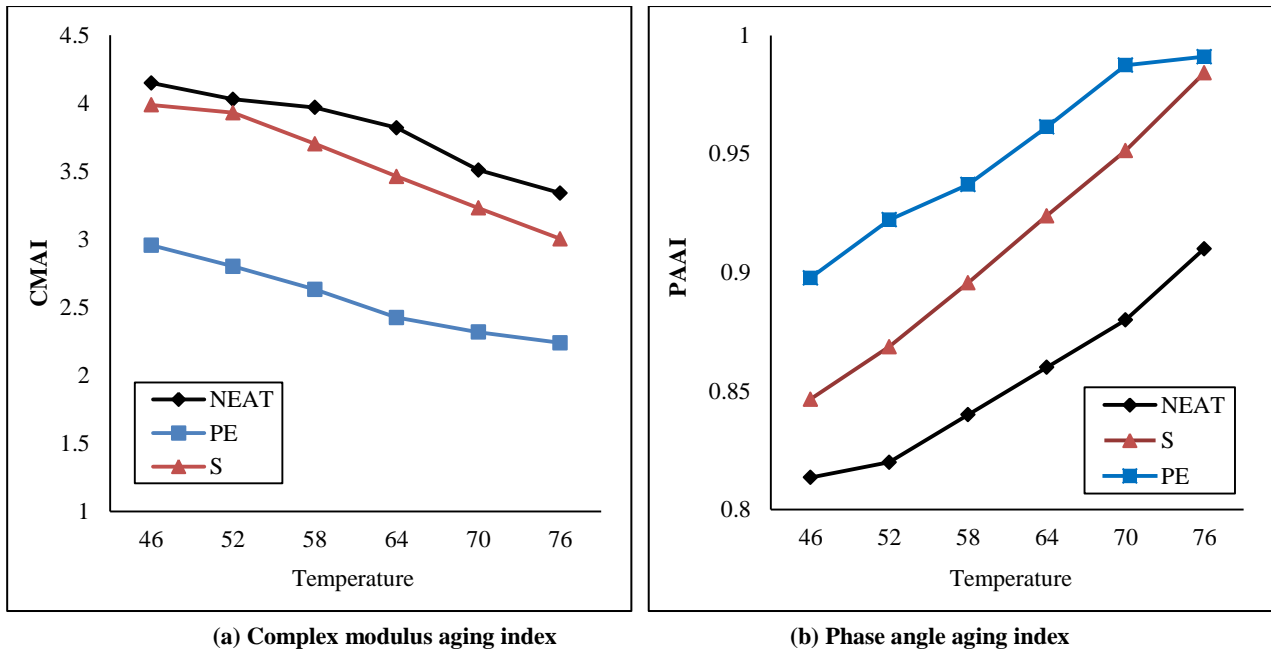


Figure 17. Rheological aging index of neat and modified bitumen

### 3.13. Determination of Failure Temperature

To determine the failure temperature of neat and modified bitumen, temperature sweep test was performed. SHRP rutting factor parameter was considered as the failure criteria when it gets below 1 kPa for unaged bitumen and 2.2 kPa for RTFO aged bitumen samples. Failing temperature of the unaged binder improved from 64°C to 70°C and 71.5°C for PE modified and S modified binder respectively. While after the RTFO, the failure temperature increased to 73.5°C for polyethylene modified binder and 75°C for sulphur modified binder. This improvement in the failure temperature, as shown in Figure 18, indicate the improved rutting resistance of modified binders. Performance grade of the bitumen increased from PG64 to PG70 in case of polyethylene and sulphur.

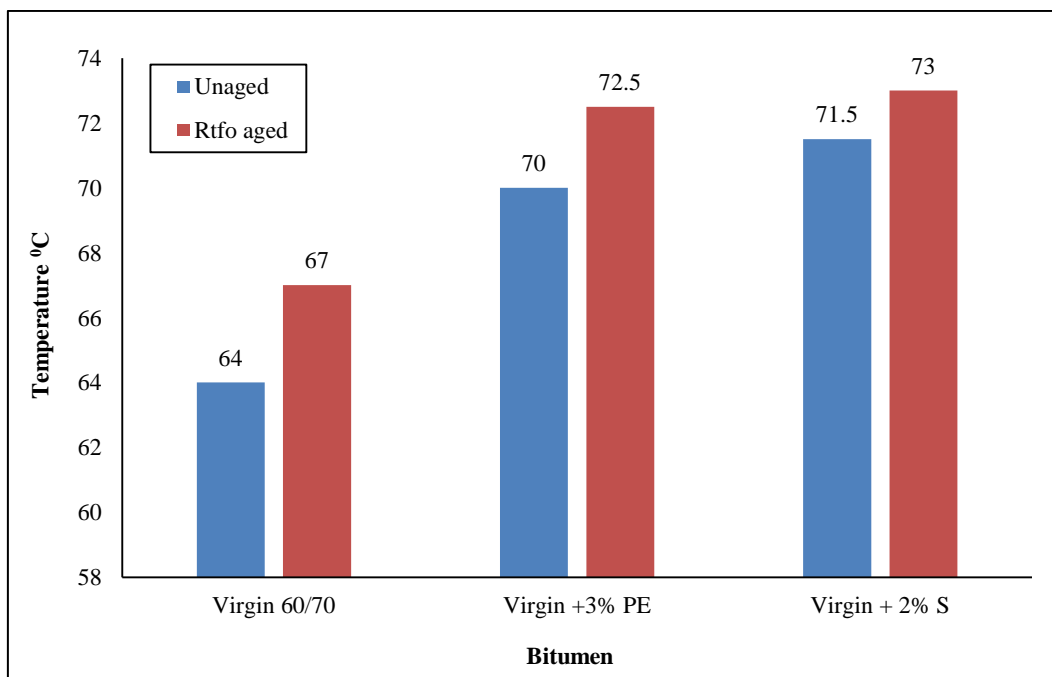


Figure 18. Failure Temperature of Neat and Modified Binders

## 4. Conclusions

Present study was conducted to determine Polyethylene and Sulphur effect on the aging properties of PARCO 60/70 grade bitumen. Increase in the performance related properties of bitumen increases the service life of roads. To observe the effect of modifiers on the Performance Grade of bitumen, performance testing of modified and unmodified bitumen was carried out. The results gave promising benefits of using polyethylene and Sulphur as bitumen modifiers. Physical properties of the modified bitumen improved as well as the rheological characteristics of modified bitumen in terms of aging enhanced greatly, thus decreasing the amount of distresses and reducing the pavement cost. The key findings are concluded as:

- All the physical characteristics of the modified bitumen improved before and after aging;
- Penetration index increased by 10% for Polyethylene modified binder and 36% for Sulphur modification which indicate better resistance against thermal cracking of the pavement at low temperatures, and lower permanent (plastic) deformation at high temperatures;
- Addition of Polyethylene and Sulphur into base binder is a Physical process;
- Aging resistance of the modified binder improved which is indicated by decrease in Carbonyl and Sulfoxide index;
- SEM analysis shows the compatibility of modifiers and their homogenous dispersion in base binder;
- Complex modulus aging index of the modified binders is less than the base binder at all temperatures which indicate higher resistance against permanent deformation;
- Phase angle aging index of the modified binders is less than the base binder which indicates improved viscous behavior and improved low temperature cracking resistance;
- Rutting resistance of the modified binders enhanced which is indicated by increase in failure temperatures;
- Performance grade of the binder improved from PG-64 to PG-70.

## 5. Funding

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## 6. Conflicts of Interest

The authors declare no conflict of interest.

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