DEVELOPMENT AND EVALUATION OF SULPHUR MODIFIED BITUMEN BINDER

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ABSTRACT

The performance of a bituminous pavement mainly depends on the properties of binder used, volumetric properties of bituminous mixtures and external factors such as environment and traffic volume. The higher traffic volume producing higher stresses and temperature variations affecting the binder performance are the main causes for pavement distresses in the form of fatigue cracking and permanent deformation. The solutions to reduce such pavement distresses are mostly in the form of modifying the normal bitumen by using certain additives to give the conventional bitumen better engineering properties and as such are helpful to extend the life span of the bituminous pavement.
In this work, an investigation has been made to use commercial sulphur available in local market to modify the conventional bitumen and the modified binder thus developed has been evaluated in the form of its rheological properties. The conventional VG 30 bitumen was used in this work for modification with sulphur at different levels (by weight of the bitumen). The rheological properties of the modified and unmodified binders were studied using a Dynamic Shear Rheometer (DSR). It is observed that the addition of only 2% sulphur with conventional VG 30 bitumen, prepared at 120^{0}C temperature results in satisfactory rheological properties. Further, as a part of DSR test, it has been possible to study the effects of aging on the rheological properties of unmodified and modified binders. It is observed that the modified binders considered in this study perform much better than the unmodified binders.

Keywords: DSR, Sulphur modified binder, complex shear modulus, phase angle, binder aging.

1. INTRODUCTION

Bitumen is widely used as a binder in constructions of highway flexible pavements due to its viscoelastic and thermoplastic properties. Bitumen normally becomes brittle at low temperature and even at an average temperature causes load associated fatigue cracking of the bituminous surface. Similarly, at relatively high temperature in summer, it becomes soft, causing rutting failure of the bituminous layer. Generally these two types of failures are very common in India particularly in pavements with high volume of heavy traffic. The characteristic performance of a bituminous pavement mainly depends on the properties of bitumen, volumetric properties of bituminous mixtures and external factors such as environment and traffic volume. Bitumen is a visco-elastic material where the temperature and rate of load application have a great influence on its behaviour. Conventional bituminous binder is exposed to a range of loading and atmospheric weather conditions. The higher traffic volume producing higher stresses and temperature variations affecting the binder performance

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are the main causes for pavement distresses, in the form of fatigue cracking and permanent deformation, which reduce the service life of the pavement and thus increase the cost of maintenance. With the quality and grading of aggregates remaining almost the same, these two failures can be attributed to the bitumen used, whose property changes with temperature and rate of loading. The contribution of the bituminous binder for the mixture performance in respect of these two failures is better addressed by the rheological characteristics. Therefore, in order to enhance the properties of conventional bitumen so as to improve the performances of bituminous mixture, it has been a common practice to modify the conventional bitumen by effectively using some modifiers. Among the different types of additives used with conventional bitumen, sulphur has been observed to be an effective extender for conventional bitumen and the basic physical properties like ductility, elastic recovery, viscosity and softening point of the bitumen are improved. It is seen that the sulphur extended bitumen has been useful in case of sand used as aggregate. This paper is an attempt to develop and explore sulphur modified bitumen that satisfies the requirements mainly in terms of rheological properties, which ultimately contributes to the viscoelastic characteristics of the resultant bituminous mixtures. Aging of bituminous binder is also a phenomenon which is now-a-days addressed before selecting a particular binder for a bituminous mix as this effect may cause serious pavement related failures before the expected design life. As per the available specifications, the binders are subjected to short term and long term aging and the aged binders thus developed are subjected to rheological tests to assess the binder characteristics which may be suitable for the paving works. This work involves several trials of preparation of this modified binder with variation in temperature and time of binder preparation and finally the optimum dosage of sulphur to result in the best binder in terms of the rheological characteristics for both aged as well as un-aged binders has been determined.

The main objectives of the present experimental work are summarized below.

- To develop a procedure for most appropriate modification of bitumen by dry sulphur with necessary temperature for mixing/blending and determine the optimum sulphur content required for modification.
- To study the rheological characteristics of sulphur modified bitumen (SMB) in terms of its rheological characteristics.
- To study the influence of sulphur on ageing characteristics of bituminous binder in terms of rheological characteristics.

2. BRIEF BACKGROUND OF LITERATURE

Chemical bonding of sulphur to bitumen leads to a new binder in which asphaltenes present a more gel-like structure resulting from a higher ability to form aggregates and decrease in dynamic mechanical properties with respect to pure binder **(Fritschy et al. 1981)**. Bitumen modification with sulphur results in improved physical properties than the conventional VG30 grade bitumen and the ageing criteria of the sulphur modified bitumen is within its permissible limits **(Kumar and Khan 2013).** The incorporation of the modified sulphur pellets, up to 40 per cent by mass of the total binder volume, does not have any effect on the low-temperature cracking property of the asphalt mixture. The sulphur extended asphalt mixtures, made with sulphur pellets show less thermal and loading-time susceptibility than the conventional asphalt mixture made with bitumen only **(Strickland et al. 2008).** Sulphur modified asphalt mixtures can be tailored to provide pavement structural enhancement through improved material properties as well as energy savings, i.e. bitumen saving, energy savings during production, and possibly pavement thickness reduction or longer pavement life **(Colange 2011).** Compared to normal mixes, sand-asphalt-fly ash-sulphur mixes have higher stability values and lower air voids. The flexural strength and fatigue life under repeated loading of some selected mixes were found to be higher than those of an asphalt concrete mix **(Mazumdar and Rao 1993)**. A study on modification of asphalt with styrene-butadiene block copolymers and sulphur suggest that sulphur increases the compatibility between polymer and asphalt by cross linking polymer chains **(Martinez et al. 2010).** Study relating to effect of long term aging on Polymer modified asphalt

binder resulted in increase of asphalt complex modulus at high temperatures and decreased modulus at low temperatures **(Ruan et al. 2003)**.
From the above review of literature it is observed that the rheological characteristics of sulphur modified bitumen prepared as per a simple procedure needs to be studied under both aging and un-aging conditions so that the viscoelastic parameters related to the binder are understood, which provides the motivation for the present work.

3. EXPERIMENTAL PROGRAM

3.1 Materials Used

In this research work bitumen considered for modification was viscosity grade VG 30 bitumen as this bitumen is commonly used for most types of roads in India and is also easily available in many places. The basic physical characteristics of VG 30 bitumen are given in Table 1. The physical properties of commercial sulphur in powder form, procured from local market and used for the modification of conventional VG 30 bitumen are given in Table 2.

Table 1: Physical properties of VG-30 bitumen used

Properties	Test Result	Specification Requirements (IS 73: 2013)
Absolute Viscosity @ 60^{0}C (Poise)	2512	2400 -3600
Kinematic Viscosity @ 135^{0}C (cSt)	449.7	350 min.
Softening Point (^{0}C)	49.5	47 min.
Penetration Value @ 25^{0}C (dmm)	58	45 min.
Ductility (cm)	>100	-
Elastic Recovery (%)	26	-

Table 2: Physical properties of commercial Sulphur used

Properties	Result
Appearance	Yellow crystalline solid
Melting point	120^{0}C
Specific Gravity	1.92

3.2 Preparation of Modified Binder

To modify VG 30 bitumen with sulphur, about 1.0 Kg of bitumen was taken in a three-liter aluminum container and gradually heated to temperatures varying from 90^{0}C to 140^{0}C. Sulphur content was varied from 1 to 8% by weight of the binder. When bitumen attains a particular pre-decided temperature, required quantity of sulphur in powder form was added to the hot bitumen slowly. Initially, the ingredients were manually stirred for about 5 minutes and subsequently, the cover with a central hole for the stirrer rod was fitted to the top part of the container. Vigorous stirring of the ingredients i.e., bitumen and Sulphur, was carried out at a pre-decided temperature for about 30 minutes using a mechanical stirrer rotating at a constant speed of about 3000 R.P.M. The time of blending of 30 minutes was decided based on several earlier trials made. The specified temperature of the binder in the container was maintained constant throughout with the help of a temperature controller. The binder thus developed is physically checked for its homogeneity.

3.3 Ageing of Binder

Ageing of both modified and unmodified bituminous binders are effected in terms of short term ageing and long term ageing using Rolling thin film oven test (RTFOT) and Pressure ageing vessel (PAV) respectively in the laboratory, in accordance with ASTM D2872 (2012) and ASTM D6521 (2013) specifications. Briefly, the short term ageing was performed under hot air flow condition at 163^{0}C temperatures for 85 minutes, while the long term ageing was performed in a pressurized and heated closed air tight vessel with air blow of 2.1 MPa at 100^{0}C temperature for 20 hours. Further, PAV residue had to undergo degassing at 170^{0}C for 30 minutes.

3.4 Testing program

The rheological properties of modified and unmodified bituminous binders thus developed for aged and un-aged conditions were assessed as described below.
A Dynamic Shear Rheometer (DSR) was used to conduct dynamic mechanical analysis as per AASHTO T315-08 (2011) procedure to determine the important rheological characteristics of the binders under control stress conditions. In DSR, Strategic Highway Research Program (SHRP) grade determination tests were conducted at a frequency of 10 rad/s. The SHRP grade determination test is essentially required for any bituminous binder to qualify for its acceptability in paving mixes as per the superpave specifications. The frequency sweeps were carried out over a range of 0.1–10 Hz at fixed stress amplitude at a temperature of 60^{0}C. Similarly, the temperature sweeps were executed from 15^{0}C to 60^{0}C with 5^{0}C increments at a fixed frequency of 10 rad/s. Parallel plate of 8 mm dia with a gap of 2.0 mm for fatigue characterization and 25 mm parallel plate with 1.0 mm of gap for rutting characterization were used. In every test, about 1.0 g of sample was applied between the parallel plates, covering the entire surface mounted in the rheometer. The sample was heated until it attains sufficient flowability and a drop of it was placed on the bottom plate, the top plate was brought into contact with the sample, and then it was trimmed. The final gap was adjusted to 1 mm and 2 mm according to the requirements. A sinusoidal stress was then applied by an actuator. The resulting viscoelastic parameters such as complex modulus (G*) and phase angle (δ) were determined through a computer software.

4. RESULTS AND DISCUSSIONS

4.1 Development of modified Binder and Evaluation of modified Binder

For development of sulphur modified binder two parameters namely, temperature of mixing and quantity of sulphur in the binder, were considered to be most important. These two parameters have been related to the basic rheological characteristics of the modified binders in terms of fatigue and rutting behavior represented by the output results of the SHRP grade determination test such as phase angle (δ) and complex modulus (G*) value as described in the following paragraphs. The modified binders have been evaluated basically with respect to these two rheological characteristics.

4.1.1 Selection of blending temperature

The temperature of blending was varied from 90^{0}C to 140^{0}C with 10^{0}C increments. This temperature range was chosen considering the viscosity pattern of normal bitumen and also more importantly of sulphur with respect to temperature. Similarly the sulphur content was varied from 1% to 8%. The variation of complex modulus which was determined as a result of SHRP grade determination test, with temperature of binder formation for binders with different sulphur content is given in Figure 1. From this figure, it is clearly seen that the maximum complex modulus results when sulphur content in the binder is 2% and temperature of binder formation is 120^{0}C. It is also observed that higher sulphur content of more than 4% though requires more temperature, yet does not result that much of complex modulus i.e., even less than that for neat bitumen. This is because of difficulty of higher sulphur content to be blended at lower temperature. The best temperatures required for proper binder formation are 120^{0}C, 130^{0}C and 140^{0}C for sulphur contents of 1% to 4%, 6% and 8% respectively. The binders thus prepared at their optimum temperatures have been used for subsequent tests.

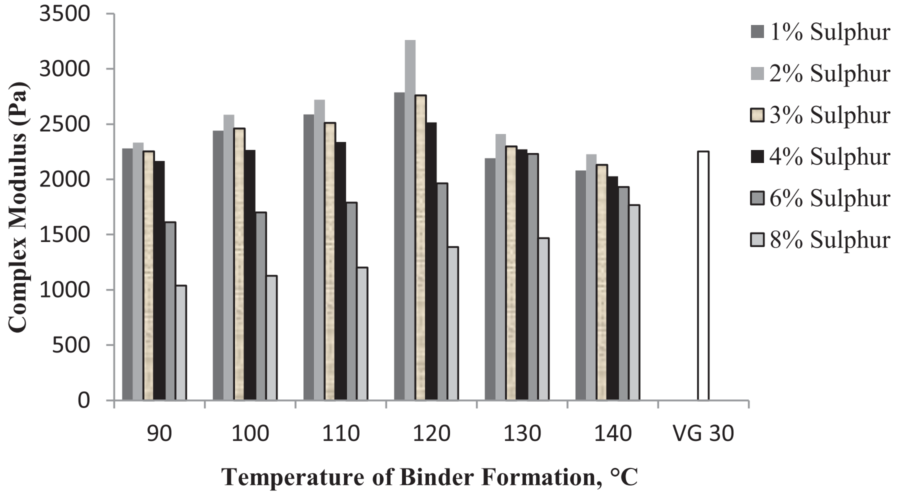

Figure 1: Variation of complex modulus with temperature of binder formation

4.2.2 Selection of optimum sulphur content

The next step was to determine the sulphur content in the binder that would result in the best binder in form of the rheological properties as determined from the SHRP grade determination test. Hence, the binders prepared at different sulphur contents at the selected temperatures were subjected to short term aging by RTFO and long term aging by PAV and the aged and un-aged binders were subjected to SHRP grade determination test in a DSR. The results of such tests in form of variations of complex modulus and phase angle with sulphur content are presented in Figures 2 and 3. It is seen that as usual, aging increases the complex modulus value and decreases the phase angle for a particular binder. It is also seen that these two parameters increase/decrease to an optimum value of sulphur content of 2% beyond which the trend reverses. This conveys that the best modification of bitumen VG 30 can be possible when the sulphur content in the binder is 2% and temperature of blending is at 120^{0}C. In fact, more sulphur content leads to a scope of more possible heterogeneity and hence inferior properties. Higher sulphur content may not lead to economy and may invite more fumes to cause air pollution

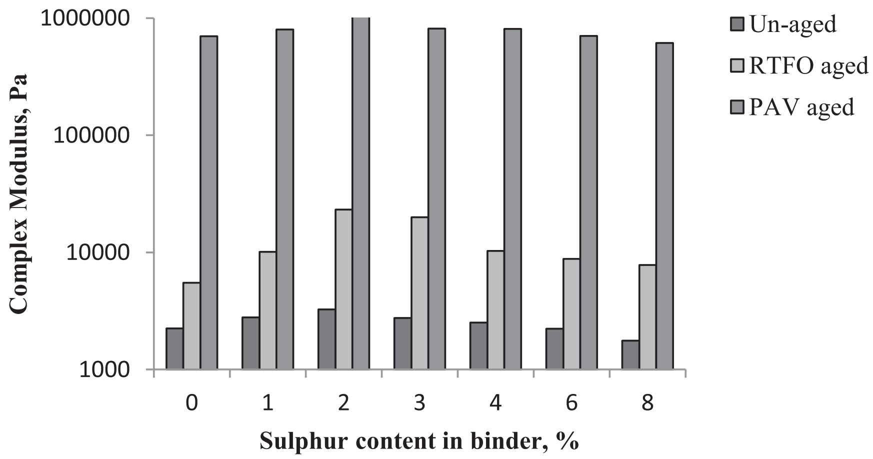

Figure 2: Variation of complex modulus with sulphur content in binder

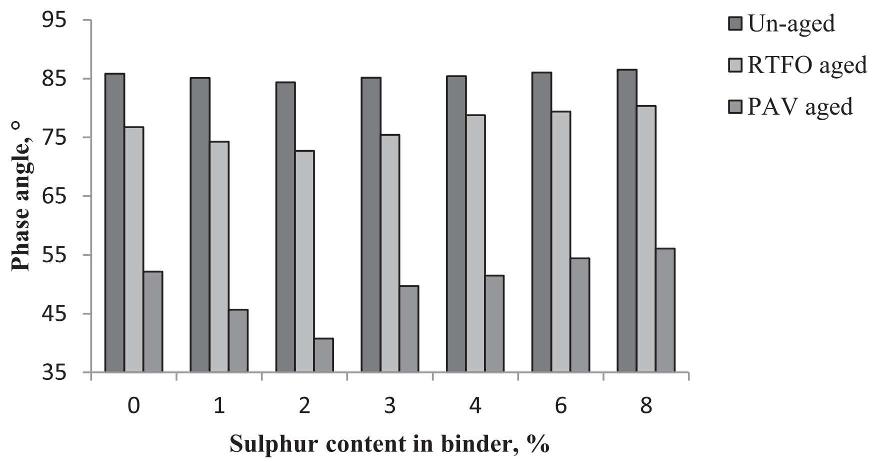

Figure 3: Variation of phase angle with sulphur content in binder

The results of SHRP grade determination test for aged and un-aged, modified and unmodified binders (2% sulphur content) are given in Table 3. It is seen that all the results presented in this table satisfy the specification requirements for the fatigue and rutting characteristics.

Table 3: Results of SHRP Grade determination tests

Binder Type	Temperature °C	Angular Frequency rad/s	Phase Angle °	Complex Modulus Pa	G*/Sin(δ) Pa	G*Sin(δ) Pa	Specifications Pa	Remarks
VG-30	60	10	85.82	2252	2258		>1000	Ok
RTFO aged VG-30	60	10	76.72	5507	5549		>2200	Ok
PAV aged VG-30	40	10	52.16	7.00E+05		5.53E+05	<5000kPa	Ok
VG-30 +2% S	60	10	84.35	3262	3278		>1000	Ok
RTFO aged (VG-30 +2% S)	60	10	72.73	2.32E+04	2.43E+04		>2200	Ok
PAV aged VG-30+2% S	40	10	40.75	1.51E+06		9.86E+05	<5000kPa	Ok

It is observed from the preceding sections that in general, the sulfur modified bitumen has higher complex modulus compared to the neat VG 30 bitumen indicating better strength behavior and similarly, the sulfur modified bitumen has less phase angle value compared to the neat VG 30 bitumen indicating better elastic behavior.

4.2 Dynamic Rheological Characteristics

The rheological characteristics of the binders have been studied with respect to the temperature, frequency and amplitude variations to take care of the realistic paving situations where the paving mixes are subjected to different temperature and loading situations.

4.2.1 Amplitude sweep

The next step was to study the rheological characteristics of normal bitumen and modified binder by subjecting the same to various sweep tests. The amplitude sweep test was undertaken first at a stress level ranging from 1Pa to 15KPa. The results of this test are presented in Figure 4.

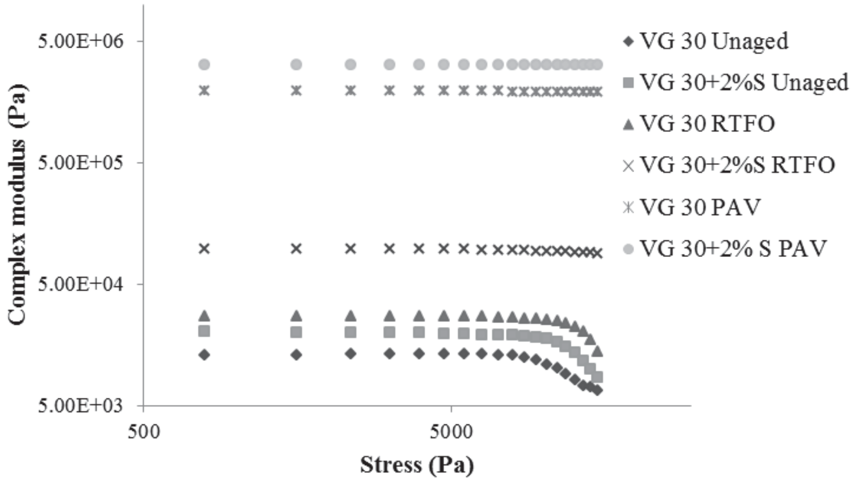

Figure 4: Results of amplitude sweep test (Complex Modulus) for binders

It was observed that the linearity range increases with sulphur modification, which means that the ability to take load increases when binder is modified with 2% sulphur. Also it is seen that for both unmodified and modified binders the linearity range increases with increase in aging effect. So a common stress of 2.5 KPa was selected from the linear range of all the category of binders for further study of temperature and frequency sweep tests.

4.2.2 Temperature sweep

In the first stage, keeping the angular speed related to frequency constant at 10 rad/sec, the DSR tests were conducted at varying temperatures to assess the effects of temperature on the rheological properties of different binders. The variations of the rheological parameters such as complex modulus and phase angle on modified and unmodified binder samples under aging as well as un-aged conditions, with temperature, are presented in Figures 5 and 6. It is observed that as usual complex modulus decreases with temperature, and increases with aging and also by sulphur modification. Similarly, the phase angle increases with temperature, and decreases with aging and sulphur modification. In Figure 5, it is clearly seen that there is a linear increase in complex modulus, G*, over respective temperature after being aged through RTFOT and PAV, respectively. The increase in G* after PAV ageing is reasonably greater than after RTFOT ageing due to the prolonged ageing process in the PAV. There is also a significant decrease in the phase angle (δ), after PAV ageing. This may be due to the fact that δ is normally considered to be more sensitive as a result of change in chemical structure **(Airey, 2003)**.

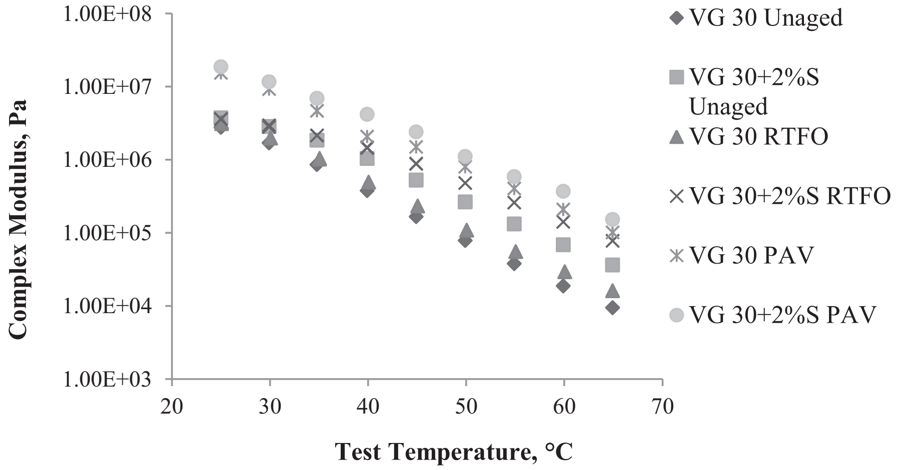

Figure 5: Results of Temperature sweep test (Complex Modulus) for binders

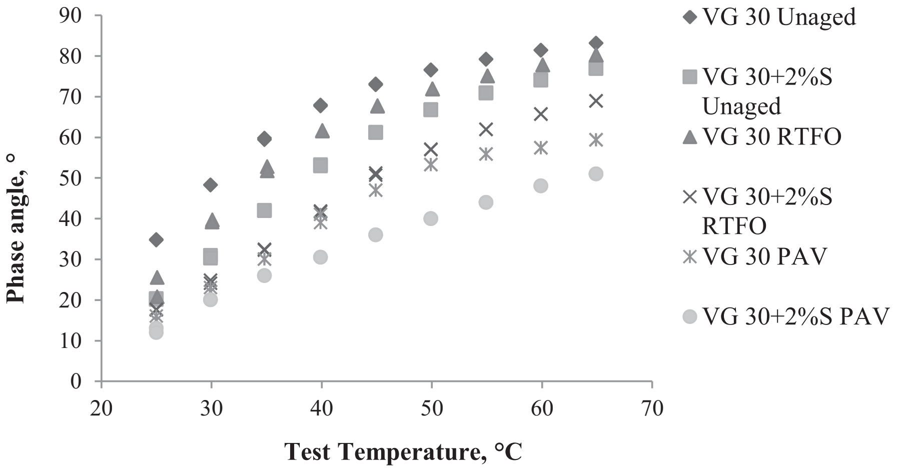

Figure 6: Results of Temperature sweep test (Phase angle) for binders

4.2.2 Frequency sweep

Oscillatory frequency sweeps test was carried out to identify and analyse the nature of structural response for modified and unmodified binders at high temperatures, frequency sweep tests (0.1–10 Hz) were conducted. The test temperature of 60^{0}C was chosen to be maintained since the bituminous pavement usually subjected to such high temperature in summer, except for PAV aged binders that were tested at 40^{0}C. The results of the frequency sweep tests are presented in Figures 7 and 8 for complex modulus and phase angle respectively.

The viscous behavior of the conventional bitumen binder increases after being subjected to short-term ageing, as shown by the raised phase angle curve in the frequency ranges and there exist a significant shift of complex modulus. In the long term ageing process, the complex modulus curve is seen to be raised over the whole applied loading frequency range and the phase angle curve is lowered similarly.

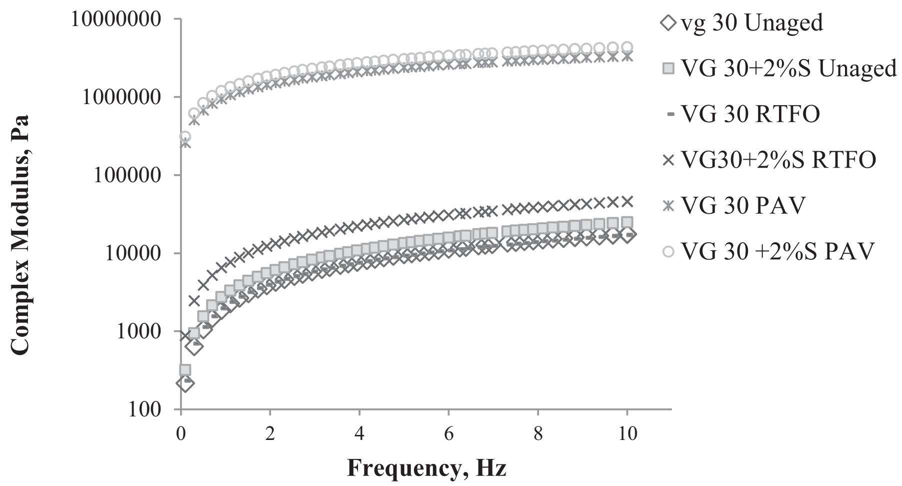

Figure 7: Results of Frequency sweep test (Complex modulus) for binders

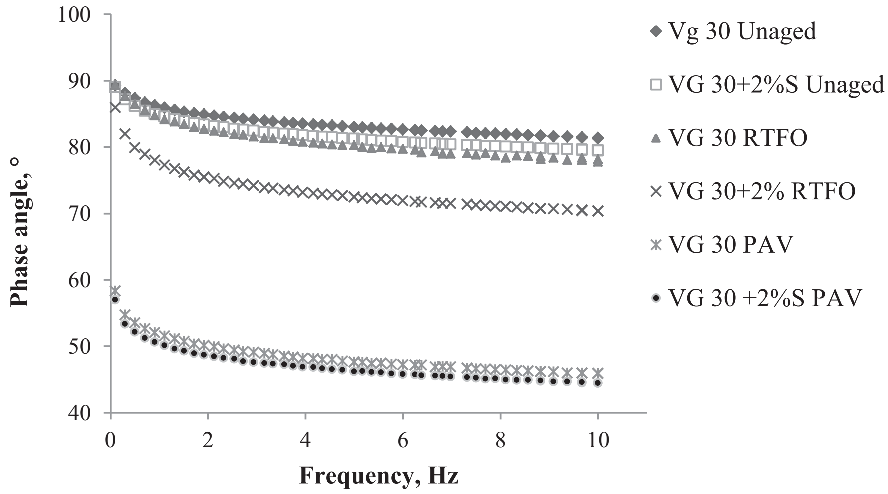

Figure 8: Results of Frequency sweep test (Phase angle) for binders

The fluctuating trends of the complex modulus curve for aged binders are similar to that of VG-30 bitumen. It is clearly seen that the modified binders offer improved rheological properties in that the complex moduli are generally higher, at least in terms of rutting behavior.

5. SUMMARY OF OBSERVATIONS

In this study sulphur has been used as a modifier for conventional VG 30 bitumen. As per the procedure developed, addition of 2% dry commercial sulphur by weight to bitumen at 120^{0}C followed by vigorous mixing using a mechanical stirrer for about 30 minutes at about 3000 rpm results in a homogeneous modified binder. The binder thus developed has been evaluated in terms of improvements in rheological properties which have been studied as per relevant standard procedures. The binders thus developed have been evaluated in terms of SHRP grade determination tests and dynamic rheological tests. The major influences of ageing in short term and long term processes on rheological behavior of sulphur modified bitumen have also been studied. It is observed that, the modified binders become more susceptible to oxidative ageing under dynamic shear. Owing to the increase in the viscous behavior of the aged binders, the low-temperature cracking resistance of the sulphur-modified bitumen may also improve in comparison with the conventional bitumen after ageing. The sulphur modified binders show much higher potential to resist permanent deformation characteristics. In general, the performance characteristics of modified binders are found to be satisfactory as per the superpave specification requirements. Sulphur is thus found to be a good modifier by enhancing the performance of the conventional bitumen.

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