Evaluating Physical, Rheological and Chemical Properties of Modified Bitumen

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Abstract--- *In India, the methods for rheological characterization of bituminous binders are inadequate to characterize the bitumen. Hence a complete rheological study and characterization of bitumen using dynamic shear rheometer would be helpful. Also there is limited insight about the chemistry of modified bitumen. Modification of asphalt binders can serve several purposes. It can increase the overall performance of a binder by widening the range between the binder's high and low-temperature grades. In this paper VG30 bitumen and two polymers: Styrene Butadiene Styrene (SBS) block copolymer and Ethylene Vinyl Acetate (EVA) polymers were used as modifiers. SBS copolymers derive their strength and elasticity from physical and cross linking of molecules into three dimensional networks. Increasing the SBS content results in increased polymer swelling, which in turn produces increase in asphaltenes and reduction in maltene content resulting in harder and viscous matrix whereas EVA modifies bitumen by forming tough, three dimensional, rigid network to resist deformation. The change in physical properties such as penetration, softening point, penetration index and mass loss were studied and compared before and after modification. Rheological parameters such as complex modulus and phase angle before and after modification were studied by using Dynamic Shear Rheometer. The results indicate that polymer modification leads to decrease in penetration value, and increase in softening point and rutting parameter (G*/Sinδ). Modifiers used for bitumen modification are normally polymeric materials which have different structures such as atactic, isotactic and syndiotactic. These structures give characteristic features in spectroscopy analysis. Thus, Infra Red Spectroscopy techniques was employed in identifying the structure and functional groups present in polymeric materials.*

Keywords--- *Complex Modulus, Dynamic Shear Rheometer, Infra Red spectroscopy, Modified bitumen, Phase Angle*

I. Introduction

HOT Mix Asphalt (HMA) concrete is a mixture of bitumen and aggregate. In a road pavement, aggregate composes 94 to 95% by weight of the mix while asphalt makes up the other 5 to 6%. Moisture damage and permanent deformation are the primary modes of distress in HMA pavements. Loss of cohesion and stiffness of asphalt film and failure of the adhesive bond between aggregate and asphalt are the main mechanisms of moisture damage in asphalt pavements. Therefore high strength and durable mixes are required for airfields and express highways [1]. The use of polymer modified bitumen (PMB) to achieve better asphalt pavement performance has been observed for a long time [2] Modification by polymers can enhance the properties of conventional bitumen. Modification of asphalt binders can serve several purposes. It can increase the overall performance of a binder by widening the range between the binder's high and low-temperature grades, or it can target a specific improvement in a binder's performance in response to a particular severe-service condition, such as a pavement carrying a very high traffic volume or a high percentage of slow-moving, heavy vehicles. The improved functional properties include fatigue and low temperature cracking [3, 4], stripping [5], permanent deformation [6, 7], wear resistance [8] and ageing [9,10]. The properties of modified bitumen depend on the polymer characteristics and content and base bitumen and also upon the blending process [11, 12, 13]. Many diverse materials are added to neat asphalt cement as modifiers. In recent years, different kinds of polymers have been used to modify properties of asphalt mixtures. For a polymer to be effective in road application it should properly blend with bitumen to produce a homogenous mix to improve its resistance to rutting, stripping, cracking, fatigue, ageing etc. The use of a modifier should also be cost-effective. Despite the large number of polymeric products, there are relatively few types which are suitable for bitumen modification. Polymers are classified into two groups: (i) elastomers and (ii) plastomers. SBS is classified under elastomers and are those modifiers which increase the elasticity and strength of binder by cross linking of molecules into three dimensional network [14].EVA come under the category of plastomers which form a three dimensional rigid network to impart toughness to the binder [15].

In this paper an attempt has been made to compare various physical, rheological and chemical properties of neat and modified bitumen. For comparing the physical properties various tests such as penetration, softening point, penetration index and mass loss on heating were done. To study the rheological parameters, values of G*/Sinδ were determined and compared and chemical properties were determined using infra red spectroscopy through formation of various functional groups.

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II. MATERIALS

VG 30 paving grade bitumen obtained from Mathura refinery was used in the study for preparing various mixtures. The physical properties of VG 30 are listed in Table 1.

Table 1: Properties of Base Bitumen

Properties	*Standard*	*Results*
Penetration(0.1mm,100g,5s,25^{o}C)	ASTM D5	67
Softening Point(^{o}C)	ASTM D36	49
Penetration Index(PI)	-	-0.698
Specific gravity	ASTM D70	1.01

A. Preparation of Ethylene Vinyl Acetate Modified Binder

Ethylene Vinyl Acetate (EVA) a plastomer was used to develop modified bitumen. VG 30 was used as base bitumen and three levels of EVA were used namely 3% (3E), 5% (5E) and 7% (7E) by weight of bitumen. Mixing was performed in the laboratory using high shear mixer capable of maintaining temperature and regulating stirring speed. About 400g of bitumen was heated at 165^{o}C for 30 min. As the bitumen attained a temperature of 165^{o}C, EVA was added slowly in the required amount to avoid agglomeration of polymer. The mixture was then vigorously agitated for 1 hr at 3000rpm. Care was taken to maintain the temperature between 160-170^{o}C. After the blend was prepared the uniformity of the mix was determined by passing it through ASTM 100# sieve and on confirmation of uniformity it was stored in aluminum containers. It was found that the asphalt binder thus prepared can be stored for future use.

B. Preparation of Styrene-Butadiene-Styrene Modified Binder

Styrene butadiene styrene (SBS) an elastomer was used to develop modified bitumen. VG 30 was used as base bitumen and three levels of SBS were used namely 3% (3S), 5% (5S) and 7%(7S) by weight of bitumen. The polymer used was in the form of pellets. Mixing was performed in the laboratory using high shear mixer capable of maintaining temperature and regulating stirring speed. The asphalt binder was heated to 150^{o}C for 1hr with mixer speed maintained at 200 rpm. After the mixing temperature of 180^{o}C was reached, the modifier was added slowly in the required amount to avoid agglomeration of polymer and the mixing was continued for next 1.5 hr at 500 rpm.[16]. After the blend was prepared the uniformity of the mix was determined by passing it through ASTM 100# sieve and on confirmation of uniformity it was stored in aluminum containers. It was found that the asphalt binder thus prepared can be stored for future use [17].

III. TEST RESULTS AND DISCUSSION

A. Physical Properties

i. Penetration

The penetration of a bituminous material is the distance in tenths of a millimeter that a standard needle will penetrate vertically into a sample of the material under standard conditions of temperature, load and time. Penetration test is the most commonly adopted test on bitumen to grade the material in terms of its hardness. The tests were conducted as per IS: 1203-1978.

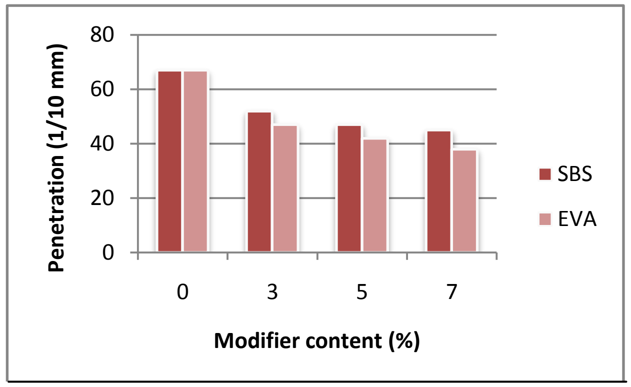

Figure 1: Variation of Penetration with Modifier Content

As can be seen from the figure 1 it is clear that the penetration value decreases significantly on addition of modifier and as the modifier content increases the penetration value decreases. The decrease is more prominent in case of EVA compared to SBS.

ii. Softening Point

The softening point is the temperature at which the substance attaining a particular degree of softening under specified condition of test. The softening point of bitumen is usually determined by Ring and Ball test. The tests were conducted as per IS: 1205-1978.

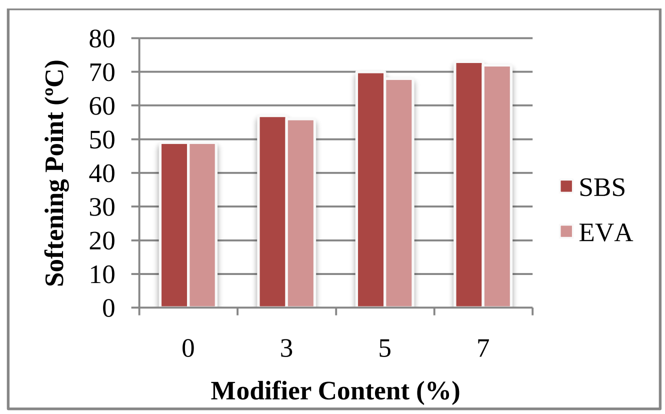

Figure 2: Variation of Softening Point with Modifier Content

iii. Penetration Index

It can be calculated by using following equation

$$P.I = \frac{20 - 500A}{1 + 50A}$$

Where

$$A = \frac{log\,800 - log\,Pen(25\,℃)}{Temp(R\&B)\ - 25\,°}$$

For paving bitumen the P.I value lies in between +2 to -2.

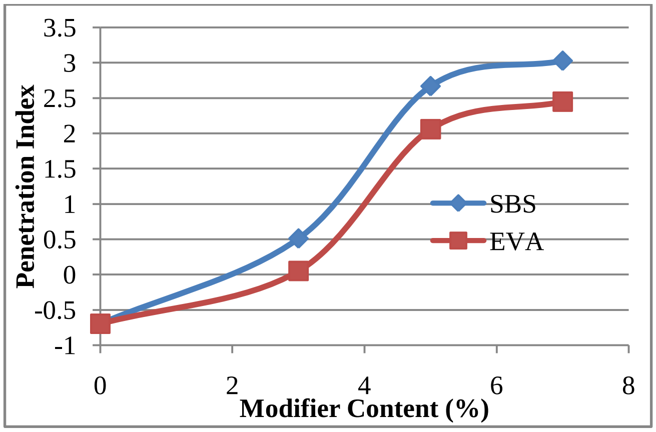

Figure 3: Variation of Penetration Index with Modifier Content

Variation of penetration index (PI) with increase in modifier content is represented graphically in figure 3.PI value increases as the modifier content increases. SBS modifier gives higher PI for all percentages of modifier compared to EVA. But as per recommendations the value of penetration index should lie between +2 and -2, therefore only 3% and 5% EVA and 3% SBS modified bitumen fulfills the criterion.

iv. Mass Loss

The Thin-Film Oven Test (TFOT) simulates short-term ageing by heating a film of asphalt binder in an oven for 5 hours at 163^{o} C (325^{o} F). The standard TFOT is AASHTO T 179 and ASTM D 1754: Effects of Heat and Air on Asphalt Materials. The effects of heat and air are determined from changes incurred in the physical properties measured before and after the oven treatment including change in sample mass. The method indicates approximate change in properties of asphalt during conventional hot- mixing at about 150^{o} C. It yields a residue which approximates the asphalt condition as incorporated in the pavement. Loss in weight is another important parameter which is used to judge the effect of aging on the bituminous binders. The loss of volatile fractions contributes to the difference in weights between original and aged sample. The maximum loss in weight should be 1% as per IRC: SP: 53:2002. [18] The weight loss after conducting TFOT on the SBS and EVA modified bitumen in tabulated in Table2.

Table 2: Mass Loss of Neat and Modified Bitumen before and after TFOT

Binder	Weight before TFOT	Weight after TFOT	Mass Loss (%)
VG 30	50.238	49.987	0.5
VG 30+3%SBS	50.231	50.186	0.09
VG 30+5%SBS	50.183	50.158	0.05
VG 30+7%SBS	50.041	50.021	0.04
VG 30+3%EVA	50.312	50.092	0.08
VG 30+5%EVA	50.171	50.151	0.04
VG 30+7%EVA	50.017	50.007	0.02

As represented by table 2, the mass loss after the introduction of modifier in bitumen is reduced indicating that the modified bitumen is more stable compared to conventional bitumen. Among SBS and EVA, percentage mass loss in EVA is less compared to SBS.

B. Rheological Properties

Asphalt Rheometer Model MCR 101 was used for measuring the dynamic rheological properties in this study. This rheometer can describe the linear visco-elastic properties of bituminous binders over a range of temperatures and loading times. During loading a sinusoidal shear stress is applied to bituminous sample sandwiched between two parallel plates. The resulting sinusoidal shear stress is monitored as a function of temperature and frequency. Based on these stress and strain measurements, stiffness and viscosity can be obtained at different temperatures, frequency and strain levels. 25mm parallel plate geometry was used and measurements were done in a temperature range of 46^{o}C to 82^{o}C. The gap width was set at 1 mm and measurements were done at a frequency of 10 rad/s as per AASHTO TP5 (1994). The parameters obtained from DSR were complex shear modulus (G*) and phase angle (δ). In accordance with SHRP specifications the relation G*/Sinδ at 10 rad/s represents the permanent deformation of the sample and is controlled by limiting its value to 1kPa and 2.2 kPa in case of unaged and short term aged specimens. Based on these values the performance grades of the samples were determined.

The Superpave Performance Grade (PG) of bitumen is based on climate. The temperature at which G*/Sinδ attains a value of 1kPa of unaged sample determines its PG. The PG of VG 30 bitumen was 64, whereas that for 3%SBS, 5%SBS and 7%SBS meet the specification requirements of PG 70, PG 76 and PG 76 respectively as shown in Fig.2. G*/Sinδ is an indicator of rutting resistance. It is evident from the figure the rutting resistance parameter G*/Sinδ of SBS modified binders are higher than those of neat bitumen at all test temperatures. This shows that modified binder is stiffer at all temperatures than neat asphalt. The rutting resistance further increases with increase in modifier content from 3% to 7%, but the percentage increase in resistance is more when the modifier content is increased from 3% to 5% compared to percentage increase from 5% to 7%. The PG for 3%EVA, 5%EVA and 7%EVA meet the specification requirements of PG 76, PG 82 and PG 82 respectively as shown in Figure 5. Comparing figures 4 and 5, it is seen that EVA modified binders has higher G*/Sinδ than those of SBS at all test temperatures. This shows that EVA modified binder is stiffer at all temperatures than SBS.

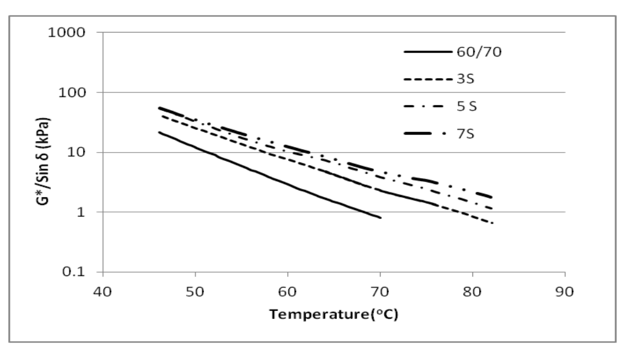

Figure 4: Relation between G*/Sin δ and Temperature for SBS Modified Bitumen

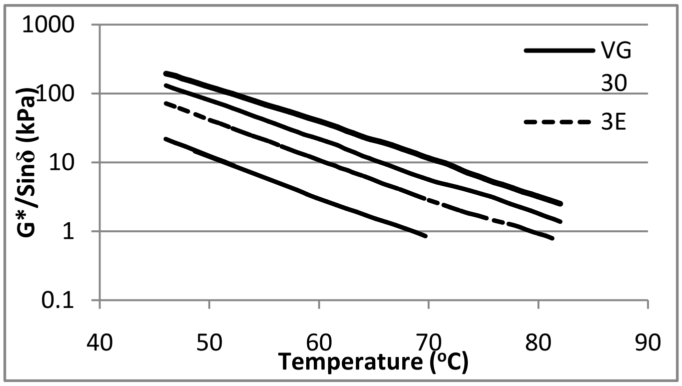

Figure 5: Relation between G*/Sin δ and Temperature for SBS Modified Bitumen

C. Chemical Analysis

i. Infra Red Spectroscopy (IR)

Fourier transform infrared spectroscopy (FT-IR) is a simple analytical technique that has been widely applied to study chemical and structural modifications in different samples and allows revealing the functional groups present in various material formations. In this study FTIR analyses were performed with a Nicolet Magna 550 spectrometer, in the transmission mode. Bitumen films were prepared on sodium chloride plates using a controlled temperature hot plate. The scanning was performed in the Middle Infrared Region (MIR, 400–4000 cm^{-1}), with a resolution of 4cm^{-1}; each spectrum is an accumulation of 32 spectra. A computer software program "Omnic" was used to process the Attenuated Total Refraction (ATR) interferogram into an absorption diagram (spectrum) through Fourier Transformation function, thus the name ATR/FTIR. We applied this methodology to study bond formation on addition of SBS and EVA to VG 30 grade bitumen. The infra red spectroscopy study was also carried out on pure modifiers and neat bitumen. The spectra were analyzed in order to monitor functional and structural changes in the fraction of binders due to modification by SBS and EVA. This monitoring was done considering structural indices, instead of band areas, because of the variations of sample film thickness. The plots of IR have been obtained with X-axis representing the wave number i.e frequency of radiations in cm^{-1} and Y-axis representing transmittance in percentage

ii. VG 30

The FTIR spectrum of the base VG 30 asphalt is given in Figure 6 below. As bitumen is a complex mixture of asphaltenes and maltenes, it contains number of compounds with various functional groups, each having its own characteristic peak in the IR spectra. The strong peaks within 2850–2960 cm^{-1} region were typical C-H stretching vibrations in aliphatic chains. The peak at 1603.6 cm^{-1} was attributed to C=C stretching vibrations in aromatics. The C-H asymmetric deforming in CH_2 and CH_3, and the C-H symmetric deforming in CH_3 vibrations were observed at 1458.2 cm^{-1} and 1375.2 cm^{-1} respectively. The peak at 1030 cm^{-1} was ascribed to S=O stretching vibrations. The small peaks within 740–910 cm^{-1} region were typical C-H vibrations of benzene ring.

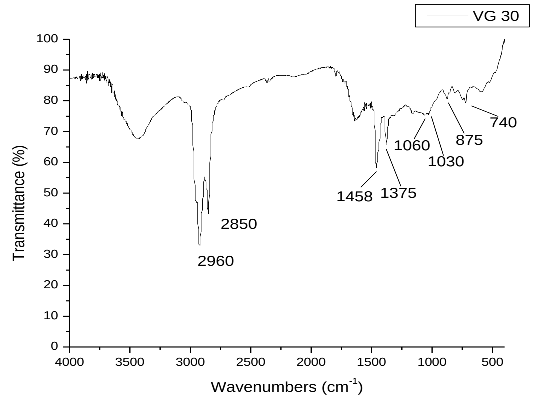

Figure 6: IR Spectrum of neat VG 30

iii. SBS

As shown in Figure 7 the main bands for characterizing the butadiene segment within SBS are CH_2 scissoring at 1449 cm^{-1},trans-1,4 C=C out of phase deformation at 966 cm^{-1}, =CH stretching at 3005 cm^{-1}, C–H stretching at 2916 and 2844 cm^{-1} and the stretching vibrations in vinyl-PB at 1640 cm^{-1}. Regarding the PS segments, styrene absorption occurs at 700 cm^{-1}, C–H out of plane deformation occurs at 3060 cm^{-1} and at 1600 cm^{-1} aromatic C–C stretching occurs.

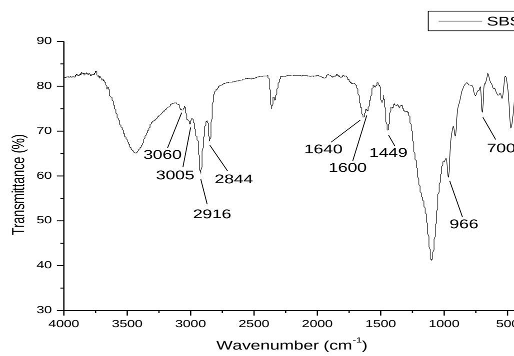

Figure 7: IR Spectrum of SBS

iv. EVA

Based on the infrared (IR) spectrum of EVA (see Fig. 8), the determination of VA content appears to be obvious. The characteristic absorbances of some bands assigned to the VA units (1740 cm^{-1}, 1240 cm^{-1}, 1020 cm^{-1}, 610 cm^{-1}) and can be related to the absorbances of the ethylene groups (2920 cm^{-1}, 2850 cm^{-1}, 1470 cm^{-1}, 720 cm^{-1})

The thinner the EVA films are, the more bands are suitable for the infrared spectroscopic measurements. The simplest way to prepare thin foils is by calendering and pressing at an appropriate temperature. Because of these difficulties of sample preparation and measurement, a simple technique was developed for the determination of the VA content of thick, commercial EVA films (< 100 mm) without special preparation.

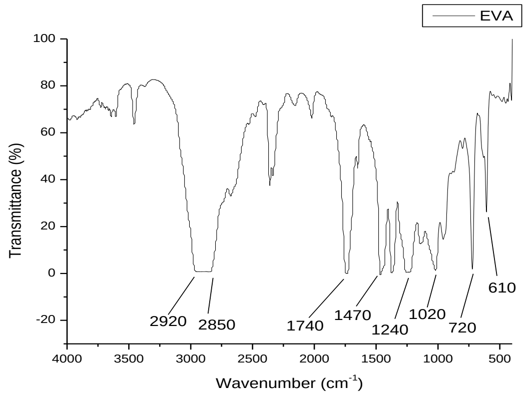

Figure 8: IR Spectrum of EVA

v. Modified SBS bitumen

Previous study [16] on SBS polymer modified found that the spectrum of SBS physical modified asphalt is the simple superposition of the SBS spectrogram and asphalt spectrogram. There is only physical mixing without any chemical reaction between SBS and matrix asphalt. 1375cm^{-1}, 810cm^{-1} of asphalt and 966cm^{-1},699cm^{-1} of SBS could be used for quantification as shown in Figure 9.

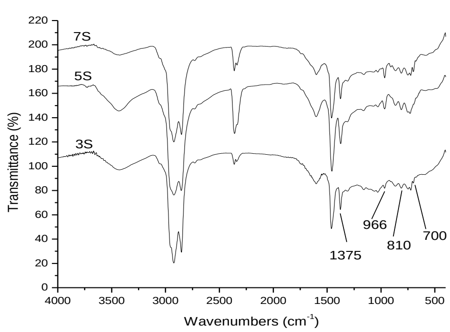

Figure 9:IR Spectrum of VG 30 Modified with various Percentages of SBS

vi. Modified EVA bitumen

Comparing the spectrum of base bitumen and EVA modified bitumen, the peaks of the base bitumen and EVA modified bitumen show few difference and it seems that the peaks transmittance are partly strengthen or weaken, no new transmittance peaks appear and no transmittance peaks disappear as indicated by Figure 10. So it can be verified no reactions have happened between the EVA and the bitumen in the system of EVA modified bitumen.

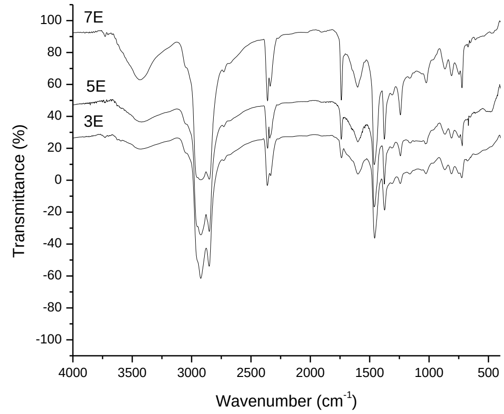

Figure10: IR Spectrum of VG 30 Modified with various Percentages of EVA

IV. Conclusions

The following conclusions are drawn based on the results obtained in the present study:

1. The physical properties of bitumen such as penetration and softening point are improved with addition of polymers. SBS modified binder gives higher softening point and EVA modified binder gives lower penetration value indicating better temperature susceptibility of modified bitumen than conventional VG30.
2. The penetration index (P.I) is increased with increase in percentage of modifier. The SBS modified binder give the highest value of P.I. with the same percentage of modifier as compared to EVA modified binders.
3. After short-term ageing mass loss in EVA is less compared to SBS indicating higher stability at higher temperatures.
4. EVA modified bitumen has higher G*/Sinδ value for all temperatures and all modifier contents compared to SBS indicating that EVA modified bitumen have higher rutting resistance to deformation under loading as compared to SBS.
5. Infrared analysis of modified bitumen indicates retaining of covalent bonding between modifier and bitumen. This suggests the stability and durability of modified binders to sustain climatic changes during its course of life.
6. Comparing the Infrared spectrum of neat bitumen and modified bitumen it is concluded that there is only physical mixing without any chemical reaction between modifiers (SBS and EVA) and matrix asphalt

References

[1] P.K. Jain, Sangita, S. Bose, and I.R. Arya, "Characterization of polymer modified asphalt binders for roads and airfields."STP No. 1108, American Society of Testing and Materials (ASTM), Philadelphia,Pp.341-355,1992.

[2] U. Isacsson and X. Lu, "Testing and appraisal of polymer modified road bitumens — state of the art", Mater. Struct. 28, Pp.139–159,1995.

[3] C.P. Valkering, W.C. Vonk and C.D. Whiteoak," Improved asphalt properties using SBS modified bitumens", Shell Bitumen Rev. 66,Pp.9–11,1992.

[4] S.H. Carpenter and T. VanDam, "Laboratory performance comparisons of polymer-modified and unmodified asphalt concrete mixtures", Transportation Research Record 1115, TRB, National Research Council, Washington, DC, Pp. 62–74,1987.

[5] G. Beecken, Ten years' experience with Caribit in Germany, Shell Bitumen Rev. 66, Pp.12–15,1992

[6] N.P. Khosla and S.Z. Zahran, "A mechanistic evaluation of mixes containing conventional and polymer modified (styrelf) asphalts", Proc. Assoc. Asphalt Paving Technologists 58, Pp.274–302,1989.

[7] R.L. Terrel and J.L. Walter, "Modified asphalt pavement materials — The European experience", Proc. Assoc. Asphalt Paving Technologists 55, Pp.482–518, 1986.

[8] T. Blomberg, "Better wear resistance with polymer modified bitumen", Proc. RILEM Residental Seminar, Dubrovnik (Yugoslavie), Pp. 315–317,September 1988

[9] J.P. Harlin, J.L. Jariel and J.C. Blondel, "Twelve years service life without specific maintenance for the bitumen Cariflex" TR–1101 bound wearing course of the Saint–Quentin Bridge, Proc. 4th Eurobitume Symp. Madrid 1, Pp.125–127,1989

[10] W.C. Vonk, M.C. Phillips and M. Roele, "Ageing resistance of bituminous road binders: benefits of SBS modification", Proc. 5th Eurobitume Cong. Stockholm 1A,Pp. 156–160,1993

[11] X. Lu and U. Isacsson, "Chemical and rheological evaluation of ageing properties of SBS polymer modified bitumens", Fuel 77, Pp. 961–972,1998

[12] G.N. King, H.W. King, O. Harders, W. Arand and P.-P. Planche, "Influence of asphalt grade and polymer concentration", J. Assoc. Asphalt Paving Technologists 62, pp.1–22,1993

[13] B. Brule, Y. Brion and A. Tanguy, "Paving asphalt polymer blends: relationships between composition, structure and properties", Proc. Assoc. Asphalt Paving Technologists 57, Pp.41–64, 1988

[14] U. Isacsson and X. Lu, "Testing and appraisal of polymer modified road bitumens: state of the art", Mater Struct, Pp.28:139–59, 1995

[15] [15] Mahabir P, Mazumdar M.," Engineering properties of EVA modified bitumen binder for paving mixes", J Mater Civil Eng, 11:131–5, 1999

[16] Baha Vural Kok and Mehmet Yilmaz, "The effects of using lime and styrene–butadiene–styrene on moisture sensitivity resistance of hot mix asphalt", Construction and Building Materials 23,Pp.1999–2006,2009

[17] V.S. Punith, and A. Veeraragavan,," Behavior of asphalt concrete mixtures with reclaimed polyethylene as additive", J. Mater. Civ. Eng.,19(6), Pp.500–507,2007

[18] IRC SP: 53 "Guidelines on Use of Polymer and Rubber Modified Bitumen in Road Construction", Indian Road Congress, New delhi,2002.