Interrelationship between Chemistry and Performance Grade Properties of Blended Bitumen

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ABSTRACT

Manifestation of rheological properties of bituminous binders over a wide a range of temperature in real life pavements can be attributed to various factors viz. crude source, processing methods, oxidative aging and chemical composition. A clear understanding of the fundamental chemical and rheological properties of bitumen and their inter-relationship is important to address issues related to binder characterization and performance. In this study, blended bitumen samples were prepared using three different crude sources and three blend proportions of PDA pitch and Heavy Extract. All the samples were subjected to both short term aging and long term aging. Corbett's fractionation procedure was conducted to evaluate the chemical composition of the bituminous samples at unaged, short term aged and long term aged conditions. Further, Performance Grading (PG) tests were conducted on all the samples at both high and intermediate temperatures as per ASTM procedure. An attempt was made to develop an inter-relationship between the PG properties and chemical composition of bitumen. From the results, the role of asphaltenes on the rheological behavior of blended bitumen was clearly evident

Keywords: Bitumen, Rheology, Chemistry, Viscosity, Aging, Viscoelasticity sources.

INTRODUCTION

India is currently constructing the largest ever bituminous based national highway project. Rational binder and mixture specifications and quality control measures are needed at the earliest so that increased cost in maintaining the pavements can be prevented. Few empirical tests are being used currently for categorizing the wide varieties of bitumen processed in India. Since bitumen processed in India has been investigated very little, a study tuned towards developing a fundamental understanding on its chemistry and rheology is a necessity. Bitumen is processed from crude either by straight vacuum distillation or air blowing or blending. Some of the refineries in India follow the blending procedure. In blending, Propane DeAsphalting (PDA) is used. PDA pitch is typically blended with heavy extracts (residuum stream of lubrication oil unit) to result in bitumen of suitable penetration/viscosity grade. A binder of desired grade can be produced using the blending process, but the issue related to compatibility between individual blend components, dosage rate of the PDA pitch, effect of crude source and the blending process on its rheology is a challenge. A clear understanding on the fundamental chemical and rheological properties of blended bitumen is necessary to address these issues and this investigation is tuned towards this goal (Rajan*et.al.* 2008).

During 1987, the United States (US) congress initiated a five year $150 million product driven research effort called SUPERPAVE (SUperiorPERformingPAVEments) under the Strategic Highway Research Program (SHRP) which includes development of performance based specification for binders. On similar lines, India needs to develop performance linked specifications for binders in the near future [2]. Until now very little work has been done in India to establish a connection between field performance and the index properties of bitumen. This task includes collection of significant database related to different rheological properties of bitumen including the information about the crude source, processing method and chemical composition as a first step. The specification parameters currently followed in India are measurements carried out at discrete sets of temperatures with little connectivity to the field requirements [1]. For instance, grading systems such as penetration or viscosity can be met by changing the proportion of pitch to heavy extract (blending) or blowing temperature, air pressure, circulation rate and use of catalyst (air blowing). By this one can produce the same penetration/viscosity grade of bitumen from a wide variety of crude sources but cannot produce similar performance grade (PG) properties from such crudes without significant changes in the production process. PG binder specification is theoretically based directly on performance rather than on empirical relationships between basic physical properties and observed performance. Performance graded binders are selected based on climate in which the pavement will serve. The physical property requirements are held constant and only test temperature changes to meet the specifications. For example, a binder classified as PG 64-22 means the binder will meet the high temperature physical property requirements up to a temperature of 64 ºC and the low temperature physical property requirements down to 22 ºC. (Sairam and Krishnan 2009).

The objectives of this study is to investigate the influence of crude source and blend proportions on the chemical composition and the PG properties of blended bitumen under different aging conditions and to develop an interrelationship between chemical composition and rheological properties of blended bitumen for different stages of aging, crude source and blend proportions. Three blend proportions 90:10, 85:15 and 75:25 were manufactured spanning from three different crude sources viz. Basra Light, Upper Zakum and Arab Mix. All the blended samples were subjected to short-term aging and long-term aging using a Rolling Thin Film Oven (RTFO) and Pressure Aging Vessel (PAV) respectively in the laboratory.

LITERATURE REVIEW

The earliest work related to bitumen chemistry seems to have been carried out by Boussingault (1837). He did some of the earlier experiments on the composition of bitumen and classified it into two groups, namely Petrolene and Asphaltene depending upon the type of solvents used to separate these hydrocarbons. 85 percent weight of the distillable fraction he called petrolene and of 15 percent weight of the solid fraction, he called asphaltenes (Krishnan and Rajagopal, 2003). To clearly conceptualize the connection between bitumen chemistry and rheology it is essential to have a microstructural model for bitumen. The earliest model is due to Nellensteyn in which bitumen was assumed to be a colloid. The asphaltenes were assumed to be suspended in saturate oil stabilized by the less polar components aromatics and resins (Nellensteyn, 1924). Further contributions were made by a number of researchers to the colloidal theory of bitumen followed by Nellensteyn which includes the well–known works of Mack (1934), Pfeiffer and Saal (1940) and Traxler (1961). Significant contribution on the colloidal theory for bitumen was given by Pfeiffer and Saal (1940). They explained the difference in rheological properties between what they called sol and gel bitumens. Sol bitumens exhibited Newtonian behaviour, whereas gel bitumens (generally blown ones) were highly non-Newtonian. Between these two extremes, a majority of bitumens was found to have an intermediate behaviour due to a mixed "sol–gel" structure (called in fact "gel–sols" or "elastic sols" by Pfeiffer and Sal. Figure 1 (a), (b) and (c) below shows the

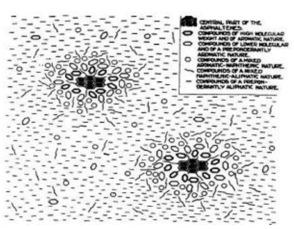

Figure 1 a. Schematic representation of peptized Asphaltene micelles

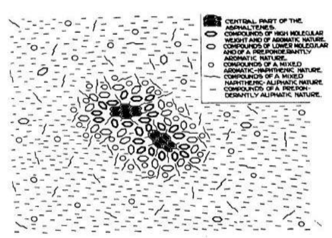

Figure 1.b Schematic representation of flocculated Asphaltene micelles

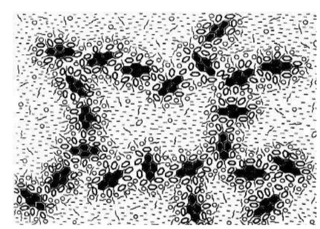

Figure 1. c.Schematic representation of the structure of an blown asphaltic bitumen

schematic sketch of the original colloidal models conceptualized by Pfeiffer and Saal (1940).

The rheological behaviour of bitumen was assumed to be considerably influenced by the volume fractions of asphaltenes. It is also understood now that asphaltenes play a major role in the manifestations of viscoelastic behaviour (Petersen 1984). The current fractionation scheme for bitumen which separates it into four generic components is mainly due to Corbett as given in figure 2(a). The effect of vacuum reduction on composition is shown in figure 2(b). It will be noted here that both saturates and naphthene-aromatics decrease as distillation progresses, whereas the polar-aromatics and asphaltenes tend to increase by concentration. Figure 2(c) taken from Corbett (1969) shows the effect of crude source on composition. In this case all four bitumens have about the same penetration and softening point, while each inherently contains different amounts of the four generic fractions. It is understood that saturates and naphthene-aromatics are liquid in nature whereas the polar-aromatics and asphaltenes are solids. This has prompted the added description that saturates and naphthene-aromatics are soft or plasticizing type components whereas the polar-aromatics and asphaltenes are hard components (Corbett 1969) Fractional separation techniques provide a method for following changes in bitumen during refinery processing, field mixing, field aging or recycling (Rajan*et.al.*, 2010). In

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controlled studies such as the one attempted here in this investigation, the information gained is very informative and gives one a clear understanding about what to expect during various blending techniques and blend proportions. It is also to be clearly noted that since all the chemical fractions are procedurally defined, one cannot extend the observations related to these fractions to areas beyond their validity.

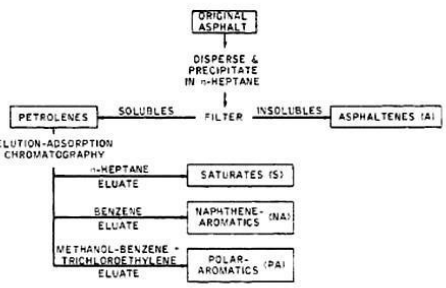

Figure 2(a) Scheme for separation into four generic components

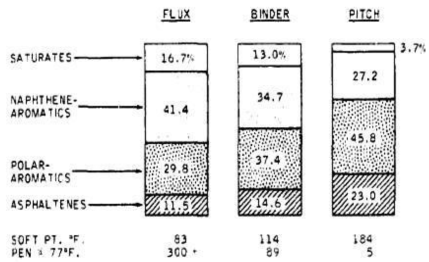

Figure 2(b) Effect of vacuum reduction on composition

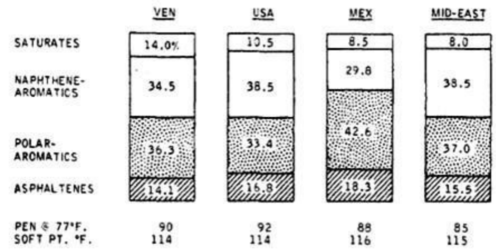

Figure 2(c) Effect of crude source on composition

In this study, to understand the inter-relationship between chemical composition and rheological properties of bitumen, a chemical composition analysis using Corbett’s fractionation procedure was conducted. The blended bitumen samples were separated into four generic component fractions viz. saturates, naphthene aromatics, polar aromatics, and asphaltenes. Performance Grade (PG) tests were conducted as per ASTM D6373 (2007) procedure at both high and intermediate temperatures. Inter-relationships between asphaltenes, and the PG properties of the binders were developed and reported.

MATERIALS AND EXPERIMENTS CONDUCTED

Three blend proportions 90:10, 85:15 and 75:25 from three different crude sources viz. Basra Light, Upper Zakum and Arab Mix were manufactured from three different crude sources using a line blending process at CPCL Research and Development (R & D) laboratory, Chennai. The samples were subjected to both short term aging using a Rolling Thin Film Oven (RTFO) (ASTM D2872- 2004), and long term aging using a Pressure Aging Vessel (PAV) (ASTM D6521-2008). Both the unaged and aged samples were subjected to chemical composition analysis and PG tests as detailed below.

Chemical Composition Analysis: The chemical composition analysis for this study was conducted in the R & D laboratory of CPCL, Chennai using a Chromatographic Column for Separation of Bitumen by Elution-Adsorption (ASTM D4124-2001). CG-20 chromatographic grade, calcined at 413 °C for 16 h and stored in an evacuated desiccator was used. Four generic fractions in the order of their increasing molecular polarity as saturates, naphthene aromatics, polar aromatics, and asphaltenes were separated from the bitumen samples.

PG Tests: A Rolling Thin Film Oven (RTFO), Pressure Aging Vessel (PAV), Brookfield Rotational Viscometer (BRV) and Dynamic Shear Rheometer (DSR) were used as per the test sequence and testing protocols to evaluate the PG properties of blended bitumen. Test properties viz. viscosity of unaged binders at an average mixing and compaction temperature of 135 ºC using a BRV, high pavement service temperature satisfying the rutting resistance criteria $G^*/\sin\delta > 1$ kPa forunaged binders using the DSR and intermediate pavement service temperature for fatigue cracking resistance criteria i.e. $G^*.\sin\delta < 5000$ kPa for PAV aged binders using the DSR were measured (ASTM D6373-2007).

RESULTS AND DISCUSSION

Chemical Composition: Table 1 below reports the results of the chemical composition (SARA fractions) of blended bitumen samples and PDA Pitch at unaged, RTFO aged and PAV aged conditions.

Table.1.Chemical Composition Analysis of Blended Bitumen and PDA Pitch (Rajan*et.al.* 2010)

Crude source	Basra Light (BL)			Upper Zakum (UZ)			Arab Mix (AM)			PDA Pitch		
Blend Proportions	90:10	85:15	75:25	90:10	85:15	75:25	90:10	85:15	75:25	BL	UZ	AM
	Unaged									Unaged		
Saturates, wt%	1.9	2.8	5.7	1.9	2.5	3.3	4.8	4.4	4.0	1.2	1.4	2.8
Naphthene aromatics, wt%	49.4	50.5	61.4	48.0	50.2	53.6	56.8	58.1	61.1	49.7	45.3	53.9
Polar aromatics, wt%	36.7	36.4	23.5	40.0	37.8	35.0	30.5	29.8	28.5	36.4	42.2	32.0
Asphaltenes, wt%	12.0	10.3	9.4	10.1	9.5	8.1	7.9	7.7	6.4	12.7	11.1	11.3
	RTFO aged									RTFO aged		
Saturates, wt%	1.2	1.4	4.2	1.2	1.5	2.9	3.4	3.1	3.8	0.7	1.3	2.6
Naphthene aromatics, wt%	45.6	47.4	52.7	44.6	46.2	48.1	50.7	53.7	49.5	44.3	40.1	45.0
Polar aromatics, wt%	39.5	38.3	32.3	42.8	39.8	37	34.8	32.4	36.6	40.2	44.6	39.2
Asphaltenes, wt%	13.7	12.9	10.8	11.4	12.5	12	11.1	10.8	10.1	14.8	14.0	13.2
	PAV aged									PAV aged		
Saturates, wt%	1	1.2	3.9	1	1.3	2.7	3.8	3.2	4.5	0.6	1.3	3.0
Naphthene aromatics, wt%	42.8	45.5	46.7	43.8	45.2	47.2	42.7	47.6	52.5	38.2	39.3	35.8
Polar aromatics, wt%	34.7	34.1	31.6	35.3	34.7	33.1	35	33.3	28.4	38.4	38.6	40.6
Asphaltenes, wt%	21.5	19.2	17.8	19.9	18.8	17	18.5	15.9	14.6	22.8	20.8	20.6

PG Properties: Figures 3 (a), (b), (c), (d) and Table 2 below depicts the results of PG properties of unaged and PAV aged blended bitumen samples at both high temperature and intermediate temperature. The PG temperature ranges for different bitumen samples were reported. From the results, one can make the following observations. Basra Light crude 90:10 blends exhibits the superior high temperature rutting resistance property satisfying the G*/sinδ> 1.0 kPa criteria whereas it shows a relatively poor intermediate temperature behavior of 27.6ºC for resistance against fatigue cracking. But compared with all the other blends, Basra Light 90:10 exhibits the highest PG temperature range of 53.9 ºC. Arab Mix crude 75:25 blends shows the lowest high temperature rut resistance temperature behavior (56.9 ºC) whereas it shows a superior intermediate temperature behavior (8.2 ºC) for resistance against fatigue cracking. Upper Zakum blends show an in-between rut resistance and fatigue resistance behavior for both high temperature and low temperature ranges. The blends were designated based on their respective high temperature behavior and reported in Table 2. From the results, one can conclude that Basra Light crude based blends are stiffer materials showing a viscoelastic solid like behavior and Arab Mix crude blends are relatively softer blends exhibiting a viscoelastic fluid like behaviour. Also, higher the PDA Pitch content (90% in 90: 10 blends) results in increased stiffness of blends. Figure 3(d) shows the apparent viscosity values for different blended unaged samples at 135 ºC for a shear rate of 70 RPM measured using a Brookfield rotational viscometer [15]. The apparent viscosity values of the samples are well within the 3 kPa criteria as per the PG specification requirement. Also as observed already, Basra Light crude based blends show the highest apparent viscosity values and Arab mix crude blends shows the lowest apparent viscosity values. Similarly 90:10 blends shows very high apparent viscosity values as compared to 85:15 and 75:25 blends indicating the influence of PDA Pitch on the rheology.

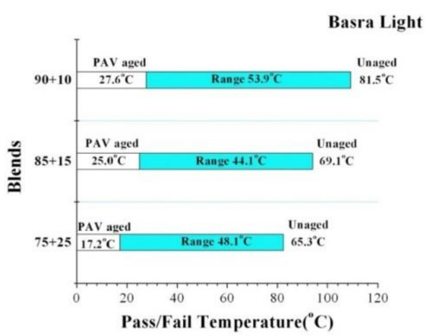

Figure.3(a).PG Pass/Fail Temperature- Basra Light 90:10,85:15,75:25 blends

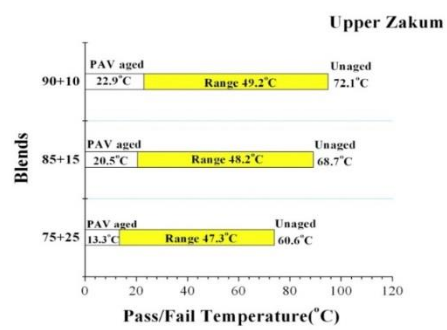

Figure.3(b).PG Pass/Fail Temperature- Upper Zakum 90:10, 85:15,75:25 blends

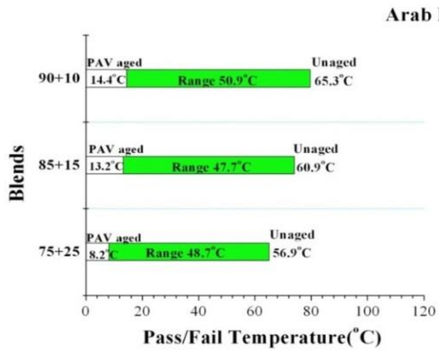

Figure 3(c) PG Pass/Fail Temperature- Arab Mix 90:10, 85:15, 75:25 blends

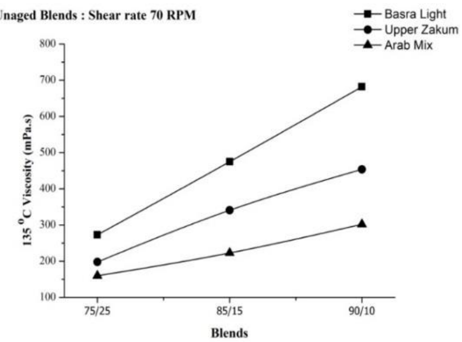

Figure 3(d) Apparent Viscosity at 135 ^{0} C for different blends

Table.2.PG Results of Blended Bitumen Samples

Samples	Critical Pass/Fail HT	Critical Pass/Fail IT	PG Temperature Rangein ºC	PG Grade (Based on HT only)
Basra Light 90:10	81.5	27.6	53.9	PG 76
Basra Light 85:15	69.1	25.0	44.1	PG 64
Basra Light 75:25	65.3	17.2	48.1	PG 64
Upper Zakum 90:10	72.1	22.9	49.2	PG 70
Upper Zakum 85:15	68.7	20.5	48.2	PG 64
Upper Zakum 75:25	60.6	13.3	47.3	PG 58
Arab Mix 90:10	65.3	14.4	50.9	PG 64
Arab Mix 85:15	60.9	13.2	47.7	PG 58
Arab Mix 75:25	56.9	8.2	48.7	PG 52

Asphaltenes and PG Properties: Figure 4 (a), (b), (c) below illustrates the interrelationship between asphaltene content (%) and different PG properties viz. critical pass/fail high temperature for resistance to rutting, critical pass/fail intermediate temperature for resistance to fatigue cracking, and 135 ºC viscosity values. From figure 4(a) one can observe that with increase in asphaltenes the critical pass/fail high temperature value for rut resistance criteria steeply increases and this was predominantly seen in blends from Basra Light crude source followed by Upper Zakum and Arab Mix. The effect of PDA pitch proportions is also clearly evident. In figure 4(b) with increase in asphaltene content as an effect of long term aging, the materials shows poor fatigue cracking resistance. The material may fail due to load associated fatigue cracking even in normal room temperature ranges of 25 to 30^{O} C for blends like Basra Light with higher PDA pitch contents. From the figure 4(c) one can observe significant changes in the viscosity values with increase in asphaltenes for different blend proportions of bitumen from different crude sources at unaged conditions. As asphaltenes are produced in oxidative aging of bitumen, the addition of more asphaltene (through more PDA pitch) essentially creates bitumen that is likely to fail much earlier due to cracking. On the other hand, blends with higher PDA pitch content (90:10) (more asphaltene content) can withstand the plastic deformation normally expected in the initial life of the pavement. But from this one cannot conclude that asphaltenes are fully responsible for the viscoelastic behavior of bitumen. Considering the fact that bitumen is made up of different component fractions as discussed above from the literature, one can argue that it is the association of asphaltenes with the remaining component fractions that holds the key and such associations have not been understood fully until now (Rajan*et.al.* 2010).

SUMMARY AND CONCLUSIONS

Blended bitumen samples from three crude sources were manufactured using three blend proportions of PDA Pitch and Heavy Extract at a pilot plant at R& D laboratory at CPCL, Chennai for this study. All the samples were subjected to short term (RTFO) and long term (PAV) aging. A chemical composition analysis was conducted using the Corbett's fractionation procedure and the blended bitumen samples were separated into four component fractions viz. Asphaltenes, Polar aromatics, Napthene aromatics and Saturates. PG tests were conducted as per ASTM procedure on the blended bituminous samples. An attempt was made to understand the interrelationship between the chemical composition and PG properties of blended bitumen. From the results, the influence of crude source, processing methods and aging on the chemistry and rheology of bitumen was clearly understood. The role of asphaltenes on the PG properties of binders was clearly evident.

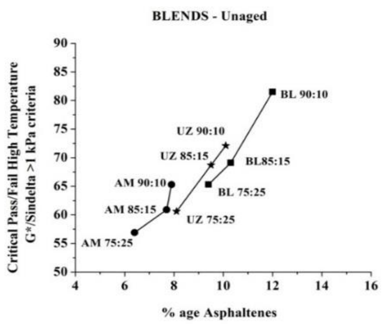

Figure 4(a) Asphaltenes Vs. High Temperature (HT) For Rut Resistance

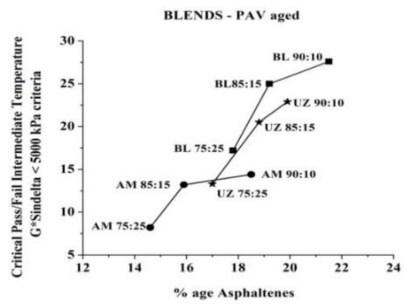

Figure 4(b)Asphaltenes Vs. Intermediate Temperature (IT) For Fatigue Cracking Resistance

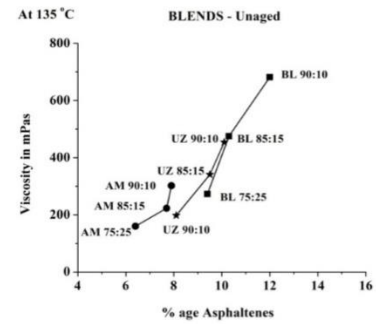

Figure 4(c) Asphaltenes Vs.135 ^{0}C Viscosity

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