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Intermolecular Bonding Study of Bituminous Material using Compositional Analysis

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ABSTRACT. *Bitumen is amorphous, black-coloured visco-elastic material, composed principally of hydrocarbons having high molecular weight characterized by "asphaltenes, resins and oils". Investigation on the composition of Bitumen having same grade taken from different Refineries i.e., NRL, ARL as Virgin Binder (VB) and RAP (extracted from the pavement). Also the careful examination of the Intermolecular Bonding of the Bitumen Microstructure by a review of studies and correlation with its composition. In research methodology, firstly SARA analysis was performed by Column chromatography on each type of bitumen. Secondly, microstructure intermolecular bonding was investigated theoretically from the literature of methods Scanning Electron Microscopy (SEM), ESEM etc. and its critical analysis was conducted. From the research results, it has been found out that there are solid and liquid phases having different percentage compositions of the bitumen that are Saturate, Aromatic, Resin, and Asphaltenes (SARA) according to their polarizability and polarity of each type of bitumen. Asphaltene is a solid phase while the other three are in liquid phases that are basically taken from Maltene. Then Compared SARA Results of VB with RAP. Data obtained from compositional analysis of asphalt help us to handle the problems related the stability of bitumen structure. While microstructure intermolecular bonding study theoretically from the literature using techniques like SEM, ESEM etc. helped to understand the internal nature of the bitumen when it is aged, unaged and modified by many modifiers like CNF, SBS, SBR latex fibre etc.*

Keywords: SARA Analysis, Scanning Electron Microscopy (SEM), Bitumen, Microstructure

1. INTRODUCTION

Bitumen has been used in road construction and engineering since the days of early Babylon [1]. Currently, it's one of the main road transportation infrastructure products. Approximately 95 percent of worldwide bitumen supply (approximately 100 Mt/year) is utilized as asphalt mixtures for the paving business [2]. Bitumen is a complicated substance, and its characteristics appear to be different based on source, process of production, contaminants, and additional chemical-physical treatment. The complicated chemical composition of bitumen makes most analytical approaches difficult beyond the point of applicability.

A commonly known analytical method is to classify bitumen into a Saturated, Aromatic, Resin, and Asphaltene fraction (SARA) due to same chemical behavior. SARA methodology of analysis which separates elements of crude oil according to their polarity and polarization. SARA research is a very wide area for studying bitumen and related properties of bitumen compositions. Asphaltene is the insolvable n-heptane and toluene dissolve portion of bitumen while in n-heptane this portion is called Maltene. Maltene consists of the Saturates, Aromatics and Resins that are separated by column Chromatography. It is the procedure of bitumen isolation which is most accepted and effective.

Scholarly work on bitumen as well as its bonding demonstrates and provides strong proof that bitumen really has a significant composition and micro-structure that can be evaluated and visualized using different techniques. Such methods are “Small Angle X-ray Scattering (SAXS)”, and studies with “Small Angle Neutron Scattering (SANS)” have shown beyond doubt that there are organized structures and configurations in bitumen. Although Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM) showed a distinctive and reproducible presence morphology that is sometimes defined as 1–5 μm "bee-like" structures [3].

“Confocal Laser Scanning Microscopy (CLSM) has uncovered the existence of fluorescent centres in bitumen of 1–10 μm size [4]. CLSM is effective of monitor highly localized fluorescence emission as well as enables for comprehensive examination of the asphalt bitumen [5]. This may be utilized to accurately visualize bitumen microstructure as well as the structural impacts of bituminous alteration [6]. In this research, SARA compositional analysis of given bitumen have been performed in details and their correlation with the literature investigation of intermolecular bonding of bitumen have been explained.

2. LITERATURE REVIEW

SARA analysis is crucial for examining how the bitumen and crude oil's characteristics relate to composition. SARA fractions effects rheology properties like dynamic modulus rises by increase in asphaltenes or resins. Also, SARA analysis helps to make an approach for the study of microstructure of bitumen. A Scientist [7] researched the impact of fractions in 1979 by introducing asphaltenes in varying proportions to the original asphalt. This study revealed that asphalt binder viscosity increased with the increase in asphaltenes content and reduced with the increase in Maltene content. SARA fractions in correlated with microstructure of bitumen by fluorescent approach [4]. They had taken the five different grade bitumen and did CLSM on it. They used the excitation radiation of wavelength 488 mm and after that they observed the emission radiation from bitumen of wavelength 500-530 and by these radiations, they got the image that was showing the microstructure image of the bitumen. In the study, they separated the bitumen in the Asphaltene and Maltene and Maltene further separated in Saturates, Aromatics, Resins and found that resin and aromatic phases are the only elements able to produce adequately intense fluorescent emissions. It is a clear justification for a complicated internal micro-structure which consists of an aromatic mantle covering an inner core [8]. Various microscopic techniques, such as optical microscopy, SEM, ESEM etc. used in past and now a days for microscopic intermolecular analysis. Gaskin, et al. used ESEM not just to asphalt binder but also bitumen percentage fraction including asphaltenes, maltenes, and waxes. The network structuring has been seen at varying temperatures [9].

Bitumen is the typical kind of rheological material. When comparing the rheological properties with the SARA fraction of modified asphalt binders shown that they have a greater impact on dynamic modulus and Phase Angle. The dynamic modulus increases when frequency increase and achieves a steady value whenever the frequency is relatively high [10]. Asphalt is usually considered to be a colloidal structure consisting of fractions of SARA. Various asphalt fractions obey a colloidal rule [11]. The colloidal instability index (CII) is an approach to determine the instability of heavy oil which is based on the chemical composition of crude oil. It is reflecting or showing the stability index of the bitumen Fractions like Maltene or Asphaltene. Stability of crude oil can be analyzed by the equation (1).

$$Colloidal\ instability\ index\ (CII) = \frac{Saturates + Asphaltenes}{Aromatics + Resins} \quad (1)$$

The crude oil or bitumen stability can also be evaluated by using the SARA fractions. When the CII is lesser than 0.7 then it is recognized as stable while when CII value is 0.9 then the bitumen is unstable [12].

3. METHODOLOGY

The methodology includes the material selection and specific experimental testing that are used for investigation purpose. In This study comprises on two phases, first describes the materials and second is related to experimental work.

3.1. Materials

Three types of asphalt binders were used. They are RAP (Reclaimed asphalt pavement) that are extracted from detritus Road of Taxila, and its Grade is checked during testing by penetration grade and compared with the virgin binder (penetration grade 60/70) (PG-58-22) from Attock (ARL) & Karachi (NRL) refineries.

RAP was extracted according to ASTM D2172 and ASTM D5404. The aggregates and asphalt binder has been separated from RAP by centrifuge extraction method using the trichloroethylene (TCE) solvent according to ASTM D2172. TCE was vaporized from the extracted material by rotary evaporator in accordance with ASTM D5404.

3.2. Experimental Program:

Analysis of bitumen fractions using SARA analysis test according to ASTM D4124 is shown in Figure 1. While rheology study would be done by DSR tests and critically analysis from literature and investigation of the microstructural behavior of bitumen would also be done by Scanning Electron Microscopy (SEM) and ESEM literature study theoretically and then would correlate them by compositional analysis (SARA) testing data.

3.2.1 SARA Analysis:

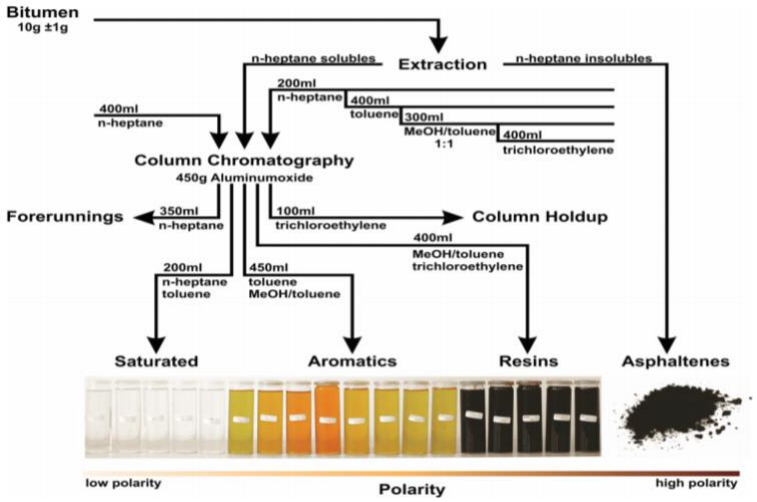

Fig-1: Schematic SARA analysis Procedure according to ASTM D4124

3.2.2. Rheological Analysis:

Rheological Properties test was carried out on the Anton Paar Peltier dynamic shear Rheometer (DSR) by which the program investigates the Performance Grading (PG) of the bitumen and also Frequency sweep test (FST). Using this test, the stiffness or resistance of the bitumen against deformation under the repetitive load according to ASTM D7175− 15 can be evaluated. The samples for all three types of asphalt were made that were then used in the experimental study. The sample made is 25 mm in diameter and 1 mm thick. To determine the time / temperature responsiveness Frequency sweep test have been performed. This analysis expresses the oscillatory shear stress at a constant strain level as well as calculates the volume and failure modulus at a specified frequency and temperatures scale. Schematic procedure of using DSR is given below in fig 2 and fig 3.

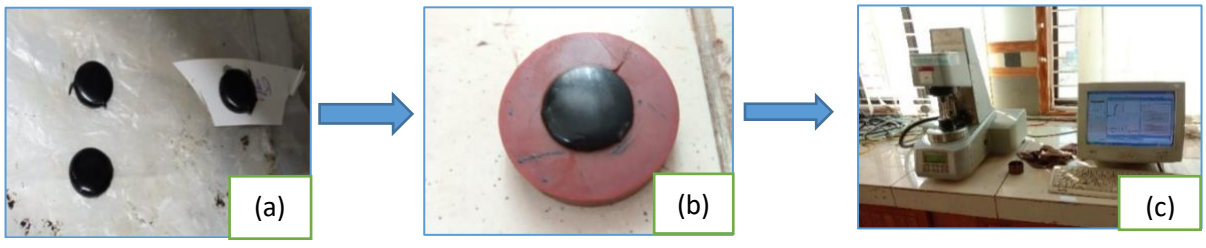

Fig-1: From left to Right (a) Asphalt Samples, (b) Mould for making specimens, (c) DSR Machine

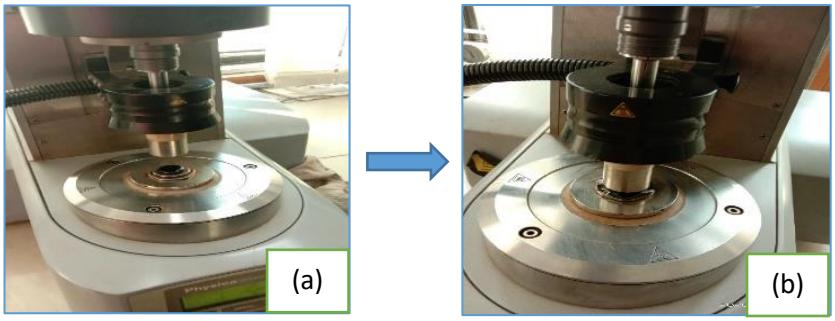

Fig-3: From left to Right: (a) sample placing, (b) Applying Loading

3.2.3. SEM Analysis:

The region that has been micro-analysed is treated by a SEM equipment with a closely aligned electron ray, which might have travelled across the surface or dynamically in a raster. The whole SEM Analysis technique is depicted in the schematic image below.

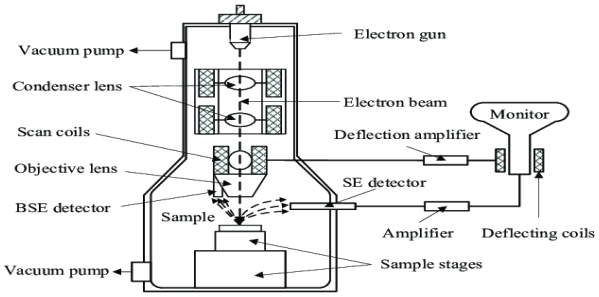

Fig-4: schematic diagram of SEM Analysis [13]

4. RESULTS AND DISCUSSIONS

SARA fractions of the Asphalt binder were isolated by using the method of Column Chromatography. The Results of SARA fraction and their stability index according to ASTM D4124 are shown in the following charts.

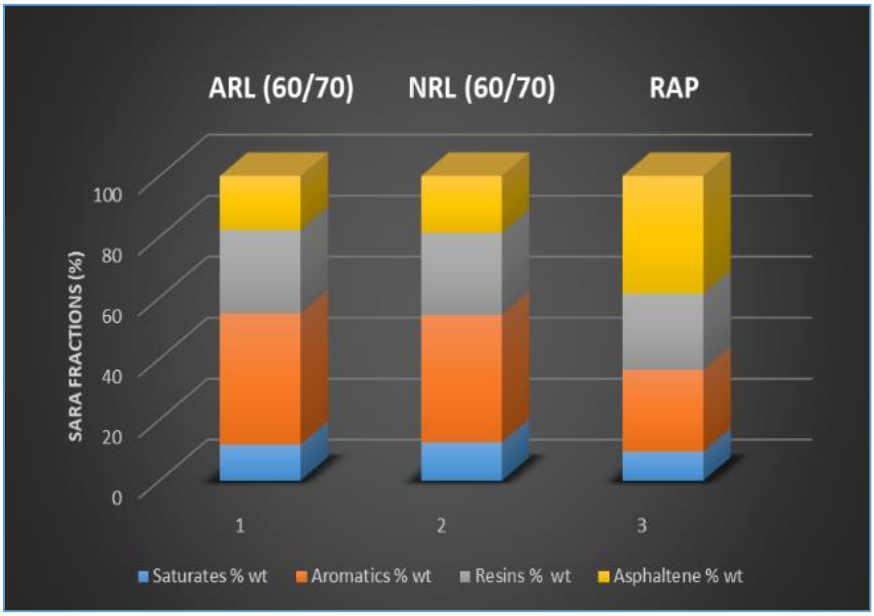

Fig-5: Bar Chart of SARA Fraction of Virgin Binder (60/70) ARL, NRL & RAP Binder

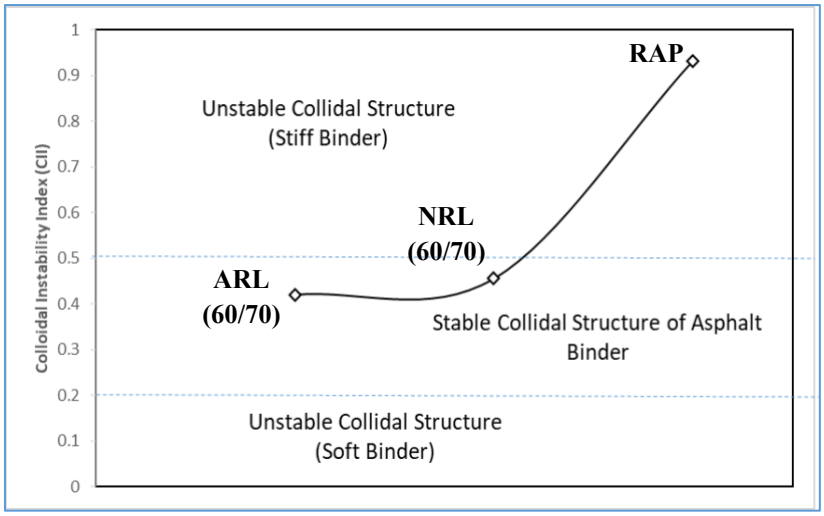

Fig-6: Colloidal instability Index (CII) Chart of Virgin Binder (60/70) ARL, NRL & RAP Binder

The value of Saturates in all three binders approximately near each other and it is also decreasing from ARL to RAP. While aromatics values of VB have almost equal and a significant change in the RAP value that make RAP less viscous. Also, the RAP has maximum value of Asphaltene that make the RAP stiffer than ARL and NRL. From CII curve it can be seen that the RAP is unstable in nature as compared to VB because of the high value of asphaltenes content. This high value asphaltenes also showed that the dispersion/scattering of the asphaltenes is week. Rheology properties of RAP has higher performance Grading temperature that was about the 88 ^{0}C.

As far as microstructural analysis investigation of bitumen concerns, it has been done by reviewing the past studies of many researchers. A lot of researchers did study from last 20 to 30 years on the microstructure of the bitumen of different grades using SEM and ESEM techniques.

In 2013, A researcher used SEM analysis to investigate CNF (Carbon Nano-modifiers) modified HMA. The results show that when CNF amount increases the binder density increases. That means the interconnectivity would strong and good internal structure would be made. This is showing in Fig. 5 in the form of the linear CNF structure. But at the root of the CNF, SEM shows the cone shaped structure of the modified binder. This shows that the high adhesion in the Binder [14]. The study carried out in 1997 by modifying bonder using SBS, SBR latex polymer was investigated using ESEM. They noted that the fibril or small slender fibre type structure have been made due to the concentration of the fibre. Due to the SBR addition a significant change in the microstructure of binder. Because of this, the density of the fibril structure grows, and a particularly special type of deformation called elongation rather than necking results as shown in Figure 6. These types of morphology are very helpful in the asphaltic concrete to which the cracks that are producing can be healed easily [15].

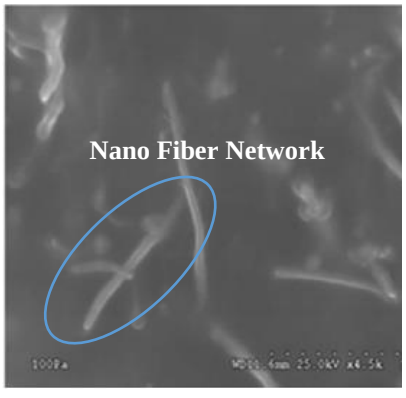

Fig-7: CNF Linear Microstructure [14]

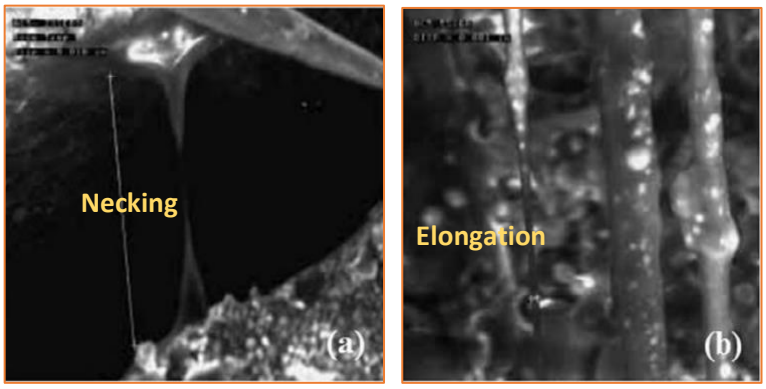

Fig-8: (a) deformation mechanism of necking with fibril and (b) Deformation mechanism of Elongation with fibril [15]

Theoretical investigation on the Rheological properties like PG, FST etc. was conducted. The results showed that when the binder in its original form they have the extreme high and low temperature. Like change of PG '80-16' to PG '70-10' But with the addition of the rejuvenator like Sulphur, etc. the PG can be set on the standard range. While Asphaltene has greater impact on FST property of the binder that dynamic modulus rises with the rise in quantity of asphaltenes. At low frequencies the differences between various modulus curves are greater than at higher frequencies [7].

5. CONCLUSIONS

- RAP has maximum value of Asphaltene compared to Virgin Binders that makes RAP solid in nature and unstable than Virgin Binders. While CII of RAP is 0.931 that make its stiffer binder. This high value of asphaltenes shows that the dispersion/scattering of the asphaltenes is week.
- Temperature for Rheology characteristics such RAP greater performance grade was about 88 C. The quantity of asphaltenes has an effect on rheological parameters such as PG and FST, among others. With more asphaltenes present, the FST property of the binder is more significantly affected, and the dynamic modulus increases.
- When an asphalt binder is altered and artificially aged, the bonding structure of the material manifests itself differently. SEM, ESEM, CLSM, AFM, and other techniques and apparatus have a stronger influence on the binder's microstructure.
- Using the modifiers like CNF, SBS, SBR latex fibre, increases the density of asphalt binder by making the network and fibre thread like structure. These types of morphology are very helpful in the asphaltic concrete to which the cracks that are producing can be healed easily.

REFERENCES

[1] Abraham H. Asphalts and allied substances, 4th edn. D. Van Nostrand Company Inc., New York; 1920.

[2] Lesueur D. The colloidal structure of bitumen: consequences on the rheology and on mechanisms of bitumen modification. Adv Colloid Interface Sci. 2009 January; 145:42–82.

[3] Wilson A, Champion-Lapalu L, Fuchs G, Martin D, Planche JP. Cryo-scanning electron microscopy: a new tool for interpretation of fracture studies in bitumen/polymer blends. Energy Fuels. 2002; 16:143–147. doi: 10.1021/ef010122s

[4] Bearsley S, Forbes A, Haverkamp RG. Direct observation of the apshaltene structure in paving-grade bitumen using confocal laser-scanning microscopy. J Mi-crosc. 2004; 215:149–155

[5] Lackner R, Spiegl M, Blab R, Eberhardsteiner J. Is low-temperature creep of asphalt mastic independent of filler shape and mineralogy? Arguments from multiscale analysis. J Mater Civ Eng. 2005; 17:485–491

[6] Sengoz B, Isikyakar G. Analysis of styrene-butadiene-styrene polymer modified bitumen using fluorescent microscopy and conventional test methods. J Hazard Mater. 2008; 150:424–432. doi:10.1016/j.jhazmat.2007.04.122

[7] John M. Dealy. Rheological properties of oil sand bitumen. The Canadian Journal of Chemical Engineering. 1997; 57:677-683

[8] Florian Handle et al. The bitumen microstructure: a fluorescent approach. Materials and Structures. 2016; 49:167–180

[9] Gaskin J. On bitumen microstructure and the effects of crack healing. UK: University of Nottingham. 2013; Ph. D thesis.

[10] Yongli Xu, Ph.D.Enhao Zhang and Liyan Shan, Ph.D. Effect of SARA on Rheological Properties of Asphalt Binders. Journal of Materials in Civil Engineering. June 2019; Volume 31 Issue 6.

[11] Lesueur, D. The colloidal structure of bitumen: Consequences on the rheology and on the mechanisms of bitumen modification. Adv. Colloid Interface Sci. 2009; 145 (1 –2): 42–82.

[12] S. Verdier. Experimental study and modelling of asphaltene precipitation caused by gas injection (Ph.D. thesis). Technical University of Denmark. 2006.

[13] Yao, Sheng & Hai, Li &Shuiquan, Pang & Zhu, Benliang& Zhang, Xianmin&Fatikow, Sergej. A Review of Computer Microvision-Based Precision Motion Measurement: Principles, Characteristics, and Applications. IEEE Transactions on Instrumentation and Measurement. 2021; PP. 1-1. 10.1109/TIM.2021.3065436.

[14] Khattak, A. Khattab, P. Zhang, H.R. Rizvi, T. Pesacreta. Microstructure and fracture morphology of carbon nano-fiber modified asphalt and hot mix asphalt mixtures. Materials and Structures. 2013 December; 46: 2045–2057. DOI:10.1617/s11527-013-0035-3

[15] A. Bhurke, E. Shin, L. Drzal. Fracture morphology and fracture toughness measurement of polymer-

modified asphalt concrete. Transportation Research Record: Journal of the Transportation Research Board. 1997 January; 1590:23–33.