EFFECT OF POLYMER MODIFICATION ON THE MICROSTRUCTURE OF BITUMEN

Juan Camilo Munera, Mónica Alvarez Lainez, Alex Ossa
Engineering Materials Research Group, School of Engineering, Eafit University, Medellin - Colombia

ABSTRACT

Polymer modification of bitumen has been commonly performed since the 1980's in order to decrease the susceptibility of bitumen (and pavements) to high and low temperatures, reducing common failure mechanisms as rutting and cracking. Despite of the widespread use of polymer modified bitumens, it is narrow the understanding of the interactions between polymer modifiers and bitumen at the micro and nano scales. In this study, Atomic Force Microscopy (AFM) on the non contact mode was used to study the effect of modification of bitumen with additions of i) Polyethylene wax; ii) SBS rubber; and iii) crumb rubber at different mass fractions and mixing conditions, on the microstructure of the material. The addition of Polyethylene wax showed to have a direct effect over the asphaltene phase morphology and distribution over the bitumen, making it stiffer. On the other hand, addition of rubber (both SBS and crumb rubber) showed to produce a length and size reduction on the asphaltene phase chains, while the maltene phase interacted with the elastomeric materials responsible for the elastomeric behavior of polymer modified bitumen at the macro scale.

Keywords: Polymer modified bitumen, atomic force microscopy, bitumen microstructure, rubber, polyethylene wax

1. INTRODUCTION

Bitumen is a material with adhesive properties, which can be found on different forms in nature, or can be produced by oil refining processes. This material consists of a mixture of different hydrocarbons, which are divided into four fractions according to their chemical affinity: e. g. Saturates, Asphaltenes, Resins and Aromatics. Asphaltenes, are the higher molecular weight components and are solid at room temperature. Bitumen has a colloidal structure in which asphaltenes are dispersed in a continuous matrix formed by the remaining components, called maltenes. Bitumen properties therefore change according to the nature and proportion of these constituents [1]. Optical microscopy has been a technique widely used to study the microstructure of different materials, however bitumen has not received much attention from microscopists because of its opacity and adhesive characteristics. At best conditions, the resolution limit of optical microscopy is about 200nm, in contrast, atomic force microscopy (AFM) can solve atomic and molecular resolution. The AFM technique, since its appearance in the 1980’s, has been an important tool for studying the structure of materials at the micro and nano scales. Based on local interactions between the tip and the surface of a sample provides images of surfaces with high spatial resolution in real time. For this reason, AFM has been used in the characterization of materials to determine their physical properties and morphological surface characteristics [2]. The aim of this study was to identify, by means of atomic force microscopy AFM, structural changes occurring in the asphalt by addition of three different polymers commonly used in the modification of bitumen for practical purposes.

2. MATERIALS AND METHODS

2.1 Materials.

The bitumen used in this study was an 80/100 penetration grade material from Colombia, processed at the Barrancabermeja-Ecopetrol refinery. Three different polymers were used as modifiers: styrene-butadiene-styrene (SBS) with a ratio 70/30 butadiene/styrene, polyethylene wax (PEW) and crumb rubber (CR) with a particle size 25 mesh retained (0.71mm).

2.2 Preparation of mixtures.

The polymer-bitumen mixtures were prepared in an open mixer, using Heidolph mechanical stirrers. A defined quantity of bitumen was preheated about 135 ^{o}C to molten state. Then the temperature was increased between 180 and 190 ^{o}C and the agitation started, followed by the addition of the polymer modifier. Stirring continued at 2000 rpm for a time period of 2 hours. The blends of bitumen and polymer were prepared at three different weight proportions: 3%, 6% and 9% for each polymer.

2.3 Preparation of films for AFM analysis.

Bitumen films were prepared by the application of a bead of bitumen into microscope slides. Then, it was heated for 1 minute on a heater-controlled plate at about 90 ^{o}C, a temperature high enough to melt the bitumen, but not so high as to oxidize it. The films were then cooled down to room temperature for a minimum of 24 hours before taking them to the AFM. This annealing process allowed for the ordering of the asphaltenes responsible for steric hardening [3].

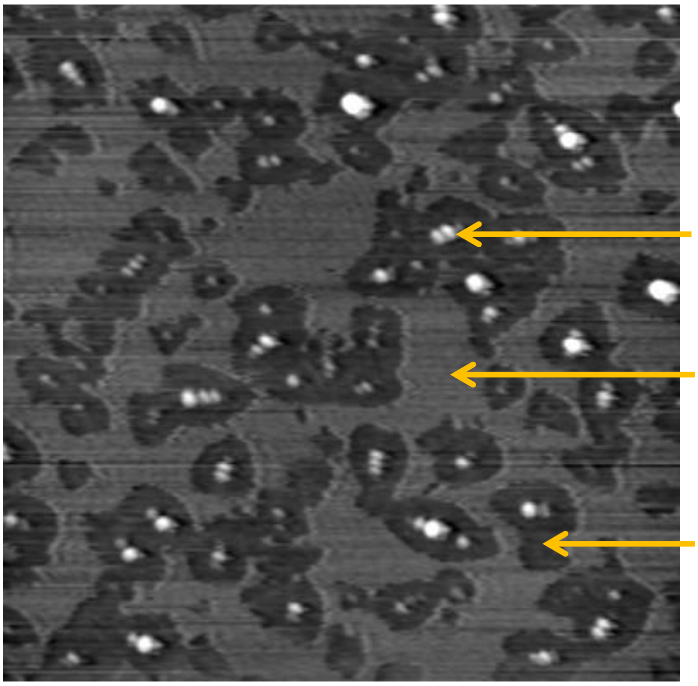
2.4 Atomic force microscopy.

The atomic force microscope used was a Nanosurf Easyscan2, operating in the mode AFM-NC (non contact mode). Vistaprobe silica probes T90 with beam-shape, having a spring constant and free resonance of 48N/m and 190 khz, respectively were also used. Topographic images of 40 x 40 um, and 10 x 10 um were obtained in tapping mode at room temperature for each of the polymer-modified bitumens prepared.

3. RESULTS AND DISCUSSION

3.1 Microstructure of neat and oxidized bitumen.

Figure 1 shows the microstructure of neat bitumen. It shows three characteristic phases which have been identified in previous studies (e.g. Catanphase, Pheriphase and Paraphase,) [3]. All these phases are related with the presence of SARA fractions (saturates, aromatics resins and asphaltenes). The catanphase corresponds to a dispersed phase with appearance similar to chains, these represent the hardest regions of bitumen and are related to asphaltenes. This phase was called: "bee structure " by Loeber and colleagues [4] and later named "catanphase" due to its wavy morphology [5] (see also Figure 2). Asphaltenes have soft and hard spots with a spacing of about 500 to 1000 nm and heights of 40 nm approximately (Figure 2). The second phase, called "periphase" is the dark region that surrounds the asphaltenes and corresponds to the resins, polar organic compounds with lower hardness than asphaltenes. They are responsible for chemical stabilization of asphaltenes [6]. Finally, the continuous matrix that surrounds the two aforementioned regions consists of a sea of low molecular weight organic compounds, and corresponds to saturated and aromatic hydrocarbon oils. This phase is called “Paraphase” and is the softer phase of the material, and also characterizes the thermal susceptibility of the asphalt. Even though this technique has not been able to quantify each fraction of saturates, resins, aromatics and asphaltenes (SARA) present in the bitumen, it allowed finding a close relationship with their viscoelastic properties as was evidenced in previous studies [7]. The phase that has generated more research interest has been the "bee- phase" or "catanphase", as it has been found that this phase has a close relation with the material stiffness. That is, as the amount of catanphase increases, so does the stiffness of the material. The morphological characteristics of this phase have been attributed to the content of metals such as vanadium and nickel in the bitumen by Masson et.al. [3, 5].



“bee-structure” or *catanphase*. Phase region corresponding to asphaltens.

Paraphase, region corresponding to saturate and aromatics oils.

Pheriphase, region corresponding to Resins.

Figure 1. Neat Bitumen topography, the arrows indicate the various phases present in bitumen (40 x 40um).

Figure 3 shows the bitumen surface after a hot air blowing process knew as oxidation. This process is commonly used to increase the stiffness and reduce the thermal susceptibility of bitumen. This process generates a breaking of molecular chains, being the saturated and aromatic fractions the compounds more sensitive to this process [6]. The result is the generation of higher molecular weight compounds. This figure shows a considerable increase in asphaltene amount and length, with a reduction on the matrix regions composed of light oils, as compared to neat bitumen (Fig. 1). This produces an increase in viscosity, which is reflected in the increase of hardness and thermal susceptibility decrease as reported in previous studies [8,9]. The bitumen phases constituted for the organic compounds are highly dependent on temperature so changes on the structure or distribution in the saturates, aromatics, resins and asphaltenes generated a marked effect on mechanical and rheological bitumen properties [9].

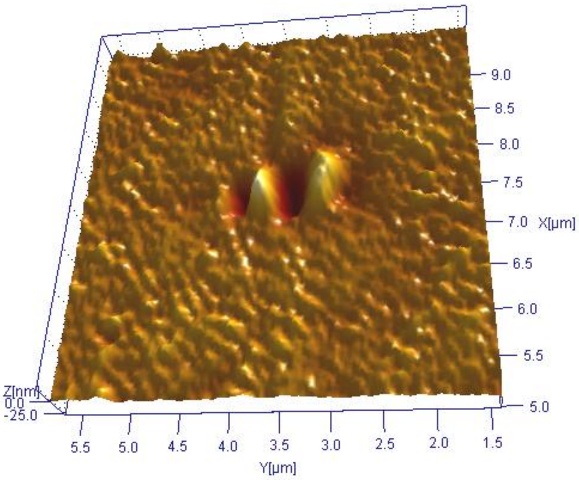


Figure 2. 3D Image corresponding to asphaltenes chain, called “bee-structure”.

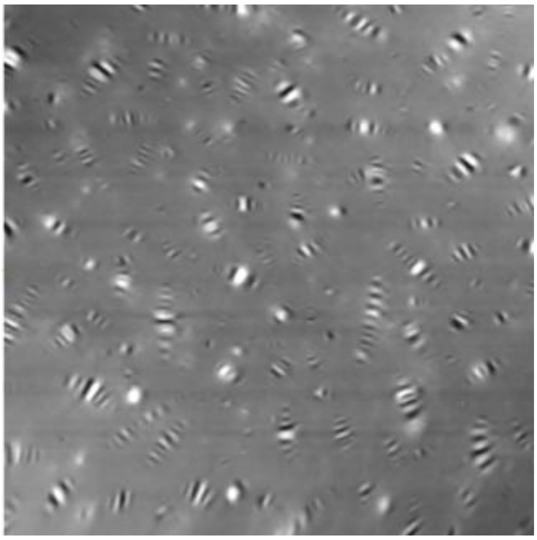


Figure 3. Bitumen after blowing process (40 x 40um)

3.2 Microstructure of bitumen - polyethylene wax mixtures

Figures 4 to 7 show the effect of addition of polyethylene wax (PEW) in proportions of 3 and 6 % w / w on the bitumen morphology. The PEW used in this mixture corresponds to an oligomeric polyethylene, which is partially miscible with the asphaltenes because of their similar molecular weight. This miscibility has been evident in the size and length increment suffered by the asphaltenes regions (see figures 5 and 7). This increase in size and length of the chain like structures on the material has a direct effect on the increase on stiffness of the PEW modified bitumen in comparison to the non-modified one.

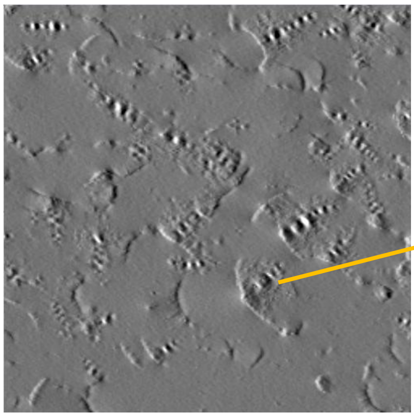


Figure 4. Bitumen + 3% PEW (40x40µm)

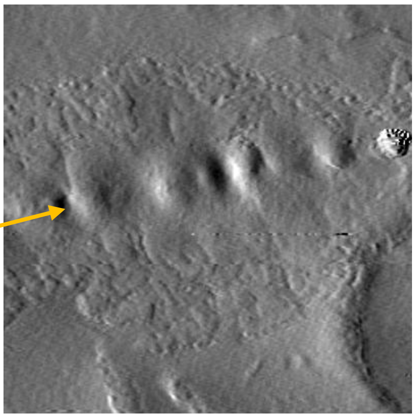


Figure 5. Bitumen + 3% PEW (10x10µm)

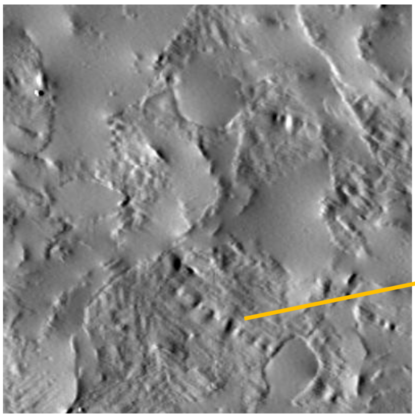


Figure 6. Bitumen + 6% PEW (40x40µm)

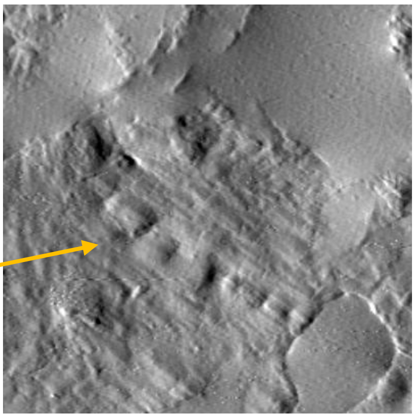


Figure 7. Bitumen + 6% PEW (10x10µm)

Figures 8 and 9 show the topography for a bitumen modified with 9% w / w PEW, with the arrow pointing towards an asphaltene chain. For this high content of PEW it is seen a significant change on the microstructure of the material, having a surface rich in wax around the asphaltenes.

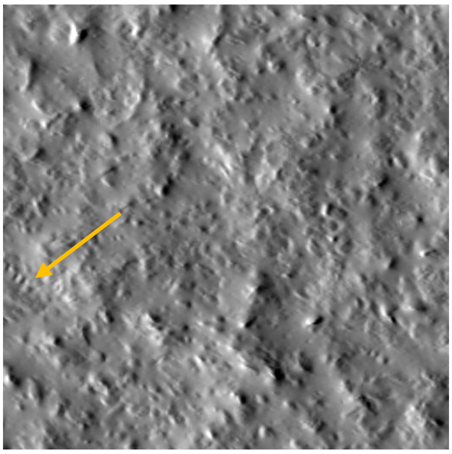


Figure 8. Bitumen + 9% PEW (40x40µm)

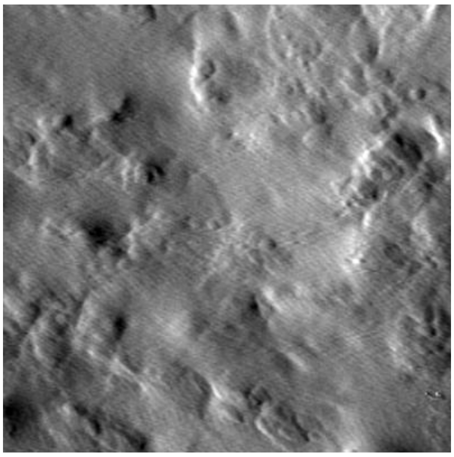


Figura 9. Bitumen + 9% PEW (10x10µm)

3.3 Microstructure of bitumen - SBS mixtures

Figures 10 and 11 show the three characteristic bitumen regions mentioned in section 3.1. The apparent asphaltene chains invariance can be attributed to the SBS interaction with the aromatic oils present in asphalt [6]. This interaction creates a swelling of the elastomeric fraction in the SBS copolymer, producing a modification of the region corresponding to the maltenes (Paraphase) [9]. Figure 12 shows a mixture with 3% w/w SBS where the asphaltene and maltene regions can be identified. The swollen SBS corresponds to the maltene region (periphase), and this region is responsible for the elastomeric behavior of SBS modified bitumens.

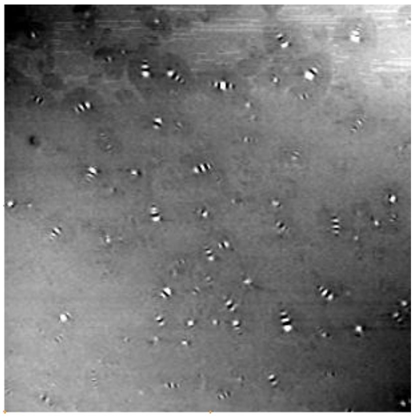


Figure 10. Bitumen + 3% SBS (40x40µm)

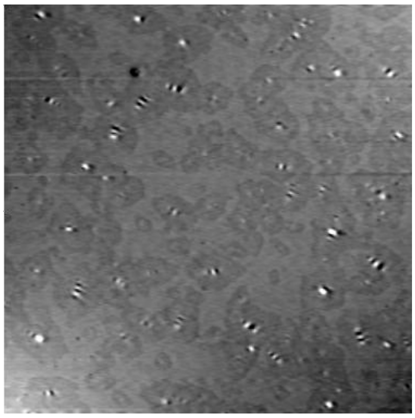


Figure 11. Bitumen + 6% SBS (40x40µm)

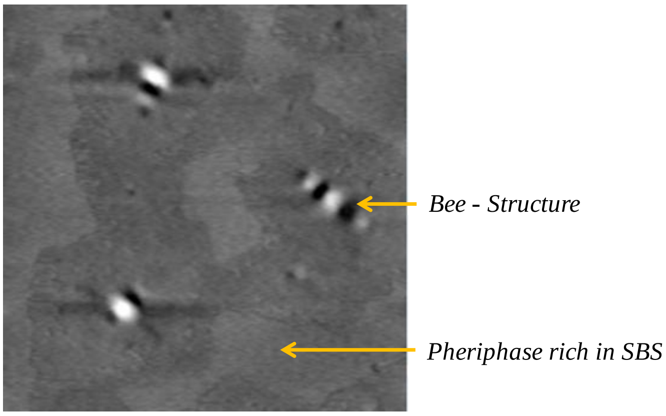


Figure 12. Bitumen + 3% SBS (10x10µm)

3.4 Microstructure of bitumen – Crumb rubber mixtures.

Figures 13 to 15 show the effect of crumb rubber addition to bitumen on its microstructure. Asphaltene structures reduce their chain length and size to about 100-300 nm, which leads to greater dispersion, affecting the macroscopic properties, reducing the stiffness and thermal susceptibility of the material.

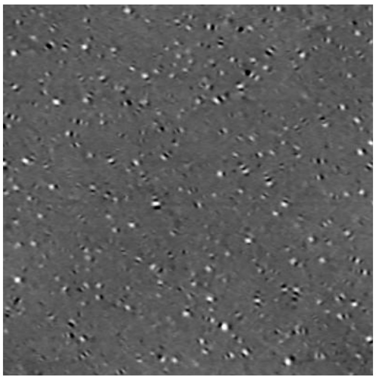


Figure 13. Bitumen + 3% CR (40x40µm)

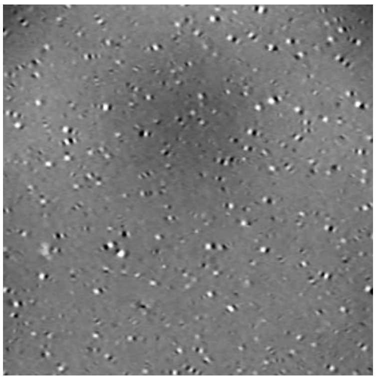


Figure 14. Bitumen + 6% CR (40x40µm)

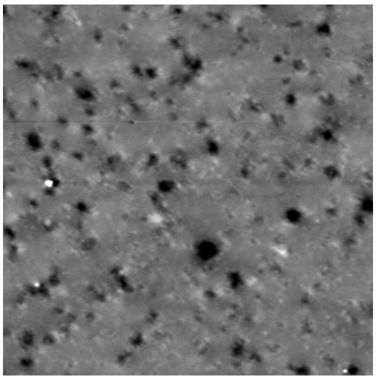


Figure 15. Bitumen + 9% CR (40x40µm)

4 CONCLUSIONS

Atomic force microscopy (AFM) allowed the study and analysis of the morphological changes of the different bitumen phases with addition of polymer modifiers, and also due to an oxidation process. The images obtained by AFM allowed identifying three characteristic regions in the neat bitumen (asphaltenes, resins and maltenes). The interaction and miscibility between polymer modifiers and components of asphalt is reflected in the changes of structure, proportion and distribution of these regions. These changes have a marked effect on the mechanical and rheological properties of the modified asphalts.

5. ACKNOWLEDGMENTS

The authors would like to thank Industrias Cascabel S.A for providing the materials used in this study. We also want to acknowledge the financial support received from Eafit University and the Department of Science, Technology and Innovation, Colciencias (Colombia) by means of the grant No 577-2009.

REFERENCES

[1] R.M. German, “Shell Bitumen Handbook”; 1996, John Wiley and Sons, Inc.

[2] R. Garcia and R. Perez, “Dynamic atomic force microscopy methods”; Surface Science Reports, Vol. 47 (2002), p. 197-301.

[3] J.F. Masson, V. Leblond and J. Margeson, “Bitumen morphologies by phase-detection atomic force microscopy”; Journal of Microscopy Vol. 221 (2006) p. 17–29.

[4] L. Loeber, O. Sutton, J. Morel, J.M. Valleton, G. Muller “New direct observations of asphalts and asphalt binders by scanning electron microscopy and atomic force microscopy”; Journal of Microscopy, Vol. 182 (1996) p. 32-39.

[5] J.F. Masson, V. Leblond, J.C. Margeson, S. Bundalo-Perc.; “Low-temperature bitumen stiffness and viscous paraffinic nano-and micro-domains by cryogenic AFM and PDM”; Journal of Microscopy, Vol. 227 (2007), p. 191-202.

[6] D. Lesueur, “The colloidal structure of bitumen: Consequences on the rheology and on the mechanisms of bitumen modification”; Advances in Colloid and Interface Science, Vol. 145 (2009), p. 42-82.

[7] J. C. Múnera, M. Álvarez-Láinez y E. A. Ossa. “Fabricacion y análisis de asfaltos modificados con polímeros”; Anales SAM/CONAMET, 2010.

[8] M. García-Morales, P. Partal, F.J. Navarro, F. Martínez-Boza, C. Gallegos, “Linear Viscoelasticity of Recycled EVA-Modified Bitumens”; Energy and Fuels, Vol. 18 (2004), p. 357-364.

[9] A. Jäger, R. Lackner, Ch. Eisenmenger-Sittner, “Identification of four materials phased in bitumen by atomic force microscopy”; Road Materials and Pavement Design, (2004) p. 9-24.