REOLOGICAL AND STRUCTURAL CHARACTERIZATION OF BITUMEN MODIFIED WITH REACTIVE POLYMERS

Filipa Antunes Luz[1], António Correia Diogo[1], Cátia Mendes Duarte[2], Jorge Reis Moura[2]

[1]Universidade Técnica de Lisboa - Instituto Superior Técnico 5 *[2]Galp Energia/ Probigalp - Ligantes Betuminosos, SA*

ABSTRACT

The addition of reactive polymers pretends to improve the properties of bitumen due to the conditions of application to which they are subject to, with a severe performance tending to reduce the thickness of layers on pavement roads, due to the increase of traffic and its constant need for maintenance. Thus, bituminous mixtures were prepared from different refineries, with concentrations addition of 1% and 3% of reactive polymers. These mixtures were compared with SBS modified bitumen. In this essay were studied the changes in structure and properties that may occur with these changes, through rheological tests, observation by atomic force microscopy and tests of specification.

Therefore it was found that there are actually changes in properties and structure in bitumen modified with reactive polymer. The tests of specification indicated changes in various properties of bitumen, with a decrease in penetration and an increase of the softening temperature, viscosity and elasticity. Modified bitumen with prepolymers also have a good performance in storage and when subjected to aging.

The rheological measurements indicated that the addition of reactive polymer increases the conservative and dissipative components of the cut module, improving elasticity and viscosity of bitumen. The AFM images also allowed observing their morphological multiphase structure, with three distinct phases: one phase dispersed a perifase and a parafase contiguous to them. Thus, there was a heterogeneous mixture that depends on the nature and concentration of the modifier used, and also the source of bitumen.

Keywords: Bitumen, Modified Bitumen, Reactive Polymers, Bitumen Rheology, Atomic Force Microscopy.

1. INTRODUCTION

Bitumen is defined as a viscous non-volatile material soluble in toluene, derived from crude oil or from bitumen natural lakes, mostly composed by a complex mixture of some thousands of hydrocarbons. Bitumen has a black or brown color and displays excellent waterproofing and adhesive properties. It is resistant to oxidation and environmental agents which results in good durability properties. The major areas of application of bitumen are road paving and waterproofing insulation. [1-2]

Bituminous products are originating from different sources: by consequence, their properties present a wide range of variability according to the source from which they are extracted. Most of the bitumen consumption comes from oil refining industry: bitumen is the residue from the last stage of the distillation process, the so-called vacuum residue.[1-2] By consequent, the composition of the bitumen depends on the geographical origin of the crude as well as the way the full refining process was driven.

Due to the huge amount of chemical components present in bitumen, its chemical composition is commonly given in terms of a small number of fractions extracted by use of some chosen solvents. Different methodologies can be used. One of the most popular ones is the SARA analysis [3]: i) the fraction called "maltenes" is soluble in alkanes such as hexane or heptane; ii) the maltenes are further separated in saturates, aromatics and resins, by increasing order of polarity and aromaticity; iii) the fraction insoluble in hexane or heptane is constituted by the asphaltenes (the most polar and aromatic components). SARA is the acronym provided by the first letter of each one of these four fractions (saturates, aromatics, resins, asphaltenes) by increasing order of aromaticity and polarity.

The microstructure of bitumen is usually described by the so called "colloidal model"[1-2,5]. According to this model, bitumen is considered as a colloidal system constituted by micelles of asphaltenes dispersed in a continuous medium constituted by the maltenes. It is believed that the most polar components of the maltenes (e.g. resins) have a peptizing effect on the asphaltene micelles, which results in stabilization of the dispersion.

The construction and maintenance of paving roads are two major applications of bituminous materials [2,6].In both cases, performance is directly related to the viscoelastic properties of bitumen [6-11], and how they can resist to a number of environmental factors: traffic, temperature cycles, rain, solar radiation, etc. Pavement rehabilitation[12], is another major application of bituminous materials. Here the challenge is how to rejuvenate the bitumen in order to recover the original characteristics as close as possible.

For a number of applications, the viscoelastic properties of bitumen can be enhanced and adjusted by mixing it with other components, yielding modified bitumen. Bitumen can be modified in several ways. Most of the bitumen modifiers fall in the following classes: natural or synthetic rubber, ground (recycled) rubber, thermoplastics and block copolymers.[9-11] Recently a new class emerged: modified bitumen with reactive polymers and prepolymers (e.g. polyurethane precursors), which presents very interesting rheological properties.[13-15]

Bitumen modified with the styrene-butadiene-styrene (SBS) elastomers presents a number of improved properties: the softening point is higher and the penetration index is smaller, there is an increase of flexibility and toughness at low temperatures. By consequence, it can be used in a wider range of temperatures than the one of conventional bitumen. These bituminous blends also show an increase in resistance to fatigue and permanent deformation, and enhanced resistance to aging. [8-10]

Prepolymers are a new class of modifiers, highly reactive, with strong adhesive properties due to the presence of free isocyanate groups. These prepolymers show higher compatibility and are more easily miscible; due to the formation of chemical bonds with the bitumen components, segregation is prevented to a large extent. It is expected that some fraction of the isocyanate groups bind chemically to the asphaltene molecules, improving bitumen stability by this way.[15]

A very interesting and challenging question is to compare the properties and performance of bitumen modified with SBS copolymers and with some chosen reactive prepolymers. Rheological testing as well as engineering tests are currently considered for this purpose.[1,7,10] Since the presence of the modifiers may affect bitumen microstructure, we also considered Atomic Force Microscopy data which are expected to provide the required information.[16,17] In this paper we will present some preliminary results concerning the microstructural, rheological and engineering properties of both kinds of modified bitumen.

2. EXPERIMENTAL

2.1 Materials

Bitumen used in all experiments was provided by Galp Energia. The bitumen sources were the Sines and Porto oil refineries. Bitumen originating from these refineries exhibits different characteristic properties and composition, due to the different sources of the crude from which it is obtained, as well as different refining procedures. The bitumen considered in the present work had penetration index of 35/50 and 50/70 (dmm).

The reactive prepolymers used for bitumen modification were synthesized at Instituto Superior Técnico (Chemical Engineering Department). Different prepolymers were considered: A0815 is a linear isocyanate prepolymer (MW ~ 3000 g/mole) with functionality f = 3.4; A2715 is a linear isocyanate prepolymer (MW = 2700 g/mol) with the same functionality; AT2125 is a three arm isocyanate prepolymer (MW = 6500 g/mol) with functionality f = 5.1. The modifier contents of bitumen were 1% and 3% w/w.

The other modifier was a copolymer of styrene-butadiene-styrene (SBS), provided by Probigalp.

2.2 Specification Tests

The mixtures of bitumen and reactive prepolymers were prepared as follows: first, the raw bitumen was heated with stirring up to 90ºC; then, by keeping the stirring constant, the prepolymers were added until a homogeneous mixture was obtained. Typical mixing times were 15 to 20 minutes.

The SBS modified bitumen mixtures were prepared at 175°C in a thermostatic container inside a heating blanket. First, the bitumen was heated up to 175ºC and stirred for better homogenization. Then the SBS modifier was added to bitumen, keeping stirring constant. Samples were taken every 30 minutes for penetration and softening temperature testing. The final mixing time was 150 min.

For each mixture, dynamic viscosity, elastic recovery, and storage RTFOT tests were performed. All experiments followed the standard procedures.

2.3 Rheological Tests

Rheological experiments were carried out in a mechanical spectrometer RMS-800 from Rheometrics. Most of the experiments were done using the parallel plates fixture.The determination of the relevant material functions was performed by testing the bitumen samples in the following three regimes: transient tests (stress relaxation), dynamic tests (strain sweep at constant frequency, frequency sweep) and steady tests (shear viscosity at different rates). In this paper we will only present the data obtained at room temperature.

2.4 Atomic Force Microscopy

Atomic Force Microscopy (AFM) experiments were performed in a Veeco-di CPIIatomic force microscope. Etched silicon probes with nominal radius of less than 10nm, a spring constant of 40 Nm^{-1} and a nominal resonance frequency of 300 kHz were used. Typical scans covered areas from 5x5 μm^2 to about 15x15 μm^2 in the bitumen samples. Imaging was performed in tapping mode (intermittent contact) at room temperature.

Both topographic and phase difference microscopy (PDM) images were recorded and further analyzed. Image analysis was done using MOCHA software. Topographic images measure the surface topography as sensed by the tip. PDM images provide the phase lag of the cantilever oscillation relative to the drive signal. The bitumen samples were circular films with an average diameter of 10 mm.

3. Results and Discussion

3.1 Bitumen characterization

Tables 1 and 2 display the results of the changes in penetration index and softening temperature caused by modification of a 35/50 bitumen, either with reactive prepolymers (Pp) or with SBS. Bitumen from Sines is considered in Table 1, and bitumen from Porto is considered in Table 2.

Table 1 - Penetration index and softening temperature for bitumen 35/50 from Sines (raw and modified).

Bitumen	Penetration [dmm]	Softeningtemperature[ºC]
S35/50 raw	45	52
S35/50+1%SBS	32	53
S35/50+3%SBS	31	59
S35/50+1%Pp	(42) 32	54
S35/50+3%Pp	31	57

Table 2 -Penetration index and softening temperature for bitumen 35/50 from Porto (raw and modified).

Bitumen	Penetration [dmm]	Softeningtemperature[ºC]
P35/50 raw	42	51
P35/50+1%SBS	34	54
P35/50+3%SBS	24	57
P35/50+1%Pp	31	53
P35/50+3%Pp	27	56

Tables 3 and 4 display analogous data about the changes in penetration index and softening temperature caused by modification of the 50/70 bitumen, either with reactive prepolymers (Pp) or with SBS. Data about modified bitumen from Sines refinery is provided in Table 3, and data about bitumen from Porto refinery is given in Table 4.

Table 3 – Penetration index and softening temperature data for 50/70 bitumen from Sines (raw and modified).

Bitumen	Penetration [dmm]	Softeningtemperature[ºC]
S50/70 (raw)	62	49
S50/70+1%SBS	48	54
S50/70+3%SBS	38	58
S50/70+1%Pp	50	54
S50/70+3%Pp	(51) 36	57

Table 4 – Penetration index and softening temperature data for 50/70 bitumen from Porto (raw and modified).

Bitumen	Penetration [dmm]	Softeningtemperature[ºC]
P50/70 (raw)	70	46
P50/70+1%SBS	57	50
P50/70+3%SBS	48	52
P50/70+1%Pp	53	49
P50/70+3%Pp	48	51

These results show a decrease in the penetration index and an increase in the softening temperature of modified bitumen, as compared to the raw one. The changes are more intense as the concentration of the modifier increases. It may be noted that the bitumen from Porto presents greater sensitivity to modifiers as compared to the one from Sines, as sensed by penetration index.

In general, both the reactive modifiers and the SBS modifiers produce analogous changes in penetration and softening temperature, for the same w/w percent composition. At this level, the advantage of the use of reactive prepolymers comes from the much more easy modification procedure. A word of caution about the use of reactive prepolymers is now in order. In some cases, the chemical reaction of the reactive prepolymer is slow and it only ends some hours or even days after the preparation. In Tables 1 and 3, the penetration data given in parenthesis was obtained in circumstances where the reaction of the prepolymer was not still finished; the remaining values are the final ones.

In general, aging causes further decrease of the penetration index and further increase of the softening temperature, for the modified bitumen.

Raw and modified bitumen were also tested for storage stability. Sinesbitumen modified with 3%SBS displayed a noticeable phase separation, with most of the SBS in the top. In all experiments, the bitumen modified with reactive polymers showed improved stability in storage, as compared to the SBS modified one. In fact, one of the driving forces for segregation comes from the difference of density between the SBS modifier and the bitumen; the other is the fact that bitumen is a poor solvent for SBS, so phase instability is very likely to occur, particularly at low temperature. Both these factors play a minor role in bitumen modified with reactive prepolymers; here, most of the modifier is chemically bonded to the bitumen constituents, which prevents phase instability and segregation.

Elasticity tests show that the bitumen modified with SBS stands out clearly with a very significant elastic recovery, being even more evident for the 3% w/w composition.

The results of the viscosity tests indicated that amounts of only 3% of modifier can double the viscosity of raw bitumen. It also appears that the modified bitumen with a higher percentage of prepolymer obtained values slightly higher than those that were modified with SBS.

3.2 Rheological Tests

All rheological tests presented in this section were performed using the parallel plates fixture of the RMS-800 mechanical spectrometer.

Figure 1 displays the results of a strain sweep experiment (at constant frequency) on raw bitumen at room temperature. The material functions displayed are the real part of the complex shear modulus (conservative modulus, G') and the imaginary part of the complex shear modulus (dissipative modulus, G").The complex shear modulus is therefore G* = G' + i.G". This experiment is mandatory for determination of the range of strain where linear viscoelastic behaviour is found. On the other hand, the strain dependence of the viscoelastic material functions can also provide some insight into the microstructure of the material: for instance, the strain dependence shown in fig.1 is quite common in multiphase systems where the dispersed phase changes its shape as the matrix is deformed.

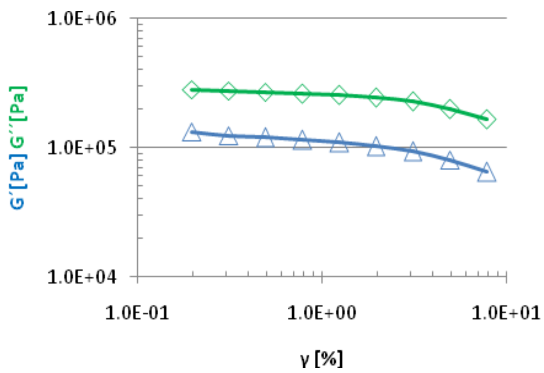

Fig.1–Strain sweep of raw bitumen at room temperature and constant frequency. G' is the conservative shear modulus and G" is the dissipative shear modulus.

In figure 2, the frequency dependence of the moduli G' and G" is presented, as well as the modulus (now in mathematical sense…) of the complex viscosity: $\eta^* = |G^*|/\omega$ where ω is the angular frequency.

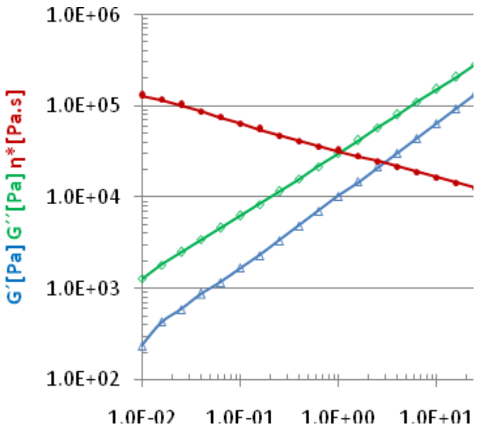

Fig.2–Frequency sweep of raw bitumen. G' is the conservative shear modulus, G" is the dissipative shear modulus and η* is the modulus of the complex viscosity.

Figure 3 presents the changes produced in bitumen material functions by modification with reactive prepolymer A0815 (superimposed to the raw bitumen data).

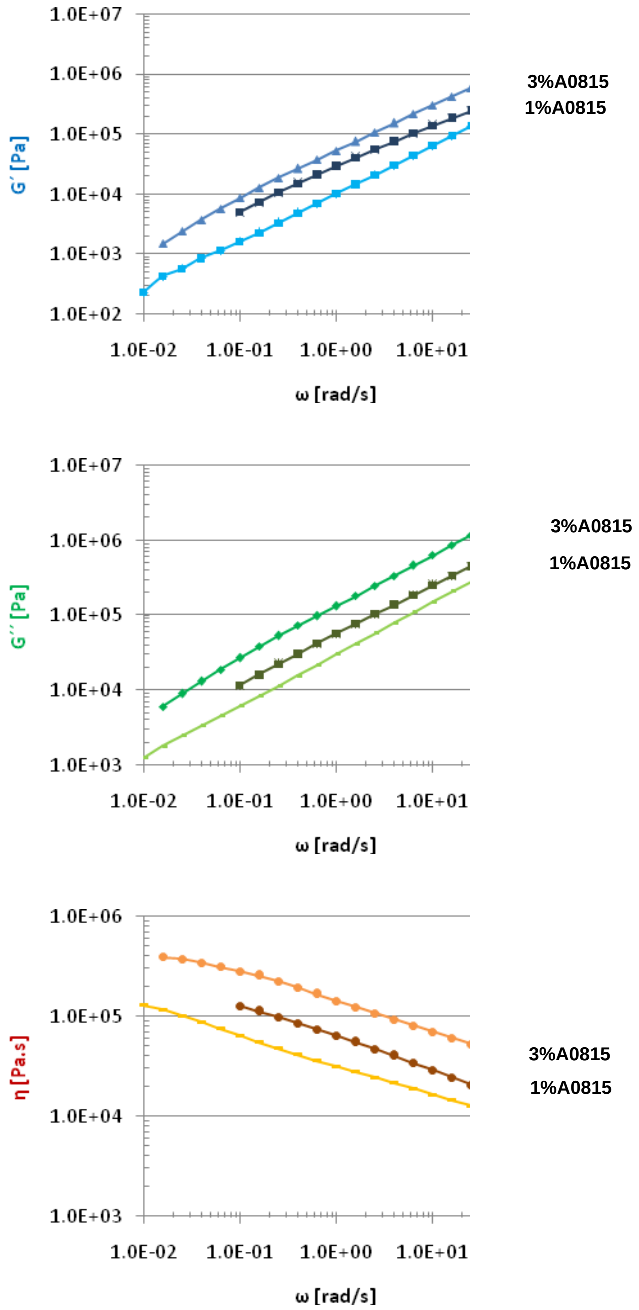

Fig.3 - Frequency sweep of raw bitumen and modified bitumen with 1% and 3% of A0815 (by increasing order). G' is the conservative shear modulus, G" is the dissipative shear modulus and η* is the modulus of the complex viscosity.

Figure 4 presents the changes produced in bitumen material functions by modification with reactive prepolymer A2715 (superimposed to the raw bitumen data).

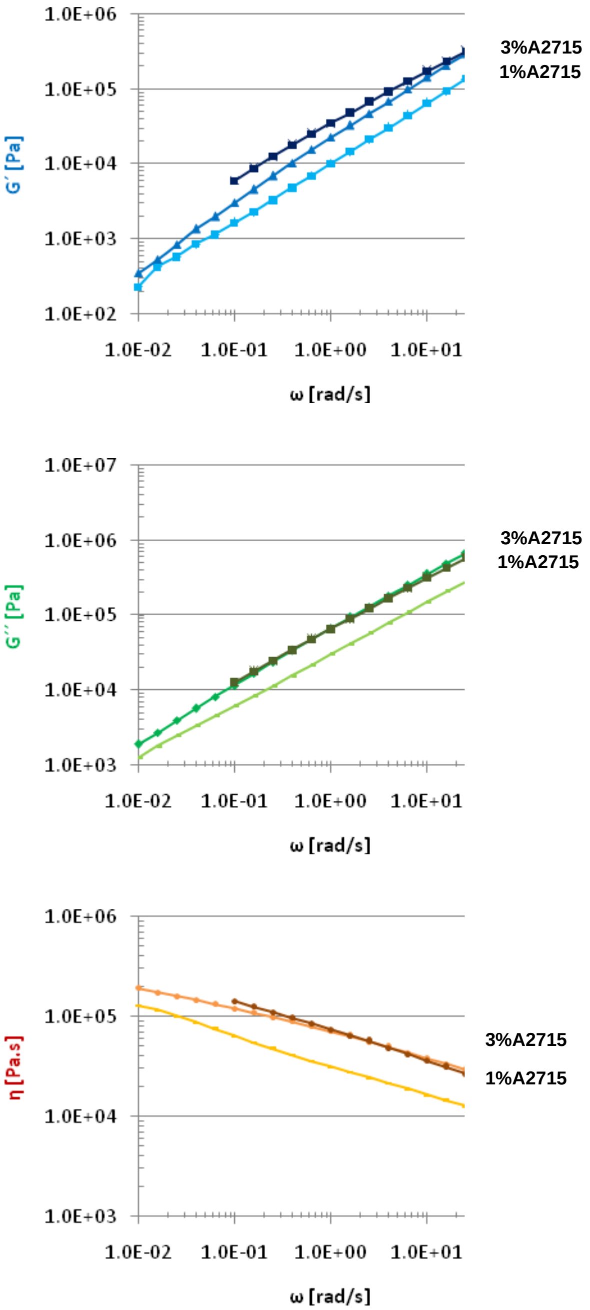

Fig.4 - Frequency sweep of raw bitumen and modified bitumen with 1% and 3% of A2715. G' is the conservative shear modulus, G" is the dissipative shear modulus and η* is the modulus of the complex viscosity.

Figure 5 presents the changes produced in bitumen material functions by modification with reactive prepolymer AT2115 (superimposed to the raw bitumen data).

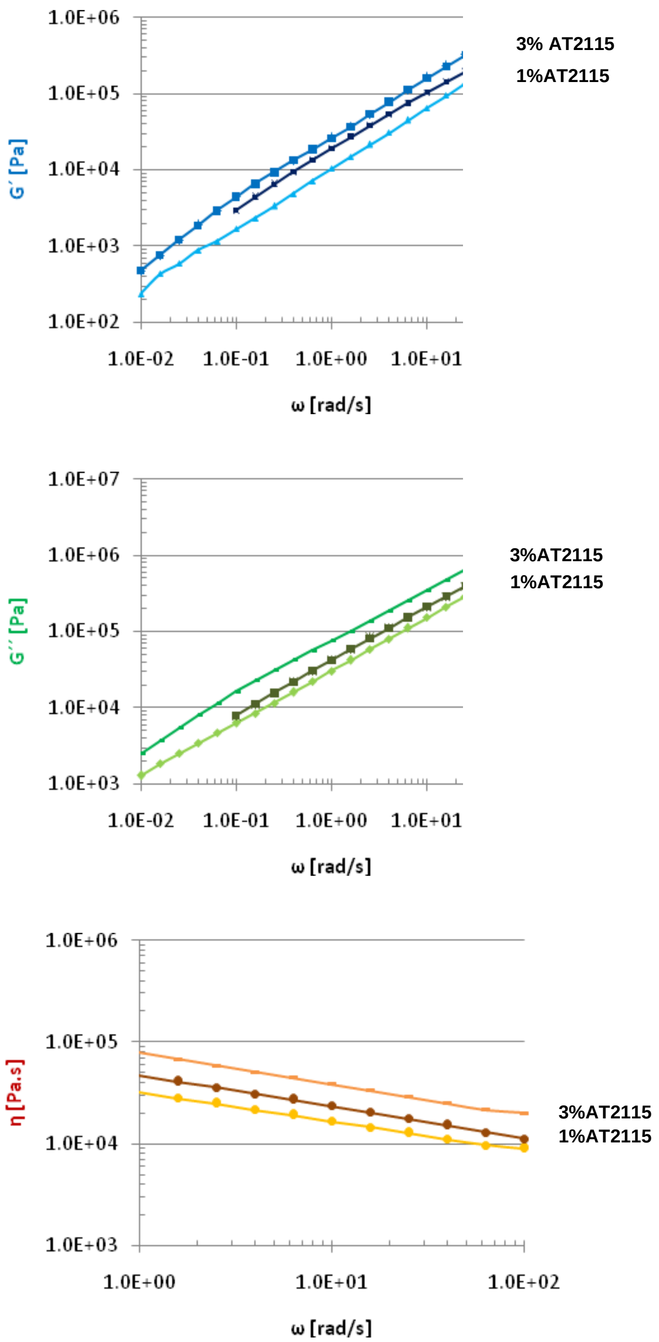

Fig.5 - Frequency sweep of raw bitumen and modified bitumen with 1% and 3% of AT2115. G' is the conservative shear modulus, G" is the dissipative shear modulus and η* is the modulus of the complex viscosity.

The main feature presented by the data shown is the large change in the rheological material functions caused by the prepolymers even at low contents. The effect caused by the introduction of 1% w/w reactive prepolymer is an increase by a factor of 2-3 of the elastic modulus and of the viscosity.

3.3 Atomic Force Microscopy

Figure 6 displays PDM and topographic AFM images of a 50/70 raw bitumen from Sines refinery. In the topographic images shown here, the darker areas correspond to valleys and lower areas of the surface profile, while the lighter areas correspond to peaks.

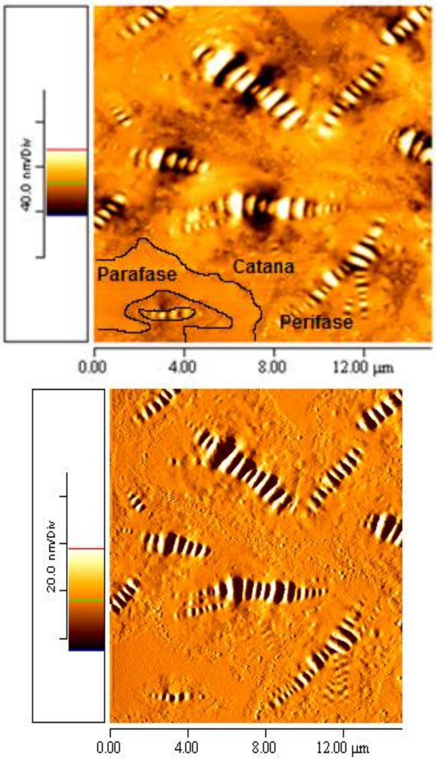

Fig.6 - AFM topographic image (top) and phase difference (PDM) image (bottom) of a conventional bitumen 50/70 Pen from Sines refinery.

AFM images show that bitumen is a multiphase material. Three phases can be identified. The catana phase represented by the bee-shaped structures with a succession of alternated dark and light stripes, the periphase which surrounds the catana domains, and the paraphase which is in contact with the periphase but does not contact with the catana domains. The AFM pictures support only qualitatively the standard description of bitumen structure provided by the colloidal model. As a matter of fact, the total number of phases is three (sometimes four) instead of two. On the other hand, the compositions provided by SARA methodology do not agree with the contents of the different phases in the AFM images obtained, as given in Table 5.

Table 5 – Phase percentage of modified bitumen (AFM data)

Bitumen	Catana [%]	Periphase [%]	Paraphase [%]
S50/70 Base	18,8	79,1	2,1
S50/70+1%A0815	18,2	79,6	2,2
S50/70+3%A0815	15,5	80,9	3,7
S50/70+1%A2715	21,7	73,8	4,5
S50/70+3%A2715	17,7	73,7	8,6
S50/70+1%AT2115	17,4	73,4	4,2
S50/70+3%AT2115	18,0	74,8	7,2

Analysis of PDM images suggest that catana phase should include the most polar and aromatic components, i.e. catana domains are the best places for finding asphaltene components. However the catana content (~18%) is much higher than the asphaltene content (6.5% for both bitumen materials considered), which strongly suggests that, besides asphaltenes,catana domains include almost one third of the resins content (total resin content ~33%). The paraphase content is generally smaller than saturates content(11%), which indicates that the periphase, besides aromatics fraction shall include some fraction of saturates and resins too.

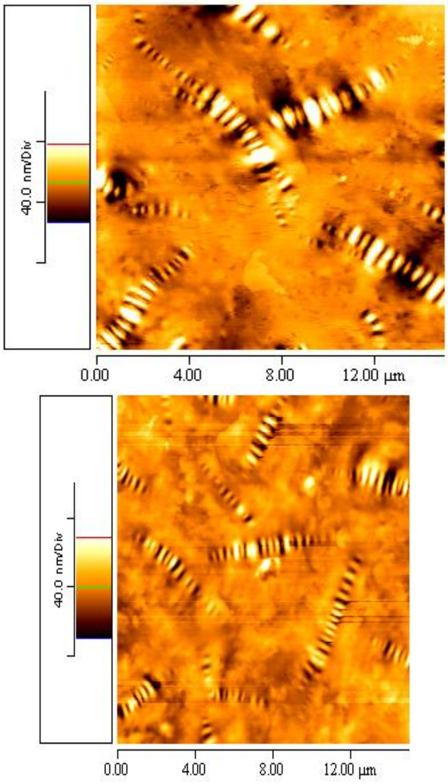

Fig.7 - AFM topographic images of a 50/70 bitumen modified with 1% (top) and 3% (bottom) of A0815.

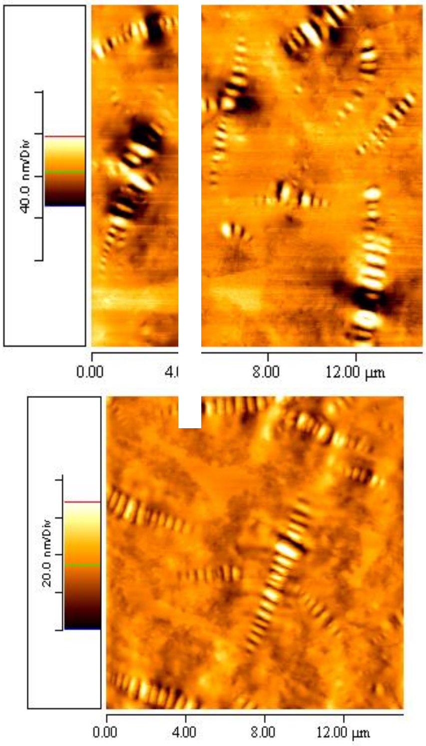

Fig.8 - AFM topographic images of a 50/70 bitumen modified with 1% (top) and 3% (bottom) of A2715.

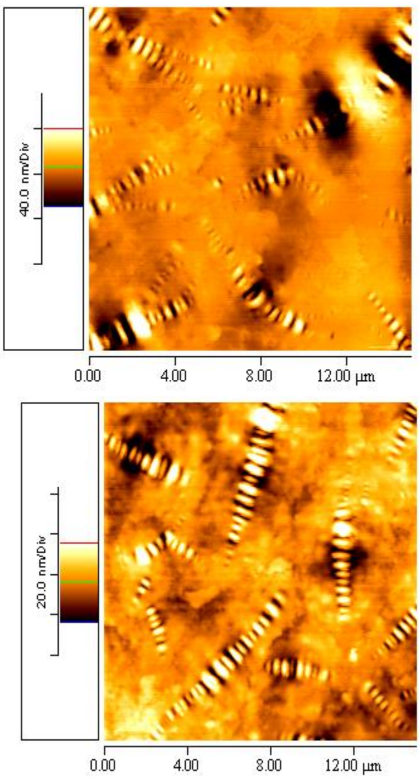

Fig.6 - AFM topographic images of a 50/70 bitumen modified with 1% (top) and 3% (bottom) of AT2115.

4. CONCLUSIONS

We presented preliminary results of a comparative study of the microsctucture, rheological and engineering properties of modified bitumen obtained either by modification with reactive prepolymers or by mixing with SBS elastomers.

In what concerns engineering properties, bitumen modified with reactive prepolymers is of much more easy preparation and shows improved storage stability and lower elastic recovery when compared to SBS modified bitumen. A follow up of the changes observed in the main rheological properties shows that both modifiers induce substantial changes in the rheological behaviour of bitumen. In general, the introduction of reactive prepolymers in the bitumen yields an increase of the elasticity and viscosity of bitumen.

AFM data of raw bitumen and bitumen modified by reactive polymers gives evidence that the standard colloidal model (asphaltenes peptized by resins and aromatics in a sea of saturates) is an oversimplification in view of the data provided by AFM and PDM images. It was found that the amount of catana phase peri-phase and para-phase depends on the source of the crude used to produce the bitumen, in good agreement with the results of reference [17]. Moreover, it is shown that reactive modifiers added to the bitumen do change the existent microphase structure. Thermal ageing may also change the microphase structure displayed in AFM images [16].

Acknowledgements

The authors are grateful to Dr Cristina Correia, Dr Nuno Correia and eng. Olga Ferreira for synthesising the reactive polymers used in this work, and to Prof. J. Bordado for helpful discussions.

Galp Energia is acknowledged for providing the bitumen samples.

References

[1] Lesueur, D - The colloidal structure of bitumen: Consequences on the rheology and on the mechanisms of bitumen modification, Advances in Colloid and Interface Science **145** (2009) 42-82.
[2] Read, J. e D. Whiteoak - The Shell Bitumen Handbook, Shell Bitumen, UK, 2003.
[3] *ASTM. 1995. Annual Book of Standards*. American Society for Testing and Materials: Philadelphia, PA; Method D-2007.
[4] Thomas, R.F. - Modern Petroleum Technology, G.D. Hobson, Institute of Petroleum, Ed.; John Wiley & Sons, pp.905-931, 1992.
[5] Loeber L. et al. - Bitumen in colloid science: a chemical, structural and rheological approach, Fuel **77** (1998) 1443-1450.
[6] European Asphalt Pavement Association (EAPA) and National Asphalt Pavement Association (NAPA)- The Asphalt Paving Industry: A Global Perspective (2009)
[7] X. Lu, U. Isacsson - Modification of road bitumens with thermoplastic polymers, Polymer Testing, **20** (2001) 77-86.
[8] B. Sengoz, G. Isikyakar - Evaluation of the properties and microstructure of SBS and EVA polymer modified bitumen; Construction and Building Materials,**22** (2008) 1897-1905.
[9] Airey, G. - Styrene butadiene styrene polymer modification of road bitumens, Journal of Materials Science, **39** (2004) 951-959.
[10] A. Adedeji, T. Grunfelder, F. S. Bates and C. W. Maccosko - Asphalt Modified by SBS Triblock Copolymer: Structures and Properties, Polymer Engineering and Science **36**(1996) .
[11] YetkinYildirim - Polymer modified asphalt binders; Construction and Building Materials, **21** (2007) 66–72.
[12] Kandhal PS, M. Stroup-Gardiner(eds) –Flexible Pavement Rehabilitation and Maintenance, ASTM STP-1348,(1998).
[13] F.J. Navarro et al. - Bitumen modification with a low-molecular-weight reactive isocyanate-terminated polymer; Fuel **86** (2007) 2291-2299.
[14] F.J. Navarro et al. - Bitumen modification with reactive and non-reactive (virgin and recycled) polymers: A comparative analysis, Journal of Industrial and Engineering Chemistry**15** (2009) 458-464.
[15] Barbosa, T.; Baptista, E.; Bordado, J.; Diogo, A.C. -Rheological characterization of asphalt bitumen modified with reactive polyurethanes; Les Cahiers de Rhéologie, Vol. XVI-1(1998),527-532.
[16] Costa E R, R. Colaço, A. Correia Diogo - Bitumen Morphology as Observed by Phase-detection Atomic Force Microscopy, Materials Science Forum 587-588 (2008) 981-985
[17] Masson J-F, Leblond, V.; Margeson J. - Bitumen morphologies by phase detection atomic force microscopy, Journal of Microscopy 221(2006) 17-29