THERMO-RHEOLOGICAL BEHAVIOR OF MODIFIED BITUMENS ADDING VIRGIN AND WASTE POLYMERS

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ABSTRACT
The use of recycled polymers for replacing virgin polymers has been employed in the road building contributing to asphalt performance and lower environmental pollution. In this work the copolymers ethylene vinyl acetate (EVA) and a recycled EVA copolymer from industry (EVAR) were used as modifying agents of the Brazilian bitumen. Other additive as a cashew nut shell liquid (CNSL) was also added in order to evaluate its use as bitumen modifiers. The rheological properties of the modified binders were analyzed by means of dynamic shear rheometer (DSR) and accelerated ageing experiment (RTFOT). Differently to the original the modified binders showed non-Newtonian behavior. The results obtained reveal that EVAR can be considered as an interesting substitute of EVA not only as a mean of effecting improvement but also from an economic and environmental point of view. The use of the original EVA and EVAR waste polymers helped to improve the aging resistance. The rutting factor ($G^*/\sin \delta$) suggest that the polymers and waste can improve the elasticity of the asphalt. The activation energy of the viscous flux (Ef) for the samples oscillated between 58 and 70 KJ/mo land showed that the additive CNSL can reduce the viscosity and thermal susceptibility of the modified binder.

Keywords: rheology, modified binders, waste polymers, CNSL additive

1. INTRODUCTION

The use of synthetic polymers as additives, via chemical or physical blending, has shown to greatly improve the performance of conventional bitumen [1]. Polymer modified binders have been used with success in road paving applications at locations of high stress (e.g., airports, vehicle weigh stations, and race tracks) [2] or as paving contractors seek to improve pavement performance in the face of an increase in traffic loads. Ethylene vinyl acetate copolymer (EVA) can be used for this purpose and it has been demonstrated to improve bitumen properties [3]. The viscoelastic characteristics of the binder at high temperatures are modified, resulting in more resistant pavement regarding to permanent deformation pavement more resistant to permanent deformation. The thermoplastic nature of this polymeric has the ability to combine elastic, strength and adhesion properties to increase road life. Improved properties also include greater resistance to aging and stability at high temperatures. It is also considered that the incorporation of cashew nut shell liquid (CNSL) to the binder can be advantageous, in terms of improving the compatibility of the material as well as from an economic stand point. CNSL is obtained as a by product of cashew process industries. Typically, the composition of technical CNSL is approximately 52% cardanol rich oil, 10% cardol and 30% polymeric material. It is also believed that the addition CNSL with antioxidant characteristic can help to decrease the oxidative ageing and improve the homogeneity of the mixture. The objective of the present work is to study the benefit of modifying binder adding the copolymer EVA virgin and EVAR combined with CNSL additives. It will be evaluated the performance of EVAR compared with EVA. For this purpose the effect of additives on the viscous and rheological properties of the binders before and after ageing process were investigated. The parameters are correlated to the thermal susceptibility, elastic properties and resistance of the material to permanent deformation.

2. EXPERIMENTAL

2.1 Materials

The neat bitumen used as a base for modification was a 50/70 penetration grade from Campo Fazenda Alegre (FA), State of Espírito Santo and processed by Petrobras/Lubnor at the State of Ceará -Brazil. Two different types of polymers: a semi-crystalline copolymers such as poly (ethylene-co-vinyl acetate) (EVA), provided from Politeno containing vinyl acetate 28 wt% and a waste recycled EVA copolymer (EVAR) from industry of sandals located at Ceará State were used as polymer modified bitumens. The EVAR (which passed through the sieve 24 Mesh size) contain additives as low density polyethylene (PEBD), $CaCO_3$ and inorganic fillers. The other additive was: Cashew Nut Shell Liquid (CNSL) provided from CIONE; The concentration of the polymers and additive were: (1) EVA 4% w/w; (2) EVAR 4,5% w/w; (3)EVA 4% w/w and cashew nut shell liquid (CNSL) 2% w/w. All the additives are provided from local industry. The blends were prepared using a FISATON reactor using low shear mixing and processed for 2 hours at 160 ± 5 °C and 544 rpm. The five samples evaluated are denoted by B+4%EVA, B+4,5%EVAR (to reach EVA content of 4%), B+4%, B+4%EVA+2 CNSL.

2.2 Aging

Short-term laboratory aging of the binder and modified binders were performed using the rolling thin film oven test (RTFOT) in accordance with the ASTM D2872 specification [4]. For the standard simulated aging process the material was submitted to heating at 163°C for 85 minutes. The aged bitumen's were evaluated by measuring their rheological characteristics.

2.3 Viscosity and Activation Energy

The viscosity of the selected binders was measured using a Brookfield DV-II+ programmable rotational viscometer with THERMOSEL control system according to ASTM D4402 [5]. The measurements were performed at 135°C, 150°C and 175°C. Two different spindles were used: SC4-21 and SC4-27, for bitumen and bitumen modified, respectively. To evaluate the susceptibility of the binders the samples were submitted to a shear rate of 2.5, 5, 10, 20, 30 and 40 rmp. The dependence of viscosity on temperature was used to obtain the activation energy of the flow (E_f) from the Arrhenius-like equation [6]. This parameter has been selected to differentiate asphalt binder and rank their thermal susceptibility to predict the compaction effort in mixes [7].

2.4. Dynamic Mechanical Analysis

Dynamic rheological measurements were performed in a stress-controlled TA Instrument AR 2000 using parallel plates with 25mm diameter and gap of 1 mm. Experiments were carried out in the temperature range of 46 to 100°C) at frequency of 10 rad/s, according to AASHTO TP5 [8]. Dynamic shear modulus (G*), phase angle (δ) and rut factor (G*/sin δ) were calculated. Tests were performed on original samples and after ageing.

2.5. Atomic Force Microscopy (AFM)

Original and modified binders were first dissolved in chloroform P.A. at room temperature. Mica was immersed.in the solution to form a thin film on it. The samples were dried at room temperature for a minimum of 12 hours and covered to prevent dust before imaging. The atomic force microscope was a Nanoscope Multimode IIIa (Digital Instruments – Santa Bárbara – CA) with a scanner J lateral resolution of 125 µm. For each sample images of 15 x 15 μm^2 and 5 x 5 μm^2 was acquired in intermittent contact mode or *tapping mode* under ambient conditions. A *cantilever* (40 N/m) set-point amplitude was adjusted to 15 nm.

3. RESULTS AND DISCUSSION

3.1 Effects of additives on the viscous properties

Figures 1-3 shows the experimental values of the viscosity versus shear rates for the original and modified binders before and after RTFOT, at 135-175°C.

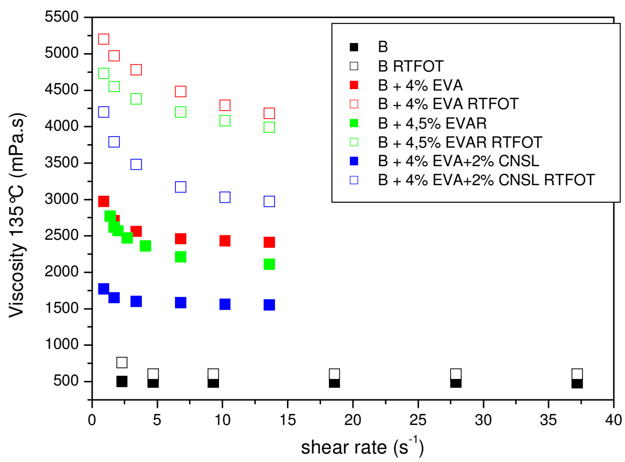


Figure 1: Viscosity 135°C versus shear rate before and after RTFOT.

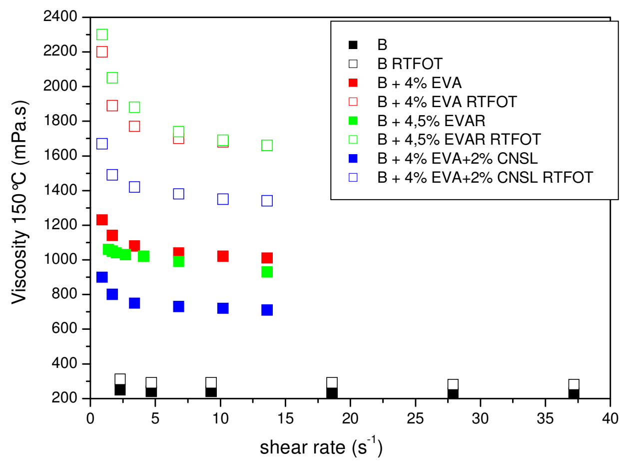


Figure 2: Viscosity 150°C versus shear rate before and after RTFOT.

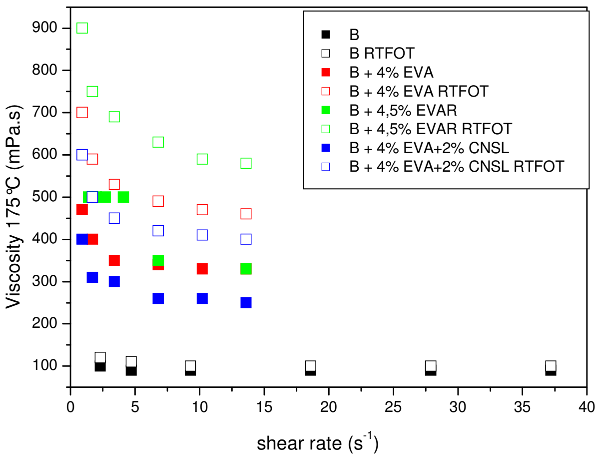


Figure 3: Viscosity 175°C versus shear rate before and after RTFOT.

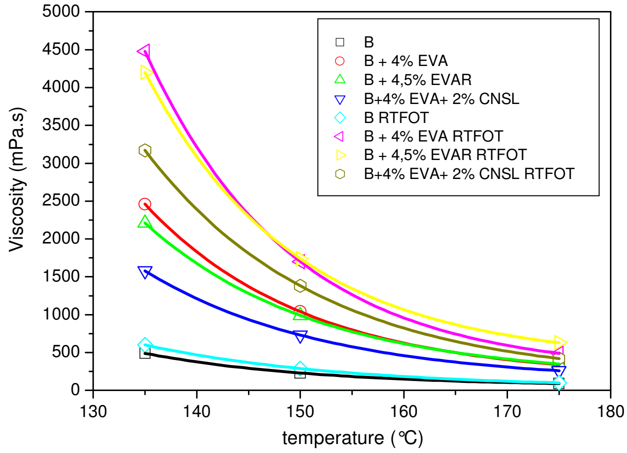


Figure 4: Viscosity *versus* temperature before and after RTFOT.

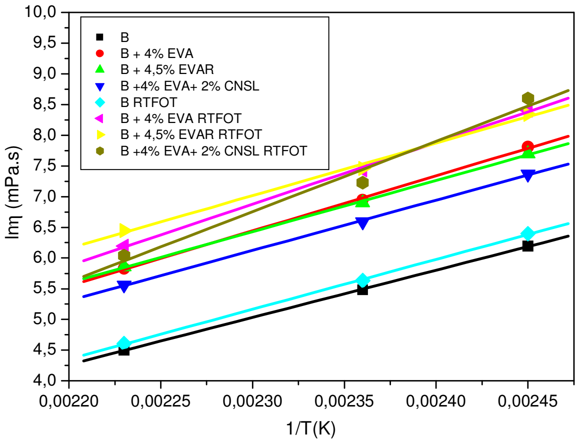
Unmodified binder showed a Newtonian behavior on the studied conditions. The modified binders presented a non-Newtonian behavior, i.e, their viscosity depends on the shear rate. It implies that zero shear viscosity (ZSV) must be a suitable method to determine the temperature of mixing and compaction [9].The shear dependence showed in this study is commonly observed for modified binders [10]. The results showed that the original binder itself has the lowest viscosity and the modified polymer binder with EVA 4.5% have the highest. This is a typical characteristic of addition of thermoplastic EVA polymer to the binder. According AASHTO MP1 (1993) the limit for viscosity values for modified binders at 135°C is 3000 mPa.s to avoid consequences on its handling and pumping process and on its in-service performance. In addition all of the samples underwent a remarkable increase in viscosity after RTFOT (Figure 4), indicating a hardening of the asphalts during ageing process as expected. This result may be related to the increase in the asphaltene concentration due to malthenic fraction oxidation. Hence, the modifications of the rheological properties of asphalts during their ageing processes depend basically on the changes in their relative composition of aromatics, resins and asphalthenes [11]. As may be seen the addition of CNSL decreased the viscosity of the EVA modified binder. The surfactant properties of the CNSL [12] probably induces to a rearranging of the molecules decreasing its flow resistance. From the results discussed above, it can be seen that the viscosity behavior of the modified binders added EVAR is similar to that displayed by modified binder added EVA. Then, in this way the EVA can be replaced by waste EVAR.

3.2 The activation energy of viscous flow (E_f)

The effect of temperature on bitumen viscosity was calculated according to the Arrhenius equation [6]:

$$\ln \eta = E_f/RT + \ln A \quad (1)$$

By plotting ln η *versus* 1/T, the activation energy for flow of neat bitumen and modified bitumen before and after RTFOT are calculated from the slope of plots (Figure 5) and shows in Figure 6. To minimize the effects of the shear rate, at each temperature, the viscosity at the plateau at the highest shear rate was used for data analysis.



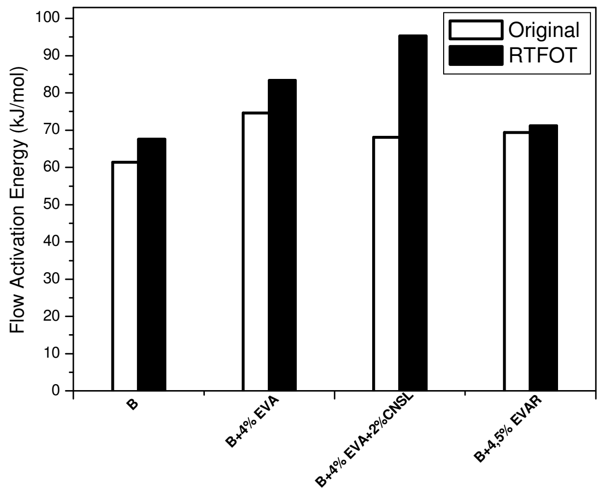


Figure 5: Arrhenius Plot for neat bitumen and modified bitumen after and before RTFOT.

Figure 6: Effect of aging on the activation energy for flow.

As shown in Figure 6, different modification of the asphalt results in different activation energies for flow. B+4%EVA and B+4,5%EVAR showed the highest values of Ef. The Ef of modified binders was higher than that of original binder. Some authors [6] found a decreasing on activation energy for polymer modified binders differently of the behavior shown here. It must be due to the polymer critical concentration. After aging, all bitumen showed higher activation energy. Oxidation increases the number of polar molecules in the asphalt binders. The higher concentration of polar molecules increases the intermolecular forces leading stronger interactions. These stronger interactions within the asphalt binder result in a higher resistance to flow consequently higher activation energy for flow. The activation energy has a special significance in numerous practical cases, e.g., when estimating a temperature effect on the stability of technological process of bitumen mixing with mineral fillers [13]. The E_f of the binders can also be related to the energy involved in bitumen application and compactation. In that sense the use of the additive CNSL is advantageous, particularly for EVA polymer modified bitumen in order to get proper values during the mixing operation to reduce the high cost of energy. The E_f has been related to the binder thermal susceptibility of different asphalt mixtures [6] [10] [14]. In the present study the rank of thermal stability was: B < B+4%EVA+2% CNSL <B+4,5%EVAR< B+4%EVA. It can be noted that EVAR modified binder presented better performance than that with EVA modified binder after ageing.

3.3 Dynamic Rheological Characterization

Figure 7 shows the complex modulus (G*) and phase angle (δ) as a function of temperature for the bitumen and modified bitumen.

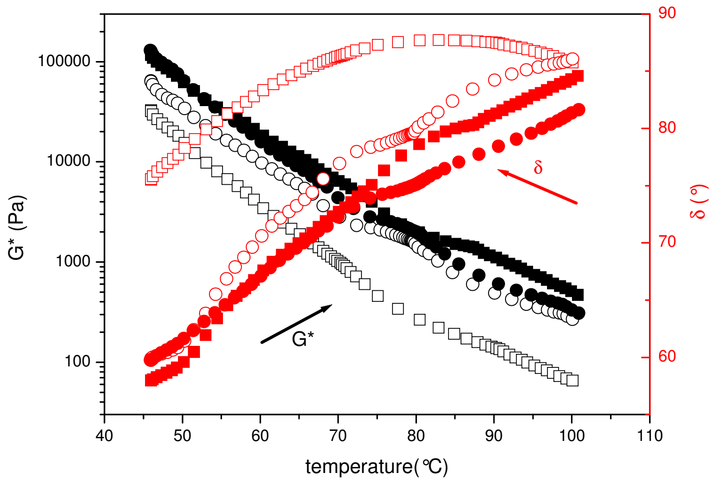


Figure 7: G* e δ as a function of temperature for bitumen (□□), B+ 4%EVA (■■), B+ 4% EVA+ 2%CNSL (○○) and B+4,5% EVAR (●●) .

The modified binders showed an increase of *G** and a decrease of δ in relation compared to the original binder enhanced rheological properties. Polymers addition improved the resistance to permanent deformation or rutting, although also increased elasticity (*G** is a measure of the overall resistance to deformation of a material, while *G'* and *G"* provide information on the elastic and viscous responses of a material, respectively. The viscoelastic character of the material is characterized by δ). The B sample showed less thermal susceptibility compared to the modified bitumens as shown by the slope of the complex modulus versus temperature relationship. This behavior could explain the activation energy data.

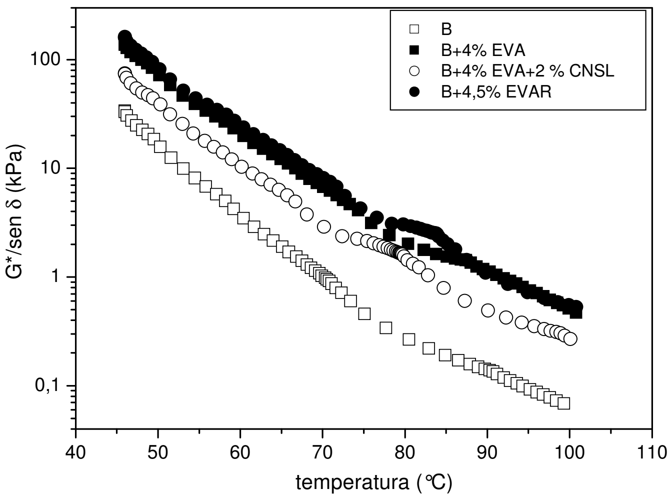


Figure 8: G*/ sin δ as a function of temperature for neat bitumen and modified bitumen.

Plots of G*/sinδ versus temperature are displayed in Figure 8. According to a SHRP test, the temperature at which G*/sinδ =1 kPa marks the maximum temperature for a good viscoelastic performance of the binder on the pavement. Road pavements in the northeast of Brazilt can undergo very high temperatures (approximately to 70°C), which can cause permanent deformations or ''rutting'' defects. Results of Fig. 8 reveal that the maximum temperature is improved when any of the copolymers is used as a modifier [15].

3.4 Performance Grade

Table 1 shows the values of the grade performance for the original and modified bitumens. According to the ASTM D 6373 [16], it was verified that the modified binders increased the resistance to the permanent deformation related to the original binder.

Amostra	B	B+4%EVA	B+4%EVA +2%CNSL	B+4,5%EVAR
T(°C), before RTFOT (G*/senδ > 1KPa)	70	>88	>88	88
T(°C), after RTFOT (G*/senδ>2,2KPa)	64	>88	>88	88
PG	64	>88	>88	88

Tabela 1: Classification of the bitumen for grade performance.

3.5 Atomic Force Microscopy (AFM)

To understand the changes on the rheological properties of the bitumens, modified binders microstructures were observed by using AFM images it was observed the microstructure of the samples using AFM images. Figure 9 shows an area on the surface of the film of binder deposited on the mica. The mica is a standard substratum for analysis in AFM due to the fact that an extremely plain surface film can be obtained (after the removal of some atomic layers) an extremely plain surface. Allied to this, it's the high chemical stability of mica guarantees reduced influence of the substratum in the morphology of the thin film formed on it this. In this image it is possible to visualize the "bee" structure already reported in literature [17] [18] attributed to asphalthenes the most aromatic and highest molecular weigh compounds in bitumen distributed uniformly at the dispersed phase. This profile is composed for regions marked for an undulation in the surface of the sample, a sequence of rises and valleys.

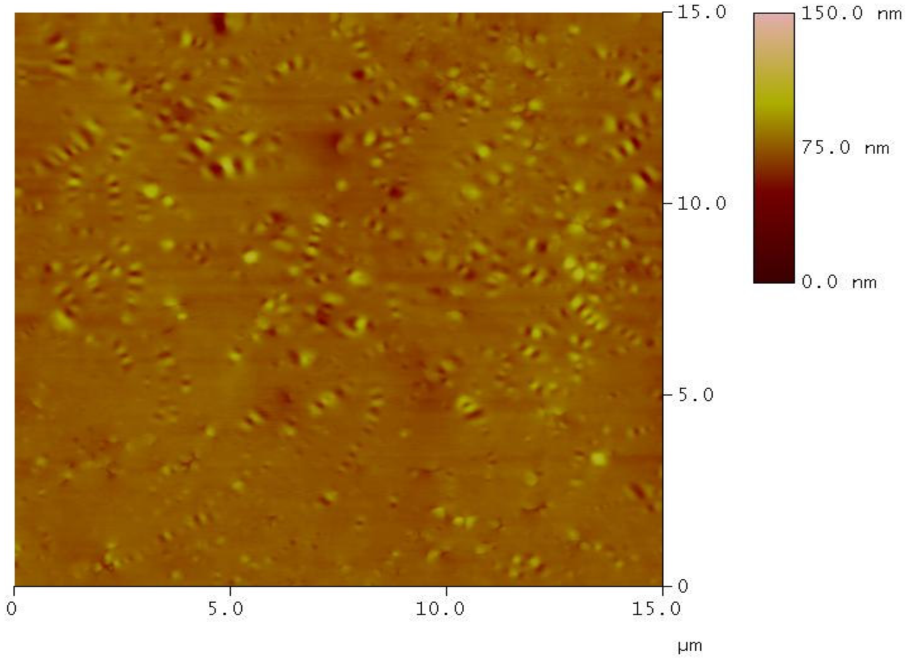


Figura 9: AFM image (15 x 15 μm^2) of bitumen on mica after being dissolved in chloroform at concentration of 200 g/L. The phase with "bees" profile (asphaltenes) is evidenced in the image.

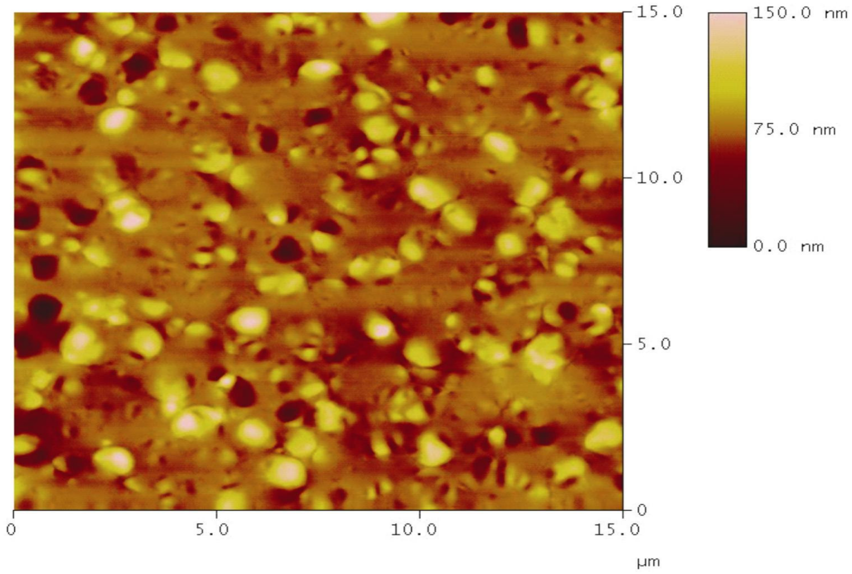


Figura. 10: AFM image (15 x 15 μm^2) of B+4%EVA +2%CNSL. The phase with "bees" profile (asphaltenes) still is evidenced in the image, however in less amount.

Figure 10 shows to the surface of the same bituminous binder with polymer EVA 4% and 2% of LCC. It is noted the presence of big bore in the surface which was not detected previously. Such particles represent the phase due to polymer. Also in this image the bee-like structure (asphalthenes) is present but in a less dispersed number. The image suggests probable association between the asphalthene and polymer, suggesting that the polymer can aggregated to the asphalthenic phase. Average A and L measures resulted in 28.55 nm and 1,13 μm respectively. The average diameter of particles of EVA in mixture B+4%EVA+2%CNSL was around 1.15 μm. This fact demonstrates the sweeling of the polymer that is probably due to adsorption of part of the malthenic fraction of the ligante [19]. The analysis of the film of EVA deposited on the surface of the mica can be seen in Figure 4. An inferior uniform plain phase is noted probably due to polymer layer. The average diameter of the particles was found around 970 nm.

4. CONCLUSIONS

Polymer added EVA, EVAR and CNSL showed an improvement of the rheological properties of bitumen, such as elastic responses and resistance to permanent deformation (increased complex modulus and decreased phase angle). Oxidative aging process increased the activation energy for flow probably due to the formation of polar molecules in the asphalt binder causing an increase in the intermolecular forces and, consequently, causing the hardening of the binder. The activation energy for flow was used to rank the relative thermal susceptibility of the binders. The EVA and EVAR modified binders presented higher values of activation energy. It was observed that the use of CNSL can be considered a suitable alternative to decrease the thermal susceptibility of the modified EVA binder. The polymers EVA and EVAR markedly increased the viscosity of the binder, although the values of the viscosity are not above the limit [8].As a preliminary result EVAR can be considered an alternative to replace virgin EVA as modifier bitumen not only for its performance but also for environmental and economical points of view.

5. ACKNOWLEDGEMENTS

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