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Rheological Properties of Asphalt Binders Modified With Natural Fibers and Oxidants

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***Abstract*—The thermal and rheological behaviors of asphalt binder modified with natural fibers and antioxidants obtained from the Amazon rain forest are analyzed through Thermogravimetry (TG), Differential Scanning Calorimetry (DSC) and Dynamical Shear Rheometer (DSR) tests. The addition of modifiers alters considerably the physical and rheological properties of the modified binders. The main results are: a good thermal stability and miscibility with asphalt cement (AC), significant increase of G* at low frequencies, decrease of δ and increase of the viscosity. The results are compared with that of asphalt binder modified with SBS polymer.**

Keywords — Asphalt binder; SBS copolymer; cutia-chesnut fiber; ucuúba fat; rheology

I. INTRODUCTION

Asphalt cements has been used successfully in highways and airport pavements worldwide due to their viscoelastic and adhesion properties [1]. In order to improve the mechanical properties of these materials, modifiers such as polymers [2-4] including plastics, elastomers, extenders, antioxidants and fibers [5-9] are under intense investigation. The asphalt modification by polymers improves their mechanical properties, as for example, the reduction of the thermal susceptibility, the permanent deformation and the enhancement of the resistance to cracking at low temperatures [10,11].

Particularly, the addition of antioxidant and fiber minimize the negative effects of oxidation and act as reinforcement and prevent the yielding, respectively [12]. It has been observed that fibers improve the rheological characteristics of asphalt: the creep compliance and rutting resistance [13,14]; the low-temperature anti-cracking properties, fatigue life, and durability of AC mixtures [15-17]; dynamic modulus [20] and elasticity [21]. Since 1960 different approaches have been used to incorporate crumb rubber modifier (CRM) in road paving materials. After seminal research works by [22], Bahia and Davies [23,24], the application of CRM to improve the rheological characteristics of the asphalt pavement has attracted a lot of interest of the scientific community worldwide [24-29].

A. Objective and Scope

The aim of the present work is to improve the rheological characteristics (complex modulus, phase angle and viscosity) of the asphalt binder AC 50/70, modifying it with raw materials from the Ama-zon biodiversity, with the perspective of sustainable use of natural resources. The mechanical properties of AC 50/70 modified with those materials were compared with those of pure AC 50/70 and that modified with styrene-butadiene-styrene (SBS) copolymer.

As one of the natural modifier material we used natural fiber obtained from the shell of a fruit popularly known as Cutia-Chesnut (Couepia Edulis - Prance), with fibrous characteristics, found in the western Amazon (Figure 1). Its shell has high level of lignin, a polymer of aromatic nature with high molecular weight, with great potential for use as asphalt binder modifier. The lignin behaves as an asphalt antioxidant and gives to the asphalt binder large compressive strength [30]. Its capability as an asphalt oxidant comes from their phenolic structures (benzene rings with attached hydroxyl groups), which has the ability to neutralize the free radicals contained on oxygen [31], by donating either a proton (positive hydrogen ions H+, which technically is just a proton) or an electron [32].

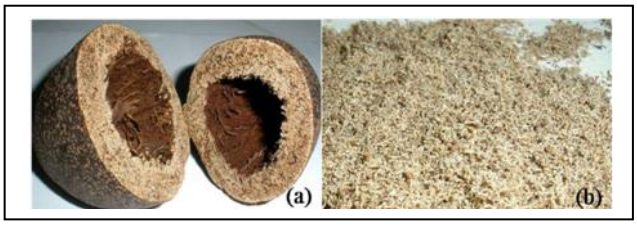

Fig. 1. *(a) Cross-section of the Cutia-Chesnut (Couepia Edulis - Prance) shell; (b) Fiber obtained from the Cutia-Chesnut shell.*

Additionally we used a second natural modifier material as an antioxidant to minimize the negative effects of the oxidative aging, which causes the asphalt to become hardened and brittle. The additive is a fat that was extracted from the ucuúba (Virola Surinamensis) fruit almond, a natural species from the Amazon forest (Figure 2). The addition of ucuúba fat yields a mixture which is more homogeneous, without segregation of the Cutia-Chesnut fibers.

Fig. 2. *Fat extracted from ucuúba* (*Virola surinamensis*).

II. MATERIALS AND METHODS

The materials used in the present study are the following: the asphalt binder AC 50/70, the SBS copolymer, a natural fiber of Cutia-Chesnut (*Couepia Edulis* - Prance) (CEF) and a fat extracted from ucuúba (*Virola Surinamens*is) (UF). We analysed the rheological properties of four mixtures of asphalt binder AC with SBS, CEF and UF, named as ACSBS, MS3.0, MS2.5 and MS2.0, whose proportions by mass are presented in subsection II.E.

A. The Asphalt Binder

The asphalt binder AC 50/70 was obtained from the Brazilian oils *Campo Fazenda Alegre* and *Ceara-Mar*, presenting the following physical properties: a) Penetration 58.0 (100g, 5s, 25 ^{o}C, 0.1 mm - ASTM D5); b) Fire and Flash Point 300 ^{o}C (ASTM D92); c) Softening Point 49:8 ^{o}C (ASTM D36).

B. SBS Copolymer

As a polymeric material we used the styrene-butadiene-styrene (SBS) copolymer (34% stirene and 66% butadiene). The rheological properties of the asphalt binder modified with natural fibers and oxidants will be compared with those of SBS. This copolymer is classically used as an AC modifier, whose elastomeric characteristic and thermoplastic behavior enhance the resistance of the mixture to permanent deformations. The SBS copolymer molecular weight are presented in Table 1 [33].

TABLE I. CHARACTERISTIC OF SBS COPOLYMER

Numerical molar mass (Mn)	1.1 x 10^5
Weight molar mass (Mw)	1.4 x 10^2
Average molar mass (Mz)	1.7 x 10^2
Polydispersion	1.3

C. Cutia-Chesnut (Couepia Edulis - Prance) Fiber (CEF)

The cutia-chesnut is originally from Amazon forest. In order to obtain the fiber of its nut the following steps were performed. Initially the shell was separated from the almond by pressing. Then the shells were triturated using a knife mill. Finally, the granularity of the triturated material was set to values near those of SBS polymer, separating the material retained on the sieve # 0.297 mm, whose particle size distribution is shown in Figure 3. Their dry and natural densities in g/cm^3 are 1.100 and 1.200, respectively. The composition by mass of CEF (cellulose, lignin, extractive-free, humidity, ashes and silica) are presented in Table 2.

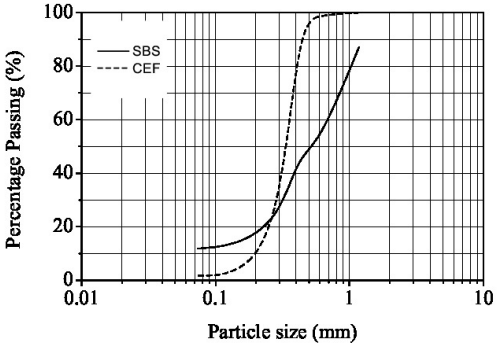

Fig. 3. *Grain size curve for SBS and CEF.*

TABLE II. COMPOSITION OF CUTIA-CHESNUT (CEF) FIBER

CEF Composition	% (mass)
Cellulose	56.78 ± 0.1
Lignin	33.26 ± 0.2
Extractive-Free	6.24 ± 0.4
Humidity	10.30 ± 0.3
Ashes	0.87 ± 0.01
Silica	0.15 ± 0.02

D. Ucuúba (Virola Surinamensis) Fat (UF)

The ucuúba fat, used as a binder extender agent, was extracted by mechanical pressing of the almond fruit of Virola Surinamensis, whose physicochemical characteristics are presented in Table 3 [34].

TABLE III. PHYSICOCHEMICAL CHARACTERISTICS OF UCUÚBA FAT.

Ucuúba Fat(UF)	Gross
Acid index (mg KOH/g oil)	32.6±0.3
Saponification index (mg KOH/g oil)	259.6±0.4
Peroxide index (meq/kg oil)	8.6±0.1
Iodine index (g I_2/100 g sample)	0.79±0.09
Unsaponication (%)	3.0±0.2
Density(g/cm^3)	0.93±0.02

E. Modified Asphalt Binder (AC 50/70))

The asphalt binder AC 50/70 was mixed with the SBS polymer, Cutia- Chesnutfiber and ucuúba fat using a mechanical mixer model Fisato 647. In Table 4 we present the modifier levels for three modified samples (MS), which are called MS3.0, MS2.5 and MS2.0.

TABLE IV. LEVELS OF SBS POLYMER, CUTIA-CHESNUT FIBER AND UCUÚBA FAT IN THE MODIFIED ASPHALT BINDER AC 50/70.

Sample	SBS (%)	CEF(%)	UF(%)
ACSBS	5.0	0.0	0.0
MS2.0	2.0	3.0	1.0
MS2.5	2.5	2.5	1.0
MS3.0	3.0	2.0	1.0

In the preparation of the mixtures the binder was heated to facilitate the addition of the modifiers, and then it was transferred to the mixer. The materials previously homogenized were subjected to an angular velocity of 560 rpm for 2 hours at a temperature of 160±5 ^{o}C.

F. Thermal Analysis

The thermogravimetric curves for the SBS copolymer, Cutia-Chesnut fiber, ucuúba fat and for the asphalt binder samples, pure (AC 50/70) and modified (MS3.0, MS2.5 and MS2.0), were obtained according to ASTM-E537, using the equipment DTG 60H from Shimadzu Corporation, under an air flux of 50 ml/min. Samples with approximately 10±0.1 mg were used, heated at a rate of 10 ^{o}C/min and temperature range from 25 ^{o}C to 700 ^{o}C. The differential scanning calorimetry (DSC) was performed according to ASTM-E1131, in a Perkin Elmer Pyris 6 DSC, using aluminium crucible and samples mass of approximately 10±0.5 mg. The DSC curves were obtained in a nitrogen atmosphere, with flow of 40 ml/min, a heating rate of 5 ^{o}C/min and heating from 40^{o}C to 80 ^{o}C.

G. Rheological Tests with Dynamical Shear Rheometer

To perform the rheological tests according to ASTM D 7175, a TA Instrument Asphalt Rheometer CSA II was used, maintaining the operating temperature at 60 ^{o}C. In order to obtain the complex modulus G*, the phase angle δ, the storage modulus G' and the loss modulus G", the samples were subjected to the oscillatory shear tests, with frequency sweep in the range of 0.1 Hz to 40 Hz, at a shear rate equal to 0.1 s^{-1}. The viscosity was measured when the material reached a steady state of flow, with shear rate in the range 0.1 s^{-1} to 20 s^{-1} and temperature ranging from 25 ^{o}C to 700 ^{o}C.

III. RESULTS AND DISCUSSION

A. Thermal Analysis

The thermogravimetric curves of the modifier agents SBS, CEF and UF obtained at temperatures range from 25 ^{o}C to 700 ^{o}C in an inert N_2 atmosphere are shown in Figure 4. The SBS polymer presents good thermal resistance in inert atmosphere, with the occurrence of only one decomposition event for which the initial and final temperatures are 403 ^{o}C and 486 ^{o}C, respectively. At the end of the test, the residue content represents approximately 4.2% of the initial mass.

The CEF thermogravimetric curve presents three decomposition events. Until the temperature of 100 ^{o}C there is a mass reduction of approximately 10%, as is shown by the left arrow in Figure 4. This mass reduction, which occurs at the boiling-water temperature, is attributed to the loss of moisture of the vegetable fibers (dehydration intramolecular and intermolecular reactions). The moisture content of 10±3 % for natural CEF exhibited in Table II corroborates this assertion. As there is no water content in SBS at room temperature, this event is absent in the SBS thermogravimetric curves. A pronounced mass reduction of 43% occurs above 255 ^{o}C, due to the decomposition of hemicelluloses and the breaking of the chemical bonds of the cellulose. The last step occurs above 375 ^{o}C due to the decomposition of the final cellulose and lignin, with final waste content being equal to 20% of the initial mass. The thermal behavior displayed by the CEF fibers is similar to that of the main natural fibers used in paving, such as sisal fiber [35] and coconut fiber [36].

The thermogravimetric profile of UF presents three stages of mass loss, which can be attributed to the volatilization and/or the decomposition of the fat. Initially there is a loss of volatile products until 200 ^{o}C followed by three events associated with the decomposition processes of highly saturated glycerides, between the temperatures of 194 ^{o}C and 401 ^{o}C.

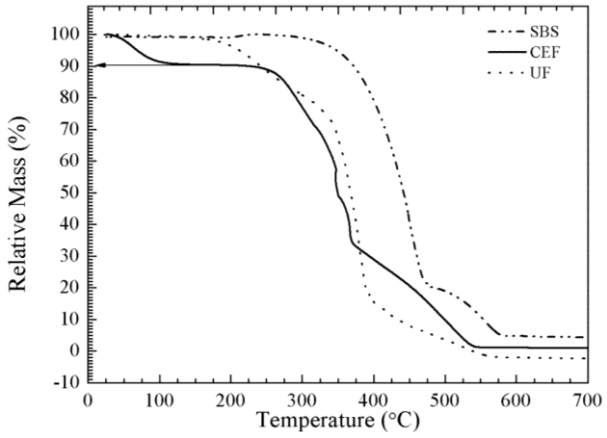

Fig. 4. *Thermogravimetric curves for the modifier agents: SBS copolymer, Cutia-Chesnut fiber (CEF) and ucuúba fat (UF), in an inert N_2 atmosphere with heating rate of 5 ^{o}C/min and flow of 50 ml/min. .*

The thermogravimetric curves of asphalt binders, pure (AC 50/70) and modified (MS3.0, MS2.5, MS2.0 and ACSBS), under an inert N_2 atmosphere, are shown in Figure 5. The profile of the TG curve for the AC 50/70 presents only one thermal decomposition process, starting at 352 ^{o}C (limit of thermal stability) and ending at 492 ^{o}C, with a mass loss of 78.1%. This behavior is typical of organic materials of the class

belonging to high molecular weight hydrocarbons, therefore with good thermal stability, which ensures the use of modifiers under aggressive temperature conditions, as occurs in the production plant and in the pavement.

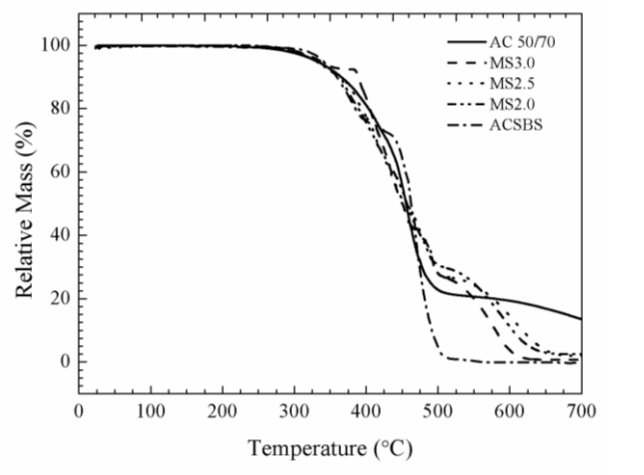

Fig. 5. *Thermogravimetric curves of AC 50/70 and modified binders (MS3.0, MS2.5, MS2.0 and ACSBS) in an inert N_2 atmosphere, with heating rate of 10 ^oC and gas flow of 50 ml/min.*

It is observed that for the mixtures MS3.0, MS2.5 and MS2.0, which contain 2%, 2.5% and 3% of CEF, respectively, no event is observed for pure CEF at 100 °C, due to the loss of moisture present in vegetable fibers, as was shown in Figure 4. In this case the moisture of the fibers was lost during the preparation of the samples. The heat resistance of the modified binders increases with the amount of fiber content in the following order: MS3.0> MS2.5> MS2.0. However, it was noted that, with respect to AC 50/70 and ACSBS, the degradation temperatures of these modified materials present a little reduction at elevated temperatures, which would not be a drawback, since it exceeds the processing temperature of the binders. According to Figure 6, there were no significant events for the pure (AC 50/70) and the modified binders (MS3.0, MS2.5 and MS2.0). On the asphalt with ucuúba fat (UF), the results indicated that the events can be correlated to its thermo-oxidative decomposition, with melting of their components. In relation to the miscibility with AC 50/70, it was noted that UF does not recrystallize due to the amorphous characteristics of the asphalt cement.

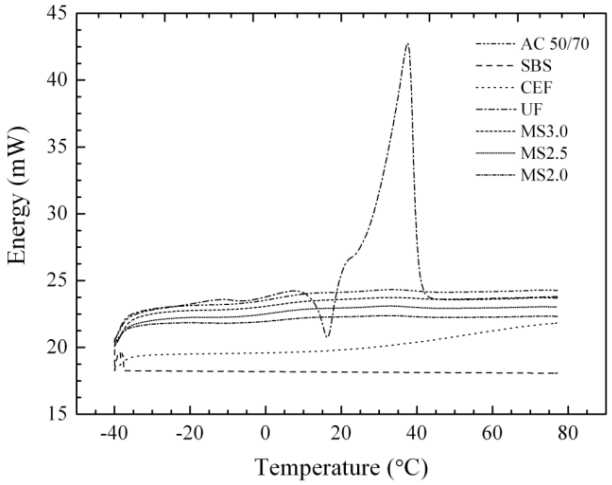

Fig. 6. *Heating curves obtained by Differential Scanning Calorimetry (DSC) for pure AC 50/70, the modifiers SBS, CEF and UF, and the modified binders MS3.0, MS2.5 and MS2.0.*

B. Rheological Tests

From the dynamic shear rheometer (DSR) test we obtained the rheological properties such as the complex modulus (G*) and the phase angle (δ). Thereby, we calculated the storage or elastic modulus G' (G'= G*cosδ) and the loss or viscous modulus G" (G"= G*sinδ) and the viscosity of both pure (AC 50/70) and modified (MS3.0, MS2.5, MS2.0 and ACSBS) binders. Such parameters allow us to evaluate the performance of the modified AC compared to pure AC at typical pavement temperature and traffic frequencies.

The complex modulus G*, which represents the total resistance to deformation under load, is plotted as a function of frequency in Figure 7. It exhibits a more pronounced increase in the values of G* for lower frequencies, most notably in the sample MS2.0. The highest fiber content of Cutia-chesnut (CEF) in MS3.0, MS2.5, MS2.0 samples provide the formation of a network of the binder layer adsorbed to the fiber surface, providing a change in the microstructure of

TABLE V. COMPLEX MODULUS PARAMETERS.

Sample	G^*_g(GPa)	f_c(rad/s)	k	m_e	R
MS2.0	1.015	$11.910x10^3$	0.1155	1.126	2.935
MS2.5	0.262	$5.137x10^3$	0.1313	1.193	2.700
MS3.0	0.747	$11.010x10^3$	0.1194	1.164	2.935
ACSBS	0.318	$5.836x10^3$	0.1151	1.038	2.715
AC 50/70	0.535	$10.240x10^3$	0.1331	1.228	2.777
SBS [37]	1.000	$1.923 x10^3$	0.1050	1.000	2.878

the binder modified with SBS polymer and ucuúba fat. DSR and SST (Simple Shear Test) test results for 36 different mixtures produced from nine selected modified binders and four types of aggregates, over various frequency and temperature ranges has been analysed [37]. It is observed that these materials obey a master curve and proposed a generalized model to represent their complex modulus and phase angle. Our measured rheology data results for AC 50/70 modified with SBS and natural fibers also present the pattern given by the above curve. According to the authors [37]), the complex modulus G^* of binders as a function of the reduced frequency f' (defined as the frequency divided by the temperature-shift factor [37] is represented by the function

$$G^* = \frac{G_g^*}{\left[1+\left(f_c / f'\right)^k\right]^{m_e/k}}, \quad (1)$$

where G^*_g is the complex modulus in the limit $f' \to \infty$, f_c is a frequency location parameter, and k and m_e are dimension less shape parameters. Since the temperature is fixed (60 °C) in our study, the reduced frequency is the frequency itself. The parameters f_c, k and m_e are estimated using a minimum squared error fitting procedure. This function presents a spectrum which increases monotonically from zero, at $f' = 0$, until its saturation at G^*_g as $f' \to \infty$. The width of the relaxation spectrum is characterized by a shape index defined as $R = (m_e/k)\log 2$. The higher this index, more gradual is the transition from the elastic behavior to the viscous behavior. The solid lines in Figure 7 represent the fitting to Equation (1) for each sample. The parameters G^*_g, f_c, k, m_e and R, from the fitting results are presented in Table 5, where we observe that the parameters $G^*_g \approx 1.0$ GPa and $m_e \approx 1.0$, as is to be expected for a linear viscoelastic fluid [38]. The parameters k, m_e and R are consistent with the results obtained in [37].

The phase angle δ is shown in Figure 8. There is a decrease in δ as the frequency increases. All samples of modified binders present phase angle lower than the pure binder AC 50/70 for all frequencies, indicating an enhancement in the elasticity due to the polymers added to the asphalt binders [39]. According [37], the model equation for the phase angle in given by

$$\delta = 90I - (90I - \delta_m)\left\{1+\left[\frac{\log(f_d / f')}{R_d}\right]^2\right\}^{-m_d/2}, \quad (2)$$

where δ_m is a phase constant, f_d is a frequency location parameter, m_d and R_d are shape parameters and $I = 0$ if $f' > f_d$ or $I = 1$ if $f' \geq f_d$. Equation (2) fits well with the phase angle data for all samples, as is shown in Figure 8, where the solid lines represent the fitting.

In Table 6 we present the parameters δ_m, f_d, m_d and R_d obtained from the fitting to Equation (2). The parameter f_d represents an in flexion in the relationship between logarithmic frequency and phase angle, and δ_m corresponds to the phase angle at $f' = f_d$. In Figure 8 this inflexion is more evident for the MS2.5 and MS3.0 curves, which occur at 2.173 rad/s and 1.089 rad/s, respectively.

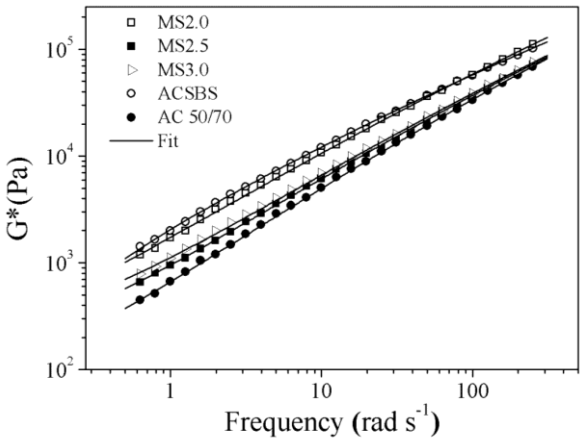

Fig. 7. *Grain size Complex modulus G* as a function of frequency for AC 50/70 and modified binders MS3.0, MS2.5, MS2.0 and ACSBS. The solid lines represent the fitting to Equation (1), whose parameters are shown in Table 5.*

The elastic modulus G' of the modified binders as a function of frequency are shown in Figure 9. All samples obey a power law as a function of frequency. The sample of AC with 5% of SBS (ACSBS) presents the highest value of G' as a function of frequency, which is used as reference to the other modified binders MS2.0, MS2.5 and MS3.0. The modified binder MS2.0 presents G' lesser than pure AC for all frequencies. The elastic modulus of MS3.0 is higher (lesser) than that of pure AC for low (high) frequencies. The best result is represented by MS2.5, whose elastic modulus is greater than that one obtained for pure AC for any frequency.

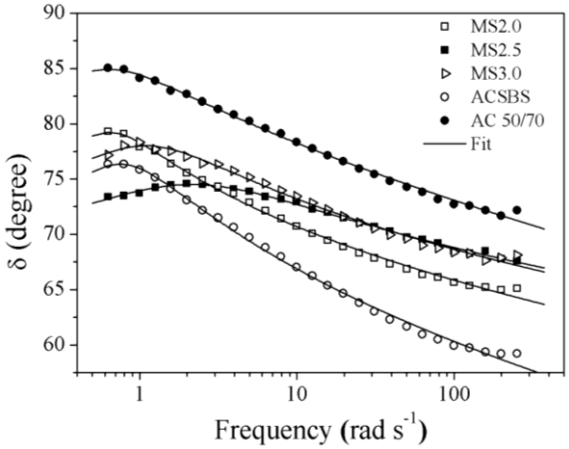

Fig. 8. *The phase angled as a function of frequency for AC 50/70 and modified binders MS3.0, MS2.5, MS2.0 and ACSBS. The solid lines represent the fitting to Equation (2), whose parameters are shown in Table 6.*

TABLE VI. PHASE ANGLE PARAMETERS..

Sample	δ_m(°)	f_d(rad/s)	R_d	m_d
MS2.0	79.23	0.639	0.604	0.379
MS2.5	74.51	2.173	1.517	0.314
MS3.0	78.02	1.089	0.977	0.371
ACSBS	76.37	0.746	0.750	0.412
AC 50/70	84.95	0.636	0.741	0.626

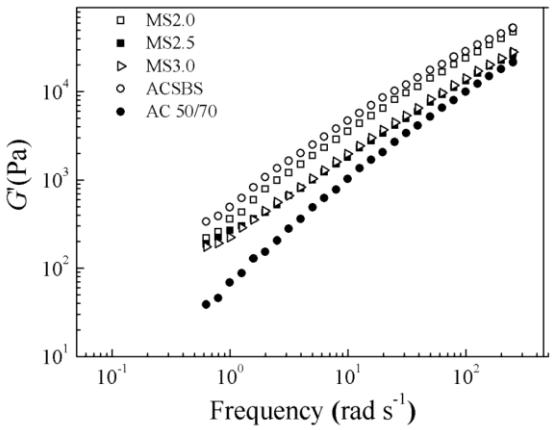

Fig. 9. *Elastic modulus G' as a function of frequency for AC 50/70 and modified binders MS3.0, MS2.5, MS2.0 and ACSBS..*

It is observed in Figure 10 that the viscous or loss modulus (G") of the modified binders depends on the content of SBS polymer, as is evident by the increasing viscous modulus for the samples MS2.0, MS2.5 and MS3.0, with increasing SBS polymer content 2% w/w, 2.5% w/w and 3% w/w, respectively. For high frequencies, the loss modulus of all samples approaches the behavior of the pure AC, irrespective of the presence of the modifiers.

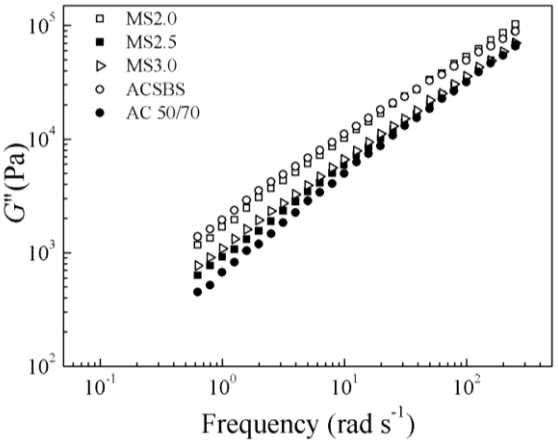

Fig. 10. *The Viscous modulus G" as a function of frequency for AC 50/70 and modified binders MS3.0, MS2.5, MS2.0 and ACSBS.*

The viscosity as a function of the shear rate for AC 50/70 and modified binders MS3.0, MS2.5, MS2.0 and ACSBS, is presented in Figure 11. The viscosity of the modified binders increases in relation to the viscosity of the AC 50/70. For low and intermediate frequency, AC 50/70 behaves as a Newtonian fluid. The addition of SBS, CEF and UF induces a non Newtonian behavior to the modified binders. The increase of the modified binder viscosity may influence the resistance to the permanent deformation of the pavements, since they can withstand higher temperatures. It was observed that the presence of the additive UF reduces the viscosity of the mixtures compared with ACSBS.

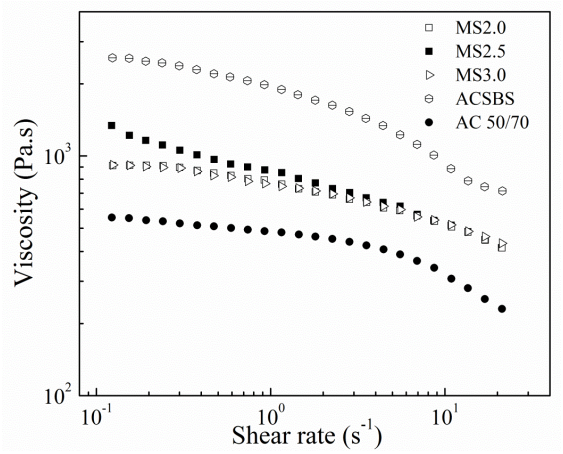

Fig. 11. *Viscosity as a function of shear rate for AC 50/70 and modified binders MS3.0, MS2.5, MS2.0 and ACSBS.*

C. The role of CEF on the modified binder

The insertion of fibers in the binder creates a secondary network or a new equilibrium system, changing the properties of the asphalt cements [40]. The degree of modification depends on the concentration and the characteristics of the fibers, as well as on the nature of the original AC. Different types of fibers have been used in the asphalt modification, for example cellulose, minerals and polyester fibers. Studies have shown that fibers inside the binder increase their surface area and behave as binder thickening agents, providing mechanisms for asphalt hardening, thereby minimizing the permanent deformation and fatigue cracking [41,42]. The role of CEF within the asphalt binder occurs in two ways: chemically and physically. The benzene rings, with attached hydroxyl groups, contained in the lignin, neutralize the free radicals contained on oxygen by the reception of a proton, i.e., a positive hydrogen ions H^+, or an electron. These free radicals are undesirable because they actively break apart the chemical structures of the asphalt binders. The antioxidant behavior of lignin contained in CEF increases the strength of the asphalt binders. On the other hand, the fiber forms a three-dimensional network structure within the asphalt binder. The adhesion between fiber network and the asphalt enhances the performance of the fiber modified asphalt binders [41].

IV. CONCLUSIONS

The complex modulus G* and the phase angle δ of the modified binders, change with the content of SBS and natural fiber (CEF). For all mixtures (MS3.0, MS2.5, MS2.0 and ACSBS), G* is higher and δ is lower than the corresponding values for pure AC 50/70. Hence, the inclusion of natural fiber and SBS polymer increases the rigidity and the elasticity of the mixture, which results in better resistance to permanent deformation. The best performance is for the sample MS2.0, made with higher CEF content. Also it is verified that G* and δ as a function of the frequency ω fit very with the equations (1) and (2) proposed in [36].

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