Evaluation of the Cashew Nut Shell Liquid (CNSL) antioxidant characteristics for asphaltic materials using different aging procedures

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ABSTRACT

The asphalt cement (AC) aging is a natural process mainly caused by volatilization of lighter fractions and oxidation reactions. It is known that, over the years, the asphalt mixtures age and become more rigid. This stiffening may decrease the fatigue crack resistance in asphalt pavements, and thus, can make them more resistant to permanent deformation. The cashew nut shell liquid (CNSL) is a "green additive", coming from a renewable and biodegradable source and has antioxidant characteristics. In the literature, there are some studies that highlight the CNSL antioxidant characteristics, however, few consider its application in paving services. In this study, the CNSL is proposed as a modifier of the AC 50/70 for the purpose of assessing their antioxidant potential. The asphalt mixes, the conventional AC and the AC modified with 2% of CNSL were analyzed before and after various aging processes. The asphalt mixtures were aged in different conditions: compacted and loose samples. After the aging processes and the AC recovery, they were evaluated in relation to their empirical and rheological properties and compared with those obtained for the virgin AC. Furthermore, the effects of oxidative aging was analyzed by infrared spectroscopy - FTIR (Fourier Transform Infrared) and changes in the SARA composition (Saturates, Aromatics, Resins and Asphaltenes) through chromatography. The asphalt mixtures containing conventional AC and AC modified with 2% of CNSL, after the aforementioned processes of aging, were characterized mechanically using resilience modulus (RM), tensile strength (TS), fatigue life, dynamic modulus and flow number (FN). The results for the AC tests indicate that the CNSL acts as an antioxidant for the short-term period, but it does not show the same behavior for the long-term period. After analyzing the results achieved for the asphalt mixtures, it can be said that the CNSL caused a slight reduction in stiffness of these mixtures and, possibly, it was polymerized when subjected to the oven aging process. The most aggressive process of aging was obtained when subjecting the loose mixture to the long-term aging for nine days.

Keywords: Additives, Ageing, Asphalt, Chemical properties, Mechanical Properties

1. INTRODUCTION

The aging of bitumen is a natural process caused, generally, by oxidation reactions Oxidized bitumen has a higher viscosity when compared to unoxidized one. This happens because the bitumen is a colloidal solution stabilized by the combination of its molecules, which undergo alterations in the process (the resins are converted into asphaltenes and the aromatics are converted into resins). The increased amount of asphaltenes causes increased rigidity of the bitumen and this increase is the main aging indicator. The bitumen aging study is important since this is usually the most onerous asphalt component and the one that undergoes changes by aging.

Some methodologies (or protocols) of aging are carried out trying to predict, in the laboratory, aging that happens in the field. The short-term aging simulates the asphalt mixture process and application and the long-term aging can simulate up to three years of pavement service life. The most used methodologies are: (i) aging and chemical analysis performed only on the bitumen (ii) asphalt aging and subsequent analysis of bitumen recovered from this aged material, (iii) asphalt aging and mechanical characterization. The tests carried out for aging analysis are usually those that assess the degree of aging through changes in the rigidity of the bitumen or of the asphalt.

It is observed in the literature that there are inconsistencies regarding the aging methods used in the laboratory because the asphalt's aging can be influenced by the bitumen aging, but this does not mean that the behavior of aged asphalt as a whole is equal to the behavior of the aged bitumen sample [1]. Some factors, as well as changes undergone in the bitumen, may also influence the aging process of asphalts such as: (i) the type of aggregate used can influence the aging through exudative stiffening (due to loss of the bitumen oily part due to the aggregate porosity of it), (ii) asphalt air voids percentage (Vv), (iii) the bitumen film thickness, among other factors [2].

The need to improve the pavements performance and quality, making them more resistant and safe, has led some researchers to evaluate the addition of alternative materials as additives for asphalt material. In an attempt to reduce the bitumen aging, some modifiers have been used, such as lime, lignin, phenols, amines and polymers [3, 4, 5].

Cashew nut shell liquid (CNSL) is a regional, renewable material and a low cost product obtained as a by-product of the cashew industry. CNSL is an oil composed of a mixture of phenols with a long alkyl substitution at the *meta*-position and it is often considered as the better and cheaper material for unsaturated phenols. Hindered phenolic compounds (ArOH) represent the family of antioxidants and it has been used as an additive in polymers and lubricants [6, 7] and also applied to gasoline stabilization [8]. Many of its application are being studied by researchers from Ceará – Brazil. CNSL was used in this research as a potential aging retardant considering the benefits of its use and especially the previous studies being studied by researchers from Ceará – Brazil as an asphalt materials modifier [9, 10, 11]. It was observed that the CNSL stabilizes styrene-butadiene-styrene (SBS) modified bitumen [9] and has potential benefits with respect to its moisture damage resistance [10]. Use of different type of vegetable oil has been studied as rejuvenator of bitumen for cold recycling [12] and also in several applications with good results [13,14].

The stiffening asphalts can cause, in some cases, a lower fatigue resistance, reducing the pavement life cycle, but it can also cause a greater resistance to permanent deformation. The problem that motivated this research was the lack of consensus between the protocols of aging methods used for the asphalts characterization. Even so, the need of slowing this aging, when it acts in a negative way, impairs the mechanical properties of asphalts.

The proposed research was carried out in two independent tasks. Each of the tasks was carried out simultaneously and motivated by specific objectives. The first one has the objective to evaluate the potential of CNSL, an agro-based raw material, as an aging retardant for asphaltic materials. The second has the general objective to evaluate different methods of aging motivated due to the lack of consensus between the protocols of aging methods used for the asphalts characterization.

2. MATERIALS AND METHODS

2.1 Materials

The bitumen used in this research is classified by penetration as a 50/70 and through Superpave classification as a PG 64-XX. The CNSL technique used was obtained in *Fábrica de Castanha Iracema Ltda.* located in Fortaleza, Brazil. 2% of CNSL was added to the bitumen by weight, yielding two distinct bitumens: (i) conventional bitumen, and (ii) BITUMEN + 2% CNSL. Bitumens have been modified using a temperature of 160 ± 5ºC rotating at 1,000 rpm during 1 hour. The aggregates used were: 3/4" gravel, 3/8" gravel and rock dust.

2.2 Asphalts mixtures design

The asphalts investigated in this study have particle sizes that fall in range C of the *Departamento Nacional de Infraestrutura de Transportes* (DNIT) - Brazil, being a asphaltic mixture with dense graduation, with aggregate nominal maximum size (NMS) equivalent to 12.5 mm. The aggregates proportion for the elaboration of the project curve was 20% 3/4" gravel, 44% 3/8" gravel and 36% rock dust. The samples compaction process was performed using the Superpave gyratory compactor (SGC). The samples (100m in diameter and 60mm in height) were compacted using 100 gyrations trying to simulate a volume of medium to high traffic. The asphalts mixtures have 6.0% of bitumen by weight (for both conventional bitumen as well as BITUMEN + 2% CNSL), which generated a Vv of approximately 4.0±0.4%.

Larger samples were also produced (100mm diameter by 150mm height), molded also using a SGC in order to carry out the dynamic creep (DC), and the dynamic modulus (|E*|) tests. In order to produce those larger volume samples, keeping the ratio between the bitumen percentages and aggregates, the compaction process did not take into account the number of gyrations, but rather the Vv and the samples height. Even after aging, keeping the loose asphalt in oven during nine days at 85°C (the most severe aging protocol conducted for this research), the number of gyrations did not exceed the value of 25. For the DC testing, the Vv used was 7% and for the |E*| testing, the Vv used was 4%.

2.3 Bitumen extraction and recovery process

After the performance of the different asphalt aging processes, it was necessary to perform a bitumen extraction and recovery process so that the characterization test could be performed. The bitumen extraction was carried out using the Soxhlet extractor. The material recovered during the extraction (BITUMEN+solvent) passed through the centrifugation process with a rotation de 1,930rpm for 30 minutes. Subsequently, the distillation of bitumen was carried out using the Abson method [15].

2.4 Aging processes used and bitumen characterization

The rheological tests (viscosity and complex modulus) as well as the spectroscopy of Fourier Transform Infrared (FTIR) for the structural analysis were performed for the evaluated bitumen before and after various aging processes. Table 1 presents the bitumen identification used throughout this study and the aging processes to which they were submitted.

Table 1: Specifications of the analyzed bitumen

Pure BITUMENS Code	**BITUMEN type**	**Aging time**		**Aging process**	
		Short-term	**Long-term**	**Long-term**	**Reference**
INITIAL	Conventional BITUMEN Conventional BITUMEN + 2% of CNSL	N/A	N/A	N/A	N/A
RTFOT	Conventional BITUMEN Conventional BITUMEN + 2% of CNSL	85 min at 163ºC	N/A	N/A	[16]
PAV	Conventional BITUMEN Conventional BITUMEN + 2% of CNSL	85 min at 163ºC	20h at 2.1MPa and 110ºC	20h at 2,1MPa and 110ºC	[17]
Recovered BITUMENS Code	**BITUMEN type**	**Aging time**		**Aging process**	
		Short-term	**Long-term**	**Long-term**	**Reference**
BLANK	Conventional BITUMEN Conventional BITUMEN + 2% of CNSL	2h at 150ºC	N/A	N/A	*Superpave*
5 DAYS	Conventional BITUMEN Conventional BITUMEN + 2% of CNSL	4h at 135ºC	5 days at 85ºC	Compacted asphalt mixture sample in a conventional oven	[18]
9 DAYS	Conventional BITUMEN Conventional BITUMEN + 2% of CNSL	4h at 135ºC	9 days at 85ºC	Loose asphalt mixture in a conventional oven	[19]
5 MONTHS	Conventional BITUMEN + 2% of CNSL	2h at 150ºC	5 months	Compacted mixture aged in the open air	[9]
12 MONTHS	Conventional BITUMEN	2h at 150ºC	12 months		

2.5 Aging process used and asphalt mixtures characterization

For the asphalt mixtures mechanical characterization, the resilient modulus (MR), the tensile strength (TS), the fatigue life (FL), the dynamic modulus |E*|, and the dynamic creep (DC) tests were performed. The materials and the aging process used in this study are presented in Table 2. Three samples were evaluated for each test performed.

Table 2: Analyzed asphalts mixtures and aging processes used

Mixture Code	BITUMEN type	Aging time		Aging process*	
		Short-term	Long-term	Long-term	Reference
MRC	Conventional BITUMEN	2h at 150ºC	-	Without aging	Superpave
MRL	Conventional BITUMEN + 2% of CNSL				
M3mC	Conventional BITUMEN	2h at 150ºC	3 months	Compacted asphalt mixture samples aged naturally	[9]
M3mL	Conventional BITUMEN + 2% of CNSL		3 months		
M5mC	Conventional BITUMEN		5 months		
M5mL	Conventional BITUMEN + 2% of CNSL		5 months		
M9mC	Conventional BITUMEN		9 months		
M12mC	Conventional BITUMEN		12 months		
Mc5dC	Conventional BITUMEN	4h at 135ºC	5 days at 85ºC	Compacted asphalt mixtures aged in a conventional oven	[18]
Mc5dL	Conventional BITUMEN + 2% of CNSL				
Ms2dC	Conventional BITUMEN	4h at 135ºC	2 days at 85ºC	Loose asphalt mixture aged in a conventional oven	[19]
Ms2dL	Conventional BITUMEN + 2% of CNSL				
Ms5dC	Conventional BITUMEN		5 days at 85ºC		
Ms5dL	Conventional BITUMEN + 2% of CNSL				
Ms7dC	Conventional BITUMEN		7 days at 85ºC		
Ms7dL	Conventional BITUMEN + 2% of CNSL				
Ms9dC	Conventional BITUMEN		9 days at 85ºC		
Ms9dL	Conventional BITUMEN + 2% of CNSL				

* The short-term aging was conducted for loose asphalts mixtures samples.

3. RESULTS AND DISCUSSIONS

3.1 Bitumen viscosity

The viscosity measurements as a function of temperature of conventional bitumen and of bitumen modified with CNSL, before and after the RTFOT and PAV, are shown in Figure 1. In general, it is observed that the aging caused an increase of bitumen viscosities. Bitumen modified with 2% of CNSL, both before and after the RTFOT, had lower viscosity values compared to the values found for the conventional bitumen. This is in agreement with the results reported by Fernandes (2011). The CNSL addition decreased the bitumen viscosity, probably due to the CNSL surfactant properties. In Figure 1, it can also be observed that the effect of increasing the bitumen viscosity (due to the aging process) was reduced in the presence of CNSL, after RTFOT.

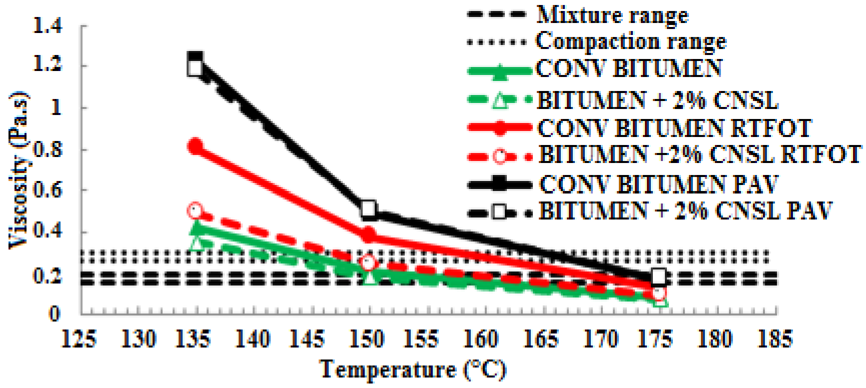


Figure 1: Viscosity (Pa.s) versus temperature for conventional BITUMEN and BITUMEN + 2% CNSL before and after RTFOT and PAV aging process

After PAV aging process, the conventional bitumen viscosity was practically the same viscosity of the bitumen modified with 2% CNSL. Possibly, the CNSL polymerization process occurred when it was subjected to long-term aging, causing modified bitumen viscosity increase. The CNSL polymerization, which occurs with aging, is the consequence of polymerization reactions which occurred in the unsaturated constituents.

The rate of aging for the conventional bitumen and the bitumen modified with 2% of CNSL was calculated. This index from the relationship between viscosity values before and after short-term aging conducted in RTFOT, for each bitumen, was obtained. As seen in Table 3, it is clear that bitumen modified with CNSL was more resistant to short-term aging, thus presenting lower values for the aging index.

Table 3: Aging index at 135°C, 150°C and 175°C for conventional BITUMEN and BITUMEN + 2% CNSL

Bitumen	Aging index (Viscosity after RTFOT/Viscosity before RTFOT)		
	135ºC	150ºC	175ºC
CONV BITUMEN	1.9	1.8	1.6
BITUMEN + 2% CNSL	1.4	1.3	1.3

Viscosity tests were also performed on the bitumen (conventional and modified with 2% CNSL) recovered from the aged asphalt mixtures. Observing Figure 2, it can be seen that both the CONV BITUMEN BLANK as well as the BITUMEN CNSL BLANK showed the lowest viscosity values of the recovered bitumen groups. This is due to the fact that these bitumens underwent, only, the short term aging (2 hours in an oven) and the recovery process. The bitumen with the highest viscosity was the modified bitumen with 2% CNSL, extracted from the asphalt mixture that underwent aging for nine days at 85°C in the oven. The increase in the viscosity for these samples may have been caused by the CNSL polymerization, as previously discussed.

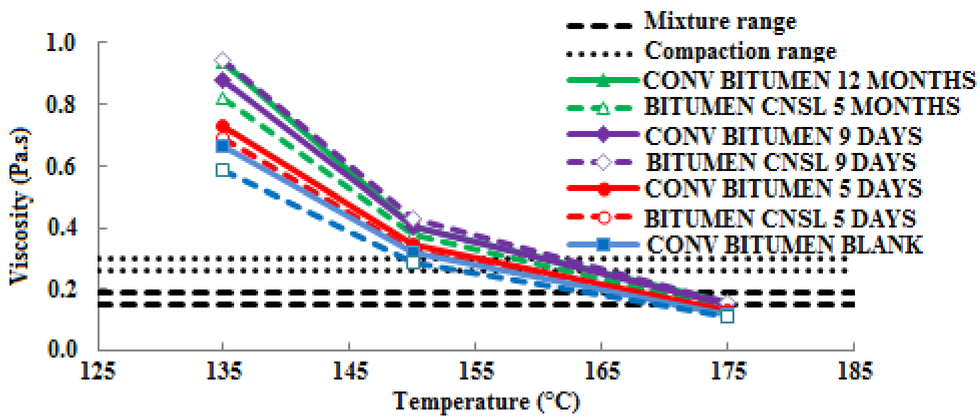


Figure 2: Viscosity (Pa.s) Viscosity versus temperature of Conventional BITUEM and BITUMEN + 2% CNSL after extraction/recovery of the same from aged asphalt mixture

The long-term aging, subjecting the loose asphalt mixture to heating in the oven during nine days caused the conventional bitumen to increase 42% of its viscosity at 135°C compared to the viscosity found for the CONV BITUMEN BLANK. Concerning the aging process of the compacted asphalt mixture samples, aged in an oven for five days, caused an increase of approximately 10% of viscosity at 135°C for CONV BITUMEN 5 DAYS when compared to the viscosity of CONV BLANK. In this way, as expected, the nine-day oven-aging process of loose asphalt was more aggressive than the five-day oven-aging process of compacted asphalt mixtures. It can still be seen that the viscosity results for the conventional bitumen recovered from the loose asphalt mixture samples submitted to nine days of oven heating was similar to the viscosity results found for the conventional bitumen recovered from the compacted asphalt mixtures aged naturally during 12 months.

3.2 Structural characterization of bitumen by FTIR

The bitumen analysis using FTIR was carried out through analysing the main bands representative of the aging process: sulfoxides (wavenumber 1,030cm^{-1}) and carbonyls (wavenumber 1,700cm^{-1}) that increase with oxidative aging. These functional groups have been known to contribute to the bitumen stiffness [20]. Figure 3 shows the spectra of the aged conventional bitumen aged evaluated in this study. This figure has an insertion on the X-axis to enhance visualization of the bands of greater interest in the analysis of the aging process: sulfoxides (1,030cm^{-1}) and carbonyls (1,700cm^{-1})

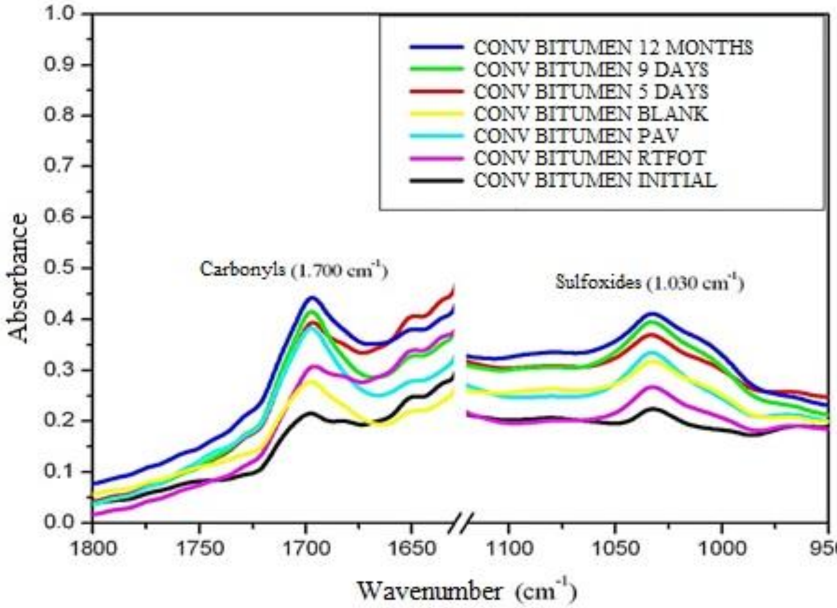


Figure 3: Spectra of conventional bitumen for the various aging processes, highlighting the carbonyl and sulfoxide absorbances

In general, it can be seen that the bitumen aging processes, performed in the laboratory, short (RTFOT) and long (RTFOT and PAV) terms, were less severe compared to aging undergone by the bitumen recovered from aged asphalt mixture. It is believed that the contact with the heated aggregates may have caused a greater aging of the recovered bitumen. The aging of conventional bitumen recovered from the compacted asphalt mixtures samples, naturally aged during twelve months, presented the highest absorbance bands for the carbonyls and for the sulfoxides. It is believed that the UV rays and rain intensity increased the aging of these samples when compared to the others. In the research conducted by Qin et al. (2014), the carbonyls and the sulfoxides absorption bands for the aged bitumen, through RTFOT and PAV, also showed less intensity when compared to the same absorbance bands of the bitumen aged naturally during eight years, regardless of the depth at which the bitumen was found in the pavement [20].

Table 4 shows the carbonyl ($A_{C=O}$) and sulfoxide ($A_{S=O}$) areas calculated for all the analyzed samples. The first interval between 1,674 and 1,720cm^{-1} was used for the carbonyls calculation and the second interval between 1,008 and 1,053cm^{-1} was used for the sulfoxides calculation. The carbonyls and the sulfoxides areas were presented individually, as well as the sum of these two areas. It can be seen that the bitumen (conventional and modified with 2% CNSL) recovered from the asphalt mixture that went through an oven-aging process during nine days presented almost the same absorbance areas. Thus, it is believed that when the aging is more aggressive, CNSL does not show a significant aging retardant effect.

Table 4: Carbonyl ($A_{C=O}$) and sulfoxide ($A_{S=O}$) areas for the analyzed bitumen

Conventional bitumen code	Bitumen type	Area		
		$A_{C=O}$	$A_{S=O}$	$A_{C=O}+A_{S=O}$
INITIAL	Conventional bitumen	2.01	0.62	2.63
	Conventional bitumen + 2% CNSL	1.30	0.42	1.72
RTFOT	Conventional bitumen	2.99	1.18	4.18
	Conventional bitumen + 2% CNSL	2.44	1.13	3.57
PAV	Conventional bitumen	4.20	1.66	5.86
	Conventional bitumen + 2% CNSL	3.86	1.30	5.16
Recovered bitumen code	Bitumen type	Area		
		$A_{C=O}$	$A_{S=O}$	$A_{C=O}+A_{S=O}$
BLANK	Conventional bitumen	2.91	1.02	3.93
	Conventional bitumen + 2% CNSL	2.47	0.84	3.31
5 DAYS	Conventional bitumen	3.65	1.15	4.80
	Conventional bitumen + 2% CNSL	2.69	0.98	3.67
9 DAYS	Conventional bitumen	4.69	1.46	6.16
	Conventional bitumen + 2% CNSL	4.79	1.41	6.19
12 MONTHS	Conventional bitumen	4.07	1.27	5.33
5 MONTHS	Conventional bitumen + 2% CNSL	3.85	1.19	5.04

3.3 Bitumen rheological tests results

The master curves constructed from the rheological tests performed on the bitumen samples were practically overlapping, indicating that the CNSL did not cause a great effect on the conventional bitumen stiffness. Table 5 shows the complex modulus (G*) values for the frequency of 1.59Hz (or 10rad/s) obtained from the master curves constructed for the reference temperature of 60°C, in order to improve the visualization of the rigidity reduction caused by the addition of 2% CNSL to the bitumen.

It is observed that the addition of 2% CNSL to bitumen, in general, reduced subtly the G* values indicating lower stiffness for such modified bitumen. The lower the G* value, the lower the bitumen stiffness should also be. Except for the aged samples in the PAV, which had practically the same stiffness (1.5×10^4Pa and 1.4×10^4Pa, for the conventional and modified bitumen, respectively). The modified bitumen with 2% CNSL stiffness, after PAV (found, also, by the viscosity test), can be associated with the polymerization process sustained by the CNSL in high temperatures [21]. It can be seen that the bitumen recovered from asphalt mixtures aged during nine days in an oven showed the highest stiffness (1.1×10^4 and 8.9×10^3Pa, for conventional and modified bitumen, respectively), followed by the results found for the conventional bitumen extracted from the asphalt mixtures aged naturally during twelve-months (1.1×10^4Pa).

Table 5: G* values versus frequency for bitumen before and after aging processes performed in this study

Conventional bitumen code	Bitumen type	*G** at 60ºC (Pa)
INITIAL	Conventional bitumen	2.5×10^3
	Conventional bitumen + 2% CNSL	2.2×10^3
RTFOT	Conventional bitumen	7.0×10^3
	Conventional bitumen + 2% CNSL	4.0×10^3
PAV	Conventional bitumen	1.5×10^4
	Conventional bitumen + 2% CNSL	1.4×10^4
Recovered bitumen code	Tipo de CAP	*G** at 60ºC (Pa)
BLANK	Conventional bitumen	5.2×10^3
	Conventional bitumen + 2% CNSL	3.8×10^3
5 DAYS	Conventional bitumen	7.4×10^3
	Conventional bitumen + 2% CNSL	5.9×10^3
9 DAYS	Conventional bitumen	1.1×10^4
	Conventional bitumen + 2% CNSL	8.9×10^3
12 MONTHS	Conventional bitumen	1.1×10^4
5 MONTHS	Conventional bitumen + 2% CNSL	8.1×10^3

3.4 Asphalt mixtures resilient modulus (RM) results

RM tests were performed in asphalt mixtures samples containing conventional bitumen and bitumen modified with 2% CNSL, before and after the aging processes. As can be seen in Figure 4, the highest RM values were found for the asphalt mixture aged naturally during twelve months (5,643MPa) and for the asphalt mixture aged in an oven during nine days (6,889MPa). The addition of 2% CNSL to bitumen in asphalt mixtures caused, in general, the reduction (a maximum of 21%) in RM values. Figure 4 presents the RM values found as well as a reference line that represents the expected RM value for a dense asphalt mixture (bitumen 50/70, range C of *DNIT*), which varies around 3,033MPa [22].

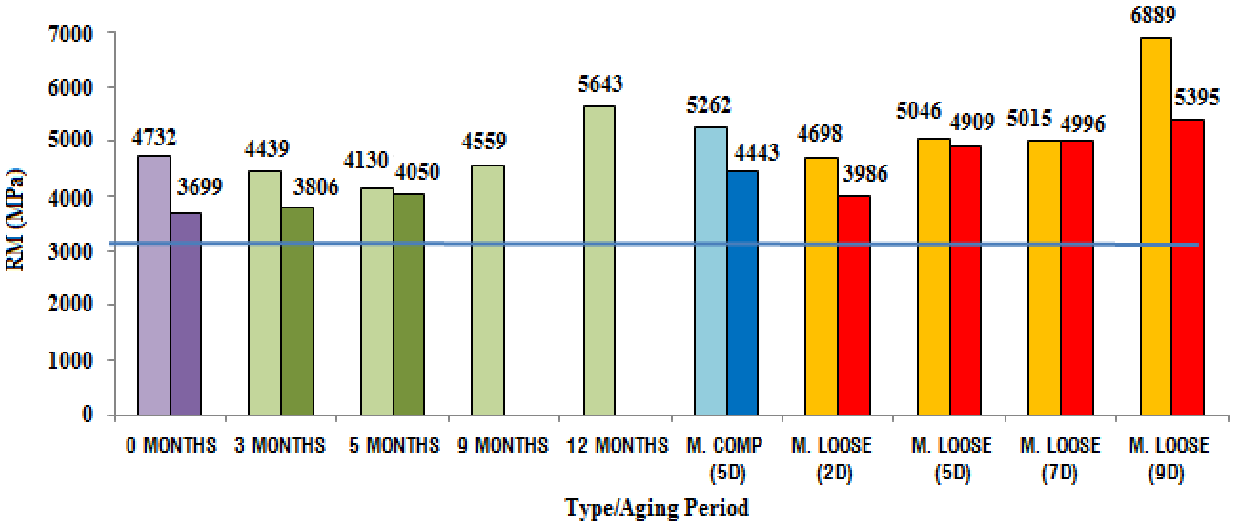


Figure 4: RM values for the analyzed asphalt mixtures (light colors correspond to conventional bitumen and dark colors correspond to bitumen modified with 2% CNSL)

3.5 Asphalt mixtures tensile strength (TS) results

TS tests for asphalt were performed according to the standard [23]. The samples were subjected to the TS test, before and after having passed through the aging processes. In general, the aging of the asphalt mixture caused the increase of the TS values. As can be seen in Figure 5, through the reference line, the asphalt mixtures tested presented TS values that exceeded the minimum accepted by the national standard protocol (0.65MPa at 25ºC).

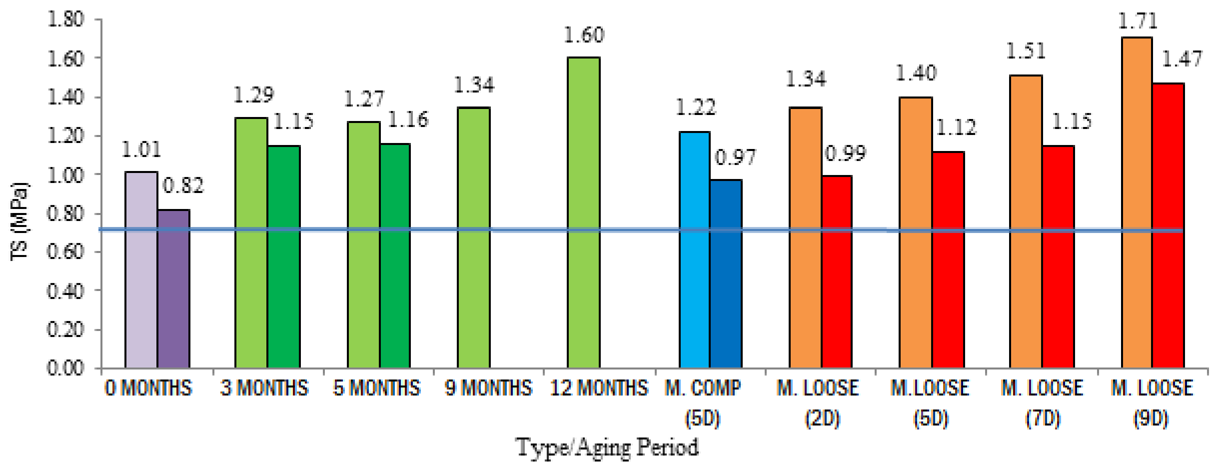
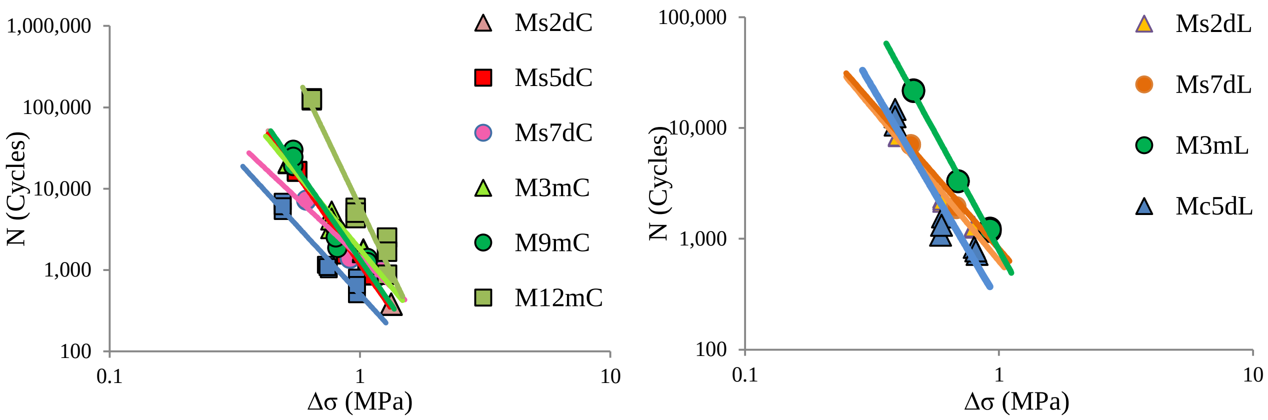


Figure 5: TS values for the analyzed asphalt mixture

It can be seen in Figure 5 that the asphalt mixture with conventional bitumen aged during nine days had the highest value of TS (1.71MPa), followed by the TS value obtained for the sample aged naturally during twelve months (1.60MPa). Observing, also, the results found for the aged sample, it can be seen that the sample containing bitumen modified with 2% CNSL did not has its TS values increasing in the same manner as the sample containing conventional bitumen. Thus, it can be said that the CNSL probably helped to reduce the TS of the sample aged naturally and in the oven (loose and compacted asphalt mixtures).

3.6 Asphalt mixtures fatigue life (FL) results

FL tests were performed in samples containing conventional bitumen and those containing bitumen modified with 2% CNSL, before and after the aging processes. It is important to remember that this is an empirical test and, for this research, the load applied on the sample took them to the complete rupture. Three specimens were tested for each stress amplitudes. In this way, for each analyzed asphalt mixture, nine samples were tested. Figure 6 shows the curves coming from the tests conducted on samples containing conventional (6a), and modified bitumen (6b).



(a) (b)

Figure 6: Fatigue life for asphalt mixture samples containing bitumen and conventional bitumen + 2% CNSL

It can be observed that the asphalt mixture samples, which underwent twelve months of natural aging, exhibited a FL curve above the curve coming from the sample aged in an oven, according to the methodology proposed by Bell et al. (1994) (compacted asphalt mixtures) and by Partl et al. (2012) (loose asphalt mixtures). The higher the values the RM or TS, greater the FL for the samples tested under controlled stress mode of loading. In this case, samples aged during twelve months (subjected to sunlight and rain) had higher TS and FL values when compared to the samples aged in the laboratory.

3.7 Asphalt mixtures dynamic modulus |E*| results

The dynamic modulus tests were performed on samples: (i) compacted aged in an oven; (ii) coming from the aged loose asphalt mixtures in an oven; and (iii) without aging, called reference asphalt mixtures. With the results, it was possible to construct the |E*| master curves for each analyzed asphalt mixtures (Figures 7 and 8).

It can be said that, for the lower frequencies, the results found for most aged asphalt mixtures were positioned above those found for the less aged asphalt mixtures for both samples containing conventional BITUMEN as well as for samples containing BITUMEN + 2% CNSL. This means that the most aged asphalt mixtures have greater stiffness at low frequencies and at high temperatures when compared with those aged less.

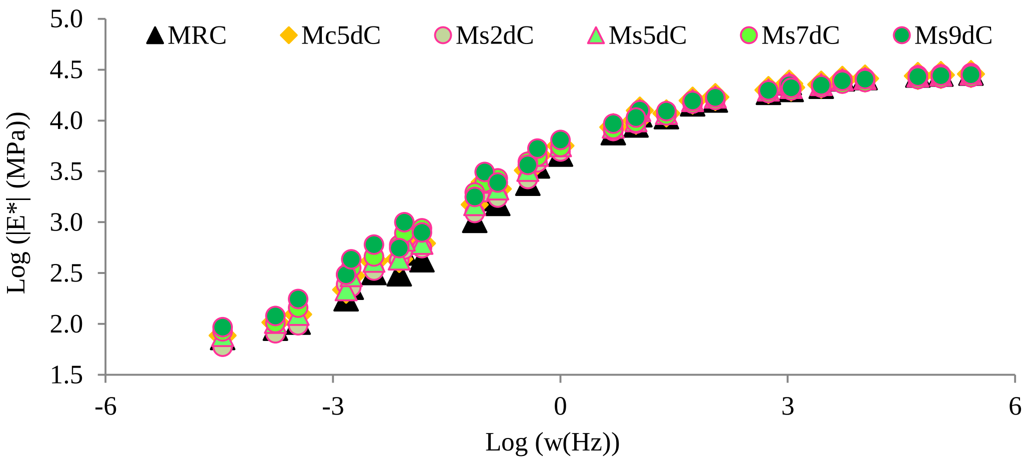


Figure 7: |E*| master curves for asphalts mixtures with conventional BITUMEN

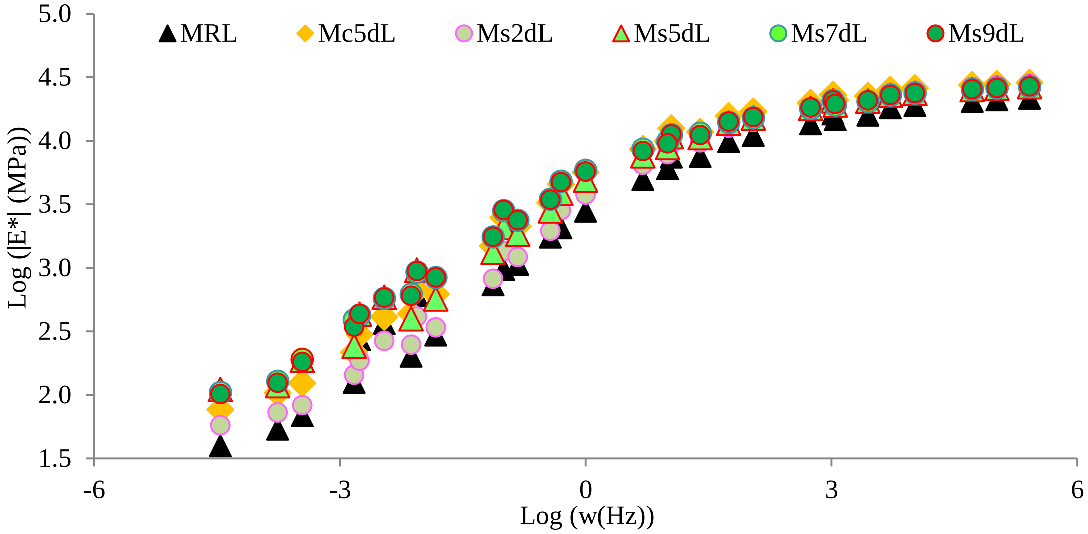


Figure 8: |E*| master curves for asphalts mixtures with BITUMEN + 2% CNSL

3.8 Asphalt mixtures dynamic creep (DC) results

The DC test was conducted at a temperature of 60ºC in triplicate. In triplicate the flow number (FN) was obtained. The FN values found were below 300, in other words, below the level considered as suitable for asphalts mixtures used for pavements undergoing medium traffic [24]. It can be seen in Figures 9 and 10 that asphalt mixtures analyzed in this research do not satisfy this condition.

The compacted asphalts mixtures aged in an oven, according to the methodology suggested by Bell et al. (1994), containing bitumen + 2% CNSL showed an elevated resistance to permanent deformation (FN) compared to the other asphalts mixtures subjected to the same test. This same asphalt mixture also presented superior FL (for smaller values of Δσ), when compared to that obtained for the asphalt mixture subjected to the same aging process, but containing conventional bitumen in its composition.

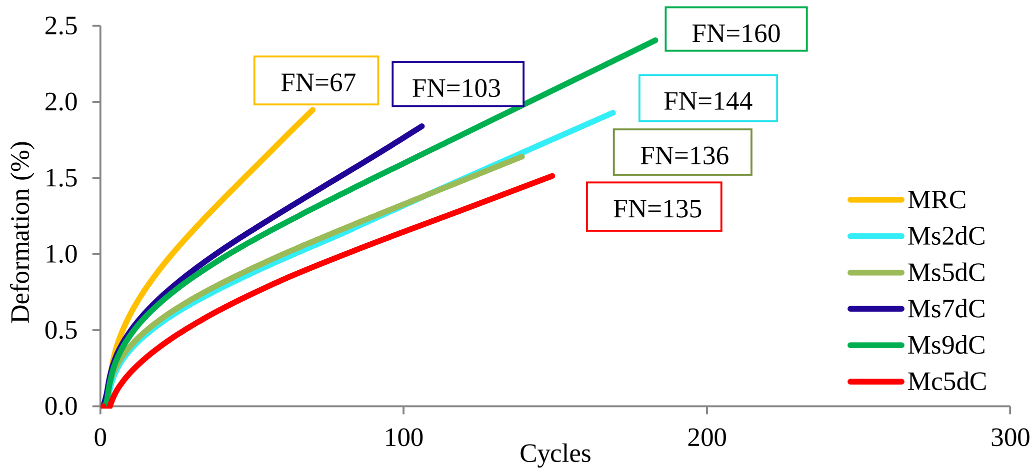


Figure 9: FN values for asphalts mixtures with conventional bitumen

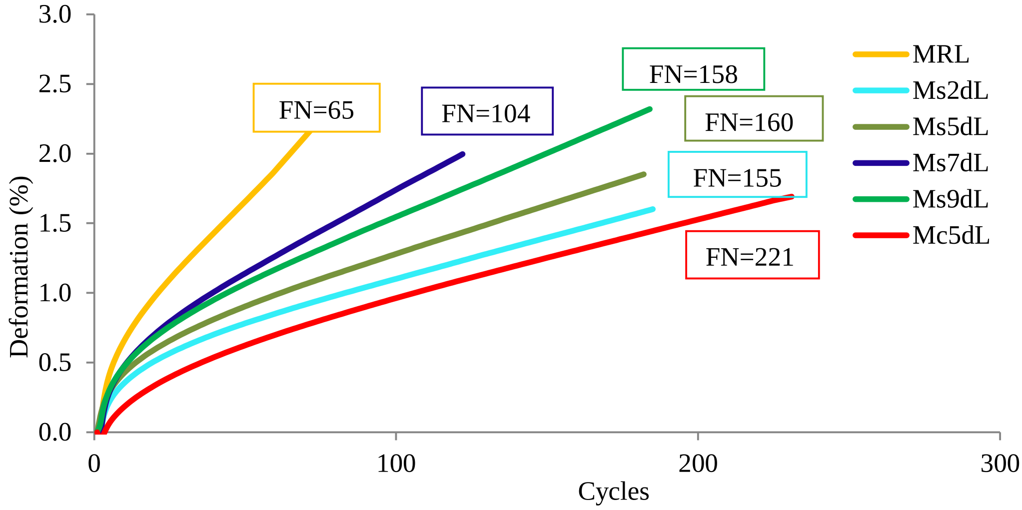


Figure 10: FN values for asphalts mixtures with BITUMEN + 2% CNSL

As previously mentioned, FN values for the tested asphalts mixtures were below 300. One of the reasons that may have influenced this result was the amount of gyrations executed during the compression process (up to 25 gyrations). It is advisable that the number of gyrations for compressing large samples (100mm×150mm), to determine FN (Vv=7.0%), should vary between 30 and 60 [24]**.** For the analyzes carried out in the asphalts mixtures, it is important to consider the different geometries (different number of gyrations) for the samples. It is believed that this difference may have influenced the presented results.

4. CONCLUSIONS

At the end of this study it is observed that the CNSL can be consider a potential aging retardant for asphaltic materials (bitumen and asphalt mixtures). This observation was greater when the aging methods processes were less severe (RTFOT and aging performed for compacted asphalt mixtures in an oven during five days). Yet when the aging methods processes used for these materials were more aggressive (PAV and aging of loose asphalts mixtures in an oven during nine days), CNSL did not show the same effect.

Comparing the chemical and rheological parameters of conventional bitumen and bitumen modified with 2% CNSL by weight: virgin and aged through use of RTFOT (short term) and PAV (long term), it can be concluded that CNSL contributed to decrease the bitumen, aged in RTFOT, stiffness. The tests results performed on samples after PAV aging, have already shown that CNSL did not reduce the bitumen stiffness in the same manner, with similar characteristics to those found for conventional bitumen. Most likely, the increased stiffness of the modified bitumen is associated with the CNSL polymerization derived from more aggressive heating caused by the PAV aging process.

Comparing the chemical and the rheological parameters of the bitumen samples recovered from asphalts mixtures (i) without long-term aging, (ii) naturally aged (open air) during different periods and (iii) aging in an oven (loose and compacted asphalt mixtures), it is possible to conclude that: the results of the tests carried out in bitumen recovered after the asphalt mixtures aging processes showed that the CNSL contributed to reduce the bitumen stiffness with the exception of the modified bitumen recovered from the asphalt mixture aged during nine days in an oven. It is believed that in this particular case, the CNSL polymerization process has occurred.

The bitumen properties most affected by the aging processes were the viscosity and the thermal-oxidative reactions represented by the carbonyls areas (in the oxidative process, the formation of carbonyls was prevalent). It can also be concluded that the bitumen process of extraction and recovery causes the same aging.

The results of the rheological tests carried out in conventional bitumen showed that there was equivalence between the aging processes performed in the asphalt mixture aged in an oven (nine days), and natural aging of samples during 12 months. This indicates that, taking into consideration the conventional bitumen, these aging processes showed similar results to the asphalts mixtures cited. Still analyzing conventional bitumen, one can conclude that the most aggressive aging processes were PAV, aging loose asphalt mixtures in an oven during nine days and natural aging of compacted asphalt mixtures during 12 months.

The testing of structural characterization of bitumen by FTIR showed to be capable of representing the aging of conventional bitumen. Through this test it was verified that the aging of conventional bitumen recovered from the compacted asphalt mixtures naturally aged during twelve months, showed the highest absorbance bands for the carbonyls and for the sulfoxides. It is believed that the climate weathering (intensity of UV rays and rain) and the interaction with the heated aggregates increased aging of these samples when compared to others.

The asphalts mixtures containing modified bitumen showed a tendency of stiffness reduction. This tendency was observed through the RM, TS and FL tests results. Yet, for the |E*| and the DC tests, the CNSL addition did not significantly alter the aged asphalt mixtures stiffness. It can be said, still, that the CNSL addition improved (even if subtly) the asphalt mixtures resistance to permanent deformation. It is believed that this gain is also associated with the aforementioned CNSL polymerization process.

Analyzing the asphalts characterization results, one can conclude that the aging process that most closely resembles the natural aging process conducted over a year is the aging of loose asphalt mixture in an oven (during nine days) at 85°C. It can also be concluded that the natural aging conducted over a year for asphalts mixtures led to a gain in resistance to fatigue cracking, given that the sample evaluated had higher FL.

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