Petroleum Plant Sap as an Asphalt Modifier for Pavement Applications

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Abstract-- **This research work aims to contribute to the development of a bio-binder for use at the paving industry, from the modification of a petroleum based asphalt by the sap of *Euphorbia Tirucalli* (Petroleum Plant). Thus, a base asphalt (PG 64-28) was modified with 3%, 5% e 10%, by weight, of sap of the petroleum plant. The functional groups present in the sap were characterized by Fourier Transformed Infrared Spectroscopy. The parameters chosen for the analysis of the modified binders were the empirical characteristics (softening point, penetration); the rheological behavior (Brookfield viscosity, complex module, phase angle); and the effects of oxidative aging (all the properties before and after aging at RTFOT). It was also carried out specific rheological tests for the determination of Performance Grade (PG) and the behavior related to permanent deformation by Multiple Stress Creep and Recovery (MSCR) test. The results showed that it was possible to replace up to 10% of the asphalt binder by sap without observe significant changes in the rheological properties, and still reducing the compaction and mixing temperatures. This result implies on major environmental and economical effects, once a material from renewable source reduces the consumption of fossil asphalt binder, and decreases the fuel expenditure for the mixing and compaction procedures as well.**

Index Term-- **Bio-binders, *Euphorbia Tirucalli*, Asphalt Modifiers, Alternative Materials**

I. INTRODUCTION

Around the world, issues such as global warming, greenhouse gases, significant increase in population, depletion of natural resources and the demanded expansion of urban infrastructure have generated great discussion regarding sustainable development and the creation of environmental friendly technologies. In this context, the search for products from renewable resources, less harmful to the environment and capable of replacing the petroleum based asphalt becomes increasingly important.

Since the 80´s, researchers are trying to develop the bio-binders, alternative materials from renewable sources [1], [2], with properties similar to traditional bituminous materials, in particular the viscoelasticity [3]. Bio-binders can be used in three different ways: as asphalt modifiers, when used in low concentrations; as asphalt extenders, replacing 25-75% of the binder; or as surrogate binders, replacing 100% petroleum based asphalt [4].

Studies conducted in order to fully replace the asphalt binder have focused on two different methods: (i) processing (decomposition, pyrolysis, distillation and liquefaction) of different types of biomass [1], [4], [5], [6]; (ii) the combination of fatty acids and resinous materials, [2], [3], [7] - [11].

From 2011, studies regarding the formulation of bio-binders were focused on modifying bituminous binders with additives from vegetal and animal origin. Some additives to be mentioned are: soybean acidulated soapstock [12], [13], waste cooking oil [14], [15]; cotton biodiesel, cotton oil, castor oil, palm oil, lignin [15], carnauba wax [15], [16], waste coffee ground [17], biomass from different sources [18]-[20]; sugarcane waste molasses [21], swine manure [22], [23], among others. When used as asphalt modifiers, some of these materials have changed consistency, thermal susceptibility and/or the workability of conventional asphalt binders [12], [13], [15], [16], [22].

The addition of larger amounts (10% to 60%) of bio-products in asphalt binders is also being investigated. The partial asphalt replacement with 10%, 30% and 60% of polymerized cooking oil promoted a decrease on the stiffness of the base asphalt, reducing the rutting and fatigue resistance, whereas increasing the thermal cracking resistance [14]. On the other hand, the use of wood biomass as asphalt extender (10% to 70%) seems to improve the rutting performance, but diminishes the fatigue and thermal cracking resistance [23].

Among the Brazilian northeastern flora there is a plant popularly known as “Petroleum Plant”, whose sap has high viscosity and adhesion. This plant, whose Latin name is *Euphorbia Tirucalli*, is a shrub used in ornamental gardening, with great adaptability to desert and high salinity environments [24]. The name Petroleum Plant was given by Calvin [25], when he discovered that its latex has hydrocarbons with molecular weight similar to those found in petroleum, and can be separated into various fractions potentially able to replace petrochemical products, such as gasoline. Regarding to productivity, plants with only 1 year old yields 10 to 20 barrels of sap per acre (1 acre = 4046.86 m²), in a year [25].

Due to high production capacity, the renewable nature, the presence of hydrocarbons and similar behavior to bituminous binder, the Petroleum Plant sap has potential for producing a green binder for pavement applications. A production of a bio-binder based on this sap enables sustainable development in underprivileged desert areas, as well as technologies that can reduce costs for road projects. The objective of this work is to produce an alternative bio-binder for use in asphalt pavement, from the modification of petroleum asphalt binder with the addition of different contents of sap produced by *Euphorbia Tirucalli*, and study their effects according to empirical and Superpave specifications applied to conventional asphalts.

II. MATERIALS AND TESTING METHODS

The base binder used in this research was a PG 64-28, with 50/70 penetration grade. The *in natura* sap of Petroleum Plant was oven dried at 60°C for 60 hours, and then mechanically fragmented to break up the lumps formed in the dehydration process. The dry sap has softening point of 87ºC.

The analysis of the functional groups of the dehydrated sap was performed by the Fourier Transform Infrared Spectroscopy (FTIR), in a Shimadzu® FTIR-8300 spectrometer, using K-Br pellets. The analysis was conducted using absorbance spectrum, in the region of 4000-400 cm^{-1} wave numbers, in transmission module.

The modified asphalts were prepared using an IKA RW20 low shear mixing reactor, at 160±5ºC and 1500rpm, for 60 minutes. The contents of sap used for bitumen modification were 3%, 5% and 10% w/w (weight/weight). Samples were denoted as “3%”, “5%” and “10%”, respectively.

The neat and modified asphalt samples were submitted to short term aging on rolling thin film oven (RTFO), following the recommendations of ASTM D2872 [26], to simulate the hardening and oxidative aging that occurs during mixing and compaction procedures.

The empirical characterization of the samples was conducted through penetration and softening point. The penetration was measured in a semi-automatic penetometer using a standard needle, according to ASTM D5 [27]. The softening point was determined using a ring and ball apparatus, following ASTM D36 [28].

The rotational viscosity determination of the neat and modified binder, unaged and RTFOT aged, was held in Brookfield® viscometer, DVII+ model coupled to a Thermosel control system and followed the recommendations of ASTM D 4402 [29]. The tests were performed using spindle 21, at 135ºC, 150ºC and 177ºC and shear rates of 20, 30, 40, 50 e 60 rpm, in order to evaluate the binder shear rate susceptibility. The measurements performed at 20 rpm were taken into account for comparison between the tested samples, at all temperatures. It was also determined the mixing and compaction temperature, according to ASTM D 2493 [30], using Asphalt Institute Method.

A Dynamic Shear Rheometer (DSR), TA Instruments® AR 2000 model, was adopted to investigate the rheological properties of the samples. The rheological tests performed were:

- Frequency Sweep, to measure the complex shear modulus (G*) and phase angle (δ) of the binders over a range of frequencies (0.01-100Hz) under stress-controlled mode (120 Pa), in accordance with ASTM D7175 [31]. The samples were tested at high temperatures only (45ºC –85ºC), on 25 mm parallel plates with 1.0mm gap. The results were presented in master curves, built by Time-Temperature Superposition Principle (TTSP) at the reference temperature of 65ºC.
- Establishment of Performance Grade (PG) and Continuous Grade, followingASTM D7175 [31], ASTM D6373 [32] and ASTM D7643 [33].
- Multiple Stress Creep Recovery (MSCR) to evaluate rutting potential of the RTFOT aged samples at the PG temperature. The parameters analyzed were the percent recovery (R%) and the non-recoverable creep compliance (J_{nr}), after 10 creep and recovery cycles of 100 Pa and 3200Pa, as described atASTM D7405-15 [34].

III. RESULTS AND DISCUSSION

A. *Chemical Characterization of the Petroleum Plant Sap*

The FTIR spectrum of the petroleum plant sap is shown in Fig. 1, and the absorbance bands with the associated functional groups are presented at Table I.

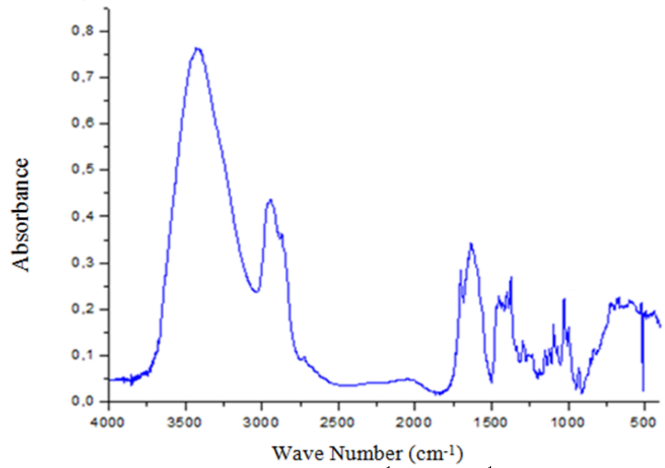


Fig. 1.FTIR *spectrum* of the sap, from 4000cm^{-1} to 400 cm^{-1}wave numbers

Table I
Functional groups from FTIR *spectrum* of the sap of Petroleum Plant

Wave Number (cm^{-1})	Functional Group
3431	ν O-H
2941	ν C(sp3)-H
2864	ν C(sp3)-H
2722	ν C(sp2)-H de aldehyde
1701	ν C=0
1637	ν C=0, tertiaryamides; δ O-H
1451	δ CH_2
1375	δ CH_3
1297	ν C-N of aliphatic
1151	ν C-O, tertiary alcohols
1123	ν C-O, aliphatic esters
1093	ν C-O, secondary alcohols
1068	ν C-O, primary alcohols
1026	ν S=O
725	Angular chain deformation -$(CH_2)_n$-

Although the sap has been pre-dried, a broad absorption band in 3431 cm^{-1}, associated with O-H axial deformation, herewith the band in 1637 cm^{-1}, indicates the presence of water. The strength of the 3431 cm^{-1} band may suggest the existence of hydroxyls of different natures, such as water and alcohols.

There is evidence of CH_3 and CH_2 groups of aliphatic chains, due to C-H axial deformation bands (2941 cm^{-1} and 2864 cm^{-1}) and angular deformation bands (1451cm^{-1} and 1375 cm^{-1}), respectively. The signal at 725 cm^{-1} may also indicate the presence of saturated chains. The axial deformation of the C-H group in aldehydes is observed as well, at 2722 cm^{-1}.

Bands associated with the C=C group were not observed, neither in aliphatic chains (between 1675 cm^{-1} to 1645 cm^{-1}), nor in aromatic rings (two or four bands at 1600 cm^{-1}, 1580 cm^{-1}, 1500 cm^{-1} and 1450 cm^{-1}).

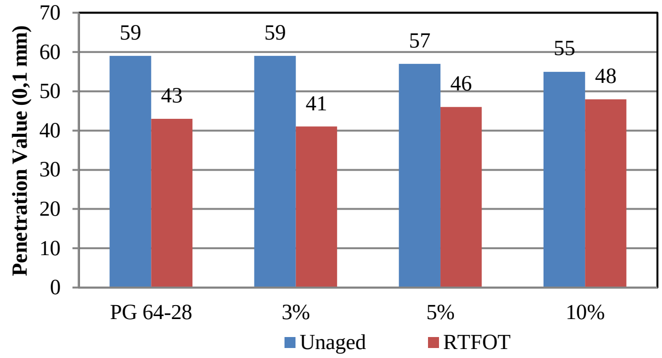
There is a band in 1701 cm^{-1}, concerning the carbonyl group (C=0). Due to the proximity to 1700, it is likely that this band is associated to ketones and aldehydes. The band observed in 1637 cm^{-1}may indicate C=O axial deformation on tertiary amides too. The presence of amides is important, once this organic function is related to enhance the adhesive properties of asphalt binders.

The sulfoxyde group (S=O) was detected on 1026 cm^{-1}, as well as a series of bands indicative of C-O group of sterols (1123 cm^{-1}) and alcohols (1068 cm^{-1}, 1093 cm^{-1}, 1151 cm^{-1}). Carbonyl and sulfoxyde groups are indicative of hardening and oxidative aging of asphalt binders. The occurrence of these groups on the sap would naturally increase the presence of the compounds on the modified binders, without necessarily promoting any aging effect. Thus, the FTIR analysis did not prove to be adequate for evaluating the aging process on petroleum plant modified binders.

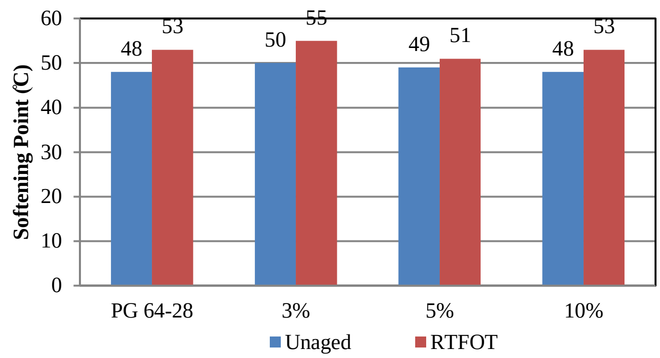
B. Empirical Properties of Neat and Modified Asphalt Binders

The results of the empirical tests (penetration and softening point), for pure and modified asphalt binder, unaged and RTFOT aged, are shown in Fig. 2. The addition of the sap promoted small changes in the consistency of the asphalt binder, making it slightly stiffer.

The addition of the sap caused a small decrease in the penetration in the order of 2 tenths of a millimeter for each 5% of additive. The addition of carnauba wax also causes a reduction in penetration asphalt binders, but at significant higher magnitudes: 4% of wax reduced the penetration from 68 to 45 tenths of a millimeter in [15], whereas 5% of wax decreased from 52 to 26 tenths of millimeters in [16].Different results occur when vegetable oils or biomass are added to the binder. Cotton oil, biodiesel, waste cooking oil [15] and *Nigella Sativa* Biomass [18] all increased the penetration measurements, the largest effect being observed with the last one (penetration enlarged from 70 to 160 tenths of millimeters).



(a)



(b)

Fig. 2.Empirical Properties of Neat and Modified Binders, Unaged and RTFOT Aged: (a).Penetration; (b). Softening Point

After RTFOT, however, the modified binder samples showed higher penetration than the original binder, resulting in an increase in retained penetration from 70.3% to 87.3%, when 10% of sap is applied. This indicates that, at the beginning of the service life, the modified binder is more flexible at 25°C than the original binder.

It was observed that the addition of the sap increased softening point (in only 2°C) just in low concentrations. This observation was unexpected, since the softening point of petroleum plant sap is 87ºC, much larger than the asphalt binder. The result was consistent, qualitatively and quantitatively, with vegetal oil results in [15], where the increment of 1.5°C at the softening point occurred with 3% and 5% of oil.

The different behaviors observed on the penetration and softening point may be due to the test temperatures. At 25ºC (penetration test), the sap showed changes in binder compatible with those observed with the addition of wax, while at higher temperatures (softening point test), the sap led to similar results to those obtained with vegetable oils.

C. Rotational Viscosity

The flow curves at 135°C for the original and modified binders are shown in Fig. 3. The linear relationship between the shear stress and the shear rate shows that the addition of the sap did not modified the Newtonian behavior of the asphalt binder, at high temperatures. The flow curves also indicate that the sap promoted a reduction in the viscosity of the binder, since that lower slopes are observed for the modified sample.

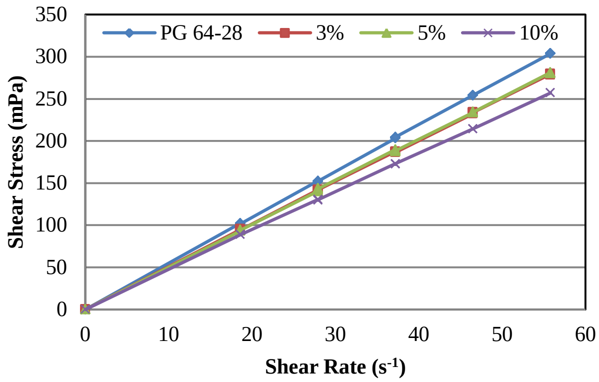


Fig. 3.Flow Curves of Original and Modified Binder at 135°C

The viscosity-temperature charts presented in Fig. 4 confirm the viscosity diminishment, especially at 135°C and 150°C. It was also observed that higher contents of sap led to larger decreases on viscosity, indicating improvement on the binder workability. At 177°C, although, the modified samples have viscosity values very close to that obtained for the original binder, indicating that the sap could have been degraded, by this temperature.

Other bio-additives that enhance the flow capability of the asphalt binders are carnauba wax [15], [16], acidulated soy soapstock [12], [13], and cashew nut shell liquid (CNSL) [35], [36]. On the other hand, some vegetal oils like biodiesel, castor oil, palm oil, cotton oil and waste cooking oil increased the viscosity of asphalt binders in [15].

The effect of viscosity reduction with the sap is not so pronounced on the RTFOT aged samples as it was for the unaged ones. For all the samples, the viscosity-temperature curves became more close to each other, after aging process. Therefore the modified samples viscosity is more susceptible to short-term aging than the original binder.

The decrease on viscosity of the modified samples reflected on the mixing and compacting temperatures. As it can be noted on Table II, the addition of sap, in all contents, led to a reduction on both mixing temperature (MT) and compacting temperature (CT). The larger benefits were observed from the addition of 10% of sap, with the reduction of 6ºC on mixing process and 7ºC on compaction. The reductions of 6ºC to 7ºC on mixing and compaction temperatures with the addition of petroleum plant sap are consistent with those obtained with other vegetal additives such as CNSL [35], soybean acidulated soapstock [12], and carnauba wax [16]. These results show that the petroleum plant sap has potential to be used as workability improver, from the environmental and economic point of view. With lower temperatures, it is possible to save energy, once less fuel is required for heating the material. In addition, lower heating of the asphalt binder can prevent excessive aging.

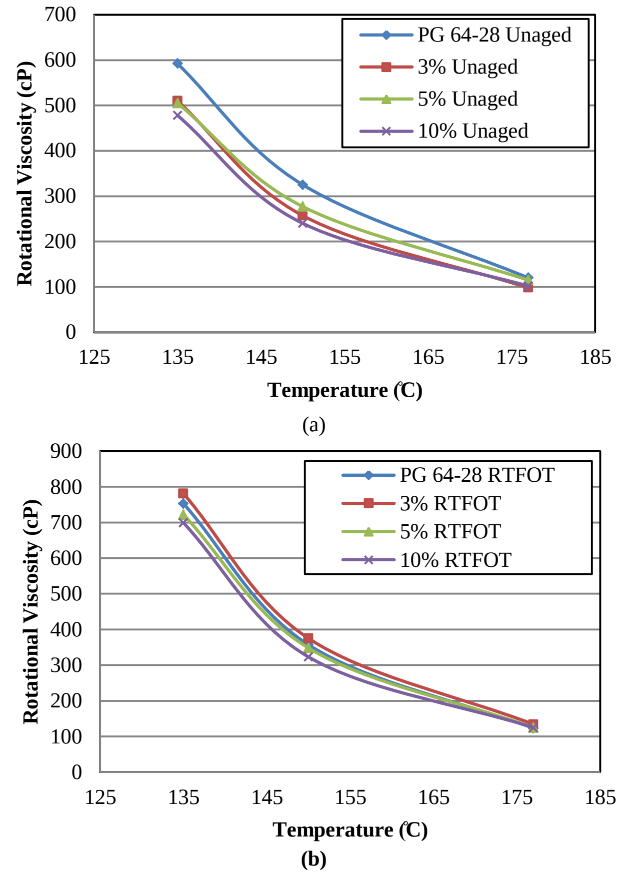


Fig. 4.Viscosity-Temperature Charts of Unaged (a) and RTFOT aged (b) Binders

Table II
Mixing and Compaction Temperatures for neat and modified binders

Sample	MT	CT
PG 64-28	168± 3	154± 3
3%	162± 3	148± 3
5%	165± 3	150± 3
10%	162± 3	147± 3

D. Rheology Analysis

The Frequency Sweep results (G*, δ) for unaged and RTFOT aged samples are presented by their master curves in Fig. 5. The reference temperature is 65°C, once only high temperatures (45°C to 85°C) were scanned. The master curves show that the Time-Temperature Superposition Principle remained valid for samples, even after modification. This was possible because the modified samples also exhibited viscoelastic behavior in the temperature range studied.

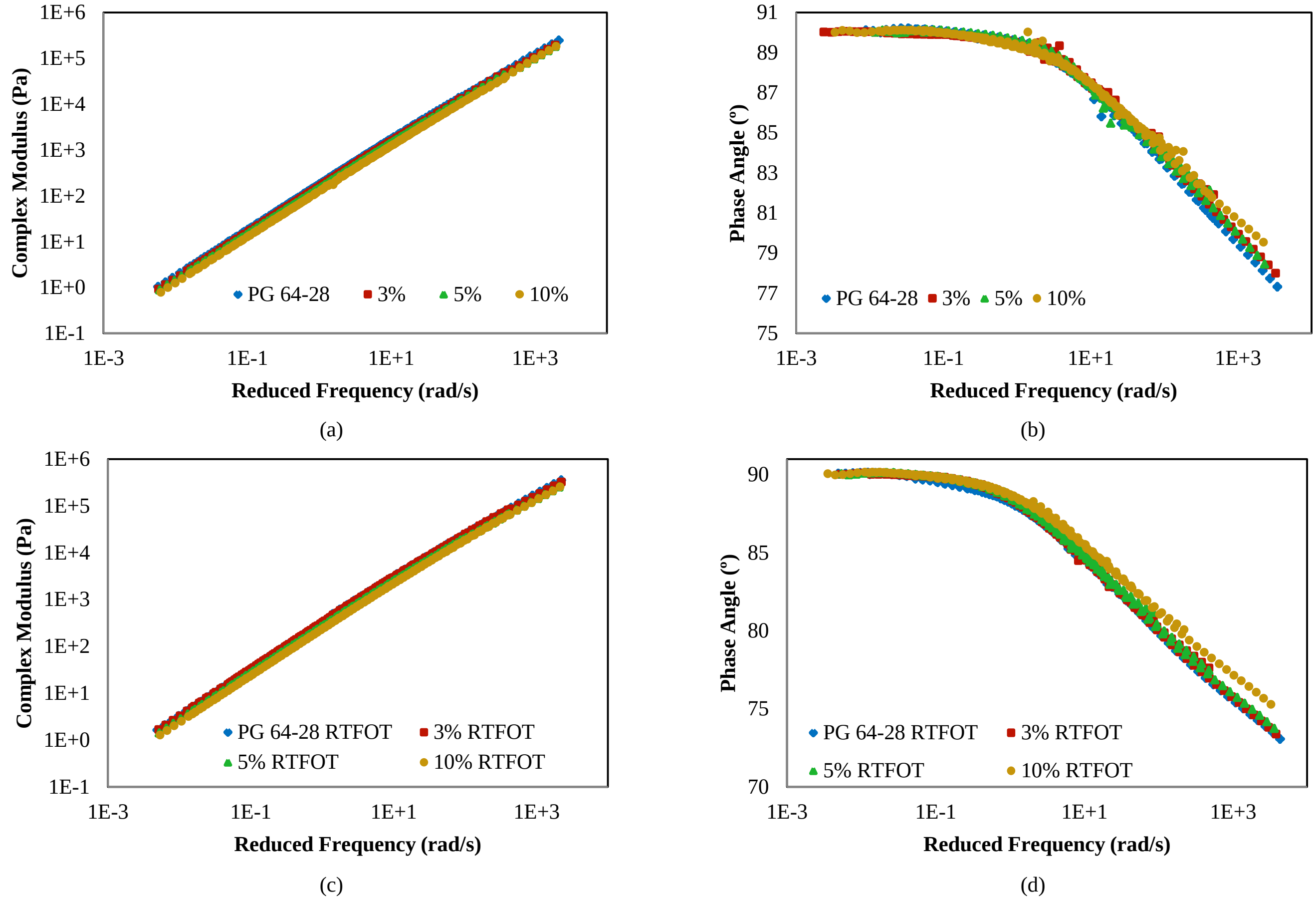


Fig. 5.Master Curves as Function of Frequency at 65ºC: (a) G* and (b) Phase Angle for Unaged Samples; (c) G* and (d) Phase Angle for RTFOT Aged Samples

Although all the G* master curves presented themselves almost overlapped on both aged and unaged samples, a small shift toward lower Complex moduli could be noticed, indicating that the applied sap has a slight tendency of softening the asphalt binder, over all the frequency (and temperature) range. This lower stiffness is desirable for improving the fatigue resistance and the thermal cracking, but opposes to rutting performance. The modified samples have upper phase angles at high frequencies (low temperatures) than the neat binder, what makes them more vulnerable to viscous deformations. At RTFOT samples, the raise on phase angle values at high frequencies is even more prominent. Lower stiffness and higher phase angles indicates that the sap tends to have solvency action on the asphalt binder.

The reduction on the asphalt binder stiffness caused by the sap is consistent with the effect of most bio-additives: soybean acidulated soapstock [12], swine manure [23], biolubricant residue [37], waste cooking oil [14] and *Nigella Sativa* biomass [18] all diminished the stiffness, being the carnauba wax [16] and CNSL [35] exceptions that increases G* values. Regarding the phase angle, rises were observed after the addition of soybean acidulated soapstock [12], but reductions were noted with carnauba wax [16], biolubricant residue [37], swine manure [32] and CNSL [35]. Nevertheless, the magnitude of these effects, raising or dropping G* and δ, were much pronounced than the ones observed with the addition of the petroleum plant sap and waste coffee ground [17], where G* curves for all samples were almost superimposed.

PG Grade and Continuous Grade Establishment

The high temperature of Performance Grade (PG) of asphalt binders is determined as the first temperature from a preselected set (52°C, 58ºC, 64ºC, 70ºC, 76ºC, 82ºC and 88°C) at which the parameter value G*/senδ is higher than 1.0kPa and 2.2 kPa for unaged and RTFOT aged samples, respectively. These values are reference that at this given temperature, the asphalt binder has suitable resistance to rutting. It is also possible to estimate (for interpolation, as described in [33]) the exact temperature were the parameter G*/senδ reaches the reference values. This temperature is denoted as the Continuous Grade (CG).

The Performance Grade and the Continuous Grade of the original and modified samples are presented at Table III. In accordance with the master curves analysis, the highest addition of sap (10%) lessened about 2ºC on Continuous Grade, and yet it was not sufficient for downgrading the Performance Grade. Thus, all the samples of this research are classified as PG64, characterized at high temperature only.

Table III
Performance Grade and Continuous Grade of neat and modified asphalt binders

Specification	PG 64-28		3%		5%		10%	
	PG	CG	PG	CG	PG	CG	PG	CG
T (°C) for G*/senδ (kPa) ≥ 1.00 (Unaged)	64	68.1	64	67.9	64	66.9	64	66.6
T (°C) for G*/senδ (kPa) ≥ 2.20 (RTFOT)	64	66.3	64	65.6	64	66.5	64	64.3
Performance Grade	64		64		64		64	
Continuous Grade	66.3		65.6		66.5		64.3	

Multiple Stress Creep and Recovery

The results of the MSCR tests for binder sample and its blend with petroleum plant sap are available on Table IV.

Table IV
MSCR test results for neat and modified asphalt samples at 64ºC

Sample	R100 (%)	R3200 (%)	J_{nr} 100 (KPa^{-1})	J_{nr} 3200 (KPa^{-1})	R_{diff} (%)	$J_{nr-diff}$ (%)
PG 64-28	2.4	0.6	3.41	3.58	75.4	4.8
3%	6.9	0.6	3.77	4.31	90.8	14.1
5%	19.9	1.5	2.32	3.66	92.7	57.8
10%	6.1	0.5	3.93	4.63	91.2	17.9

The percent recovery represents the amount of the elastic response to a given stress, and the non-recoverable creep compliance measures the ratio between the permanent deformation and the stress applied. The percent difference in recovery (R_{diff}) and in non-recoverable creep compliance ($J_{nr-diff}$) between 0.1 kPa and 3200 kPa represents the susceptibility of these parameters to the increase of tension.

The studied asphalt binder has a low percent recovery and high non-recoverable creep compliance, on both 100 Pa to 3200 kPa, indicating that the material has low elasticity and is susceptible to permanent deformation. The non-recoverable compliance at 3200 kPa is quite close to the limit value of 4 kPa^{-1}, which indicates that at 64ºC this material has rutting resistance for standard traffic only. However, this binder has shown to be very resistant to stress variations, since the percent difference of the non-recoverable compliance ($J_{nr-diff}$) was 4.84%, much lower the prescribed limit of 75%.

The addition of 3% and 10% of the sap did not provide any improvement in parameters related to permanent deformation. There was a slight increase in the percent recovery values at low stress, but at high stress the recovery stood practically the same. It was also found that non-recoverable compliance increased, showing these blends more vulnerable to permanent deformation. Otherwise, the content of 5% of sap improved the rut resistance at low stress, with higher percent recovery and lower non-recoverable compliance at 100 Pa. However, raising the stress to 3200 kPa, this blend has behaved just like the original binder. Furthermore, the percentage differences of the non-recoverable compliance ($J_{nr-diff}$) and percent recovery (R_{diff}) increased, showing that all contents of sap made the binder more susceptible to stress variations.

Generally, the MSCR test results indicated that the addition of petroleum plant sap reduced the resistance to permanent deformation, even though the binder had already low rutting resistance. The studied properties suffered little variations, from the practical point of view, like it was observed on master curves and Continuous Grade establishment. Regarding to rut resistance, the petroleum plant sap showed similar behavior to polymerized waste cooking oil [14] and *Nigella Sativa* biomass [18].

IV. Conclusions

There were identified evidences of aliphatic chains, water, esters, alcohols, aldehydes, and tertiary amides on the dehydrated sap of petroleum plant. The presence of carbonyl and sulfoxyde groups also identified on the sap made unfeasible the FTIR analysis for measuring the aging properties of the modified binders.

The petroleum plant sap tends to soften the base binder at high in service temperature, even though the magnitude of the changes is almost negligible, even at higher contents. At mixing and compaction temperatures, although, the addition of the sap improved the binder workability, decreasing the required temperatures at about 6ºC.The temperature limits on which the base binder and the modified binders begin to have more distinguished behavior seems to be higher than 85ºC, probably around the softening point of the sap, at 87°C.

The additive apparently does not protect the properties of the sample from the short-term aging effects, since modified binders showed almost the same properties as the base binder after RTFOT aging (except for the penetration test). Possibly, this is a reflection of the harsh conditions of the mixing process: temperature of 160°C for a period of 60 minutes is a very similar condition to those applied in the aging process in RTFOT. Another prospect is that the antioxidant complexes are volatilized during the oven drying process of the sap or during mixing with the asphalt binder.

In practical terms, it was possible to replace up to 10% of the asphalt binder by the sap of petroleum plant, without observing significant variations in the behavior at usual in-service temperatures, and still reducing the compaction and mixing temperatures. This result implies on major environmental and economical effects, once a material from renewable source reduces 10% of the total consumption of fossil asphalt binder, and decreases the fuel expenditure for the mixing and compaction procedures as well. The application of the petroleum plant sap on asphalt binders would also allow local production arrangements in desert and non productive areas, promoting vegetation recovery on barren wasteland and economical development at the same time.

V. ACKNOWLEDGMENTS

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