THE USE OF VEGETAL PRODUCTS AS ASPHALT CEMENT MODIFIER

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ABSTRACT

The use of different vegetal products is being studied as asphalt binder improver. They are tested without refining, with different goals: thermal susceptibility improver, warm mix additive and antioxidant. Blends of asphalt cement with these materials were analyzed according European and American asphalt binder specifications. The binders were exposed to ultraviolet rays using the equipment Suntest – Atlas to measure the benefits of the vegetal materials as antioxidant. The bituminous mixtures made with them where submitted to Superpave hot mix design. The cores obtained with these mixtures were tested in relation to fatigue life, dynamic modulus and flow number. The rheological tests on the asphalt binders and mechanical tests in the bituminous mixtures showed good results.

Keywords: vegetal products, asphalt binder, bituminous mixtures, antioxidant, SUPERPAVE, thermal susceptibility

1. INTRODUCTION

Bioasphalt is an asphalt alternative made from non-petroleum based renewable. The vegetal sources can be used partially or totally replacing the bitumen. Examples of these renewable products used in paving roads were already done in different countries since last century. One of them is GEO320™, which is made from Sugar and Molasses, but it also possesses good mechanical and rheological properties to be applied on the road [1]. Colas developed Vegecol, which is an entirely vegetable based alternative to bitumen and petroleum resin binders and so carries massive potential for the pavement sector, used as warm mixes as well. In Europe, use of Vegecol has extended to surface and base course asphalts [2]. Shell developed Floraphalte that belongs to a new generation of binders used to produce colored pavements, which is composed of vegetable products, including polymers in order to bring high performance to paved roads [3]. The Patent US 2008-0006178 is also related to this kind of product, constituted of natural resin of vegetable oil, but exempt of synthetic elastomer [4]. The partial use of renewable source can be seen in fluxing oils and cutbacks. Fluxing oils derived of methyl esters of fatty acids obtained by transesterification or even formulated with fatty acids from vegetable sources are being patented to be used blended with asphalt binder in surface treatments, where the hardening of the binder after spreading is obtained by crosslinking of the thinner in the presence of atmospheric oxygen and metallic catalysts [5, 6]. The cutbacks asphalt can be diluted with a sufficient amount of biodiesel instead of kerosene or diesel oil producing cold patch material which is free of added liquid petroleum [7]. Composition sealant to rejuvenating and preserving wearing courses that includes soybean oils and terpine hydrocarbons as thinner of asphalt binder are developed as well [8, 9]. It is important to empathize that the use of vegetable products show benefits from both health and environmental perspectives, are abundantly available (do not compete with the food chain) and provide at least equivalent technical performance in bituminous applications.

The main objectives of this work were to identify and develop different vegetal products as asphalt binder additives. Primarily, vegetal products were added to asphaltic residue or asphalt binder in the proportion from 3 to 20% as thermal susceptibility improver. They are vegetable oils without refining, biodiesel and used frying vegetable oil. Secondly, vegetable waxes were blended with asphalt binder to act as warm mix additive, and also to enhance the fuel resistance of the pavement. Crude carnauba wax (without clarification process) was used for this purpose in the proportion 2 to 6%. Finally, a sub product derived from sugar cane bagasse acid digestion, known as black liquor that contains 30% of lignin was added to asphalt binder to improve aging resistance. Circa of 15% of the dehydrated black liquor was added to asphalt binder.

2. MATERIALS

2.1 Asphalt binders

Different asphalt binders were used in each case: sample of asphalt cement, penetration 50/70 with PG grade 64-16 was used in the carnauba wax study, sample of hard asphalt, penetration 10/20 with PG grade 70-4 and 30/45 penetration (PG 70-10) sample were used in the vegetable oils study, sample of penetration 50/70 with PG 70-22, known as an asphalt with bad aging resistance was employed in the lignin study.

2.2 Vegetable additives

Carnauba wax

It is a wax originated from the gross dust waxing process, bleeding from straw palm, whose Latin name is Copernicia prunifera M. Straws are cut from palm tree, the dust contained in the straw results in a natural yellow wax. Ripe Top straws in array shape produce brown wax. The refining process is composed of several filtration steps to adequate the wax to the desired type. According to purity grade, color and refining process, there are different types of waxes to be offered to the market. Constituted of long paraffinic chains, with 68 to 84 atoms de carbon, they contain carbonyls of fatty esters/acids/amides, unsaturated carbons of olefins and aromatics, aliphatic carbons bonded to oxygen also joined with esters/ ethers/ alcohols with melting point above 85ºC. [10, 11]. The type of carnauba wax employed in this study was the brown wax to reduce the cost of raw material.

Vegetables oils, Used frying oil and Biodiesel

The fatty acids existing in the natural vegetable oils differ in chain size and unsaturated bonds number. Besides, functional groups can make part in its composition. Natural triglycerides are biodegradable and enough efficient as lubricants. The more common fatty acids from triglycerides have 12, 14, 16 or 18 carbon atoms. An interesting example is the castor oil composed mainly of ricinoleic acid $CH_3(CH_2)_5CH(OH)CH_2CH{=}CH(CH_2)_7COOH$, in its triglycerides (circa 90%), according Table 1. The reasons of thermal instability of vegetable oils are the double bonds in the fatty acid and the β-CH groups in the alcohol no component (Figure 1). Double bonds are specially reactive and react immediately with air oxygen, whereas the hydrogen atom β is easily eliminated from the molecule structure. It leads to ester breakage in olefins and acids. [12] (Silva J.A. 2006). The palm oil, castor oil and dark cotton oil were chosen as additive in asphalt cement in this work.

Table 1 – Properties of vegetables oils and its derivatives

Properties		Castor oil	Cotton oil	Palm oil	Soybean oil
Fatty acids, % , C; =					
Myristic	14:0	-	0.4 - 2	-	0.1
Palmitic	16:0	1	17 - 31	5.7 - 7	10.3
Stearic	18:0	1	1 - 4	3 - 4	4.7
Oleic	18:1	3	13 - 44	20	22.5
Ricinoleic	18:1	89. 5	-	-	-
Linoleic	18:2	4.2	33 - 59	53	54.1
Linolenic	18:3	0.3	0.1 – 2.1	< 0.1	8.3
Classification		unsaturated	polisaturaded	polisaturaded	polisaturaded
Viscosity at 37.8ºC, cSt		285	37.5	37	36.8

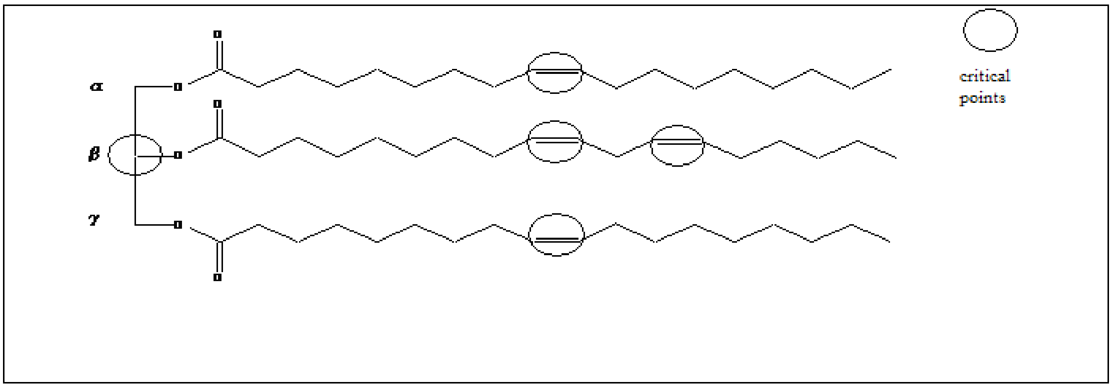

Figure 1 – Typical structure of a vegetal oil and its instability (critical points)

Biodiesel is an alternative fuel for diesel engines consisting of the alkyl monoesters of fatty acids from vegetable oils or animal fats. Most of the biodiesel that is currently made uses soybean oil, methanol, and an alkaline catalyst. Animal and plant fats and oils are typically made of triglycerides which are esters containing three free fatty acids. In the transesterification process, the alcohol is deprotonated with a base to make it a stronger nucleophile. Commonly, ethanol or methanols are used. As can be seen, the reaction has no other inputs than the triglyceride and the alcohol, according Figure 2 [13]. The biodiesels derived from castor and cotton oil were used as susceptibility enhancer in asphalt cement. The typical properties of biodiesel of different sources compared with diesel oil characteristics are described in Table 2.

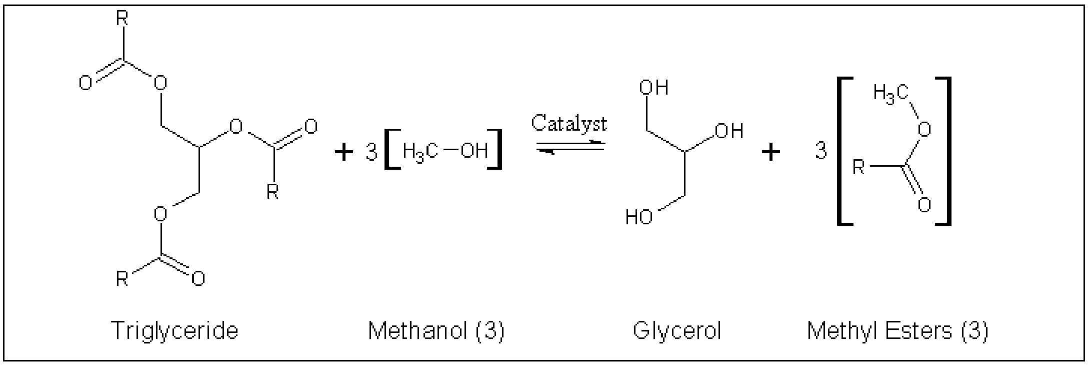

Figure 2 – Transesterification reaction

Food fats and oils are (from a chemical point of view) mixtures of triacylglycerols (non-polar components), which are composed of fatty acids and glycerol. Such triacylglycerols are affected by oxygen and heat, whereby, due to oxidation and polymerization more polar compounds like free short-chain fatty acids, mono- and diglycerides, aldehydes, ketones, polymers, cyclic and aromatic compounds are formed. Some of these compounds are responsible for the pleasant flavor of the deep-fried products. At the same time however, oxidation products such as short-chain fatty acids lead to a decrease of the smoke point, so that the fat starts smoking at clearly lower temperatures than the fresh fat. In addition it develops a gritty taste. Polymeric components lead to the formation of foam and increase the viscosity [14]. The used frying oil employed in this study was derived from several vegetable oil.

Table 2 Typical properties of biodiesel of different sources compared with diesel oil characteristics

Properties	Biodiesel		Diesel Oil
	Castor oil	Cotton	
Density at 20ºC, g/cm^3	0.9190	0.8750	0.8497
Viscosity at 37.8ºC, cSt	21.6	6.0	3.04
Distillation at 50%, ºC	301	340	278
Distillation at 90%, ºC	318	342	373
Conradson Carbon residue, %w/w	0.09	-	0.35

Lignin

Lignin, a complex phenolic polymer, is important for mechanical support, water transport, and defense in vaseular plants. Lignin is a complex hydrophobic network of phenylpropanoid units, according Figure 3 that is thought to result from the oxidative polymerization of one or more of three types of hydroxycinnamyl alcohol precursors [15]. Its strucutural schme is showed in Figure 4. Asphalt pavements undergo long-term aging due to oxidation of the asphalt binder. The use of an antioxidant in an asphalt binder could retard aging, thus increasing the pavement's service life. Lignin is a known antioxidant and is highly available from timber and many agricultural products. A wet-mill ethanol process produces several co-products, some of which contain lignin. The utilization of lignin from an ethanol plant could provide benefit to asphalt pavements, along with increasing the value of these lignin. McCready related that asphalt-lignin blends were evaluated according to Superpave specifications and performance-graded on a continuous scale. The blends were also tested for separation tendencies. The results illustrate that the addition of lignin has a slight stiffening effect on the binder. The more lignin added, the greater the stiffening. The lignin has an overall effect of widening the performance grade range of the asphalt binders [16]. Bagasse, a non-wood consist mainly of cellulose (50%), hemicellulose (30%) and lignin (20%). Lignin is an amorphous large, cross-linked, macromolecule with 54 molecular masses in the range 1000 g/mol to 20,000 g/mol. In Brazil, sugar cane bagasse is an abundant natural solid lignocellulosic residue after extraction of juice from sugar cane stalk. A large amount of bagasse is currently burnt as a low-grade fuel for energy recovery; only a limited quantity has been used to make pulps, broad materials and composites. Bagasse acid digestion generates black liquor, as sub product. The black liquor comprises 15% solids by weight of which 10% are inorganic and 5% are organic. Normally the organics in black liquor are 40-45% soaps, 35-45% lignin and 10-15% other organics [17].

Two types of lignin were used as antioxidants, one is commercial with 95% purity and the other is the material resulted from black liquor lyophilization, the last was formed as sub product from acid digestion of sugar cane bagasse. The lignin concentration in the dry material should be about 15%.

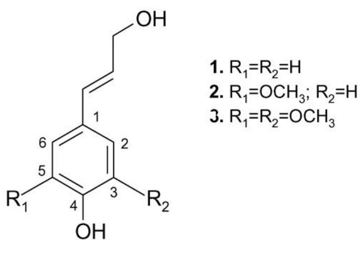

Figure 3 – Phenylpropanoid units from Lignin

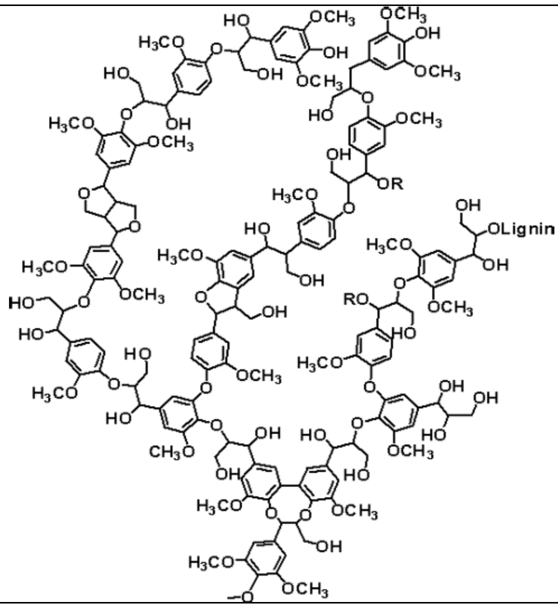

Figure 4 - Structural scheme for lignin

2.3 Modified asphalt binders with vegetable additives

The modified asphalt binders with above renewable modifiers were prepared in the laboratory. The prepared blends are codified according Table 3. The asphalt cements samples used are classified by penetration according EN 12591 and EN 13924. There were two different 50/70 asphalt cement samples, one with excellent thermal susceptibility but poor aging resistance and the other with thermal susceptibility satisfactory. The operational conditions of mixture comprise the following steps:

- Asphalt binders melting at 135ºC
- Adding the modifier - 3 to 5% w/w to all blends, except the Black liquor lyophilized that was used as 15% of the blend due to low lignin content in this dry material and the commercial lignin employed as standard (95% purity) was used as 1.5% of the blend
- Temperature control at 135ºC in an thermal controlled reactor
- Stirring speed and time – 1500 revolutions per minute for 20 minutes

Table 3 – Identification of modified asphalts

Asphalt binder	Modifier	Code	Modified asphalt
50/70	Carnauba wax	11	35/50
15/25	Cotton biodiesel	21	30/45
15/25	Cotton oil	22	30/45
15/25	Palm oil	23	30/45
15/25	Castor oil	24	30/45
15/25	Soybean used frying oil	25	30/45
50/70	Commercial Lignin	A	50/70
50/70	Black liquor lyophilized - lignin	B	50/70

2.4 Aggregates

The mineral aggregates used are granites, from Sepetiba stone quarry, whose properties are described in Table 1.

Table 1: Properties of mineral aggregates used in bituminous mixtures

Properties	**Test method**	**Results**
Flat and elongated particles coarse aggregates (1:5), %	ASTM D 4791/99	1.0
Los Angeles abrasion loss, %	ASTM C 131/03	43.3
Coarse aggregates effective specific gravity	ASTM C 127/04	2.792
Coarse aggregates bulk specific gravity	ASTM C 127/04	2.666
Absorption of coarse aggregates, %	ASTM C 127/04	0.80
Fine aggregates effective specific gravity	ASTM C 128/04a	2.781
Fine aggregates bulk specific gravity	ASTM C 128/04a	2.693
Absorption of fine aggregates, %	ASTM C 128/04a	3.01
Clay content, %	ASTM D 2419/95	84.0

2.5 Bituminous mixes

The Superpave mix design of bituminous mixture with modified carnauba wax asphalt binder (code 11) and the vegetable modified asphalt (code 21, 22, 23, 24 and 25) were done in the gyratory compactor. The content of carnauba wax in the binder was 4% mix. The dense mix with 19 mm maximal nominal size was employed. The figure 5 shows the 0.45 power gradation chart with control limits and restricted zone of the aggregate structure.

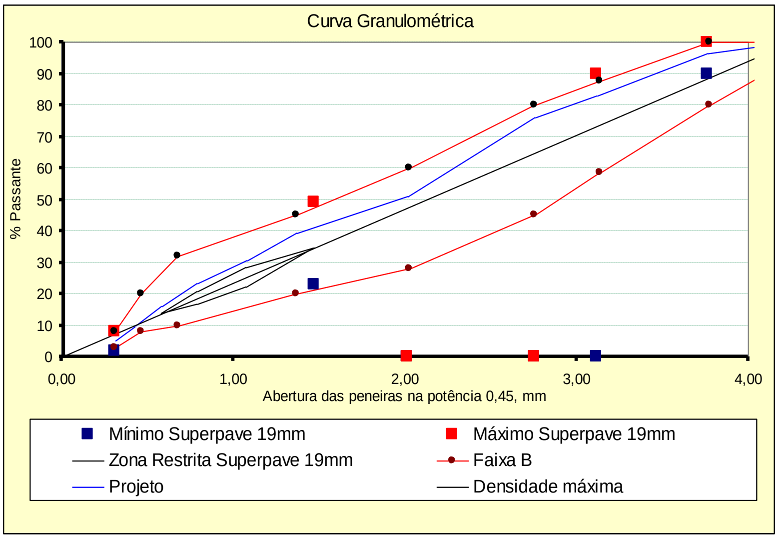

Figure 5 – SUPERPAVE gradation for 19 mm mixture

4. LABORATORY WORK AND ANALYSES

4.1 Binder properties

The asphalt binders were submitted to the following tests:

- Rotational viscosity at 135ªC – ASTM D 4402;
- Viscosity by vacuum capillary viscometer at 60ºC – ASTM D 2171;
- Penetration at 25ºC (100g, 5s) (Pen)- ASTM D 5;
- Softening point (RB) - ASTM D 36;
- Effect of heat and air (rolling thin film (RTFOT) - ASTM 2872;
- Test methods of specification for performance graded asphalt binders - ASTM 6373;
- Flexural Creep Stiffness using the Bending Beam Rheometer (BBR) after 24 hours at low temperature to give time to paraffin crystallization - ASTM D6648 [18];
- Multiple Stress Creep and Recovery (MSCR) – ASTM 7405;
- Master curve using dynamic Shear Rheometer (DSR). Frequency sweep tests were performed on asphalt binders in original and RTFOT condition. They were tested from the high PG temperature until + 5°C. The samples were all poured and trimmed at the PG temperature. The tests were run on 25-mm parallel plates with a 1.0 mm gap at temperatures between PG grade and 35ºC and were run on 8-mm parallel plates with a 2.0 mm gap at temperatures between 30 to 5ºC. The sample was allowed to equilibrate for ten minutes at each temperature prior to testing [19];
- Penetration index according equation (1) below

$$PI = \frac{\log 800 - \log Pen(25°C)}{RB - 25} \qquad (1)$$

- Resistance to fatigue damage by means of cyclic loading employing a linearly ramping amplitude sweep test. The amplitude sweep is conducted using DSR at the continuous intermediate temperature performance grade of the asphalt binder. The test method is done with the material aged using ASTM 2872 to simulate the estimated aging for in-service asphalt pavements. Viscoelastic Continuum Damage (VECD) coefficients can be easily obtained by applying a logarithmic transformation to the damage curves. The use of this linearization technique eliminates the need of iterative optimization tools that required initial guesses for estimation of the model coefficients. Both Excel Solver and the linearization method were used to determine *C1* and *C2* for the asphalt binders tested using all strains according figure 6 [20].

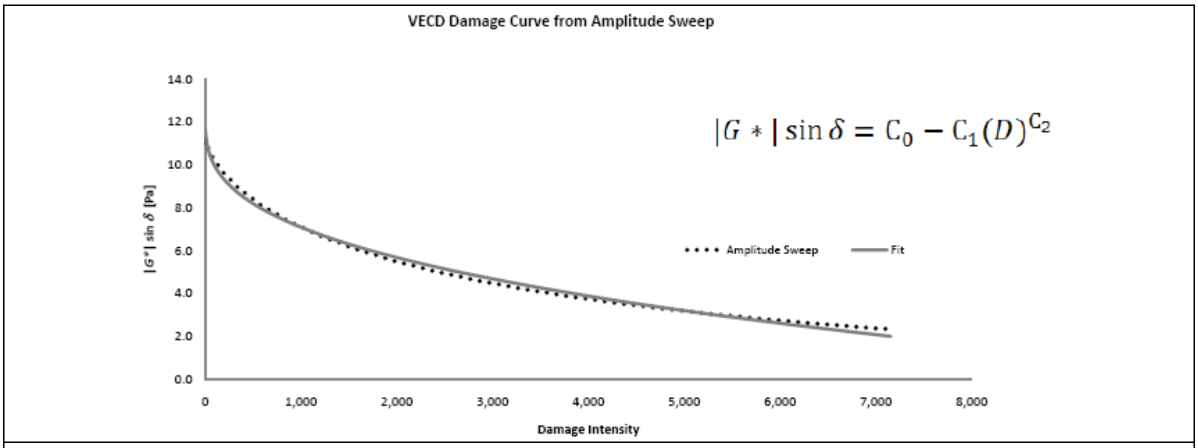

Figure 6 – VECDdamage curve from amplitude sweep

- Immersion test of asphalt binder in jet fuel in order to quantify the mass loss [21]. In order to verify the asphalt binder solubilization in carburants, the test consists in the molding of traditional and modified asphalt binder in the rings of the softening point test. After the immersion for 30 and 60 minutes the mass loss is quantified;
- The aging effect of ultraviolet and visible irradiation (700 a 15 nm) was done in the ATLAS Suntest equipment, primarily developed for lubricants oils. The influence of antioxidant effect of lignin in the asphalt binder was evaluated using Suntest chamber at 60ºC for 48 hours under xenon lamp with 500 W/m2 power. The aging effect was evaluated by the carbonyl bands using FTIR and rheological measures – master curve of samples with and without lignin [22].

4.2 Mechanical tests

In SUPERPAVE mix design AASHTO M 323-04, the specimen was submitted to 100 gyrations (design number) in order to achieve 4% voids. Besides the voids in mineral aggregates - VMA and voids filled with asphalt - VFA met the requirements. The optimal binder content was determined. The following tests were done in the several cores compacted using the final mix design:

- Repeated load uniaxial test – Flow number at 60ºC [23]
- Dynamic modulus at 25ºC and 60ºC - AASHTO TP 62-05;
- Fuel strength test for asphalt mixes - EN 12697-43

Dynamic modulus were determined at frequency of 10 e 5 Hz and the *Flow Number* was done at maximal stress of 204 kPa. European test EN 12697-43 consist of two steps: the first is the core partial immersion for 24 hours, followed by water rinsing, oven drying for 24 hours, then the surface is observed and the mass loss is determined, and in the second step the core surface that was exposed to fuel immersion is submitted to 30 seconds brushing with steel bristle, then more 30 seconds brushing and more 60 seconds, finally the mass loss is determined. There is a criteria with established limits for each step. It was already used at LNEC studies [24].

5. RESULTS

The physic-chemical and rheological results of carnauba wax modified asphalt binders are compared with the conventional asphalt 50/70 used in the modification, these data are presented in the table 4. Immersion test results of carnauba wax modified binder in jet fuel in order to quantify the mass loss are showed in Table 5. The results of five vegetable modified asphalt binders are compared with the conventional asphalt 30/45 of same crude oil used to produce the original 15/25 used in the vegetable modification, this comparison is showed in table 6.

Table 4 – Comparison between conventional 50/70 and carnauba wax modified asphalt

Tests	**50/70 + 2% wax**	**50/70 + 4% wax**	**50/70**
Rotational viscosity at 135ºC, cP	280.0	244.5	325
Rotational viscosity at 155ºC, cP	124.3	109.5	177
Mixing temperature (2P), ºC	148	143	156
Penetration at 25ºC, (Pen) 1/10mm	49	45	68
Penetration index	- 0.3	+ 1.8	- 1.5
Softening point, ºC (RB)	54.1	65.2	46
Dynamic shear - G*/sen $\delta \geq 1.0$ kPa,ºC Test temperature, ºC	1.5 64	2.6 64	0.8 64
After RTFOT			
Mass loss, %m/m	- 0.104	- 0.096	- 0.150
Dynamic shear - G*/sen $\delta \geq 2.2$ kPa,ºC Test temperature	2.45 64	4.071 64	1.53 64
Softening point, ºC	58.8	67	50
MSCR at 64ºC $J_{nr\ 3200} < 4$ Standard – S $J_{nr\ 3200} < 2$ Heavy – H $J_{nr\ 3200} < 1$ Very heavy – V	0.06	0.04	3.8
After RTFOT + PAV			
Dynamic shear - G*sen $\delta \leq 5$ MPa,ºC Test temperature, ºC	3700 25	-	3200 25
Creep stiffness - S $\leq$ 300 MPa and m $\geq$ 0.300, ºC Test temperature, ºC	-6	-6	-6
After 24 hours at -6ºC Creep stiffness - S $\leq$ 300 MPa and m $\geq$ 0.300, ºC Test temperature, ºC	-	0.308 -6	0.316 -6
Performance grade – PG	64-16	67-16	58-16

The figure 7 shows the number cycles of fatigue life for two vegetable modified asphalt binders (cotton oil code 22 and biodiesel code 21) in comparison with conventional 30/45 and 50/70. The test method used was the linearly ramping amplitude sweep test – LAS.

Table 5 - Loss weight after immersion test with Jet fuel

Results	**Conventional 50/70**	**50/70 with 4% Carnauba wax**
After 30 minutes, %	29	5
After 60 minutes, %	48	10

Table 6 - Comparison between conventional 30/45 and vegetable modified asphalt

Tests	**30/45**	**Biodiesel**	**Used frying oil**	**Castor oil**	**Cotton oil**	**Palm oil**
Rotational viscosity at 135ºC, cP	430	493.5	444	484	450	455
Penetration at 25ºC, (Pen) 1/10mm	37	40	40	37	42	37
Penetration index	-1.4	-0.8	-0.9	-0.8	-0.8	-1.0
Softening point, ºC (RB)	52	53.7	53.5	54.3	53,5	53.4
Dynamic shear - G*/sen δ ≥ 1.0 kPa,ºC Test temperature, ºC	1.2 70	1.2 70	1.0 70	1.1 70	- 67	- 67
Mass loss, %m/m	-0.1	-0.9	-0.7	-0.5	-0.1	-0.1
Dynamic shear - G*/sen δ ≥ 2.2 kPa,ºC Test temperature	2.5 70	3.7 70	2.5 70	2.8 70	- 67	- 67
Softening point, ºC	56	62.4	-	61.3	57.6	57.6
Dynamic shear - G*sen δ ≤ 5 MPa,ºC Test temperature, ºC	31	28	28	28	25	28
Creep stiffness, S≤ 300 MPa m ≥0.300, ºC Test temperature, ºC	0	0	0	-6	-6	-6
Performance grade – PG	70-10	70-10	70-10	70-16	67-16	67-16

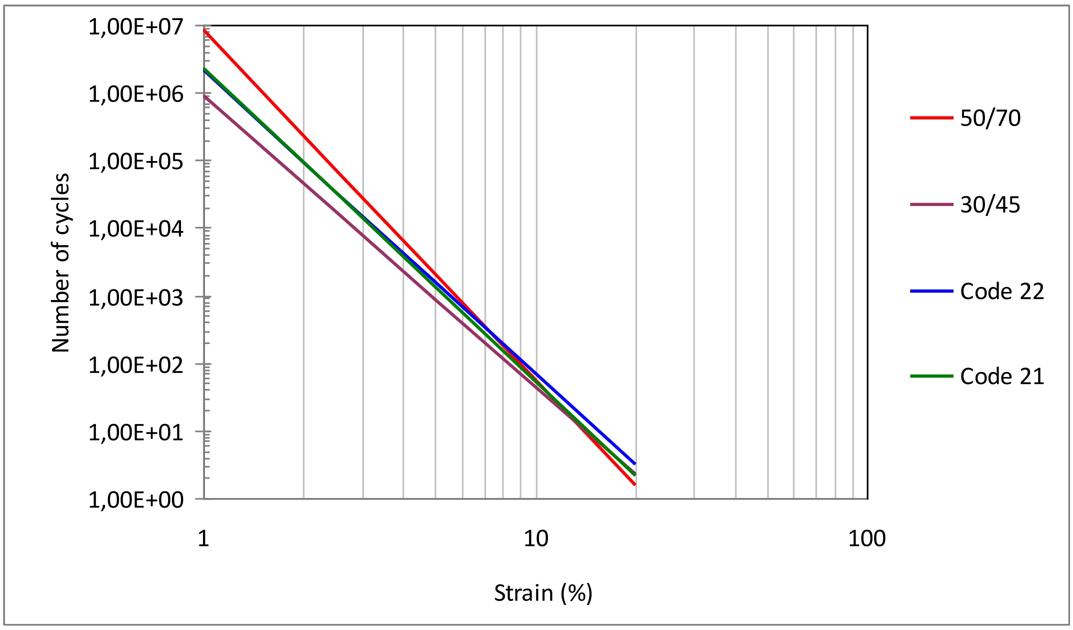

Figure 7 – Fatigue life - cycles number of vegetable modified asphalt binders x conventional asphalt cements

Lignin A (commercial) and B (Black liquor lyophilized – lignin – that contains 15% of lignin) were added to a sample in the concentration of 1.5 and 15% respectively. Theses three samples (without additive, sample with additive A and sample with B) were submitted to effect of air and temperature (RTFOT) and then to the UV irradiation for 48 hours and 60ºC in the Suntest chamber (PS). The virgin samples, RTFOT samples and PS samples were tested in the DSR in order to construct a master curve. The three samples after the UV aging (PS) were submitted to carbonyl index determination. The results of carbonyl index are presented in table 7 and the rheological behaviour of the samples after short and long term aging with the use of the two additives are showed in the figures 8 and 9.

Table 7 – Results of carbonyl index after PS

Samples	Carbonyl index
Conventional 50/70	9
50/70 + 1.5% commercial lignin - A	0,5
50/70 + 15% material resulted from black liquor lyophilization - B	3,3

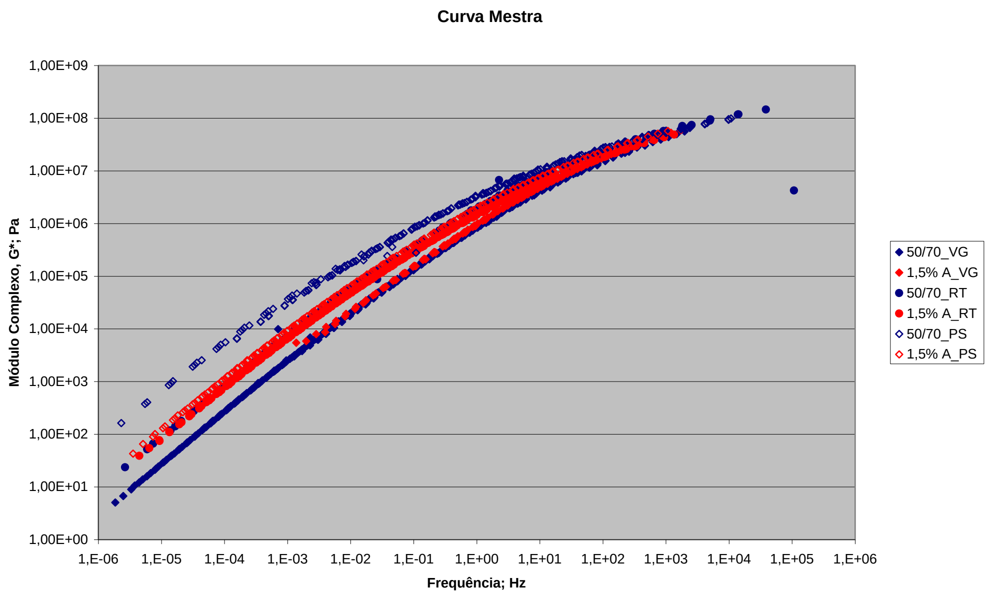

Figure 8 – Master curve of virgin, RTFOT and PS sample with additive A in comparison with 50/70 sample

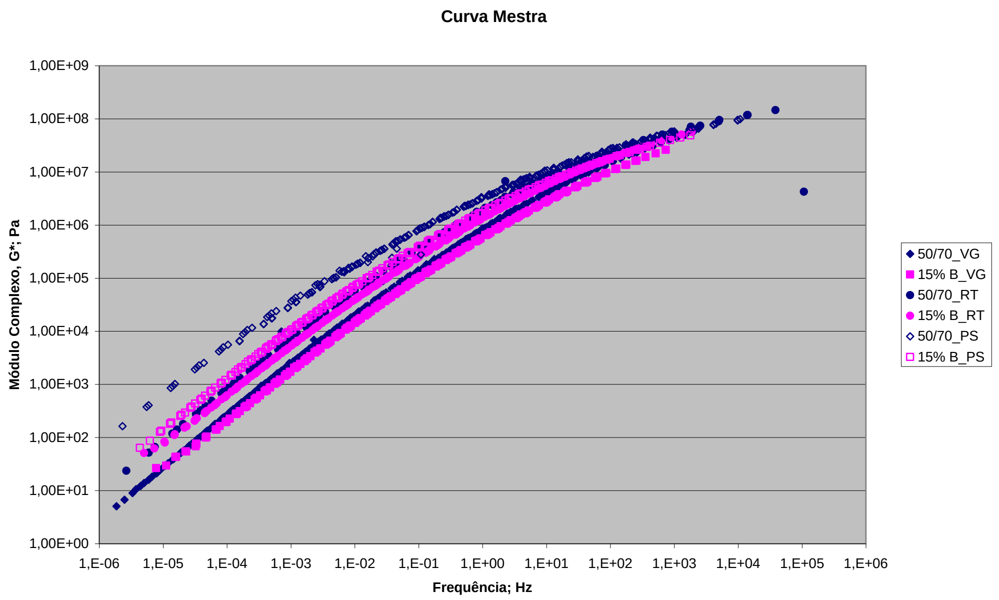

Figure 9 – Master curve of virgin, RTFOT and PS sample with additive B in comparison with 50/70 sample

The bituminous mixes derived from vegetable modified asphalt binder samples (code 11, 21, 24 and 25) were submitted after SUPERPAVE mix design to mechanical tests of dynamic modulus at 25ºC and 60ºC and flow number test as well. The results of these samples are compared with results of mixes prepared with conventional binders 30/45 and 50/70, presented in Table 8.

Table 8 – Comparison of mechanical tests results of vegetable modified binders and conventional asphalt cements

CARNAUBA WAX						
25°C			60°C			FN
E* @ 10Hz	Phase angle	E* x sen delta	E* @ 5Hz	Phase angle	E* / sen delta	
6921			807			240
CASTOR OIL						
25°C			60°C			
E* @ 10Hz	Phase angle	E* x sen delta	E* @ 5Hz	Phase angle	E* / sen delta	FN
10923	18,28	3426,1	416,1	33,54	753,1	225
BIODIESEL						
25°C			60°C			
E* @ 10Hz	Phase angle	E* x sen delta	E* @ 5Hz	Phase angle	E* / sen delta	FN
9147,9	19,00	2978,3	356,9	32,82	658,5	178
USED FRYING OIL						
25°C			60°C			
E* @ 10Hz	Phase angle	E* x sen delta	E* @ 5Hz	Phase angle	E* / sen delta	FN
8469,3	19,63	2845,2	311,3	31,82	590,4	147
50/70						
25°C			60°C			FN
E* @ 10Hz	Phase angle	E* x sen delta	E* @ 5Hz	Phase angle	E* / sen delta	
5412			215			78
30/45						
25°C			60°C			FN
E* @ 10Hz	Phase angle	E* x sen delta	E* @ 5Hz	Phase angle	E* / sen delta	
12455			638			360

The EN 12697-43 was done in the carnauba wax modified bituminous mixture. The results of the first step for modified and conventional mixes are presented in table 9. The maximal limit of this step is 5%.

Table 9 – The results of EN 12697-43 test

Bituminous mixes	**Mass loss in the first step**	**Classification relative to the fuel strength**
4% Carnauba wax modified binder	6	marginal
Conventional 50/70	14	low

6. DISCUSSIONS

The results obtained lead to the following comments:

- The addition of Carnauba wax allows mix with aggregates in the asphalt plants at lower temperatures due to viscosity reduction obtained with the wax. This fact will provide fuel consumption reduction in the asphalt plant, fumes and fuel combustion emission reduction, increase of aging resistance of the asphalt binder;
- The Carnauba wax did not affect the crystallization properties of the asphalt binder because the creep stiffness temperature did not change with 24 hours cooling time;
- The PG grades of the modified binders improved with the wax addition, that means rutting resistance enhance. The same occurred with the Carnauba wax asphalt mix. The flow number was better than the conventional mixture with 50/70 asphalt cement;
- The mass loss test done with the wax modified binder showed less mass loss than the conventional binder. In terms of bituminous mixes, the European test relative to the fuel resistance of the asphalt mixes presented marginal result for the Carnauba wax mixture whereas the conventional mix resulted in higher mass loss;
- The material resulted from black liquor lyophilization (15% concentration) showed similar effect to the commercial lignin (1.5% concentration) in respect to antioxidant influence in the asphalt cement

50/70. The carbonyl index was reduced with the lignin addition and the complex modulus presented less results than the conventional binder after RTFOT and PS aging;

- The thermal susceptibility of asphalt binders is improved with the addition of vegetable oils, biodiesel and even used frying oil. This thermal susceptibility can be seen by increase of penetration index or PG grade;
- The LAS fatigue tests proposed to replace the rheological parameter of ASTM D 6373 specification (G* sen δ) showed that the vegetable oil modified binders improved the fatigue life, they are classified as 30/45 but theirs cycles numbers are between the 30/45 and 50/70 asphalt cement;
- The mechanical tests done with the vegetable modified mixes shoed a good behaviour. Flow number superior to the original 50/70 and modulus between the 30/45 and 50/70. The castor oil seems to be more rutting resistance, then followed by biodiesel. The used frying oil could have lost some good properties of vegetable oils when submitted to cooking, its behaviour was the poorest among them.

7. CONCLUSIONS

Adding vegetable and renewable products in asphalt cement can improve its properties related to thermal susceptibility, fatigue and rutting resistance and antioxidant properties.

Carnauba wax modified binder showed jet fuel resistance in terms of mass loss and viscosity reduction, that can be suggested its use in warm mixes. Besides its addition improve the PG grade and rutting resistance without affect the cold properties of the binder.

The vegetable oil enhances the thermal susceptibility of asphalt cements, whose crude source leads to low penetration index. The castor oil is in the first range whereas the used frying oil is in the last position probably due to the properties loss during cooking process.

The black liquor resultant from ethanol secondary production from bagasse sugar cane showed similar behaviour to commercial lignin related to reduce the carbonyl index (oxidation) after aging and reduce the complex modulus (hardening) caused by short and long term aging.

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