Rheological behavior of vegetable oil-modified asphaltite binders and mixes

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ABSTRACT

This paper focuses on the development of a viscoelastic bituminous binder by blending hard natural bitumen (asphaltite), waste vegetable oil and a small amount of hard petroleum bitumen. The optimization of the composition of this mixture allows obtaining binder with similar needle penetration as classical paving grade bitumen. The obtained product is expected to be an alternative to the consumption of the classical petroleum bitumen and a new way to recycle waste vegetable oils. Two waste vegetable oils (rapeseed and sunflower) have been used for this issue. The appropriate composition of the blends has been firstly determined based on the conventional penetration and softening point tests. The volatility of the constituents of the binders has been measured thanks to a thermo-gravimetric analyses (TGA). The linear viscoelastic properties of the binders and the corresponding asphalt concretes have been also measured. In addition, theirs performances regarding the resistance to the permanent deformation and the water sensitivity have been evaluated. It has been found that the produced binders and the corresponding mixes have lower stiffness modulus than the classical 35/50 paving grade bitumen. The rutting depths, the stripping resistances as well as the stiffness modulus obtained with the new binders comply with the actual standard 13108-1, except the stiffness modulus obtained with the waste rapeseed oil.

Keywords: Bleeding, Modified Binders, Natural asphalt

1. Introduction

Bitumen is the favorite binder for the common applications in road building. It consists of about 5% of the asphalt concrete mass but provides to this later one all the viscoelastic properties require for the good behavior of the pavement structure. The mechanical performances and the durability in terms of ageing of the asphalt concrete depend on the choice of the binder and the time evolution of its properties. So, the choice of the binder is of prime interest to guarantee minimum performances of the structure.
The bitumen consumption is estimated to be about 85 Mt/year in the world. 90% of this consumption is dedicated to the road applications [1]. It is an oil refining byproduct, then, its production is seen as nonrenewable natural resources consumption and as a high impact on the CO_2 emissions. Since the last decades, the research on the alternative binders' development gains interest for several reasons: forecasting the depletion of the natural nonrenewable resources, valuation of industrial waste products … The purpose of this study is to make a focus on the use of bio-oils and natural bitumen on mixture design.
Traditionally, natural bitumen are used as additives to harden paving grade bitumen. According to Yilmaz et al. [2], the addition of 60 % Trinidad lake natural bitumen (TLA) or 10% Iranian Gilsonite or 9.5% USA Gilsonite in a 34/58 paving grade bitumen provides a new binder. A series of mechanical tests (water sensitivity, resistance to fatigue, rutting, direct tensile strength and stiffness modulus) show that performances are improved compared to the reference bitumen. Recently, the Albanian Selenniza natural bitumen has been found to be a hardener and an ageing inhibitor when adding in soft petroleum bitumen [3].
Furthermore, recent studies show the capability of the vegetable oils to rejuvenate hard aged bitumen and to provide more flexibility to the final product [4, 5]. The conclusions of these studies are based on the measurements of conventional properties (Penetration, softening temperature R&B), on the rheological properties (complex modulus, ductility, creep) and on the resistance to fatigue. Similar results were obtained on site and laboratory by Bailey et al. [6] when adding 5% vegetable oil (UVO and Vegetex) into aged bitumen. Then, the increase of the percentage of vegetable provides sometime better properties than the use of original bitumen. However, according to Bailey et al. [6], the miscibility and the stability of the colloidal structure of the binder is not always guaranteed. However, it can be verified by determining the colloidal stability index IC from chromatography analysis which allows to get the SARA fractions of the mixture (IC = (asphaltenes + saturated)/(aromatic + resins)). A first chemical and rheological investigation on the role of waste rapeseed and linseed oil in 50/70 paving grade bitumen has been addressed by Tachon [7].
The purpose of the current study is to develop new binders by blending Selenizza' natural bitumen and two waste vegetable oils (rapeseed and sunflower). The composition of the constituent materials of the binders will be optimized first to get similar needle penetration (according to EN 1426) to classical paving grade bitumen. Rheological and mechanical properties of the binders and the mixes will be investigated.
This paper is organized as follows:
The first part focus on the binders' characterization and the second part to the mixes' properties and performances evaluation. The conclusions about the conformity of the performances to the requirements of the product standard EN 13108-1 will be drawn.

2. Materials

The binders consist of natural bitumen (asphaltite) from Albanian's Selenizza quarry mixed with waste rapeseed or sunflower oils and hard bitumen 15/25 (0.1mm). The composition of the blended binders is given in the Table 1. This composition has been optimized in preliminary study to select binders whose penetrations (noted pen) are between 35 and 50 (0.1mm) as common bitumen used in France. The natural bitumen consists of a blend of hydrocarbon fraction (80%) and mineral fractions (15-18%) [3], which provide hardness to the asphaltite (pen ≈ 0 mm). Hard 15/25 paving grade bitumen has been added to the asphaltite. The amount of added bitumen is exactly equals to the content of the mineral material in the natural asphalt. The use of waste vegetable oils allows to soften the final blended binder. Figure 1 a) and b) shows a part of the constituents materials used to produce the binders.
The binders manufacturing process consist firstly to preheat the natural bitumen into a mixer at 190°C. The waste oil and the hard 15/25 bitumen are added into the melted natural bitumen. The blend of these constituents is mixed for 30 minutes duration to get a liquid homogeneous binder (figure 1 c)).

Table 1: Composition of the binders

Constituent materials	Natural bitumen		Waste vegetable oil	Hard bitumen
	hydrocarbon	Mineral fraction		
Percentage	71.4%	14.3%	14.3%	14.3%

a) Overview of the wastes oils

b) Selenizza's quary of natural bitumen (Alnania)

c) Example of blended binder with waste sunflower oil

Figure 1: Main constituents of the binders

3. Binders' characterization

3.1 Conventional properties

Two binders which contain respectively waste rapeseed oil and sunflower oil have been produced. Theirs compositions comply with Table 1. Theirs penetrations and softening temperature have been measured and represented on figure 2. These results show that the binder which contains sunflower oil is harder than the rapeseed oil binder. Nevertheless, theirs penetrations are close to the 35/50 (0.1mm) petroleum bitumen commonly used in France. However, theirs softening temperatures exceed the values obtained from the conventional petroleum bitumen. Therefore, these binders cannot be classified as conventional bitumen. The higher softening temperature of these binders is due, in part, to the mineral filler of the natural bitumen ($R\&B_{asphaltite}$ =119°C [3]). The penetration versus softening temperature (R&B), represented on the figure 3, shows the location of the produced binders compared to paving grade bitumen, hard bitumen (10/20 to 160/220) and multigrade bitumen (MG 20/30-64/74, MG 35/50-57/67) (defined in standards EN 12591, EN 13924). As it can be observed, the produced blends cannot be classified between the classical bitumen because of theirs higher softening temperatures at a given needle penetration.

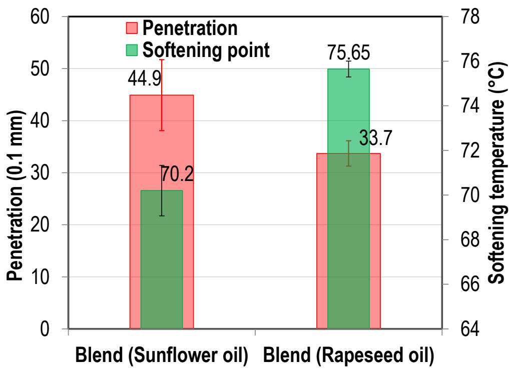

Figure 2: Conventional properties of the blends

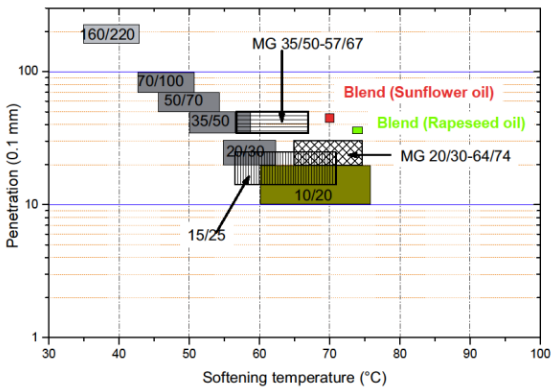

Figure 3: Comparison between the blends and classical bitumen

3.2 Volatility of the constituents of the binders

The volatility of the constituents of the binders have been investigated thanks to thermo-gravimetric analyses (TGA) and represented on figure 4. Six samples have been characterized: the rapeseed oil, the sunflower oil, the asphaltite, the 15/25 bitumen and the blended binders. The tests have been carried out from 32 °C to 800 °C at a constant heating rate of 10 K / min. As expected, all the constituents seem nonvolatile for temperatures below 250°C. These results prove that no significant degradation of the constituents of the binders occurs during the binders' production and during the mixes manufacturing step at 190 °C. It can be assumed, because of the non-volatility of the waste vegetable oils that the hardness recovery on the blended binders is due to the cross-linking of the double bonds of the vegetable oil in the presence of oxygen.

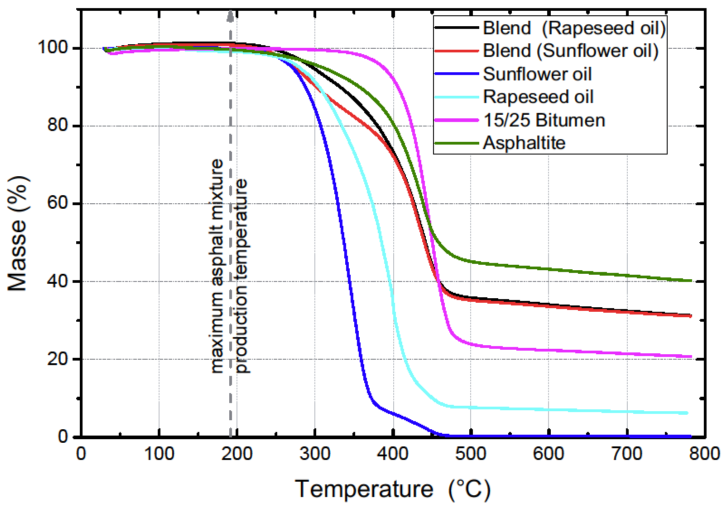

Figure 4: Evolution of the mass of the constituents of the binders' versus temperature

3.3 Complex modulus

Frequency sweeps have been carried out from 1 to 80 Hz at 10 different frequencies using Metravib apparatus over a temperatures range from -20°C to 60°C at 10°C intervals. From -20°C to 20°C a cyclic tensile-compression test has been performed on the specimen (see Figure 4 a)). From 20°C to 60°C, the shear test has been carried out (see Figure 4 b)). The results have been represented in the Black's and Cole-Cole spaces to check the validity of the time-temperature superposition principle (TTSP) (see figure 6 and 7). The black space diagram is a convenient way to quantify the changes in the rheological behavior of a bituminous binder due to vegetable oil, additives, ageing, …The produced binders exhibit a lower phase angle at any given modulus value. For, classical this behavior is generally indicative of the binder that is becoming less viscous or more brittle. However for the produced binders, this correlation is not proved because theirs phase angles are higher than that of the reference binder for the high frequency (~low temperature) as represented on figure 8. The relatively continuous evolution of the experimental data for each binder on figure 5, confirms the validity of the TTSP and allows building the master curves of complex modulus and phase angles (figure 8). The reference temperature of 15°C has been chosen for this issue.

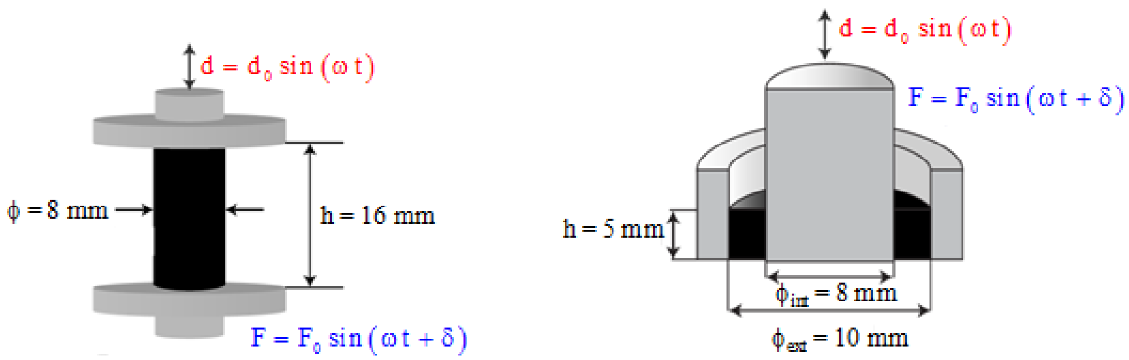

Figure 5: Principle of measuring binders complex modulus with METRAVIB apparatus : tensile-compression test (left) and shear test (right)

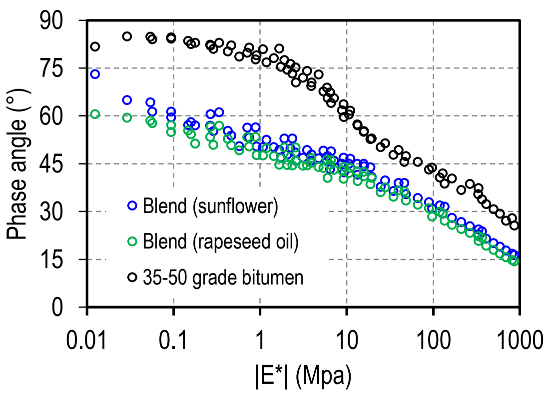

Figure 6: Results represented in Black space

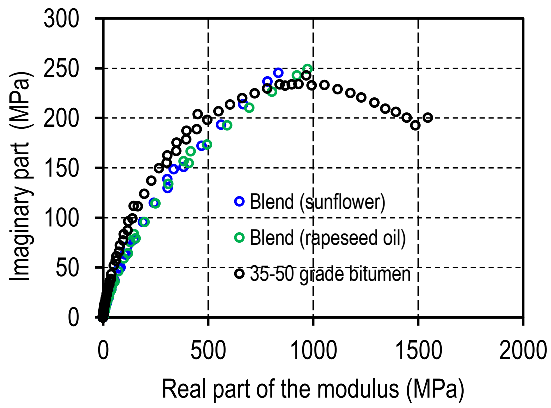

Figure 7: Results represented in Cole-Cole space

The binders' complex modulus and phase angle master curves are represented on figure 8. It appears that the reference bitumen is stiffer than the blended binders in the temperature range between -20°C to 60°C. However, the blended binders have relatively similar stiffnesses regarding the accuracy of the data. The evolution of the phase angles represented on the figure 8, shows that the blended binders have lower phase angles than reference bitumen for T≥20°C and higher phase angle at T≤20°C. It can be observed that the produced binders' phase angles are not equal zero, this means that viscous effect are not negligible compared to reference bitumen. Then, at low temperature they cannot be assumed to be a purely elastic materials. This could be an advantage for stress relaxation at low temperature compared to the reference bitumen.

To compare the rheological behavior of the different binders, the rheological index (R) and the crossover frequency ($\omega_c=1/\tau_\beta$) have been assessed and given in Table 2. The crossover frequency (ω_c) is defined as the frequency at which the phase angle is 45° at the reference temperature and τ_β is the relaxation time. It is an indicator of the hardness of the bituminous binder. Lower (ω_c) values indicate a softer binder. The rheological index (R) is an indicator of the flatness of the master curves and is given by R=Gg-Gc. Where Gg is the glassy modulus and Gc the modulus at ω_c [8]. As shown is Table 2, all R values of the produced binders are higher than the R value of reference binder.

Table 2: Rheological parameters of the Christensen's model [8]

	Rheological index, R	Crossover frequency ω_c (rad.s^{-1})
Blend (rapeseed oil)	2.18	1.69
Blend (sunflower oil)	1.91	11.86
35-50 bitumen	1.33	3.9

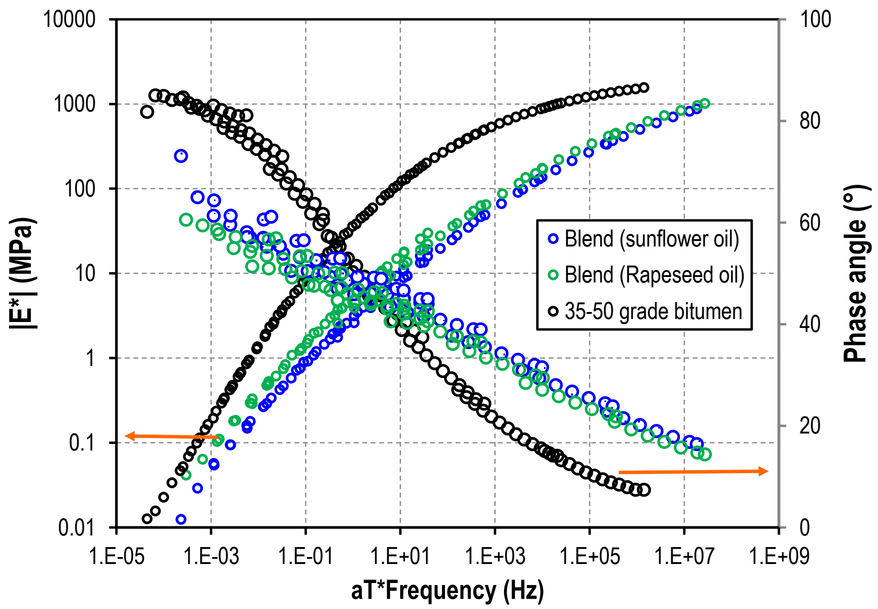

Figure 8: Blends complex modulus and phase angles master curves at 15°C

4. Mixes characterization

French asphalt concrete BBSG 3, 0/10 according to the EN 13108-1 (2007) has been manufactured according to the mix composition described in Table 3. The mixture is obtained by mixing the aggregates and the binder during 3 minutes at 190 °C. According to the laboratory mixing standard EN 12697-35 which defines the manufacturing temperatures, a 35/50 penetration bitumen shall be heated at a maximum temperature of 170°C. However, it has been found that this standard is not applicable to the mixes produced because the produced binders are still viscous at 170°C compared to a 35/50 petroleum bitumen. At 190°C these binders are relatively liquid and allows good coating of the aggregates.

Table 3: Composition of the mixes

BBSG3, 0/10 according to the EN 13108-1 (2007)	
Granular fractions	Pourcentages
0/2	26.1 %
2/6	23.7 %
6/10	42 %
Filler (limestone)	1.9 %
Binder (Asphaltite + oil + Bitumen)	6.3 %

4.1 Resistance to permanent deformation

The resistance of a bituminous material to permanent deformation is grasped by measuring the rut depth induced by the repeated passage of a wheel on a mix plate at a reference temperature of 60 °C according to the standard 12697-22 (Large size device). It allows simulating in the laboratory the effect of traffic on a roadway. The plates used have been manufactured and compacted thank to a roller compactor. For each asphalt concrete, the test is carried out on two plates. The temperature has been measured during the experiment to be sure that no overheating occurs during the test. The rutting depth has been measured with a depth gauge as a function of passes. The first 1000 passes are carried out at room temperature, and the others at 60 °C. The results are represented on figure 9. The rutting depths of the mixes produced with the blended binders are smaller than these obtained with the reference bitumen.
According to the standard NF EN 13108-1, the percentage of rut depth for a BBSG 3, 0/10 shall be smaller than 5% at 60 °C for 30 000 cycles. Therefore, the results obtained with the produced binders, represented on figure 9, comply with the standard contrary to these obtained from reference bitumen. These better resistances to the permanent deformation are probably due to the asphaltite even if the real mechanisms that occur are not known yet. This improvement of the resistance to permanent deformation observed is supported by the conclusions of previous studies on the natural asphalts [2, 9, 10].

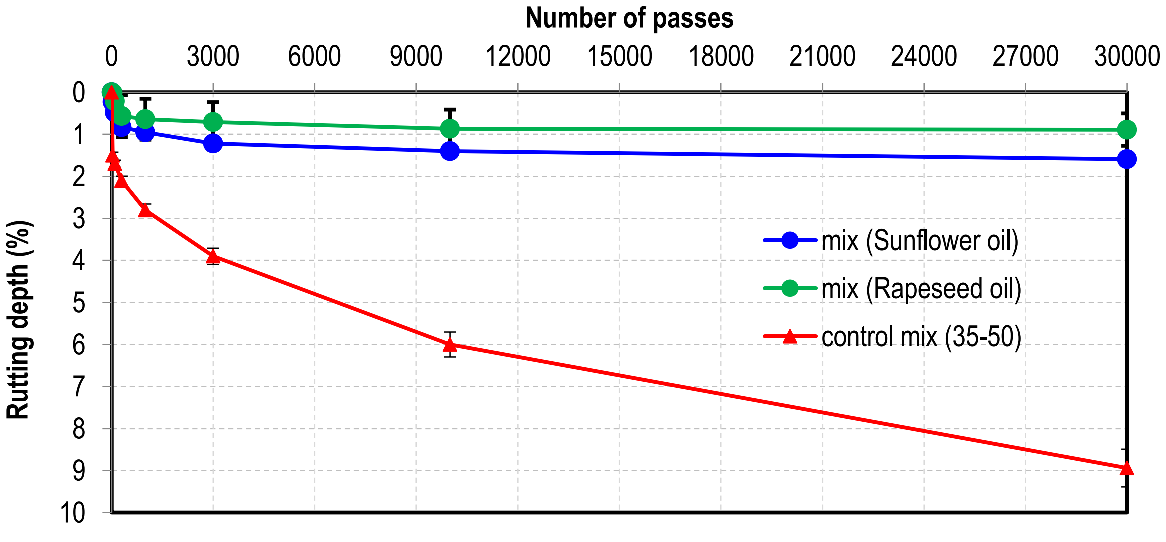

Figure 9: Evolution of the rutting depth

4.2 Stiffness modulus

The stiffness moduli have been determined following the standard EN 12697-26 annex E (DT-CY method). The stiffness modulus test consist of applying uniaxial tensile loads on cylindrical specimens of asphalt concrete (of 200 mm high and 80 mm diameter) at given temperatures (-10°C, 0°C, 10°C, 15°C, 25°C and 40°C) and loading times (1s, 3s, …, 300s). The specimens have been cored from plate compacted with roller compactor. A preliminary study is conducted to determine the strain amplitude which shall be applied during the test. According to the standard EN 12697-26, this maximum deformation depends on the temperature as reminded in the Table 3. The experiment has been carried out in accordance to the Table 4.

Table 4: Strain to be applied during a controlled rate test in accordance with the stiffness determined by a preliminary test to 50 microstrain (according to EN 12697-26)

Temperature θ °C	Stiffness modulus at 10°C and 3s		Stiffness modulus at 10°C and 300s	
	<7.5 GPa	≥7.5 GPa	<1 GPa	≥1 GPa
	Amplitude of deformation in micro-strain			
θ≤10°C	100	50	-	-
10°C≤θ≤20°C	-	-	200	100
20°C≤θ≤40°C	-	-	300	200

The results recorded for each temperature and time sweeps have been used to build the master curves of the stiffness modulus at the reference temperature of 15°C. They have been built by shifting the isothermals in the time domain. They are represented on figure 10. It can be seen that the reference mix obtained with the 35-50 bitumen is stiffer than the two others. This is consistent with the evolution of the complex modulus of the binders on figure 8. However, an inconsistency due to the difference between the stiffness of the mixes produced compared to the complex modulus of the binders is observed. Let’s precise that during the experiment following guidance given on Table 4, two specimen containing blended binder with rapeseed oil have been broken respectively à 25°C and 40°C. It is suspected for these temperatures that the experiment has been carried out on the nonlinear behavior domain of the samples produced with the waste rapeseed oil. More investigations need to be conducted to check the suitability of following the guidance of the standard EN 12697-26 (sum up in Table 3) for these materials.
The estimated value of the stiffness modulus at 15 °C for a loading time of 0.02s for the mixes are respectively: 5678 MPa, 8233 MPa and 13171 MPa for the mixes with rapeseed oil, sunflower oil and 35-50 grade bitumen. Then, the stiffness modulus of the rapeseed oil asphalt concrete does not comply with the requirement of EN 13108-1 which requires, for a BBSG 3, 0/10, a minimum stiffness modulus of 7000 MPa.

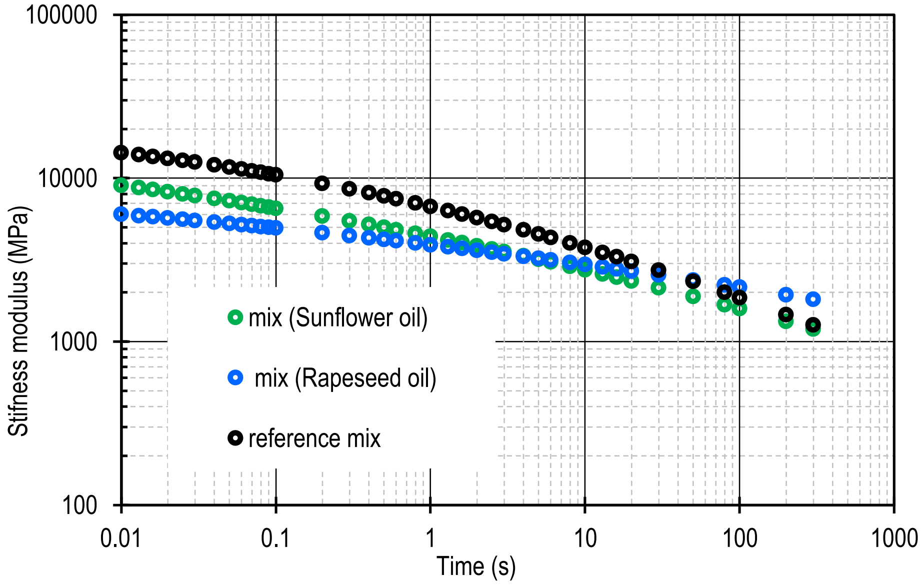

Figure 10: master curves of the stiffness modulus of the mixes at 15°C

4.2 Water sensitivity

Ten cylindrical samples, with 120 mm diameter, have been manufactured with each binder. For each mixture, half of the specimen has been cured in thermoregulated chamber at 18°C and the other ones have been immersed in water at 18°C. After seven days conservation, compression tests have been carried out on the samples in accordance with the standard EN 12697-12, to measure the failure strength. The maximum resistances recorded are presented on the figure 11 for samples cured in air (C) and samples cured in water (i). The ratios i/C have been estimated and represented in conjunction with the compression strengths on the figure 11. Since the ratios i/C exceeds 0.7, all the results comply with the standard EN 13108-1 requirements.

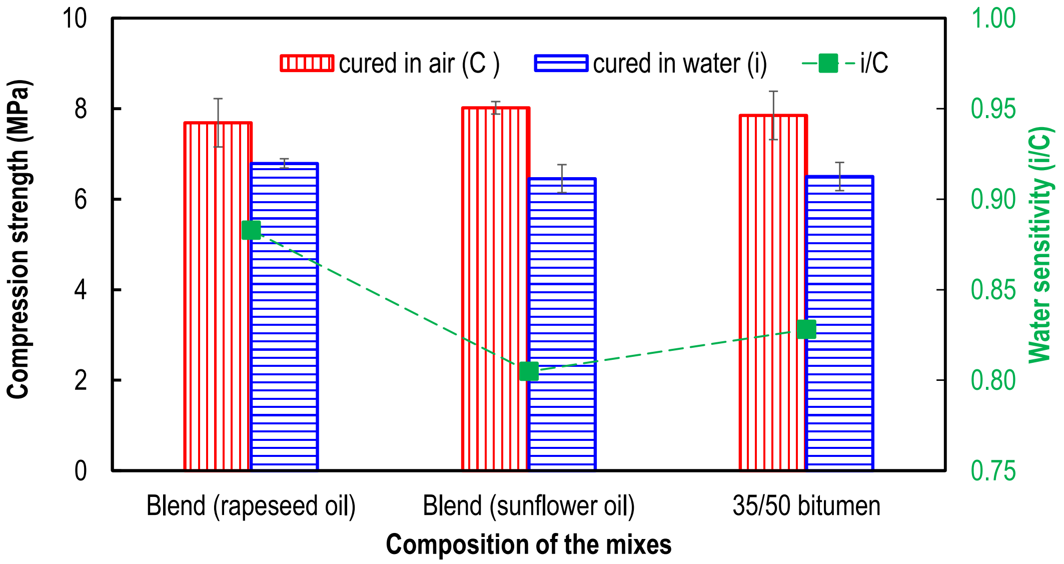

Figure 11: Compression resistances and water sensitivity of the mixes

5. Conclusion

The aim of the study presented in this paper was to produce new binders for road building applications by modifying natural bitumen by waste vegetables oils and a small amount of hard petroleum bitumen. For 71.4 % of asphaltite, 14.3 % of waste oil and 14.3% of hard bitumen, the produced binders have similar needle penetration as classical 35-50 grade bitumen. The viscoelastic properties of the binders and the mixes have been also characterized. It was found that the produced binders are softer than the 35-50 bitumen.
Asphalt concretes have been manufactured and their stiffness modulus, resistance to permanent deformation and water sensitivity measured. Except the stiffness modulus obtained with the waste rapeseed oil, all the results comply with the standard EN 13108-1 requirements.
However, this study shall be continued to study the ageing, the fatigue and the low temperature properties of these mixes. Further study shall be done to analyse the viability and the economic feasibility of this technology.

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