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New Binders Using Natural Bitumen Selenizza

Edith Tartari

Selenice Bitumi Sha, R&D Department, Rruga Gjik Kuqali, Pallati Melrose, Tirana 1019, Albania

Highlights

- The natural bitumen Selenizza is an additive that strongly affects the mechanical behavior of road bitumen. It hardens the modified bitumen, improves its performance, and decreases its susceptibility to aging.
- A new type of binder was developed using natural bitumen Selenizza and waste vegetable oil.
- Combining the hardening and anti-aging effect of natural bitumen Selenizza with the regenerating properties of vegetable oil, a rejuvenating agent was obtained which made possible the production of asphalt mixture containing 100% RAP aggregates.

Abstract: The purpose of this paper is to highlight the benefits of using natural bitumen as part of the emerging environmental sustainability innovations and trends in asphalt mixture design. Various recent studies have analyzed the characteristics of natural bitumens showing that they are totally compatible with bitumens from refineries and their influence may be compared to that of chemical additives. More particularly, the use of natural bitumen Selenizza, not only increases the binder consistency, viscosity, and stability, but it confers on the modified bitumen, increased resistance to aging, and leads to an improved low-temperature behavior compared to equivalent penetration grade straight run bitumen. The high modulus asphalt mixes obtained with binders modified with natural bitumen, allow successfully facing up the growing volume of the traffic while achieving efficient pavement structures with thinner and more durable layers. This paper specifically presents the main conclusions of recent research work focusing for the first time on the use of vegetable oils (rapeseed and sunflower) to soften natural bitumen Selenizza aiming to develop a new type of binder for asphalt mixes and introduces an experimental investigation of a new High Modulus Asphalt Concrete (HMAC), incorporating 100% reclaimed asphalt pavement (RAP) aggregates thanks to a rejuvenator composed of waste vegetable oil and natural bitumen Selenizza which reverses the aging rheological binder properties and restores the fresh bitumen values.

Key words: Natural bitumen, aging, vegetable oil, rejuvenator, RAP, Selenizza.

1. Introduction

The hot-mix asphalt (HMA) industry, in the context of global environmental change, has renewed its focus on perpetual HMA pavement construction promoting the development and testing of innovative concepts, methods, and technologies. The increasing transportation demands in terms of traffic volume and loads have resulted in substantial challenges to meet, creating the need to devote our research efforts to further enhance the design of HMA and improve the selection of the materials used in highway construction. The production of asphalt mixes with a high content of reclaimed asphalt pavement (RAP) appears as one of the main applications in the current trends and developments in the flexible pavement design that provide greater economic and environmental benefits.

The bituminous binders and the time evolution of their physical and rheological properties contribute significantly to the principal viscoelastic characteristics of asphalt mixtures and play a key role in ensuring their performance. Within a general framework where efforts are currently focused on energy saving and the development of low-carbon technologies for asphalt pavement construction, French researchers investigated the possibility to develop a new type of binder produced by mixing natural bitumen and waste vegetable oils, thus circumventing the use of oil refined bitumen whose production implies the consumption of nonrenewable

Corresponding author: Edith Tartari, Master of Science, research fields: road construction materials.

natural resources with high impact on CO_2 emissions. Combining the hardening and anti-aging properties of natural bitumen Selenizza, with the capability of vegetable oils to provide more flexibility to bitumen, a new type of bituminous binder was obtained whose rheological and mechanical properties were similar to a traditional 35/50 road bitumen. The behavior of asphalt concrete Job Mix Formula (JMF) using the new binder was characterized in terms of stiffness modulus, rutting resistance, and water sensitivity performance.

In parallel, a research project was conducted recently by Erfurt University in Germany, studying and experimenting new wearing course mix design with the use of 100% RAP asphalt, and a rejuvenating agent composed of vegetable oil and natural bitumen Selenizza. In this study, the mechanical and viscoelastic behavior of 12 variants of asphalt concrete with the same aggregates and grading curve as well as their respective binders, was analyzed before aging, after aging, and after the introduction of the rejuvenating agent. A significant improvement of the fatigue resistance, as well as a reduced risk of low-temperature cracking, was observed in JMF variants added with the rejuvenating agent after the aging, compared to the reference and aged variants.

2. Hardening Effect and Anti-aging Properties of Natural Bitumen Additive Selenizza

For a long time, there has been limited professional interest shown on the potentiality of natural asphalts to be used as bitumen modifiers and their application in road construction has been underestimated and massively ignored. It is only recently that researchers began addressing this issue due to the leading challenges for sustainable development in highway construction with the need to provide high serviceability roads all by preserving the environment. The market growth for high modulus mix asphalts associated with an increasing demand for hard bitumen has revealed the need to use natural bitumen as a useful alternative to polymeric additives and other modifiers of straight run bitumen.

Santarelli and Scarsella [1] from the University of Rome “La Sapienza” have studied the nature of changes that occur when modifying distillation bitumen with natural asphalts using rheological and thermal measurement techniques. Three of the most commonly used types of natural asphalt were analyzed: Gilsonite from Utah deposit (USA), Selenizza (Albania), and Trinidad Lake Asphalt (Central America). To investigate the nature of the modification and the efficiency of these natural asphalts as modifiers, 10% (in weight) of each natural asphalt, was added to a standard penetration grade bitumen 80-100 and mixed at a minimum temperature of 150-180 °C to guarantee the complete solubility.

As expected, for the three cases, the resulting modified bitumen was characterized by higher softening point (R&B temperatures) and lower penetration values, compared to the original standard bitumen, due to the presence of high percentages of asphaltenes content in the natural asphalts. There was observed a proportional relationship between the percentages of asphaltenes, present in the modified samples of bitumen, and the respective values of the softening point.

The dynamic rheological tests indicated that the rheological behavior in medium and high temperatures (50 ÷ 160 °C) does not depend on the quality of the modifier but exclusively on its asphaltene content. The trends of the complex viscosity values in function of temperature, for the original bitumen and samples modified with three natural asphalts, reflect the increase in the viscosity values after the modification. Compared to the viscosity curve of standard bitumen, the viscosity curves of the modified samples shift upwards, but they remain with the same shape and the slope and are parallel to one another, for all sample types (Fig. 1). This means that the modifiers do not affect the internal interactions between the asphaltene

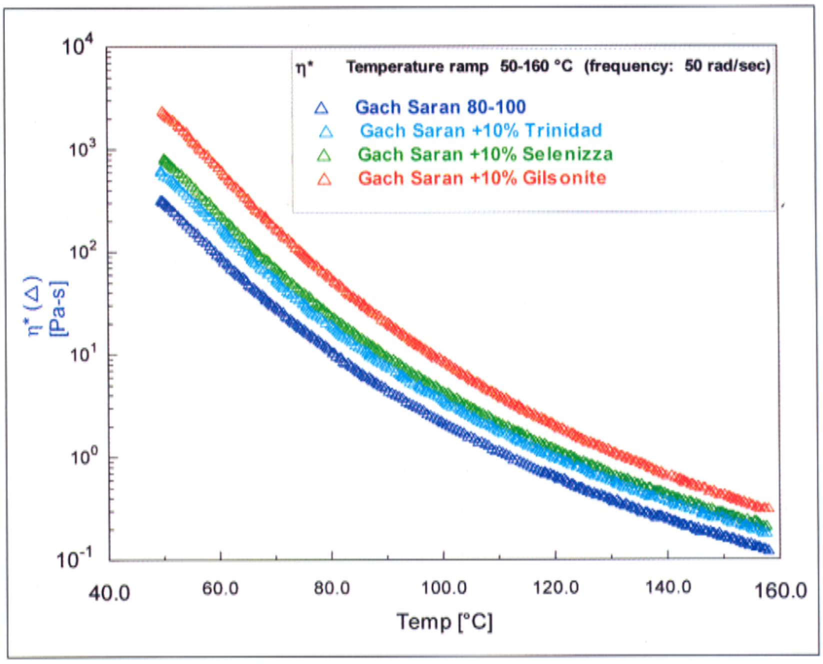

Fig. 1 Complex viscosity η* versus temperature.

components in the modified bitumen, a typical phenomenon for the compatible additives.

The Modulated Differential Scanning Calorimetric (MDSC) analysis demonstrates that the rheological behavior of the straight run bitumen, does not result particularly affected at low temperatures by the addition of natural bitumen, but it is significantly modified at hot temperatures.

The comparison of softening temperatures (from the reversing curves between the original bitumen and modified samples), showed that the addition of natural asphalts Trinidad and Selenizza, due to the lower molar mass of their maltenic phases (compared to those of reference bitumen), lowered the inferior limit of the reference bitumen softening range, with a dilution effect on the latter. As the maltenic phase of base bitumen begins to soften at 55.8 °C, its mixture with Trinidad was observed to start softening at 45.9 °C whereas that with Selenzza, at even lower temperature, inferior to 45.9 °C. In contrast, it was observed that Gilsonite does not influence the melting temperatures of different maltenic and aphaltenic phases, but expands the softening range of the original bitumen to higher temperatures.

This study demonstrated that the nature of changes produced by the addition of natural asphalts is ultimately determined by their composition, and more particularly, their asphaltene content. The modified bitumen is characterized by increased values of consistency, viscosity, and stability conferring to the asphalt mix, better resistance to permanent deformation.

A more recent research work carried out at the University of Strasbourg France, investigated the potential of using the natural bitumen Selenizza mined in Albania, in the production of hard bituminous binders and high modulus asphalt mixes.

In this study by Themeli et al. [2], the asphaltene content values of Selenizza were determined using IATROSCAN analysis. To better characterize the natural bitumen quality throughout the entire volume of the deposit, were analyzed raw and purified bitumen samples, collected from the depth and near-surface areas of the deposit (Table 1).

The colloidal instability index I_c values indicate that the organic phases of Selenizza have a sol or sol-gel character, with enough quantity of resins to peptize the asphaltenes.

Table 1 SARA fractional composition—IATROSCAN method.

		Saturated	Aromatic	Resin	Asphaltene-i	I_c
Purified sample-depth	Average	1.7	24.8	35.1	38.4	0.67
	Standard deviation	0.35	2.29	1.35	1.88	
Purified sample-surface	Average	1.5	22.7	37.2	38.6	0.67
	Standard deviation	0.14	1.37	1.90	1.58	
Raw sample-depth	Average	1.6	23.8	34.6	40.01	0.71
	Standard deviation	0.29	1.40	1.16	1.99	
Raw sample-surface	Average	1.6	19.7	37.9	40.8	0.73
	Standard deviation	0.24	2.02	1.60	2.74	

Table 2 Evolution of the vitreous transition of modified bitumen according to the added Selenizza percentage.

	Total heat flux				
	T_g1 (°C)	T_g (°C)	T_g2 (°C)	ΔT_g (°C)	$\Delta\Phi$ (W/g)
Petroleum bitumen 50/70	-31.9	-22.9	-13.2	18.6	0.022
Mixed with 5% Selenizza	-30.9	-23.1	-13.8	17.1	0.019
Mixed with 10% Selenizza	-30.3	-23.1	-13.3	17.0	0.018
Mixed with 15% Selenizza	-32.1	-23.3	-13.4	18.8	0.019
Natural asphaltite Selenizza	-12.6	-1.1	16.2	28.8	0.021

Results from the survey show that in physical and chemical terms, Selenizza is similar to petroleum bitumen (forming with the latter stable mixtures) but with a higher content of resins and asphaltenes which confers upon the natural bitumen, higher stiffness, and higher vitreous temperatures.

The differential calorimetric analysis was used in this research work to determine the vitreous transition of bitumen modified with the different percentages of natural bitumen Selenizza. The glass transition temperature T_g is correlated to the mechanical bitumen behavior at low temperatures. In Table 2 was investigated the evolution of vitreous transition of 50/70 samples modified with Selenizza.

From the table, it can be seen that T_g, ΔT_g, and $\Delta\Phi$ do not vary and that the addition of Selenizza, does not affect the glass transition of bitumen. At the same time, with the increase in the modification rate, it was observed a slight decrease in the crystallizable fractions. It is interesting to note that this analysis revealed a value of glass transition temperature of the 35/50 bitumen modified with Selenizza T_g = -23.1 °C, lower than that of the reference petroleum bitumen with equal paving grade 35/50, whose glass temperature was found to be T_g = -19.3 °C. This seems to indicate that the bitumen modified with Selenizza, at a percentage of 5%, has increased resistance to low temperature cracking compared to petroleum bitumen of equivalent grade.

As the hard bitumen manufactured by refineries often features relatively high susceptibility to aging, a characteristic which plays an important role in pavement performance, the study particularly focused on the analysis of the evolution of bitumen modified with natural bitumen during the artificial aging process and the capability of the latter to avoid this defect.

A specimen of 50/70 bitumen, modified with different percentages of Selenizza, as well as the respective equivalent normal paving grade bitumen, was submitted to accelerated artificial aging RTFOT followed by PAV. After the tests, the aged bitumen samples were submitted to different tests (penetration, R&BT, rheology, etc.) to evaluate the evolution of these parameters due to the aging. Normally, a road paving bitumen loses a penetration grade after the RTFOT aging.

The results of the measurement of penetration and softening temperatures before and after artificial aging are shown in Table 3.

The aging was also manifested by an increase of complex modulus and by a greater elasticity (decrease

Table 3 Penetration and softening temperature before and after aging.

Description	Penetration (0.1 mm)			R&B (°C)		
	New binder	After RFTOT	After PAV	New binder	After RFTOT	After PAV
50/70 bitumen	54	37	19	49	53.4	61.4
50/70 with 5% Selenizza	38	27	15	52.6	57.2	66.0
50/70 with 10% Selenizza	28	21	13	56.2	60.8	68.8
50/70 with 15% Selenizza	20	14	11	61.6	65.4	72.2
Normal 35/50	40	27	12	52.6	56.8	66.2
Normal 20/30	23	12	7	60.0	67.0	78.8
Normal 10/20	18	9	5	65	72.6	86.0

Table 4 Composition of binders.

Constituent materials	Natural bitumen		Waste vegetable oil	Hard bitumen
	Hydrocarbon	Mineral fraction		
Percentage	60.7%	10.7%	17.9%	10.7%

of phase angle values). The analysis of the evolution after the aging of complex modulus and phase angles of different samples modified with Selenizza and of those of equivalent penetration grade conventional petroleum bitumens showed the same trend in changes.

These tests have demonstrated that after the aging, the changes that occur in the modified bitumen are lower compared to the changes in the initial bitumen 50/70. Also, for the modified specimen, the changes are attenuated with the increase of the modification rate. The comparison between the modified bitumen and the equivalent normal bitumen shows that the modified bitumens are characterized by minor changes, which means that Selenizza, lessens the aging effect and acts as an aging inhibitor.

3. The Development of a New Type of Binder Using Waste Vegetable Oil and Natural Bitumen

Bitumen, as a by-product of petroleum refining, is increasingly scarce as a non-renewable source and may result in a shortage of supply. To tackle this trend, specialists are considering new ways to find substitutes or modifiers of the traditional bituminous binders. Utilizing waste vegetable oils to partially substitute bitumen can not only reduce bitumen consumption but also improve the pavement performance. Recently published papers indicate that waste oils can restore the properties of aged asphalt binder and provide more flexibility to the final binder. According to some authors, the Aromatics, Resins and Saturates fractions content in vegetable oils (except for the Asphaltene), are similar to those of petroleum bitumen, ensuring good compatibility between the two types of product. On the other hand, the high asphaltene content in the natural bitumen Selenizza, along with its anti-aging property, makes it a suitable choice to combine with the rejuvenating properties of waste vegetable oils (mainly composed of aromatics, resins and saturates) for the development of innovative binders.

In a research study conducted jointly by the French Centre for Studies and Expertise CEREMA and Institute for Science and Technology IFSTTAR [3], was developed a new type of binder using 71.4% natural bitumen Selenizza, blended with 17.9% of rapeseed or sunflower waste vegetable oil and 10.7% hard bitumen P15/25.

The new binder consisted of natural bitumen Selenizza, mixed with two types of waste vegetable oils, rapeseed and sunflower, and a hard bitumen P15/25, which was added to the mixture to compensate the inorganic matter contained in Selenizza. The composition of the mixtures is given in Table 4.

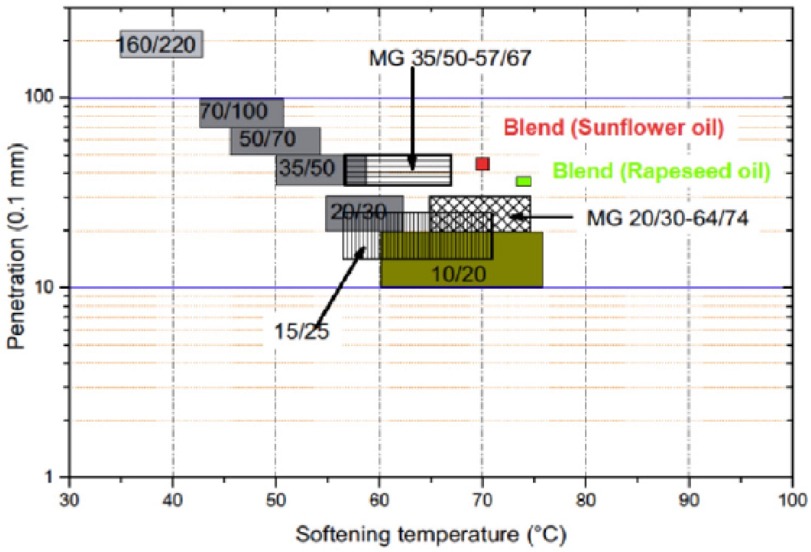

Fig. 2 Comparison between blends and classical bitumen.

In this study were examined the rheological and mechanical properties of the new binder as well as the performance of the asphalt mix manufactured with the new binder.

The binder manufacturing process consisted in preheating the natural bitumen Selenizza at 190 °C into the mixer and then adding the waste oil and hard bitumen P15/25 into the melted Selenizza, by mixing all the ingredients during 30 minutes until obtaining a homogenous blend. The measurement of the penetration and softening temperature for the two types of binders (with sunflower and rapeseed oil), showed that the engineering properties of the newly produced binders were close to a P 35/50 standard petroleum bitumen, but with the particularity that the softening temperatures of the new binder are higher than those of the conventional bitumen (Fig. 2).

The volatility of the binder constituents was determined using thermo-gravimetric analysis from 32 °C to 800 °C at a constant heating rate of 10 K/min on specimens of vegetable oils, Selenizza, hard bitumen P 15/25 and the newly produced binders. The testing results showed that no one of the samples resulted to be volatile for temperatures lower than 250 °C, demonstrating thus that no significant degradation of the constituents occurs during the binder productions and mixes manufacturing at 190 °C.

The analysis of binder thermal behavior was conducted, using differential scanning calorimeter (DSC) in a temperature range from -80 °C to 200 °C. It was observed that the newly developed binders have lower glass transition temperatures compared to the reference bitumen which leads to better low-temperature behavior such as thermal cracking. The better relaxation capability of the new binder is due to the contribution of vegetable oils whose glass transition temperatures are lower compared to those of conventional bitumen [4].

Using Metravib analyzer, frequency sweep tests have been conducted at 10 different frequencies in the range from 1 to 80 Hz. From -20 °C to 20 °C, the tensile-compression complex modulus E* was determined, and from 20 °C to 60 °C, the shear complex modulus G* was measured. Master curves were built at a reference temperature of 15 °C using software developed by IFSTTAR. Binder's complex modulus and phase angle master curves (Fig. 3) indicate that the reference bitumen is slightly stiffer than the new binders in temperatures that range between -20 °C and 60 °C. The phase angles of the new binders are lower than those of reference bitumen for the reduced frequency $a_T \times f \leq 2.5$ Hz (e.g. $T \geq 20$ °C) and higher for the reduced frequency $a_T \times f \geq 2.5$ Hz (e.g. $T \leq 20$ °C).

Also it was noticed that at very low temperatures, the phase angles of the newly produced binders are not equal to zero, which means that the viscous effects are not negligible compared to reference bitumen. Consequently, at low temperatures, the newly produced binders' behavior can not be assumed to be that of a purely elastic material and this property may be advantageous for low-temperature stress relaxation.

For the mix characterization, a Semi Coarse Asphalt Concrete (BBSG 0/10) was designed with the new binders, whose composition is described in Table 5. The aggregates and the binder were mixed for 3 minutes at 190 °C.

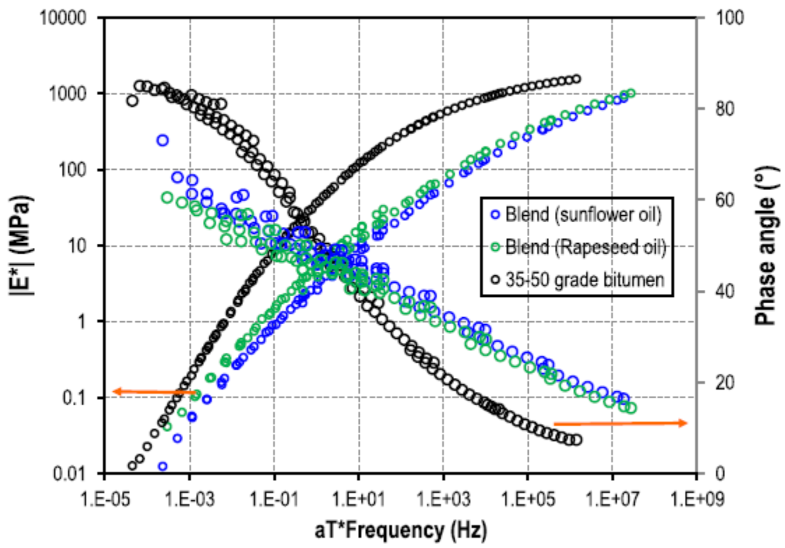

Fig. 3 Binders complex modulus and phase angle master curves at 15 °C.

Table 5 Composition of asphalt mixes.

BBSG3 0/10 according to EN 13108-1	
Granular fractions	Percentage by mass
0/2	26.1%
2/6	23.7%
6/10	42%
Filler (limestone)	1.9%
Binder (Selenizza + waste oil + P15/25 bitumen)	6.3%

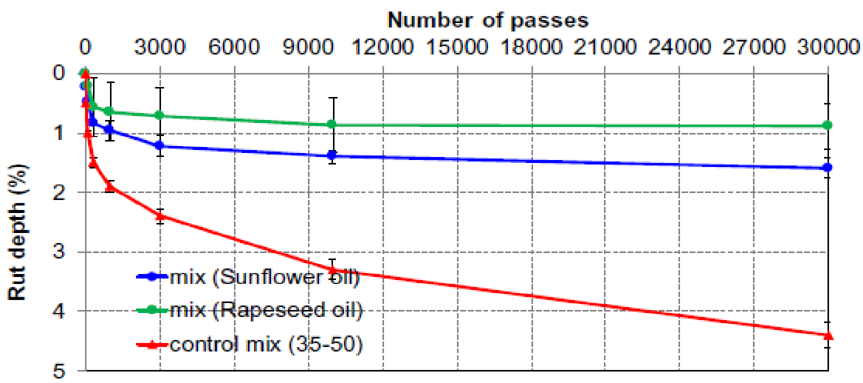

Fig. 4 Evolution of the rut depth.

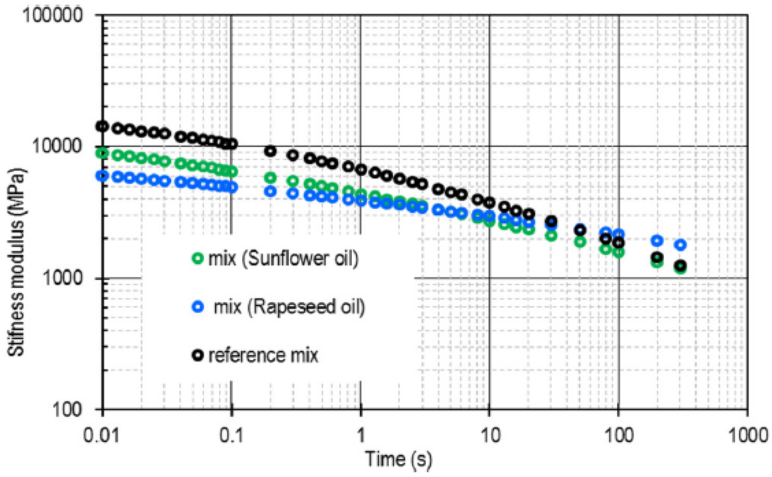

Fig. 5 Master curves of stiffness modulus of mixes at 15 °C.

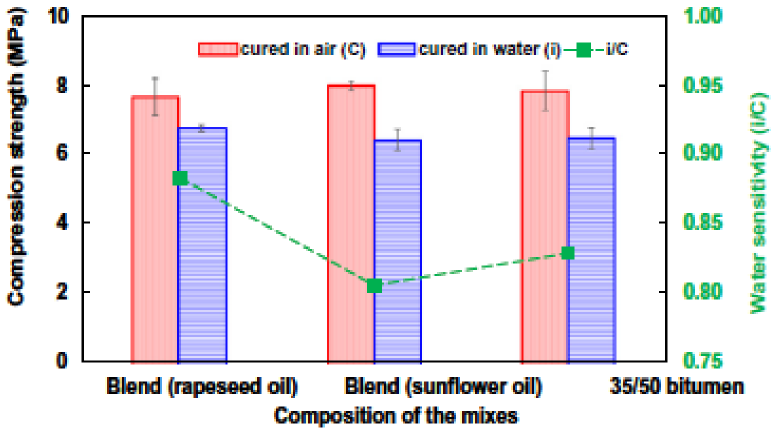

Fig. 6 Compression resistance and water sensitivity of the asphalt mixes.

The resistance to the permanent deformation was determined using the wheel tracker large device. For each asphalt concrete, the test was conducted on two plates, compacted by a roller compactor. The rut depth was measured using a depth gauge as a function of passes. The rut depths (at 60 °C) of the mixes manufactured with the newly produced binders are lower than the control mix (with 35/50 bitumen) rut depth (see Fig. 4), which is incompatible with the results of stiffness modulus measurements. The better resistances to the permanent deformation obtained with the newly produced binders can probably be attributed to the high asphaltene content in natural bitumen [5], but the real mechanism that occurs, is not known yet.

The mixtures stiffness modulus was determined using DT-CY (direct tensile test) according to the standard EN 12697-26 annex E. The experiment was conducted at -10 °C, 0 °C, 10 °C, 15 °C, 25 °C, 40 °C, and at 1 s, 3 s, …, 300 s loading times. Beforehand was determined the strain amplitude which must be applied during the tests to preserve the linear elastic behavior of the samples. The results of each temperature and time sweeps have been used to build the master curves at the reference temperature of 15 °C. As shown in Fig. 5, the reference asphalt mix was stiffer (following the evolution of binders complex modulus) 13,171 MPa (at T_{ref} = 15 °C and loading time 0.02 s) compared to the two other asphalt mixes, whose modulus values were respectively 8,233

MPa and 5,678 MPa for the sunflower and rapeseed oil. The stiffness modulus of the rapeseed oil-based asphalt concrete did not comply with the minimum value (7,000 MPa) required by the standard EN 13108-1 (2007).

To assess the water sensitivity of asphalt mixes, cylindrical samples with 120 mm diameter were manufactured to assess the bitumen to aggregate bond. The test specimens for each type of asphalt mix were divided into two batches, one batch being stored in water at 18 °C for 7 days and the other stored in air for 7 days at 18 °C, inside a temperature-controlled chamber. The specimens were then subject to compression tests and maximum resistances were recorded for the wet batch (*i*) and the dry batch (*C*). No significant difference between the vegetable oils mixes and the reference mix is observed regarding water sensitivity (Fig. 6). For all the asphalt mixes, the ratios *i/C* exceeded 0.7, in compliance with the requirements of the standard EN 13108-1 (2007).

This study must be further developed and completed, especially focusing on the fatigue resistance, aging, and low temperature cracking of the asphalt mixes with the new binder.

4. Example of Innovative Asphalt Mix Design for Surface Layers Using 100% RAP Aggregates and a Binder Composed Only of Vegetable Oil and Natural Bitumen Selenizza

Recycling asphalt pavements creates a material reusing system that optimizes the use of natural resources. The use of reclaimed asphalt pavement (RAP), reducing the need to use virgin aggregate (which is a scarce commodity in some areas), as well as the amount of costly new asphalt binder, has experienced rapid and sustained growth in recent years because of the enormous economic and environmental benefits.

A recent study carried out by Riedl and Sorge [6] from Erfurt University, as a part of a national innovation program, proposed and evaluated an innovative asphalt mix using 100% RAP aggregates with the addition of a rejuvenator. The newly developed rejuvenator aimed to restore the rheological properties helping to rebalance the composition of aged binder that has lost its maltenes during the asphalt mix manufacture process and its service period, restoring the original characteristics of the fresh bitumen and its effectiveness. While it should have a high percentage of aromatics that are necessary to keep the asphaltene dispersed, the new binder should contain a low content of saturates which are highly incompatible with asphaltenes and highly detrimental to the rheological properties of aged asphalts [7]. The rejuvenating agent investigated in this study was composed of waste vegetable oil and natural bitumen Selenizza. For this project, 12 variants of an asphalt concrete AC 11 DN and the associated binders, without a rejuvenator and the same, aged mixtures, with 3, 4, and 8% rejuvenator content by mass of the bitumen in the asphalt, were investigated. In Table 6 (Fig. 7), JA refers to reference variants of asphalt mixtures, JB to the aged variants and JC, to the aged asphalt mixes added with a rejuvenator.

The purpose of the test program was to determine the effect of aging and assess the efficacy of using the rejuvenating additive.

To simulate the accelerated aging of bitumen and asphalt mixtures the following methods were used in the laboratory:

- Rolling Thin Film Oven Test (RTFOT) according to DIN EN 12607-1:2013;
- Pressure Aging Vessel (PAV) according to DIN EN 14769:2012;
- Standard Practice for mixture conditioning of hot mix asphalt (AASHTO R 30);
- Braunschweiger process for the aging of asphalt mix (practical method of asphalt mix aging developed at the Technical University Braunschweig).

To be able to determine the effects of aging and the use of the rejuvenating additive, and then subsequently

Table 6 Different variants of AC 11 DN.

Variant	Asphalt mix	Binder	Binder content [M-%]	Additive content [M-%]
JA1	AC 11 DN	Shell B 50/70	6.2	-
JA2	AC 11 DN	BP3 B 50/70	6.2	-
JA3	AC 11 DN	Olexobit PmB 25/55-55	6.2	-
JB1	AC 11 DN	Shell B 50/70-BSA	6.2	-
JB2	AC 11 DN	BP3 B 50/70-AASHTO R 30	6.2	-
JB3	AC 11 DN	Olexobit PmB 25/55-55-AASHTO R 30	6.2	-
JB4	AC 11 DN	RC-Elxleben	6.2	-
JC1	AC 11 DN	Shell B 50/70-BSA	6.2	4.0
JC2	AC 11 DN	BP3 B 50/70-AASHTO R 30	6.2	8.0
JC3	AC 11 DN	Olexobit PmB 25/55-55-AASHTO R 30	6.2	8.0
JC4.1	AC 11 DN	RC-Elxleben	6.2	3.0
JC4.2	AC 11 DN	RC-Elxleben-BSA	6.2	3.0

Fig. 7 JA: reference asphalt mixture, JB: aged asphalt mixture, JC: asphalt mixture with rejuvenator.

deduct the recipes for the production in the mixing plant, the following methodology was used iteratively:

- Production of rejuvenator additive variants;
- Investigation of rejuvenator additive impact on fresh bitumen;
- Examination and validation of aging bitumen and asphalt mixtures;
- Investigation of the additive adding in the binder;
- Investigation of dosing levels impact in the asphalt mix;
- Preparation of trial segment, investigation of different developed asphalt mixtures.

The bitumen binder contained in the bituminous mixture during its full lifetime faces different aging processes mainly due to interactions with the environment. The mechanism of aging includes oxidation, evaporation, and physical hardening. The evaporating aging is a purely physical process that involves the evaporation of low-viscosity oil components from the bitumen. The process depends on the type of bitumen, the temperature, and the specific surface area. During the asphalt mixture, when thin asphalt film comes into contact with aggregates at temperatures of 150 °C or higher, aromatic fractions rapidly evaporate and asphaltenes generally increase between 1 and 4 wt.%. The process leads to an increase in viscosity and a reduction in adhesion. However, today's penetration grade bitumens are relatively non-volatile, thus during in-service pavement use, this type of aging is negligible. Although volatilization occurs primarily during the mixing, it may also occur during storage, transportation, and laying. The oxidative aging is purely an irreversible chemical process that is triggered primarily by the reaction with atmospheric oxygen and occurs under the influence of photo-oxidation and thermal oxidation processes. The subsequent release of oxygen and reactive gases (ozone, nitrogen oxides, sulfur dioxide, and trioxide) that split bitumen components, is crucial for the aging intensity. The sunshine has a major influence. The oxygen bonds are split by light and carbon-hydrogen or carbon-carbon bonds are split by UV radiations. As a result, asphaltenes are formed from petroleum resins unbalancing the existing system and enhancing colloidal instability. Although the depth of sunlight exposure is only of 5 μm, they can contribute to the creation of free radicals that penetrate to deeper layers. Also, there is a great influence of the temperature on the reaction rate which doubles for every 10 °C rise in temperature. Due to the abovementioned unbalance in the bitumen colloidal structure, so-called structural aging occurs. This effect is to be regarded as a combination of distillation and oxidative aging and less as an independent form of aging. The colloid-ally dispersed particles (micelles) enlarge and coalesce into larger aggregates. As the asphaltene content in the bitumen structure increases, that of the maltenes decreases. This is called the transition from the original sol state to the gel state. Due to this process, the bitumen continuously gains in structural viscosity, thus aging, gaining more and more hardness and at the same time, loses its ability to relax. There is also the physical or structural hardening, an independent and reversible process that changes the rheological properties of bitumen without altering its chemical composition. It involves the crystallization (steric hardening) of paraffin and paraffin-like constituents contained in the bitumen at temperatures below 90 °C attributable to the crystallization of linear alkanes present in asphaltene fractions. As a result of this effect, the bitumen hardens and increases in rigidity. At ambient temperatures, physical hardening is very slow, but it can speed up at low temperatures.

Chemical aging which leads to global hardening of the material and increases cracking-problems is classified into two categories: short-term aging, which is rapid chemical aging during asphalt mix manufacturing process, and long-term aging, which occurs during the service life of the road.

The above considerations were taken into account when formulating the rejuvenator agent.

To complement and verify the results of asphalt mix aging, the used binder was aged in parallel to the asphalt mixture with the same parameters. For this purpose, a thin binder film (≤ 0.5 mm), was poured into silicone molds and aged parallel to the asphalt mixtures.

The aging procedure for the practical oxidative aging of the mix was developed in the Institute of Road Engineering of the Technical University of Braunschweig. In this aging process, the asphalt mixture previously produced in a compulsory mixer was laid in thin even layers of 2.0 cm, on a metal rack with size mesh 0.5 cm, and stored in an oven set at a constant temperature of 80 °C with good air circulation, for 96 hours (Fig. 8). After the warming, the asphalt mix was granulated again and heated slowly and uniformly in intervals in the compulsory mixer, to the production temperature of 145 °C.

The newly developed rejuvenator agent consists of finely ground natural bitumen Selenizza and a vegetable oil rich in unsaturated acids (Fig. 9). The addition of vegetable oils as a rejuvenator to the binder has been widely described in the literature. Several series of tests have reported that fatigue resistance can be significantly increased by the application of used vegetable oil as a rejuvenator in RAP. At the same time, the increased use of vegetable oil can result in a reduction of the stiffness of the asphalt mixture and a higher potential of rutting occurrence due to the weakened bond between the binder and aggregates in the mixture. The rejuvenator needs to act not merely as a softening agent, but it must completely restore the chemical and rheological properties of aged bitumen. To this effect, natural bitumen Selenizza was also used (to an adequate amount) in conjunction with the vegetable oil to produce the rejuvenator agent aiming to rebalance the SARA composition and correct the physicochemical characteristics of the resulting binder, with the double benefit of achieving high anti-rutting performance and also leading to a composite bituminous phase, less subjected to aging phenomena (thanks to the high asphaltene content anti-aging properties of natural bitumen). The maximum amount of RAP to be reused in the asphalt mix will depend on the capability of the

Fig. 8 Braunschweig aging method.

Fig. 9 Rejuvenator production in laboratory.

rejuvenator to correct the physical and chemical characteristics of the aged bitumen.

Also, the ratio of the two components has a considerable influence on the storage capacity of the rejuvenator as well as on binder and asphalt mix properties.

Considering the significant influence of aging on bitumen properties, various tests were carried out on the binder to investigate the aging behavior and the influence of the rejuvenator, which was successively added, leading to one first validation of suitable formulations for the asphalt mix.

Due to the aging, the softening temperatures of aged binders (JB1, JB1.2, and JB2) increased in comparison with (JA1, JA2) reference variants and the penetration decreased. The addition of the additive leads to a significant reduction of softening point (JC1, JC2) as well as a significant increase in penetration (Figs. 10 and 11).

In addition to the conventional test methods, a large part of performance-oriented tests was conducted with the Dynamic Shear Rheometer (DSR). From the test results of the DSR analysis at a load frequency of 1.59 Hz and temperature range of 20 °C to 65 °C, it was observed that aged variants (JB) have a greater rigidity

Bitumen type	*20/30*	*30/45*	*50/70*	*70/100*
Softening point [°C]	*63 - 55*	*60 - 52*	*54 - 46*	*51 - 43*
JA1			50,6	
JB 1	59,2			
JB 1.2	63,6			
JC1		53,4		
JD1			50,2	
JE1			46,0	
JA2			50,6	
JB2	67,0			
JC2	58,4			

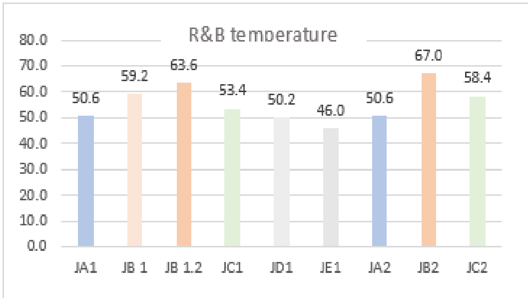

Fig. 10 Softening point.

Bitumen type	*20/30*	*30/45*	*50/70*	*70/100*
Penetration [0,1 mm]	*20 - 30*	*30 - 45*	*50 - 70*	*70 - 100*
JA1			60	
JB 1	19			
JB 1.2	20			
JC1		44		
JD1			55	
JE1			60	
JA2			55	
JB2	20			
JC2		40		

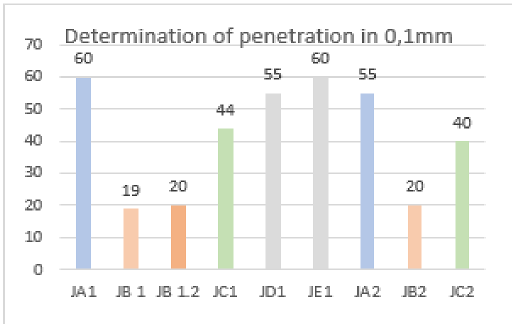

Fig. 11 Penetration.

compared to reference variant (JA) over the entire temperature range. The rejuvenated variants (JC) are again in the range of the initial values (Fig. 12).

The phase angle test results for temperature sweeps at a frequency of 1.59 Hz in the temperature range from 20 °C to 65 °C are shown in Fig. 13. It can be seen that the aged variants (JB), in particular, compared to the reference variants (JA), have a lower phase angle over the entire temperature range. The rejuvenated variants (JC) are again in the range of initial values.

In previous researches, some authors argue that asphaltenes produced during the aging are somewhat different from the asphaltenes initially present in bitumen and that the ratio of asphaltene to maltene of the rejuvenated binder is significantly different from that of the virgin bitumen, affecting the long-term performance of RAP mixture. The action of the rejuvenator consists of diluting the asphaltenes created during the aging process, by the addition of new maltenes. According to some authors, a better rejuvenation is attained when the percentages of resins and aromatics are higher in the mixture. The diffusion of rejuvenator in the bituminous binder may follow two phases mechanism. As a first step is the diffusion of the oil in the maltenes phase of bitumen and then, the migration of bitumen asphaltenes into the rejuvenated maltenes.

In this study, the respective SARA composition of variants JB1 and JC1 was determined using Iatroscan analysis. For each sample, five replicate individual scans were performed and the average value of the five readings was considered as the result. It was observed that the addition of the additive leads to a difference in the percentage distribution of the main SARA groups. It was found that the rejuvenation process leads to an increase of the polarizable fractions, i.e., resins (at a higher level) and asphaltenes (slighter increase), accompanied at the same time, by a reduction of the aromatics and saturates (Fig. 14).

Subsequently, comparison tests were carried out to investigate the asphalt mix behavior and the changes of mixture performance versus a reference asphalt mixture.

A major part of the experimental program consisted of investigating and evaluating the stiffness and fatigue behavior of asphalt mixes using the dynamic axial tensile test according to DIN EN 12697-24 and DIN EN 12697-26.

Fatigue cracks are one of the most common damage manifestations of asphalt pavements. They occur when cohesive bond energy of asphalt binder and the adhesive bond energy between asphalt aggregate and binder of an aggregate-asphalt matrix are affected by the heavy traffic load (stresses of mechanical origin) and rapid cooling of the bituminous mixture (cryogenic stresses). The superposition of mechanical and thermogenic stresses leads to the increase of the resulting tensile stress which increases the risk of cracking. Studying the behavior of the mechanical properties of asphalt mixtures at low and intermediate temperatures is vitally important. In this research work, indirect tensile fatigue tests investigated the fatigue and dynamic characteristics of asphalt mixtures. The determination of the fatigue function of all the variants was carried out under the same experimental conditions at a test temperature of 20 °C and a load frequency of 20 Hz. The fatigue functions of the splitting tensile strength test at 20 °C are shown in Fig. 15. On the ordinate axis are shown the values of load cycles until failure and on the abscissa axis, the initial elastic strain. It was observed that the rejuvenated variants (JC) compared to the aged variant (JB) and reference variant (JA), for the same elastic initial strain, endure more load changes up to the macro cracking.

The equivalence between test temperature and load frequency regarding the stiffness was established using the time-temperature superposition principle to predict the stiffness modulus for different combinations of temperature and load frequency. Extracts from stiffness-temperature functions for 10 Hz, in the

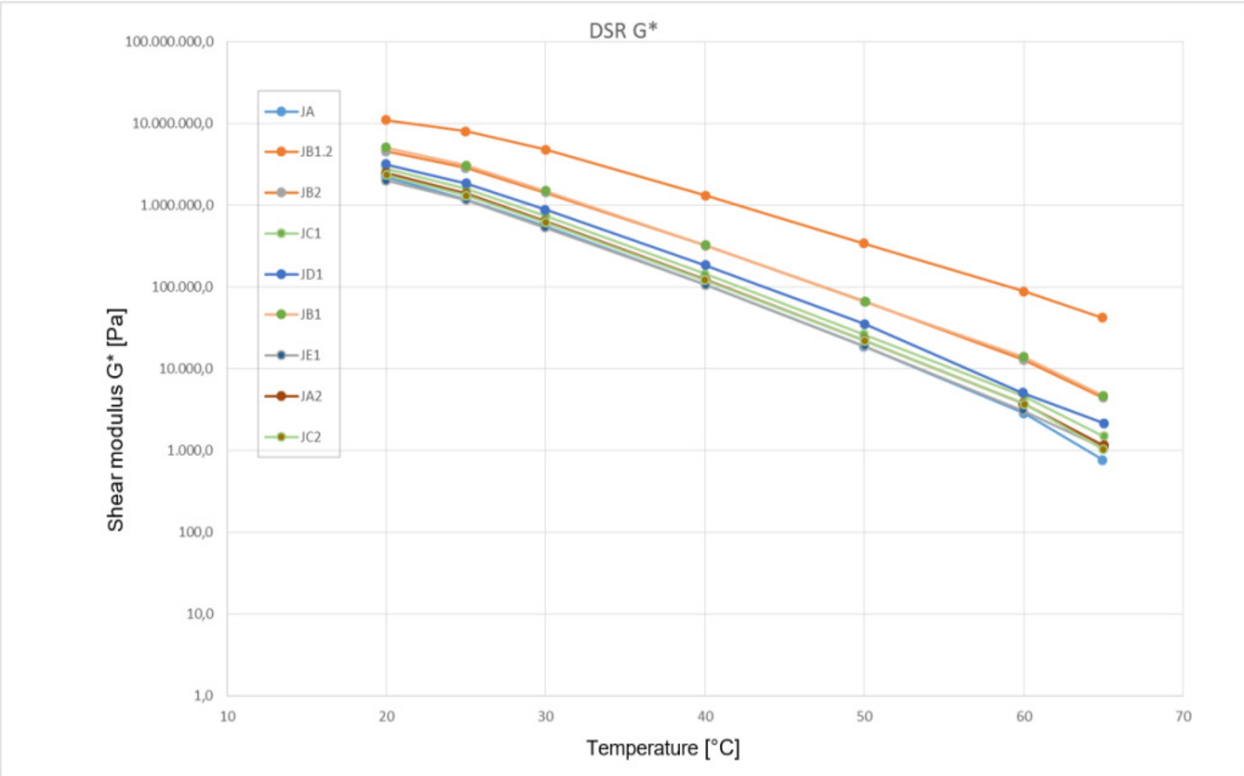

Fig. 12 Temperature-sweep G*.

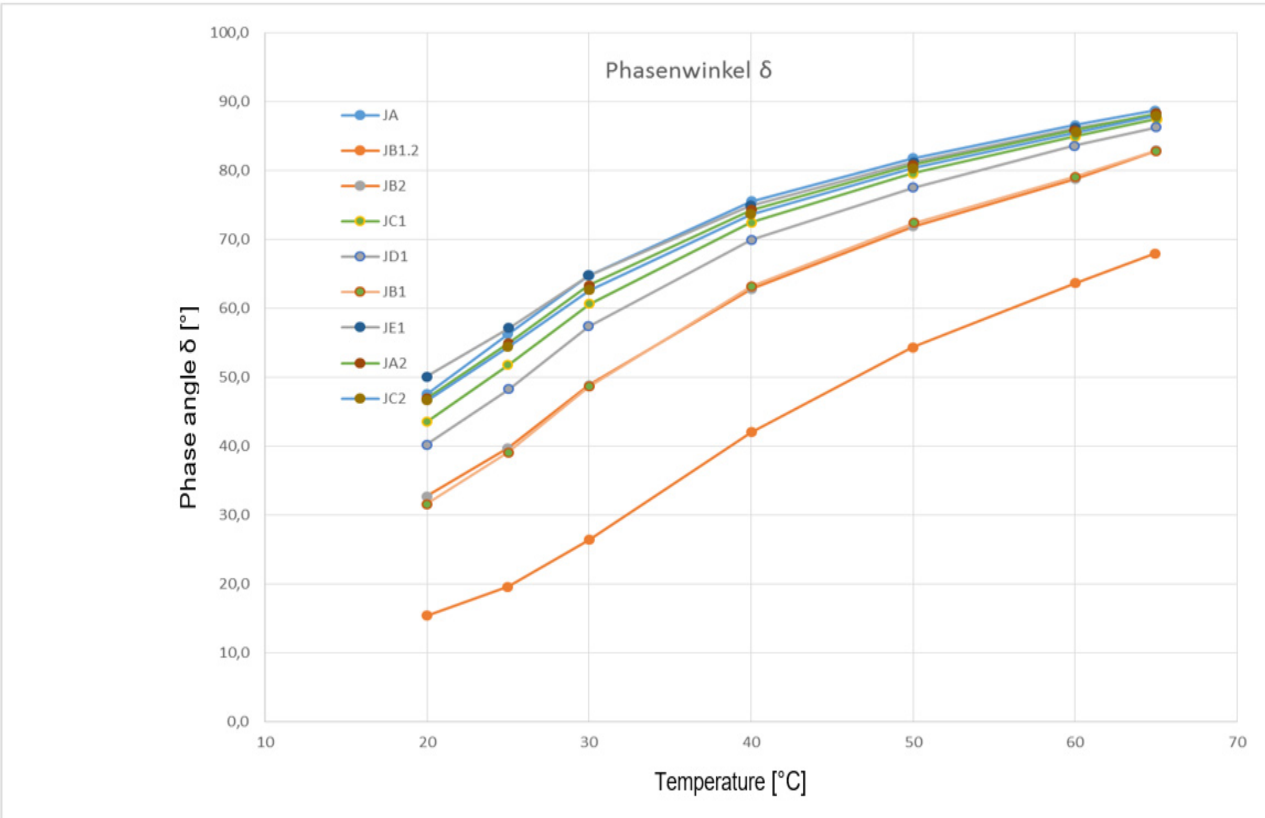

Fig. 13 Temperature-sweep phase angle.

Variation JB 1	Average (%)	Standard deviation
asphaltenes	27.548	0.233
resins	35.635	1.205
aromatics	33.763	0.801
saturates	3.056	0.635

Variation JC 1	Average (%)	Standard deviation
asphaltenes	28.179	0.240
resins	39.675	0.111
aromatics	29.423	0.972
saturates	2.723	0.621

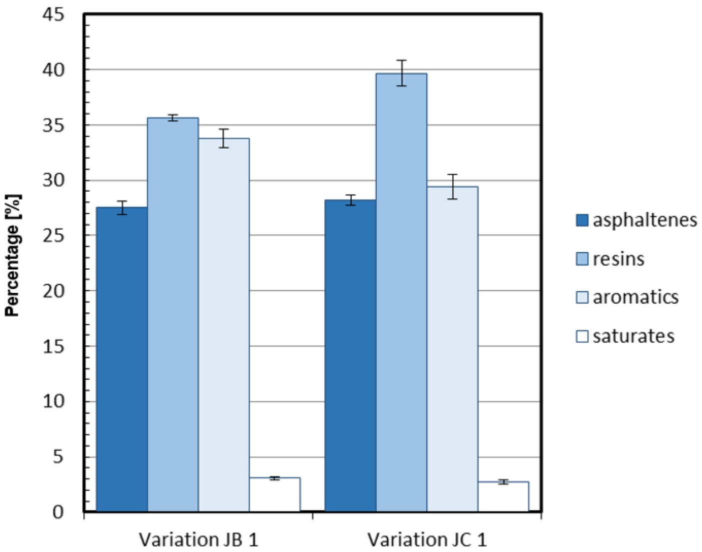

Fig. 14 SARA analysis-graphical comparison.

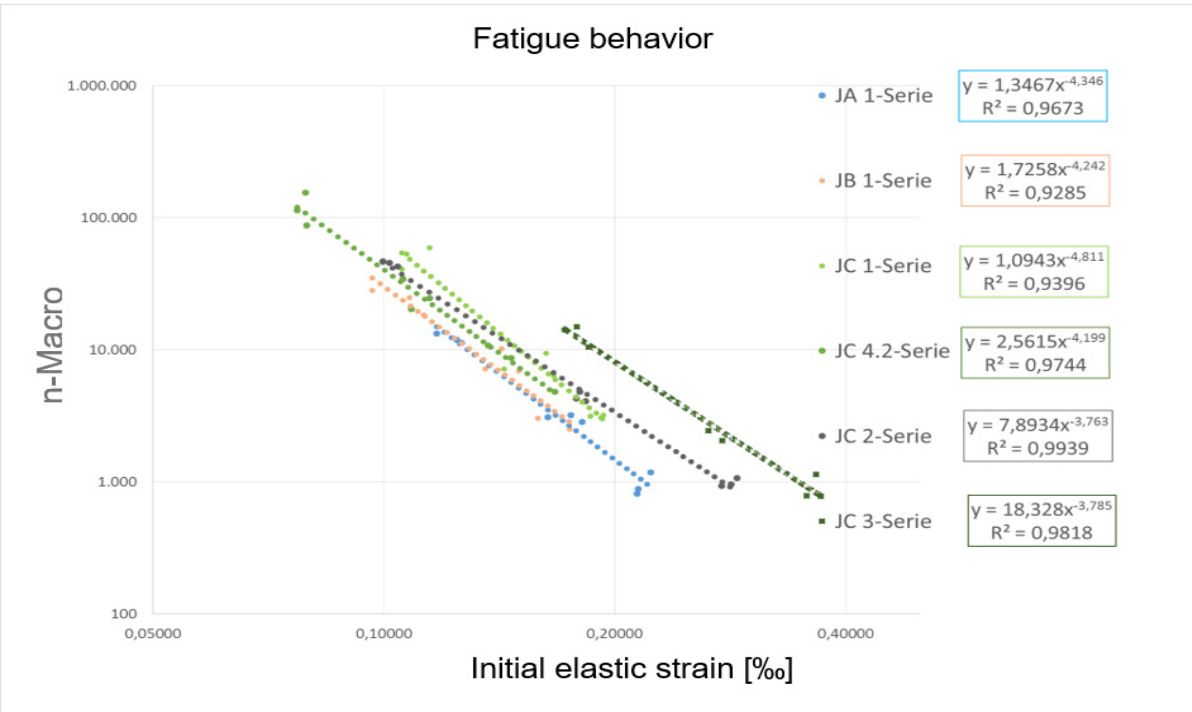

Fig. 15 Fatigue behavior of dynamic splitting tensile tests.

temperature range -20 °C to ±30 °C, are shown in Fig. 16. The aging leads to an increase of the stiffness modulus (JA to JB) in the temperature range under consideration while there is a reduction in stiffness modulus after the addition of the additive (JB to JC). Comparing the rejuvenated variant to the reference variant (JC-JA), it was observed that the values after rejuvenation, are in the range of the reference variants or even below.

The asphalt mixtures were tested for rutting resistance. The partial results of the wheel track test after 10,000 cycles are shown in Fig. 17. It was observed that no variant reached the 8 mm rut depth failure criteria and that they were all within the authorized standard range.

To investigate the effect of the rejuvenating additive on the adhesion bond in the interface between bitumen and aggregates, a rolling bottle test was carried out according to EN 12697-11. The degrees of bitumen coverage are shown in Table 8, where there are only small deviations of the values. Compared to the reference variant JA, the variant JC (24-72 h) has 5% to 10% more coating.

To verify the results of this research work, a test section with the implementation of an upper layer using 100% RAP with vegetable oil and Selenizza, has been laid in Greußen, near Erfurt (Fig. 18).

This research work will be further continued with *in situ* long-term observations on the laid test section over the upcoming years to clarify and better map the process improvement that will lead to better outcomes and potential savings of the technology developed in this project. Furthermore, it will be necessary to develop a general production and use guide on an industrial scale, providing the basis to establish uniform procedures that can be implemented in other mixing plants to guarantee the uniform quality of the asphalt mixture.

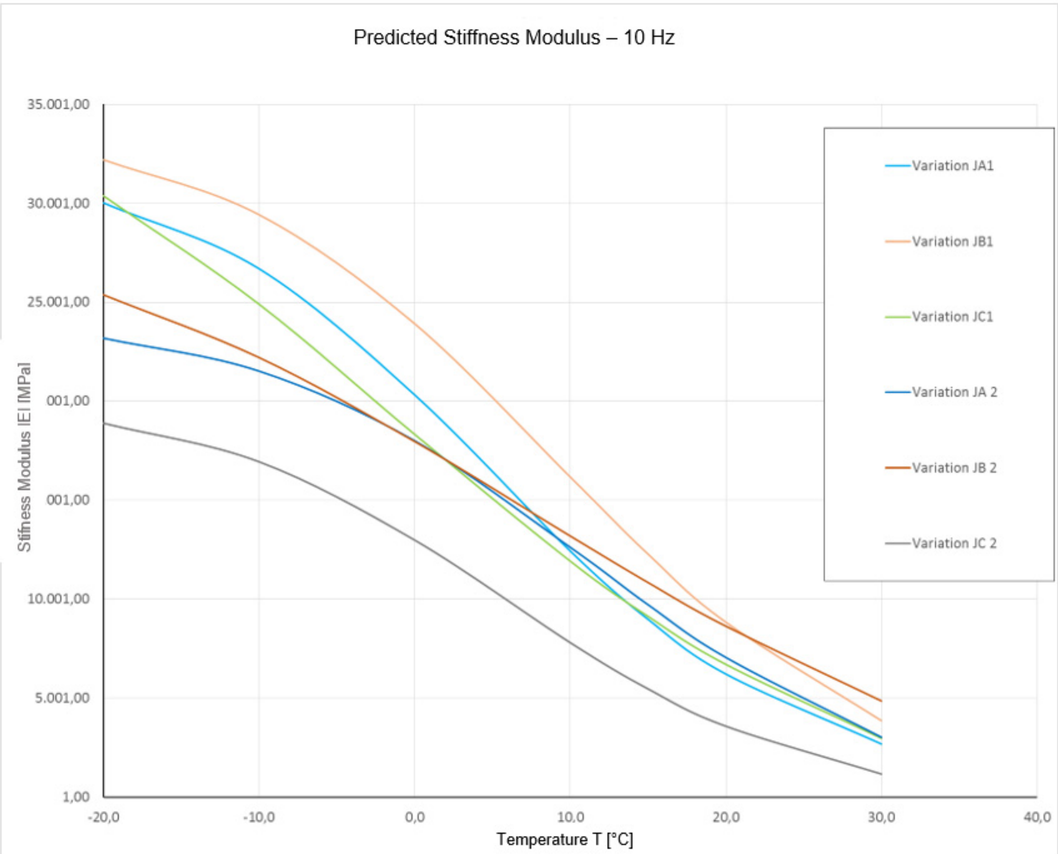

Fig. 16 Stiffness modulus-temperature function.

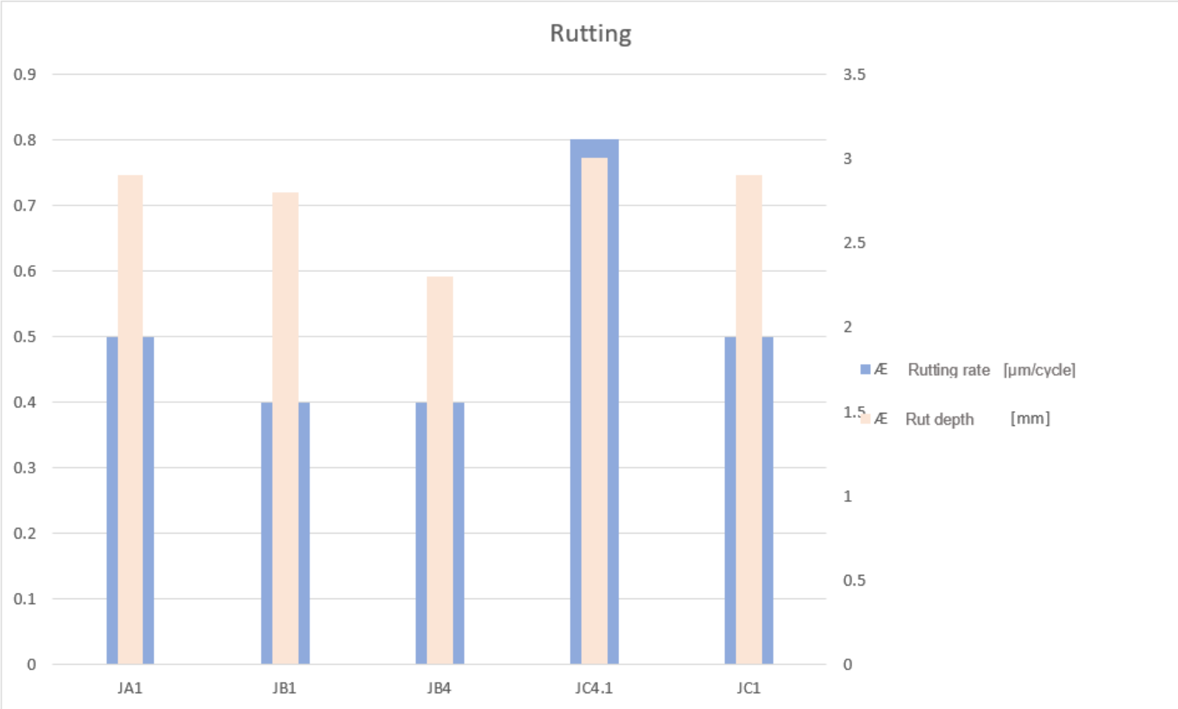

Fig. 17 Wheel tracking test.

Table 8 Degree of bitumen coverage.

		Rolling time [h]			
		6	24	48	72
Coverage [%]	Var. JA1	80	55	45	40
	Var. JA2	80	55	45	40
	Var. JB1	80	60	50	45
	Var. JB1.2	75	55	45	40
	Var. JB2	75	55	50	45
	Var. JC1	80	60	55	45
	Var. JC2	80	60	50	45

Fig. 18 Test session in D-99718 Greußen.

5. Conclusions

Recent research works have focused on alternative bituminous binders such as the binders derived from natural bitumen and vegetable oils.

In particular, it was found that natural bitumen Selenizza strongly affects the mechanical behavior of bitumen and decreases the susceptibility to the aging of modified bitumen as the percentage of natural bitumen content increases. Thus, for equivalent penetration grades, crude oil bitumen mixed with Selenizza, results more resistant to aging compared to traditional road bitumen.

The hardening and anti-aging properties of natural bitumen were advantageously used to develop new binders combining the high performance mechanical and durability properties of Selenizza with the rejuvenating capability of waste vegetable oils, whose Aromatics, Resins and Saturates fractions contents, are relatively close to those of petroleum bitumen.

A new binder made from natural bitumen Selenizza and waste vegetable oil was developed in the laboratory. Its characteristics were similar to traditional 35/50 straight run bitumen, with higher values of softening temperature.

Another line of inquiry, reversing the percentages of natural bitumen Selenizza vs. the waste vegetable oil, examined the production of a rejuvenator based on waste vegetable oil and natural bitumen Selenizza allowing designing asphalt mixes with a high content of RAP content. Mixtures containing 100% RAP aggregates were successfully implemented with the addition of a newly developed rejuvenator.

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