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Bio-Degradable Wax to Modify Asphalt Binder for Warm Mix Asphalt

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Abstract: In order to reduce production and compaction temperatures, as well as to increase the resistance to permanent deformation, synthetically refined waxes are commonly used as additives in asphalt pavements. This study focuses on the capability of replacing synthetically refined wax with bio-degradable wax. Ten different bio-waxes (called Biomer) with varying melting ranges and composition, as well as three conventional waxes (Sasobit®, Licomont®, and Asphaltan) are mixed with a virgin bitumen of standard type 50/70. Different conventional and rheological properties are determined for these viscosity-modified binders to evaluate the effect of the waxes. Two promising Biomer waxes (BIT111 and BIT140) were identified, which show almost identical results compared to Sasobit® and Licomont®, respectively. The results indicate that replacement of synthetic wax by bio-degradable wax is technically feasible. Additionally, the potential of asphalt pavements to form a source of microplastic is evaluated in this study. It is found that bitumen and wax cannot be considered as a source of microplastic.

Keywords: Biomer; bitumen; bio-degradable; wax modification; DSR

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1. Introduction

The concept of sustainability has gained public attention in recent years. Significant sustainable measures in road pavement construction have already been, and continue to be steadily implemented, mostly based on energy-saving construction methods and an increased use of reclaimed asphalt materials. The use of temperature-reduced asphalt mixtures with viscosity-changing additives, for example, enables asphalt mixtures to be paved at lower temperatures, thereby reducing the amount of required heating fuels, and energy costs. Additionally, emissions of aerosols from the asphalt binder are significantly reduced, thus avoiding odours and protecting the health of personnel.

Organic waxes are often used as viscosity-reducing additives, which can be basically divided into three groups: Amide waxes (e.g., Licomont®), Montan waxes (e.g., Asphaltan) and Fischer-Tropsch waxes (FT waxes, e.g., Sasobit®). A large part of the raw materials for these waxes is obtained from lignite (brown coal) or mineral oil. These resources are finite and associated with environmental concerns, and therefore have triggered public debate. As an alternative to synthetically refined waxes, bio-degradable, oxidized waxes (which are called Biomer) from natural raw materials have been developed. The production of Biomer waxes is based on natural waxes, such as sugar cane or natural paraffin. Different Biomer types are available on the market, with melting ranges from 60 to 140 °C. The possibility of using (bio-degradable) waxes in combination with high amounts of reclaimed asphalt as warm mix asphalts (as, for example, mentioned in [1]), imply even more positive ecological effects. However, experience in using bio-degradable wax for asphalt pavement applications is currently rather limited.

Within the scope of this study, a comparison is carried out of the properties of wax-modified bitumen, considering commercially available waxes Sasobit®, Licomont®, and

Asphaltan and Biomer as an alternative. The testing program includes conventional and rheological asphalt binder tests, including a conventional unmodified asphalt binder, and the variants of this binder modified with different waxes. The objective of this study is to compare different available Biomer waxes with synthetically refined waxes, with regards to their basic applicability for asphalt pavement application, and to identify the ideal bio-degradable replacement for typically used waxes.

In addition to waxes, polymers are often used as additives in asphalt road construction. About 25% of asphalt consumption in Europe is polymer modified bitumen (PmB) [2], and polymer modification is mostly realized through thermoplastic elastomers (e.g., styrene-butadiene-styrene). These polymers improve the performance properties of the asphalt in a way that meets all technical requirements. In the context of polymers, the formation of "microplastic", and its potential impacts on the environment and human beings, is currently being debated in public and scientific circles. This paper discusses the terms "plastic/polymer" and "microplastic" in order to provide appropriate definitions and classifications; it assesses whether and to what extent bitumen, polymer- or wax-modified bitumen must be classified as a harmful source of microplastic; and it questions if the use of bio-waxes can potentially reduce the amount of microplastic.

2. Background

2.1. Polymer

The scientific overall term "polymer" (meaning: many-part, from the Greek: *poly*—much and *meros*—the part) mainly covers plastics (thermoplastics/plastomers and thermosets/duromers) as well as elastomers (rubber). The components that form the polymer are called monomers and can come from a variety of substance groups, which are linked by polymerization. For example, polyolefins are a group of polymers formed by monomers which are called alkenes (olefins). The two most common polyolefins are polyethylene (PE) and polypropylene (PP) [3], which consist of the alkenes ethene and propene, respectively. Another group of substances used as monomers for polymerization is aromatic hydrocarbons. Styrene is an unsaturated aromatic hydrocarbon, which is used for the production of styrene-butadiene-styrene (SBS) [4].

The European Chemicals Agency defines polymers as substances that are made from monomers, and which meet certain criteria regarding their molecular weight distribution. The weight distribution (resulting from the chain length of the polymers) can be controlled during polymerization to obtain the desired technical properties.

The durability of a product made from synthetic polymers is an essential property required for its application. At the end of the product's lifetime, however, the durability of its components may become a problem. This is especially true if the product is not disposed of properly. Since the degradation of synthetic plastics in the environment takes decades to centuries [3], and incorrect disposal results in significant amounts of plastics entering the environment, public debate about the use of plastics has recently gained attention.

The EU has provided a political framework for a circular economy as part of the "First Circular Economic Action Plan", launched in 2015. Part of this plan is the establishment of the "EU Plastics Strategy" by the EU Commission, in January 2018 [5]. The EU Plastics Strategy aims to protect the environment and reduce marine waste, greenhouse gas emissions, and dependence on imported fossil fuels. The EU will support more sustainable and safer consumption and production patterns of plastics. The EU Plastics Strategy also aims to transform the way plastic products are designed, manufactured, used, and recycled in the EU. Thus, the ability to recycle materials or, where this is not possible, the degradability of products in the environment, makes the properties of synthetic polymers and the fields of application in which they can be further used in the long term [5] even more relevant.

2.2. Polymers in Asphalt Pavements

For road pavement application, bitumen can be modified with polymers to change its elasto-viscous behavior, and as such is designated as polymer modified bitumen (PmB).

PmBs are produced by mechanical mixing or chemical reaction of bitumen and one or more polymers, in a percentage usually ranging from 3% to 10% [6]. Due to their high stiffness and elasticity, polymers can significantly increase the plasticity range of bitumen. In addition, the added polymers potentially increase stability and resistance to deformation in a high service temperature range, and improve low-temperature performance by reducing brittleness [6].

There are a variety of polymers that are used to modify bitumen, as shown in Table 1. The properties of the resulting PmB are influenced by the properties of the polymers [7,8], but also by the polymer content and various parameters during mixing [9]. According to Table 1, the polymers are classified as elastomers, thermoplastics, and thermosets. In most European countries, styrene butadiene styrene (SBS), which can be considered as a thermoplastic elastomer, is the most commonly used polymer for road construction purposes [8,10].

Table 1. List of polymers used for modification of bitumen (extracted from [7,8]).

Type of Modifier	Polymer	Abbreviation
elastomer	styrene–butadiene elastomer	SBE
	styrene-butadiene-styrene (linear or radial)	SBS
	styrene–isopropene-styrene	SIS
	styrene–ethylene–butadiene–styrene	SEBS
	polyisobutene	PIB
	polybutadiene	PBD
	ethylene propylene rubber	EPR
	ethylene propylene diene rubber	EDPM
thermoplastic	ethylene vinyl acetate	EVA
	ethylene methyl acrylate	EMA
	atactic polypropylene	APP
	polyethylene	PE
	polypropylene	PP
thermoset	epoxy resin	
	polyurethane resin	PU

2.3. Microplastic

Although microplastics in the environment were already recognized as a problem in the 1970s [3], scientific research has massively expanded over the last 10 years. In this context, formation, accumulation, and prevention of microplastics in the environment have been studied, as well as their effects on human beings and nature.

The first definition of the term "microplastic" goes back to 2008, although it was initially only based on properties such as shape and size [3]. There is not yet a comprehensive, internationally recognized, and accepted definition that includes, for example, chemical constituents and substance groups [11]. There have been several initiatives to standardize the definition of microplastics, together with related research methods to harmonize the increasing number of findings [11,12].

In general, microplastics are defined as a heterogeneous mixture of objects made of plastics that occur under normal conditions as solid particles, fragments, fibers, granules, or pellets. The definition of a maximum particle size of 5 mm is widely accepted, as particles smaller than 5 mm can be easily ingested by organisms [11]. According to Table 2, plastics with particle sizes larger than 5 mm can be considered as "macroplastics" or "plastic litter" [3], while particles smaller than 5 mm can be categorized in "mesoplastic", "microplastic" and "nanoplastic", based on their particle size. To date, it is difficult to set thresholds for minimum sizes because most commonly used measuring devices cannot detect microplastics [5]; for the detection of such small particles, measuring technology and methods are currently still being developed.

Table 2. Categorization of plastics by size [11].

Designation	Size
Macroplastic	>5 mm
Mesoplastic	≤5 mm to >1 mm
Microplastic	≤1 mm to 0.1 µm
Nanoplastic	<0.1 µm

General agreement can be found in the definition of primary and secondary microplastics. Primary microplastics are produced in the appropriate size (e.g., friction bodies in cosmetics or plastic pellets), while secondary microplastics are produced by weathering and fragmentation of larger objects, such as plastic waste [3,13].

Considering composition, microplastic is an overall term for a large group of substances (polymers), which have different chemical and physical properties and enter the environment from different sources in different forms, causing various impacts. Based on the study of Wagner and Lambert [11], five criteria can be gathered that are commonly applied to define microplastics. Microplastics are:

1. Made of synthetic materials with a high polymer content,
2. Solid particles,
3. With a size of <5 mm,
4. Insoluble in water,
5. Non-degradable.

However, with respect to the first criterion, synthetic materials with a high polymer content would include all polymers, thus also including elastomers (rubber).

With regards to the pavement sector, scientific debate continues over whether tire abrasion should be included in microplastics [11]. The guidance document for Monitoring Litter in European Seas does not count tire abrasion as microplastics [11]; however, there are many studies that look at rubber, especially from tire abrasion, as a source of microplastics (e.g., [3,14]).

2.4. Waxes in Asphalt Pavements

Waxes are typically used as viscosity-changing additives in highly stressed road sections (highways) to increase resistance to permanent deformation [15–17]. Typically used wax types include Amide waxes, Montane waxes, and FT-waxes [16].

FT-wax (also called FT-paraffin) is synthesized during the conversion of natural gas or syngas over metal catalysts, to a mixture of hydrocarbons [18]. Due to the starting materials and manufacturing process, Fischer-Tropsch-synthesis cannot be assigned to classical polymerization. Additionally, polymers and paraffins can clearly be distinguished since paraffins have relatively small chain lengths, in the order of 10^1 to 10^3 hydrocarbon atoms [19], while the chain length of polymers is in the order of 10^5 hydrocarbon atoms [4]. Accordingly, paraffins are not considered as plastics or polymers [20,21].

Amide and Montane waxes consist of alkanoic acids, which are reacted with a different molecule (an amine or an alcohol) to form the wax. They are very similar to paraffins, but contain an additional carbon chain. The functional groups of alkanoic acid amines and alcohols influence chemical composition and properties in such a way that the waxes cannot be considered as polymers [21,22].

3. Materials and Methods

The practical part of this study compares the properties of modified binders using biodegradable waxes (Biomere) and conventional waxes (Sasobit®, Licomont®, and Asphaltan).

Conventional tests and rheological tests are performed to compare the effects of different waxes on bitumen properties. From a selection of different Biomer waxes, suitable products for use as viscosity modifying additives, and to replace conventional refined wax in asphalt road construction, are identified. The technical equivalence between selected Biomer products and conventional waxes is demonstrated, and the classification of viscosity modified binders, according to the German standards [23], is verified.

3.1. Materials

The bitumen used in the tests is a standard penetration graded bitumen 50/70, with a Softening Point Ring and Ball value of 51.3 °C, and a needle-penetration value of 64 1/10 mm. For modification, the conventional waxes Asphaltan A (from the Romonta company), Licomont® (from the Clariant company), and Sasobit® (from the Sasol company) are used. In addition, different Biomer waxes are used, which are produced and provided by Deurex® AG (Elsteraue, Germany). The Biomer waxes consist of different proportions of natural paraffins, sugarcane waxes, and their fatty acids. For example, wax BIT140 consists only of paraffin, while wax BIT111 is a mixture of paraffin and sugarcane wax. Through oxidative treatment, the carbon chain is changed and, depending on the chain length and different acid value, the biodegradability can be adjusted. The name of the Biomer waxes is derived from the melting range, prefixed with the acronym "BIT". In Table 3, all waxes are listed with the associated characteristic values, according to the manufacturer's specifications and delivery form.

Table 3. Used waxes with properties according to manufacturer's specifications.

Wax	Melting Range [°C]	Crystallinity [%]	Color	Delivery Form
BIT60	60	44	Brown	Granulate
BIT70	70	51	White	Granulate
BIT80	80	52	Brown	Granulate
BIT90	90	62	White	Granulate
BIT100	100	67	White	Granulate
BIT110	110	68	White	Granulate
BIT111	110	86	White	Powder
BIT120	120	84	Yellow	Granulate
BIT140	140	70	White	Granulate
BITBB	60–140	62	Brown	Granulate
Asphaltan A	125	75	Brown	Granulate
Licomont®	140	70	White	Granulate
Sasobit®	100	85	White	Granulate

Addition rate of wax to bitumen 50/70 is 3 wt.%.

For sample preparation, an amount of approximately 200 g of bitumen is heated to 160 °C, which is above the melting temperature of the waxes considered. While keeping the temperature constant, the respective wax is added to the heated bitumen and stirred at 200 rpm for three to five minutes, using a laboratory mixer with propeller blades. After the wax and bitumen have been mixed and homogenized properly, appropriate specimens for the conventional and rheological tests are prepared.

3.2. Testing Program

The testing program consists of six different test methods, as shown in Table 4.

Needle-penetration and Softening Point Ring and Ball are determined for all 14 material variants, according to European standards [24,25]. The penetration value is used to evaluate the effect of the wax on the hardness of the modified binder in the average temperature range, while the temperature of the softening point is a measure of the plasticity range.

Table 4. Testing program.

Material Variant	Conventional Tests Needle-Penetration	 Softening Point Ring and Ball	 BTSV Values	Rheological Tests Using DSR Phase Transition Temperature T_{PT}	 T-f-Sweep Test	 Relaxation Test
50/70	X	X	X	X	X	X
50/70 + 3% BIT60	X	X	X	X		
50/70 + 3% BIT70	X	X	X	X	X	X
50/70 + 3% BIT80	X	X	X	X		
50/70 + 3% BIT90	X	X	X	X	X	X
50/70 + 3% BIT100	X	X	X	X		
50/70 + 3% BIT110	X	X	X	X	X	X
50/70 + 3% BIT111	X	X	X	X	X	X
50/70 + 3% BIT120	X	X	X	X		
50/70 + 3% BIT140	X	X	X	X		X
50/70 + 3% BITBB	X	X	X	X		
50/70 + 3% Asphaltan A	X	X	X	X		
50/70 + 3% Licomont®	X	X	X	X		X
50/70 + 3% Sasobit®	X	X	X	X	X	X

3.3. Rheological Tests

Rheological tests are performed using a Dynamic Shear Rheometer (DSR). DSR test methods include the Binder-Fast-Characterization-Test, the determination of the phase transition temperature, temperature-frequency-sweeptests, and relaxation tests. The Binder-Fast-Characterization-Test (BTSV—in German "Bitumen-Typisierungs-Schnell-Verfahren) is performed according to European Standard prEN 14,763 [26]. As a result of the test, the temperature is determined at which the complex shear modulus G* equals 15 kPa, designated as T(BTSV), together with the respective phase angle δ(BTSV), at a frequency of 1.59 Hz. The temperature T(BTSV) is a measure for the binder hardness, while the phase angle δ(BTSV) provides information about the viscoelastic behavior of the material. Two replicates are performed for each material and the mean values are reported.

The phase transition temperature (T_{PT}) is the temperature where a viscosity modified binder shows a discernible increase in stiffness during cooling of the material, which can be attributed to the crystallization of the inherent organic wax. The phase transition temperature is determined by using a standardized procedure from Germany [27], using DSR in rotational mode. A parallel-plate geometry, with a diameter of 25 mm and a gap of 1 mm, is used with a constant shear rate of 2 s^{-1}. During the test, the test temperature is continuously decreased from 150 to 70 °C with a temperature rate of −0.02 K/s, and the shear stress is recorded at a measurement rate of 1 s^{-1}. The point at which the shear stress on a double-logarithmic scale, plotted against the temperature, disproportionately increases can be determined graphically, or by calculation as the phase transition temperature [27]. The phase transition temperature allows us to compare the temperature at which the wax in the modified binder begins to solidify. The arithmetic mean of two replicates is given as the phase transition temperature T_{PT}.

Temperature-frequency-sweep tests (T-f-Sweeps) are performed according to EN 14770 [28] to analyze the temperature-dependent viscoelastic behavior of viscosity modified binders, using the oscillation mode in DSR. The analyzed temperature ranges from −30 to +90 °C, and the frequency ranges from 0.1 Hz to 10 Hz. In the temperature range from +30 to +90 °C, a test geometry with a diameter of 25 mm and a gap of 1 mm is used. Parallel plates with diameters of 8 mm and 4 mm, with a gap of 2 mm, are used to test the temperature ranges from −10 to 40 °C and from −30 to 0 °C, respectively. Strain controlled mode is used for 25 and 8 mm geometries, and stress controlled mode is used for 4 mm geometry with strain and stress values within the LVE-range (linear viscoelastic range) of the material. Values of the complex shear modulus G* and the phase angle δ are reported as mean values from two replicates for the interpretation of stiffness and viscoelastic behavior over the entire temperature range. In this study, only the test frequency 1.59 Hz is considered.

Relaxation tests are performed in the DSR to evaluate the low temperature performance of the modified binders. The test is currently being prepared to be included in German technical regulations for bitumen and mastic testing [29–34]. The relaxation test is performed with the 4 mm parallel-plate geometry with a gap of 2 mm in a quasi-static mode. A constant shear strain of 0.1 % is applied to the specimen for a duration of 60 min, while the temperature is held constant (−15 and/or −20 °C). During the test, the shear stress resulting from the shear strain slowly decreases due to stress relaxation. From the results, the percentual decrease of the resulting shear stress after 60 min can be derived as a characteristic value for the relaxation capacity of the material. High values of percentual stress relaxation indicate favorable material behavior, which is attributed to an increased resistance to low temperature cracking [30].

4. Results

4.1. Conventional Tests

The results from Penetration and Softening Point Ring and Ball tests are presented in Figure 1. The red box indicates allowed specification values of binder 50/70, according to EN 12591 [35]. The tested bitumen 50/70 is exactly within the specified range.

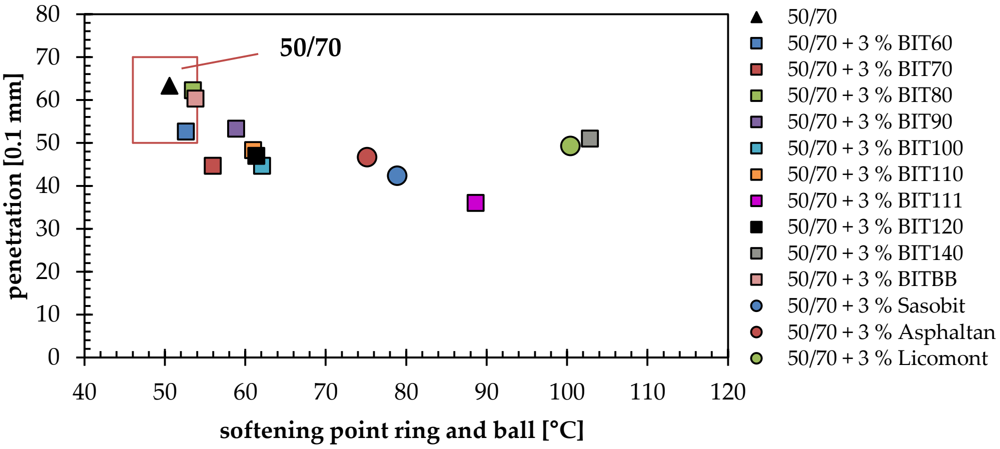

Figure 1. Softening Point Ring and Ball and Penetration values of different wax modified bitumen.

In all cases, the addition of wax leads to lower penetration values and increased softening point temperatures, demonstrating the stiffening effect at intermediate and high temperatures. However, the stiffening effect varies significantly in terms of the wax used. Biomer BIT 111 leads to the highest decrease in penetration, while Biomer BIT140 and Licomont® show the highest increase in softening point temperatures.

4.2. BTSV

BTSV results are illustrated in Figure 2, presenting the values for T(BTSV) on the *x*-axis and δ(BTSV) on the *y*-axis. In addition to the test data, boxes with black lines indicate typical ranges of BTSV-values for virgin asphalt binder grades [36,37]. The equi-shear modulus temperature T(BTSV) for all wax-modified binders is above the temperature of the unmodified bitumen, indicating the stiffening effect of the waxes. The largest increase in temperature T(BTSV) is observed for Biomer BIT111, which is very similar to the effect of Sasobit®. The phase angles δ(BTSV) of the modified binders are lower than those of the unmodified bitumen, as the binders become slightly more elastic due to the addition of wax. The variants modified with BIT140 and Licomont® show very similar BTSV-values.

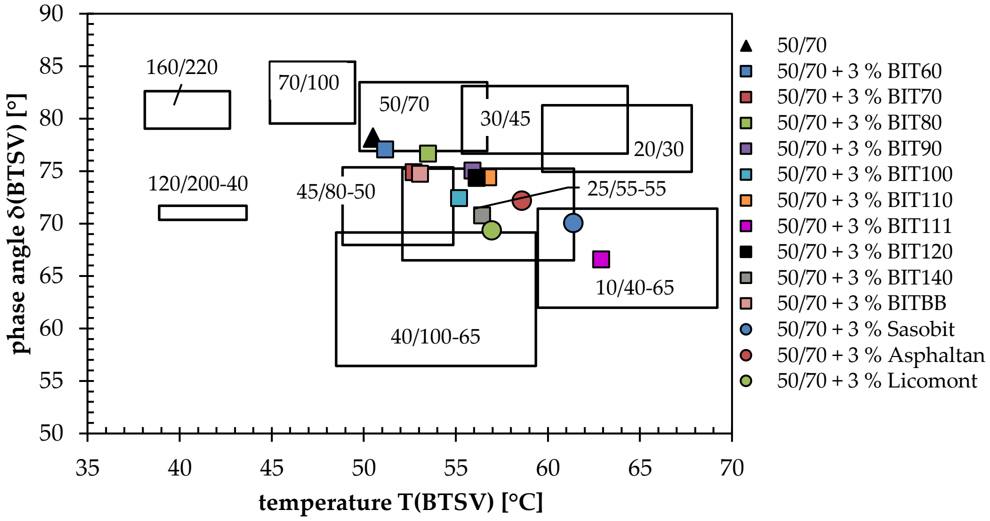

Figure 2. BTSV values of different wax modified bitumen.

4.3. Phase Transition Temperature

The results of the phase transition temperature (T_{PT}) tests from four different materials are shown in Figure 3. For the unmodified bitumen 50/70, a quasi-stationary increase of the shear stress can be observed with decreasing test temperature, while the shear stress is an indicator of the current material viscosity. For BIT140 and Licomont®, the shear stresses are below the one from plain bitumen above T_{PT}, demonstrating the viscosity reducing effect of the wax. At temperatures of 117 and 117.5 °C, a sudden and disproportionate increase in shear stress can be observed, which is designated as T_{PT} for these materials. Additionally, below around 105 °C for both materials, the stiffening effect of the added waxes is observed with a viscosity above that of the unmodified binder. While the curves of Biomer BIT140 and Licomont® are almost similar, Biomer BITBB shows a T_{PT} around 100 °C.

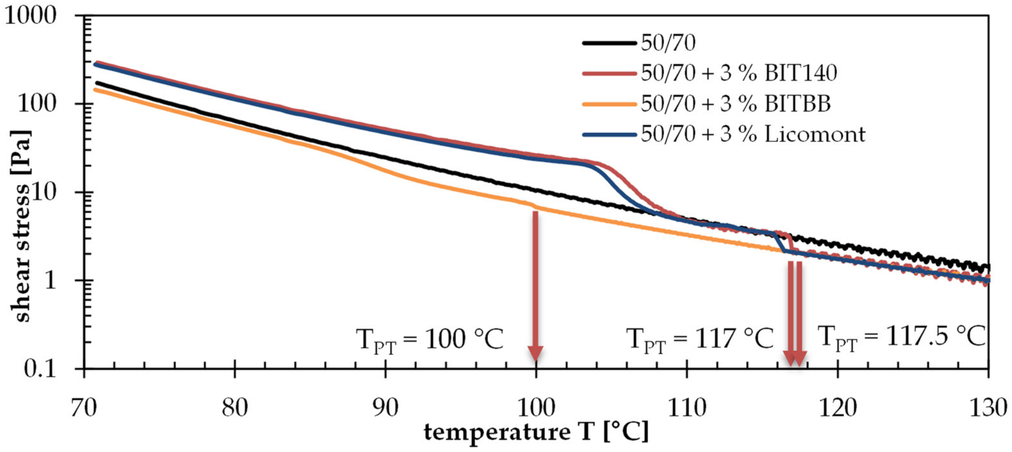

Figure 3. Test results of the determination of the phase transition temperature T_{PT} of unmodified bitumen 50/70 and variants 50/70 + 3% BIT140, 50/70 + 3% BITBB, and 50/70 + 3% Licomont®.

For many of the Biomer waxes included in this study (BIT60, BIT70, BIT80, BIT90, BIT100, BIT110, and BIT120) no T_{PT} can be determined within the viscosity range of the modified binder, since no disproportionate increase in shear stress is observed. For the variant 50/70 + 3% Asphaltan, it is possible to determine a T_{PT} of 84.5 °C, but no other variant of the tested Biomer waxes shows a similar behavior. When increasing the addition rate of Biomer to 6% a phase transition becomes visible for some binders, however, such addition rate is unrealistic for field application due to economic and technical reasons.

Figure 4 presents the shear stress curves of the variants with BIT111 and Sasobit®. These variants show similar behavior and the determined T_{PT} are in a similar temperature range, as T_{PT} = 85 °C for the binder with Sasobit® and T_{PT} = 87 °C for the binder with BIT111. The viscosity reducing effect of the waxes can be seen in the temperature range $T > T_{PT}$ due to shear stress, which is smaller than for the unmodified bitumen. After the increase of the phase temperature, the shear stress curve moves upwards, which demonstrates the stiffening effect of the waxes.

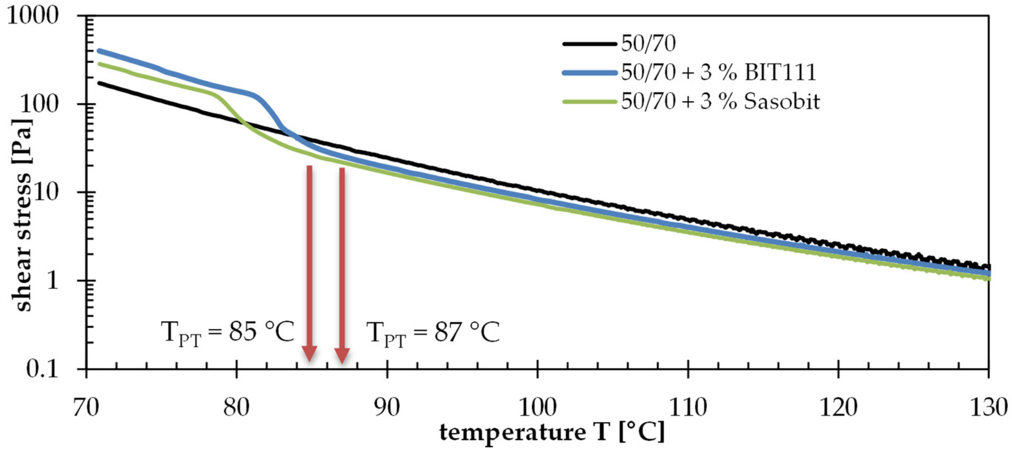

Figure 4. Test results of the determination of the phase transition temperature T_{PT} of unmodified bitumen 50/70 and the variants 50/70 + 3% BIT111 and 50/70 + 3% Sasobit®.

4.4. T-f-Sweep Tests

The following Figures present the complex shear modulus (G*) and the corresponding phase angle (δ) at a frequency of 1.59 Hz for a temperature range of −30 to 90 °C, which are composed of the individual test results of different test geometries.

Figure 5 presents the curves of G* and δ of unmodified bitumen 50/70 and of the one modified with 3% Biomer BIT70. With regards to the shear modulus evolution, an effect of the wax is observed at temperatures above 0 °C. From 0 to 60 °C, G* is higher compared to the unmodified bitumen, while from 60 °C onwards the curve of the wax-modified binder is below the curve of the unmodified bitumen. Initially, the wax has a stiffening effect, but as the temperature increases, the melting point of the wax (around 70 °C) is approached and the viscosity-reduction can be recognized by a reduced stiffness. As concerns the curve of δ, the effect of the wax is seen in a temperature range from −10 to 60 °C. In this range, δ is smaller compared to the unmodified bitumen, indicating an increased elastic behavior due to the wax.

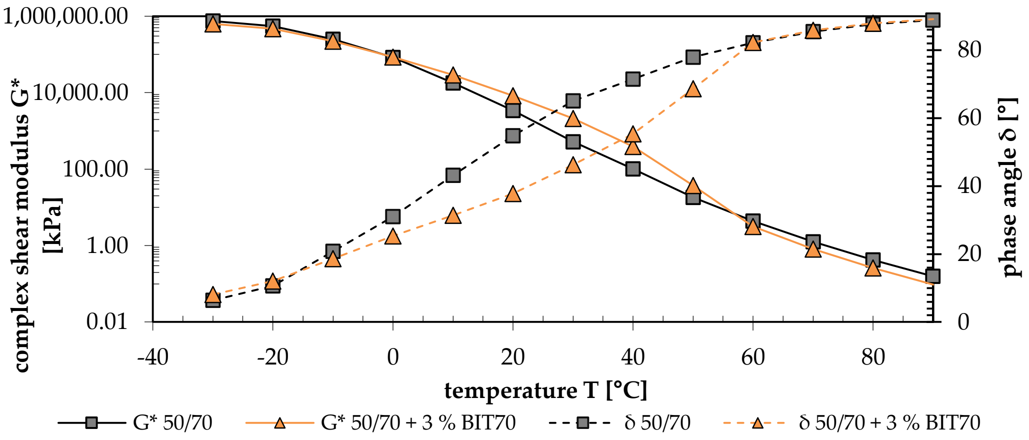

Figure 5. Complex shear modulus G* and phase angle δ for a frequency 1.59 Hz of unmodified bitumen 50/70 and the variant 50/70 + 3 % BIT70, as obtained from T-f Sweep tests in the DSR.

Figure 6 shows the test results of T-f-Sweep tests for the variants with BIT90 and BIT110 waxes, in comparison with the unmodified bitumen 50/70. Generally, G* and δ curves of these two wax variants are very similar. Above a temperature of 10 °C, an increase in G* is noticeable for both modified binders, which approaches G* of the unmodified bitumen in the range of high temperatures 80 °C and 90 °C. The viscosity-reduction of both waxes is not really visible since the test temperatures are below the expected melting points of the waxes. The δ of the variants shows the effect of the wax from a temperature of 0 °C onwards. As δ is reduced due to the addition of wax, the material behaves more elastic. In the high temperature range, however, the curves of δ of modified and unmodified bitumen converge.

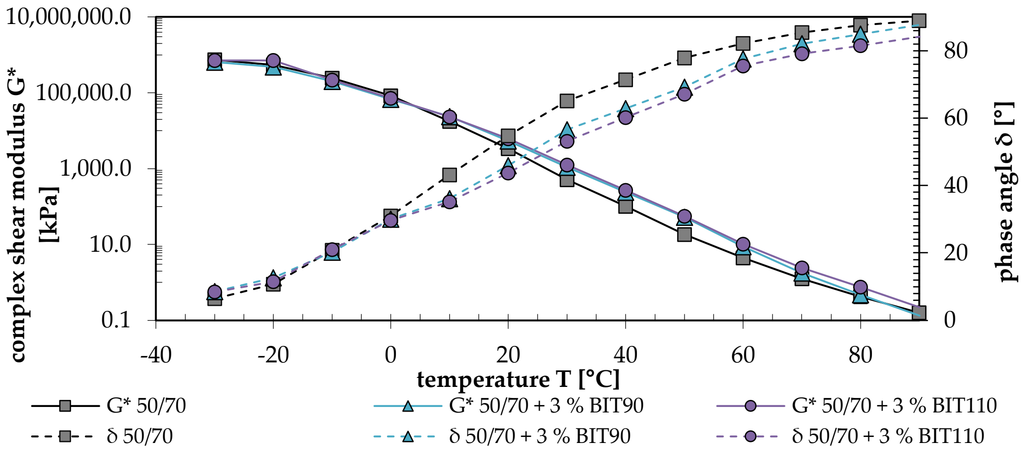

Figure 6. Complex shear modulus G* and phase angle δ for a frequency 1.59 Hz of unmodified bitumen 50/70, and the variants 50/70 + 3 % BIT90 and 50/70 + 3 % BIT110, as obtained from T-f-Sweep tests in the DSR.

The results of the T-f-Sweep tests of the modified binders with BIT111 and Sasobit® are illustrated in Figure 7. Both waxes show very similar effects on the rheological parameters. From a temperature of 0 °C onwards, the stiffening effect of the waxes is observed by higher shear modulus values, compared to the unmodified bitumen. The modification with waxes BIT111 and Sasobit® shows the greatest influence on δ of all waxes. The effective range of the wax begins at −10 °C, while the difference between the phase angles of the wax-modified binders and the unmodified bitumen becomes more and more distinct. The difference to the unmodified bitumen of approximately 20° is most distinct in the high temperature range. The material behavior becomes more and more elastic compared to the unmodified bitumen.

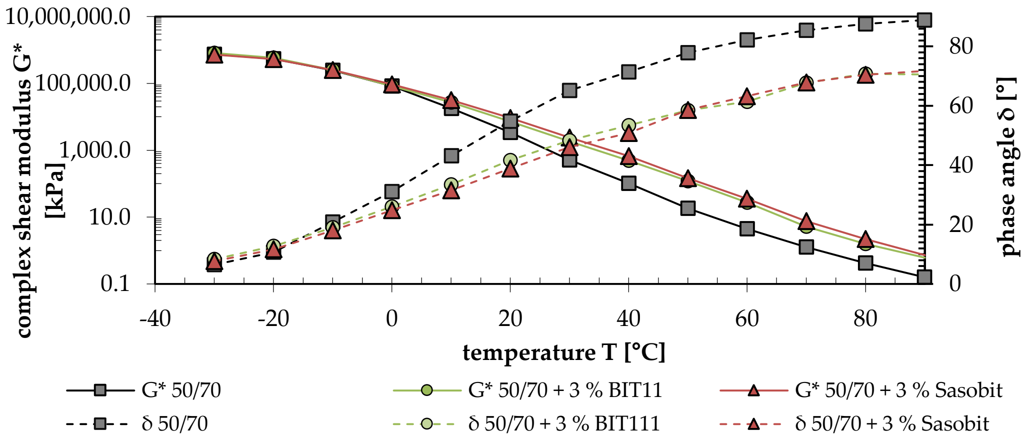

Figure 7. Complex shear modulus G* and phase angle δ for a frequency 1.59 Hz of unmodified bitumen 50/70, 50/70 + 3 % BIT111, and 50/70 + 3 % Sasobit®, as obtained from T-f-Sweep tests in the DSR.

4.5. Relaxation Tests

In T-f-Sweep tests, very similar rheological behaviors in terms of shear modulus G* and phase angle values δ are observed for wax-modified and unmodified bitumen in the low-temperature range from −30 to −10 °C. These values, however, do not ensure good low-temperature performance in terms of resistance to low-temperature cracking; therefore, relaxation tests are carried out for selected material variants. The stress relaxation observed after 60 min is shown in Figure 8, as observed for the investigated variants and the unmodified bitumen, including the mean value and the absolute deviation of the maximum and minimum values as error bars. It can be observed that all wax-modified binders show a lower stress relaxation than the unmodified bitumen, which indicates a disadvantageous influence on the low-temperature behavior. This influence varies depending on the variant. The variant with the wax BIT70 has a stress relaxation after 60 min of approximately 93%, and with a difference of 2% it shows the smallest deviation from the unmodified bitumen (stress relaxation $_{60\ \mathrm{min}}$ = 95%). Inferior low-temperature behavior is observed for the variant with Biomer BIT90, where a stress relaxation of 91% is found. The scatter of the individual results is <1%, so that a clear differentiation of the different materials is possible.

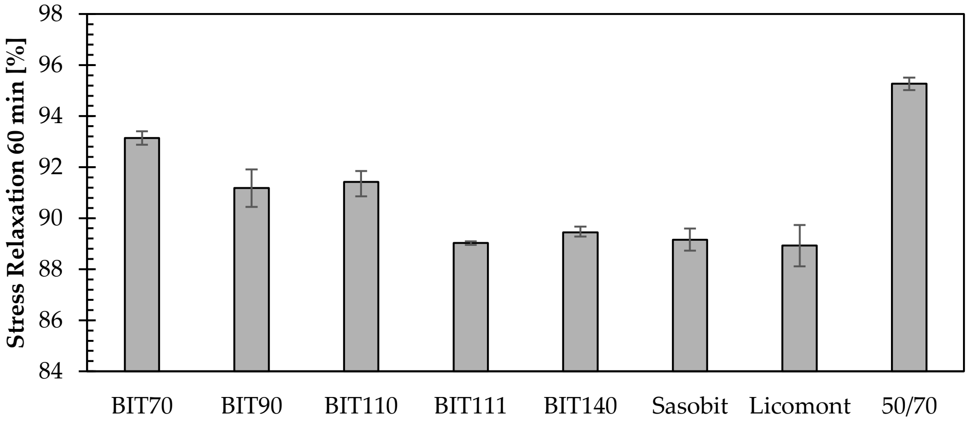

Figure 8. Results of stress relaxation tests for unmodified bitumen 50/70 and the variants 50/70 + 3% BIT70, 50/70 + 3% BIT90, 50/70 + 3% BIT110, 50/70 + 3% BIT111, 50/70 + 3% BIT140, 50/70 + 3% Sasobit®, and 50/70 + 3% Licomont®. The average values and the scatter of the individual measurements are shown.

The variants BIT140, BIT111, Licomont®, and Sasobit® all show very similar low-temperature behaviors, with a stress relaxation after 60 min of approximately 89%. The inferior relaxation capability can be explained by the higher crystallinity of the variants.

5. Discussion

All Biomer waxes clearly affect the binder properties, considering an addition rate of 3 wt.% to bitumen 50/70. Below the melting temperature, the Biomer usually increases the stiffness and elasticity, while above the melting temperature the Biomer decreases the stiffness (viscosity-reducing effect) and increases the viscous behavior. However, the modifying effect significantly differs throughout the different products, mainly because of the corresponding melting range of the wax, but also due to its molecular composition and origin. Based on the results presented, the Biomer BIT111 and Biomer BIT140 seem suitable for replacing conventionally refined waxes. The product BIT140 shows almost identical results to conventional wax Licomont®. With regard to DSR test results, the product BIT111 shows almost identical properties to the conventional wax Sasobit®.

In Germany, viscosity-modified binders can be classified according to the “recommendations for classification of viscosity-modified binders” [23], which is based on the same conventional and rheological binder properties as used in this study. Since the base bitumen considered in this study is of the type 50/70, the resulting modified bitumen can be classified either as 35/50 VL or 35/50 VH, where VL and VH stand for viscosity modified bitumen with low phase transition temperature and high phase transition temperature, respectively. The differentiation between VL and VH is based on the phase transition temperature obtained via DSR, considering a phase transition temperature of 100 °C as a distinguishing value. Based on the recommendations for classification in Germany [23], the Biomer BIT111 achieves all specification requirements for a binder 35/50 VL when added with 3 wt.% to 50/70. Likewise, the Biomer BIT140 achieves all specification requirements for a binder 35/50 VH, with the exception of the penetration value, which was 1 dmm above the specification limit.

Resistance to low-temperature cracking is an important property for the service life of asphalt pavements, and can be addressed by a binder relaxation test. Based on the results from relaxation tests in this study, it can be stated that wax modified binders show a generally unfortunate influence on low-temperature performance, compared to unmodified bitumen [16]. This is explained by crystallinity of the variants. The value represents the proportion of molecules in the wax that have arranged themselves in a crystalline structure, which can be determined by differential scanning calorimetry (DSC). The higher the degree of crystallinity, the stiffer and more brittle is the variant [38]. This behavior is clearly seen in relaxation test results. The variants with a lower degree of crystallinity show higher, and the ones with higher degrees of crystallinity show lower stress relaxation after 60 min (see Table 3 and Figure 8). However, the bio-degradable waxes show no adverse effects compared to conventionally refined waxes.

In Figure 9, the crystallinities of the waxes are compared to the characteristic rheological values T(BTSV) of the modified binders, which reliably represents binder stiffness/hardness. The results indicate a linear correlation between the crystallinity of the wax and the equi-shear modulus temperature T(BTSV) of the corresponding modified binder. Consequently, the crystalline molecule structure of the wax governs the modified binder stiffness; the correlation can be used to determine the optimum amount of a specific wax to achieve the desired binder properties.

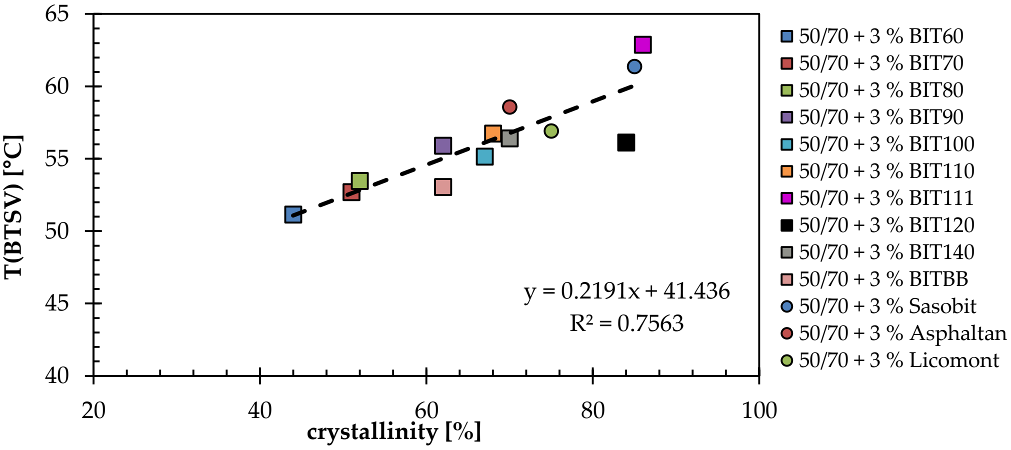

Figure 9. Comparison of the binders' characteristic value T(BTSV) to crystallinity as a property of the pure wax.

Microplastic in Asphalt Pavements

Asphalt mixture is the most frequently used material for road pavements, and is composed of petroleum-based materials (asphalt binder composed of bitumen and bitumen modifiers, where appropriate) and natural materials (aggregate). While it is well known that tire abrasion provokes significant emission of microplastic during pavement service-life (see Section 2.3), it is unclear if, and to what extent, the asphalt binder components contribute.

Bitumen consists of a vast variety of hydrocarbons that form large complex molecule structures. In general, bitumen is not assigned to polymers, as their molecules have not been polymerized from monomers, and have no defined weight distribution (see Section 2.1). Thus, bitumen cannot generate microplastic.

Waxes used for bitumen modification are also not polymers (see Section 2.4), and hence, they do not contribute to microplastic formation.

Polymers, conventionally used as bitumen modifiers (see Section 2.2), must be considered as a potential source for microplastic formation. However, the most frequently used polymer is styrene-butadiene-styrene (SBS), which is a (thermoplastic) elastomer and formally does not belong to the substance group of plastics (see Section 2.1). Obviously, depending on the formal definition of substance groups, polymer modifiers can be considered as a source of microplastic, or not.

To evaluate the microplastic hazards of road asphalt materials, share and particle size distribution of the substance used for asphalt mixtures need to be considered. Conventional waxes and polymers (thermoplastics and elastomers) typically melt within the hot bitumen during production, and are eventually well dispersed in the homogeneous composite. Ideally, the additive is completely dissolved, and is no longer visible in the binder composite by microscope. As particles within the binder composite cannot be identified, classification of microplastics in terms of share and particle size distribution is impossible.

Another important aspect when evaluating microplastic hazards, is bio-degradability of material components in function of time under specific environmental conditions. Bitumen itself is long-term bio-degradable [39], and is classified as not hazardous to water. It is unlikely that parts of bitumen are washed out from the asphalt mixture and penetrate the subbase layers with time. Similarly, polymer modifiers are not classified as hazardous substances by EU regulations [40]. Petroleum-based polymers are not bio-degradable [41].

By definition, microplastic is non-bio-degradable (see Section 2.3). Due to high stability and durability, polymeric materials accumulate rather than degrade in the environment [42]. While the bio-degradability of long-chain n-alkanes and iso-alkanes, paraffin waxes, and polyethylene waxes, have been successfully observed under laboratory conditions, their actual behavior in the environment is almost unknown. Paraffin-rich waxes show slight degradation when exposed to marine environment for 16 months [20]. In general, Fischer-Tropsch waxes are hardly bio-degradable [43,44]. According to the producer, the Biomer waxes used in this study all reach a value of at least 66% bio-degradation after 28 days of testing using the OECD 301B testing method [45], which indicates an advantage compared to the conventional waxes.

Regarding the amount of substance emitted from road pavements, current available data are limited. It is assumed that significant asphalt binder abrasion from the pavement surface occurs immediately after releasing the virgin pavement to traffic, when the thin binder film on the aggregate is rubbed off by tires, while it is rather limited during pavement service life, especially when compared to the share of tire abrasion. In most studies, tire and brake abrasion is investigated [46], while road abrasion quantification is focused on aggregate mineral dusts [47]. However, reported emissions from asphalt binder range from 1.5 to 228 g per inhabitant and year (g/cap·a), while tire abrasion is in the range of 1228.5 g/cap·a [3].

6. Conclusions

In this study, 10 different bio-degradable waxes (called Biomer) were added with 3 wt.% to bitumen 50/70 and compared to conventional synthetically refined waxes with regard to key rheological properties, such as needle-penetration, Softening Point Ring and Ball, BTSV values, phase transition temperature, T-f-Sweep, and relaxation test data. The following conclusions can be derived, based on conventional and rheological tests of the viscosity modified binders:

- The effect of Biomer waxes on bitumen properties was significantly affected by the composition and origin of the wax, and by the specific melting point of the Biomer. Below its melting point temperature, the Biomer increased stiffness and elasticity of the bitumen, while above the melting point temperature the Biomer decreased stiffness (viscosity-reducing effect) and increased viscosity. However, for many of the Biomer products considered in this study, no phase transition temperature was identified for the viscosity-modified binder, indicating that the effect of the Biomer is superimposed by the temperature dependent bitumen properties;

- Biomer BIT111 and Biomer BIT140 were identified as promising candidates to replace synthetic waxes Sasobit® and Licomont®, respectively, since the resulting properties of the viscosity-modified binders were quite similar. Additionally, the two types of Biomer waxes could also be used to create viscosity-modified binders, according to standard specifications. Based on the binder properties investigated in this study, selected bio-degradable waxes have the potential to completely replace conventionally refined waxes with no disadvantages regarding the binder properties;
- Replacing conventional FT waxes with Biomer waxes seems to have a negligible effect with regard to the reduction of microplastic. Instead, it is supposed to focus on the development of substitutes for polymer-modified bitumen, or on massively reducing tire abrasion. However, the application of Biomer as an alternative to FT waxes provides advantages in terms of environmental protection and resource conservation, since they are bio-degradable. Moreover, they are partly manufactured from renewable resources, as the raw material for Biomer is a waste product of sugar production. Hence, the use of Biomer supports the goal of an enhanced circular economy.

In order to ensure full suitability of Biomer waxes for practical road building applications, investigations should be extended to asphalt mastic and asphalt mixture testing by also including different base bitumen. Specifically, asphalt mixture performance should be analyzed with Biomer present, and the aging behavior should also be examined. Optimally, the wax-modified binder with Biomer should be applied in a test section, in order to be able to describe the behavior of the wax in the asphalt under in-situ conditions.

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