AN EXPERIMENTAL STUDY OF THE IMPACT OF AGING ON GILSONITE AND TRINIDAD EPURÉ MODIFIED ASPHALT BINDERS PROPERTIES

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Abstract. The tests and analyses presented in the paper are related to the 20/30, 35/50 and 50/70 penetration grade road bitumens as well as the asphalt binders obtained through modification of the 35/50 and 50/70 bitumens. The latter were modified by adding to it 3%, 5% and 7% of the Gilsonite natural asphalt and 15%, 25% and 35% of the Trinidad Epuré Z 0/8 natural asphalt. The aim of the study was to assess the changes in the functional and rheological properties of the road bitumens that were modified by adding to them the Gilsonite and Trinidad Epuré natural asphalts. The modified asphalt binders were subjected to the laboratory simulated short-term and long-term aging, where two methods, designed as part of the Strategic Highway Research Program, were used, i.e. the Rolling Thin Film Oven Test and the Pressure Aging Vessel, respectively. The study of the asphalt binders both those that were subjected to aging and those unaged includes thermal susceptibility (the Penetration Index) and resistance to cracking at low temperatures by tests carried out using the Bending Beam Rheometer. The analysis of the results revealed that the unfavourable impact of the aging process on the asphalt binder properties is limited if a suitable amount of the natural asphalt is used as a modifier.

Keywords: aging, low-temperature properties, modified binders, natural asphalt, temperature susceptibility, thermal cracking.

1. Introduction

Heavy traffic, especially, that of heavy vehicles, leads to the deterioration of the asphalt pavement in the form of cracks and permanent deformation. Therefore, to improve its durability various modifiers of asphalt binders are used ranging from the very popular ones such as polymers (Wang *et al.* 2015b), through the natural asphalts (Yilmaz, Çeloglu 2013), natural rubber (Al-Mansob *et al.* 2014) to the very specific ones such as, for example, the tourmalines (Wang *et al.* 2015a) or polyaminoamide (Haritonovs 2015). However, when modifying bitumen it is necessary to make an effort to find out what the effect of the added modifier on the aging process of the asphalt binder might be in manufacturing, paving of the asphalt mixture and operation of the asphalt pavement. For example, it is possible to determine whether the modifier added weakens or intensifies the aging of the asphalt binder by the changes observed in the values of the Penetration Index (*PI*), the Stiffness Modulus obtained at low temperatures or the critical temperature determined using the Bending Beam Rheometer (BBR) method.

The authors of this paper took on a task to assess the impact of the short and long-term aging on the changes in the functional and rheological properties of the asphalt binders manufactured using road bitumens modified by adding to them the Gilsonite and Trinidad Epuré natural asphalts. The aim of the paper is the assessment of the changes in the functional and rheological properties that were brought about by the aging of the asphalt binders modified by the selected natural asphalts. The benefits and risks related to the use of the Gilsonite and Trinidad Epuré natural asphalts as bitumen modifiers were presented, too. Therefore, the determination of the asphalt binder resistance to cracking at low temperatures due to the significant stiffening properties of the selected additives was of the paramount importance to the authors. Furthermore, a mathematical correlation between the content of the modifier and the critical temperature was also determined.

Yilmaz *et al.* (2013) described the benefits of using the asphaltites as modifiers of the asphalt binder. They contribute to the decrease of the negative influence of the short and long-term aging. On the other hand, however, they enhance the likelihood of cracking of asphalt mixtures at low temperatures.

Gilsonite (named after Samuel H. Gilson, the discoverer of the mineral deposits) also known in academic circles as Uintaite or Uintahite is mined in the north-eastern part of

Utah (USA) in the Uintah Basin. Gilsonite is a shiny, black and solid hydrocarbon from the asphaltite group. The mineral is a natural compound of (based on product weight): carbon – 85%, hydrogen – 10%, nitrogen – 3% as well as oxygen, sulphur and other elements in an amount of about 2% (Boden, Tripp 2012; Nciri *et al.* 2014). After being crushed, it is delivered to customers in the form of granules with a grain size of 0/2 mm or as a powder (Cholewińska, Iwański 2011). A very high content of pure asphalt binder is the characteristic feature of Gilsonite, i.e. about 98% by its weight. A mineral with very similar characteristics exists in Iran where it is called Iranian natural bitumen (Iranian Gilsonite) (Ameri *et al.* 2011). Due to its origin, chemical composition and high molecular mass Gilsonite shows a strong affinity with petroleum bitumen. The use of this additive to modify petroleum bitumen results in the decrease of the penetration value and the softening point rise (Słowik *et al.* 2012). The addition of Gilsonite causes an increase in resistance of asphalt binders containing it, before and after aging, to permanent deformation at high temperatures (an increase in the value of the $\frac{G^*}{\sin\delta}$ parameter). Asphalt mixtures modified by adding Gilsonite are characterised by greater stability and narrower range of permanent deformation. Therefore, they are more resistant to ruts and at the same time they do not show any tendency towards fatigue and low temperature cracking (Aflaki *et al.* 2014; Ameri *et al.* 2012; Babagoli *et al.* 2015).

Trinidad Epuré natural asphalt is dug out from Trinidad Pitch Lake located near the town of La Brea on Trinidad Island on the Caribbean Sea (Yilmaz, Çeloglu 2013). The excavated asphalt is subjected to a refining process to soften it, evaporate unbound water and chemical compounds dissolved in it as well as to separate mineral and organic impurities such as stones or wood. This technology allows obtaining the final product in the form of purified asphalt known as Trinidad Epuré (TE) or Trinidad Lake Asphalt (TLA). The content of its weight is as follows: the asphalt binder – from 53% to 55%, mineral dust – from 36% to 37%, ash – from 9% to 10%. The trade name of Trinidad Epuré Z 0/8 is interpreted as TE natural asphalt crushed to the grain size of 0/8 mm with the addition of an anti-caking agent – diatomaceous earth (amorphous silica) with the grain size <0.063 mm. This anti-craking agent does not alter the composition of the product discussed (according to the 2013 *Laborhandbuch für Trinidad Naturasphalt* Laboratory Manual for Trinidad Naturasphalt). Research conducted by Liao *et al.* (2014) and Widyatmoko, Elliott (2008) concerning the modification of road bitumens by adding Trinidad Epuré showed that this additive reduces the penetration value, increases the softening point and resistance to permanent deformation at high temperatures (an increase in the value of the $\frac{G^*}{\sin\delta}$ parameter). An improvement in the workability and ability to compact of the asphalt mix was observed in the case of road pavement made of asphalt mixture that was prepared using an asphalt binder with the addition of Trinidad Epuré (Danowski 2009). This modifier also has a positive effect on increasing adhesion between the asphalt binder and the aggregate resulting in greater resistance of the asphalt mixtures to an adverse impact of water (Feng *et al.* 2014). Asphalt binder aging is a complex process that affects the changes that occur in the composition and chemical structure of bitumen with time. As a result of aging the quality of the asphalt binder is deteriorated. The intensity of the changes occurring during aging is affected by the chemical composition of the asphalt but also the length of time during that the factors determining this process such as temperature or the exposure to oxygen from the air are active. While examining the aging of the asphalt binder, two different stages are distinguished, i.e. the short-term and long-term aging. The latter refers to those changes that affect the asphalt binder during the production of the asphalt mixture, its transportation, paving and compacting of the road pavement layer. Then bitumen is exposed to high temperature (usually in the range 140–200 ºC) and the oxygen coming from the air. As a result of this exposure, various aging processes such as evaporation of the oil fractions and bitumen oxidation occur (Nivitha *et al.* 2015; Wang *et al.* 2015b). The aging of the asphalt binder takes from a few to several hours. One of the laboratory tests developed as part of the Strategic Highway Research Program (SHRP) to simulate short-term aging processes is the Rolling Thin Film Oven Test (RTFOT) described in *EN 12607-1:2014 Bitumen and Bituminous Binders. Determination of the Resistance to Hardening under Influence of Heat and Air. RTFOT Method.* The long-term aging, on the other hand, refers to gradual changes in the properties of the asphalt binder during the whole lifetime of the road pavement. The intensity of this process is greatly influenced by the location of the asphalt layer in the road pavement structure. The greatest changes in the properties of the asphalt binder are observed in the wearing course. The interaction between asphalt binder and the oxygen coming from the air leads to gradual oxidation of its components, finally resulting in the irreversible changes in its composition and chemical structure. Furthermore, the process is also intensified by adverse weather conditions, exposure to solar radiation and the environmental factors such as water or chemicals used for de-icing the roads. The temperature of the road pavement while in use rarely exceeds 60 °C and therefore this is not a factor of crucial importance to the long-term aging. The type and amount of bitumen used in the asphalt mixture, the voids in the asphalt pavement layer as well as the type of the aggregate and its grain size influence the process discussed to a far greater degree (Nivitha *et al.* 2015; Xiao *et al.* 2012). The laboratory test method, which is most often used to simulate the long-term aging, is the method designed as part of the SHRP, i.e. Pressure Aging Vessel (PAV) described in *EN 14769:2012 Bitumen and Bituminous Binders. Accelerated Long-Term Ageing Conditioning by a Pressure Ageing Vessel (PAV).*

2. Experimental

2.1. Materials

Three petroleum road bitumens 20/30, 35/50 and 50/70 penetration grade were selected for the examination. All three of them were made of Russian (Uralic) crude oil. The bitumens 35/50 and 50/70 penetration grade were modified by the addition of the powdered Gilsonite natural asphalt and the Trinidad Epuré Z 0/8 natural asphalt.

The procedure of preparing the asphalt binders consisted in initial preheating of the containers with the 35/50 and 50/70 bitumens to the temperature specified for the modifier used. When Gilsonite was the modifying agent, the temperature was 185 °C for both bitumens. In the case of Trinidad Epuré, the 35/50 bitumen was heated to 175 °C while the 50/70 one to 165 °C. Next, natural bitumens in appropriate proportions were added and such modified asphalt binders were further heated in a laboratory oven. Then, a laboratory blender was used to make the asphalt binders obtained earlier homogeneous (speed – 400 rpm, blending time – 3 min).

The amount of the Gilsonite and Trinidad Epuré natural asphalts added to the road bitumens 35/50 and 50/70 penetration grade was calculated in such a way so as to obtain asphalt binders with similar penetration values, i.e. it was assumed that the differences in the determined penetration values will be less than 2 mm/10. After a series of preliminary tests carried out to determine penetration at 25 °C for the asphalt binders containing various amounts of natural asphalt, only those samples that contained 3%, 5%, 7% of Gilsonite and 15%, 25%, 35% of Trinidad Epuré were selected.

Next, the asphalt binders obtained were labelled accordingly, first giving the penetration grade of the petroleum bitumen and then the content and type of the modifier used. Gilsonite was labelled as GIL for short and Trinidad Epuré as TE. Here is a sample description of the specimens:

– 35/50 penetration grade bitumen with the addition of 3% of Gilsonite – labelled as 35/50+3% GIL;

– 50/70 penetration grade bitumen with the addition of 25% of Trinidad Epuré – labelled as 50/70+25% TE.

2.2. Test methods

2.2.1. Temperature susceptibility

To determine temperature susceptibility of the asphalt binders that was examined in the paper, the values of the *PI* were calculated according to Eq (1) given in *EN 12591:2009 Bitumen and Bituminous Binders. Specifications for Paving Grade Bitumens* using the penetration values determined according to *EN 1426:2007 Bitumen and Bituminous Binders. Determination of Needle Penetration* and values of softening point determined according to *EN 1427:2007 Bitumen and Bituminous Binders. Determination of Softening Point. Ring and Ball Method.*

$$PI = \frac{20 T_{R\&B} + 500 \log(Pen_{25}) - 1952}{T_{R\&B} - 50 \log(Pen_{25}) + 120}, \qquad (1)$$

where Pen_{25} – penetration at 25 °C according to *EN 1426*, mm/10; $TR\&B$ – softening point according to *EN 1427*, °C.

2.2.2. The investigation of low-temperature behaviour using the Bending Beam Rheometer

The experiment was carried out using the BBR according to *EN 14771:2012 Bitumen and Bituminous Binders. Determination of the Flexural Creep Stiffness. Bending Beam Rheometer (BBR)* at –32 °C, –24 °C, –16 °C and –8 °C on asphalt binders that were not subjected to aging and those that underwent the process using the RTFOT and the PAV methods. The test using the BBR involves the determination of the stiffness modulus by measuring a deflection in the function of time of the bitumen beam bent under a constant load at low temperatures.

A simply supported beam is loaded at its centre with the force of 980±50 mN for 240 s. Bending occurring in the middle of the beam (between the supports) is constantly recorded during the test. It serves as a basis for calculating the values of the stiffness modulus expressed in Pascal according to Eq (2) as well as the quantity that is characteristic of the intensity of stiffness changes as a function of loading time *m*-value *m(t)* according to Eq (3).

$$S_m(t) = \frac{PL^3}{4bh^3 \delta(t)}, \text{MPa}, \qquad (2)$$

$$m(t) = \frac{\log S_m(t)}{\log(t)}, \qquad (3)$$

where P – loading of the specimen, P = 981±10 mN; L – distance between the supports, L = 101.6 mm; b – width of the specimen, b = 12.7 mm; h – height of the specimen, h = 6.3 mm; $\delta(t)$ – deflection of the specimen at time t.

The values determined for the stiffness modulus and the *m*-value of the asphalt binders tested were used to calculate the critical temperature T_{cr} according to Eq (4), by the regulations developed as part of the American research programme SHRP and the Superpave specifications

$$T_{cr} = \max(T_{s=300\text{MPa}}, T_{m=0.3}) - 10, \text{°C}, \qquad (4)$$

where $T_{s=300\text{MPa}}$ – temperature at which the stiffness modulus determined after time t = 60 s reaches the value of 300 MPa; $T_{m=0.3}$ – temperature at which the *m*-value determined after time t = 60 s reaches the value of 0.3.

2.2.3. Aging process

The test known as the RTFOT and carried out according to the *EN 12607-1* standard is designed to simulate short-term aging processes of the asphalt binder under laboratory conditions. This method consists of exposing a thin layer of asphalt binder to hot air for 75±1 min. Glass bottles with the samples of the asphalt binder are placed in a special disc that rotates at 15.0±0.2 rpm located in a laboratory oven. The samples of asphalt binder in bottles are subjected to a temperature of 163±1 °C as well as compressed

air with the flow rate of 4.0±0.2 l/min and the maximum pressure of 200 kPa.

Before aging using the PAV method, the asphalt binder is aged using the RTFOT method. As a result of such a procedure, first the binder is subjected to the process of short-term aging (that occurs during the process of manufacturing and paving of the asphalt mixture) and after that the process of long-term aging (that occurs during the operation of the pavement made of asphalt mixture).

The PAV test according to the *EN 14769:2012* standard involves subjecting a bitumen specimen to the atmospheric pressure of 2.1±0.1 MPa for 20 hrs at a temperature of 90±0.2 °C, 100±0.2 °C or 110±0.2 °C (in the tests carried out for the purpose of the present study the temperature of 100±0.2 °C was applied). The whole process is supposed to simulate the changes taking place in the structure of bitumen during 5–10 years of the asphalt pavement operation.

3. Test results

3.1. Temperature susceptibility

Tables 1 and 2 show the results of penetration determined at 25°C according to the *EN 1426:2007* and softening point

determined according to the *EN 1427:2007* of the unaged and aged asphalt binders as arithmetic means and measure uncertainties at a significance level of α = 0.05 (Słowik 2010). The penetration values at 25 °C decreased (Fig. 1) and the softening point values increased (Fig. 2) as a result of the aging of the asphalt binders using the RTFOT and the PAV methods. Figure 3 shows the values of the *PI* calculated by Eq (1).

3.2. Behaviour at low temperatures

Tables 3 to 6 show the results of the determination of the stiffness modulus and the *m*-value using the BBR method as arithmetic means and measure uncertainties at a significance level of α = 0.05 (Słowik 2010). The tests of the reference asphalt binders and those modified by natural bitumens, both unaged and aged by the RTFOT and the PAV methods were carried out at –24 °C, –16 °C and –8 °C. The values for which disadvantageous results were obtained are printed in bold. They are labelled disadvantageous with regard to their resistance to the formation of the thermally induced cracks (at low temperature) in an asphalt mixture that is to be used in the road pavement. According to the Superpave specification the asphalt

Table 1. The values of penetration and softening point for the Gilsonite modified asphalt binders

Asphalt binder	Penetration at 25 °C, mm/10			Softening point, °C		
	unaged	after		unaged	after	
		RTFOT	RTFOT+PAV		RTFOT	RTFOT+PAV
20/30	25.6±0.5	19.9±0.7	8.7±1.5	63.6±0.2	71.0±0.4	82.3±0.5
35/50	40.8±0.3	25.5±0.8	17.0±1.8	55.9±0.5	61.7±0.3	72.3±0.9
35/50+3% GIL	27.2±0.3	21.0±0.3	10.8±0.7	61.1±0.2	65.9±0.3	76.4±0.4
35/50+5% GIL	24.4±0.5	17.7±0.3	8.8±0.5	62.9±0.3	69.1±0.3	78.5±0.6
35/50+7% GIL	19.8±0.3	17.0±0.3	7.8±1.4	65.3±0.2	71.3±0.8	81.4±0.5
50/70	55.9±0.7	36.7±1.1	20.5±1.5	51.6±0.2	57.1±0.3	67.2±0.4
50/70+3% GIL	38.6±0.3	26.7±0.3	15.4±0.8	55.8±0.4	61.1±0.4	71.9±0.6
50/70+5% GIL	32.6±0.4	21.5±0.3	13.0±0.6	57.2±0.3	65.2±0.3	74.2±0.3
50/70+7% GIL	26.6±0.7	18.7±0.3	12.2±0.3	60.4±0.4	67.3±0.7	77.0±0.3

Table 2. The values of penetration and softening point for the Trinidad Epuré modified asphalt binders

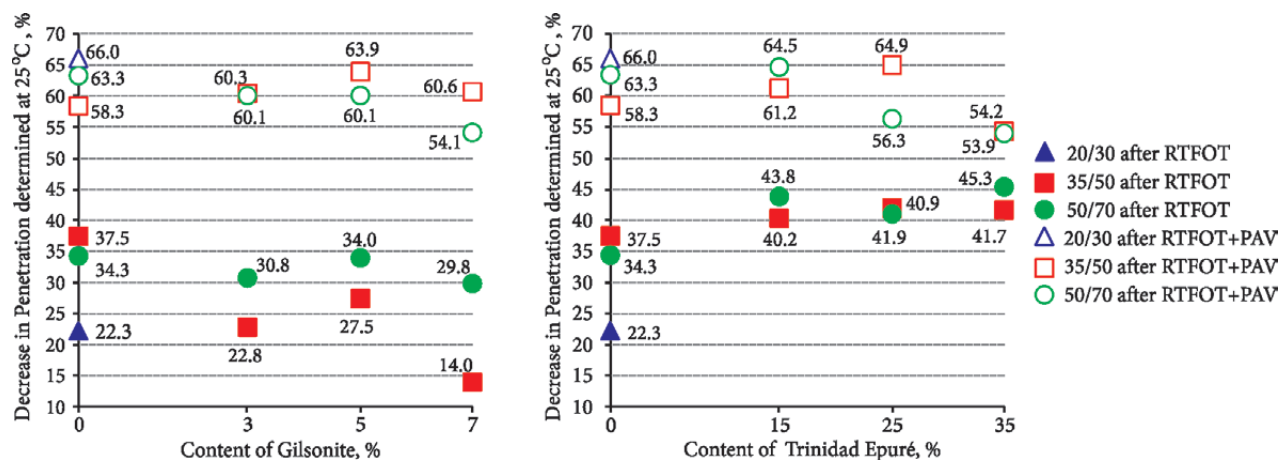| Asphalt binder	Penetration at 25 °C, mm/10			Softening point, °C		
	unaged	after		unaged	after	
		RTFOT	RTFOT+PAV		RTFOT	RTFOT+PAV
20/30	25.6±0.5	19.9±0.7	8.7±1.5	63.6±0.2	71.0±0.4	82.3±0.5
35/50	40.8±0.3	25.5±0.8	17.0±1.8	55.9±0.5	61.7±0.3	72.3±0.9
35/50+15% TE	28.6±0.7	17.1±0.3	11.1±0.7	57.5±0.3	66.5±0.4	77.3±0.2
35/50+25% TE	24.8±0.3	14.4±0.4	8.7±0.7	59.5±0.2	68.0±0.3	81.8±0.6
35/50+35% TE	19.2±0.5	11.2±0.6	8.8±1.4	62.0±0.2	70.1±0.3	83.8±0.3
50/70	55.9±0.7	36.7±1.1	20.5±1.5	51.6±0.2	57.1±0.3	67.2±0.4
50/70+15% TE	39.7±0.6	22.3±0.7	14.1±0.7	53.3±0.3	62.1±0.3	74.4±0.5
50/70+25% TE	32.0±0.6	18.9±0.7	14.0±1.0	55.7±0.3	64.4±0.4	77.1±0.6
50/70+35% TE	25.8±0.6	14.1±0.8	11.9±6.0	58.6±0.4	67.1±0.3	78.9±0.3

Fig. 1. A decrease in the penetration value at 25 °C of the Gilsonite and Trinidad Epuré modified asphalt binders as a result of aging using the RTFOT method and aging using both the RTFOT and the PAV methods
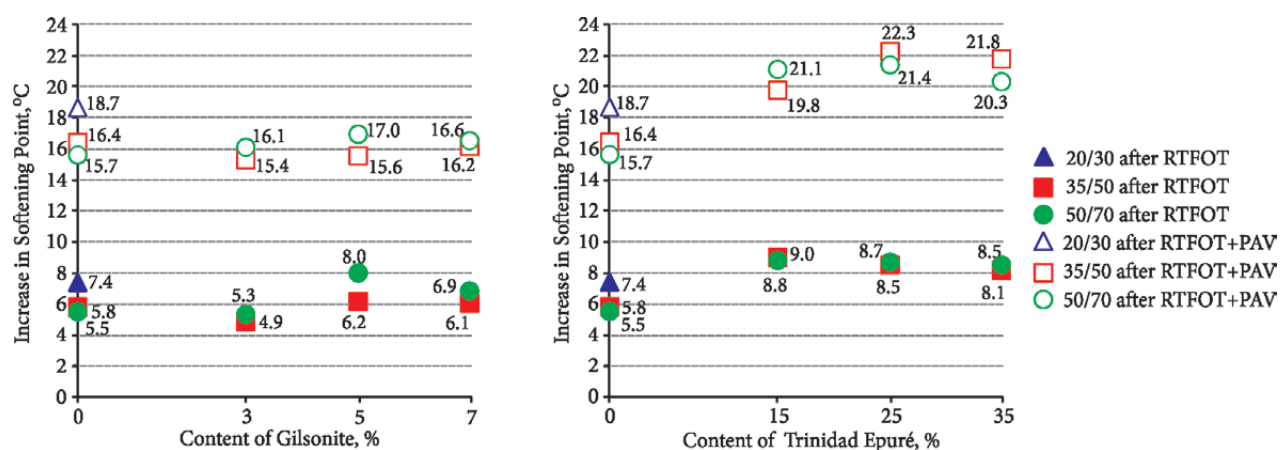

Fig. 2. The softening point rise of the Gilsonite and Trinidad Epuré modified asphalt binders as a result of aging using the RTFOT method and aging using both the RTFOT and the PAV methods
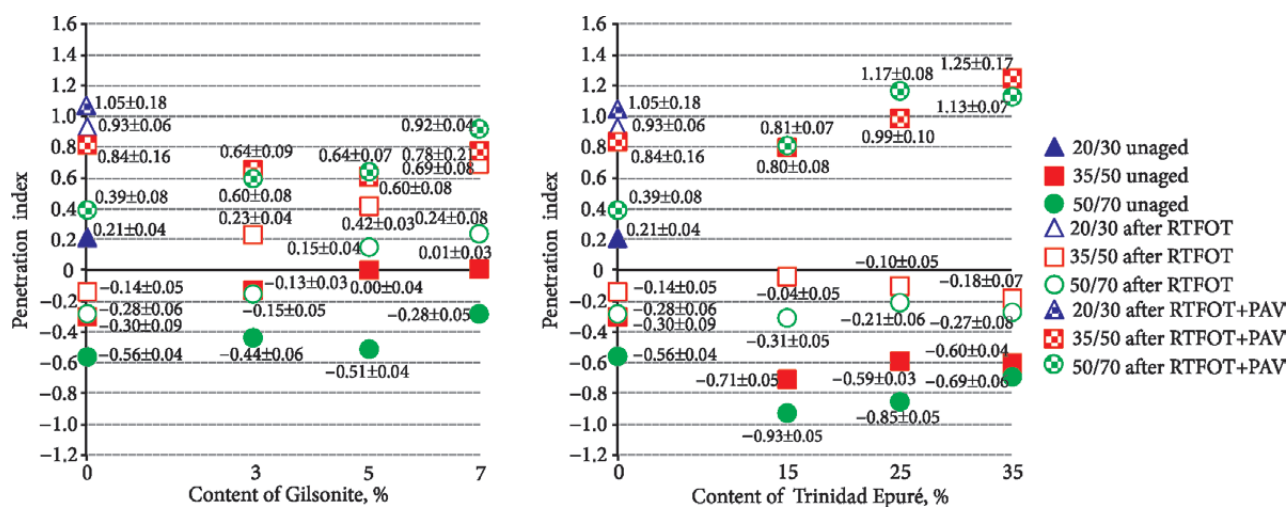

Fig. 3. The values of the Penetration Index for the Gilsonite and Trinidad Epuré modified asphalt binders

binder shows resistance to cracking at low temperature, when values of $S_m > 300$ MPa and $m < 0.3$ (determined at the loading time $t = 60$ s). In the case of unaged 50/70 penetration grade bitumen the lack of results for the stiffness modulus and the m-value at –8 °C is caused by exceeding the standard allowable deflection of the specimen during the test. Therefore, an additional test was performed to determine the values of the parameters mentioned above at –32 °C. The following results were obtained: the stiffness modulus $S = 880\pm112$ MPa and $m = 0.199\pm0.016$.

Table 3. Results of the stiffness modulus determination at –24 °C, –16 °C and –8 °C for the Gilsonite modified asphalt binders

Asphalt binder	Stiffness modulus determined after 60 s of loading, MPa								
	–24 °C			–16 °C			–8 °C		
	unaged	after		unaged	after		unaged	after	
		RTFOT	RTFOT+ PAV		RTFOT	RTFOT+ PAV		RTFOT	RTFOT+ PAV
20/30	451±28	513±32	562±4	208±13	244±8	279±16	63±4	98±9	110±11
35/50	427±29	507±8	535±8	150±7	182±8	240±3	46±5	52±3	86±4
35/50+3% GIL	526±26	554±9	551±2	186±8	231±7	268±5	66±1	85±1	101±2
35/50+5% GIL	588±29	631±28	590±7	217±9	244±23	296±2	71±4	88±1	114±7
35/50+7% GIL	590±45	644±34	612±9	250±9	255±16	322±8	86±9	92±8	125±3
50/70	421±17	481±21	495±18	128±9	166±13	197±2	–	44±3	70±4
50/70+3% GIL	510±16	528±24	537±7	172±15	200±14	243±6	52±6	63±6	84±2
50/70+5% GIL	555±23	616±4	559±10	198±4	222±11	266±9	57±4	76±4	92±2
50/70+7% GIL	558±17	599±70	586±10	231±14	252±20	289±3	69±6	88±9	110±2

Table 4. Results of the stiffness modulus determination at –24 °C, –16 °C and –8 °C for the Trinidad Epuré modified asphalt binders

Asphalt binder	Stiffness modulus determined after 60 s of loading, MPa								
	–24 °C			–16 °C			–8 °C		
	unaged	after		unaged	after		unaged	after	
		RTFOT	RTFOT+ PAV		RTFOT	RTFOT+ PAV		RTFOT	RTFOT+ PAV
20/30	451±28	513±32	562±4	208±13	244±8	279±16	63±4	98±9	110±11
35/50	427±29	507±8	535±8	150±7	182±8	240±3	46±5	52±3	86±4
35/50+15% TE	601±63	620±25	628±9	209±6	257±38	305±16	66±5	78±5	116±4
35/50+25% TE	687±18	738±51	726±9	251±8	317±12	366±5	86±2	108±5	165±7
35/50+35% TE	830±50	905±16	800±8	329±15	382±21	432±13	105±8	156±20	186±4
50/70	421±17	481±21	495±18	128±9	166±13	197±2	–	44±3	70±4
50/70+15% TE	550±77	598±18	609±9	187±8	212±6	278±9	50±4	55±4	112±4
50/70+25% TE	668±24	718±55	710±2	244±13	287±23	335±10	68±8	87±8	144±5
50/70+35% TE	801±58	862±43	797±8	319±14	374±22	413±7	96±3	128±7	181±2

Table 5. Results of the *m*-value determination at –24 °C, –16 °C and –8 °C for the Gilsonite modified asphalt binders

Asphalt binder	m-value$\cdot 10^{-3}$ after 60 s of loading								
	–24 °C			–16 °C			–8 °C		
	unaged	after		unaged	after		unaged	after	
		RTFOT	RTFOT+ PAV		RTFOT	RTFOT+ PAV		RTFOT	RTFOT+ PAV
20/30	243±4	236±16	206±6	314±6	291±13	258±22	404±9	348±10	304±6
35/50	276±10	243±38	225±13	355±5	328±4	279±6	458±5	431±9	348±13
35/50+3% GIL	243±8	224±6	220±9	355±10	301±3	263±10	426±6	383±3	331±4
35/50+5% GIL	222±3	212±0	210±4	319±3	292±3	253±4	413±3	367±3	329±4
35/50+7% GIL	216±6	213±8	209±13	301±5	289±13	246±22	400±3	363±3	316±3
50/70	292±10	255±4	244±4	385±3	355±10	310±16	–	456±9	382±9
50/70+3% GIL	261±3	240±3	232±1	356±8	333±3	285±3	459±3	424±8	365±3
50/70+5% GIL	247±10	227±3	218±13	348±3	320±3	268±4	450±8	395±3	350±3
50/70+7% GIL	233±4	215±8	210±13	323±5	298±5	267±4	426±5	389±5	340±6

Table 6. Results of the *m*-value determination at −24 °C, −16 °C and −8 °C for the Trinidad Epuré modified asphalt binders

Asphalt binder	*m*-value·10⁻³ after 60 s of loading								
	−24 °C			−16 °C			−8 °C		
	unaged	after		unaged	after		unaged	after	
		RTFOT	RTFOT+ PAV		RTFOT	RTFOT+ PAV		RTFOT	RTFOT+ PAV
20/30	**243±4**	**236±16**	**206±6**	314±6	**291±13**	**258±22**	404±9	348±10	304±6
35/50	**276±10**	243±38	**225±13**	355±5	328±4	**279±6**	458±5	431±9	348±13
35/50+15% TE	**243±16**	**227±8**	**212±10**	332±3	305±4	**263±10**	431±5	394±10	325±3
35/50+25% TE	**230±13**	**210±13**	**207±3**	315±3	**289±1**	**253±6**	415±3	372±6	**288±4**
35/50+35% TE	**219±22**	**202±10**	**192±4**	**297±10**	**269±10**	**240±4**	401±3	350±4	**289±9**
50/70	**292±1**	**255±4**	**244±4**	385±3	355±10	310±16	–	456±9	382±9
50/70+15% TE	**269±1**	**240±6**	**220±10**	361±11	332±6	280±10	472±5	431±9	335±6
50/70+25% TE	**240±3**	**225±16**	**204±10**	335±8	307±10	264±6	453±8	401±4	**298±6**
50/70+35% TE	**227±13**	**204±13**	**203±4**	321±10	**287±13**	**247±1**	425±6	380±9	**298±6**
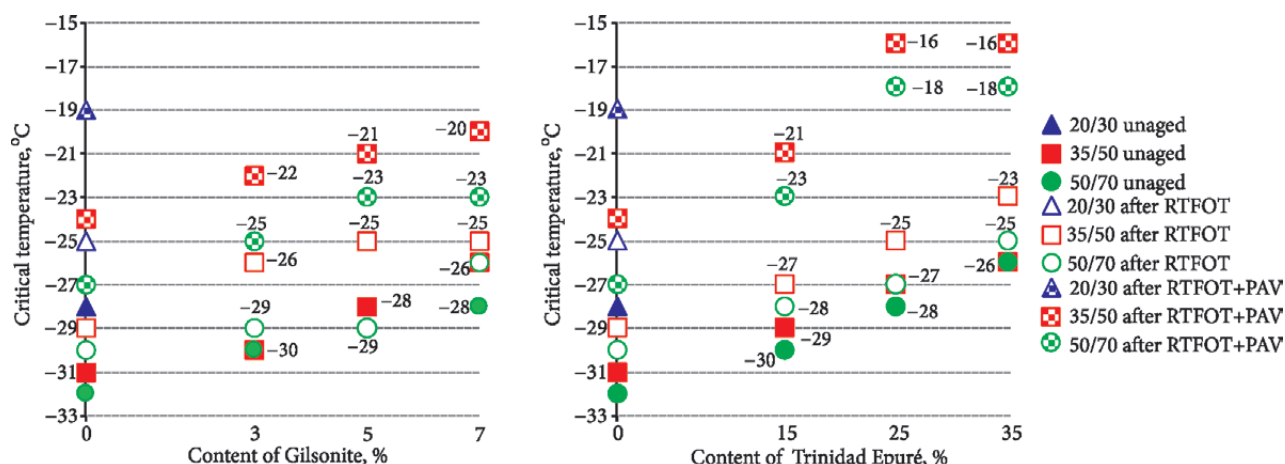
Fig. 4. Mean values of the critical temperature determined for the Gilsonite and Trinidad Epuré modified asphalt binders using the BBR method

Figure 4 shows mean values of the critical temperature as determined by the BBR method according to the Eq (4) for the asphalt binders modified with the natural bitumen additives discussed.

Table 7 shows the values of the *a*, *b* and R^2 coefficients of the linear regression determined for the dependence of the mean critical temperature on the content of the Gilsonite and Trinidad Epuré additives. The coefficient *a* indicates the intensity of the changes in the average value of the critical temperature. The coefficient *b* indicates the average value of the critical temperature for the asphalt binders with no natural bitumen additives (*C* = 0). The coefficient of determination R^2 assumes values from 0 to 1 and it is an indicator of the quality of the linear regression fit (the higher the value the better fit).

Tables 8 and 9 show average values of the critical temperature determined in accordance with the principles described in the SHRP and the Superpave specifications. Additionally, the tables present values calculated according to Eq (5) on the basis of the parameters of the trend line for the dependency of the mean critical temperature on the content of the natural asphalt additive.

$$T_{cr,\ c} = a\ C + b\ , \ °C, \tag{5}$$

where $T_{cr,\ c}$ – value of the calculated critical temperature, °C; *a* – linear regression coefficient; *C* – content of the natural asphalt additive, % of its weight; *b* – linear regression coefficient (the value of T_{cr} for *C* = 0).

Table 10 shows mean values of the critical temperature for the 20/30 and 35/50 penetration grade bitumens as well as the 35/50 and 50/70 ones modified with Gilsonite and Trinidad Epuré natural asphalts. The content of the above-mentioned additives was calculated using Eq (5) and the average value of the critical temperature for the unmodified bitumens. The use of Eq (5) made it possible to calculate the maximum amount of the natural asphalt additive to be used with the selected bitumen in a way to obtain asphalt binder with the same resistance to low temperatures as the unmodified bitumen.

Table 7. The values of the coefficients *a*, *b* and R^2 of the linear regression determined for the dependence of the critical temperature mean value on the content of the Gilsonite and Trinidad Epuré additives

Asphalt binder	unaged			after RTFOT			after RTFOT+ PAV		
	a	*b*	R^2	*a*	*b*	R^2	*a*	*b*	R^2
35/50 with addition of GIL	0.720	−31.449	0.939	0.589	−28.458	0.863	0.570	−23.888	0.994
50/70 with addition of GIL	0.570	−31.888	0.994	0.505	−30.393	0.757	0.617	−26.813	0.925
35/50 with addition of TE	0.148	−31.019	0.980	0.172	−29.224	0.989	0.252	−23.981	0.911
50/70 with addition of TE	0.172	−32.224	0.989	0.138	−30.093	0.984	0.280	−26.757	0.922

Table 8. The values of the average critical temperature determined by tests in the BBR and calculated for asphalt binders modified by adding Gilsonite

Asphalt binder	Critical temperature, °C								
	unaged			after RTFOT			after RTFOT+ PAV		
	determined	calculated	Δ	determined	calculated	Δ	determined	calculated	Δ
35/50+3% GIL	−30	−29.3	0.7	−26	−26.7	0.7	−22	−22.2	0.2
35/50+5% GIL	−28	−27.8	0.2	−25	−25.5	0.5	−21	−21.0	0.0
35/50+7% GIL	−26	−26.4	0.4	−25	−24.3	0.7	−20	−19.9	0.1
50/70+3% GIL	−30	−30.2	0.2	−29	−28.9	0.1	−25	−25.0	0.0
50/70+5% GIL	−29	−29.0	0.0	−29	−27.9	1.1	−23	−23.7	0.7
50/70+7% GIL	−28	−27.9	0.1	−26	−26.9	0.9	−23	−22.5	0.5

Table 9. The values of the average critical temperature determined by tests in the BBR and calculated for asphalt binders modified by adding Trinidad Epuré

Asphalt binder	Critical temperature, °C								
	unaged			after RTFOT			after RTFOT+ PAV		
	determined	calculated	Δ	determined	calculated	Δ	determined	calculated	Δ
35/50+15% TE	−29	−28.8	0.2	−27	−26.6	0.4	−21	−20.2	0.8
35/50+25% TE	−27	−27.3	0.3	−25	−24.9	0.1	−16	−17.7	1.7
35/50+35% TE	−26	−25.8	0.2	−23	−23.2	0.2	−16	−15.2	0.8
50/70+15% TE	−30	−29.6	0.4	−28	−28.0	0.0	−23	−22.6	0.4
50/70+25% TE	−28	−27.9	0.1	−27	−26.6	0.4	−18	−19.8	1.8
50/70+35% TE	−26	−26.2	0.2	−25	−25.3	0.3	−18	−17.0	1.0

Table 10. The average critical temperature of the unmodified and modifies asphalt binders along with an equivalent content of modifier

Asphalt binder	unaged			after RTFOT			after RTFOT+ PAV		
	T_{cr}, C	content of additive		T_{cr},°C	content of additive		T_{cr},°C	content of additive	
		Gilsonite	Trinidad Epuré		Gilsonite	Trinidad Epuré		Gilsonite	Trinidad Epuré
20/30 35/50 + additive	−28	5	20	−25	6	25	−19	9	20
35/50 50/70 + additive	−31	2	7	−29	3	8	−24	5	10

4. Discussion

A comparative analysis of the effect of the addition of Gilsonite and Trinidad Epuré on the road bitumen 35/50 and 50/70 penetration grade was based on the assumption that one of the characteristics of the asphalt binders obtained as a result of modification will be their similar penetration values (Tables 1 and 2), i.e. the differences between them will not exceed 2 mm/10.

The values of penetration determined at 25 °C and the softening point for the tested asphalt binders confirm the stiffening properties of the analysed natural asphalts described by Ameri *et al.* (2012) and Babagoli *et al.* (2015).

The decrease of the penetration value shown in Fig. 1 was caused by stiffening of the asphalt binder as a result of the aging processes. It has been noticed that bitumens with the addition of Gilsonite show a smaller degree of stiffening as a result of short-term aging than those with the addition of Trinidad Epuré (15% on the average). An increase in the asphalt binder stiffness arising from long-term aging is comparable for the two natural asphalts discussed and falls within the range of 53.9% to 64.9%.

When analysing the data presented in Fig. 2 it has been found out that the addition of Gilsonite slightly alters the softening point gradient as a result of aging, i.e. the increment values are ±1 °C for the asphalt binders containing bitumen 35/50 and ±2.5 °C for the asphalt binders containing bitumen 50/70. Due to the aging processes, bitumen with the addition of Trinidad Epuré is characterized by a greater rise of the softening point. The maximum softening point gradient equals to 3.5 °C for the short-term aging and 5.9 °C for the long-term one.

When analysing the data presented in Fig. 3 it has been noted that adding Gilsonite to 35/50 and 50/70 penetration grade bitumen results in the increase of the *PI* both before and after aging, which means that the tested asphalt binders show lower temperature susceptibility. The exception is the 35/50 bitumen containing Gilsonite in which case the value decreases after aging using the RTFOT and the PAV methods together, and this might be associated with very substantial stiffening of the tested asphalt binder. As a result of adding Trinidad Epuré to bitumen a slight decrease in the value of the *PI* is observed and this results in the increased temperature susceptibility of the analysed binders. It has been seen that aging using the RTFOT method eliminates the adverse effects of using Trinidad Epuré as a bitumen modifier. Moreover, aging using the RTFOT and the PAV methods used simultaneously causes a reduction of the temperature susceptibility of the modified bitumen in comparison to the reference one.

The analysis of the results of the tests carried out using the BBR at –32 °C, –24 °C, –16 °C, –8 °C (Tables 3–6) showed that the modification of the road bitumen by adding Gilsonite and Trinidad Epuré results in the linear increase in stiffness modulus values in the function of the modifier content both before and after short-term and long-term aging. Excessive stiffness of the asphalt binder may lead to enhanced susceptibility to low temperature cracking. Therefore by the principles developed as part of the SHRP and the Superpave it is assumed that the value of the stiffness modulus for the asphalt binders aged with the RTFOT and the PAV methods together should be less than 300 MPa and the *m*-value should not be less than 0.3. Furthermore, it has been noticed that none of the asphalt binders tested meets the requirements presented above at a temperature of –24 °C, even those unaged. At –16 °C the requirements above are satisfied only by the unmodified 50/70 bitumen. It should be noted, however, that at a temperature of –16°C after aging using the RTFOT and the PAV methods together the requirements are not met by:

the 20/30 bitumen, the 35/50 bitumen with 5% and 7% of Gilsonite as well as 25% and 35% of Trinidad Epuré, the 50/70 bitumen with 7% of Gilsonite and 35% of Trinidad Epuré. The 35/50 bitumen with 35% of Trinidad Epuré stiffens so considerably that if it is unaged it reaches the *m*-value lower than 0.3 already at –16 °C. It has been also found that the requirements outlined in the Superpave for –8 °C are not met by the bitumen that contains 25% and 35% of Trinidad Epuré. This, in turn, is likely to result in their higher susceptibility to cracking at temperatures below 0 °C. Based on the results presented in Tables 3–6, it was observed that the 35/50 bitumen with 3% and 5% of Gilsonite as well as 15% of Trinidad Epuré are alternatives to the hard bitumen 20/30 used in the asphalt mixtures. It is also possible to replace the 35/50 bitumen with the 50/70 one containing 3% or 5% of Gilsonite or 15% of Trinidad Epuré. Furthermore, the 35/50 bitumen can be replaced with the 50/70 one containing 3% or 5% of Gilsonite or 15% of Trinidad Epuré. Analysing the results of the determination of the stiffness modulus at –24 °C an interesting phenomenon was recorded in the case of the bitumens containing 5% or 7% of Gilsonite as well as 25% or 35% of Trinidad Epuré. Namely, it turned out that the value of the stiffness modulus of these asphalt binders had increased considerably as a result of aging that was carried out using the RTFOT method and then dropped when the PAV method was applied. Moreover, it is also claimed that the stiffness modulus of the unaged binders and those that were aged using the RTFOT and the PAV methods together does not exhibit any statistically significant differences about the cases discussed above. The causes of the process described above lie in the substantial stiffness of the modified binders tested ($S_m > 550$ MPa). On the other hand, however, they are related to softening resulting from the high pressure to which the binder specimens are subjected during the tests in which the PAV method is used.

Upon studying the results of the critical temperature determination it was noticed, as shown in Fig. 4, that the modification of the tested road bitumens 35/50 and 50/70 penetration grade containing Gilsonite and Trinidad Epuré leads to an increase in the mean value of the critical temperature. The increase of the critical temperature in the function of the modifier content (GIL or TE) is linear. In the case of Gilsonite, the maximum increase in T_{cr} for both bitumens modified is 5 °C before aging and 4°C after both short-term and long-term aging. A greater increase in the mean value of the critical temperature was recorded for Trinidad Epuré addition. The maximum increase in T_{cr} is 5 °C for the unaged 35/50 bitumen and 6 °C for the 50/70 one, 6 °C for the 35/50 bitumen after short-term aging and 5 °C for the 50/70 one and finally, 9 °C for the 35/50 bitumen and 8 °C for the 50/70 one after long-term aging. In the case of the modified bitumens containing 3% and 5% of Gilsonite and the 35/50 bitumen with the addition of 15% of Trinidad Epuré, increases in T_{cr} are less than for the bitumens with equivalent penetration values, i.e. 20/30 and 35/50, respectively. Taking into consideration the behaviour of the asphalt binder

at low temperatures the critical temperature before and after aging by means of the RTFOT and using Gilsonite is on average 1 °C lower than in the case of Trinidad Epuré . The difference that occurred between the critical temperature for Gilsonite and Trinidad Epuré rises to 5 °C after aging using the RTFOT and the PAV methods together. It must be added that these values were recorded for the asphalt binders modified with natural asphalts whose characteristic feature is their equivalent penetration value.

Having studied the data included in Tables 8 and 9 it was found that the addition of Gilsonite and Trinidad Epuré natural asphalts causes a linear increase in the critical temperature. The average difference between the value of T_{cr} determined in the BBR and calculated in accordance with Eq (5) is of 0.4 °C while the maximum is 1.1 °C. By means of the linear regression coefficients presented in Table 7 it is possible to accurately determine the amount of natural asphalt in a modified asphalt binder, which corresponds to a particular value of the critical temperature. By the data included in Table 10, it is claimed that as a result of short-term and long-term aging the 35/50 bitumen with the addition of 9% of Gilsonite and 20% of Trinidad Epuré has got the same value of T_{cr} as the 20/30 bitumen. The same values of T_{cr} after aging as for the 35/50 bitumen are also characteristic of the 50/70 bitumen containing 5% of Gilsonite and 10% of Trinidad Epuré. Moreover, it has been observed that the potential amount of the modifier that is added in the case of Gilsonite gets greater and greater as the aging processes progress while in the case of Trinidad Epuré such an increase is detected only when the 50/70 bitumen is used. Based on the data presented in Table 10, it has been found that an appropriate content of the Gilsonite or Trinidad Epuré natural asphalt is conducive to mitigate the effects of asphalt binder aging.

The results obtained confirm the possibility of using the 35/50 bitumen containing 5% of Gilsonite as an alternative to the 20/30 as well as the 50/70 bitumen containing 3% of Gilsonite as an alternative to bitumen 35/50. In the case of Trinidad Epuré an originally suggested content of the modifier should be reduced by 5%. It is then possible to use the asphalt binder consisting of 35/50 bitumen and 20% of Trinidad Epuré as an alternative to 20/30 bitumen and an asphalt binder containing bitumen 50/70 and 10% of Trinidad Epuré as an alternative to the 35/50 penetration grade bitumen.

Modified bitumens subjected to tests were considered including the possibility to use them in selected asphalt mixtures such as high modulus asphalt concrete or mastic asphalt. These hot mix asphalts require low penetration grade bitumens. For this reason, in the research, only 20/30, 35/50 and 50/70 penetration grade bitumens were analysed. It is also possible using natural asphalts to modify high penetration grade bitumens like 70/100 or 100/150. Such modified bitumens that are characterized by penetration grade similar to the bitumens analysed in the paper must be prepared with the usage of much more amounts of natural asphalt. It results in significant increase of production costs of such modified bitumens.

The authors of the present paper did not analyse the bitumen-natural asphalt colloidal stability because from the technological point of view the modification of bitumen takes place in the mixer during the production of hot mix asphalt. Polymer-modified bitumens are produced in refineries as a separate product otherwise than natural asphalt modified bitumens. However, according to the research conducted by Yılmaz *et al.* (2015) natural asphalts modified bitumens are characterized by a greater storage stability than polymer-modified bitumens.

5. Conclusions

1. Modified asphalt binders containing Gilsonite show a smaller degree of stiffening resulting from short-term aging than those containing Trinidad Epuré. However, if the long-term aging is taken into consideration, then the increased stiffness of the asphalt binder for both additives is comparable.

2. The addition of Gilsonite has no effect on the changes in the softening point gradient resulting from the aging of the modified asphalt binders. Such an effect was observed when Trinidad Epuré was used as a modifier.

3. Gilsonite modified bitumens display lower thermal susceptibility of the unaged asphalt binders and those, which underwent aging using the Rolling Thin Film Oven Test method. In the case of Trinidad Epuré modified bitumens, such lowered susceptibility was recorded for the asphalt binders after aging using the Rolling Thin Film Oven Test and the Pressure Aging Vessel methods together.

4. It is reasonable to use 3% and 5% of the Gilsonite additive as well as 15% of the Trinidad Epuré to modify the 35/50 and 50/70 penetration grade bitumens. Such an amount of those additives allows obtaining asphalt binder with comparable resistance to cracking at low temperatures as is exhibited by the 20/30 and 35/50 penetration grade road bitumens. This was verified by the tests carried out using the Bending Beam Rheometer.

5. A process of a significant increase in the stiffness modulus values determined using the Bending Beam Rheometer at –24 °C as a result of the Rolling Thin Film Oven Test method aging. Values of stiffness modulus are reduced after the Pressure Aging Vessel aging process in the case of asphalt binders containing 5% and 7% of Gilsonite or 35% of Trinidad Epuré.

6. Modifying 35/50 and 50/70 penetration grade road bitumens by adding to them Gilsonite and Trinidad Epuré results in a linear increase of the critical temperature. Using an appropriate mathematical formula it is possible to accurately determine the content of the selected additive in an asphalt binder, which corresponds to a particular value of the critical temperature.

7. The 35/50 bitumen modified by adding 5% of Gilonite or 20% of Trinidad Epuré are regarded as an alternative to using the 20/30 penetration grade bitumen while the 50/70 bitumen is containing 3% of Gilsonite or 10% of Trinidad Epuré as an alternative to the 35/50 penetration grade bitumen.

References

Aflaki, S.; Hajikarimi, P.; Fini, E.; Zada, B. 2014. Comparing Effects of Biobinder with Other Asphalt Modifiers on Low-Temperature Characteristics of Asphalt, *Journal of Materials in Civil Engineering* 26(3): 429–439.
https://doi.org/10.1061/(ASCE)MT.1943-5533.0000835

Al-Mansob, R. A.; Ismail, A.; Alduri, A. N.; Azhari, C. H.; Karim, M. R.; Yusoff, N. I. M. 2014. Physical and Rheological Properties of Epoxidized Natural Rubber Modified Bitumens, *Construction and Building Materials* 63: 242–248.
https://doi.org/10.1016/j.conbuildmat.2014.04.026

Ameri, M.; Mansourian, A.; Ashani, S. S.; Yadollahi, G. 2011. Technical Study on the Iranian Gilsonite as an Additive for Modification of Asphalt Binders Used in Pavement, *Construction and Building Materials* 25(3): 1379–1387.
https://doi.org/10.1016/j.conbuildmat.2010.09.005

Ameri, M.; Mansourian, A.; Sheikhmotevali, A. H. 2012. Investigating Effects of Ethylene Vinyl Acetate and Gilsonite Modifiers Upon Performance of Base Bitumen Using Superpave Tests Methodology, *Construction and Building Materials* 36: 1001–1007. https://doi.org/10.1016/j.conbuildmat.2012.04.137

Babagoli, R.; Hasaninia, M.; Namazi, N. M. 2015. Laboratory Evaluation of the Effect of Gilsonite on the Performance of Stone Matrix Asphalt Mixtures, *Road Materials and Pavement Design* 16(4): 889–906.
https://doi.org/10.1080/14680629.2015.1042016

Boden, T.; Tripp, B. T. 2012. *Gilsonite Veins of the Uinta Basin. Utah.* Salt Lake City: Utah Geological Survey. 50 p.

Cholewińska, M.; Iwański, M. 2011. Modification of Petroleum Road Bitumen 50/70 with natural asphalt Gilsonite, *Structure and Environment* 3(2): 5–10.

Danowski, M. 2009. Nawierzchnie z dodatkiem asfaltu naturalnego Trynidad [Pavements with Addition of the Trinidad Natural Asphalt], *Nawierzchnie asfaltowe* 2: 7–13, in Polish.

Feng, M.; Zhen, F.; Lilong, W. 2014. Asphalt-Aggregate Adhesion Work of Natural Asphalt Modified Asphalt, *International Journal of Pavement Research and Technology* 7(6): 456–460.
http://dx.doi.org/10.6135/ijprt.org.tw/2014.7(6).456

Haritonovs, V. 2015. Evaluation of Polyaminoamide as a Surfactant Additive in Hot Mix Asphalt, *Baltic Journal of Road and Bridge Engineering* 10(2): 112–117.
https://doi.org/10.3846/bjrbe.2015.14

Liao, M. C.; Chen, J. S.; Airey, G. D.; Wang, S. J. 2014. Rheological Behavior of Bitumen Mixed with Trinidad Lake Asphalt, *Construction and Building Materials* 66: 361–367.
https://doi.org/10.1016/j.conbuildmat.2014.05.068

Nciri, N.; Song, S.; Kim, N.; Cho, N. 2014. Chemical Characterization of Gilsonite Bitumen, *Journal of Petroleum & Environmental Biotechnology* 5(5): 1–10.
https://doi.org/10.4172/2157-7463.1000193

Nivitha, M. R.; Prasad, E.; Krishnan, J. M. 2015. Ageing in Modified Bitumen Using FTIR Spectroscopy, *International Journal of Pavement Engineering* 17(7): 565–577.
https://doi.org/10.1080/10298436.2015.1007230

Słowik, M. 2010. Analiza Niepewności Pomiarowych Przy Ocenie W*łaściwości* Asfaltów Drogowych [Analysis of Measurement Uncertainty in Assessment of Properties of Road Bitumens], *Poznan University of Technology, Archives of Institute of Civil Engineering* 7: 129–144, in Polish.

Słowik, M.; Grabowski, W.; Bilski, M. 2012. Road Bitumen Modified with Natural Asphalt Trinidad Epuré and Gilsonite Addition, in *the 5ᵗʰ Eurasphalt & Eurobitume Congress.* 13–15 June, 2012, Istanbul, Turkey.

Wang, C.; Wang, P.; Li, Y.; Zhao, Y. 2015a. Laboratory Investigation of Dynamic Rheological Properties of Tourmaline Modified Bitumen, *Construction and Building Materials* 80(1): 195–199. https://doi.org/10.1016/j.conbuildmat.2014.12.105

Wang, Y.; Sun, L.; Qin, Y. 2015b. Aging Mechanism of SBS Modified Asphalt Based on Chemical Reaction Kinetics, *Construction and Building Materials* 91: 47–56.
https://doi.org/10.1016/j.conbuildmat.2015.05.014

Widyatmoko, I.; Elliott, R. 2008. Characteristics of Elastomeric and Plastomeric Binders in Contact with Natural Asphalts, *Construction and Building Materials* 22(3): 239–249.
https://doi.org/10.1016/j.conbuildmat.2005.12.025

Xiao, F.; Amirkhanian, S. N.; Juang C. H.; Hu, S.; Shen, J. 2012. Model Developments of Long-Term Aged Asphalt Binders, *Construction and Building Materials* 37: 248–256.
https://doi.org/10.1016/j.conbuildmat.2012.07.047

Yilmaz, M.; Çeloglu, M. E. 2013. Effects of SBS and Different Natural Asphalts on the Properties of Bituminous Binders and Mixtures, *Construction and Building Materials* 44: 533–540.
https://doi.org/10.1016/j.conbuildmat.2013.03.036

Yilmaz, M.; Kök, B. V.; Kuloğlu, N. 2013. Investigation of Mechanical Properties of Short- and Long-Term Aged Asphaltite Modified Asphalt Mixtures, *Journal of Materials in Civil Engineering* 25(5): 563–572.
https://doi.org/10.1061/(ASCE)MT.1943-5533.0000626

Yilmaz, M.; Kök, B. V.; Yamaç, Ö. E. 2015. Determination of Rheological Properties of Polymer and Natural Asphalts Modified Binders After Storage Stability Test, *Journal of Engineering and Natural Sciences* 33: 157–165.