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Structuring role of F-T synthetic wax in bitumen

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Abstract. The reduction in asphalt mixture production and placement temperatures can be achieved by modifying bitumen 35/50 with the Fischer-Tropsch synthetic wax. To identify the role this modifier plays in the bitumen 35/50, a series of tests has been performed. The experiment was carried out for wax doses from 1.5% to 4.0%. Analysis of the modified binder properties such as ductility at 5, 15 and 25°C, complex modulus G* with the parameter G*/sinδ and LSV, susceptibility according to MSCR procedure, morphology and group type analysis helped describe the structuring function of the F-T wax in the binder. The optimum F-T wax content of 2.5% has been identified to provide the desired parameters required for modified binders.

Key words: bitumen, synthetic wax F-T, ductility, rheology, morphology, group type.

1. Introduction

The most commonly accepted modifier used to improve the properties of road bitumens, increase their workability and ensure proper performance of the pavement upper layers in winter low temperatures and summer high temperatures is the styrene-butadiene-styrene (SBS) block copolymer [1–3]. Modifiers of this type are used within the traditional range of mix production and placement temperatures [4]. Present hot mix technologies distinguish a high energy consumption during the technological process [5]. Today's striving for the reduction in manufacturing energy costs and environmental emissions, of CO_2 in particular, has turned engineers' attention towards low-viscosity modifiers used in Warm Mix Asphalt (WMA) technologies [6–8]. These additives decrease the viscosity of the binder above 100°C and as a result aggregate grains are coated with bitumen binder at temperatures 20–30°C lower than the traditional temperature of approximately 165°C. The temperature of asphalt mixture placement while constructing pavement structural layers is also lower compared with the conventional process. The modifiers increase viscosity of the binder at pavement service temperatures thus making structural layers more resistant to plastic deformation – rutting. One of the low-viscosity modifiers is the Fischer-Tropsch synthetic wax [9–11].

Fischer-Tropsch synthetic waxes are co-products in fuel production, obtained by the Fischer-Tropsch process. Their chain lengths are considerably longer (up to C_{100}) than those of paraffins contained in bitumen (from C_{22} to C_{45}), their structure is more microcrystalline and their molecular weight is approximately 40% higher than that of natural waxes present in bitumen. Long hydrocarbon chains crystallise at higher temperatures, short chains crystallise at lower temperatures. Owing to their microcrystalline form, F-T waxes have an ability to disperse uniformly and provide the bitumen phase with the desired stiffness [12]. Fisher-Tropsch waxes increase the n-paraffin fraction ratio in the asphalt mix, increasing the bitumen molecular weight [13]. The optimal content of the synthetic wax in a bitumen affects a satisfactory level of its low temperature resistance [14]. Their action, being similar to that of asphaltenes, reduces the mobility of asphaltene fraction in relation to malthene fraction [15,29]. The mix homogenic nature is dependent on the wax composition, the base bitumen formulation, polar character of the wax and its ability to interact with bitumen [16].

To evaluate the versatile benefits arising from the F-T synthetic wax application as a modifier in WMA, the mechanism of its effect on the binder has to be identified.

2. Design of experiment

The tests were performed on bitumen 35/50, commonly used in asphalt mixtures intended for the use in pavement binder courses and bases. To evaluate the mechanism of the influence of the F-T synthetic wax on the properties of bitumen 35/50, a research programme was developed which involved determining the following significant characteristics of the modified binder: ductility at 5, 15 and 25 °C with force load measurement, complex shear modulus G* with the elastic portion G*/sinδ, LSV (low shear viscosity), phase shift angle, rheological characteristics in the MSCR test, morphology and group types. The tests were performed at 50°C, 60°C and 90°C, which are the temperatures relevant in terms of the binder performance in service and during the bitumen layers placement process.

Identification of the effect of F-T synthetic wax on the ductility of bitumen 35/50 is of significant importance because it provides information about the cohesion of the binder. The influence of the modifier on the ductility changes and maximum force load were evaluated using a 3×5 full factorial design (Fig. 1).

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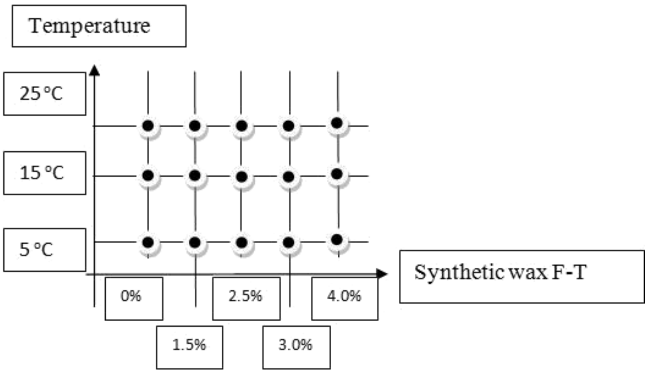

Fig. 1. Design of experiment

The ductility of the modified bitumen 35/50 was studied at temperatures 15°C and 25°C and at the tensile speed of 50 mm/min. During initial tests it was established that in order to perform the ductility test at 5°C, the speed had to be reduced to 5 mm/min. During the tension test, the bitumen specimen was continuously monitored for elongation and tensile stress.

A complex evaluation of the rheological properties of the binder (viscoelastic material) can be performed using the complex shear modulus G*, which is a vector sum of two components [17]. One of them is the elastic modulus and the other one is the loss modulus (viscous portion). There is a phase shift between these two values, a phase angle. Complex modulus at different temperatures may have the same value but will vary with respect to the ratio of the elastic portion to the viscous portion. Therefore, at higher temperatures the viscous portion will prevail in the evaluation of the complex modulus, which results from the uptrend of the phase angle value. Complex modulus is a measure of a certain propensity for changes in the binder, but it defines them too extensively. To characterise the binder in a better way, the evaluation should include the phase shift angle change or the function determined with the phase shift angle, which are associated with the loading time (frequency). The values of the bitumen complex modulus at low phase angle indicate the definite predominance of the elastic component over the viscous one. The distribution of the complex modulus G* for the angle of more than 70° indicates the predominance of the viscous component.

The Multiple Stress Creep Recovery (MSCR) test was performed in accordance with the AASHTO TP70 specification. MSCR procedure, based on the Strategic Highway Research Program (SHRP), has been developed in the United States to verify the complex modulus and phase shift angle tests for modified binders. The test quantifies the non-linear performance of the binder and produces results that are closely correlated with the actual mix performance (wheel tracking test) [15, 18]. This method helps to assess the levels of susceptibility to permanent deformation and the relaxation of the binder incorporated in the asphalt mixture under loading conditions simulating service conditions, and non-linear viscoelastic character of the bitumen within a broad range of stress. The binder's potential for permanent deformation was measured with the application of two stress levels, a 1-second stress of 100 and then 3200 Pa, followed by the measurement of elastic recovery for 9 seconds at a temperature of 60°C. The entire cycle for one stress level took 100 seconds. The rut/permanent deformation resistance value J_{nr} (irreversible portion of the strain divided by the stress applied) and the value of elastic recovery $R\%$ (percentage relative elastic strain which is the ratio of the strain at 1 second at the beginning of the cycle to the strain value measured at 10 seconds) were finally determined.

The structural analysis of the modified bitumen 35/50 was performed by UV exposure using an AxioScope A.1 microscope in accordance with EN 13632.

Spectroscopy, which identifies group types within the binder, was used to evaluate the influence of F-T synthetic wax on the properties of the modified bitumen. The following characteristics were adopted as the reliable values for the binder evaluation [19]: carbonyl index, aliphatic structures index, aliphatic index, and sulphoxide index.

3. Results and analysis

3.1. Force ductility test on F-T synthetic wax modified bitumen 35/50. The force ductility test was performed to EN 13589 with the use of a DDA-3m ductilometer to automatically measure the force and the specimen's elongation. During the measurement, the maximum elongation was recorded together with the tension force and the strain work at breaking. The final stage of the ductility test was aimed at achieving the minimum level of tension force equal to 100 mN. The results varied within the range of 5% (Fig. 2).

It is important to note that the ductility level of the modified bitumen 35/50 changes with temperature (Fig. 2). The ratio of the binder elastic behaviour to the strain plastic behaviour increases proportionally to the temperature drop [20]. At a temperature of 25°C, the plastic strain is relatively high. That is why in the chart, its magnitude is limited to 200 mm (tension force <100 mN). At the transition from 25°C to 15°C, a three-fold increase in the maximum force was recorded at a considerable reduction in ductility. Within the temperature range from 15°C to 5°C, this increase reached approximately 40%. The binder's ductility decreased by about 20%. Compared with the 2.5 F-T synthetic wax modified binder, the ductility drop in the control bitumen 35/50 was 40%. This is associated with the high level of structural viscosity and a fast transition towards the steady-state flow. A rapidly increasing level of the maximum force during the experiment confirms this phenomenon. In this way, the ratio of elastic component to viscous component will grow up to the elastic-brittle state, appropriate for the cement concrete model. The maximum force increase in the modified binder 35/50 will have a direct influence on the extension of the asphalt pavement relaxation period under the load and on its elastic character at intermediate service temperatures.

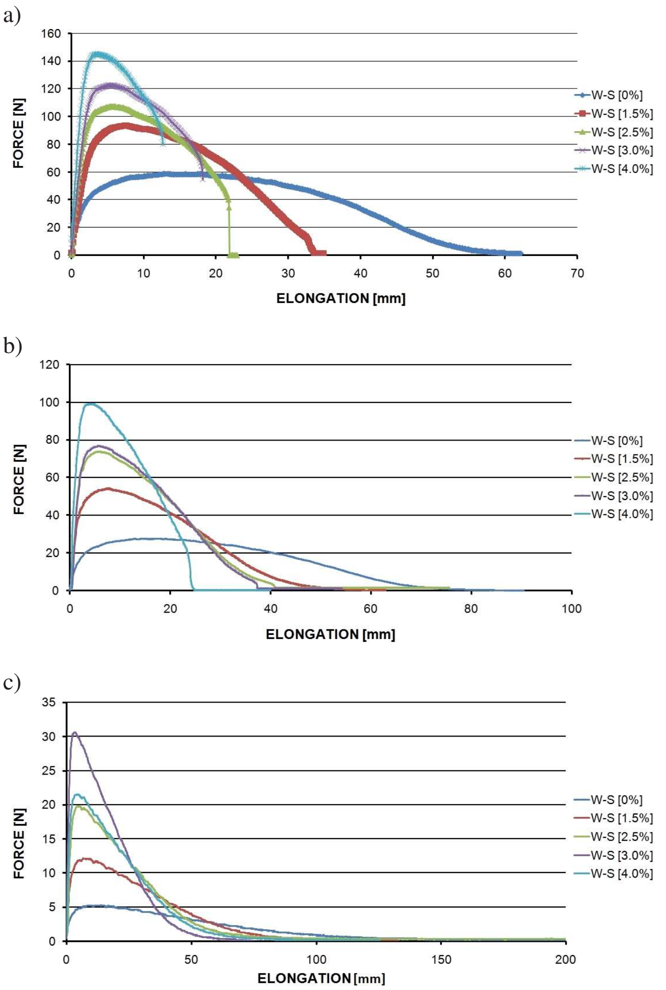

Fig. 2. Force ductility of synthetic wax modified bitumen 35/50; maximum force at a) 5°C, b) 15°C and c) 25°C

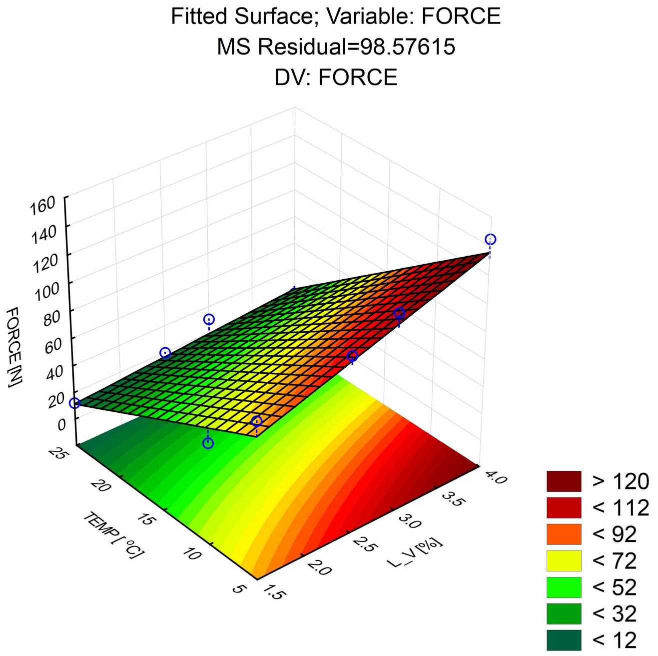

Fig. 3. Ductility of F-T wax modified bitumen 35/50 at 5, 15, 25°C

A more detailed analysis of the changes in force ductility of F-T synthetic wax modified bitumen 35/50 involved finding the mathematical model. Based on the chosen optimization method [21], it was assumed that, for the case investigated (research scope), the following mathematical model will be most adequate

$$y = b_o + \sum_{i=1}^{n} b_i \cdot x_i + \sum_{i=j=1}^{n} b_{i=j} \cdot x_i \cdot x_j + \sum_{i=1}^{n} b_{ii} \cdot x_i^2. \quad (1)$$

The response surface will be the second degree polynomial expressed as [22]

$$y = b_o + b_1 \cdot x_1 + b_2 \cdot x_2 + b_3 \cdot x_3 \cdot x_1 + b_4 \cdot x_1^2 + b_5 \cdot x_2^2, \quad (2)$$

where x_1 – temperature level [°C], x_2 – F-T synthetic wax content [%], b_o–b_5 – values of experimental coefficients.

Graphical interpretation of the modified bitumen ductility model is presented in Fig. 3.

Results of statistical analysis indicate that the second degree polynomial is the most adequate model in terms of temperature for describing the changes in the synthetic wax modified bitumen 35/50. The analysis of fit results is shown in Table 1.

Table 1
Results of the statistical fit assessment for the regression model of ductility changes in F-T synthetic wax modified bitumen 35/50

Regression	df	Type I sum of squares	R^2	F value	Pr > F
Linear	2	22392	0.9029	185.18	<.0001
Quadratic	2	1631.109865	0.0658	13.49	0.0020
Crossproduct	1	233.590711	0.0094	3.86	0.0809
Total Model	5	24256	0.9781	80.24	<.0001

The result of the ductility changes model fit for F-T wax modified bitumen 35/50, defined using the coefficient of determination $R^2 = 0.9687$, shows a good fit of the regression model and confirms satisfactory assumptions made for the experimental domain. The next stage of the analysis involved an evaluation of parameters of the regression model used (Table 2).

Table 2
Evaluation of estimation parameters of the ductility model for the F-T synthetic wax modified bitumen 35/50

Parameter	df	Estimation	Standard error	t value	Pr > |t|
Intercept	1	62.051049	10.666740	5.82	0.0003
TEMP	1	−0.437360	1.360217	−0.32	0.7551
W-S	1	−25.704089	5.474148	−4.70	0.0011
TEMP*TEMP	1	0.170550	0.042589	4.00	0.0031
W-S*TEMP	1	−0.354382	0.180292	−1.97	0.0809
W-S*W-S	1	3.835701	1.159581	3.31	0.0091

The mathematical model developed indicates the statistically significant influence of the non-linear temperature variation, while the changes in ductility of the modified bitumen 35/50 in terms of the F-T synthetic wax content, remain approximately linear. Further analysis indicates the lack of significant influence of the synergy of both factors on the overall level of the binder ductility. The action of either of the factors (W-S – F-T synthetic wax content, TEMP – temperature) shows a low interaction level. Thus the measurement temperature does not affect the F-T wax concentration level, which might result in the change of the ductility value. The temperature levels will definitely affect the bitumen cohesion. The crystalline phase of the F-T wax remains insensitive within the set temperature interval from 5°C to 25°C, and its influence on the modified bitumen 35/50 is approximately constant.

Another element of the study comprised the evaluation of the F-T wax influence on the maximum tension force acting on bitumen 35/50. Based on the statistical analysis, a second degree polynomial was taken to describe the changes in this relationship (Fig. 4). The model fit evaluation is presented in Table 3.

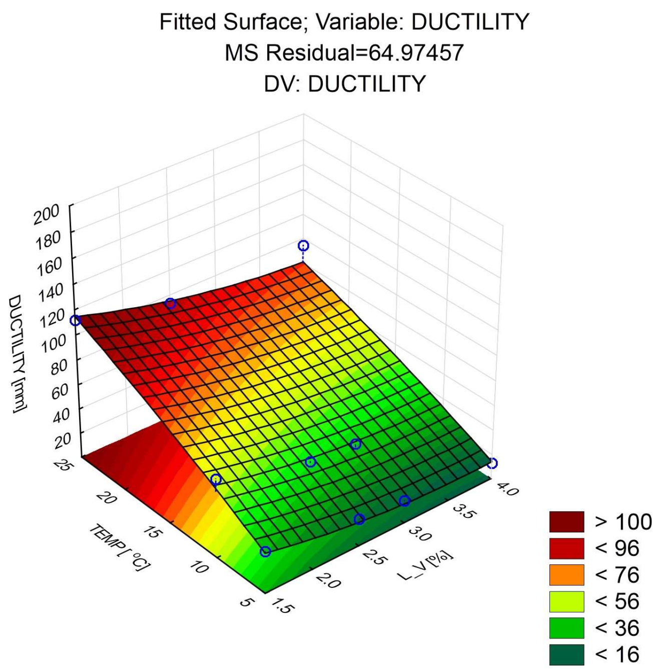

Fig. 4. Influence of F-T synthetic wax on the value of the ultimate tensile strength of bitumen 35/50 modified with F-T synthetic wax at temperatures of 5, 15, and 25°C

Table 3
Results of the statistical fit assessment for the regression model of the maximum tension force for the F-T synthetic wax modified bitumen 35/50

Regression	df	Type I sum of squares	R^2	F value	Pr > F
Linear	2	25078	0.9432	412.66	<.0001
Quadratic	2	71.950673	0.0027	1.18	0.3496
Crossproduct	1	1165.887505	0.0438	38.37	0.0002
Total Model	5	26316	0.9897	173.21	<.0001

The fit of the model was established using the coefficient of determination $R^2 = 0.95$, which indicated the good fit of the regression model and confirmed satisfactory assumptions made for the experimental domain. In the next step, the parameters of the regression model were evaluated. The model described the influence of the F-T synthetic wax on the maximum tension force for the modified binder at temperatures of 5, 15, 25°C (Table 4).

Table 4
Evaluation of parameters of maximum tension force estimation for bitumen 35/50, modified with F-T synthetic wax

Parameter	df	Estimation	Standard error	t value	Pr > |t|
Intercept	1	62.706297	7.562014	8.29	<.0001
TEMP	1	−1.268215	0.964304	−1.32	0.2210
W-S	1	27.544868	3.880809	7.10	<.0001
TEMP*TEMP	1	−0.045400	0.030192	−1.50	0.1669
W-S*TEMP	1	−0.791720	0.127815	−6.19	0.0002
W-S*W-S	1	−0.268658	0.822066	−0.33	0.7513

Similarly to the case of ductility test, the values of the maximum tension force change linearly in terms of the F-T synthetic wax amount added to bitumen 35/50. The mathematical model developed for the modified bitumen 35/50 is indicative of the influence of temperature non-linear variation factor. The result of interaction between the test temperature factor and the F-T synthetic wax amount factor in bitumen 35/50 is a relevant aspect of the analysis. Unlike in the ductility test, the synergy effect (W-S*TEMP) is statistically significant. All this is an indication that the presence of the crystalline phase guaranteed by the F-T synthetic wax content is supported by temperature-induced changes that occur in the bitumen. These interrelated factors have an effect on the magnitude of the maximum tension force and on the structure of the modified bitumen 35/50.

3.2. Complex modulus G* of the F-T synthetic wax modified bitumen. Bitumen complex modulus is a comprehensive measure of the susceptibility of binders as viscoelastic materials. The analysis covered the evaluation of changes in the complex modulus of bitumen 35/50 modified with the F-T synthetic wax as a function of frequency, which represents the loading time by a vehicle axle. The results from the complex modulus measurement analysis for modified bitumens at 50°C, 60°C, and 90°C are shown in Fig. 5.

Increased amount of F-T synthetic wax F-T leads to the increase in the value of complex modulus. The frequency interval from 0 to approximately 2 Hz is characteristic here. This interval represents time for which the pavement is loaded by vehicles moving at a speed of up to 60 km/h and this frequency interval is where the pavement is exposed to damage. Asphalt mixtures as viscoelastic materials are characterised by creep and relaxation. This phenomenon involves slow dispersion of energy accumulated during loading. Long loading time in the creep process magnifies the level of irreversible accumulated strains in the asphalt mixture. For temperatures 50°C and 60°C, the sensitivity of the bitumen to the loading time for the binder modified with more than 2.5% F-T synthetic wax is 10-fold lower than that for the original bitumen 35/50. It is important to note that the main objective behind bitumen modification is creating the binder of low sensitivity in terms of the complex modulus, within the range of up to 2 Hz.

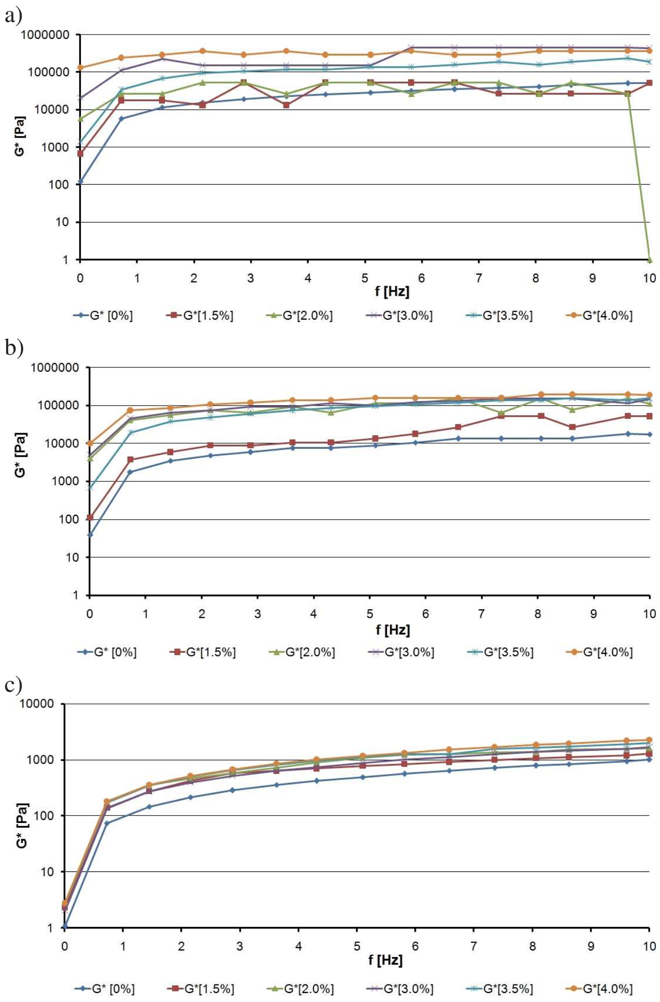

Fig. 5. Influence of F-T synthetic wax on complex modulus G* of bitumen 35/50 at specific test temperatures: a) at 50°C, b) at 60°C, c) at 90°C

It has to be noted that for frequencies from 2 to 10 Hz, the complex modulus change establishes at a similar level. This is associated with the extension of relaxation time in relation to the loading time. For the test temperature of 60°C, the stucturing influence of 2.5 to 4% F-T synthetic wax prolonged the relaxation time significantly, the result being the approximately constant level of the complex modulus of the modified bitumen (semi-logarithmic scale) with respect to the loading frequency from 1 Hz. The same phenomenon in unmodified/original bitumen 35/50 was observed at a loading frequency of 2 Hz. At a temperature of 50°C, the structuring character of the F-T synthetic wax magnifies this phenomenon by affecting the relaxation period extension and limiting the creep process. The test temperature has an important influence on the magnitude of the bitumen complex modulus.

At a temperature of 90°C, loading frequency significantly affects the change in complex modulus G*. This characteristic influence of temperature caused a 100-fold drop in the complex modulus of the modified bitumen 35/50 at 60°C. The very short relaxation time is also characteristic.

The change in complex modulus value depending on the phase angle of the F-T synthetic wax bitumen 35/50 is shown in Fig. 6.

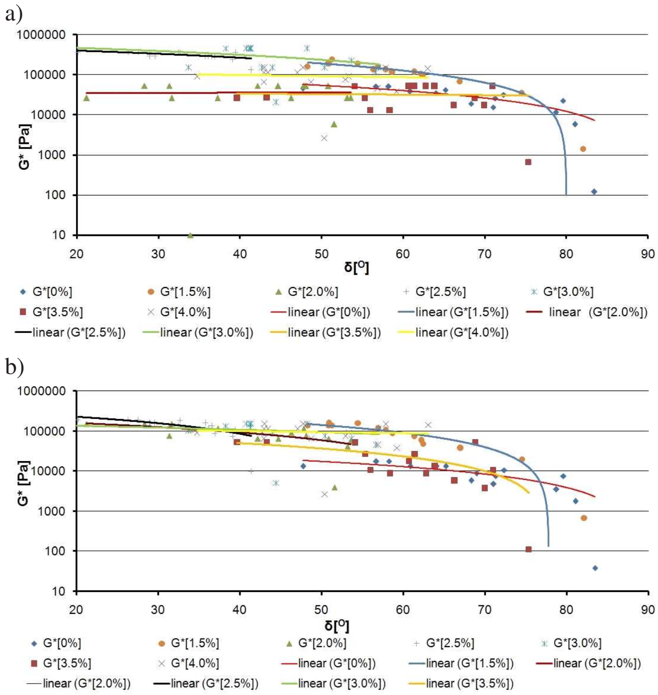

Fig. 6. Influence of F-T synthetic wax on the complex modulus value of bitumen 35/50 at a) 50°C, b) 60°C

A comparison of the characteristics presented in Fig. 5 suggests the conclusion that despite similar values of the bitumen 35/50 complex modulus, the phase angles change significantly. At a temperature of 50°C, bitumen 35/50 containing approximately 2% F-T synthetic wax reaches the phase angle level of below 30°. At a temperature of 60^{o}C, the phase angle values have a similar distribution but they are arranged in a better way. This results from the fact that at 50°C measurement limiting values are reached on a viscometer with coaxial cylinders. Similar changes in the complex modulus can be observed regardless of the temperature (Fig. 6a,b). But with increasing amount of the F-T synthetic wax incorporated in the binder 35/50, the value of the phase angle decreases continuosly. The phase angle value for bitumen 35/50 at 60°C ranges from 70 to 85°. Bitumen modification with 4% synthetic wax makes that value range from 20 to 40°. Bitumen 50/70 modified with F-T synthetic wax also demonstrates more elastic behaviour, but the influence of the modifier is less significant within the given experimental domain than it is for bitumen 35/50.

A comparable level of the complex modulus G* at the decreased range of the phase angle for the modified bitumen

35/50 is indicative of the growing value of the complex modulus elastic component (G*/sinδ) relative to the viscous component. In that case a similar level of complex modulus G* for bitumen 35/50 and decreasing phase angle range will suggest a large portion of elastic resonse of the binder 35/50 in service. This fact may support the conclusion that F-T synthetic wax has a considerable effect in the asphalt concrete rutting process, and that the binder together with the strengthened structure will take up part of the shear stress from the asphalt concrete pavement [23].

The tests for the bitumen 35/50 modified with F-T synthetic wax at the cyclic loading frequency of 1.56 Hz (corresponding to loading time for 60 km/h) at various temperatures were performed in accordance with SHRP procedures. SHRP functional tests include the criteria that eliminate too sensitive bitumens, and according to which non-aged binders should have sufficient stiffness that reflects the level of parameter (G*/sinδ) higher than 1000 Pa. The results form the modified bitumen 35/50 tests at temperatures ranging from 50 to 90°C at the frequency of 1.56 Hz are shown in Fig. 7.

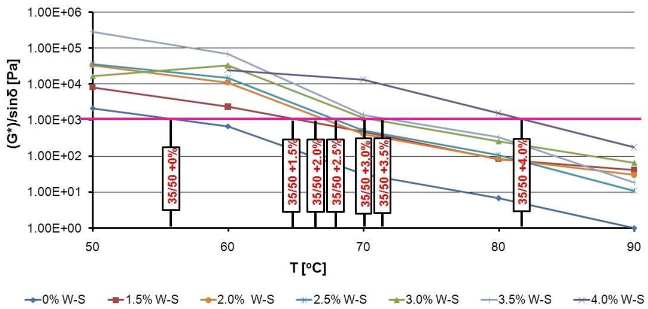

Fig. 7. Influence of F-T synthetic wax on changes in the elastic component (G*/sinδ) of the complex modulus for bitumen 35/50 as a function of temperature

The results from the tests for the complex modulus elastic component (G*/sinδ) demonstrate that at a temperature of 60°C, bitumen 35/50 is below the critical value (line that conforms to the value of 1000 Pa) and thus the viscous component of the complex modulus will not be large and will not affect the rutting test result obtained at 60°C to a significant extent. The modified bitumen 35/50, even at the minimum F-T wax content of 1.5%, meets the SHRP criteria and modulus value is higher than the required value at 60°C. Modification of bitumen 35/50 with 2.5% synthetic wax will result in the asphalt mixture containing this binder being more resistant to permanent deformation at a temperature as high as 70°C. For bitumen 35/50 modified with 4% F-T synthetic wax, parameter (G*/sinδ) $=$ 1000 Pa is achieved at a temperature of 80°C. This result is associated with the presence of the F-T synthetic wax crystalline phase, which influences the structure of bitumen 35/50 to a significant degree. The results from the bitumen susceptibility tests, carried out to SHRP procedures, and LSV explain a similar phenomenon associated with high viscosity of the original bitumen structure. Linear correlation analysis results (semi-logarithmic scale) for parameter (G*/sinδ) and LSV for the modified bitumen 35/50 at the temperature ranging from 50°C to 90°C are shown in Fig. 8.

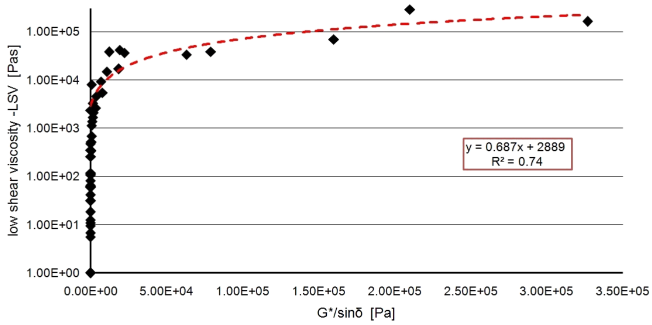

Fig. 8. Correlation between the results of modulus G*/sinδ (at a frequency of 1.56 Hz) and viscosity values at small shear stresses for bitumen 35/50, modified with F-T synthetic wax

The analysis confirms the statement that there is a strong correlation between the results obtained from the G* real part tests and LSV for the bitumen 35/50 modified with the F-T synthetic wax. It is important to note that, due to a different behaviour of polymer bitumen, the low correlation of parameter G*/sinδ according to SHRP in relation to the rutting results predication has been frequently signalled [24, 25]. The level of the coefficient of determination $R^2 = 0.74$ in the simplest linear model revealed good correlation of the results from both tests for the modified bitumen 35/50. Thus the result obtained for the F-T wax modified bitumen 35/50 can be used to evaluate the binder susceptibility to permanent deformation [26, 27].

3.3. Role of the F-T synthetic wax in bitumen creep according to MSCR procedure.

The values of the susceptibility to strain Jnr100 (stress 100 Pa), Jnr3200 (stress 3200 Pa) and elastic recovery R [%] of the modified bitumen 35/50 were determined based on the MSCR procedures in the process of applying and removing the load from the binder at 60°C (Fig. 9).

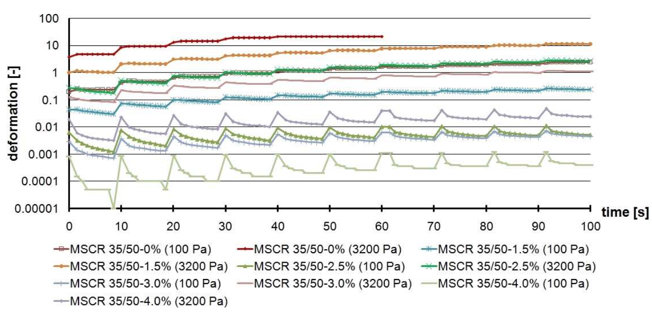

Fig. 9. Influence of F-T synthetic wax on changes in strain of binder 35/50 for the set dynamic stress

The test temperature in the MSCR procedure refers to the highest in-service pavement temperature and is a very important characteristic in the rutting test [27]. At 60°C, bitumen 35/50 is in the rheological sol-gel state. Thus to describe its behaviour, strain changes in particular, the Maxwell model was used. This model describes relaxation very well and is a simple tool in an evaluation of the relationship between the loading time and the relaxation time [28]. Under the tangential stress, immediate strain occurs with the value of τ/G (ratio between tangential stress and the shape elasticity module), whereas the damping element deforms uniformly at the deformation increase rate τ/η (the ratio of tangential stress to viscosity).

After transformation of the Maxwell model assumptions, the equation takes the form

$$\varepsilon = \frac{\tau}{G} + \frac{\tau}{G} \cdot \frac{t}{\theta} \cdot n, \tag{3}$$

where τ – tangential stress, G – shape elasticity modulus, t – loading time, θ – relaxation time, n – number of loading cycles.

A complete model of changes can be described using a linear function

$$y = a \cdot x + b, \tag{4}$$

where

$$a = \frac{\tau}{G} \cdot \frac{t}{\theta} \cdot n, \qquad b = \frac{\tau}{G}.$$

As parameters τ, G are constant values of the bitumen, the ratio of loading time to relaxation time can be determined. The low value of the ratio t/θ suggests the binder's trend to excessive plastic deformation. The higher the "a" parameter of the regression fucntion, the higher the binder's susceptibility and the shorter the relaxation time.

The results of the model parameters for the modified bitumen 35/50 are shown in Table 5 and 6.

The results of the linear regression model parameters fit for bitumen 35/50 suggest a significant difference in their values depending on the F-T wax content. As for the influence of the the tangential stress of 100 Pa (Table 5), the relative variation level of the deformation rate expressed by parameter "a" between 0% and 1.5% F-T wax concentration (loading variation against relaksation time) is approximately 90.26% for the bitumen 35/50. In other cases, the difference is bigger than 95% (compared with 0% F-T wax content in bitumen 35/50). This indicates the extension of the binder relaxation time (at tangential stress of 100 Pa) with the increase in F-T synthetic wax content. The difference in the parameter "a" value (slope) between 0% and 2.5% synthetic wax amount contained in the bitumen 35/50 is about 10-fold, and when the relation 0% and 4.0% synthetic wax content in the binder is compared, the ratio is 1000-fold. The use of original and modified bitumen 35/50 makes the results different relative to the level of "a" (varied susceptibility). The values of parameter "b" decrease with the increase in F-T synthetic wax content in the bitumen 35/50, which indicates a growing value of the binder complex modulus.

As for the test for the high tangential stress values, 3200 Pa (Table 6), the variation of coefficient "a" is lower than that for the tangential stresses of 100 Pa. This is associated with a quick disarrangement of the binder's structure due to the stress (3200 Pa) in the modified bitumen 35/50 with a lower F-T synthetic wax content. Therefore, stresses generated in the binder have values close to the limiting stress value at which the binder tested will work beyond the linear viscoelasticity range. When the LVE (linear visco-elasticity) is exceeded, it is impossible to perform a comparative analysis due to non-laminar flow of the bitumen during the measurements.

Table 5
MSCR test regression model parameters for bitumen 35/50 modified with F-T synthetic wax at = 100 Pa

Parameter of the model	Synthetic wax content [%]				
	0	1.5	2.5	3.0	4.0
a	0.023744242	0.002313515	4.11515E-05	4.17936E-05	4.5447E-06
b	0.002066667	0.010606667	0.001306667	0.0004418	−3.35667E-05
R^2	1.00	1.00	0.96	1.00	0.99
relative difference to 0% F-T wax	–	90.26	99.83	99.82	99.98

Table 6
MSCR test regression model parameters for bitumen 35/50 modified with F-T synthetic wax at =3200 Pa

Parameter of the model	Synthetic wax content [%]				
	0	1.5	2.5	3.0	4.0
a	0.034341212	0.003711697	6.20606E-05	1.48256E-05	7.25921E-06
b	0.003933333	0.024466667	0.001406667	0.000281253	6.37133E-05
R^2	1.00	1.00	0.99	0.99	0.99
relative difference to 0% F-T wax	-	89.19	99.82	99.96	99.98

3.4. Bitumen structural analysis under a fluorescence microscope. The spectroscopic images obtained from the fluorescence microscope suggest that the presence of the crystalline phase of the F-T synthetic wax plays an important role of a very fine temperature-controlled filler. Temperature increase makes the bitumen stiffer due to the formation of an internal crystalline structure. The observations of the F-T wax modified bitumen 35/50 spectrum under the fluorescence microscope are presented in Fig. 10.

The results obtained using the microscope are the digital data. It is thus possible to perform a quantitative analysis of the structures obtained, characteristic of F-T wax in bitumen 35/50. The assessment of the variation between lengths of F-T synthetic wax structures in bitumen 35/50 was carried out through the analysis of variance (ANOVA), presented in Table 7.

Analysis of variance (Table 7) indicated that the amount of F-T synthetic wax has a significant influence on the length of its crystalline forms in bitumen 35/50. The evaluation of the results revealed that the length of these structures increases with the increasing F-T synthetic wax content. The nature of the distribution (skewness) is the same for each of the cases. The quantity of the F-T synthetic wax structures larger than the average length, represented by the median (50% population), will increase with the increasing F-T wax concentration, which is manifested as growing irregularity in longer and shorter forms quantities. This phenomenon can be interpreted as an aggregation of smaller structures with the progress of time. The level of this aggregation is controlled by the resin phase in the bitumen. The magnitude of the standard deviation (red diamond) increases, but at the levels from 3.5% to 4% it remains the same. With progress of time this informs about increasing saturation of the bitumen phase with F-T synthetic wax forms.

The results from the comparative analysis performed using Tukey's test for identification of quantitative distribution of the F-T synthetic wax forms contained in the bitumen 35/50 are shown in Fig. 11, with the circles representing range intervals.

The size of the set of results represented by the interval range is negligible, which suggests a significant variability of subsequent values (for the given dosage) of the mean polyethylene structure lengths in the binder.

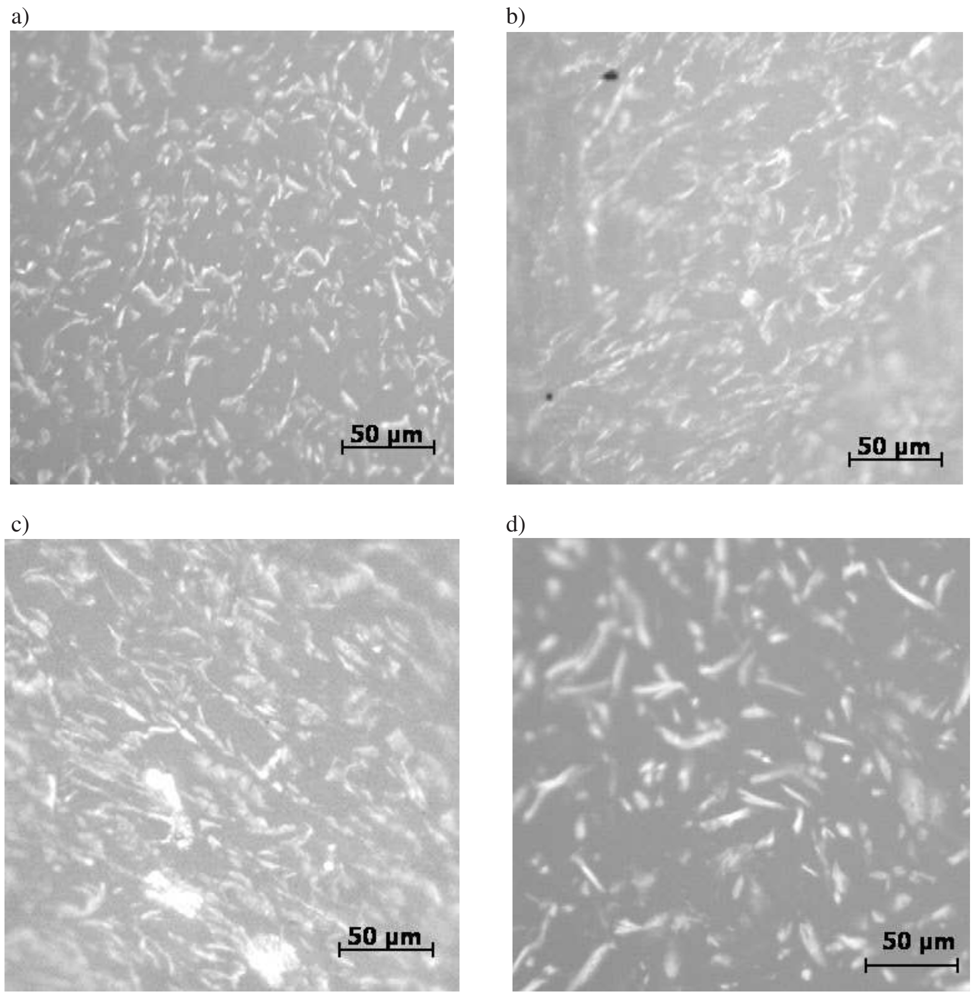

Fig. 10. Photographs of the synthetic wax phase present in the bitumen 35/50 phase recorded using a fluorescence microscope for synthetic wax contents: a) 1.5%, b) 2.5%, c) 3.5%, d) 4.0%

Table 7
Analysis of variance (ANOVA) – the influence of the modifier amount contained in bitumen 35/50 on the length of F-T synthetic wax structures

Source	df	Sum of squares	Mean of squares	F value	Pr > F
Model	3	3150.10024	1050.03341	38.74	<.0001
Error	432	11710.48132	27.10760		
Total corrected	435	14860.58156			
W-S (F-T wax content)	3	3150.100239	1050.033413	38.74	<.0001

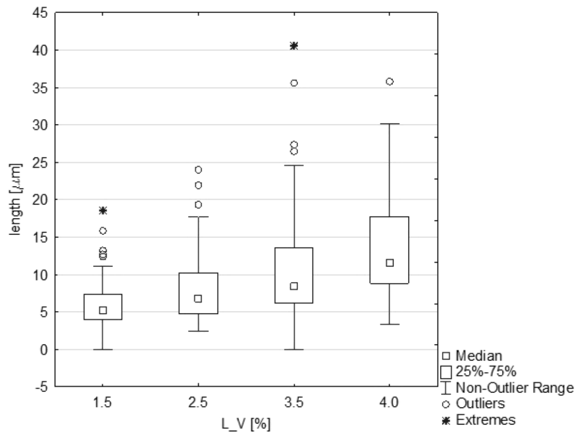

Fig. 11. Quantitative analysis of the recorded structure lengths (F-T synthetic wax F-T) in bitumen 35/50

Quantitative analysis revealed that an increase in the F-T synthetic wax amount at its certain concentration may lead to the formation of crystals which through the excessive aggregation will stiffen the modified bitumen 35/50 up to the level of its increased brittleness. Therefore the value of the "length" parameter may be decisive in determining the critical amount of F-T synthetic wax F-T added to bitumen 35/50. The presence of the binder coating the crystals of the F-T synthetic wax is responsible for the lubrication effect that occurs among them providing the structure of the binder with an elastic character at low temperatures.

3.5. Spectroscopic evaluation of the F-T synthetic wax modified bitumen composition. The aim of the test was to establish the character of change in the proportions of bitumen 35/50 group components as a result of the modification with F-T synthetic wax, which causes the change in the transmittance of the wave number of specific atom bonds in the chemical compounds of the binder (Fig. 12).

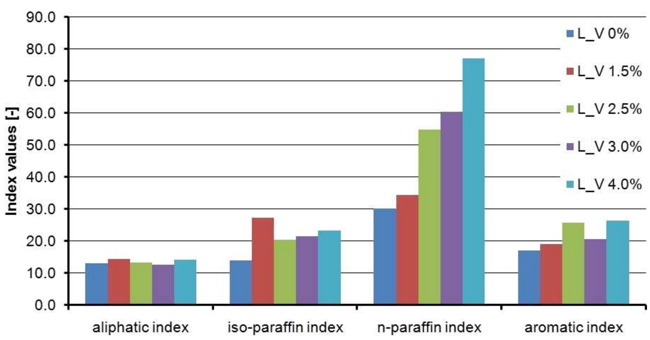

Fig. 12. Structural compounds indices for bitumen 35/50 at varied F-T synthetic wax content

Group type analysis of the modified bitumen 35/50 (Fig. 12) indicates that the most significant changes occur in the binder aliphatic fraction ranges, that is, in the ranges that also constitute the structure of the F-T synthetic wax.

It is important to note that the branch structure index of the bitumen 35/50 modified with different amounts of F-T synthetic wax did not change considerably in relation to the original binder, and the variation value does not exceed 10%. However, this value increases dynamically in relation to the aliphatic structure index of the modified bitumen 35/50 with long chains. The change compared with non-modified 35/50 is higher of even 70%. This describes the nature of the modifier's dispersion in the binder phase. It has to be noted then that the composite that consists of F-T synthetic wax and bitumen 35/50 is not subject to a full chemical homogenisation. Aliphatic hydrocarbons undergo a process of dissipation and do not react with bitumen 35/50. Aromatic index does not show any significant level changes in comparison with branch aliphatic hydrocarbons index or long-chain aliphatic hydrocarbons. Thus this modifier type indicates the existence of the phase of long-chain aliphatic hydrocarbons, which act as fine filler in bitumen 35/50. Therefore crystalline structures of F-T synthetic wax are visible at low temperatures. Owing to its range of phase change, this type of modifier facilitates controlling the viscosity of the entire bitumen composite.

Harrington's utility function [22] was used to determine the F-T synthetic wax content that would ensure optimum properties of bitumen 35/50

$$U^{III} = \exp\left[-\exp\sum_{i=1}^{m} w_i \cdot \left(-\frac{y^{(i)} - y_G^{(i)}}{y_L^{(i)} - y_G^{(i)}}\right)\right], \tag{5}$$

where $y^{(i)}$ – investigated properties of the modified bitumen 35/50, $y_L^{(i)}$ – worst value of the i-th property being investigated, $y_G^{(i)}$ – best value of the i-th property being investigated, w_i – weights assigned to individual properties $y^{(i)}$, $0 \leq w_i \leq 1$; $i = 1, 2, \ldots, m$; $\sum_{i=1}^{m} w_i = 1$.

It was assumed that all properties of the modified bitumen 35/50 are the same significant. Thus all the functional properties of the binder were assigned the same weights. The analysis of the results from the binder functional tests, obtained using Harrington functions indicates that the most beneficial amount of the F-T synthetic wax used to modify bitumen 35/50 is 2.5%.

4. Conclusions

The following conclusions can be formulated based on the tests evaluating the influence of F-T synthetic wax on the properties of bitumen 35/50:

- F-T synthetic wax has a positive influence on the ductility of bitumen 35/50 and allows modelling the rheological state of the binder in terms of structural viscosity, complex modulus and the phase shift angle;
- an addition of 1.5–4.0 % F-T synthetic wax increases the structural viscosity of bitumen 35/50 by extending the range of the material's linear viscoelasticity behaviour;
- F-T synthetic wax acts as filler with a crystalline phase, the form magnitude of which depends on its content in the binder and on temperature;
- the use of 1.5% to 4.0% synthetic wax as a bitumen 35/50 modifier extends the binder relaxation time thus affecting the asphalt mixture plastic deformation range;
- the group types analysis of the F-T synthetic wax modified bitumen 35/50 clarified the mechanism of making the binder more structured;
- F-T synthetic wax has a significant influence on the potential for deformations Jnr100 (stress 100 Pa) and Jnr3200 (stress 3200 Pa) and the value of elastic recovery R [%] of the modified bitumen 35/50, determined based on the MSCR procedures used during strain tests in the process of load application and removal at a temperature of 60°C;
- the optimisation using the Harrington test helped determine the most advantageous F-T wax content of 2.5% for the modification of bitumen 35/50. This amount of the F-T synthetic wax will guarantee high quality of the warm mix asphalt (WMA).

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