THE INFLUENCE OF RHEOLOGICAL PROPERTIES OF BITUMEN WITH SYNTHETIC WAX ON CHANGING RESILIENT MODULUS OF ELASTICITY OF ASPHALT CONCRETE

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ABSTRACT

The papers presents the assessment of correlation between the viscoelastic properties of low-viscosity bitumen and thermal susceptibility of the resilient modulus of elasticity. Tests were carried out on the asphalt concrete AC 11 S in accordance with PN-EN 13108-1. The experiment was conducted on samples of bitumen which penetration was 35/50. Six variants of the modification were prepared by application the low-viscosity modifier (obtained in process of Fisher-Tropsh synthesis) in the range of 1.5 % to 4 % with steps 0.5 %. The asphalt concrete was compacted at temperature range between 110°C and 145°C. The framework of mineral mix in all samples was identical. The following properties of bitumen binders were considered: complex modulus $G^*$, phase angle $\delta$ in frequency range of 0,01 to 10 Hz. Moreover, bitumen tests were supplemented by assessment of additional properties such as: dynamic viscosity versus shear rate in temperature range of 110°C and 145°C, penetration grade, softening point and breaking point temperature. The following properties of asphalt concrete were tested: void fraction content, resilient modulus of elasticity at temperature range of -5°C to 25°C. In results of research process was found that viscoelastic properties of low-viscosity bitumen considerable affected changing the resilient modulus of elasticity in relation to the reference asphalt concrete. The evaluation of test results revealed that thermal susceptibility of resilient modulus of elasticity was mainly depend on concentration of synthetic wax content in virgin bitumen which in significant way stiffen the asphalt concrete.

Keywords: bitumen, asphalt concrete, viscoelastic properties, low-viscosity modifier, Fisher-Tropsh synthesis
1. INTRODUCTION

Environmental aspects at the present time are one of the most important issues in road construction. In the face of increasingly high cost of processing fuels derived from the non-renewable sources force us to look for more suitable technology which delivers the ecological and the environmental protection. All the world economy, limit the amount of pollutants emitted mainly from energy generation. The situation was regulated by international agreements in the wording of the Kyoto Protocol 2005. Benefits of lowering production and compaction temperatures of the asphalt mixtures have been considered in results [1,2]. The use of asphalts of the low temperature compaction, or in other words, warm mix asphalt (WMA) provides many benefits of technological and environmental production.

For technological and manufacturing advantages benefits can be listed as:
- Decreased levels of aging bitumen due to the reduction of temperature in the manufacturing process, the lowering the temperature up to 10 °C causes a twofold increase of asphalt oxidation [3],
- improved workability of the mix due to the reduced viscosity at low temperatures producing asphalt,
- reduced compaction resistance makes the compacting process easier by reducing compaction temperatures,
- cooling process grows much slowly in mixtures.

The environmental benefits include:
- reduction of CO\textsuperscript{2} emissions,
- reduction of energy consumption required to bring the binder on the required level of the viscosity,
- less inconvenience due to the lower level of odor emissions oil fractions contained in the asphalt,
- easier permitting asphalt plant near inhabited areas,

There are many benefits of applying WMA technologies. Generally, this state of affairs can be achieved by modifying the binder by means of organic modifiers, viscosity reduction by the dispersion of the binder with water vapor, or a reduction in surface tension which improve a covering of aggregate. The aim of this study is to evaluate the impact of modification of the binder by aliphatic hydrocarbon additives. From the fact that the modification of the bitumen is a fundamental element of this type of the technology (WMA) the part of the paper was assigned especially to the analyses of influence the wax on bitumen rheology which is a key factor for WMA technology. The changes in rheology that occurred in bitumen will have a bearing on a behavior entire asphalt concrete.

As mentioned, an example of such WMA technology is the use of synthetic waxes obtained from the synthesis of Fischer-Tropsch (F-T). F-T synthetic waxes are varied from natural wax because F-T waxes contain more carbon atoms in the molecule (40-100) while the number of carbon atoms in natural paraffins do not exceed of 40. It should be noted that these waxes have a large number of particles ISO-paraffin affects forming the fine microcrystalline structures well-dispersed in asphalt. Additionally, the possibilities of lowering the temperature up to 10 - 30 °C, in ambient temperature, delivers a possibility maintenance of the crystal phase of the hydrocarbons which favorable hardens of the bitumen. Lowering the costs associated with increasing bitumen properties to the desired level of the viscosity influences on reducing compaction energy and simultaneously affects the rut resistance. Addition of synthetic wax modifier can increase the softening point and reduce the penetration grade of the bitumen in comparison with neat bitumen [4], which in turn influences on the thermal sensitivity of the asphalt. Moreover, the change in characteristics of the visco-elastic, describes the bitumen as a material predominantly elastic.

2. EVALUATION OF IMPACT OF THE F-T WAXES ON BITUMEN PROPERTIES

Comparative studies with different types of bitumen have been presented in [5,6,7]. The authors showed that for modification much more advantageous are softer bitumen because of their rheological nature of the sol or gel-sol. The studies showed a large share of continuous phase that it allows to make the cross-linking structure by enrichment of asphalten forms part by means of saturated high molecular weight synthetic waxes. In this paper the reference bitumen was a bitumen of penetration grade of 35/50 was used as an example that there is on the border of two rheological types: gel and gel-sol. Due to the relatively high stiffness of bitumen it can be possible exaggeration of the effect of synthetic waxes. The tests of the impact of the low – viscosity modifier on changes of the bitumen properties were carried out for the traditional 35/50 bitumen. These binder was modified by the low-viscosity modifier in the range from 1.5% to 4.0% with steps 0.5% in proportion to the amount of the bitumen. The samples were blended according to condition of production [8].

2.1 Penetration index

The penetration index reflects the thermal susceptibility of the bitumen and it is an indicator concerning assessment of rheological state of a bitumen. The penetration index has been determined on the base of two fundamental parameters in accordance with following equation:
where:
\[ P_I = \frac{20 \times T_{pk} + 500 \times \log P - 1952}{T_{pk} - \log P + 120} \]

[T_{pk} – softening point temperature [°C],
P – penetration in temperature of 25°C [x 0,1mm].

In view of the possibility of deterioration of bitumen properties at low temperatures [9] the fragility evaluation was carried out by mean of breaking point temperature test in accordance with the Fraass methodology. The evaluation of the penetration index and breaking point temperature were presented in figure 1.

On the basis of a separate analysis the correlation between the penetration index and the breaking point temperature it was registered that the correlation ratio did not reached the value of 51% in the current experiment, so it is difficult to determine its significance. The fact of hardening of the bitumen (increase IP) relates completely to the existence of the paraffin crystal forms in waxes and asphaltene structures at the current level of resin [10]. The modification of bitumen 35/50 in the amount from 2.0% to 3.5% guaranties obtaining the penetration index values between +1 and +2, and indicates on the existence of reserves of flexibility at low temperatures. The absence of negative effects of waxes in the amount of 3% in the low and medium temperature were presented in the work [7].

2.2 Complex modulus and phase angle

Complex modulus and phase angle are an assessment of the visco-elastic behavior of bitumen listed in the SHRP methodology [12]. The interrelation between the complex modulus and the phase angle is an evaluation of the elastic and viscous part of the binder. Both of these relationships change depending on the temperature and the loading time. At low temperatures, the phase angle \( \delta \to 0^\circ \), indicates an elastic-brittle behavior of the binder. At temperatures, where \( \delta \) is close to 90 degrees the bitumen tends to the Newtonian fluid state. An important issue is making a bitumen modification in such way that changing the phase angle was not too violent. Of course, the bitumen condition characterized by the phase angle is not sufficient, the modulus value is interactively important. The complex modulus decides about a possibility of receiving small deformation at high stress [16]. The results of the phase angle and the complex modulus are presented in figure 2.
In order to evaluate the increase dynamics of the complex modulus as a function of changing frequency an assessment of the slope of the complex modulus at specified frequency ranges was made. The value of the slope was calculated according to the equation:

$$\alpha_{Hz1-Hz2} = \frac{\log(G^*(Hz2)) - \log(G^*(Hz1))}{Hz2-Hz1}$$

where:
- Hz1,Hz2 - current limits of frequency ranges,
- G*(Hz) - complex modulus at current frequency.

Test results were presented in figure 3.

Complex modulus expresses the potential resistance to deformation under cyclic loading and it must be considered that the increase in its value will improve the resilient modulus of elasticity of the asphalt concrete. The test results indicate that as the load frequency increases the complex modulus increases (Figure 2). However, regardless of the temperature, the low-viscosity modifier affected the increase of the level of the complex modulus in each variant of dosage. All bitumen modification variants and the reference bitumen had a value of (elastic part) $G^*/\sin(\delta) > 1000$ Pa at a frequency of 1.56 Hz what it corresponded to the loading time at 60 km/h according to the SHRP. Compared to the reference bitumen the level of complex modulus for the amount of modifier of 3.0% has a sevenfold increase. In that situation a significant rut resistance should be expected in normal traffic conditions and at lower speeds, expressed by the time the load of 0.5 Hz (38 km/h), where at the modification of 1.5% the complex modulus was still greater than 1000 Pa. This level of hardening of bitumen guaranties the low susceptibility of asphalt concrete to permanent deformation within the confines of SHRP programme [12]. Nature of the dynamics of the complex modulus and the level of its change (Figure 3) indicates that in the range between 0.001 to 10 Hz there is a statistically significant increase in the modulus $G^*$ value. It must be noted that regardless of the amount of low-viscosity modifier (the whole of experiment domain), the rate of growth, with relation to the reference bitumen, is proportional. Variations in the frequency values are similar but in
some cases are even leaser. This state of affairs probably corresponds to the quality of fine microcrystalline synthetic waxes dispersion, whose presence does not impair the integrity of the colloidal structure of the bitumen. With respect to the phase angle the increase in value of low-viscosity content causes the reduce in value of this physical quantity. In some cases, up to 50%. It could be expected that the bitumen modified by synthetic wax had a elastic behavior with a high capacity to accumulate and release energy coming from the axle loads [10].

2.3 Low Shear Viscosity

Zero shear viscosity ZSV is an alternative parameter which predicts a susceptibility of the binder in the aspect of the possibility of occurring the plastic deformation coming from axe loads at high ambient temperatures [19]. The need of applying this parameter was established at the time when polymerized modifier was appeared. This type of asphalt has a high resistance to plastic deformation during long-time load, which did not revealed the complex modulus G* and phase angle δ that were accepted as the standard parameters. The idea behind this study was determined the structural viscosity at the shear stresses tended to zero. Due to the difficulty of fixing this parameter also flagged in [13] the further analysis was carried out by using a parameter LSV (low shear viscosity) instead of ZVS, which describes the viscosity at the very low frequency equal to 0.005 Hz. The variability of test results, determined by means of the Grubbs test [11], did not exceed 7%. The results of the LSV of the low-viscosity bitumen depending on the amount of synthetic waxes are shown in Figure 4.

![Image](image_url)

**Figure 4**: Influence of synthetic waxes on the low shear viscosity [LSV]

The results of the LVS indicate that increasing the amount of the modifier decreased the susceptibility of the plastic deformation of the bitumen. The highest growth was registered in the range from 1.5% to 2%. This may be related to obtaining by the bitumen 35/50 saturation point of paraffin crystals. Further increase of the modifier causes changes in the LSV, but their growth is not so violent.

2.3 Apparent viscosity versus shear stress

The aim of this study is identification of changes in the structure of modified bitumen. The bitumen is a colloidal compound built of particles that have various shapes [17]. Therefore, the stability of the structure of the bitumen in the visco-elastic state will depend on the level of shear stress which could breach a state of equilibrium. Relative element of this research is an evaluation the thixotropic behavior in a current stress sweep (pseudoplastic fluid). In figure 5 there are a viscosity as a function of the shear stress of the low-viscosity bitumen (F-T).
It should be noted that as the level of modification was changed the viscosity decreased in whole value range of shear stress. The increase in the apparent viscosity value, depending on the FT waxes content, shows a good correlation with the results of the LSV as signaled in Figure 4. Noticeable was the fact that the level of the viscosity in the initial phase of the shear stress level is constant and does not depend on the stress values. With increasing amounts of synthetic waxes the shear stress range, in which the level of the viscosity is constant, becomes wider. This fact indicates on behavior of material in non-disturbed phase. The observed phenomenon is related to the presence of the fine crystals of paraffin that are well dispersed in the phase of bitumen. They alternatively fill the colloidal structure like asphaltene forms in the bitumen. Such favorable cross-linking will influence on much more asphalt concrete reliability in the high operating temperature up to 60 °C. Wider range in which the bitumen has a high apparent viscosity at a low stress level will provide a lower probability of potential ruts forming. Another feature, that is noticeable, is the fact that the high level of (Newtonian) viscosity, after exceeding the level of the stress, is connected with a non-disturbed state. State viscosity at the maximum stress level of 2000 Pa, in relation to the measurement device, is still higher than the reference bitumen viscosity which was not subjected to modification.

3. DESIGN OF THE ASPHALT CONCRETE MIX

3.1 Design of the mineral mix

In order to assess the impact of the low-viscosity bitumen on properties of the asphalt the experiment was carried out for asphalt concrete of AC 11 S for the wearing coarse layer PN-EN 13108-1. The mineral mix was designed by means of the best fitting a current curve between the limit curves by using an authorial optimization algorithm made of VBA computer's language. Results of optimization with regard to increasing of grit fractions were shown in Figure 6.
The reference asphalt concrete that was designed consisted of the principal aggregate of the gabbro in amount of at 50%. A dolomite mix 0/4 and granite fractured sand were used to increase fraction contents. Composition of the mineral mixture was used in all variations of modifications of the bitumen and the compaction temperature level.

3.2 Laboratory of the asphalt concrete AC 11 S

On the basis of the mineral mix composition the amount of the bitumen has been optimized. With regard to the reference asphalt concrete the optimal amount of bitumen was 5.2% in accordance with PN-EN 13108-1 and also according to the Marshall methodology. Cylindrical samples were compacted in accordance with PN-EN 12697-10. Each side was subjected of 75 blows of the Marshall hammer. The results achieved by the reference asphalt concrete is shown in Table 1.

Table 1: The reference asphalt concrete test results

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Value</th>
<th>Coefficient of variance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Indirect tensile strength ratio ITS R</td>
<td>%</td>
<td>93</td>
<td>8.2%</td>
</tr>
<tr>
<td>Void contents WP</td>
<td>%</td>
<td>3.16</td>
<td>4.75%</td>
</tr>
<tr>
<td>Resilient modulus of elasticity at 20°C</td>
<td>MPa</td>
<td>4800</td>
<td>5.8%</td>
</tr>
<tr>
<td>according to PN-EN 12697-26</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

4.0 DESIGN EXPERIMENTS OF IMPACT OF THE LOW-VISCOSITY BITUMEN ON THE RESILIENT MODULUS OF ELASTICITY

4.1 Outline and evaluation of the request surface

The experiment was carried out basing on the factorial plan n x m (6x7). The graphic presentation of domain of the experiment is shown in Figure 7.
Figure 7: Design of experiment

When analyzing the impact of the low-viscosity modifier and compaction temperature on the resilient modulus of elasticity and additional content the void fractions, it was found that statistically significant was the linear regression and the polynomial model of second degree [14] [15]. Therefore, for further analysis the second degree polynomial model was adopted. To determine mentioned parameters, an important element of the study was homogeneity of the work. The study allows only a sample in which the voids in the group was ranged outliner results in line with the Grubbs test [11]. It should be noted that the average results for each variant of the modifier content and temperature were characterized by a coefficient of variance of lower than 15%. The following regression model was adopted:

\[ y = b_0 + b_1 \cdot x_1 + b_2 \cdot x_2 + b_3 \cdot x_1 \cdot x_2 + b_4 \cdot x_1^2 + b_5 \cdot x_2^2 \]

where:
\( x_1 \) – the low-viscosity modifier content [%],
\( x_2 \) – the compaction temperature [°C],
\( b_0 \) – values of experimental coefficients.

The graphical interpretation of regression models obtained from the resilient modulus of elasticity were presented in Figure 8.
Figure 8: Resilient modulus of elasticity at the temperatures of 2°C (E(2)), 10°C (E(10)) and 20°C (E(20))

Graphical interpretation of regression models obtained from void fraction contents were presented in Figure 9.

Figure 9: The graph of the void fraction contents (Wp)

Table 2: The Pearson's correlation $R^2$ factor and significant influence of factors on the resilient modulus of elasticity at temperatures of 2, 10, 20°C and void fraction contents

<table>
<thead>
<tr>
<th>Feature</th>
<th>$R^2$</th>
<th>Low-viscosity modifier content</th>
<th>Compaction temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resilient modulus of elasticity at temperature of +2°C (E(2))</td>
<td>0.79</td>
<td>0.2452</td>
<td>0.0033</td>
</tr>
<tr>
<td>Resilient modulus of elasticity at temperature of +10°C (E(10))</td>
<td>0.75</td>
<td>0.2403</td>
<td>0.0569</td>
</tr>
<tr>
<td>Resilient modulus of elasticity at temperature of +20°C (E(20))</td>
<td>0.82</td>
<td>0.0014</td>
<td>0.0288</td>
</tr>
<tr>
<td>Void fraction content Wp</td>
<td>0.71</td>
<td>0.3393</td>
<td>&lt;.0001</td>
</tr>
</tbody>
</table>

Analyzing the test results it should be noted that the compaction temperature has the highest impact on changes of the resilient modulus of elasticity in time of reducing the testing temperature which related to the temperature at which the asphalt concrete works. The level of the resilient modulus of elasticity decreased with rising the temperature. It is associated with reducing bitumen viscosity. Contrary to the trend of the impact of the compaction temperature, the high level of the resilient modulus of elasticity in the high measurement temperature was caused by the increase in value of synthetic waxes. Synthetic waxes at this temperature maintain relatively stable the crystalline state which could be interpreted as the presence of an additional filler in the mastic.
The existence of the fine microcrystalline waxes phase provides an increase in the rut resistance. Analyzing graphs of the resilient modulus of elasticity, it could be noted that the best results were obtained from asphalt concrete at compaction temperatures in range from 125 °C to 130 °C. This phenomenon is probably caused by the optimum level of bituminous binder viscosity. With regard to the void fraction content, as the compaction temperature increases with the interaction of increasing the low-viscosity modifier content, the lowest level was obtained. In this situation, there is noticeable the over-compaction effect of the asphalt concrete. The most statistically significant effect, regarding void fraction content, was observed for the compaction temperature. The level of the modern waxes influenced much smaller in case of this feature. Nevertheless, it was revealed the interaction effect of both factors which both influenced on the void fraction content. The level of 3.16% of void fraction content with respect to the reference compound was registered for configuration factors: the compaction temperature between 122 °C and 130 °C and the levels of low-viscosity modifier in range of 1.7% - 2.2%.

4.2 Preliminary correlational relationships of modified bitumen and asphalt concrete

On the basis of test results the correlation between the modified bitumen and the asphalt concrete properties were sought. According to this it was decided that the analysis will concern a evaluation of the asphalt concrete properties in aspects of modern wax contents and the constant temperature of compaction of 125 °C. The aim of analysis was a determination of the generalized correlations between the bitumen and the asphalt concrete properties such as:

- Resilient modulus of elasticity at +20 °C,
- Void fraction content.

Bitumen properties (factors) affecting the above-mentioned features included:

- LSV (low shear viscosity),
- Complex modulus at temperature of 60°C by frequency of 1,56Hz,
- Phase angle at temperature of 60°C by frequency of 1,56Hz,
- Penetration index.

In order to clarify the relationship between empirical values of the variables a multiple regression analysis with backward elimination method was used [14] [18]. The task of this method was to eliminate the variables with no statistically significant effect on the model and looking for the best solution, expressed by the regression, at the significance level of α = 0.1. For the analysis the regression function the current model was adopted:

\[ Y = \gamma + \beta_1 \cdot X_{i1} + \cdots + \beta_p \cdot X_{ip} + e_i \]

where:
- \( Y \) - asphalt concrete properties,
- \( X_i \) - bitumen properties, \( i=1,2,\ldots,n \),
- \( \gamma, \beta \) - regression constants,
- \( e_i \) - estimation error.

### Table 3: Assessment of the significance of the impact of bitumen properties on the characteristics of the asphalt concrete at the compaction temperature of 125 °C at the significance level α = 0.1

<table>
<thead>
<tr>
<th>Dependent explanatory</th>
<th>Resilient modulus of elasticity (E(20)) [MPa]</th>
<th>Void fraction content [Wp]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Penetration index</td>
<td>NS</td>
<td>S</td>
</tr>
<tr>
<td>Complex modulus [Pa]</td>
<td>S</td>
<td>NS</td>
</tr>
<tr>
<td>Phase angle [°]</td>
<td>S</td>
<td>NS</td>
</tr>
<tr>
<td>Low shear viscosity (LSV) [Pas]</td>
<td>S</td>
<td>NS</td>
</tr>
</tbody>
</table>

* NS – non significant, S - significant

The results in Table 3 indicate that the visco-elastic properties of the bitumen plays a main role on changes in value of mechanical properties of the asphalt concrete (resilient modulus of elasticity E (20)). Only in case of penetration index this factor did not play a significant role, while others factors had a significant influence. This state of affairs does not pose that the penetration index hasn't an important influence at all. With respect to the void fraction content the penetration index revealed a significant effect. Probably this situation is connected to the rheological character of the bitumen and a dynamic of reducing its viscosity.

5. CONCLUSIONS

Based on the analysis of the test results of asphalt concrete the following conclusions can be drawn:

- The bitumen 35/50 modified synthetic wax is characterized by an increase in penetration index in relation to...
the reference bitumen.

- With increase of the low-viscosity modifier the level of structural viscosity increases and level of the shear stress at 60 °C causing increasingly rut resistance of asphalt concrete
- The increase synthetic wax content in the amount of 2.0% significantly influenced on growth of alternative low shear viscosity parameter, complex modulus G* and phase angle.
- Synthetic waxes, incorporated into designed asphalt concrete, reduced the potential susceptibility to deformation, especially at high ambient temperatures.
- The high level of elastic resilient modulus of elasticity was caused by the interaction between the amount of the modifier and compaction temperature both of which have an impact on the viscosity during compaction. As a result of the conducted experiment at the modifier content of 2.5% the maximum resilient modulus of elasticity value was reached at the temperature of about 125 °C.
- The presence of synthetic waxes enables reducing compaction resistance and it lead to reducing of the void fraction content to the level of the reference mixture with decreasing the temperature up to 20 °C.
- Analysis of correlation points out to strong relationship between the resilient modulus of elasticity and visco-elastic properties of bitumen revealed by such parameters as LSV, complex modulus G* and phase angle.

REFERENCES