Abstract: Bituminous binders are broadly used for asphalt mixtures in construction of roads. They are often modified by synthetic polymers to improve their physical properties (to increase their softening point and decrease their breaking point). This paper deals with comparison of rheological parameters $\eta^*$, $G'$, $G''$ of selected polymer modified bituminous binders at the temperatures of 60 and 80 °C.

Keywords: polymer modified bituminous binders, rheological properties, oscillatory rheometer, complex viscosity, complex shear modulus

INTRODUCTION

Bitumen is generally material obtained as the residue of vacuum distillation process during the refining of crude oil [1]. It is broadly used as a binder in a construction of roads where it is mixed with aggregate to create asphalt mixture (Figure 1).

Bituminous binders are semi-solid at ordinary temperatures but they can be liquefied by applying heat. They are highly waterproof, durable and act as the glue that holds the road together. Mechanical properties of asphalt mixture are mostly affected by the properties of applied bituminous binder. Bitumen binder must be fluid enough at high temperature (about 160 °C) to create homogenous coating of the aggregates upon mixing. Depending on the local climate, it has to become stiff enough at the highest pavement temperature to resist rutting deformation and it must remain soft enough at low temperatures [2].

In order to obtain appropriate properties, bituminous binders are used not only in the form of pure bitumen (unmodified bitumens = paving grade bitumens, PBS) but they are modified by synthetic polymers. Polymer modified bitumens (PMB) have higher softening point and lower breaking point than unmodified ones and therefore they are recommended for construction of highly loaded roads in climates with large temperature changes [3], [4], [5].

Bituminous binders are thermoplastic liquids which behave as viscoelastic materials [3]. Their deformation behavior can be determined by their rheological parameters. The changes of both viscous and elastic properties with temperature and time are measured as the response of the material to deformation by periodic forces (during forced vibration or small-amplitude oscillatory shear). Stress and strain are not in phase, the strain delays behind the stress by a phase angle. If the oscillatory
shear is sinusoidal, shear stress $\tau$ is expressed [6], [7]:

$$\tau(t) = \tau_0 \cdot e^{i\omega t} = \tau_0 (\cos \omega t + i \cdot \sin \omega t)$$  \hspace{1cm} (1)

$\tau_0$ - stress amplitude, $\omega$ - angular frequency, $t$ - time and $i = \sqrt{-1}$.

The complex shear modulus $G^*$ [Pa] is defined as [6], [7]:

$$G^* = \frac{\tau(i)}{\gamma(i)}$$  \hspace{1cm} (2)

Equation (2) can be resolved into two parts:

$$G^* = G' + i \cdot G'' = \frac{\tau_0}{\gamma_0} (\cos \delta + i \cdot \sin \delta)$$  \hspace{1cm} (3)

The first $G'$ is in phase with strain, and the second $G''$ is out of phase with strain of angle $\delta$. Therefore, two dynamic moduli are defined [6], [7]:

$$G' = \frac{\tau_0}{\gamma_0} \cos \delta$$  \hspace{1cm} (4)

$$G'' = \frac{\tau_0}{\gamma_0} \sin \delta$$  \hspace{1cm} (5)

$G'$ is called storage modulus and its value is a measure of the deformation energy stored by the sample during the shear process. Thus, it represents the elastic behavior. Value of loss modulus $G''$ is a measure of the deformation energy used up by the sample during the shear process and therefore it represents the viscous behavior of the material. A part of this energy heats the sample and the residue is released as heat to environment. Sample with high loss modulus exhibits irreversible deformation [6], [7].

The complex dynamic viscosity $\eta^*$ [Pa.s] is defined by the equation

$$\eta^* = \frac{\tau(i)}{\dot{\gamma}(i)}$$  \hspace{1cm} (6)

$\dot{\gamma}$ [s$^{-1}$] presents the shear rate [6], [7].

This paper deals with the comparison of rheological parameters $G'$, $G''$ and $\eta^*$ in the chosen interval of angular frequencies [6].

EXPERIMENTAL MATERIAL

Rheological properties were determined and compared for three various polymer modified bituminous binders produced by different producers. Apollobit, Sealoflex and Kraton represent binders modified by synthetic polymer Styrene Butadiene Styrene [4], [5], [8], [9], [10].

Basic properties of tested materials are shown in Table 1.

<table>
<thead>
<tr>
<th>Type of binder</th>
<th>polymer modified binders</th>
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<tbody>
<tr>
<td>Softening point $[^{\circ}\text{C}]$</td>
<td>Apollobit</td>
</tr>
<tr>
<td>Penetration at 25°C [10$^{-1}$ mm]</td>
<td>min. 70</td>
</tr>
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<td>50 - 100</td>
<td>60 - 90</td>
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EXPERIMENTAL METHOD AND CONDITIONS

Measurements were performed on the oscillatory Physica Rheometer MCR301 with convection heating device CTD 450. The applied method was Frequency Sweep test (FS). FS method uses parallel plate system (PP system: lower plate is stationary, upper one is shear, performing oscillatory motion). The distance between the plates (shearing interval) is well-defined (Figure 2).

Figure 2. PP system, Physica Rheometer MCR301

FS test is run at a constant temperature. This measuring method enables simultaneous monitoring of rheological parameters $G'$, $G''$ and $\eta^*$ in the chosen interval of angular frequencies [6].

Each tested sample was placed between two parallel plates with diameter of 25 mm (PP25 system), in 1mm distance from each other (shearing interval = 1 mm). Measurements were carried out at the temperatures of 60 and 80 $^{\circ}$C. Amplitude of $\gamma$ was 5%, applied angular frequency $\omega$ was 30 – 600 s$^{-1}$.

RESULTS AND DISCUSSION OF EXPERIMENTS

The course of monitored rheological parameters $G'$, $G''$, $\eta^*$ in dependence on angular frequency is linear except for high angular frequencies 400 – 600 s$^{-1}$ at both temperatures (Figures 3 – 5). The curves $G'$ and $G''$ have no intersection point in observed interval of angular frequencies and therefore degradation which would be shown by
changes of molecular weight (as networking or macromolecular chains breaking) is not probable [6].

As we can see in Figures 3 – 5, the increase of temperature from 60 °C to 80 °C caused strong loss of parameters $G'$, $G''$ and $\eta^*$. At 80 °C, the curves expressing storage modulus $G'$ lose their linearity at the angular frequencies of 400 – 600 s$^{-1}$ (Figures 3 – 5). Sharp decrease of $G'$ means higher ratio between loss modulus $G''$ and storage modulus $G'$ (called damping factor) and it points to degradation connected with the loss of elasticity. This phenomenon is more pronounced for Sealoflex and Craton than for Apollobit modified binder.

Differences of complex viscosities of all tested samples in dependence on angular frequency $\omega$ can be seen in Figure 6 A, B. Apollobit modified binder reaches the highest values of complex viscosity at both temperatures and at both angular frequencies. All tested binders show sharp decrease of complex viscosity at higher angular frequency ($\omega = 600s^{-1}$) at lower temperature. This decrease is the strongest for Apollobit binder. On the contrary, the viscosity of Kraton binder is least dependent on angular frequency.

CONCLUSION

✓ Apollobit polymer modified binder achieves the highest values of evaluated rheological parameters $G'$, $G''$, $\eta^*$ in the considered interval of angular frequencies at the temperatures of 60 and 80 °C. The lowest values of rheological
parameters are achieved for Kraton modified binder.

- Tested modified binders show significant reduction in complex viscosity with the increase of angular frequency (Figure 6).
- According to obtained results, Apollobit seems to be the most suitable (from a set of tested binders) in asphalt mixtures for highly traffic loaded roads that will be resilient to prevent permanent deformation during hot weather.

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