ASSESSMENT OF THE VISCOELASTIC PROPERTIES OF MODIFIED BITUMENS CONTAINING STYRENE-BUTADIENE-STYRENE COPOLYMER

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Abstract. The viscoelastic behaviour of styrene-butadiene-styrene copolymer modified asphalt binders during tensile test and inverse creep test (retarded strain recovery after unloading) has been analysed in the presented paper. Laboratory tests have been conducted on two specimens of road bitumen: 20/30 and 50/70 penetration grade, which have been subjected to modification with the additive of 9% concentrate of SBS elastomer modified bitumen. When the two were mixed, the samples of polymer modified binders containing 3% or 6% by mass of the SBS elastomer were obtained. Force-ductility (tensile) test that has been followed by the extended procedure for the determination of elastic recovery, has been used as the research method. The results of the study have showed a significant improvement of the effect of modifications on the elastic properties and the temperature susceptibility reduction obtained only in the case of binders, where the polymer constitutes a dispersing phase forming a continuous network throughout the bitumen. Moreover, the temperature susceptibility coefficients, defined on the basis of the tensile test results, have been proposed as an alternative or extension to the previously widely used parameter, the Penetration Index.

Keywords: bitumen, copolymer, rheology, viscoelasticity, tensile, inverse creep, temperature susceptibility.

1. Introduction

Modern asphalt pavements have to satisfy more and more demanding requirements resulting from the fact that the conditions, in which they are used, are quite difficult and bearing this in mind they have to be made durable enough. The most important reasons for the degradation of Polish road pavements are steadily increasing traffic loads and a very unfavourable, as far as a pavement behaviour is concerned, influence of climatic conditions that occur in Poland. Asphalt mixtures, put in layers of pavement structure, have to show a sufficient resistance to all the factors that may lead to their destruction. The most important properties of hot mix asphalt include resistance to permanent deformation at high temperatures (Kalyoncuoglu, Tigdemir 2011), resistance to cracking at low temperatures (Isacsson, Zeng 1998), resistance to fatigue at repeated loading (Awanti *et al.* 2007; Liao *et al.* 2012; Zhou *et al.* 2013) as well as resistance to water and frost (Iwański, Pobocha 2008). Since the content of asphalt binder volume in the hot mix asphalt usually does not exceed 15%, these are the bitumen characteristics that have a great impact on the durability of asphalt pavements. The most crucial of them are the following, good adhesion to the surface of aggregate grains and bitumen-filler interactions (Yiqiu *et al.* 2012), low temperature susceptibility and resistance to aging,

occurring during technological processes (production, transport, paving and compaction), and long-term use of the asphalt pavement (Chai *et al.* 2014; Wang *et al.* 2015; Wu *et al.* 2009; Zhang *et al.* 2011). Road bitumen has also to meet a number of requirements that are related to their rheological properties: cohesion, dynamic viscosity, stiffness modulus, and elasticity.

In order to improve the properties of the bitumen, created by the distillation of crude oil (petroleum bitumen), various modifiers are added to their structure. At present, polymers, especially elastomers, which significantly improve the elastic properties of bitumen (Judycki 1989), as well as rubber from waste tires, natural asphalt or bio binder (Aflaki *et al.* 2014) are commonly used to modify bitumens. However, since the 1980s the most widely used and at the same time the most effective road bitumen modifiers have been thermoplastic elastomers that have been manufactured in the form of a block copolymer of styrene-butadiene-styrene (SBS). When an SBS elastomer is added to hot bitumen, it absorbs maltenes (resins and oils) from the bitumen and swells by up to nine times its initial volume. At content of about 5–6% by mass of SBS, the swollen SBS elastomer represents a major volume fraction of the bitumen forming a continuous polymer network throughout the bitumen. At lower SBS concentrations, the polymer

network may not be continuous throughout the bitumen. However, in a fragmented form, it still forms a substantial volume of the bitumen and consequently significantly modifies its properties (Valkering *et al.* 1992).

Bitumen modification, by the SBS copolymer addition on an industrial scale, takes place in refineries or, less frequently, in special installations which road construction companies are equipped with. Manufacturers of hot mix asphalt (Bražiūnas, Sivilevičius 2010) where elastomer modified bitumen is used as a binder, have three options to get this product. The first option is to buy polymer modified bitumen, ready for direct use in hot mix asphalt. In that case they order bitumen of the appropriate class, characterized by the properties compatible with the technical specifications, designed for the execution of a particular contract – construction or repairs of the road pavement. The second possibility is the self-production of modified bitumen from raw materials, i.e. road bitumen of appropriate hardness and copolymer, following a special technological process. This procedure is available only if you have an expensive equipment for the production of polymer modified bitumens. The third option, a compromise between the two previously mentioned, is to buy highly-modified bitumen, commonly known as the "concentrate" containing, eg 9% or 12% by mass of the SBS copolymer. After mixing (thinning) the concentrate with unmodified bitumen, modified asphalt binder with a reduced content of SBS copolymer, depending on the proportions of the two used components, is received. It is possible to combine the concentrate with bitumen of different hardness and to obtain a wide range of the final product (polymer modified bitumen) with variable values of penetration determined at 25 °C, and different levels of modification. Despite the above advantages, this method is not popular in Poland yet. The necessity to have equipment for mixing the concentrate and the bitumen may be a hindrance. However, in this case the production process is considerably simplified in comparison with the self-modification of bitumen, because a bitumen modification process is carried out in a refinery. The only thing, which remains to be done, is "thinning", i.e. the reduction of the concentration of copolymer in the modified bitumen, by mixing it with the appropriate amount of an unmodified one.

The purpose of the research and analysis presented in this study has been to assess the viscoelastic properties of modified bitumens with different content of SBS copolymer, obtained by mixing, in different proportions, unmodified bitumens of different hardness with the concentrate containing 9% by mass of SBS copolymer. This objective has been accomplished by carrying out a tensile test with the force data collecting (force-ductility test) and, then, observing the inverse creep occurring after unloading, i.e. cutting the binder specimens into halves. These tests, as a penetration test, have been conducted on bitumen specimens at two temperatures: 10 °C and 25 °C, in order to evaluate their temperature susceptibility. Finally, microscopic images of selected modified bitumen structures were also examined.

2. Experimental

2.1. Materials

Two road bitumen made from Russian crude oil, 20/30 penetration grade (in Poland usually used in Mastic Asphalt, or in the high modulus asphalt concrete, designed according to the French technology EME, enrobes à module élevé) and 50/70 penetration grade (in Poland usually used in asphalt mixtures laid in wearing course of the pavements for a light to medium traffic load), have been selected as base materials. For modification of the above mentioned road bitumen, the concentrate of bitumen modified with the block copolymer SBS (styrene-butadiene-styrene) having a linear structure, and the concentration in bitumen (9.0±0.2)% by mass (in accordance with the manufacturer's specifications), has been used. For practical reasons, it is important that the process of modification of bitumen with SBS copolymer would be performed following an industrial method (in the refinery), while the process of mixing the concentrate with unmodified bitumens may take place in the laboratory.

Samples of bitumen-polymer composites have been prepared by heating the base binders to the appropriate temperature: bitumen 50/70 – 145 °C, bitumen 20/30 – 155 °C, 9% concentrate of SBS copolymer – 190 °C and, then, weighing out the components in suitable proportions and precise mixing of them together using the laboratory stirrer with a rotational speed of 150 rpm. These bitumen have been combined with the concentrate in the two proportions, i.e. 2:1 and 1:2, thus obtaining the modified binders containing 3% or 6% by weight of SBS elastomer, respectively. Table 1 shows a list of all samples used in the research program.

Table 1. List of asphalt binder specimens subjected to testing

Asphalt binder	Components content, %			Resulting concentration of the SBS elastomer in the bitumen, %
	20/30	50/70	Concentrate	
20/30	100.0	0	0	0
20/30 (3% SBS)	66.7	0	33.3	3.0
20/30 (6% SBS)	33.3	0	66.7	6.0
50/70	0	100	0	0
50/70 (3% SBS)	0	66.7	33.3	3.0
50/70 (6% SBS)	0	33.3	66.7	6.0
Concentrate (9% SBS)	0	0	100.0	9.0

2.2. Research methods

The main part of the study has been carried out using a ductilometer with load cells at four measuring stations. The test procedure has been composed of two steps.

Step 1. The tensile test with force data collecting (force-ductility test) of asphalt binders' specimens at a constant rate, according to *EN 13589:2008 Bitumen and Bituminous Binders – Determination of the Tensile Properties of Modified Bitumen by the Force Ductility Method*. On the basis of the achieved results, the following four specific parameters have been determined: a maximum value of the tensile force, occurring at the elongation of 10 mm to 20 mm, the final value of the force at the elongation of 20 mm, and the deformation energy calculated as the surface area under the graph showing the relationship between force and the elongation at the sections of 0 mm to 200 mm and from 100 mm to 200 mm.

Step 2. Determination of strain recovery, as well called an inverse creep test after cutting the samples previously stretched to 200 mm, according to *EN 13398:2010 Bitumen and Bituminous Binders – Determination of the Elastic Recovery of Modified Bitumen* into two halves. The normalized procedure has been modified by using samples with constant cross section dimensions (10×10 mm) in the part subjected to stretching (Fig. 1a).

The tests have been conducted respecting the following measurement conditions:

- temperature of the tests – 10 °C and 25 °C maintained with an accuracy of ±0.5 °C;
- stretching speed – 50 mm/min;
- maximum elongation – (200±0.5) mm; it corresponds to the maximum value of strain $\varepsilon_{max} = 6.667$ (666.7%);
- tensile force data collected at intervals of 1 s;
- cutting the specimens into halves, right after stretching and reaching elongation value of 200±0.5 mm;
- strain recovery has been measured at the time t – 0.5 min; 1 min; 2 min; 5 min; 10 min; 15 min; 20 min; 25 min; 30 min; 40 min; 50 min; 60 min; 75 min; 90 min; 105 min and 120 min after cutting the specimens.

In order to determine the accurate and reliable values of strain recovery of the tested binders, the test stand has been expanded by adding a specially designed instrument. The stretched samples (after being cut in half) have been placed on the 10 mm thick glass plate with a measuring scale. Brass pins that have been attached to the glass plate, have allowed the precise placement of the specimens in positions corresponding to the elongation of 200 mm (Fig. 1b). All the measurements have been taken using six independent samples of each type of asphalt binder subjected to the tests.

As a complementary investigation, the penetration at 10 °C and 25 °C (Pen_{10} and Pen_{25}, respectively) in accordance with *EN 1426:2007 Bitumen and Bituminous Binders – Determination of Needle Penetration* and the Softening Point by the "ring and ball" method ($T_{R\&B}$) – in accordance with *EN 1427:2007 Bitumen and Bituminous Binders – Determination of the Softening Point – Ring and Ball Method*, have been determined. Six measurements of penetration have been carried out at any set temperature and four measurements of softening point have been taken for each asphalt binder.

3. Results and discussion

Table 2 shows the results of penetration determined at 10 °C and 25 °C, as well as R&B Softening Point, in the form of the arithmetic mean and the uncertainty of measurement calculated at a confidence level of $P = 95\%$, in accordance with the procedure described by Słowik (2010).

The last column of Table 2 shows the suggested classification of the examined modified bitumen, according
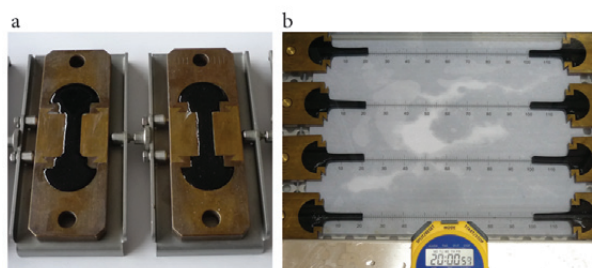

Fig. 1. The selected details of the procedure for stretching test with force data collecting and strain recovery determination: a – bitumen samples with constant cross-sectional dimensions prepared for testing; b – example of a picture facilitating reading the strain recovery values (20 minutes after cutting the samples), using a glass plate with the measuring scale

Table 2. Results of the determination of basic properties of the tested asphalt binders

Asphalt binder	Pen_{25}, mm/10	Pen_{10}, mm/10	$T_{R\&B}$, °C	Classification of polymer modified binders according to *EN 14023:2010*[*]
20/30	24.1±0.4	5.7±0.4	63.5±1.1	–
20/30 (3% SBS)	32.5±0.4	8.5±0.5	62.7±0.5	PMB 25/55-60 or 10/40-60
20/30 (6% SBS)	51.0±0.3	13.9±0.5	93.3±0.8	PMB 25/55-80 or 45/80-80
50/70	68.8±0.5	13.0±0.5	49.2±0.6	–
50/70 (3% SBS)	68.7±0.7	17.8±1.0	51.3±0.4	PMB 65/105-50 or 45/80-50
50/70 (6% SBS)	80.2±0.4	20.1±0.6	79.5±0.5	PMB 65/105-75
Concentrate (9% SBS)	78.5±0.6	25.9±0.7	97.5±1.5	PMB 65/105-80 or 45/80-80

Note: *EN 14023:2010 Bitumen and Bituminous Binders – Specification Framework for Polymer Modified Bitumens.*

to *EN 14023:2010*, taking into account the values of penetration at 25 °C and a softening point. By combining (in an appropriate proportion) the concentrate and a conventional bitumen, the obtained polymer modified binders vary in their hardness (penetration at 25 °C) and degrees of modification as concluded from the large differences in the values of Softening Point.
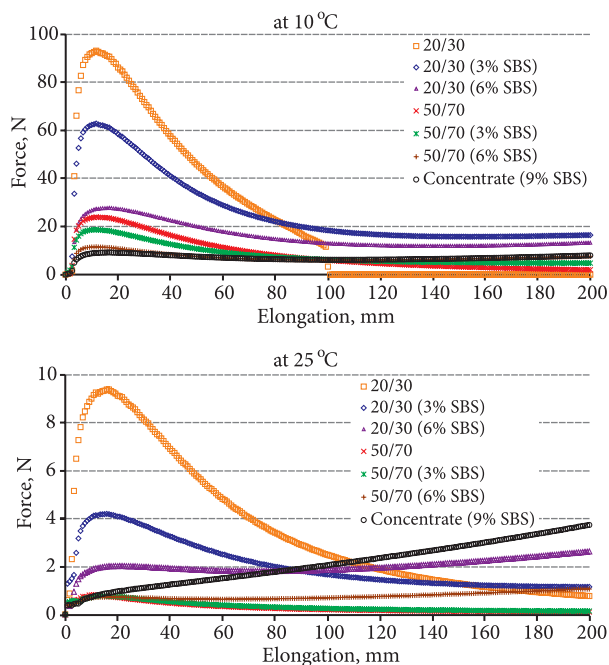

Fig. 2. Tensile force versus elongation curves

The results of the tensile test with force data collecting, carried out at 10 °C and 25 °C, are shown in Fig. 2, in the form of graphs presenting the relationship between the force and elongation values. Upon analysing the changes in tensile force (Fig. 2), a considerable variation in curve shapes for various binders as well as a significant decline in force values while increasing the test temperature from 10 °C to 25 °C have been observed. Samples of unmodified bitumens, after reaching the maximum, show a steady decline of the force values (samples of 20/30 penetration grade bitumen examined at 10 °C have broken at an average elongation of 100 mm). Specimens of modified bitumen containing SBS elastomer behave in a different way. After reaching the maximum (at an elongation of about 10 mm), an initial decrease followed by another increase of the tensile force values was noticed. This was most clearly seen in the case of binders with high elastomer concentration (6% or 9%). The first maximum is linked to the properties of the asphalt binder, whereas the observed reinforcement results from the SBS elastomer properties, for which the force versus elongation relationship is differently compared with the bitumen. An increase in the force during the second stage of stretching is gentle, but the reached force values are, in some cases, much greater than those which have been obtained at the first maximum.

Tables 3 and 4 show values of the parameters (listed below) that characterize properties of the examined binders:
– the maximum tensile force obtained during the first stage of the test at the elongation between 10 mm to 20 mm (in the case of concentrate, tested at 25 °C,

Table 3. Tensile force and deformation energy of the tested binders determined at 10 °C

Asphalt binder	$F_{10\,(max)}$, N	$F_{10\,(200\,mm)}$, N	$DE_{10\,(0-200\,mm)}$, J	$DE_{10\,(100-200\,mm)}$, J
20/30	93.3±8.3	–	4.8±0.4	–
20/30 (3% SBS)	63.0±4.4	16.5±1.5	5.2±0.3	1.63±0.12
20/30 (6% SBS)	27.9±1.5	13.3±0.4	3.2±0.1	1.24±0.04
50/70	24.0±4.0	2.0±0.3	1.7±0.3	0.35±0.05
50/70 (3% SBS)	18.7±0.4	4.7±0.2	1.6±0.1	0.52±0.04
50/70 (6% SBS)	11.6±0.6	7.6±0.2	1.4±0.1	0.66±0.02
Concentrate (9% SBS)	9.2±0.5	8.0±0.2	1.4±0.1	0.68±0.02

Table 4. Tensile force and deformation energy of the tested binders determined at 25 °C

Asphalt binder	$F_{25\,(max)}$, N	$F_{25\,(200\,mm)}$, N	$DE_{25\,(0-200\,mm)}$, J	$DE_{25\,(100-200\,mm)}$, J
20/30	9.4±1.2	0.80±0.10	0.71±0.08	0.140±0.020
20/30 (3% SBS)	4.2±0.6	1.20±0.20	0.41±0.06	0.130±0.020
20/30 (6% SBS)	2.0±0.1	2.60±0.30	0.40±0.03	0.220±0.020
50/70	0.8±0.2	0.08±0.02	0.06±0.02	0.011±0.003
50/70 (3% SBS)	0.8±0.1	0.14±0.03	0.07±0.01	0.018±0.004
50/70 (6% SBS)	0.7±0.1	1.10±0.10	0.15±0.01	0.086±0.008
Concentrate (9% SBS)	1.0±0.1	3.70±0.20	0.42±0.03	0.290±0.020

the value is not maximum but the inflection point) – $F_{10\,(max)}$ and $F_{25\,(max)}$;
- the tensile force at the moment of achieving the assumed maximum elongation value of 200 mm – $F_{10\,(200\,mm)}$ and $F_{25\,(200\,mm)}$;
- deformation energy, calculated as the surface area between the line showing the relationship between the tensile force and elongation and the horizontal axis (in the sections from 0 mm to 200 mm – $DE_{10\,(0–200\,mm)}$, and $DE_{25\,(0–200\,mm)}$ as well as from 100 to 200 mm – $DE_{10\,(100–200\,mm)}$ and $DE_{25\,(100–200\,mm)}$).

All the results in Tables 3 and 4 have been presented as the arithmetic average and uncertainty values calculated at confidence level of $P = 95\%$, in accordance with the procedure described by Słowik (2010).

The results of inverse creep tests, conducted at 10 °C and 25 °C, have been shown graphically in Fig. 3, as curves of strain recovery versus time measured from the moment of cutting the specimens. Samples of 20/30 penetration grade bitumen tested at 10 °C have not reached the assumed elongation of 200 mm as they have broken at the average elongation of 100 mm (Fig. 2) due to high stiffness. Therefore, the inverse creep has not been studied in this case. Fig. 3 shows the results of the tests using dots or lines representing the relationship of strain recovery versus time obtained as a result of mathematical modelling using the linear viscoelastic rheological model (Yusoff *et al.* 2011) consisting of two Kelvin elements (parallel combination of Hooke and Newton elements) and Maxwell element (serial connection of Hooke and Newton elements), connected in series (Fig. 4). The usefulness of this model, for the description of the inverse creep of asphalt binders, has been demonstrated by Słowik (2012).

The Dual Kelvin + Maxwell model formula used to describe the strain recovery of asphalt binders specimens which starts at the moment of unloading, i.e. cutting them into halves ($t = 0$, $\sigma = 0$), is as follows (Słowik 2012):

$$\varepsilon(t) = \frac{\sigma_0}{E_0} + \frac{\sigma_0}{E_1}\exp\left(-\frac{t}{\tau_1}\right) + \frac{\sigma_0}{E_2}\exp\left(-\frac{t}{\tau_2}\right) + \varepsilon_\infty, \quad (1)$$

where $\varepsilon(t)$ – strain of specimen at time t from the moment of cutting; σ_0 – tensile stress value just before cutting the sample, Pa; τ_1, τ_2 – retardation times, s – $\tau_1 = \frac{\eta_1}{E_1}$ and $\tau_2 = \frac{\eta_2}{E_2}$; E_0, E_1, E_2, η_1, η_2 – moduli of elasticity in Pa, and dynamic viscosity in Pa·s, respectively, according to the diagrams shown in Fig. 4; ε_∞ – permanent strain (generated in Newtonian dashpot of viscosity η_0), calculated at $t \rightarrow \infty$.

Since there was no possibility of determining the values of σ_0, the Eq (1) allowed the calculation of the following parameters of the Dual Kelvin + Maxwell model: $\frac{\sigma_0}{E_0}$, $\frac{\sigma_0}{E_1}$, $\frac{\sigma_0}{E_2}$, τ_1, τ_2 and ε_∞. The modelling was carried out

employing the smallest squares of deviation and using the *Nonlinear Least Squares Regression (Curve Fitter)* software. The results of strain determination in samples ε against time t (16 pairs of results for each approximated curve) have been served as the data used for modelling. The results of strain recovery modelling have been used in calculation of the values of two important properties, which assessment would be virtually impossible following the laboratory test method used in the study. These are immediate strain recovery ($\frac{\sigma_0}{E_0}$) and permanent strain ε_∞. On their basis, the coefficient of retardation α_s (Judycki 1989) was precisely determined and took the following modified form (Słowik 2012), symbols as in the Eq (1):

$$\alpha_s = \left(1 - \frac{\sigma_0}{E_0(\varepsilon_{max} - \varepsilon_\infty)}\right) \cdot 100, \%. \quad (2)$$

The results of modelling of the inverse creep in the form of Dual Kevin + Maxwell model parameters, values of the coefficient of determination R^2 and values of coefficient of retardation α_s calculated according to the formula (2)
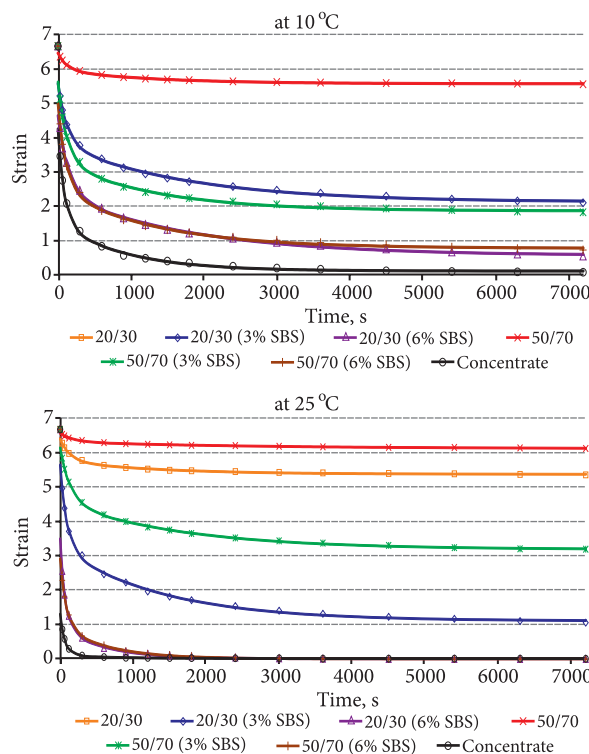

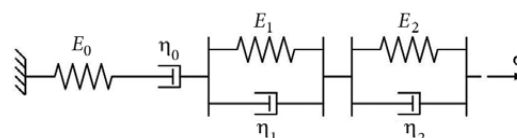Fig. 3. Strain recovery versus time curves

Fig. 4. Schematic representation of the Dual Kelvin + Maxwell linear viscoelastic rheological model used in the mathematical description of inverse creep of the tested asphalt binders

have been presented in Table 5. Moreover, the values of elastic recovery R_E were determined 30 min later, after cutting the specimens (according to *EN 13398:2010*, but the used samples with constant cross section dimensions (10×10 mm) in the part subjected to stretching – Fig. 1a) have also been shown in the Table 5.

High compatibility between the curves, obtained from mathematical modelling and the experiment results, has been observed, as the evidence of high values of the coefficient of determination R^2 in the range from 0.997 to 1.000. Three parameters, presented in Table 5, i.e. the immediate strain recovery $(\frac{\sigma_0}{E_0})$, the permanent strain ε_∞, and the coefficient of retardation α_s have been regarded as the most useful ones for the evaluation of elastic properties of the tested asphalt binders.

The values of $(\frac{\sigma_0}{E_0})$ demonstrate which part of the binder sample deformation is perfectly elastic. In the case of unmodified bitumens, the elastic component of deformation is almost non-existent and does not exceed the values of 0.3 (20/30) or 0.2 (50/70). This represents 4.5% and 3% of the specified strain, respectively. In the case of bitumen, containing 3% of mass of SBS copolymer, the values of $(\frac{\sigma_0}{E_0})$ are significantly higher and reach 1.1 (16.5%). However, this result cannot be considered satisfactory. When the content of SBS copolymer is 6% of mass, large values of immediate strain recovery up to 3.8 (57%) at 25 °C are observed. As expected, the specimens of the concentrate containing 9% of mass of the SBS copolymer showed the highest values of $(\frac{\sigma_0}{E_0})$ – 5.4 (81%) at 25 °C. The values of $(\frac{\sigma_0}{E_0})$ depend on the temperature, but at the same time the observed changes are different for different binders. It has been observed that the values of $(\frac{\sigma_0}{E_0})$

measured at 10 °C have approximately been twice as high as the ones that have been obtained at 25 °C for the bitumen 50/70 and 50/70 (3% SBS). A much higher value of the tensile force and tensile stress at a moment of unloading in the case of samples tested at 10 °C (Tables 3 and 4) is, probably, a reason for this. For the bitumen 20/30 (3% SBS) the values of $(\frac{\sigma_0}{E_0})$ at 10 °C and 25 °C are almost the same. However, in the case of bitumen, containing 6% or 9% of the SBS copolymer, the values of $(\frac{\sigma_0}{E_0})$, determined at 25 °C, are from 1.6 to 2.2 times higher than those which are obtained at 10 °C. This can be explained by the higher viscosity of bitumen at the lower temperature, which leads to damping (slowing) of the processes caused by the continuous elastomer network in the asphalt binder.

The permanent deformation ε_∞ is another interesting assessment parameter while testing bitumen behaviour. On its basis and bearing in mind long-term strain recovery conclusions about mutual relationships between reversible and irreversible deformation have been drawn. In the case of unmodified bitumens 20/30 and 50/70 penetration grade, very large values of permanent deformation (from 5.4 to 6.1) have been obtained, which amounts are from 81% to 92% of the maximum specified strain. This points to the dominant viscous characteristic and a very small elastic component of the strain in the case of unmodified bitumen. In the case of the asphalt binders, containing 3% of mass of SBS copolymer, the share of irreversible strain in the process has been much smaller, i.e. from 1.1 to 3.2 (from 17% to 48%). On the other hand, bitumen containing 6% or 9% of mass of SBS copolymer have practically showed no permanent deformation at 25 °C. Thus, the strain is totally reversible in this case.

The coefficient of retardation α_s which takes values from 0% to 100% indicates a mutual relationship between the values of the immediate and delayed strain recovery. When $\alpha_s = 0\%$, all strain recovery proceeded in a perfectly elastic

Table 5. Results of modelling the inverse creep of the tested asphalt binders

Asphalt binder	T, °C	$\frac{\sigma_0}{E_0}$	$\frac{\sigma_0}{E_1}$	τ_1, s	$\frac{\sigma_0}{E_2}$	τ_2, s	ε_∞	R^2	α_s, %	R_E, %
20/30	25	0.274	0.636	133	0.392	1339	5.365	0.998	79.0	18.0
20/30 (3% SBS)	10	1.093	1.735	125	1.714	1746	2.124	0.999	75.9	59.3
	25	1.036	2.399	93	2.126	1414	1.106	0.999	81.4	74.4
20/30 (6% SBS)	10	2.027	2.253	147	1.825	1821	0.562	0.998	66.8	81.8
	25	3.176	2.528	68	0.953	588	0.009	0.999	52.3	98.9
50/70	10	0.198	0.501	123	0.396	1312	5.572	0.999	81.9	14.9
	25	0.116	0.242	183	0.201	2719	6.108	0.997	79.2	7.0
50/70 (3% SBS)	10	1.045	2.284	118	1.472	1303	1.866	0.998	78.2	66.5
	25	0.531	1.567	141	1.386	1676	3.182	1.000	84.8	45.3
50/70 (6% SBS)	10	1.676	2.492	110	1.721	1333	0.778	0.998	71.5	81.7
	25	3.759	1.920	82	0.983	641	0.005	1.000	43.6	98.8
Concentrate (9% SBS)	10	2.413	2.723	88	1.418	914	0.113	0.999	63.2	94.8
	25	5.365	1.178	65	0.109	664	0.015	1.000	19.3	99.6

way, immediately after unloading, and the effect of retardation of strain recovery did not occur. The Maxwell's rheological model describes such a situation (Judycki 1989). On the other hand, $\alpha_s = 100\%$ when no immediate but only delayed strain recovery occurred. Analysing the values of α_s, determined at 10 °C, small differences among the tested binders have been observed. All the results are within the range from 63.2% to 81.9%. This shows the high proportion of retarded strain recovery in relation with the immediate strain recovery. The results of α_s, obtained at 25 °C, are much more diversified. In the case of unmodified bitumens and those containing 3% of mass of SBS copolymer, the results, obtained at 25 °C, do not differ significantly from those, obtained at 10°C (the maximum difference is 6.6%). The α_s values obtained for bitumens 20/30 (6% SBS) – 52.3% and 50/70 (6% SBS) – 43.6%, and, especially, for a concentrate containing 9% of SBS – 19.3% prove that in the case of highly modified bitumen the significant part of a strain recovery occurs immediately after unloading.

In order to determine mutual relationships between different parameters obtained as a result of the tests, the correlation tables have been made. The values of the Pearson correlation coefficient R, related to the results received at 10 °C (Table 6) and at 25 °C (Table 7) have been included.

It has been observed that the penetration of bitumen points to a significant correlation (in both test temperatures), only reaches the maximum tensile force. It has also been found out that there is a significant correlation between the three parameters determined in inverse creep tests, i.e. the immediate strain recovery, the permanent deformation, and the coefficient of retardation (with the exception of the relationship between α_{s25} i $\varepsilon_{\infty25}$). Furthermore, a significant correlation has been observed in the case of a relationship between the maximum tensile force and the deformation energy, determined in the elongation in the range from 0 to 200 mm, as well as between the tensile force at the elongation of 200 mm and the deformation energy, calculated at the elongation in the range from 100 to

Table 6. Pearson's coefficient of correlation R values calculated for the relationship between the selected parameters of bitumens determined at 10 °C

Properties	Pen_{10}, mm/10	$F_{10\,(max)}$, N	$F_{10\,(200\,mm)}$, N	$DE_{10\,(0–200\,mm)}$, J	$DE_{10\,(100–200\,mm)}$, J	$\left(\dfrac{\sigma_0}{E_0}\right)_{10}$	$\varepsilon_{\infty10}$	α_{s10}, %
Pen_{10}, mm/10	1.00	**−0.88**	0.06	**−0.85**	−0.02	0.62	−0.53	−0.60
$F_{10\,(max)}$, N	**−0.88**	1.00	−0.12	**0.91**	−0.10	−0.34	0.23	0.33
$F_{10\,(200\,mm)}$, N	0.06	−0.12	1.00	0.30	**0.99**	0.42	−0.49	−0.41
$DE_{10\,(0–200\,mm)}$, J	**−0.85**	**0.91**	0.30	1.00	0.32	−0.09	0.00	0.08
$DE_{10\,(100–200\,mm)}$, J	−0.02	−0.10	**0.99**	0.32	1.00	0.26	−0.34	−0.25
$\left(\dfrac{\sigma_0}{E_0}\right)_{10}$	0.62	−0.34	0.42	−0.09	0.26	1.00	**−0.94**	**−0.98**
$\varepsilon_{\infty10}$	−0.53	0.23	−0.49	0.00	−0.34	**−0.94**	1.00	**0.86**
α_{s10}, %	−0.60	0.33	−0.41	0.08	−0.25	**−0.98**	**0.86**	1.00

Note: all cases where the absolute value of the correlation coefficient exceeds a critical value 0.7545 (when the number of degrees of freedom $df = n − 2 = 5$ and a confidence level is 0.95) (Krysicki *et al.* 2002), are written in bold.

Table 7. Pearson's coefficient of correlation R values calculated for the relationship between the selected parameters of bitumens determined at 25 °C

Properties	Pen_{25}, mm/10	$F_{25\,(max)}$, N	$F_{25\,(200\,mm)}$, N	$DE_{25\,(0-200\,mm)}$, J	$DE_{25\,(100-200\,mm)}$, J	$\left(\dfrac{\sigma_0}{E_0}\right)_{25}$	$\varepsilon_{\infty25}$	α_{s25}, %
Pen_{25}, mm/10	1.00	**−0.89**	0.17	−0.74	−0.08	0.53	−0.30	−0.56
$F_{25\,(max)}$, N	**−0.89**	1.00	−0.14	**0.84**	0.13	−0.42	0.39	0.38
$F_{25\,(200\,mm)}$, N	0.17	−0.14	1.00	0.42	**0.96**	**0.87**	−0.72	**−0.86**
$DE_{25\,(0–200\,mm)}$, J	−0.74	**0.84**	0.42	1.00	0.65	0.08	−0.04	−0.10
$DE_{25\,(100–200\,mm)}$, J	−0.08	0.13	**0.96**	0.65	1.00	**0.75**	−0.61	−0.74
$\left(\dfrac{\sigma_0}{E_0}\right)_{25}$	0.53	−0.42	**0.87**	0.08	**0.76**	1.00	**−0.83**	**−0.98**
$\varepsilon_{\infty25}$	−0.30	0.39	−0.72	−0.04	−0.61	**−0.83**	1.00	0.70
α_{s25}, %	−0.56	0.38	**−0.86**	−0.10	−0.74	**−0.98**	0.70	1.00

Note: all cases where the absolute value of the correlation coefficient exceeds a critical value 0.7545 (when the number of degrees of freedom $df = n − 2 = 5$ and a confidence level is 0.95) (Krysicki *et al.* 2002), are written in bold.

200 mm. In other cases, a statistically significant correlation for both applied test temperatures has not been found.

In order to assess the temperature susceptibility of the tested asphalt binders, the coefficients describing the change in the value of selected properties obtained in the tensile test and caused by change in temperature by 15 °C have been calculated. The coefficients have been calculated as a relation of bitumen properties at 10 °C, to those, determined at 25 °C according to the following formulas:

– maximum Force Index

$$FI_{(max)} = \frac{F_{10(max)}}{F_{25(max)}}, \qquad (3)$$

– 200 mm Force Index

$$FI_{(200\ mm)} = \frac{F_{10(200\ mm)}}{F_{25(200\ mm)}}, \qquad (4)$$

– Deformation Energy Indexes

$$DEI_{(0-200\ mm)} = \frac{DE_{10(0-200\ mm)}}{DE_{25(0-200\ mm)}}; $$

$$DEI_{(100-200\ mm)} = \frac{DE_{10(100-200\ mm)}}{DE_{25(100-200\ mm)}}. \qquad (5)$$

The results of the calculations in the form of an arithmetic mean and the uncertainty, determined at a confidence level of $P = 95\%$ have been shown in Table 8. The Penetration Index (PI) has been used as a reference parameter. PI is considered to be the most popular parameter characterizing the temperature susceptibility of the asphalt binders (concerning only the temperature range occurring during asphalt pavement operation). It has been calculated on the basis of the

results obtained in penetration tests, carried out at 10 °C and 25 °C, in accordance with the following formula:

$$PI = \frac{300 - 500\Delta\log Pen}{15 + 50\Delta\log Pen}, \qquad (6)$$

where

$$\Delta\log Pen = \log Pen_{T_2} - \log Pen_{T_1}, \qquad (7)$$

and Pen_{T_1}, Pen_{T_2} – values of penetration determined at $T_1 = 10$ °C and $T_2 = 25$ °C, respectively.

On the analysis of the penetration index values, the highest temperature susceptibility has been recorded for both, unmodified bitumen tested ($PI < 0$), and the lowest one, the concentrate containing 9% of mass of SBS copolymer. However, no significant difference has been noticed between the PI values for the asphalt binders containing 3% and 6% of mass of SBS copolymer. All the results fall within the range from –0.02 to 0.40. A much greater variation for these binders has been observed in the case of the other parameters, characterizing the temperature susceptibility, obtained as the results of the tensile test. The Maximum Force Index has been recognized as the most useful, although, in this case, the value of $FI_{(max)}$ for 20/30 penetration grade bitumen has been incompatible with the expectations. In the case of the remaining parameters, their values, determined for bitumen 20/30, are not reliable due to the premature crack of the specimens tested at 10 °C. They have not achieved the objective elongation of 200 mm.

Furthermore, a correlation table containing the Pearson coefficient of correlation R has been prepared (Table 9). It specifies the relationships between the selected factors, characterizing the temperature susceptibility of the tested bitumens. All those cases, where the absolute value of the

Table 8. The values of coefficients characterizing the temperature susceptibility of the tested asphalt binders

Asphalt binder	PI	$FI_{(max)}$	$FI_{(200\ mm)}$	$DEI_{(0-200\ mm)}$	$DEI_{(100-200\ mm)}$
20/30	−0.30±0.32	10.0±0.7	–	6.8±0.7	–
20/30 (3% SBS)	0.17±0.32	15.2±2.1	14.5±2.3	12.9±1.8	12.7±1.9
20/30 (6% SBS)	0.40±0.19	10.7±1.1	5.1±0.5	8.0±0.5	5.7±0.5
50/70	−1.20±0.16	29.5±3.5	27.0±5.8	31.4±6.0	30.8±5.8
50/70 (3% SBS)	0.15±0.27	25.9±3.7	33.6±9.5	25.5±4.3	29.6±5.9
50/70 (6% SBS)	−0.02±0.15	11.0±0.6	7.2±0.7	9.6±0.6	7.7±0.7
Concentrate (9% SBS)	1.52±0.17	9.1±1.2	2.2±0.1	3.4±0.2	2.4±0.1

Table 9. The values of Pearson's correlation coefficient R characterizing the relationships between temperature susceptibility coefficients of the tested asphalt binders

Properties	PI	$FI_{(max)}$	$FI_{(200\ mm)}$	$DEI_{(0-200\ mm)}$	$DEI_{(100-200\ mm)}$
PI	1.00	−0.62	−0.63	−0.70	−0.74
$FI_{(max)}$	−0.62	1.00	**0.95**	**0.99**	**0.99**
$FI_{(200\ mm)}$	−0.63	**0.95**	1.00	**0.94**	**0.98**
$EI_{(0-200\ mm)}$	−0.70	**0.99**	**0.94**	1.00	**0.99**
$EI_{(100-200\ mm)}$	−0.74	**0.99**	**0.98**	0.99	1.00

correlation coefficient exceeds a critical value equal to 0.7545, at a confidence level of 0.95 (Krysicki *et al.* 2002), have been written in bold. It has been noted that the Penetration Index values show no correlation with any of the proposed indexes determined on basis of the tensile test results, which are closely correlated with each other ($R > 0.9$). Thus, it is possible to use them as an alternative or supplement of the Penetration Index in the assessment of temperature susceptibility of polymer modified bitumen.

Fig. 5 shows photographs of the microscopic images of the structure of the selected modified bitumens containing copolymer SBS. The pictures have been taken using a microscope, equipped with a camera recording an image formed by UV rays (fluorescence microscopy).

In the case of the asphalt binder 50/70 (3% SBS), Fig. 5a, the bitumen constitutes the dispersing phase, and the copolymer occurs as the dispersed phase in the form of a single oval concentrations which dimensions do not exceed 30 μm. Bitumen 50/70 (6% SBS), Fig. 5b. It is characterized by a balance of bituminous and polymeric phases. However, the copolymer has been identified as a dispersing phase, while the bitumen is as the dispersed phase. The SBS copolymer forms a continuous network in the structure of asphalt binder at the concentration of 6%. A similar situation has been noted down in the case of a concentrate, containing 9% of mass of the SBS copolymer, Fig. 5c. A continuous polymer network in the structure of an asphalt binder, which is much more homogeneous, has also been observed. The continuous network of the copolymer when its content is of 6% or 9% by mass in the asphalt binder explains the elastic properties much better than those observed for the unmodified bitumens and the binders containing 3% by mass of SBS copolymer (which does not form a continuous polymer network in the bitumen structure). Thus, the rheological properties of modified binders depend more on the properties of the continuous (dispersing) phase than the dispersed phase. In the case of SBS copolymer modified binders with continuous bituminous phase, the polymer is regarded only as an elastic filler. There is no image of the unmodified bitumen 50/70 structure, shown in Fig. 5, due to its consistent black appearance (only the background, bitumen, was visible, there was no reflection of UV light observed, since there is no polymer in the structure of asphalt binder).

4. Conclusions

1. The method for bitumens modification used in the research work consisting in mixing them with modified bitumen concentrate containing 9% by mass addition of SBS copolymer allowed obtaining modified asphalt binders of different hardness, and with varying degrees of modification. This confirms the usefulness of this method for the production of elastomer modified bitumens in Hot Mix Asphalt Plants.

2. The research methods used in the study, where two measurement procedures, i.e. a tensile test with force data collecting and an inverse creep test were combined into one test, allowed for a detailed analysis of the viscoelastic behaviour of the tested bitumens, including assessment of the temperature susceptibility.

3. Highly modified asphalt binders, where the SBS copolymer content is 6% or 9% by mass and which constitutes the dispersing phase forming the continuous network in the bitumen structure, showed much better elastic properties than the unmodified bitumens or those containing 3% by mass of the SBS copolymer, where the elastomer particles are dispersed in the bitumen. This regularity was confirmed most clearly by the values of immediate strain recovery and permanent strain determined on the basis of the inverse creep test and mathematical modelling using the Dual Kelvin + Maxwell rheological model.

4. The proposed temperature susceptibility coefficients, determined on the basis of the tensile test results, especially the Maximum Force Index regarded as the most appropriate, are possible to use as an alternative or extension to the previously widely used parameter, i.e. the Penetration Index, particularly for assessment of the properties of elastomer modified asphalt binders. These parameters diversify the temperature susceptibility of medium and highly modified bitumens more effectively than the Penetration Index.
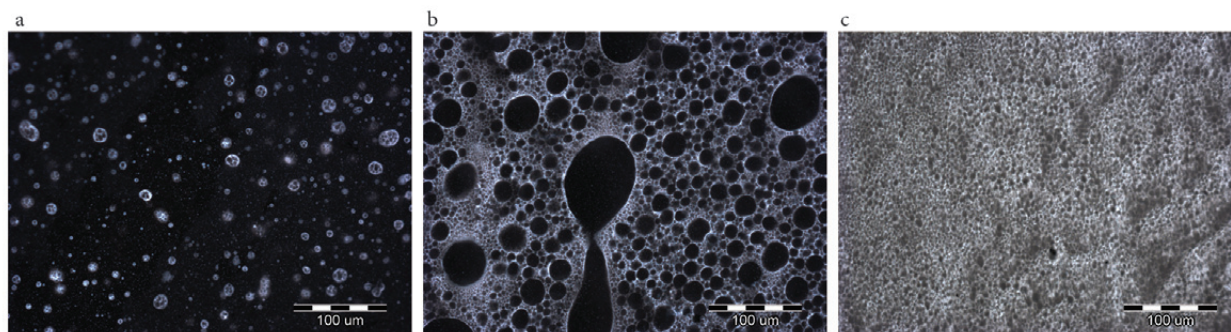
Fig. 5. Examples of microscopic images of modified bitumens structure (reference section length is of 100 μm): a – 50/70 (3% SBS); b – 50/70 (6% SBS); c – concentrate (9% SBS)

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