Evaluation of The Modification Efficiency of Bituminous Binders with SBS Polymer Based on Changes in Strain Energy in the Ductility Test

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Abstract. Road pavement layers in many cases are done of hot mix asphalt (HMA). It is mixture of mineral aggregate and asphalt binder. The content of the bituminous binder is not very significant (several percent). In fact, asphalt binder decides about every properties of hot mix asphalt in significant range. Traffic condition is still changing (traffic is growing and trucks are heavier). It is reason to find better solution to asphalt pavement and improve parameters asphalt binder. One of important attribute is sensitivity for temperature. Searching for a way to improve cohesion, viscosity and adhesion to mineral aggregate is one of the directions research. One of solution is use application of modifier. The most popular are polymers. Most frequently used copolymers to modify asphalt binder are thermoplastic elastomer styrene - butadiene - styrene (SBS). Thermoplastic polymers are used in practice, which soften upon heating and harden during cooling (reversible process), reminding in this respect the behaviour of asphalts. In article, authors have present tests results of modified asphalt binder by SBS polymer. Tests were made on two types of bitumen, one of them was distilled asphalt, second oxidised. Amount of modifier was variable and was from 0% to 6%. Results of test confirmed usefulness SBS polymer to modify asphalt. In every cases noticed increase penetration index (PI) and change structure of bitumen from sol-gel to typical gel. Effect of this is reduce thermal sensitivity. Resistance to changing of temperature is better. After tests and analyses, the authors stated that amount of polymer above 2% clearly changes asphalt parameters both hard and soft.

1. Introduction
Owing to the wide range of tasks set for asphalt binders in constantly changing traffic conditions (varied loads), it is necessary to seek solutions that would improve their properties. This primarily applies to reducing asphalt thermal sensitivity, increasing their viscosity and cohesion in the range of working temperatures and improving adhesion to mineral surfaces. These goals can, at least partly, be achieved using modifiers. Polymers constitute the most popular group of modifiers. Thermoplastic polymers are used in road technology. Like asphalts, they soften when heated and harden when cooled (reversible process). Owing to their formability properties they can be divided into elastomers and plastomers. Because of Polish weather and climate conditions copolymers are most commonly used. These are chemical compounds that consist mainly of an elastomer with a small addition of a plastomer. In some cases, it is necessary to apply a mixture of a copolymer (or an elastomer) with a small addition of a plastomer, e.g. to increase the softening point. Their use license is conditional on their compatibility.
with the binder, i.e. ability to create a homogeneous and durable physical mixture that would not disturb the colloidal balance of asphalt [1–3]. Styrene-butadiene-styrene thermoplastic elastomer, commonly referred to as SBS, is the most commonly used copolymer applied to modify asphalt binders. Polystyrene (plastomer) is a chemical compound which accounts for only approximately 23% of the copolymer. When it expands, it increases its volume nine-fold while at the same time it absorbs mainly some heavy oil fraction [4]. SBS is made up of polystyrene blocks linked with polybutadiene chains. When under load, SBS is strained. When load is released, SBS returns to its original shape and dimensions. Polybutadiene is responsible for spring-elastic properties in the elastomer. Polystyrene hardens the modifier and above 100°C it softens. It is a reversible process. When cooled again, polystyrene becomes hard again [4,5]. As a product, the modifier is available in different forms, e.g. as a granulate or powder.

2. Materials and experimental

2.1. SBS copolymer

When a polymer is introduced into a binder, it disturbs its chemical and physical equilibrium. Intensity and range of such changes is dependent on [5,6]:

− chemical composition and rheological type of the initial asphalt (e.g. proportions and ratios of constituent elements),
− structure of the polymer (molecular mass, structure),
− amount of introduced modifier.

An inappropriate selection of components can result in polymer modified asphalt lacking compatibility. It can be tested based on PN-EN 13399:2012: “Bitumen and bituminous binders. Determination of storage stability”. Lack of homogeneity disqualifies the product. If amalgamation is good (no segregation), the resulting binder acquires specific properties which are better than those of the original binder and which brings it closer to ideal binder. Characteristic changes of rheological properties of polymer modified bitumens can be observed in cohesion changes in relation between force and strain obtained in ductility test with force measurement. The effect of polymer is marked. It is linked to the changes of polymer’s deformation modulus depending on deformation magnitude (Fig. 1).

![Figure 1. Exemplary relation between tensile force and strain of: a) standard (road) asphalt b) asphalt modified with polymer](image)

Zone I characterizes the area of bitumen elastic strain. For modified bitumens in this strain range, the area under the curve increases when the amount of modifier increases relative to base asphalt. The increase can be the effect of polymer, or to be more precise, its Young’s modulus E1 (Fig. 1). As the asphalt sample expands, its cross-sectional area decreases as a result of which the force necessary to accomplish strain decreases too. The measured reduction of force acting in modified bitumens is smaller
than that of base bitumens. This is the effect of polymer, whose E2 (in zone II in Fig. 2) is greater than deformation modulus of asphalt. Further strain results in force increase in spite of sample cross-section getting smaller (strength increase). It reflects polymer behavior under deformation in zone III (Fig. 1), given heavy strain and corresponding high values of E3 modulus.

The above flow curves of “pure” elastomers (Fig. 1) and modified asphalts (Fig. 1) show that elastomer in asphalt increases Young’s modulus mainly in zones II and III. This is predominantly the result of structural changes occurring in the combined materials, i.e. the asphalt and the elastomer. The expansion of elastomer is the dominant structural process. It is caused by absorption of the oil fractions of asphalt by the stiff molecules of polystyrene. An inhibited course of the process results in miscibility (compatibility) of the two components, traditionally referred to as homogeneity. These ordinary technological issues can now be supported by physico-chemical science, and particularly by thermodynamics. The kinetic theory can be of particular use. It says that the rotation of polymer chains relative to individual bonds can occur without changes of internal energy. Therefore, any change of polymer chain length under stress is the result of entropy change.

2.2. Bituminous binders and their modifications

Two types of base asphalt were selected for the study: hard (35/50) and soft (160/220). The products were obtained using distillation (BITUMEN I) and oxidation (BITUMEN II). SBS containing below 30% of styrene and above 70% of polybutadiene was used as the modifier. It is a classic linear triblock with SB content < 1% and above 99% of SBS. A total of 24 samples of modified bitumen (with polymer content from 1 to 6%) and 4 base asphalts were prepared. The modification procedure was as follows. Asphalt was placed in a sealed container with the volume of approximately 10 dm³. The sample was heated to 180°C in an oil bath that provided uniform distribution of heat. When the required temperature was obtained, an appropriate amount of the modifier (from 1 to 6%) was added to the binder. Then the mixture was stirred with an agitator for 60 min with the constant speed of 126 rpm (Fig. 2). The mixing of bitumen and polymer was followed by maturation when the temperature of 180°C was maintained for 2 h. Samples prepared in this way were further examined. First, compatibility of the binders with the modifier was determined in a stability test.

The stability test was based on tube test to examine separation of modified bitumen stored in high temperature. The test was conducted in accordance with PN-EN 13399:2012 Polish standard. The results from all samples show that the bitumen - modifier system is stable. The applied elastomer displays high compatibility with bituminous binders obtained with distillation (BITUMEN I) and those produced using distillation and oxidation (BITUMENT II) from oil of varied origin.
2.3. Examination of SBS modified asphalts
To determine parameters of the modified asphalts, the following were determined or conducted:
- softening point in accordance with R&B,
- penetration at 25°C,
- force ductility test.

3. Results and discussions
R&B and penetration results (table 1) show that SBS modifier improves the hardening properties of binders. Greater parameter changes of R&B softening point and penetration caused by the polymer were observed for the soft bitumen (160/220). Compared to the base asphalt, the change of softening point is in the range of 80% while that of penetration is approximately 41%. Greater changes were found in distilled bitumen samples (BITUMEN I).

Table 1. Penetration and softening point results of 35/50 and 160/220 bitumen samples before and after SBS modification

| characteristic | amount of modifier, % | BITUMEN I | BITUMEN II |
|----------------|-----------------------|-----------|------------|
|                | 0                     | 35/50     | 160/220    | 35/50     | 160/220    |
| Softening Point $T_{R&B}$, °C | 1                     | 44,8      | 165,3      | 36,3      | 153,2      |
|                | 2                     | 42,7      | 139,2      | 34,4      | 146,1      |
|                | 3                     | 38,9      | 118,9      | 33,5      | 135,8      |
|                | 4                     | 36,7      | 111,3      | 31,2      | 127,3      |
|                | 5                     | 33,4      | 104,9      | 30,4      | 117,8      |
|                | 6                     | 32,1      | 97,1       | 29,7      | 105,9      |
| Penetration (25°C), ×0,1 mm | 0                     | 53,5      | 38,9       | 54,9      | 40,4       |
|                | 1                     | 54,9      | 40,9       | 56,7      | 41,5       |
|                | 2                     | 59,1      | 43,2       | 58,1      | 42,9       |
|                | 3                     | 62,3      | 47,3       | 62,5      | 45,3       |
|                | 4                     | 66,4      | 57,6       | 68,8      | 55,7       |
|                | 5                     | 71,2      | 70,5       | 74,2      | 65,7       |
|                | 6                     | 74,3      | 71,8       | 78,9      | 70,8       |

A smaller hardening influence of the modifier was observed for 35/50 bitumen, with average changes of approximately 41% for softening point and 30% for penetration. For 35/50 asphalt, the technology of binder production (distillation / oxidation) did not have a straightforward effect on the above mentioned parameters. Greater changes after polymer modification in R&B examination were observed in BITUMEN II. In terms of penetration, BITUMEN I turned out to be more susceptible to change. The positive effect of modifier (i.e. SBS elastomer) on bitumen is determined based on the changes of binder penetration index (PI), in accordance with PN-EN 12591:2010, Appendix A. PI increased in all cases and the binders underwent transition from sol-gel (or even sol) to typical gel state, which could be observed for mixtures with polymer content above 4%. As a result, temperature sensitivity decreased, i.e. the characteristics of binders became more resistant to temperature changes. Elastic recovery test results are presented in Fig. 3.
Figure 3. Effect of SBS amount on elastic recovery values of 35/50 and 160/220 bitumens

According to PN-EN 14023:2009, medium-modified bitumens should be characterized with elastic recovery of 50%. When the amount of modifier is higher, elastic recovery should not be smaller than 70%. The latter level, which is the value of PMB 45/80-65, was obtained for 2% addition of the polymer. It confirms the fact that compatibility of the product (binder and modifier) was good and met the current standards.

Force ductility tests showed that base (road) asphalts and asphalts with a small addition of modifier (of no more than 1%) did not display the existence of zone III (in line with Fig. 1), characteristic for rubber-like substances. This is the region of spring-elastic strain, which gets bigger as the amount of polymer increases. The increase of modifier amount expands the range of work in zone III and increases work in the range of plastic deformation (zone II). This is due to the increase of binder cohesion, which is reflected by the increase of maximum force measured in the ductility test. When the content of polymer in the bituminous binder is approximately 5 - 6%, work in the range of spring-elastic deformation (zones I and III) is bigger than work conducted on a sample in plastic deformation range (Fig. 4). When the amount of polymer gets bigger, no significant changes are observed in work conducted in the range of purely elastic strain, despite the fact that the maximum strain force increases. A marked correlation was found between total work conducted on a sample and the amount of polymer. The hardening effect of modifier is to a large extend dependent on the hardness of base asphalt. An interesting correlation was found between the amount of polymer and work quotient (D) conducted on a sample in the range of spring-elastic and plastic strain (Fig. 5). The work quotient value was determined from Equation (1):

\[ D = \frac{W_{SI} + W_{SIII}}{W_{SII}} \]  \hspace{1cm} (1)

where:
- \( W_{SI} \) – work conducted on a sample in the range of elastic strain (zone I as in Fig. 1), J/cm²;
- \( W_{SII} \) – work conducted on a sample in the range of plastic strain (zone II as in Fig. 1), J/cm²;
- \( W_{SIII} \) – work conducted on a sample in the range of spring-elastic strain (zone III as in Fig. 1), J/cm².
Figure 4. Work conducted on bitumen samples in tensile test accounting for deformation nature (zones as in Fig. 1), binder type and SBS amount

Figure 5. Correlation between the amount of polymer and the quotient of work conducted on a sample in the range of spring-elastic and plastic strain

Analysis of results presented in Fig. 5 shows that the mere addition of 2% of polymer to the base asphalt, both hard (35/50) and soft (160/220), significantly increases work conducted in spring-elastic range, compared to work in the plastic range. This surplus work in elastic regime does not depend on the technology of binder processing. It does, however, have an impact on the size of surplus of work conducted in elastic range over plastic regime.

4. Conclusions
Bituminous binders need to be modified to improve their properties due to increased road traffic and aggressive environmental factors. Rubber-like materials, e.g. thermoplastic polymers, are the most commonly used modifiers. Elastomers, and in particular SBS, constitute the most popular polymers in
Poland. They increase cohesion of base binders, widen their visco-elastic range towards positive and negative temperatures.

Elastic recovery and cohesion, determined in a ductilometer, are the basic parameters used to assess modification. Other useful parameters are softening point and penetration index. PN-EN 14023 standard determines total work conducted on a sample in a ductility test in defined conditions as a property of cohesion. It cannot determine the character of deformation or the stress-strain curve of an examined binder.

The force ductility test showed that if the requirements of work type conducted on a binder sample were made more precise, it could be an additional factor to classify the quality of modification. Particular attention should be paid to spring-elastic strain in zone III, which can be the indicator of modifier amount. It is particularly important in terms of surface operating in high temperatures in summer. The change of binder deformation into spring-elastic regime (including mineral-binder mixtures that contain binders) in the range of extensive deformation is a factor that will improve surface functional properties, and particularly resistance to permanent deformation.

Our findings show that 2% addition of the modifier causes quality changes in the behavior of hard (35/50) and soft (160/220) binders, regardless of their production technology (distilled and oxidized bitumens). The emergence of spring-elastic strain in zone III in a deformed sample due to the addition of polymer is the decisive factor. The above demonstrated share of polymer in bitumen, accounting for its price, can be said to be optimal, for both hard and soft asphalts.

Apart from technological and economic factors, the assessment of asphalt modified with rubber-like additions should also consider consequences of using mineral-asphalt mixtures with excessive amount of the modifier. If vehicle tyres are made of a substance modified with the same rubber-like material as road surface, excessive reboundness can lower road traffic safety and increase fuel consumption.

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