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Abstract

This paper describes application of high performance gel permeation/size exclusion chromatography (HP-GPC/SEC) for the determination of content of polymer modifiers in modified road bitumens. The obtained results were compared with the measurements based on the procedure recommended by the American Association of State Highway and Transportation Officials, which employs Fourier transform mid-infrared spectroscopy (mid-IR FTIR). Two most commonly used modifiers of paving bitumens, namely styrene-butadiene-styrene (SBS) and styrene-butadiene (SB) copolymers as well as modified bitumens sampled from various streets in the city of Gdansk (Poland) were investigated. This work confirmed the ability of GPC/SEC to distinguish modified road bitumens from unmodified ones. The developed methodology is particularly important in quality control of modified bitumens, as well as in arbitration analysis when there is a suspicion that the amount of modifier added to bitumen was lowered or that the material does not meet the specifications concerning the modifier content.

Keywords: polymer modifiers; styrene-butadiene-styrene (SBS); road bitumen; size exclusion chromatography (GPC/SEC); Fourier transform infrared spectroscopy (FTIR); thin layer chromatography coupled with flame ionization detection (TLC-FID)

1. Introduction

Bitumens belong to the group of thermoplastic and viscoelastic materials. Heated bitumens become soft and undergo a gradual transition from a solid to a liquid, while cooling turns them into a brittle-elastic solid. At intermediate temperatures bitumens exhibit the properties of both a viscous liquid and an elastic solid. The properties of road pavements called asphalts (a mixture of bitumen and aggregates) vary as a function of temperature and duration of use. Therefore, the range of viscoelastic properties of a given bitumen type should be properly matched with the expected temperatures of the bitumen in order to retain its rheological characteristics (Loeber, Muller, Morel & Sutton, 1998).

The climate of Poland has a negative impact on paved surfaces. Traditional asphalts do not fulfill all the expectations of road users. Ruts caused by slowly moving trucks during hot summer months and transverse cracks formed as a result of abrupt temperature drops in winter are a real issue for drivers. Furthermore, asphalt undergoes aging processes when exposed to oxygen, heat and ultraviolet light, resulting in changes of physical properties and chemical structure of asphalts (Lamontagne, Dumas, Mouillet & Kister, 2001; Lu & Isacsson, 1998; Ruan, Davison & Glover, 2003; Fernandes, Forte & Leite, 2008; Wang, Razaqpur, Xing & Chen, 2015), as well as, polymer-modifiers added to bitumen (Zhang, Jia, Yu & Xue, 2013; Polacco, Biondi, Stastna, Vlachovicova & Zanzotto, 2004; Airey, 2004). Consequently, the ideal bitumen should possess both a high relative stiffness at high temperatures (summer) to reduce rutting and shoving and an

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increased adhesion between bitumen and aggregates in the presence of moisture to reduce stripping (Roberts et al.,1996).

The most common method to prevent the aforementioned damage to paved surfaces is the replacement of traditional bitumens with polymer-modified bitumens, which changes the interfacial properties of the primary bituminous material (Błażejowski & Styk, 2004). The aim of bitumen modification is to improve the useful properties of the mixtures of mineral aggregates, and to extend the expected service life of paved surfaces - asphalts. This requires better pavement resilience to permanent deformation, cracking, aging, fatigue and the impact of external factors. Methods based on increasing the angle of internal friction in the mixture of bitumen and mineral aggregates, i.e. increasing the content of crushed grains and grit, and on optimizing the binder content and binder consistency do not ensure all the required properties, particularly in the case of increasing road traffic (Piłat & Radziszewski, 2007).

Polymer-modified bitumens used for paving contain a specified amount of modifier in the form of polymer which was introduced into the bitumen via dedicated technological processes (Błażejowski & Styk, 2004; Piłat & Radziszewski, 2007). The modification process is based on crosslinked modifiers at the phase boundary. The final product has properties which improve pavement resilience to rutting and cracking. Polymer-modified bitumens are mainly used for paving roads exposed to high volume traffic of heavy vehicles, bridges, roundabouts and intersections.

Application of polymer-modified bitumens increased the need for reliable quality control procedures determining the content of modifiers in bitumens. This has become one of many tasks of modern analytical chemistry dealing with the composition of complex mixtures. Chromatographic techniques are an indispensable tool in such cases, and liquid chromatography

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is the method of choice to determine low-volatility and non-volatile mixture components. The application of liquid chromatography is particularly recommended for determining the group-type composition of bitumens (Gudebska, 1999). Liquid chromatography can also be used for the determination of bitumen modifiers in asphalts.

So far, a procedure using Fourier transform infrared spectroscopy (FTIR) for determining the content of styrene-butadiene-styrene (SBS), styrene-butadiene rubber (SBR) and styrene-butadiene (SB) copolymers in modified bitumens has been developed (AASHTO T302-05, 2007). FTIR spectroscopy is well-known technique utilized widely in asphalt technology. It can be used to determine the presence and approximate content of polymers in an asphalt binder (Diefenderfer, 2006), to evaluate oxidation levels in bitumens and polymer-modified bitumens (Yut & Zofka, 2011). The FTIR allows for comparison of different types of bituminous samples (Zhang, Wang, Wu, Sun & Wang, 2009; Wu, Zeng, Ou, Yu, Lu & Xu, 2010; Izquierdo, Navarro, Martínez-Boza & Gallegos, 2012). It can be also helpful while explaining interactions occurring between the polymer modifier and bitumen (Ramalinga Chandra Sekar, Mahendran, Vasudevan & Velkennedy, 2015) and while investigating the aging resistance characteristics of polymer-modified birumens (Ouyang, Wang, Yong Zhang & Yinxi Zhang, 2006; Nivitha, Prasad & Krishnan, 2015). Size exclusion chromatography (GPC/SEC) has also been applied for similar analyses (Peramanu & Pruden, 1999). This is due to the fact that polymers with high molecular weights are used as bitumen modifiers. Furthermore, GPC/SEC is a technique commonly used in many aspects of bitumen analytics (Doh, Amirkhanian & Kim, 2008; K.W. Kim, K. Kim, Doh, & Amirkhanian, 2006). Thin layer chromatography coupled with flame ionization detection (TLC-FID) also seems to be useful for determining the modifier content. However, its major application is determination of the group composition (Paliukaitė, Vaitkus & Zofka, 2014;

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Kamiński, Gudebska, Górecki & Kartanowicz, 2003; Ecker, 2001; Masson, Price & Collins, 2001) – a so-called SARA (Saturates, Aromatics, Resins, Asphaltenes).

In the current Polish standard PN EN 14023, describing the classification rules for polymer-modified bitumens, the determination of modifier content is not required (PN EN 14023, 2009). Modified bitumens are on average 20 to 25% more expensive than traditional bitumens. Because of that, adulteration of modified bitumens by lowering the required content of modifiers is quite probable. Lack of monitoring of the amount of modifier used in paved surfaces makes tampering even more likely. Liquid chromatography, especially SEC, could be used for the determination of modifier content in bitumens. It should be noted, however, that for some purposes only highly selective and highly orthogonal separation systems can provide a satisfactory separation of the analytes allowing their quantitative analysis (Boczkaj, Jaszczołt, Przyjazny & Kamiński, 2013; Gilgenast, Boczkaj, Przyjazny & Kamiński, 2011).

In the light of the above facts, the development of the procedure for determining modifiers in bitumens is very important. In addition, the information about the actual amount of ground polymer added is important from the point of view of quality control. The basic principle of quality control concerning addition of modifiers is based on fluorescence microscopy. However, this technique only allows assessment of the technology, but does not allow determining the content of modifier added.

In contrast, this work provides the procedure for the determination of the content of modifier, but does provide any information on whether the modifier occurs in a granular form. Nevertheless, the methodology presented in this paper can be used in quality control laboratories as well as in process analytics, as a tool for the control of modifier content in road pavements.

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The results and conclusions of these investigations should also contribute to the identification of adulterated modified bitumens.

2. Materials and methods

2.1. Materials

The standards used: polystyrene (1,260,000 Da, 120,000 Da, 30,300 Da, 2,450 Da) and benzene were purchased from Merck (Germany), SBS (styrene-butadiene-styrene) and SB (styrene-butadiene) – both from Polish manufacturer. The eluents/solvents used in the investigations – dichloromethane, methanol and toluene (POCH, Poland) were analytically pure and tetrahydrofuran (Merck, Germany) was of HPLC grade. The chromatographic columns employed during the experiments were: two 250 x 7 mm LiChrogel PS1 (5 µm) columns (Merck, Germany) and two 250 x 7 mm LiChrogel PSMix columns (Merck, Germany). The PTFE disc filters (0.45µm) were purchased from Merck (Germany).

2.2. Apparatus

A Merck–Hitachi (Darmstadt, Germany) gradient liquid chromatograph equipped with an L-7100 four-channel pump, a 7450A UV-Vis diode array detector, a RID 7490 refractive index detector, a 7350 thermostat with a 7350i cooling system, a Rheodyne model RH-7725i injector with a 20-µL sample loop, a V7226 six-port two-position backflush valve (Knauer, Berlin, Germany) to switch the flow direction of the mobile phase, were used in the present work.

A FTIR NICOLET 8700 (Thermo Electron Corporation) spectrometer with Specac Golden Gate ATR accessory; an analytical balance (RADWAG Poland); an XL ultrasonic bath, a 2020 Sonificator® Misonix (USA) and a rotary evaporator Heidolph (Germany) were used.

An Iatroscan (Iatron Labs, Japan) TLC-FID analyzer equipped with Chromarod-S III rods was also used. Additional equipment included: an automated sample dispenser SES 3200/IS-01, a

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TLC rods dryer model TK-8, an analogue-to-digital converter and software for data processing (Elkor, Poland).

2.3 Samples

Unmodified bitumens: 35/50, 160/220 and modified bitumens: 25/55-60, 45/80-55 (from international supplier of bitumens) were examined. In addition, samples of asphalt from streets paved at different times (year: 2006, 2007, 2008) were investigated. The latter samples were taken from various streets in Gdansk, Poland (see Fig. 1), namely:

- modified bitumen samples were taken from: Marynarki Polskiej Street (year 2006), Grunwaldzka Street (year 2007) and Cienista Street (year 2008);
- unmodified bitumen samples – from: Spacerowa Street (year 2006), Źródlana Street (year 2007) and Kampinoska Street (year 2008).

2.4 Procedure

2.4.1. Sample preparation

a) Road pavement samples

Six samples of modified and unmodified bitumens were collected in the Gdansk area at different time points during the road construction. Samples (3-5 grams) were taken from the depth of 1 cm (sample width ca. 1 cm).

b) Bitumen solutions

The size-reduced samples (approximately 2.5 g) of collected road pavements were transferred into pre-weighed 10-mL vials and subjected to ultrasound-assisted extraction with an organic solvent - dichloromethane (DCM) for 10 minutes. The extraction was then continued until the

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mineral aggregates turned clean and bitumen was visibly dissolved. The undissolved material was vacuum filtered onto 90 mm disc filters which were subsequently washed a couple of times with dichloromethane. The filtrates were transferred into pre-weighed 100-mL round-bottom flasks and evaporated to dryness in a rotary evaporator at 40 °C. Finally, the flasks were dried in a laboratory dryer for 30 min at 120 °C and the obtained samples (of known mass) were dissolved in THF for GPC/SEC.

2.4.2 Infrared Spectroscopy (FT-IR)

Spectral analysis was performed by using the attenuated total reflectance (ATR) technique according to the modified procedure described in standard AASHTO T 302-05 (2007). Total reflectance is achieved by directing a beam of infrared radiation onto the side of a diamond optical element that constitutes the main part of a Golden Gate accessory. Samples in a solid state were placed on the surface of a crystal (diamond). Spectra were recorded at a 4cm^{-1} resolution by averaging 32 measurements in the range from 4000 cm^{-1} to 500 cm^{-1}. The maximum absorbance for bitumen should be at ca. 1375 cm^{-1}, while the peak having a maximum at 975 cm $^{-1}$ indicates the presence of SB or SBS.

2.4.3 Size Exclusion Chromatography (GPC/SEC)

Two PS-MIX (250×7 mm, d_p = 5μm) and two PS-1 (250×7 mm, d_p = 5μm) columns with tetrahydrofuran as the mobile phase, and a refractive index and a UV-DAD detectors connected in series were used in this study. All samples were separated at 20 °C. The mobile phase flow rate was 1 mL/min and the injection volume was 20 μL. The solutions were filtered through 0.45-μm PTFE membrane filters. For the determination of molecular mass, calibration curves were prepared by using molecular mass standards with known masses (1,260,000 Da, 120,000 Da, 30,300 Da, 2,450 Da, benzene). To determine the modifiers in bitumens, calibration curves

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were prepared by using solutions of bitumens in THF at 50 mg/mL with the following modifier concentrations: 1% SBS, 3% SBS, 5% SBS, 7% SBS. An analogous series of solutions was prepared using bitumens modified with SB.

2.4.4 Thin Layer Chromatography Coupled with Flame Ionization Detection (TLC-FID)

Separation of bitumens was performed according to a modified procedure published previously (Gudebska, 1999). During bitumen separation, an optimization procedure was carried out – the flow rates of hydrogen and air were changed prior to analysis of each of the ten chromarods – and the optimum flow rates for hydrogen (150 mL min^{-1}) and for air (1.8 L min^{-1}) were selected.

Chromarods were activated by passing them through a TLC-FID analyzer using a hydrogen flame just before sample application. Activated rods were spotted with 1 μL of sample solution containing: 10mg asphalt mL^{-1} dichloromethane and 1mg SBS mL^{-1} dichloromethane, using a 2-μL microsyringe. After application of spots, the rods were dried for 2 minutes in an oven at 70˚C and placed for 10 minutes in a desiccator. Next, the rod holder carrying the chromarods was placed in a TLC chamber containing the solvent – a mixture of dichloromethane: methanol 95:5 (v/v). Elution was carried out to a height of 2.5 cm. The rod holder was put in an oven at 70 °C for 2 minutes and then placed in a desiccator for 10 minutes, and after that – for 10 minutes in a TLC chamber containing toluene where the chromarods were developed up to a height of 6 cm. Next, the rod holder was transferred to an oven for 2 minutes, then to a desiccator for 10 minutes, and finally it was placed in the TLC chamber containing hexane for 5 min where the elution was carried out to a height of 10 cm.

Detection was carried out by the FID detector with digital acquisition of the detector signal.

2.4.5 Determination of SB and SBS

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Analytical conditions were optimized using solutions of road bitumen having concentrations of 0.05 g/mL and of modifiers of 0.005 g/mL in tetrahydrofuran (for GPC analysis). Next, the samples were prepared according to the procedure described in „Sample preparation FT-IR and GPC/SEC".

The limit of quantitation (LOQ) was taken as the concentration corresponding to the signal five times as great as the noise corrected for the recovery. The LOQ values (the lowest concentration of modifier that could be determined using the developed procedure) for SBS and SB were 0.46% and 0.38%, respectively. The determination of polymer content in bitumens was carried out by the external standard method. Four-point calibration curves were prepared using solutions of modified bitumens with known modifier concentrations in a typical range of 1-7%. Each determination was repeated five times. The peak area of modifiers in real samples was determined using a so-called "drop" integration method and the same method was applied for the preparation of the calibration curve. Drop method is based on drawing a perpendicular line to the baseline from the "valley" between the chromatographic peaks which are not separated.

In case of calibration curve preparation, the applied "drop" method enabled to obtain satisfactory values of determination coefficient (R^2) within the "practical" range of concentrations presented in the paper. It confirms the correctness of determinations performed with the use of the calibration curve.

2.4.6 Quality control, quality assurance

Statistical studies were carried out using Microsoft Excel Data Analysis ToolPak. The following parameters were calculated: the arithmetic mean, standard deviation (SD), relative standard deviation (RSD), limit of repeatability and parameters describing the regression, i.e. the

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value of the slope and correlation coefficients. The results are reported as the mean value from at least five independent measurements, in which the difference did not exceed 5%.

3. Results and discussion

3.1 Infrared spectroscopy (FT-IR)

Attenuated total reflection (ATR) infrared spectroscopy was used to perform spectral analysis of the samples (see Fig.2).

Spectral analysis confirmed the presence of alkyl groups as evidenced by the C-H stretching vibrations in the 3000–2850 cm^{-1} region. No bands were detected for the wavenumber values greater than 3000 cm^{-1}. Inspection of the 1760–1665 cm^{-1} range (carbonyl band position) revealed no evidence for the presence of carboxylic, ester, aldehyde, amide and ketone groups. The following characteristic bands were observed:

- ✓ C–H stretching from 3000 to 2850 cm^{-1},
- ✓ C–H bending or scissoring from 1470 to 1450 cm^{-1},
- ✓ C–H rocking from 1370 to 1350 cm^{-1}.

Bands in the 1300–900 cm^{-1} region, which is called the fingerprint region, originated from skeletal vibrations and formed a complex picture. In general, it is difficult to interpret bands in this particular region. However, each organic compound has its unique pattern, the so-called fingerprint, which can be used for its identification by comparing the compound's fingerprint with the fingerprint of the selected standard reference material (AASHTO T302-05, 2007). In the case of reference standards such as SBS and SB, the characteristic region occurs at **965cm^{-1}** and **697 cm^{-1}**, respectively. The SBS band is split, while no such feature occurs in the case of SB (Fig. 3). The polymers in the analyzed samples could not be positively identified because their content was too low and the absorption bands were blurred.

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The contents of modifiers were determined from a calibration curve (Fig. 4 prepared on the basis of data listed in Table 1) for the characteristic regions (R^2=0.9998; absorbance = f(concentration of modifier): (A1/A2) = 0.031c + 0.0286).

The concentrations of modifiers determined in all the examined samples are listed in Table 2.

3.2 Size exclusion chromatography (GPC/SEC)

Examples of chromatograms of selected bitumens (including those from road pavement) are shown in Figures 5 and 6, while Figure 7 presents chromatograms of the mixtures containing polystyrenes and the analyzed modifiers.

The chromatograms of modified bitumens reveal an additional peak compared to the chromatograms of unmodified bitumens. The peak is attributed to the presence of a modifier (Fig. 5a) and has a lower retention due to the high molecular weight of the compound (Fig. 7). The obtained molecular weight of ca. 550 kDa is not the true molecular weight of the analyzed polymer, but its relative molecular weight with respect to the molecular weight of polystyrene.

The GPC/SEC molecular weight distribution calibration curve (log M = f(V_e)) presented in Fig. 8 (blue curve) was prepared on the basis of Fig. 7a. The five points (blue dots in Fig. 8) indicated on the calibration curve refer to the obtained values of log M = f(V_e) of polystyrenes of masses: 1,260,000, 120,000, 30,300, 2,450 Da and to acetone (58 Da). The average molecular weights for the modifier and bitumens were calculated from the equation: log M= -0.4656V_e + 13.31. Using the GPC/SEC chromatograms in Fig. 5-7, it was possible to indicate on the calibration curve the ranges of elution volume characteristic of the modifier (purple line) and bitumen (black lines). Since the chromatographic peaks for bitumen (Fig. 5, 6) are not typical because they split into two fractions, there are two black lines in Fig. 8. It is likely that the first fraction (counting from right to left) represents bitumen sample components with

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lower molecular weights, while the second is the result of oxidation and polymerization process and contains sample components with higher molecular weights. It was not possible to present separately the V_e ranges for two types of the examined modifiers (SBS and SB) due to their similar molecular weights. Therefore, size exclusion chromatography is not an appropriate technique to distinguish these two modifiers.

A calibration curve (Fig. 9 prepared on the basis of data listed in Table 3) used for the determination of modifier concentration was constructed based on the GPC/SEC measurements made for four 35/50 bitumen solutions with increasing polymer contents, namely, 1, 3, 5 and 7% (R^2=0.9844, peak area = f(concentration of modifier): A = 149295c + 201.45). The obtained results, including descriptive statistics, are presented in Table 4. A comparison of chromatograms of unmodified and modified asphalts, both "unused" samples (obtained from the manufacturer) and samples collected from the roads reveals that the analytical signal in the range of the expected value of the modifier retention time was obtained only in the case of modified bitumen samples. According to the obtained results, both steps, *i.e.*, sample preparation procedure and chromatographic analysis, proved to be optimal for the intended use of the methodology presented in this study. In this way, the ability of GPC/SEC to distinguish modified road bitumens from unmodified ones was confirmed. The procedure developed in this work is particularly important in quality control measurements of modified bitumens as well as in comparative and arbitration analysis whenever there is a suspicion that the amount of modifier added to bitumen was lowered by the manufacturer or when there is a suspicion that the delivered material does not meet the specifications concerning the modifier content. Moreover, the procedure described here is also applicable to the assessment of aging of road asphalts and their degradation during usage.

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As was the case of ATR infrared spectroscopy measurements, sample 1 again displayed a lowered content of modifier when assayed by GPC/SEC. A comparison of the results obtained by FTIR and GPC/SEC shown in Tables 2 and 4 reveals that the differences between the two procedures for the average modifier content in each of the investigated bitumens are within the repeatability of the FTIR method. Consequently, the developed GPC/SEC procedure is a viable alternative to FTIR while offering an improved precision of the determinations as indicated by substantially lower relative standard deviation values.

3.3 Thin layer chromatography coupled with flame ionization detection (TLC-FID)

Table 5 summarizes the differences in group composition content resulting from the presence of the modifier. For unmodified bitumen 35/50, it can be noticed that the most abundant group are aromatic compounds (49.99%), followed by resins (21.58 %) and saturated compounds (21.27 %). In contrast, modified bitumen 25/55-60 shows significant differences in the group composition, caused by the presence of the modifier.

The TLC-FID technique is not useful for the determination of asphalt modifiers; however, it allows determining the group composition of bitumens. Comparing the results of each fraction content for both types of bitumen one can observe a decrease in aromatic compounds content and an increase in resin content in a modified bitumen sample (Table 5). These changes result from the polymer presence, because SBS – due to the presence of aromatic rings in polystyrene and the double bonds in polybutadiene – has a greater affinity to aromatic and resin fractions. Differences in group-type composition after bitumen modification may result from the conversion of bitumen constituents. SBS probably binds aromatic molecules in a molecular network, causing an increase in their weight and, therefore, shifting them to the resin fraction region.

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The polymer applied at a high concentration on the chromarods was not separated and remained at the start along with some part of the asphaltene fraction. Another attempt with a lower concentration of a polymer sample showed the presence of the signal which had the highest intensity in the range of aromatic fractions. At a high concentration (greater than 30 mg ml^{-1}) of the polymer there is a problem of polymer solubility. The mobile phase used for chromatogram development is a mixture of dichloromethane-methanol 95/5 (v/v) and the polymer is insoluble in methanol. Consequently, the presence of methanol causes SBS stoppage at the start. This limitation is only theoretical due to a relatively low concentration of the modifier in commercial bitumens.

4. Conclusions

The concept of using infrared spectroscopy for determining the content of polymer modifiers in road bitumens is valid, as supported by the published literature. Such polymer modifiers as styrene-butadiene-rubber (SBR), styrene-butadiene-styrene (SBS) and styrene-butadiene (SB) are characterized by the specific band regions at 965cm $^{-1}$ and 697 cm^{-1}. The SBS band at 965 cm^{-1} is split in contrast with the SB modifier. A positive identification of individual polymers in the analyzed samples of paving bitumens was not possible due to low analyte content and the significantly blurred bands.

The studies revealed that infrared spectroscopy should be appended with the size exclusion chromatography, as the latter results in repeatable measurements with smaller errors.

The developed procedure for the determination of polymer modifiers in paving bitumens by size exclusion chromatography requires the use of four columns connected in series, i.e. two PS1 columns and two PS Mix columns packed with a styrene-divinylbenzene copolymer, and tetrahydrofuran as the eluent. This procedure allows the separation of modifiers from other

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bitumen components, as well as the determination of modifier content. However, size exclusion chromatography does not allow simultaneous identification of SBS and SB modifiers present in the same sample because the difference between the molecular weights of these polymers is too small.

In addition, the studies carried out using thin layer chromatography coupled with flame ionization detection have demonstrated that this technique is useful for determining the composition of modified bitumens. Modified bitumens contain more so-called resins and less aromatic compounds than unmodified bitumens. This is due to structural changes in aromatic hydrocarbons interacting with polymer molecules. The TLC-FID technique does not allow the determination of the modifier content in bitumen samples because the modifier is eluted in the range of aromatic compounds and resins. Furthermore, the application of the procedure described in Polish standard PN EN 129161 (2008) using NP-HPLC also did not allow the measurement of the polymer content. In this case, the failure was caused by poor solubility of polymer modifiers in the eluent used. The developed procedures also allow determining the modifier content in road bitumens already used for road paving, as well as the rate of degradation of the modifier during its use.

This paper describes the methodological basis for the determination of modifiers content in bitumen samples collected from the roads. It is the first work allowing to perform such determination using gel permeation/size exclusion chromatography (GPC/SEC). The developed methodology will be used for monitoring the changes of modifier concentration in bitumens during road pavement aging, as well as, for comparative studies of modified bitumen supplied by different manufacturers. The results of this research will be the subject of subsequent papers.

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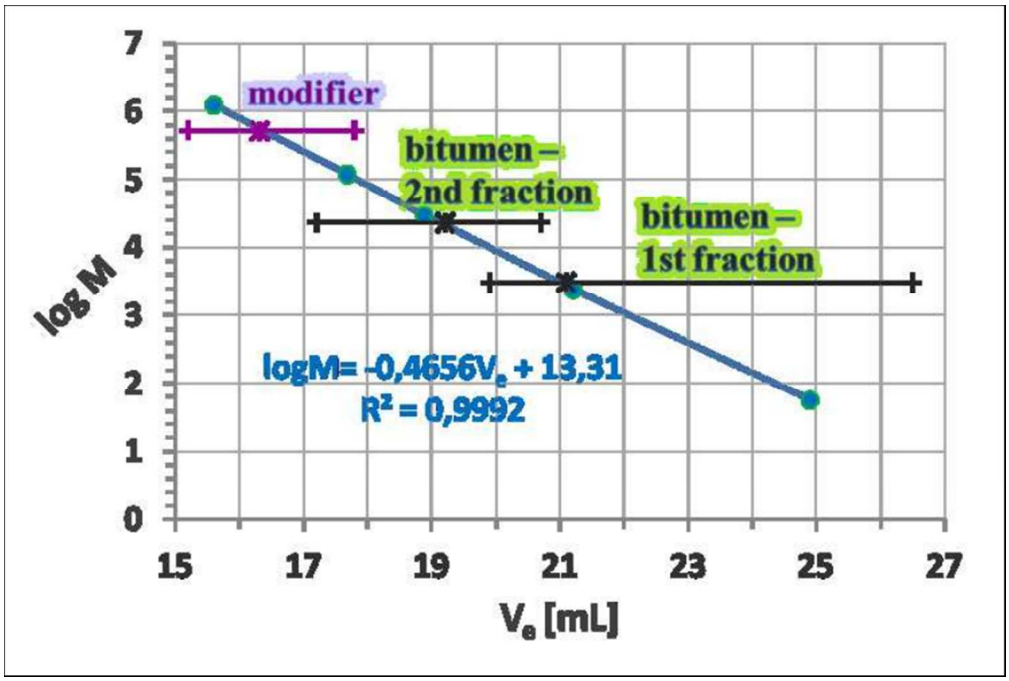

230x155mm (96 x 96 DPI)

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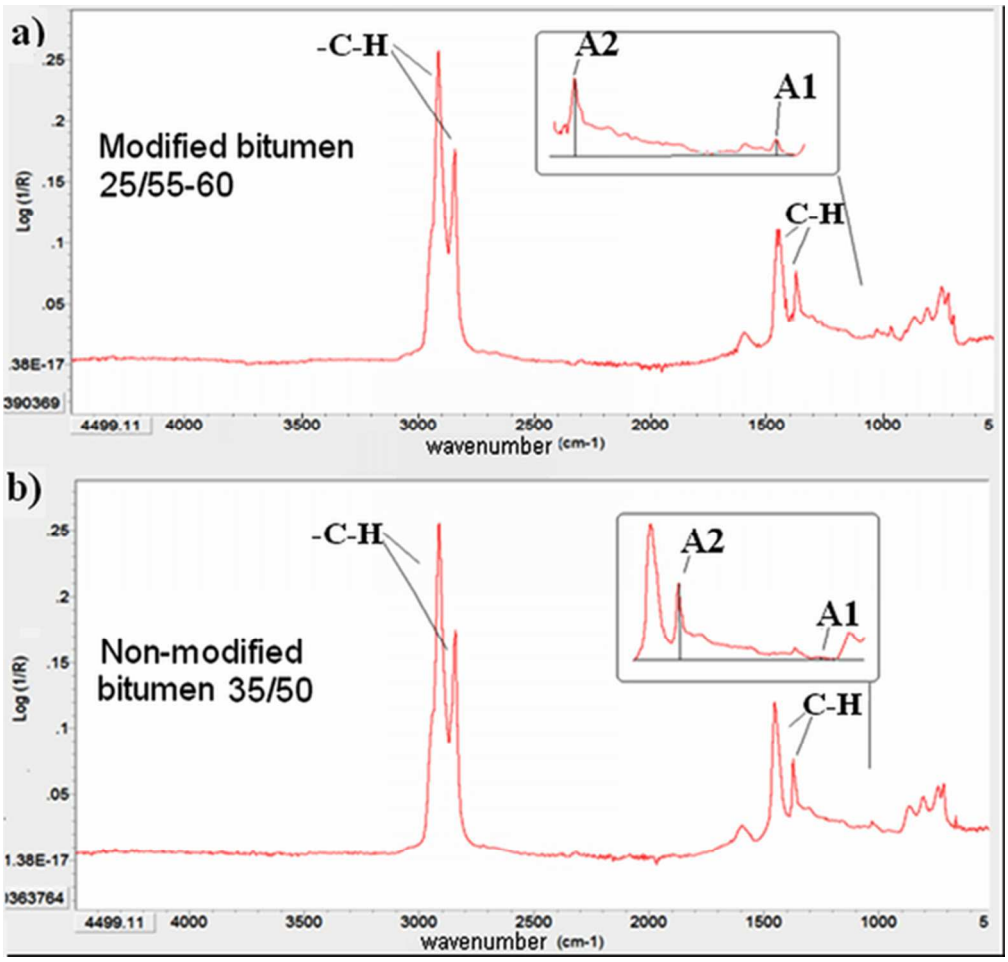
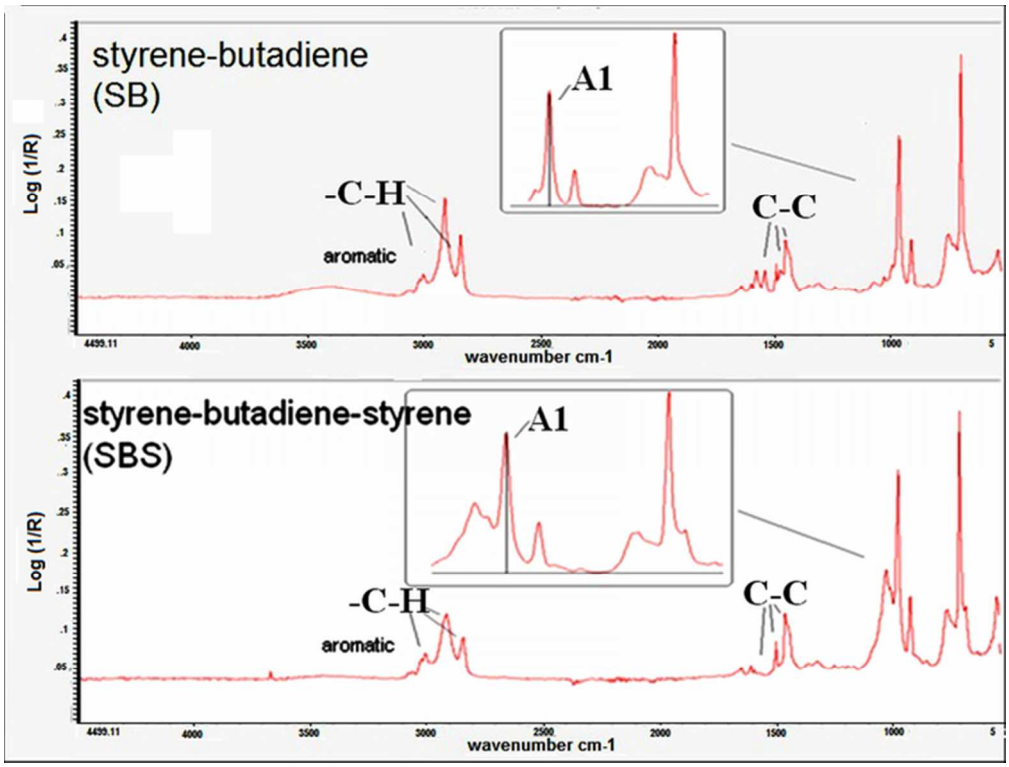
Map of Gdansk with sampling sites of modified and unmodified bitumens marked.
27x22mm (600 x 600 DPI)



ATR IR spectra with a resolution of 4 cm-1 in the range 4000–500 cm-1 of: a) modified bitumen 25/55-60 b) unmodified bitumen 35/50.
27x26mm (600 x 600 DPI)



ATR IR spectra with a resolution of 4 cm-1 in the range 4000–500 cm-1 of SB and SBS modifiers.
30x23mm (600 x 600 DPI)

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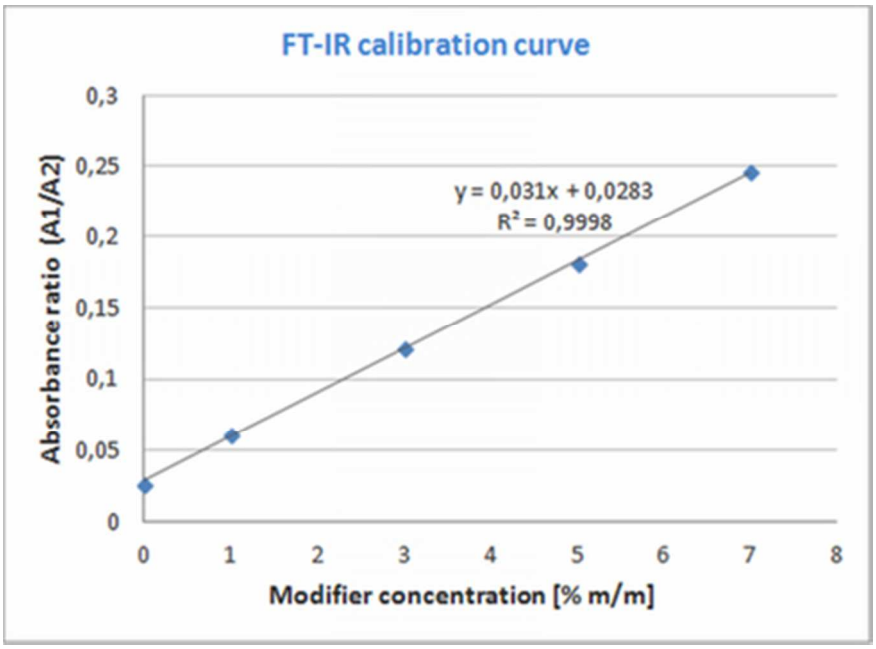

Calibration curve for FT-IR. Variable x stands for modifier concentration (in % m/m), variable y – for absorbance ratio.
18x13mm (600 x 600 DPI)

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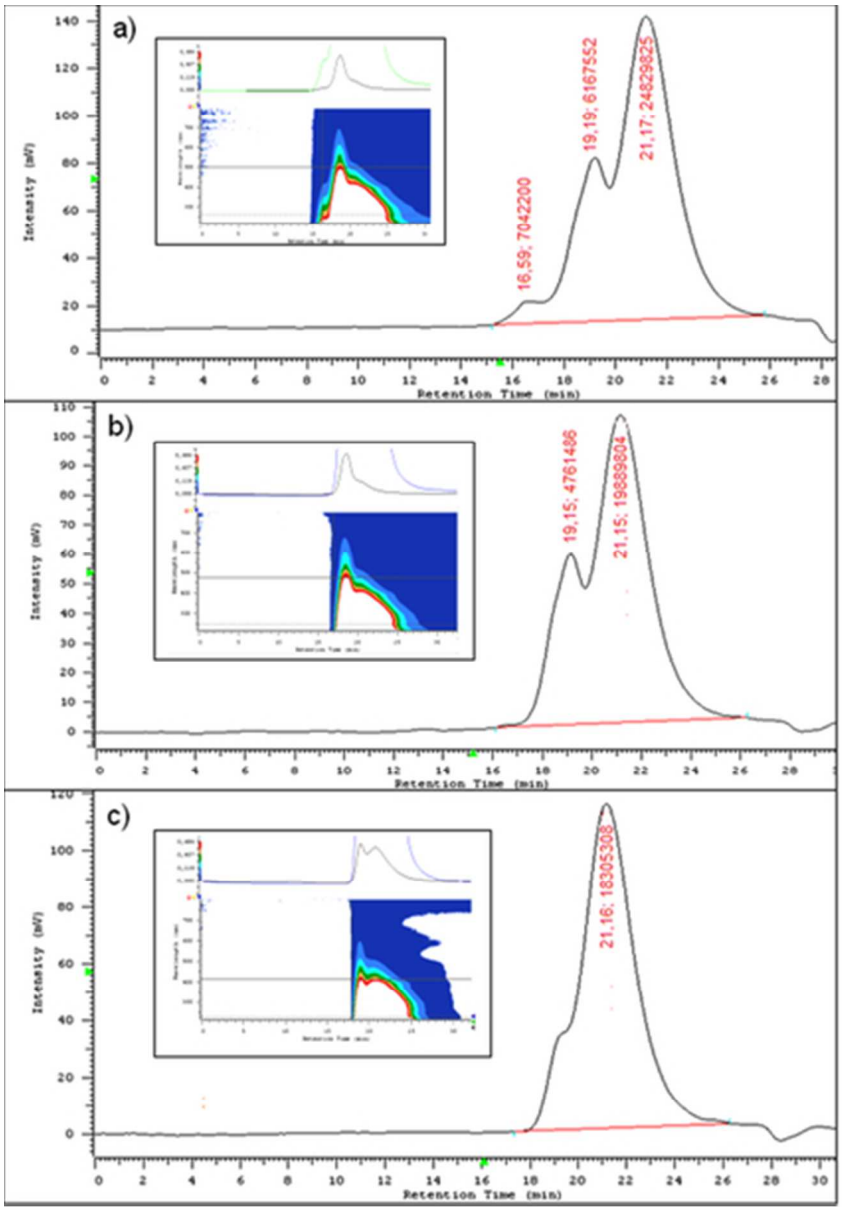
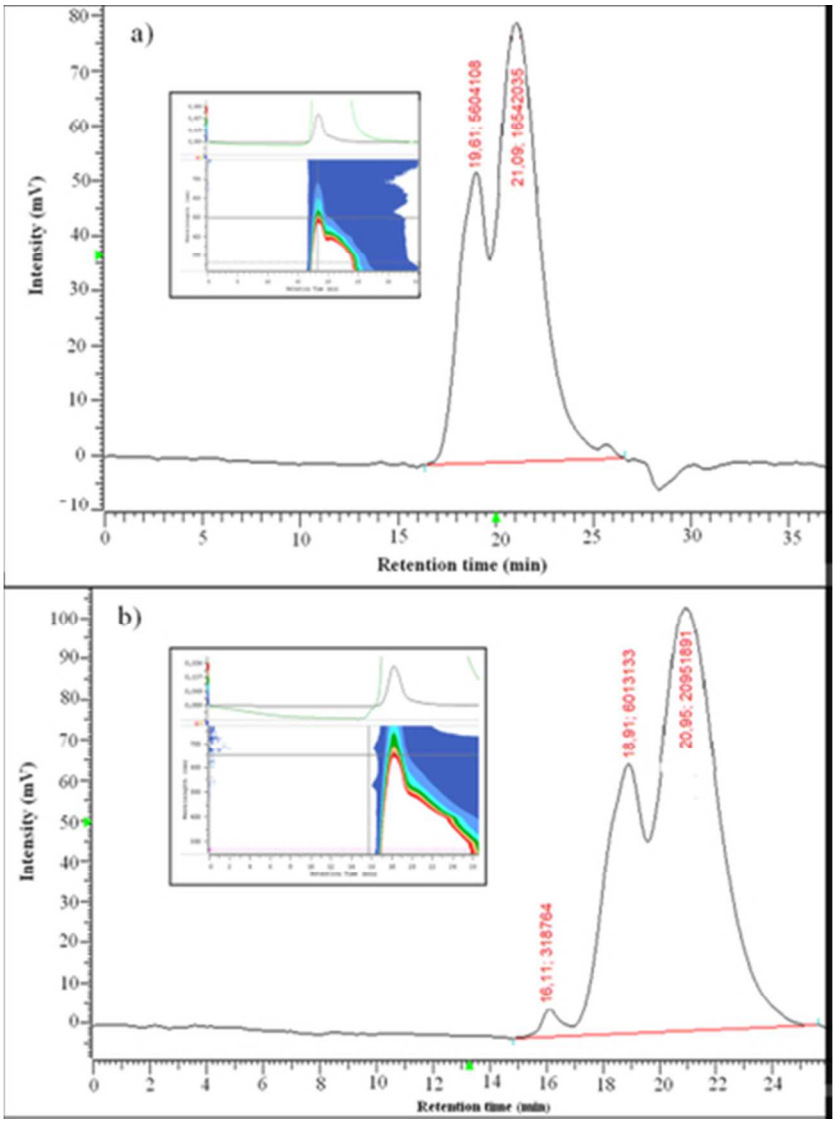
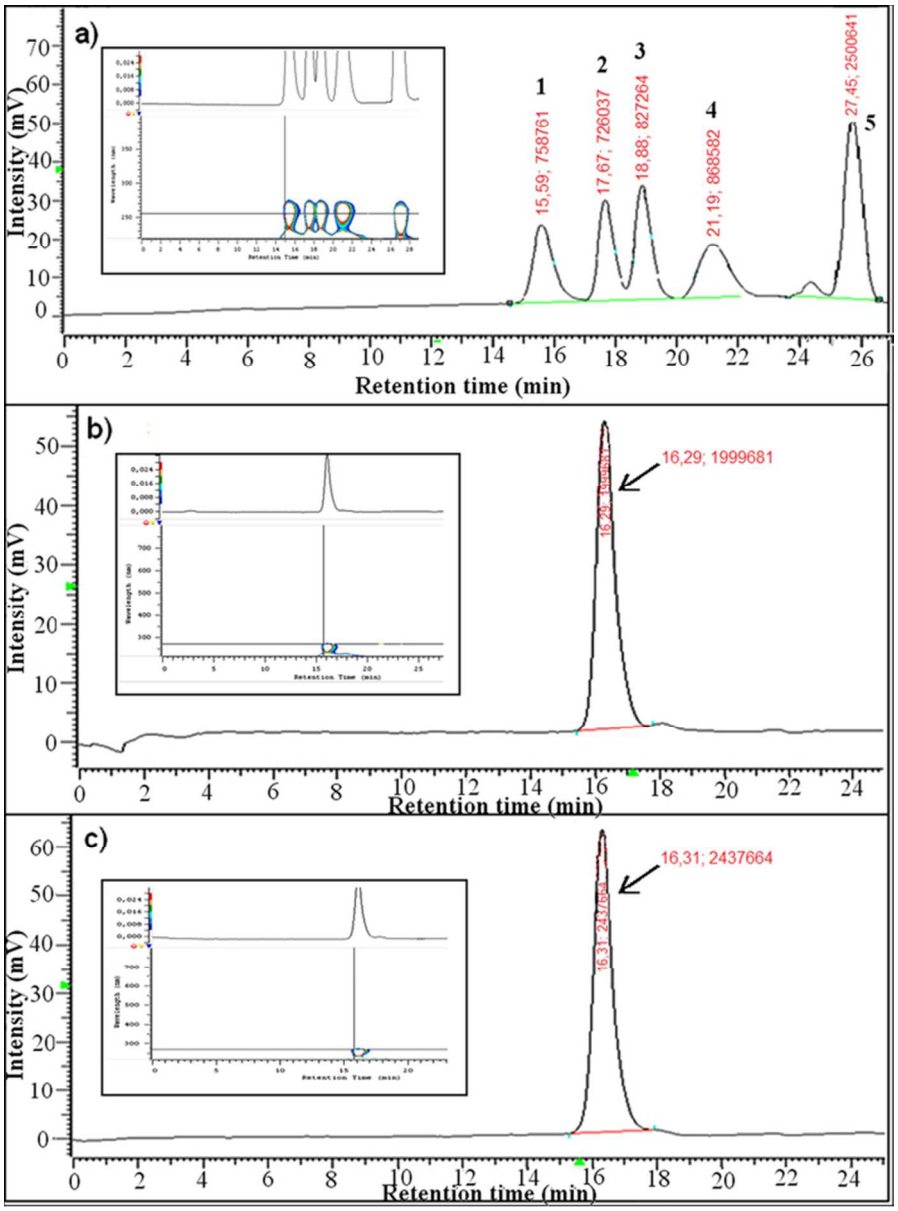


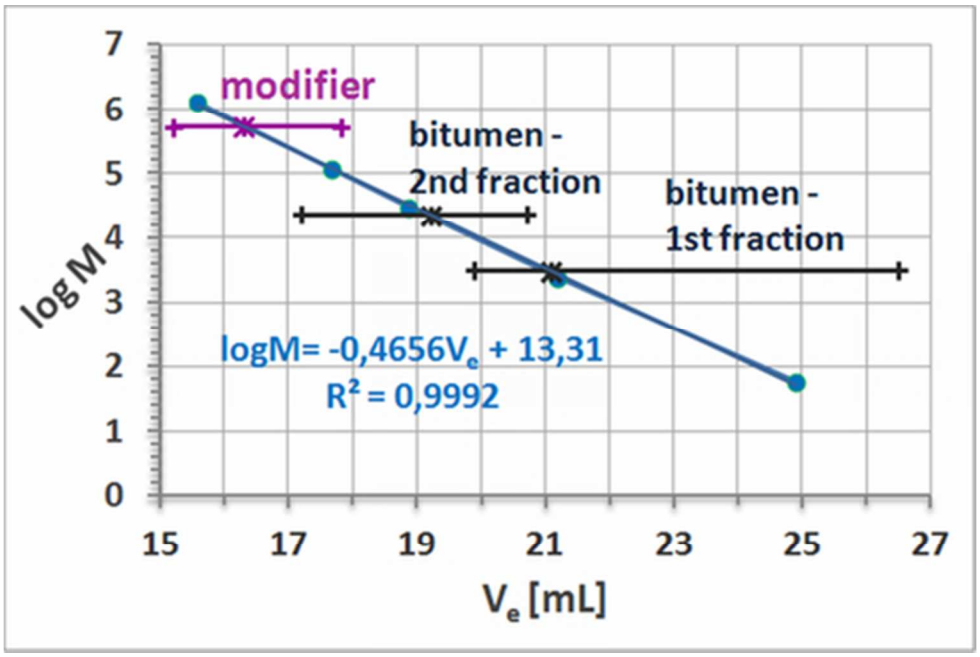
GPC/SEC chromatograms of bitumens. Columns: 2xPS1+2xPS MIX, eluent: tetrahydrofuran 1mL min-1, injection volume 20 µL, temperature 20 0C, a – modified bitumen 25/55-60 (50 mg mL-1); b – unmodified bitumen 35/50 (50 mg mL-1); c – unmodified bitumen 160/220 (50 mg mL-1).
19x25mm (600 x 600 DPI)



GPC/SEC chromatograms of bitumens. Columns 2xPS1+2xPS MIX, eluent: tetrahydrofuran 1mL min-1, injection volume 20 µL, temperature 20 0C, a – unmodified bitumen from Kampinoska Street from year 2008 (50 mg mL-1); b – modified bitumen from Cienista Street from year 2008 (50 mg mL-1).
17x23mm (600 x 600 DPI)



GPC/SEC chromatograms of polystyrenes and analyzed modifiers. Columns: 2xPS1+2xPS MIX, eluent: tetrahydrofuran 1mL min-1, injection volume 20 µL, temperature 20 0C; a–mixture of standards (where 1–4 are polystyrenes of masses: 1–1,260,000, 2–120,000, 3–30,300, 4–2,450, 5–acetone, 6–benzene) (5mg mL-1); b–SBS (5 mg mL-1); c–SB (5.3 mg mL-1).
29x40mm (600 x 600 DPI)



GPC/SEC calibration curve (log M = f(Ve); blue) for polystyrenes of masses: 1,260,000, 120,000, 30,300, 2,450 and acetone. The relevant ranges of Ve values obtained for bitumen (black, 1st and 2nd fraction, where the 1st one refers to fraction of lower molecular mass, and 2nd – to higher molecular mass; explained in text), as well as for bitumen modifier (purple) are depicted in the graph.
20x13mm (600 x 600 DPI)

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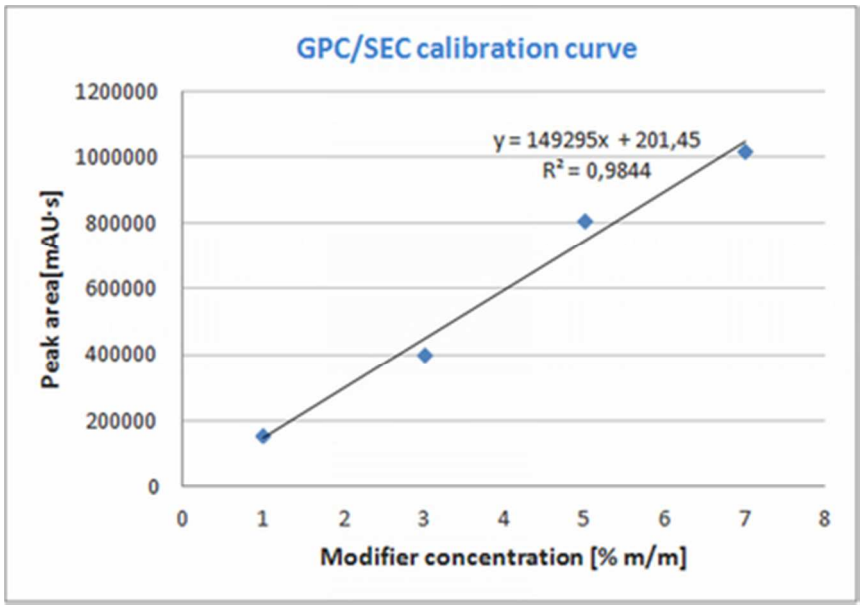

Calibration curve for GPC/SEC. Variable x stands for modifier concentration [% m/m], variable y – for peak area [mAU·s].
18x12mm (600 x 600 DPI)

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Figure captions

Figure 1. Map of Gdansk with sampling sites of modified and unmodified bitumens marked.

Figure 2. ATR IR spectra with a resolution of 4 cm^{-1} in the range 4000–500 cm^{-1} of: a) modified bitumen 25/55-60 b) unmodified bitumen 35/50.

Figure 3. ATR IR spectra with a resolution of 4 cm^{-1} in the range 4000–500 cm^{-1} of SB and SBS modifiers.

Figure 4. Calibration curve for FT-IR. Variable x stands for modifier concentration (in % m/m), variable y – for absorbance ratio.

Figure 5. GPC/SEC chromatograms of bitumens. Columns: 2xPS1+2xPS MIX, eluent: tetrahydrofuran 1mL min^{-1}, injection volume 20 µL, temperature 20 ^{0}C, a – modified bitumen 25/55-60 (50 mg mL^{-1}); b – unmodified bitumen 35/50 (50 mg mL^{-1}); c – unmodified bitumen 160/220 (50 mg mL^{-1}).

Figure 6. GPC/SEC chromatograms of bitumens. Columns 2xPS1+2xPS MIX, eluent: tetrahydrofuran 1mL min^{-1}, injection volume 20 µL, temperature 20 ^{0}C, a – unmodified bitumen

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from Kampinoska Street from year 2008 (50 mg mL^{-1}); b – modified bitumen from Cienista Street from year 2008 (50 mg mL^{-1}).

Figure 7. GPC/SEC chromatograms of polystyrenes and analyzed modifiers. Columns: 2xPS1+2xPS MIX, eluent: tetrahydrofuran 1mL min^{-1}, injection volume 20 µL, temperature 20 ^{0}C; a–mixture of standards (where 1–4 are polystyrenes of masses: 1–1,260,000, 2–120,000, 3–30,300, 4–2,450, 5–acetone, 6–benzene) (5mg mL^{-1}); b–SBS (5 mg mL^{-1}); c–SB (5.3 mg mL^{-1}).

Figure 8. GPC/SEC calibration curve (log M = f(V_e); blue) for polystyrenes of masses: 1,260,000, 120,000, 30,300, 2,450 and acetone. The relevant ranges of V_e values obtained for bitumen (black, 1st and 2nd fraction, where the 1st one refers to fraction of lower molecular mass, and 2nd – to higher molecular mass; explained in text), as well as for bitumen modifier (purple) are depicted in the graph.

Figure 9. Calibration curve for GPC/SEC. Variable x stands for modifier concentration [% m/m], variable y – for peak area [mAU·s].

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List of tables

Table 1. Actual data used for calibration curve preparation in case of FT-IR.

modifier concentration [% m/m]	**0,0**	**1,0**	**3,0**	**5,0**	**7,0**
absorbance ratio (A1/A2)*	0.027	0.061	0.122	0.182	0.246

* where A1 is characteristic absorbance for polymer modifier (965cm^{-1}), and A2 is characteristic absorbance for bitumen (1375cm^{-1})

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Table 2. Concentration of modifiers in bitumens and statistical parameters for FT-IR technique.

Parameters	modified bitumen 25/55-60	modified bitumen 45/80-55	1 (2008)	2 (2007)	3 (2006)
Modifier concentration [%m/m]	4.52	3.51	2.24	3.32	3.36
Standard deviation	0.25	0.25	0.13	0.80	0.57
Relative standard deviation	0.05	0.07	0.06	0.24	0.17

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Table 3. Actual data used for calibration curve preparation in case of GPC/SEC.

modifier concentration [% m/m]	**1,0**	**3,0**	**5,0**	**7,0**
peak area [mAU·s]*	158199	402767	811214	1017353

* the peak area are avarages for triplicate analysis

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Table 4. Concentration of modifiers in bitumens and statistical parameters for GPC/SEC technique.

Parameters	modified bitumen 25/55-60	modified bitumen 45/80-55	1 (2008)	2 (2007)	3 (2006)
Modifier concentration [%m/m]	4.41	3.16	2.11	3.28	3.57
Standard deviation	0.24	0.13	0.06	0.24	0.06
Relative standard deviation	0.05	0.04	0.03	0.07	0.01

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Table 5. Group composition of unmodified and modified bitumens.

Bitumen	Saturated compounds [%]	Aromatic compounds [%]	Resins [%]	Asphaltenes [%]
Unmodified bitumen 35/50	21.27	49.99	21.58	7.16
Modified bitumen 25/55-60	16.22	36.15	38.97	8.67

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