Materials Today Communications 49 (2025) 113719

Contents lists available at ScienceDirect

Materials Today Communications

journal homepage: www.elsevier.com/locate/mtcomm

Comparative analysis of SBS polymers and their impact on the chemical composition of modified binders

Judita Škulteckė [a,*], Audrius Vaitkus [a], Viktoras Masevičius [b], Vaidas Klimkevičius [b], Ovidijus Šernas [a]

[a] Road Research Institute, Vilnius Gediminas Technical University, Linkmenu 28, Vilnius LT-08217, Lithuania
[b] Institute of Chemistry, Faculty of Chemistry and Geosciences, Vilnius University, Naugarduko 24, Vilnius LT-03225, Lithuania

ARTICLE INFO

Keywords:
Styrene-butadiene-styrene (SBS)
Polymer modified bitumen
SBS structure
SBS molecular weight
Dispersity
Fractional composition
Copolymer composition

ABSTRACT

Styrene-butadiene-styrene (SBS) is a widely used polymer to enhance the performance of bitumen and asphalt pavements. However, notable inconsistencies in the performance of asphalt pavements with polymer modified binders (PMBs) within the same PMB class highlight a critical knowledge gap. Most previous studies have focused on SBS dosage levels with limited attention to the influence of polymer microstructure and the base binder chemistry on final PMB properties. This study addresses this gap by comprehensively evaluating eight commercially available SBS polymers differing in structure (linear or radial), styrene and vinyl content, and molecular weight. These were characterized using ^{1}H nuclear magnetic resonance (^{1}H NMR) and size-exclusion chromatography (SEC). Based on the results, four representative polymers were selected for PMB production using three chemically distinct 70/100 base binders. Twelve different PMBs were prepared with a fixed SBS content (3.5 %) to evaluate the effect of both SBS properties and base binder chemical composition on the final product. Thin-layer chromatography with flame ionization detection (TLC-FID) and Fourier transform infrared (FTIR) spectroscopy were employed to evaluate chemical changes. The results showed that linear SBS, despite lower molecular weight, induced greater redistribution of aromatics and resins due to more effective swelling and integration into the maltene phase. In contrast, radial SBS led to less pronounced changes in SARA fractions. Moreover, base binders with higher aromatic and resin content provided a more favourable medium for polymer dispersion and structural reorganization. These findings highlight the importance of considering both SBS molecular structure and base binder composition when designing PMBs to ensure consistent and optimized performance.

1. Introduction

The performance and durability of pavement structures are influenced by numerous environmental and mechanical factors, including solar radiation, precipitation, temperature fluctuations, and traffic loads. To enhance the durability of asphalt pavements and, at the same time, to reduce maintenance costs, the use of modified binders has become increasingly essential in pavement construction [1–4]. A wide range of modifiers, such as crumb rubber, nanomaterials like carbon nanotubes, nanowires, nanofibers, and nanoceramics, are used to improve binder performance [5–8]. However, among these, polymers are the most widely used [9–11].

Polymers are classified based on two main criteria: their chemical composition and their effect on bitumen properties [1,12]. The two primary types of polymers used in bitumen modification are elastomers and plastomers. Elastomers exhibit elasticity, allowing them to stretch and return to their original shape, whereas plastomers form a rigid structure that resists deformation. Thus, elastomers contribute flexibility and resilience, while plastomers provide stiffness and structural integrity under stress. Due to elastomers' superior ability to enhance bitumen's flexibility and thermal sensitivity, they are more widely used than plastomers in road engineering.

Styrene-butadiene-styrene (SBS) is the most widely used elastomer in road engineering. It is a triblock copolymer composed of styrene–butadiene–styrene segments, where the styrene blocks impart strength and rigidity, while the butadiene block provides elasticity [13]. Numerous studies have shown that SBS improves the elasticity of bitumen at high temperatures and reduces its stiffness at low

---

* Corresponding author.
E-mail address: judita.skultecke@vilniustech.lt (J. Škulteckė).

https://doi.org/10.1016/j.mtcomm.2025.113719
Received 29 August 2025; Accepted 1 September 2025
Available online 2 September 2025

temperatures [14–18]. It is also widely recognized that polymer-modified binders offer improved adhesion and cohesion, higher viscosity and stiffness, and reduced temperature susceptibility compared to unmodified binders. Consequently, asphalt mixtures incorporating polymer-modified binders demonstrate enhanced resistance to both rutting and fatigue [19–21].

Despite the well-documented advantages of SBS-modified bitumen (PMB), the performance of nominally similar PMBs and corresponding asphalt pavements often varies significantly [16,17,22]. This variation is largely attributed to the prevailing emphasis on optimizing SBS content to achieve desired performance outcomes, while the intrinsic properties of the SBS polymer itself and its compatibility with the base binder are often overlooked [15,23,24]. Previous studies have shown that SBS microstructure (linear vs. radial), styrene content, and molecular weight/dispersity govern network formation, phase continuity, and storage stability in PMBs, with clear signatures in viscoelastic properties and morphology [10,25–27]. At the same time, base binder chemistry, particularly the balance of aromatics and resins and the presence of polar functionalities, controls polymer swelling and compatibility, thereby shaping the stiffness and temperature susceptibility of the final PMB. All previous studies demonstrate strong structure–property relationships but often infer chemical changes indirectly from rheological or morphological observations. In addition, most investigations are limited in scope as they cover only a few base binders or polymer types and emphasize mechanical and rheological properties, while neglecting detailed chemical analyses. Moreover, they often rely on generic manufacturer-supplied data without a detailed analysis of the polymers themselves. As a result, there remains a limited understanding of how the characteristics of SBS and the base binder collectively influence the chemical composition of the modified binder.

This study aims to address this knowledge gap. The aim of this paper is to characterize various SBS polymers commonly used in bitumen modification and to evaluate their influence on the chemical composition of modified binders, which in turn determines their performance in asphalt pavements. For this purpose, eight commercially available SBS polymers that differ in structure, styrene and vinyl content, and molecular weight were selected and characterized using ^{1}H nuclear magnetic resonance (^{1}H NMR) and size-exclusion chromatography (SEC), and four representative polymers were subsequently used to prepare 12 PMBs with three chemically distinct base binders. Their chemical changes were then examined by SARA fractions and FTIR spectroscopy. This integrated approach provided new insight into how SBS molecular features (architecture, styrene/vinyl content, molecular weight) and distinct base binder chemistries jointly drive (i) redistribution among saturates, aromatics, resins, and asphaltenes and (ii) functional group evolution during modification.

2. Materials and methods

2.1. Materials

2.1.1. Styrene-butadiene-styrene (SBS) polymers

In this study, eight different SBS polymers produced by three different manufacturers were analysed. These SBS were selected based on a profound literature review and represent the most widely used polymers for bitumen modification in road construction. They differ in their structure, which can be either linear or radial, and in their properties, especially in the content of styrene and butadiene. The properties of SBS, which are declared by manufacturers, are given in Table 1.

2.1.2. Base binders

Three base binders within penetration grade 70/100, but with different chemical compositions, were selected for modification. Their physical and chemical properties are presented in Table 2.

Table 1
The SBS properties declared by the manufacturers.

Identification Code	Structure	Physical Form	Styrene Content, % (ASTM D5775)	Vinyl Content, % (KM 03)
I_L31	Linear	Porous pellets	31.0	–
I_L31.5	Linear	Porous pellets	31.5	Butadiene part has high vinyl content
I_R20	Radial	Porous crumb	20.0	–
I_R30	Radial	Porous pellets	30.0	–
II_L31	Linear	Porous pellets	31.0	–
II_L30	Linear block (triblock content ≥90 %)	Porous pellets	30.0	≥ 35.0
II_R23	Radial triblock	Porous pellets	23.0	–
III_L31.5	Linear	Porous pellets	31.5	–

Table 2
Properties of 70/100 base binders.

Properties	Results of 70/100 base binders		
	A	B	C
Penetration at 25 °C (dmm)	80.4	84.6	86.7
Softening point (°C)	47.9	44.6	45.9
Fractional composition:			
saturates (%)	9.13	5.95	10.27
aromatics (%)	36.00	50.45	44.39
resins (%)	36.59	25.69	30.13
asphaltenes (%)	18.27	17.99	15.21
Colloidal stability (Gaestel) index Ic	0.378	0.317	0.342

2.2. Preparation of PMBs

After a comprehensive analysis of SBS properties determined in this study, four different polymers were selected for bitumen modification. The polymers were mixed at a mass content of 3.5 % with three base binders. A total of 12 PMBs were produced and analysed. Table 3 presents the designations for all PMBs tested in this study.

All PMBs were produced using a high-shear Silverson L5M-A laboratory mixer with a general-purpose disintegrating head. At first, 600 g of base binder was preheated at 160 °C and mixed at 3000 rpm for 15 min. Subsequently, 3.5 % SBS (by weight of bitumen) was gradually added to the binder over a period of 5 min. After the addition of the polymer, the mixer speed was increased to 6000 rpm and the modification process was continued for 1 h at a temperature of 180–185°C

Table 3
Designations for produced PMBs.

Base binder (70/100)	Identification code of SBS	Designations for PMBs
A	I_L31.5	A_I_L31.5
	I_R20	A_I_R20
	I_R30	A_I_R30
	II_L31	A_II_L31
B	I_L31.5	B_I_L31.5
	I_R20	B_I_R20
	I_R30	B_I_R30
	II_L31	B_II_L31
C	I_L31.5	C_I_L31.5
	I_R20	C_I_R20
	I_R30	C_I_R30
	II_L31	C_II_L31

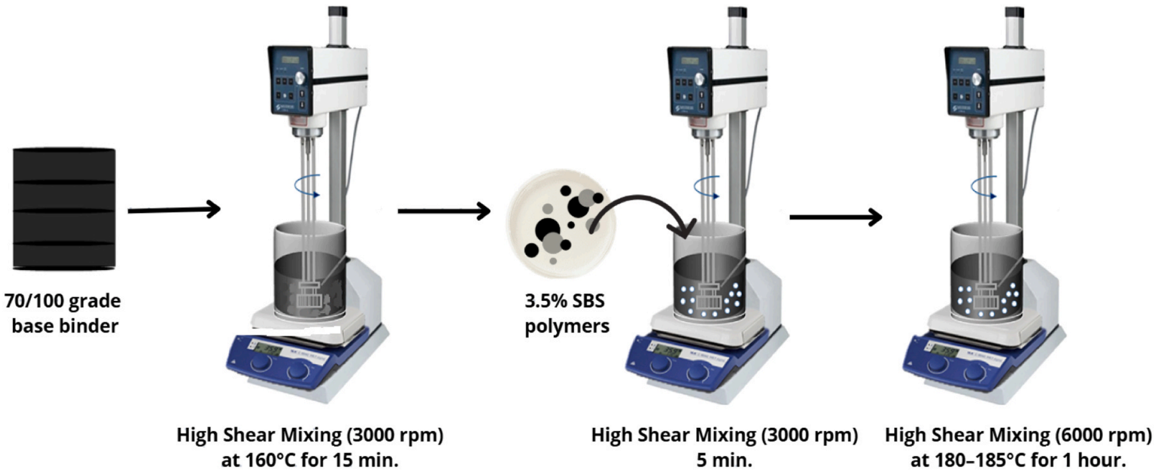

Fig. 1. Schematic illustration of PMB preparation.

(Fig. 1). This procedure ensures a homogeneity of produced PMB and minimizes the separation of polymer phase. It was proved by checking PMB properties at different modification periods.

2.3. Test methods

2.3.1. ^{1}H Nuclear magnetic resonance spectroscopy (^{1}H NMR)

^{1}H nuclear magnetic resonance (^{1}H NMR) spectroscopy is a crucial analytical technique for elucidating and studying the structure of organic compounds [28]. Therefore, to structurally analyse SBS polymers, ^{1}H NMR spectroscopy proves to be highly convenient. This technique enables both qualitative and quantitative evaluations of the structural components of the copolymer [29]. The ^{1}H NMR spectra were recorded using a Bruker 400 spectrometer operating at 400 MHz for proton resonance, with the spectra collected at 22°C from SBS samples dissolved in deuterated chloroform ($CDCl_3$). The residual non-deuterated chloroform chemical shift was chosen as an internal standard; it is noteworthy that the residual proton chemical shift of chloroform at 7.26 ppm does not significantly overlap with the aromatic protons of the styrene moiety [30]. Consequently, the integration error should not exceed 3 %, or even less. ^{1}H NMR experiments were performed using a relatively high amount of corresponding SBS samples (11–14 mg).

2.3.2. Size-exclusion chromatography (SEC)

The macromolecular parameters of SBS (number-average molecular weight, weight-average molecular weight, and dispersity ($Đ = M_w/M_n$) were determined by size exclusion chromatography (SEC). SEC measurements were carried out in THF as the eluent at 50°C using a flow rate of 1.0 mL/min. A Viscotek T6000M General Mixed column (Malvern Instruments, Malvern, United Kingdom), 300 × 8.0 mm, was used. The SEC system, OmniSEC Resolve (Malvern Panalytical, United Kingdom), was equipped with a four-detector array (OmniSEC Reveal): a refractive index (RI) detector; a light scattering (LS) detector measuring scattered light (laser 3 mW, $\lambda = 670$ nm) at two angles – right-angle (RALS, 90°) and low-angle (LALS, 7°); a four-capillary bridge viscometer (DP); and PDA UV-Vis detectors. The system was calibrated using a Viscotek PolyCAL™ TDS-Mix-NB triple detection calibration standard (PS 99 kDa in THF). Additional calibration was performed using a linear PS standards kit (ReadyCal-Kit Poly(styrene), Mp 370–252,000 Da, PSS Polymer Standards Service GmbH, Germany). SEC data were processed using OmniSEC software v.11.37 (Malvern Panalytical, Malvern, United Kingdom).

2.3.3. Saturates, aromatics, resins, and asphaltenes (SARA)

The fractional composition of binders was determined using IATROSCAN MK6s thin-layer chromatography with flame ionisation detection (TLC-FID). The method is based on dividing a fraction into four component groups by percentages: Saturates, Aromatics, Resins, and Asphaltenes (SARA). Initially, samples were prepared through dissolving 1:100 bitumen in toluene and applying 1 μL of the resultant solution onto activated quartz rods (chromarods). To ensure the removal of residual toluene, the frame containing five rods was subjected to drying at 80°C in a drying chamber for a duration of 2 min. The separation of fractional groups of bitumen was achieved by sequentially placing the frames with rods in three containers containing different solvents: container 1 contained 100 % n-heptane, which was used to extract saturates, container 2 contained 80 % toluene and 20 % n-heptane, which was used to extract aromatics, and container 3 contained 95 % dichloromethane and 5 % methanol, which was used to extract resins. Due to their high molar mass, asphaltenes adsorbed onto the surface at the bottom of the rod.

The analysis was conducted using a TLC-FID analyser. Fig. 2 shows that the identification of vertical positions was conducted at the lowest points between adjacent peaks. These vertical lines were then used to divide the chromatogram into four distinct segments, which were subsequently integrated. The concentration of each fractional component was calculated as the ratio of its peak area to the combined area of all spectrum peaks.

To understand the effect of both SBS and base binder on PMBs chemical composition, a fractional index as the ratio of difference in each SARA fraction over the same fraction of its base binder was calculated as follow.

$$\text{Fractional index} = \frac{A_{PMB} - A_{\text{base binder}}}{A_{\text{base binder}}} \bullet 100\% \tag{1}$$

It has been demonstrated by previous studies that the colloidal instability index (Ic) is an effective reflection of bitumen's colloidal properties. According to Gaestel's theory, the presence of sufficient quantities of resins and aromatics enables the complete stabilization of asphaltenes within the bitumen. The Ic was calculated based on the SARA fractions as follows:

$$I_c = \frac{A_{\text{asphaltenes}} + A_{\text{saturates}}}{A_{\text{resins}} + A_{\text{aromatics}}} \tag{2}$$

2.3.4. Fourier transform infrared (FTIR) spectroscopy

The chemical composition of binders was analysed using a Bruker Alpha II Fourier transform infrared (FTIR) spectrometer equipped with an attenuated total reflectance mode (ATR) featuring a diamond crystal. Before each measurement, a background spectrum of the clean, empty ATR crystal was recorded to ensure accurate baseline correction. After

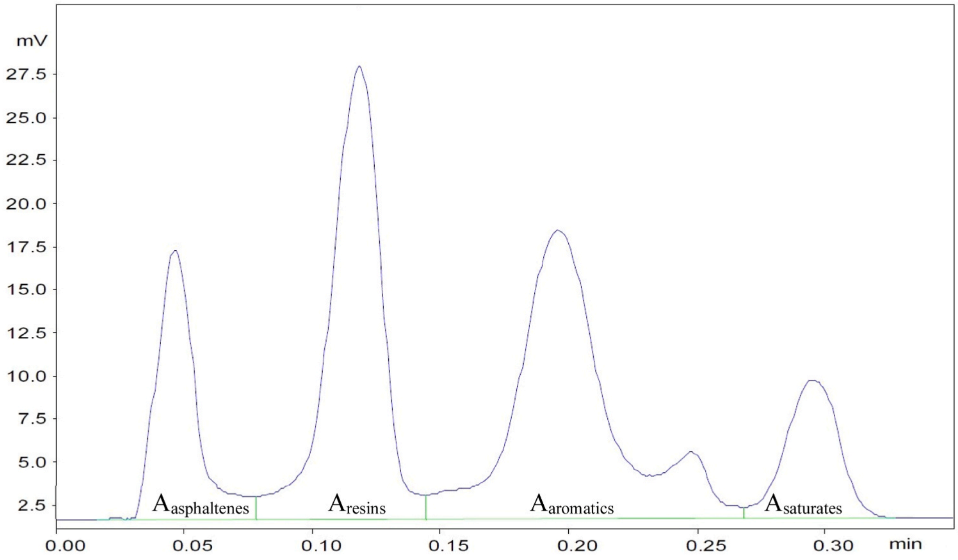

Fig. 2. Bitumen fractional component.

that, a binder sample was applied onto the ATR crystal. The spectra were recorded in absorbance mode over a wavenumber range of 4000–400 cm^{-1}, with a resolution of 4 cm^{-1} and an average of 24 scans. Each bitumen sample was subjected to four replicates, with three samples prepared for each type of bitumen. Consequently, a total of 12 spectra were recorded for each bitumen.

The received spectra were processed using the software program OPUS. Prior to data analysis, min-max normalization and baseline correction were performed on all spectra. Baseline correction was performed by setting the absorbance values at the upper wave-number limit of the carbonyl band (1753 cm^{-1}) to zero. The typical spectra of neat and modified binders are shown in Fig. 3.

The presence of SBS in FTIR spectra was indicated by the absorption peaks at approximately 966 cm^{-1}, 910 cm^{-1}, and 699 cm^{-1} [31–33]. The broad peak at 966 cm^{-1} corresponds to out-of-plane =C–H deformation of trans-1,4-butadiene and encompasses vinyl group same type of vibrational peak at 990 cm^{-1}, while the 910 cm^{-1} peak is characteristic of 1,2-vinyl-butadiene units exclusively. The 699 cm^{-1} peak arises from C–H bending vibrations in the aromatic rings of styrene, as well as rare monosubstituted benzene moiety in bitumen. Meanwhile, the broad absorption peak at 1460 cm^{-1} is present due to methylene group bending also aromatic double bond stretching vibrations. Peak at 1375 cm^{-1} could be attributed to aliphatic C–H bending vibrations of methyl group, which is not found in SBS at all. Both peaks are considered suitable as reference peaks.

Structural indices for butadiene and styrene were calculated from the areas under their respective characteristic peaks, as follows:

$$I_{PB} = \frac{A_{966} + A_{910}}{A_{1460} + A_{1375}} \tag{3}$$

$$I_{PS} = \frac{A_{699}}{A_{1460} + A_{1375}} \tag{4}$$

The carbonyl (~1700 cm^{-1}) and sulfoxide (~1030 cm^{-1}) bands, typically associated with oxidative aging of bitumen, were not analysed in this study, as the binders were in the unaged state, where such oxidation-related functional groups are not expected to change.

3. Results and discussion

3.1. Nuclear magnetic resonance spectroscopy (NMR)

The structural moieties of bitumen modifiers ensure interaction among the molecules constituting bitumen. The SBS modifier contains styrene moieties, which interact with aromatic structuring components of bitumen through $\pi-\pi$ stacking. During the analysis of the proton spectra of the studied SBS samples, six distinct ranges of chemical shift were identified. These ranges are essential for a deeper understanding of the structure of SBS polymers (Table 4).

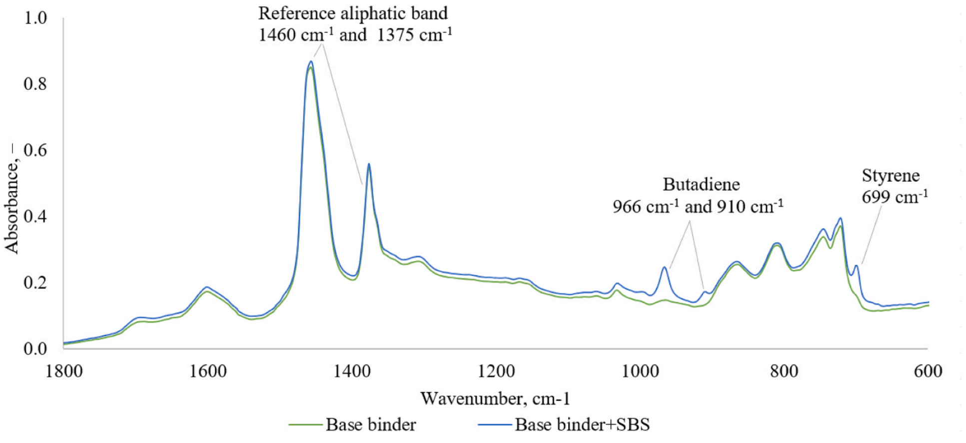

Fig. 3. FTIR-ATR spectra of binders in the wavenumber range 1800 cm^{-1} to 600 cm^{-1}.

Table 4
Structural segments of SBS copolymers in ^{1}H NMR spectra.

Range in ppm	Structural fragment or moiety of SBS
(A) 6.3–7.24	in the aromatic proton range, shifts corresponding to the styrene aromatic scaffold are detected. The styrene aromatic fragment consists of 5 protons and does not overlap with other structural elements of SBS, allowing for integration to assess the structure of the SBS copolymer based on this fragment. However, subsequent SEC analysis reveals that all tested SBS polymers contain a low molecular weight additive, presumably polystyrene.
(B) 5.49–5.64	the chemical shift of the single proton at the vinyl double bond (1 proton)
(C) 5.3–5.48	the chemical shift corresponding to non-vinyl double bond (2 protons), these protons' shifts partially overlap with those of the vinyl double bond (**B**) in high vinyl-content copolymers.
(D) 4.88–5.02	the chemical shift of the terminal protons of the vinyl double bond (2 protons) – does not overlap with other protons, making it suitable for integration and quantitative analysis of vinyl groups in copolymer.
(E) 1.7–2.2	the protons' chemical shift of the methylene group next to the alkene fragment (4 protons) and the alpha protons of the benzyl group (1 proton)
(F) 1.17–1.58	the chemical shifts observed for the most shielded methylene group protons (2 protons), which are situated between two sp^3 hybridization carbon atoms.

The presence of vinyl double bonds in SBS copolymer raises intriguing questions regarding the polymerization process. Under thermodynamically controlled conditions, specifically 1,4 addition of butadiene occurs, one would anticipate the absence of such vinyl double bonds. However, the ^{1}H NMR spectra observed vinyl moiety indicates that co-polymerization via 1,2 addition also proceeds [34]. These vinyl fragments are prone to oxidation under atmospheric conditions; however, vinyl groups possess beneficial features, such as the ability to further modify SBS if necessary [35]. Fig. 4 presents the structural scaffolds of SBS in the case of 1–4 addition and 1–2 addition.

As shown in Fig. 5, the radial SBS (I_R20) exhibited proton chemical shifts across all regions (A to F) defined in Table 4. This is consistent with all other SBS samples examined. In this sample (I_R20), butadiene is the dominant component in the SBS copolymer. The integral of aromatic styrene protons (I_A) is 0.39, while the proton shift integral of the unsaturated bond of butadiene (I_C+I_D) is 1 + 0.15. If this copolymer did not contain polystyrene additive (which it does, as confirmed by the SEC results in Fig. 7A), it could be possible to accurately determine the ratio of the copolymer segments. The ratio would be 0.39/5 with 1.15/2. Only about 12 % of the structural segments in the copolymer consist of styrene. When calculated by M_W of the respective structural moiety, the styrene accounts for 20.7 % of the sample by mass. This percentage is slightly higher than that declared by the supplier of I_R20 (Table 1). The structural composition of SBS, which includes a polystyrene additive, is calculated for the styrene moiety as follows:

$$Styrene\ wt.\% = \frac{Mw_{styrene} \times \left(\frac{I_A}{5}\right)}{Mw_{styrene} \times \left(\frac{I_A}{5}\right) + Mw_{butadiene} \times \left(\frac{I_c+I_D}{2}\right)} \times 100 \tag{5}$$

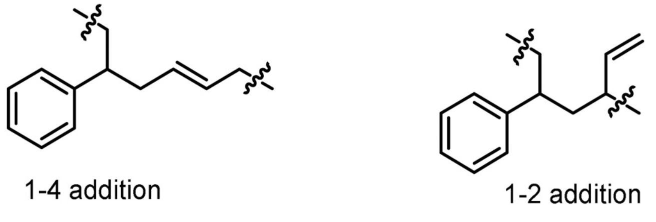

Fig. 4. Structural scaffolds of SBS in the case of 1–4 addition (left) and 1–2 addition (right).

In samples with high vinyl content, the protons of ranges B and C overlap. To accurately determine the number of butadiene structural segments, one proton from the vinyl group must be subtracted from the combined integral of ranges B and C. This is achieved by simply subtracting half the value of the integral from range D. The corrected I_c is calculated as follows:

$$I_c corrected = \left(\frac{I_C + I_B - \frac{I_D}{2}}{2}\right) \tag{6}$$

The I_R20 sample exhibits a relatively low presence of segments with vinyl moiety; integration of the fourth chemical shift range (D) gives a value of 0.15 compared to a value of 1 for the non-vinyl double bond proton range (C). In range (D), just like in range (C), there are chemical shifts of 2 protons present. This allows us to easily calculate the copolymer segments that contain vinyl structural fragments, which represent 11.5 % of the total copolymer segments in I_R20 sample. The percentage of vinyl groups in the sample is calculated as follows:

$$Vinyl\ segments\% = \frac{\frac{I_D}{2}}{\frac{I_A}{5} + \frac{I_C+I_D}{2}} \times 100 \tag{7}$$

In the analysis of the I_L31.5 sample, the ^{1}H NMR spectra (Fig. 6) reveal an evidently different profile when compared to I_R20 sample. While the butadiene fragment remains predominant, it is noteworthy that 31.9 wt% of this sample comprises styrene moieties. This finding closely aligns with the results obtained through refractometric measurements and is consistent with the data provided by the supplier of I_L31.5 (Table 1). Moreover, the manufacturer has classified this product as a high vinyl content copolymer, although no precise numeric value was specified. The ^{1}H NMR spectra substantiate this classification, indicating that as much as 31.3 % of the segments possess a vinyl double bond. Such a copolymer is not typically expected to form during conventional copolymerization processes of SBS; it is likely that the manufacturer employs anionic copolymerization at low temperatures to ensure kinetic control of the reaction rather than thermodynamic.

Other samples were analysed using the same method, and the results are presented in Table 5. All ^{1}H NMR spectra of all analysed SBS samples can be found in the electronic supplementary data. It is important to note that all analysed samples contain vinyl groups, which account for 7.3–33.7 % of the total structural moieties counted.

In summary, while some analysed copolymers may share the same structural composition as determined by ^{1}H NMR, they are not necessarily identical products. Manufacturers often differentiate these copolymers based on whether they have a linear or radial structure, even if other characteristics are the same (e.g. I_L31 and I_R30). ^{1}H NMR serves as a fast and reliable method for evaluating copolymer composition, including SBS [28]. The styrene content can be determined faster than through the refractometric method used by suppliers (ASTM D5775), which is only effective if the styrene content is less than 55 %. In samples with a high amount of styrene moieties, ^{1}H NMR provides more reliable results. Furthermore, this analysis offers accurate and essential i-formation regarding the exact quantity of vinyl groups present in the sample.

Products with a high vinyl content can be crosslinked to form a spatial structure, thereby hardening the bitumen. However, this can complicate the recycling process of such bitumen. In contrast, products with a higher proportion of styrene fragments tend to interact more effectively with resins, while those that are dominated by the butadiene component are likely to mix better with aliphatic hydrocarbons.

3.2. Size-exclusion chromatography (SEC)

The molecular characteristics of SBS modifiers – including molecular weight (M_W), molecular weight distribution ($Đ = M_W/M_n$) have a significant influence on the performance of polymer modified bitumen. The

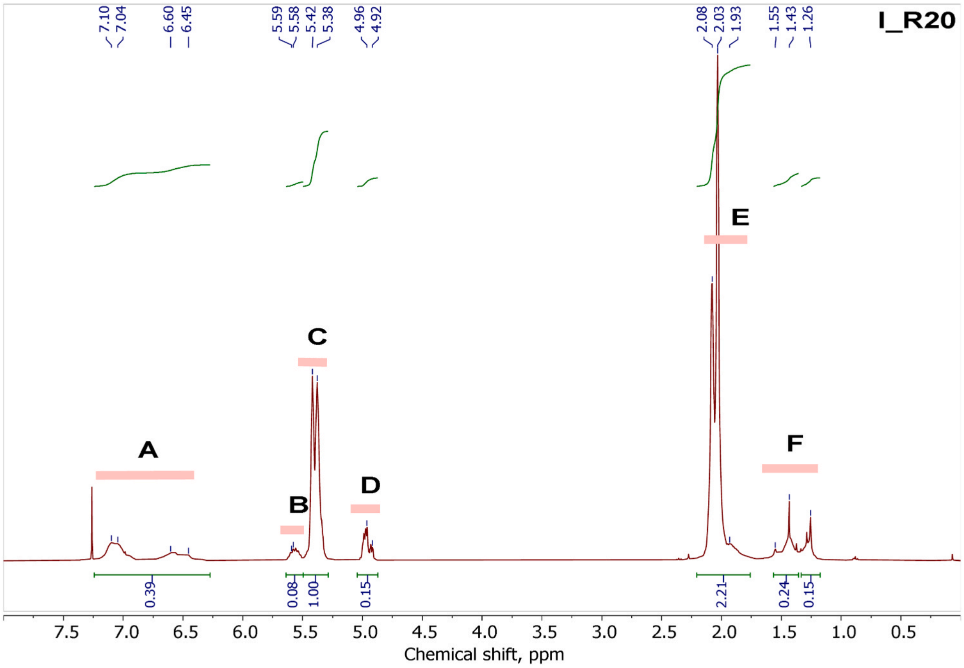

Fig. 5. ^{1}H NMR spectra of I_R20.

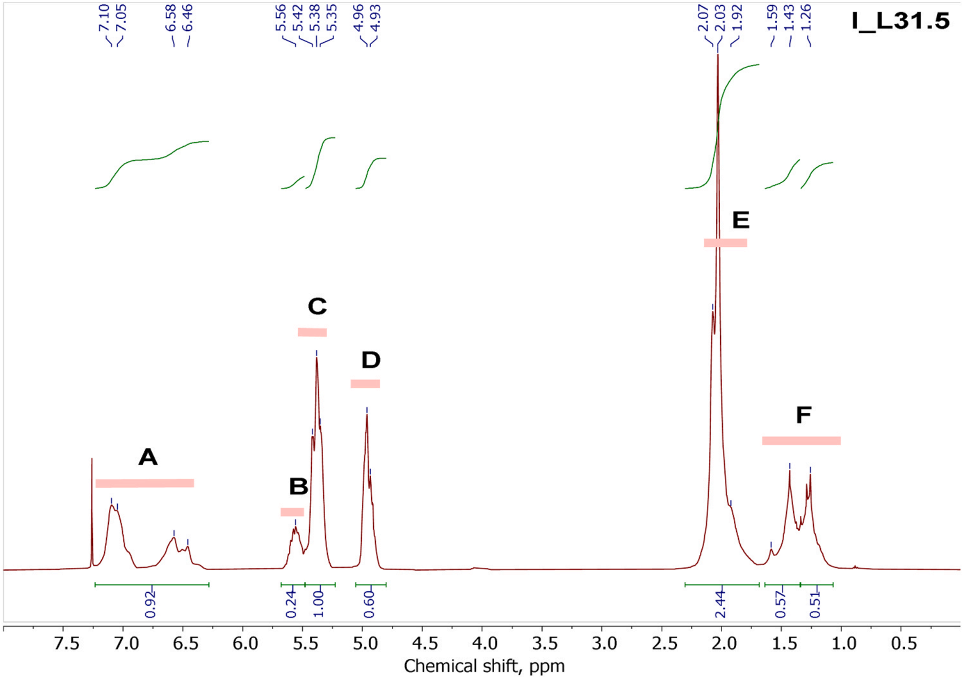

Fig. 6. ^{1}H NMR spectra of I_L31.5.

molecular characteristics of SBS samples were determined by SEC analysis, with the results summarized in Fig. 7. Initially, the samples with SEC were analysed using a triple detection system to determine their absolute molecular weights (Fig. S9 in the electronic supplementary data). However, overlapping of the light scattering signals from the main SBS fraction and the low molecular weight fraction at higher retention volumes (indicated by arrows in Fig. S9) hindered accurate molecular weight determination. To overcome this limitation, the system was calibrated using monodisperse linear polystyrene (PS) standards, and the molecular weights of the SBS samples were subsequently calculated using this conventional calibration method.

SEC analysis confirmed that all SBS samples contained a low molecular weight (LMW) fraction, independent of manufacturer or structure [34]. The relative amounts of the main polymer fraction and the low molecular weight components were determined from the SEC RI eluogram by mathematically separating and integrating the areas under the original curve (Fig. S10 in the electronic supplementary data). The low molecular weight fraction accounted for approximately 13–16 % of the total sample (Fig. 7), with molecular weights ranging from 14.5 ± 1.4 kDa in a radial sample (I_R20, Figs. 7C) to 29.3 ± 1.1 kDa in a linear one (II_L30, Fig. 7F). While excessive LMW content may reduce mechanical strength, a moderate amount can be somewhat beneficial.

Table 5
Structural segments of SBS copolymers in ^{1}H NMR spectra.

Identification Code	Structure	Styrene Content, %		Vinyl Content, %	
		^{1}H NMR	Declared by manufacturer (ASTM D5775)	^{1}H NMR	Declared by manufacturer (KM 03)
I_L31	Linear	32.1	31.0	9.9	–
I_L31.5	Linear	31.9	31.5	31.3	Butadiene part has high vinyl content
I_R20	Radial	20.7	20.0	11.5	–
I_R30	Radial	30.8	30.0	10.0	–
II_L31	Linear	32.3	31.0	7.3	–
II_L30	Linear block (triblock content ≥90 %)	31.4	30.0	33.7	≥ 35.0
II_R23	Radial triblock	23.1	23.0	7.9	–
III_L31.5	Linear	32.0	31.5	11.1	–

These LMW chains can act as compatibilizers and internal plasticizers, improving the integration of SBS into the bitumen, enhancing processability, and supporting the formation of a more uniform and effective polymer network when used alongside high molecular weight counterparts. Unfortunately, the addition of a small molecular weight polystyrene (PS) polymer does not increase the styrene structural segments in the SBS copolymer. Furthermore, the PS polymer can distribute throughout the bitumen unevenly. Consequently, the same percentage of styrene moiety in the bitumen modifier will not yield the same results as when it is incorporated as part of the SBS copolymer structure. The behaviour and characteristics of the styrene moiety are different depending on whether it is a structural component of the SBS copolymer or simply added as LMW polystyrene.

Molecular weight analysis revealed that the M_w of the main SBS fraction depended solely on the type of bitumen modifier. Radial modifiers exhibited higher molecular weights than their linear counterparts. The molecular weight of linear SBS polymers ranged from 77.1 ± 1.4 kDa (I_L31.5, Figs. 7B) to 92.8 ± 5.4 kDa (II_L30, Fig. 7F). Among the radial modifiers, the lowest molecular weight – 118.4 ± 16.1 kDa – was observed for the sample with the lowest styrene content (20.7 %, Table 1) (I_R20, Fig. 7C), while the highest – 144.4 ± 9.2 kDa – was found in the I_R30 sample with 30.8 % styrene (Table 1, Fig. 7D). Radial SBS modifiers, which exhibit higher molecular weights, contribute to stronger polymer networks within the bitumen matrix, enhancing elasticity, temperature stability, and resistance to deformation. In contrast, linear SBS modifiers typically have lower M_w and may form less robust networks, though they can still offer satisfactory performance in some applications [36] and better recyclability.

Additionally, it was observed that polymers obtained from the second manufacturer exhibited broader molecular weight distributions ($Đ = 1.083–1.18$, Fig. 7E-G) compared to those from other sources ($Đ = 1.05–1.08$, Fig. 7A-D and Fig. 7F). A narrow molecular weight distribution ($Đ \approx 1.05–1.08$) is generally favourable, as it ensures more consistent behaviour of modifiers. Broader distributions ($Đ \approx 1.08–1.18$), as seen in polymers from some manufacturers, may lead to less predictable performance.

3.3. Saturate, aromatic, resin, and asphaltene (SARA)

To understand the effect of both SBS and base binder on PMBs' chemical composition, four generic fractions (Saturates-Aromatics-Resins-Asphaltenes) were determined using the TLC-FID method. The average results of the separate fractions are given in Fig. 8. The standard deviation is less than 1 % for saturates and asphaltenes and less than 2 % for aromatics and resins. In addition to this, a fractional index as the ratio of difference in each SARA fraction over the same fraction of its base binder was determined (Fig. 9).

A closer examination of Fig. 9 reveals that the chemical composition of the base binder significantly influences the redistribution of fractions within the PMBs, regardless of the specific SBS used. The changes in the proportion of fractions were more pronounced in PMBs produced from base binders B and C compared to those from binder A. Among all base binders, binder A had the lowest initial aromatic content (36.0 %) and the highest resin content (36.6 %). When ranked by aromatic content, the binders follow the order: A<C<B. In contrast, for resin content, the trend is reversed: B<C<A. This suggests that binder A, being richer in resins and poorer in aromatics, provides a less favourable environment for SBS interaction, which may limit the extent of polymer-induced redistribution. Notably, when considering the combined content of aromatics and resins, which together represent the maltene phase most reactive to SBS, the trend among base binders is A<C<B (73 %, 75 %, and 76 %, respectively). This implies that binder B, with the richest maltene phase, offers the most chemically interactive environment for SBS dispersion and swelling. However, it should be noted that the difference in combined content of aromatics and resins among base binders is only 1–3 %.

Across all PMB samples, SBS (3.5 %) had a minimal effect on saturates and asphaltenes, in contrast to its significant impact on aromatics and resins. This trend aligns with previous findings [1,37], which suggests that SBS primarily interacts with the aromatic-rich maltene phase. As a result, modification mainly involves the redistribution of molecular components within this phase, particularly through the swelling of polymer domains and partial dissolution of polystyrene blocks.

The incorporation of SBS generally resulted in a reduction of aromatics and an increase in resins, with the magnitude of these changes depending on both the chemical composition of the base binder and the type of SBS used. The redistribution of aromatics and resins was more pronounced in PMBs produced from binders B and C than from binder A (Fig. 9). Aromatics decreased by 5–26 % (from 50.4 % to 37.1–48.0 %), by 4–23 % (from 44.4 % to 34.0–42.7 %) and by 4–9 % (from 36.0 % to 32.9–34.5 %) respectively for PMBs with base binder B, C and A (except A_I_R30, where aromatics slightly increased). Meanwhile resins increased by 14–49 % (from 25.7 % to 29.3–38.3 %), by 4–33 % (from 30.1 % to 31.2–39.9 %) and by 6–9 % (from 36.6 % to 38.8–40.0 %) respectively for PMBs with base binder B, C and A (again with exception for A_I_R30, where resins slightly decreased). The decrease in aromatics likely reflects the incorporation of aromatics into swollen polymer micelles, effectively reducing the free aromatic content. While the increase in resins can be attributed to the solvation and redistribution process that occurs during SBS dispersion, and possibly to the partial dissolution of the polystyrene blocks into the resin phase. Overall, these changes appear to be compensatory, as the combined content of resins and aromatics in the PMBs remained nearly identical to that of the base binders, regardless of the SBS used. This phenomenon was also observed by Pipintakos et al. [38].

What was unexpected is that both linear SBS (I_L31.5 and II_L31) led to a much higher change in aromatics and resins compared to radial SBS (I_R20 and I_R30), even though radial SBS is considered more branched and interactive due to its complex structure and higher molecular weights compared to linear SBS. This outcome is likely linked to the differences in vinyl content and the physical behaviour of the polymers during modification. Specifically, I_L31.5 SBS features a high vinyl content (31.3 %) in the butadiene block, which can be crosslinked to form a spatial structure. Moreover, linear SBS typically swells and disperses more uniformly within the bitumen, promoting deeper integration into the aromatic and resin fractions. In contrast, the compact, star-

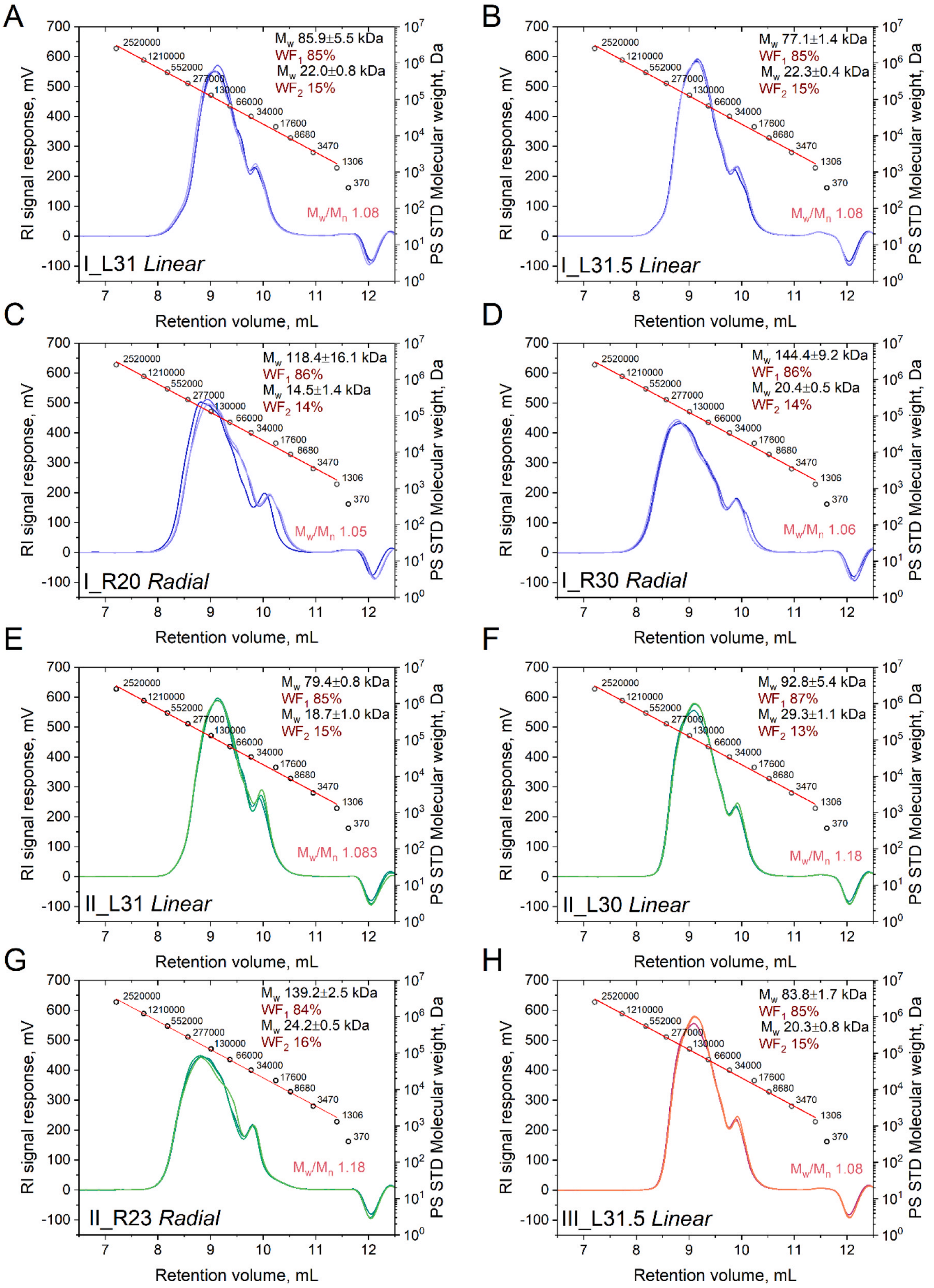

Fig. 7. The molecular weight analysis of SBS samples of different manufacturers (indexed as I, II, and III) and structures: linear (A, B, E, F, H), and radial (C, D, G).

shaped structure of radial SBS (I_R20 and I_R30) may limit its diffusion and reduce its interaction with the surrounding matrix under identical mixing conditions. Radial SBS tends to form more compact, micelle-like domains or gel networks that trap certain binder components but do not chemically alter the overall balance of aromatics and resins to the same extent. All these factors suggest that while radial SBS is effective at forming a mechanical network, which is beneficial for resistance to rutting [27,38,39], linear SBS has a greater impact on the chemical rebalancing of the bitumen, particularly within the maltene phase. It may lead to better polymer-bitumen compatibility and higher storage

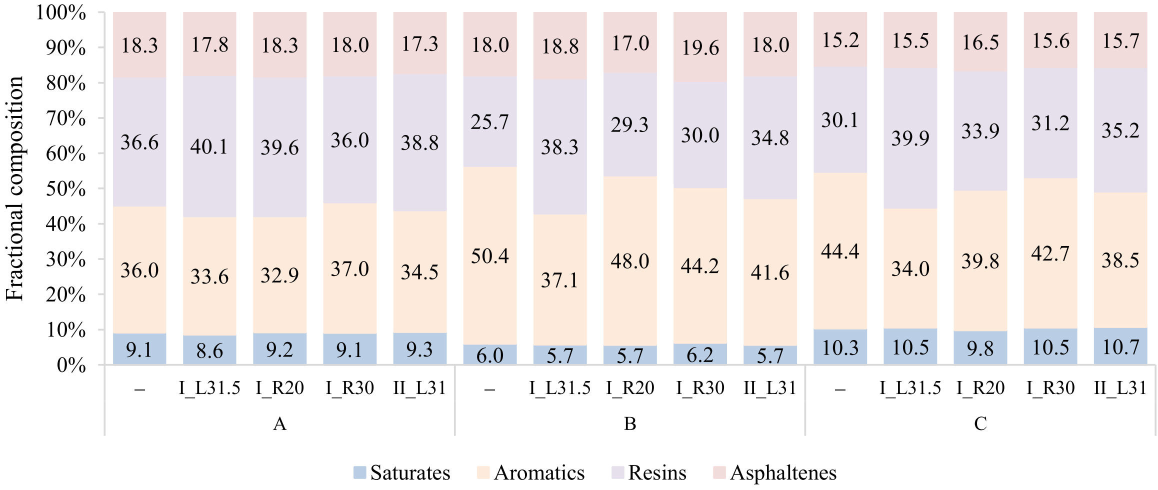

Fig. 8. SARA fractions.

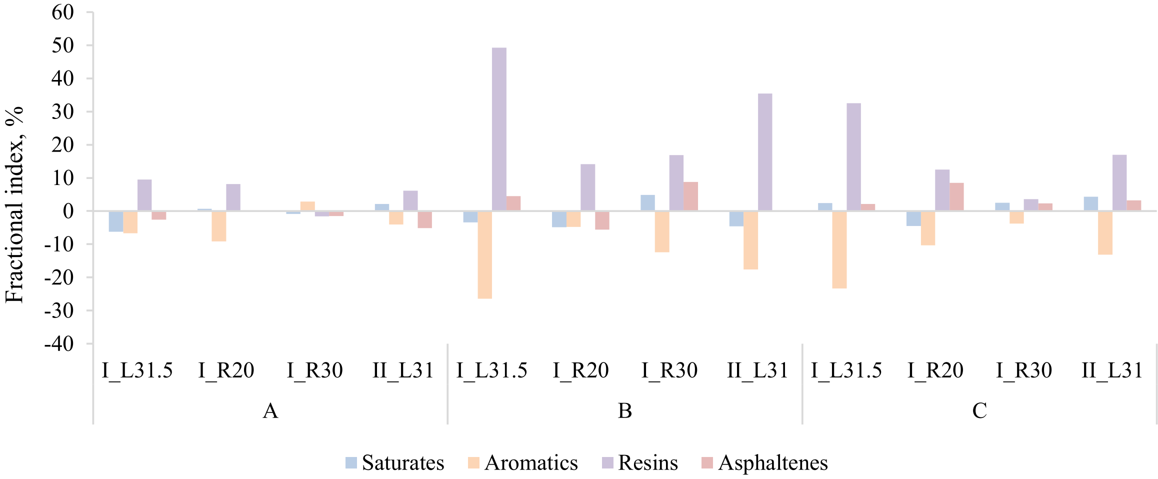

Fig. 9. Effect of SBS and base binder on SARA fractions.

stability [26].

A comparison of radial SBS with different styrene contents (I_R20 and I_R30) revealed that the effect of styrene content on the distribution of bitumen fractions is strongly influenced by the base binder. For binder B, increasing the styrene content led to a decrease in aromatics (from 48 % to 44 %) and a slight increase in resins (from 29 % to 30 %). In contrast, for binder C, aromatics increased (from 40 % to 43 %) while resins decreased (from 34 % to 31 %). This contrasting behaviour may be attributed to the higher initial aromatic content and lower resin content in base binder B (50 % aromatics, 26 % resins) compared to base binder C (44 % aromatics, 33 % resins). Base binder B likely provided a more favourable environment for polymer swelling and aromatic uptake, whereas the lower aromatic content in base binder C may have limited such interactions. These findings indicate that polymer–bitumen interactions depend not only on the polymer structure (e.g., styrene content) but also on the specific chemical composition of the base binder.

The colloidal instability index (Ic) calculated by Eq. 2 showed that all produced PMBs are colloidally stable. The Ic value varied from 0.293 (B_I_R20) to 0.379 (A_I_R_20).

3.4. FTIR spectroscopy

FTIR spectroscopy was used to assess the structural changes in the bitumen matrix induced by SBS polymers, specifically focusing on the functional groups related to styrene and butadiene units. The structural indices for butadiene (I_{PB}) and styrene (I_{PS}) were calculated from the corresponding absorption bands and are given in Table 6. In all cases, the coefficient of variation was below 2.5 %. The relative changes in these indices due to modification were expressed as percentage with respect to the corresponding base binder values and are presented in Fig. 10. Fig. 10 should be interpreted as evidence of polymer dispersion in bitumen and interaction with the maltene phase. All FTIR-ATR spectra for both the base binder and the produced PMBs are provided

Table 6
FTIR-ATR results.

Base binder	SBS	$A_{1460} + A_{1375}$	A_{966}	A_{910}	A_{699}	I_{PB}	I_{PS}
A	I_L31.5	55.731	5.550	3.114	1.819	0.155	0.033
	I_R20	56.319	6.897	4.355	3.109	0.200	0.055
	I_R30	57.175	7.351	3.662	2.742	0.193	0.048
	II_L31	56.753	7.038	3.565	2.995	0.187	0.053
B	I_L31.5	56.574	7.359	3.545	3.142	0.193	0.056
	I_R20	53.846	5.114	2.981	1.892	0.150	0.035
	I_R30	55.041	6.448	4.115	3.031	0.192	0.055
	II_L31	54.458	6.984	3.555	2.857	0.194	0.052
C	I_L31.5	55.382	5.856	3.254	2.395	0.164	0.043
	I_R20	55.140	6.450	3.351	2.872	0.178	0.052
	I_R30	51.681	4.712	2.821	1.879	0.146	0.036
	II_L31	52.505	6.035	3.995	3.082	0.191	0.059

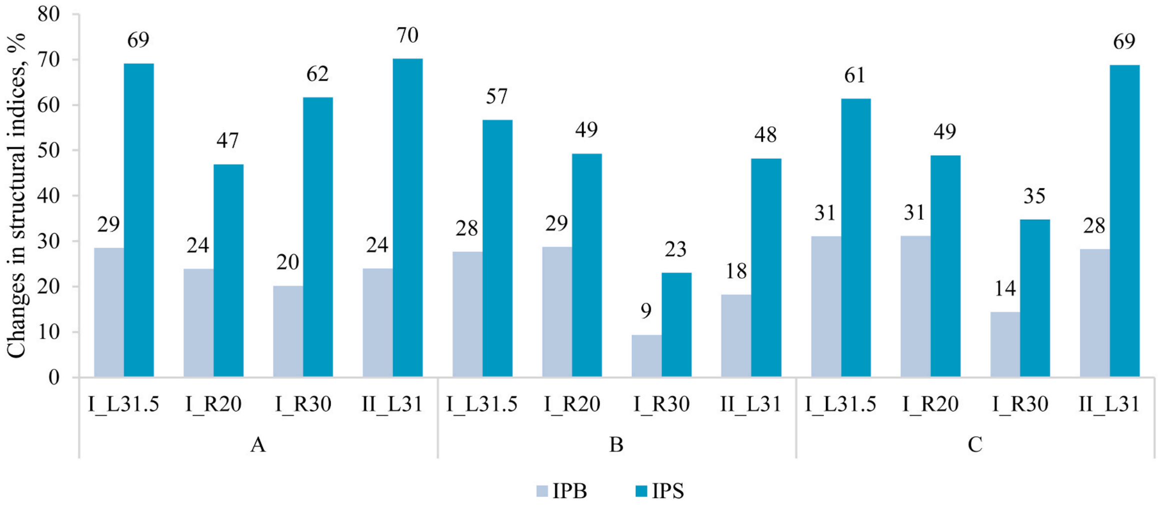

Fig. 10. Changes in structural indices due to modification.

in the electronic supplementary data.

Among all SBS-modified binders, the incorporation of SBS polymers generally led to increases in the I_{PB} and I_{PS} indices by 20–31 % and 47–70 %, respectively, compared to their base binders. However, two notable exceptions were observed. Binders B_I_R30 and C_I_R30 exhibited significantly lower I_{PB} and I_{PS} values, both falling below 0.170 and 0.050, respectively. This deviation may be attributed to the limited dispersion or reduced spectroscopic detectability of the radial SBS polymer (I_R30) within the matrices of base binders B and C. The radial structure of I_R30 likely forms more compact micellar domains that reduce the effective interaction with the bitumen's maltene phase and consequently diminish the FTIR absorption associated with butadiene and styrene functionalities.

A comparison of the radial SBS polymers (I_R20 and I_R30) revealed that higher butadiene content led to increased I_{PB} values in PMBs, regardless of the base binder. This is consistent with previous studies showing enhanced FTIR absorbance from more reactive butadiene segments [31,33,38]. However, this trend did not apply to styrene. An increase in I_{PS} values with higher styrene content was observed only in PMBs with base binder A, while PMBs with base binder B and C showed a decrease in I_{PS} values from 0.052 to 0.043 and 0.054–0.049, respectively. This suggests that in more aromatic-rich binders (B and C), radial SBS polymer may form more compact domains that limit the spectroscopic visibility of styrene blocks.

The spectral differences observed among PMBs are also related to chemical interactions at the molecular level. Linear SBS polymers (e.g., I_L31.5, II_L31) generally display stronger FTIR band intensities, indicating better molecular dispersion and a higher degree of interaction with the base binder. This aligns with findings by Schaur et al. [13] and Fernandes et al. [40], who showed that the less entangled structure of linear SBS facilitates greater swelling and partial dissolution within the maltene phase. In contrast, the compact, star-shaped structure of radial SBS tends to form localized gel-like domains with limited interfacial contact, thereby reducing the spectroscopic visibility of styrene and butadiene segments.

Among four selected and analysed SBS types, I_L31.5 exhibited a significantly higher vinyl content, as indicated by the BMR results. This was further supported by the FTIR spectra, which showed a distinctly stronger peak at 910 cm^{-1} . The absorbance ratio of the PMB to the base binder at this wavenumber was 1.4 regardless of the base binder, whereas for other polymers, it was 1.1–1.2 depending on SBS. To further estimate the vinyl-to-trans content, the ratio A_{910} / A_{966} was calculated. The results were consistent with the intensity of the 910 cm^{-1} peak, confirming that I_L31.5 had the highest vinyl-to-trans butadiene ratio among the tested polymers. It confirms a redistribution of functional groups, which reflects microstructural interactions rather than covalent chemical reactions.

The base binder type also affected the I_{PB} and I_{PS} indices, as shown in Fig. 10. Binders modified with base binder B and either I_R30 or II_L31 polymers showed smaller changes in both indices compared to those modified with base binder A or C. This may be attributed to the higher aromatic and lower resin content of binder B compared to base binder A and C, which could initially favour SBS solvation but limit further polymer swelling or structural rearrangement. However, this trend was not observed with I_L31.5 and I_R20, which likely exhibit better compatibility and dispersion regardless of the base binder.

4. Conclusions

This study presented a comprehensive comparative analysis of various commercially available styrene-butadiene-styrene polymers and their subsequent impact on the chemical composition of modified binders. The investigation revealed that the final chemical composition of polymer modified binders is not dictated by the polymer's nominal characteristics alone, but by a complex interplay between the specific molecular features of the SBS and the inherent chemical composition of the base binder. The following conclusions can be drawn from this study:

- Standard manufacturer-provided data is often insufficient for predicting polymer-bitumen interactions. This study demonstrated that ^{1}H NMR is a rapid and highly effective technique for determining the precise styrene and vinyl content of SBS copolymers, revealing significant variations (vinyl content ranging from 7.3–33.7 %) not captured in technical datasheets. Furthermore, SEC analysis confirmed that all tested polymers, irrespective of their structure, contained a significant amount of low molecular weight (LMW) fraction (13–16 %), which likely influences compatibility and dispersion within the bitumen matrix. However, attention has to be paid on styrene moiety form in SBS product – if it is a structural component of the SBS copolymer or simply added as LMW polystyrene.
- Polymer structure (linear vs. radial) influences bitumen interaction, although the extent of this effect depends on both the base binder and the specific fraction. Linear polymers, despite their lower molecular weights, induced more substantial changes in the binder's fractional composition, significantly decreasing aromatics (from 36–50 % to 34–42 %) and increasing resins (from 26–37 % to 35–40 %). This suggest stronger integration and swelling within the maltene phase. Conversely, radial polymers, with their higher molecular weight and branched structure, tend to form more discrete,

gel-like networks, leading to less pronounced chemical redistribution within the SARA fractions with difference between PMB and base binder remaining below 6 % for each fraction.

- The initial chemical composition of the base binder, particularly its aromatic and resin content, plays a critical role in the final chemical composition of the PMB. Binders B and C, with higher aromatic content (44–50 %) and lower resin content (26–30 %), showed more significant changes in SARA fractions after modification with 3.5 % SBS, with fractional index as much as 23–49 %. In contract, binder A (aromatics 36 %, resins 37 %) showed less substantial redistribution (fractional index was less than 9 % for all fractions). Although this trend was not reflected in the FTIR-derived I_{PB} and I_{PS} indices, the results clearly showed that the same SBS polymer can yield chemically distinct PMBs when blended with different base binders, highlighting that the binder is not a passive matrix but an active component in the modification process.
- Beyond confirming polymer dispersion, FTIR analysis provides a method for verifying specific polymer microstructural features within the final modified binder. The high vinyl content of the I_L31.5 polymer, initially determined by ^{1}H NMR, was directly corroborated by a significantly enhanced absorbance at 910 cm^{-1} relative to the peak at 966 cm^{-1} . This demonstrates the technique's utility for qualitatively assessing the butadiene isomer distribution after modification, thereby offering a valuable method for quality control and for confirming the presence of specific polymer functionalities in the final product.

To translate these chemical insights into performance-oriented outcomes, future research will focus on correlating the identified chemical changes in polymer modified binders with their rheological behaviour, durability, and in-service performance in asphalt pavements. Establishing these relationships will provide a more comprehensive understanding of how SBS molecular characteristics and binder composition jointly dictate pavement performance, ultimately enabling the design of more durable and sustainable asphalt mixtures.

CRediT authorship contribution statement

Audrius Vaitkus: Conceptualization, Writing – review & editing. **Judita Škulteckė:** Data curation, Methodology, Supervision, Writing – original draft. **Vaidas Klimkevičius:** Formal analysis, Methodology, Visualization, Writing – original draft. **Viktoras Masevičius:** Formal analysis, Methodology, Visualization, Writing – original draft. **Ovidijus Šernas:** Resources, Visualization, Writing – review & editing.

Funding sources

This work was supported by the Research Council of Lithuania (LMTLT), agreement No. S-MIP-23–106.

Declaration of Competing Interest

The authors declare no potential conflict of interest.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mtcomm.2025.113719.

Data availability

Data will be made available on request.

References

[1] G. Polacco, S. Filippi, F. Merusi, G. Stastna, A review of the fundamentals of polymer-modified asphalts: asphalt/polymer interactions and principles of compatibility, Adv. Colloid Interface Sci. 224 (2015) 72–112, https://doi.org/10.1016/j.cis.2015.07.010.

[2] K. Błażejowski, M. Wójcik-Wiśniewska, H. Peciakowski, J. Olszacki, The performance of a highly modified binders for heavy duty asphalt pavements, Transp. Res. Procedia 14 (2016) 679–684, https://doi.org/10.1016/j.trpro.2016.05.331.

[3] H.R. Soleymani, H. Zhai, H. Bahia, Role of modified binders in rheology and damage resistance behavior of asphalt mixtures, Transp. Res. Rec. J. Transp. Res. Board 1875 (2004) 70–79, https://doi.org/10.3141/1875-08.

[4] S. Hassanpour-Kasanagh, P. Ahmedzade, A.M. Fainleib, A. Behnood, Rheological properties of asphalt binders modified with recycled materials: a comparison with Styrene-Butadiene-Styrene (SBS), Constr. Build. Mater. 230 (2020) 117047, https://doi.org/10.1016/j.conbuildmat.2019.117047.

[5] R. Li, F. Xiao, S. Amirkhanian, Z. You, J. Huang, Developments of nano materials and technologies on asphalt materials – a review, Constr. Build. Mater. 143 (2017) 633–648, https://doi.org/10.1016/j.conbuildmat.2017.03.158.

[6] T. Xia, Y. Qin, J. Xu, L. Zhou, W. Chen, J. Dai, Viscoelastic phase separation and crystalline-to-amorphous phase transition in bitumen/SBS/PE blends, Polymers 155 (2018) 129–135, https://doi.org/10.1016/j.polymer.2018.09.042.

[7] O. Šernas, A. Vaitkus, J. Škulteckė, Performance of crumb rubber bitumen and asphalt modified in the wet process alone and in combination with SBS polymer, Road Mater. Pavement Des. (2023), https://doi.org/10.1080/14680629.2023.2180294.

[8] S. Malinowski, A. Woszuk, M. Wróbel, A. Kwaśniewska, G. Gładyszewski, J. Škulteckė, A. Vaitkus, W. Franus, Anti-ageing and rheological performance of bitumen modified with polyaniline nanofibres, Constr. Build. Mater. 437 (2024), https://doi.org/10.1016/j.conbuildmat.2024.136810.

[9] G.D. Airey, Rheological properties of styrene butadiene styrene polymer modified road bitumens, Fuel 82 (2003) 1709–1719, https://doi.org/10.1016/S0016-2361(03)00146-7.

[10] M. Liang, P. Liang, W. Fan, C. Qian, X. Xin, J. Shi, G. Nan, Thermo-rheological behavior and compatibility of modified asphalt with various styrene-butadiene structures in SBS copolymers, Mater. Des. 88 (2015) 177–185, https://doi.org/10.1016/j.matdes.2015.09.002.

[11] G. Cuciniello, P. Leandri, S. Filippi, D. Lo Presti, G. Polacco, M. Losa, G. Airey, Microstructure and rheological response of laboratory-aged SBS-modified bitumens, Road Mater. Pavement Des. 22 (2021) 372–396, https://doi.org/10.1080/14680629.2019.1621771.

[12] J. Zhu, B. Birgisson, N. Kringos, Polymer modification of bitumen: advances and challenges, Eur. Polym. J. 54 (2014) 18–38, https://doi.org/10.1016/j.eurpolymj.2014.02.005.

[13] A. Schaur, S. Unterberger, R. Lackner, Impact of molecular structure of SBS on thermomechanical properties of polymer modified bitumen, Eur. Polym. J. 96 (2017) 256–265, https://doi.org/10.1016/j.eurpolymj.2017.09.017.

[14] X. Lu, U. Isacsson, J. Ekblad, Low-temperature properties of styrene–butadiene–styrene polymer modified bitumens, Constr. Build. Mater. 12 (1998) 405–414, https://doi.org/10.1016/S0950-0618(98)00032-4.

[15] G. Cuciniello, P. Leandri, S. Filippi, D. Lo Presti, M. Losa, G. Airey, Effect of ageing on the morphology and creep and recovery of polymer-modified bitumens, Mater. Struct. 51 (2018) 136, https://doi.org/10.1617/s11527-018-1263-3.

[16] H.L. Von Quintus, J. Mallela, M. Buncher, Quantification of effect of polymer-modified asphalt on flexible pavement performance, Transp. Res. Rec. J. Transp. Res. Board 2001 (2007) 141–154, https://doi.org/10.3141/2001-16.

[17] X. Lu, S. Said, H. Soenen, A. Ahmed, H. Carlsson, Long Lasting Asphalt Pavements with Polymer Modified Bitumens, in: 7th Eurasphalt Eurobitume Congr., 15-17 June, 2021, Madrid, Spain (online), 2021: pp. 1–10.

[18] C. Celauro, R. Teresi, N.T. Dintcheva, Effect of Short-Term and UV irradiation aging on the behaviour of SBS-Modified bitumen, Sustainability 14 (2022) 6915, https://doi.org/10.3390/su14116915.

[19] O.-V. Laukkanen, H. Soenen, T. Pellinen, S. Heyrman, G. Lemoine, Creep-recovery behavior of bituminous binders and its relation to asphalt mixture rutting, Mater. Struct. 48 (2015) 4039–4053, https://doi.org/10.1617/s11527-014-0464-7.

[20] T. López-Montero, R. Miró, Differences in cracking resistance of asphalt mixtures due to ageing and moisture damage, Constr. Build. Mater. 112 (2016) 299–306, https://doi.org/10.1016/j.conbuildmat.2016.02.199.

[21] A.W. Ahmed, S.F. Said, X. Lu, H. Carlsson, Pavement performance follow-up and evaluation of polymer-modified test sections, Int. J. Pavement Eng. 20 (2019) 1474–1487, https://doi.org/10.1080/10298436.2018.1435878.

[22] J. Škulteckė, A. Vaitkus, O. Šernas, K. Liubinas, Analysis of Variation in Creep and Recovery of Polymer Modified Bitumen Used for Asphalt Mixtures Production of Various Producers, in: 8th E&E Congr., 19-21 June 2024, Budapest, Hungary, 2024.

[23] X. Lu, U. Isacsson, Chemical and rheological evaluation of ageing properties of SBS polymer modified bitumens, Fuel 77 (1998) 961–972, https://doi.org/10.1016/S0016-2361(97)00283-4.

[24] S. Zhou, J. Wang, S. Li, C. Yan, Investigating the rheological behaviour of styrene–butadiene–styrene modified asphalt, Road. Mater. Pavement Des. (2023) 1–16, https://doi.org/10.1080/14680629.2023.2287715.

[25] J. Škulteckė, A. Vaitkus, O. Šernas, Creep and Recovery of SBS Modified Bitumen Depending on the Properties of Base Bitumen and Polymer, in: 8th Int. Conf. Road Rail Infrastruct. (CETRA 2024), 15-17 May, 2024, Cavtat, Croatia, 2024: pp. 579–585. https://doi.org/10.5592/CO/CETRA.2024.1607.

[26] X. Lu, U. Isacsson, Compatibility and storage stability of styrene-butadiene-styrene copolymer modified bitumens, Mater. Struct. Constr. 30 (1997) 618–626, https://doi.org/10.1007/bf02486904.

[27] O.V. Laukkanen, H.H. Winter, H. Soenen, J. Seppälä, Rheological characterization of styrene- butadiene-styrene block copolymer modified bitumens, Annu. Trans. Nord. Rheol. Soc. 24 (2016) 53–57.

[28] S.B. Chakrapani, M.J. Minkler, B.S. Beckingham, Low-field ^{1}H NMR spectroscopy for compositional analysis of multicomponent polymer systems, Analyst 144 (2019) 1679–1686, https://doi.org/10.1039/C8AN01810C.

[29] R. Ma, L. Zhang, Molecular weight and arm number of a star-shaped styrene–butadiene block copolymer synthesized on a pilot-vessel scale, J. Appl. Polym. Sci. 103 (2007) 1853–1859, https://doi.org/10.1002/app.25352.

[30] G.R. Fulmer, A.J.M. Miller, N.H. Sherden, H.E. Gottlieb, A. Nudelman, B.M. Stoltz, J.E. Bercaw, K.I. Goldberg, NMR chemical shifts of trace impurities: common laboratory solvents, organics, and gases in deuterated solvents relevant to the organometallic chemist, Organometallics 29 (2010) 2176–2179, https://doi.org/10.1021/om100106e.

[31] S. Luo, J. Tian, Z. Liu, Q. Lu, K. Zhong, X. Yang, Rapid determination of styrene-butadiene-styrene (SBS) content in modified asphalt based on Fourier transform infrared (FTIR) spectrometer and linear regression analysis, Measurement 151 (2020) 107204, https://doi.org/10.1016/j.measurement.2019.107204.

[32] S. Weigel, M. Gehrke, C. Recknagel, D.A. Stephan, Identification and quantification of additives in bituminous binders based on FTIR spectroscopy and multivariate analysis methods, Mater. Struct. 54 (2021) 171, https://doi.org/10.1617/s11527-021-01763-1.

[33] J. Škulteckė, S. Bitarytė, K. Liubinas, FTIR-ATR spectroscopy to identify and quantify the SBS in modified bitumen, Environ. Eng. (2023) 1–6, https://doi.org/10.3846/enviro.2023.880.

[34] L.B. Canto, G.L. Mantovani, E.R. DeAzevedo, T.J. Bonagamba, E. Hage, L.A. Pessan, Molecular characterization of Styrene-Butadiene-Styrene block copolymers (SBS) by GPC NMR, and FTIR, Polym. Bull. 57 (2006) 513–524, https://doi.org/10.1007/s00289-006-0577-4.

[35] X.-K. Li, G.-S. Chen, M.-W. Duan, W.-C. Yang, S.-C. Tang, Y.-D. Cao, Y. Luo, Branched hydroxyl modification of SBS using Thiol-Ene reaction and its subsequent application in modified asphalt, Ind. Eng. Chem. Res. 56 (2017) 10354–10365, https://doi.org/10.1021/acs.iecr.7b02280.

[36] T. Xia, J. Xu, T. Huang, J. He, Y. Zhang, J. Guo, Y. Li, Viscoelastic phase behavior in SBS modified bitumen studied by morphology evolution and viscoelasticity change, Constr. Build. Mater. 105 (2016) 589–594, https://doi.org/10.1016/j.conbuildmat.2015.11.033.

[37] Y. Zeng, Q. Liu, Q. Zeng, Y. He, Z. Xu, Research on the mechanism of interaction between styrene–butadiene–styrene (Sbs) and asphalt based on molecular vibration frequency, Materials 14 (2021) 1–14, https://doi.org/10.3390/ma14020358.

[38] G. Pipintakos, J. Škulteckė, A. Vaitkus, O. Šernas, H. Soenen, W. Van den bergh, Optimising bitumen modification: how styrene–butadiene–styrene (SBS) characteristics and content affect bitumen behaviour, Road. Mater. Pavement Des. 26 (2025) 443–463, https://doi.org/10.1080/14680629.2025.2482842.

[39] V.O. Bulatović, V. Rek, K.J. Marković, Polymer modified bitumen, Mater. Res. Innov. 16 (2012) 1–6, https://doi.org/10.1179/1433075X11Y.0000000021.

[40] M.R.S. Fernandes, M.M.C. Forte, L.F.M. Leite, Rheological evaluation of polymer-modified asphalt binders, Mater. Res. 11 (2008) 381–386, https://doi.org/10.1590/S1516-14392008000300024.