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FTIR-ATR SPECTROSCOPY TO IDENTIFY AND QUANTIFY THE SBS IN MODIFIED BITUMEN

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Abstract. The aim of this paper is to demonstrate that the Fourier transform infrared (FTIR) spectroscopy with attenuated total reflexion (ATR) technique is a rapid and suitable method for identifying and preliminary quantifying the amount of styrene-butadiene–styrene (SBS). For this purpose, unmodified and modified binders were tested with FTIR-ATR spectroscopy. Both the laboratory modified binders and modified bitumen existing in the market were analysed. In addition to this, multi stress creep recovery (MSCR) test was used to demonstrate the importance of polymers and the dependency of results on the amount of SBS. The research results showed that FTIR-ATR spectroscopy is a suitable method to identify and preliminary quantify the amount of SBS in modified bitumen and that the higher amount of SBS, the better the performance of bitumen is.

Keywords: FTIR-ATR, spectroscopy, polymer modified bitumen, SBS modified bitumen, amount of SBS, MSCR test.

JEL Classification: L74 Construction.

Introduction

Bitumen is one of the main materials for pavement construction. Following climate change, bitumen needs to be more sustainable and durable. Since it influences the asphalt mixture behaviour, scientific community has big interest in bitumen and try to understand its performance from different perspectives (Hajj & Young, 2021; Redelius & Soenen, 2015). To obtain better characteristics of bitumen, it is typically modified with polymer. Asphalt pavements with polymer modified bitumen (PMB) last longer than those with unmodified bitumen since PMB has higher strain recovery and lower creep compliance, than unmodified bitumen (Ahmed et al., 2019; Błazejowski et al., 2016; Woo et al., 2007). A particularly suitable polymer for bitumen modification is styrene-butadiene-styrene (SBS). The level of bitumen improvement depends on the polymer amount (Dong et al., 2014). SBS improves performance in warm and cold weather also leads to better resistance to permanent deformation and lower aging (Celauro et al., 2022; Cuciniello et al., 2021; Yan et al., 2020; Wang et al., 2015).

SBS elastomers compound the properties of a thermoplastic resins with those of butadiene rubber. The styrene blocks supply mechanical strength and boosts the abrasion resistance, while the rubber mid-block provides flexibility and toughness. In the market, SBS are with different polymers structure (linear and radial) and different ratio of butadiene and styrene (Schaur et al., 2017). It leads to different performance of modified bitumen.

Previous researches showed the significance of bitumen's chemistry for its performance (Lu & Isacsson, 2002; Weigel & Stephan, 2018). Best way to analyse bitumen chemical groups is using Fourier-transform infrared- Attenuated Total Reflection (FTIR-ATR) method. Also, FTIR-ATR is used to evaluate diffusion behaviours of microencapsulated rejuvenator. This method is not standardised. As a result, some authors give recommendations how to perform tests with FTIR-ATR (Hofko et al., 2017, 2018; Mirwald et al., 2022). Hofko et al. (2017) showed the repeatability and sensitivity of FTIR-ATR method depending on the data analysis method.

From the previous studies it is obvious that polymers improve bitumen performance at both low and high temperatures. However, the amount and properties of the polymer used to modify bitumen are not typically specified in the documents and as a result it is not clear why asphalt pavements with the same type of polymer modified bitumen have different durability. Therefore, there is a need to have rapid and easy method to identify and preliminary quantify the amount of polymer (typically, SBS) in bitumen. This paper aims to fill this research gap by proposing FTIR-ATR method.

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Table 1. Penetration and softening point of analysed bitumen

Property	Test method	Bitumen type and amount of polymer						
		50/70			PMB 25/55-60		PMB 45/80-65	
		0%	2%	5%	A	B	C	D
Penetration, °C	LST EN 1426	59.5	49.9	39.6	55.0	40.7	55.6	51.4
Softening point, °C	LST EN 1427	49.9	58.9	70.8	74.6	65.2	70.1	60.8

1. Materials and methods

1.1. Materials

Six polymer modified bitumen and one neat bitumen, were analysed in this study. Four PMBs were taken from the market and two – were modified in the laboratory. All tested bitumen and their main properties (penetration and softening point) are presented in Table 1.

In the laboratory, bitumen 50/70 was modified with 2% and 5% of SBS (Calprene 401). It is a thermoplastic copolymer, polymerized in solution and have a radial structure. It consists of 80% butadiene and 20% styrene. The SBS modified bitumen were prepared using high speed shear mixer at constant temperature of 175±5 °C and mixed for 3 hours.

1.2. Methods

Multiple stress creep recovery (MSCR) test

Multiple stress creep recovery (MSCR) test was conducted using a dynamic shear rheometer with parallel plates (25 mm in diameter and 1 mm in gap). A test procedure followed the requirements of the European standard EN 16659 (European Committee for Standardization, 2015). Ten cycles were applied to the samples at 60 °C and 0.1 kPa and 3.2 kPa stress level. Each cycle consisted of loading (1 s) and resting (9 s). After the test, the average percent recovery (R) and non-recoverable creep compliance (J_{nr}) were calculated for both stress levels.

FTIR-ATR spectroscopy

Bruker Alpha II FTIR spectrometer equipped with an attenuated total reflection (ATR) was used to determine functional groups of analysed bitumen. Bitumen was heated at 180 °C temperature and then small samples (droplets) were applied on small pieces of butter paper and stored at dark for 10 minutes in closed container. Tests were done within one hour after samples were prepared. Spectra were recorded at room temperature. The recorded spectra were analysed using OPUS software within the absorption wavenumbers range of 400–4000 cm^{-1} with a resolution of 4 cm^{-1} and 32 scans. Each sample was scanned 3 times and 3 samples per binder were scanned. In total, 63 spectra were recorded. Spectra were normalized using min-max method.

2. Results

MSCR test results of SBS modified bitumen, which were either taken from the market or modified in the laboratory, are given in Figure 1. The error bars represent the minimum and maximum value.

As can be seen in Figure 1, polymer modified bitumen has significantly higher resistance to rutting compared to unmodified bitumen and it depends on the amount of polymer. Recovery ($R_{3.2}$) and non-recoverable creep compliance ($J_{nr\ 3.2}$) of modified bitumen was 8–79% and 0.211–1.364 kPa^{-1} depending on the polymer amount, while unmodified bitumen at 3.2 kPa did not recover at all (at 0.1 kPa it recovered only 4%) and non-recoverable creep compliance ($J_{nr\ 3.2}$) reached 4.165 kPa^{-1} (at 0.1 kPa it was 3.510 kPa^{-1}). The increase in the SBS content from 2% to 5% significantly changed the performance of bitumen. Recovery at 3.2 kPa ($R_{3.2}$) increased from 8% to 51%, and non-recoverable creep compliance ($J_{nr\ 3.2}$) decreased from 1.364 kPa^{-1} to 0.249 kPa^{-1}. Thus, the higher the SBS content, the higher the recovery and the lower the residual strain of bitumen. These findings are in line with those of previous studies (Behnood & Olek, 2017; Huang & Tang, 2015; Laukkanen et al., 2015; Lu et al., 2013).

This study also shows that on the market existing binders, which comply with the requirements of the European standards and are classified as the same type, might perform differently. For example, both PMB 25/55-60 binders had significantly different resistance to rutting. PMB 25/55-60 A recovered 4.5 times more and had about 4 times lower residual strain compared to PMB 25/55-60 B. The same trend was observed for PMB 45/50-55 binders. In addition to this, PMB 25/55-60 A performed very similarly to PMB 45/80-55 C. The difference in recovery and non-recoverable creep compliance at 3.2 kPa ($R_{3.2}$ and $J_{nr\ 3.2}$) was only 7% and 0.034 kPa^{-1}, respectively. These findings may be explained by the fact that both the amount of polymer and the type of polymer are not known for tested binders from the market (PMB 25/55-60 and PMB 45/80-55) since bitumen producers do not provide this kind of information. It is important to note that the chemical and fractional composition of bitumen also influences its performance.

The FTIR-ATR spectra of all tested binders in the wave number range from 4000 cm^{-1} to 600 cm^{-1} are given in Figure 2. Since this paper aims to determine the presence of SBS in bitumen, enlarged section in the wave number range from 1800 cm^{-1} to 600 cm^{-1} are given in Figure 3. All spectra are normalized and present the average of three specimens.

Figure 2 and Figure 3 show that all binders have absorption peaks around absorption wavenumbers of 2919 cm^{-1}, 2851 cm^{-1}, 1690 cm^{-1}, 1600 cm^{-1}, 1456 cm^{-1}, 1376 cm^{-1}, 1032 cm^{-1}, 866 cm^{-1}, 811 cm^{-1}, 745 cm^{-1}, and 721 cm^{-1}. Each absorption peak characterizes a specific functional group: aliphatic hydrocarbons, carbonyls, aromatics, sulfoxides and polyaromatics. These groups are typical to all bitumen irrespective of crude oil and additives. The scattering between the absorbance of some peaks may be explained by the elemental, structural and fractional composition of bitumen itself. In this study, these compositions were not analysed.

Figure 3 shows that contrary to neat bitumen, all modified binders have absorption peaks around absorptions wavenumbers of 966 cm^{-1}, 910 cm^{-1} and 698 cm^{-1}. These peaks indicate the presence of SBS. Absorption peaks at the wavenumbers of 966 cm^{-1}and 910 cm^{-1} attribute to the butadiene while peaks at the wavenumbers of 698 cm^{-1} attributes styrene (Luo et al., 2020; Munteanu & Vasile, 2005; Weigel et al., 2021). The highest absorption peak around absorptions wavenumbers of 966 cm^{-1} was determined for laboratory-modified bitumen 50/70 with 5% of SBS. However, at absorptions wavenumbers of 910 cm^{-1} and 698 cm^{-1} PMB 25/55-60 A taken from the market had the highest peaks.

Looking closer at the neat and laboratory-modified bitumen (Figure 4), it is clear that peaks at absorptions wavenumbers of 966 cm^{-1}, 910 cm^{-1} and 698 cm^{-1} depend on the amount of SBS. The higher amount of polymer, the higher the peaks. From the Figure 3 and Figure 4 is clear that all tested binders from market have

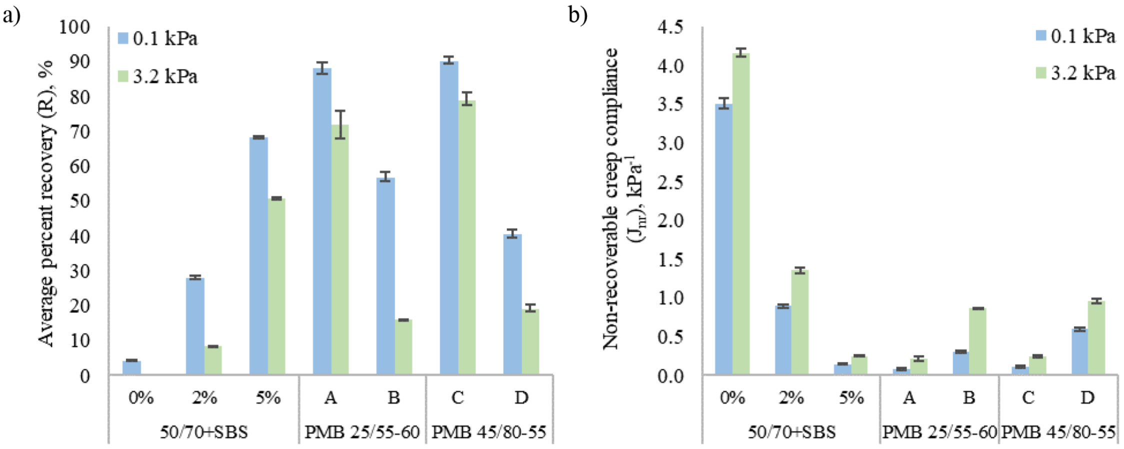

Figure 1. MSCR test results at 60 °C: a) average percent recovery at 0.1 kPa and 3.2 kPa ($R_{0.1}$ and $R_{3.2}$, respectively); b) non-recoverable creep compliance at 0.1 kPa and 3.2 kPa ($J_{nr\ 0.1}$ and $J_{nr\ 3.2}$, respectively)

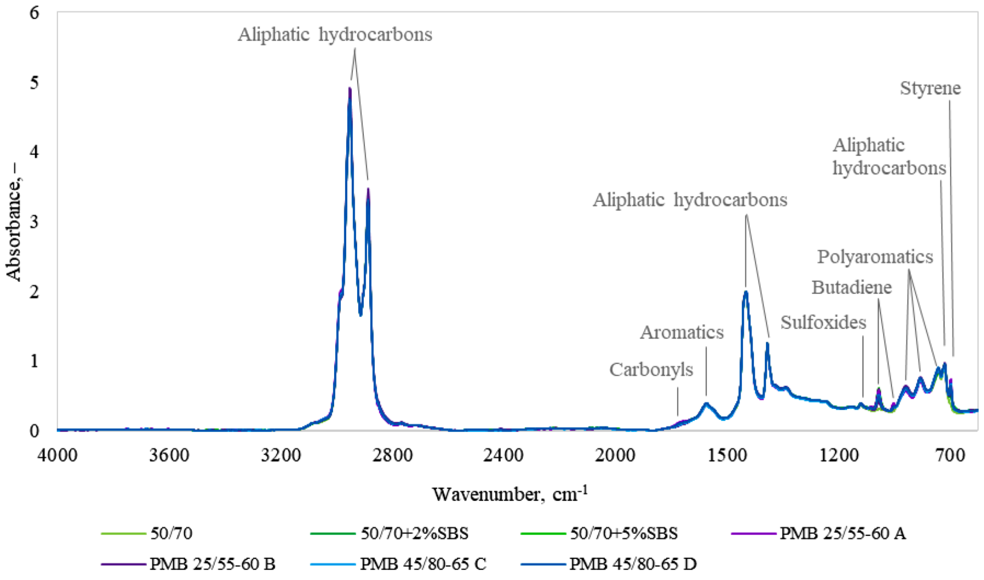

Figure 2. FTIR-ATR spectra of all tested binders in the wave number range from 4000 cm^{-1} to 600 cm^{-1} (peak labelling according to Feng et al. (2016), Mouillet et al. (2008), van den Bergh (2011), Weigel and Stephan (2017) and Weigel et al. (2021))

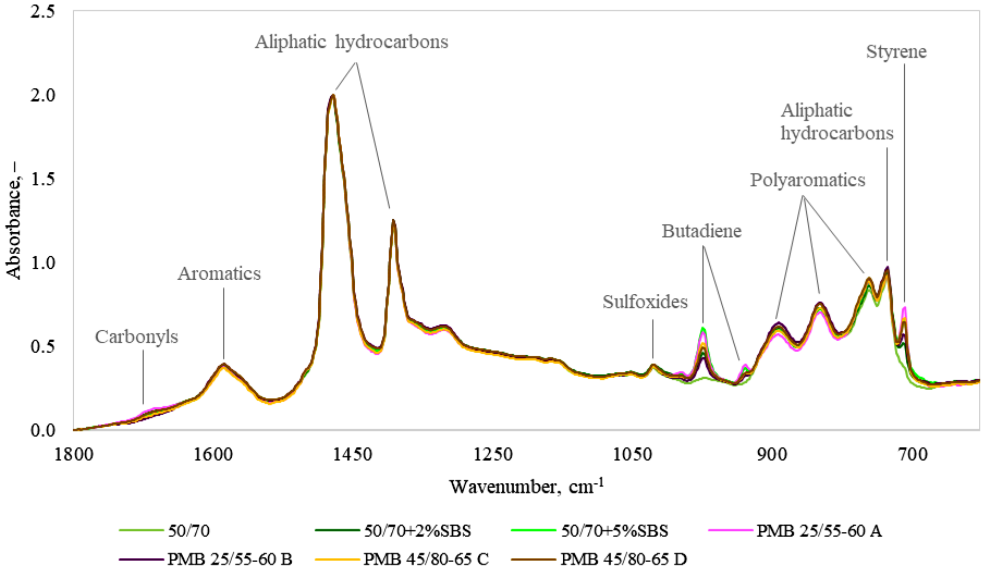

Figure 3. FTIR-ATR spectra of all tested binders in the wave number range from 1800 cm^{-1} to 600 cm^{-1} (peak labelling according to Feng et al. (2016), Mouillet et al. (2008), van den Bergh (2011), Weigel and Stephan (2017) and Weigel et al. (2021))

at least 2% of SBS and some of them (e.g. PMB 25/55-60 A and PMB 45/80-55 C) – even 5% or more. Seeking to preliminary quantify the amount of SBS in binders from the market, bitumen 50/70 was modified with 3% and 4% of SBS and additional FTIR-ATR spectra were determined. The comparison of FTIR-ATR spectra between laboratory-modified bitumen (SBS varied from 2% to 5%) and binders from the market showed that it is not possible to quantify the amount of SBS in the binders from the market based on the absorption peaks at wavenumbers of 966 cm^{-1}, 910 cm^{-1} and 698 cm^{-1} since the position at some wavenumbers may differ from the reference spectra (spectra of laboratory-modified bitumen) due to unknown chemical composition of base bitumen. Nevertheless, FTIR-ATR spectra can be used to quantify SBS, but different approach has to be considered. Recently, the peak area ratio (i.e., the peak area at 966 cm^{-1} divided by the total area at peaks 966 cm^{-1} and 813 cm^{-1}) was suggested to determine the amount of SBS (Luo et al., 2020). Multivariate evaluation was also suggested as one of the appropriate methods to quantify the SBS (Weigel et al., 2021).

Seeking to find out whether bitumen performance can be predicted based on the FTIR-ATR spectra, especially based on the absorption peaks at absorptions wavenumbers of 966 cm^{-1}, 910 cm^{-1} and 698 cm^{-1},

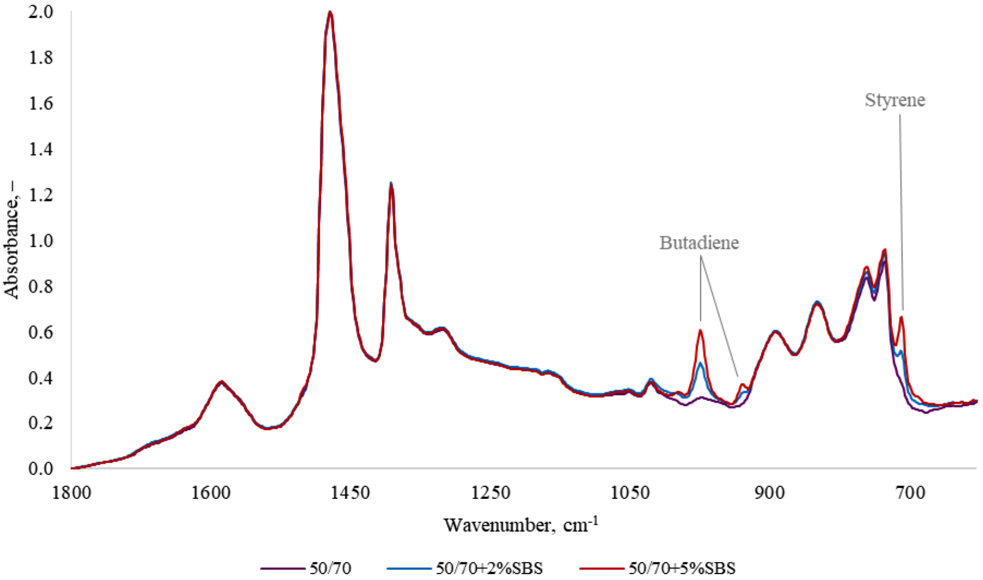

Figure 4. FTIR-ATR spectra of neat and laboratory-modified bitumen in the wave number range from 1800 cm^{-1} to 600 cm^{-1}

MSCR test results were compared with corresponding peaks. The results showed that binders with the highest peaks at absorptions wavenumbers of 966 cm^{-1}, 910 cm^{-1} and 698 cm^{-1}, which attributes to the highest amount of SBS, have high recovery and the low non-recoverable creep compliance. This was a case for laboratory-modified bitumen 50/70 with 5% SBS and two binders from the market (PMB 25/55-60 A and PMB 45/80-55 C). However, PMB 45/80-55 D did not follow this trend. Although its absorption peaks at wavenumbers of 966 cm^{-1}, 910 cm^{-1} and 698 cm^{-1} were almost the same as for PMB 45/80-55 C, it performed significantly worse in MSCR test compared to PMB 45/80-55 C. Further research is needed to answer why this happened.

Conclusions

In this study, laboratory-modified bitumen 50/70 with different amount of SBS (0%, 2% and 5%) and binders from the market (two PMB 25/55-60 and two PMB 45/80-55) were tested with FTIR-ATR spectroscopy and dynamic shear rheometer (MSCR test). The following conclusions are drawn from the conducted study:

- On the market existing polymer modified binders, which comply with the requirements of the European standards and are classified as the same type, perform differently. During MSCR test at 60 °C and 3.2 kPa, PMB 25/55-60 A recovered 4.5 times more and had about 4 times lower non-recoverable creep compliance compared to PMB 25/55-60 B and the results were very close to those of PMB 45/80-55 C (the difference in recovery and non-recoverable creep compliance at 3.2 kPa was only 7% and 0.034 kPa^{-1}, respectively). These rather contradictory results could be explained by the fact that bitumen producers are not obliged to specify the amount and type of polymer used to modify bitumen and there are no performance-based requirements in Europe.
- Using FTIR-ATR spectroscopy, the presence of SBS is identified by the absorption peaks around wavenumbers of 966 cm^{-1} (butadiene), 910 cm^{-1} (butadiene) and 698 cm^{-1} (styrene) irrespective of PMB type. The spectra of neat bitumen confirmed it, since in this case peaks around wavenumbers of 966 cm^{-1}, 910 cm^{-1} and 698 cm^{-1} were not determined contrary to the spectra of polymer modified bitumen.
- Peaks at absorptions wavenumbers of 966 cm^{-1}, 910 cm^{-1} and 698 cm^{-1} depend on the amount of SBS. The higher amount of polymer, the higher the peaks and the better bitumen performance. The increase of SBS from 2% to 5% in bitumen 50/70, increased the absorption peaks attributed to SBS about 20–30% and resistance to rutting (recovery at 60 °C and 3.2 kPa increased from 8% to 51% and non-recoverable compliance decreased from 1.364 kPa^{-1} to 0.249 kPa^{-1}). Further investigation and experimentation into peaks dependency on the both SBS amount and type is strongly recommended. In addition to this, it is recommended to consider the elemental, structural and fractional composition of base bitumen and its influence on the absorption peaks attributed to SBS.
- To determine the exact amount of SBS in binders taken from the market based on the absorption peaks at wavenumbers of 966 cm^{-1}, 910 cm^{-1} and 698 cm^{-1} is not possible due to unknown spectra of reference bitumen (spectra of base bitumen with different amount of SBS). However, this approach can be successfully used for bitumen control by bitumen producers. Seeking to determine the exact amount of SBS in polymer modified bitumen taken from the market, a different approach has to be considered.

Disclosure statement

No potential conflict of interest was reported by the authors.

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