

Laboratory evaluation of emissions from Polymer modified Bitumen

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Abstract

In addition to technical advantages of asphalt materials, the asphalt industry is placing health and safety at the forefront, especially for workers during construction. The fumes, which are generated during the manufacture of Hot Mix Asphalt (HMA), may impact occupational exposure limits. In recent years, a spotlight has been placed on bitumen fumes, and studies have been published on this subject. Polymer modified Bitumen (PmB) is being used successfully for more than 40 years and brings a lot of advantages for the durability of the pavement and long-term maintenance plan. Due to higher viscosity, PmB may require higher mixing temperature as compared to standard paving grade bitumen. This may raise the question of impact on bitumen fumes released during, manufacturing the PmB itself, the handling of the binder and manufacturing at asphalt mix plant. This paper investigates the fume emissions of Polymer modified Bitumen based on analytical testing using headspace analysis. This specific method enables to analyse the volatile components from samples and more specifically the Polycyclic Aromatic Hydrocarbons. Two types of PmB were evaluated, a commonly used PmB with 3.5% of SBS and a highly modified binder with 7.5% of special SBS. They were compared with a conventional paving grade bitumen used as a reference. These three binders were tested at different temperatures reflecting various conditions of making hot mix asphalt. The overall results shown that the total fume emissions are very dependent to the temperature, the higher the mixing temperature, the higher the level of emission. In the case of the high modified bitumen, the specifically designed SBS polymer allows to keep the viscosity in a reasonable range, despite the higher polymer load. This leads to a direct effect on the fume emissions.

1 INTRODUCTION

With the constant focus on health and safety, the paving industry is paying more attention to material and processing emissions. During the manufacture of Hot Mix Asphalt (HMA) at elevated temperatures, controlling the emissions of Volatile Organic Compounds (VOCs) is one of the key focus areas, as it may impact occupational exposure limits. In previous years, extensive studies and researches have been conducted and published to better monitor fume emissions and identify technologies that can reduce these emissions [1] [2] [3].

At the same time, the constant demand for better roads, safer, more durable and reliable, means there are requirements for high performance materials. The use of Polymer modified Bitumen (PmB) has technical proven advantages with regards to durability of the roads. However, it may lead to higher binder viscosity, which requires higher mixing temperature as compared to standard paving grade bitumen. This can have an impact on the fumes emissions released during the production of the PmB itself and later during handling and manufacturing at the asphalt mix plant. While there are already studies on fume emissions from bitumen especially to detect heavy PAH [4], there is limited data available when considered modified bitumen. However there are multiple ways of modification techniques either with additives or with polymers, and then there are different types of polymers. SBS polymer is the most widely used polymer for paving applications, thus it was considered for further investigation on its effect on emissions.

This study focused on a laboratory evaluation of the fume emissions of a SBS polymer modified bitumen as compared to standard pen grade bitumen. The goal was, comparing a neat bitumen with a standard PmB and a highly modified bitumen to record the Volatile Organic Compounds in fume emissions, and more specifically focusing on the ones that may affect occupational exposure, such as Polycyclic Aromatic Hydrocarbons (PAH). This paper describes the key outcomes of the study.

In previous studies, fume emissions on binders were evaluated using headspace analysis combined with Gas Chromatography / Mass Spectrometry (GC/MS) [5]. The headspace (HS) technique has been widely used for the analysis of volatile organic compounds in solid samples [6] [7]. This technique facilitates the characterisation and relative comparison of the volatile compounds emitted by bitumen over a range of temperatures. This approach has previously been used successfully by the asphalt industry, including characterisation of bitumen with additives [8]. The method by itself may present some limitations, as the detection limits are high, making it more suitable for high levels of volatile compounds [9]. In this study a headspace stir bar sorptive extraction (HSBSE) method was used to characterise the volatile compounds emitted by bitumen. The target compounds were Volatile Organic Compounds (VOCs) and Polycyclic Aromatic Hydrocarbons (PAHs).

2 EXPERIMENTAL PLAN

2.1 Materials

For the study, three different binders were used, a neat bitumen graded as 50/70 according to EN 12591, a PmB with 3.5 % SBS polymer graded as 45/80-55 as per EN 14023 and a highly modified bitumen with 7.5 % SBS graded as 25/55-80 as per EN 14023. The standard PmB was prepared in the laboratory with a soft base bitumen, 70/100 and 3.5% of D1101 SBS copolymer; the base bitumen was different and from a different source than the reference neat bitumen 50/70. The second PmB was a highly modified bitumen, HiMA, made with the same reference neat bitumen 50/70, used in the study, and 7.5 % D0243 SBS copolymer. This high polymer content ensures to have a rich polymer phase in the binder behaving more like polymer than bitumen. The polymer used was a high vinyl linear SBS polymer which, with its low molecular weight, enables keeping the viscosity of the final PmB in reasonable range for manufacturing asphalt mix. It has been developed to enhance further the rutting resistance and cracking performance for either surface layers or structural layers [10]. The neat bitumen used in the evaluation is assumed to represent normal emission values for these types of pure bitumen. The binders have data available in another study evaluating their physical properties. Table 1 displays the main properties of the three binders used in the study.

Table 1. Main properties of binders

Binder	Label	EN Grade	Formula	Penetration value at 25 °C	Softening point temperature
Bitumen 50/70	50/70	50/70	Pure bitumen	58 0.1mm	48 °C
Standard PmB	PmB	45/80-55	70/100 + 3.5 D1101	62 0.1mm	58 °C
HiMA PmB	HiMA	25/55-80	50/70 + 7.5% D0243	33 0.1mm	88 °C

In addition, Fourier Transform Infra-Red (FTIR) spectroscopy were performed in Attenuated Total Reflectance (ATR) to qualify the presence of the SBS in the PmB.

2.2 Fumes emission evaluation

The stir bar sorptive extraction method is based on passive sampling, placing a stir bar coated with 47 μL polydimethylsiloxane in headspace of a vial with bitumen for 30 min at 140 °C, 160 °C, 180 °C and 200 °C. Following exposure, the analytes were thermally vaporised at 300 °C for 10 min and pre-concentrated in the cold trap (Tenax) at -20 °C and then thermally desorbed at 320 °C for 5 min in the thermal desorption system (TD). Finally, the analytes were separated in the gas chromatography (GC) and detected by triple quadrupole mass spectrometry detector (MS-TQ). Figure 1 shows the setting of the equipment.



Figure 1. Thermal Desorption Gas Chromatography Triple Quadrupole Mass Spectrometry

For VOCs and PAHs, total ion chromatogram (TIC) and multiple reactions monitoring (MRM) mode were used, respectively. Experienced has shown that HSBSE method coupled to TD-GC-MS-TQ was successful applied to the characterisation of volatile compounds emission from bitumen. The HSBSE technique is simple, cost effective and can be easily implemented in most laboratories.

The PAH detection was first calibrated using a standard mixture, EPA M-610, containing the 16 EPA-PAHs, naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)-anthracene, chrysene, benzo(b)fluoranthene, benzo(k)-fluoranthene, benzo(a)pyrene, indeno(1,2,3,c-d)pyrene, dibenz(a,h)anthracene and benzo(ghi)perylene. This initial step validated that the PAHs can be detected and then calibrating the signal for each PAH with the known concentration.

As the amount of emitted volatile compounds depends on the temperature at which the binder is heated, four temperatures were considered: 140 °C, 160 °C, 180 °C, covering a wide range of manufacturing temperatures and 200 °C representing an extreme condition outside the normal temperature range. The three binders were evaluated, the neat 50/70 pen grade bitumen, the PmB and the HiMA binder. A total of twelve samples were tested to explore the matrix of four temperatures and three binders. And for each sample, the measurements were duplicated. The analysis allows the identification and relative comparison of emission levels from the samples tested. It was based on the intensity and/or compositional change of the emissions with regard to relative levels of Volatile Organic Compounds (VOCs), and Polycyclic Aromatic Hydrocarbons (PAHs).

3 RESULTS

3.1 Physical properties

The three binders were already used in a previous study evaluating the aging of PmB as compared to standard neat bitumen and will not be covered extensively here. For the purpose of the study, in addition to standard properties as per EN 14023, Brookfield viscosity at different temperatures was performed. This has been done to be able to compare the emissions at equi-viscosity. Figure 2 displays the viscosity profile for the three bitumen samples. While the HiMA binder had a higher softening point temperature (30 °C above) compared to the PmB as reported in Table 1, its viscosity is not as much higher as it could be expected, at equi-viscosity the difference in temperature is only 10 °C. This is mostly due to the nature of the high vinyl content and low molecular weight SBS polymer used. In order to compare the bitumen at equi-viscosity, the temperature for the PmB and the HiMA binder should be respectively about +35 °C and +45 °C higher than for the 50/70 bitumen.

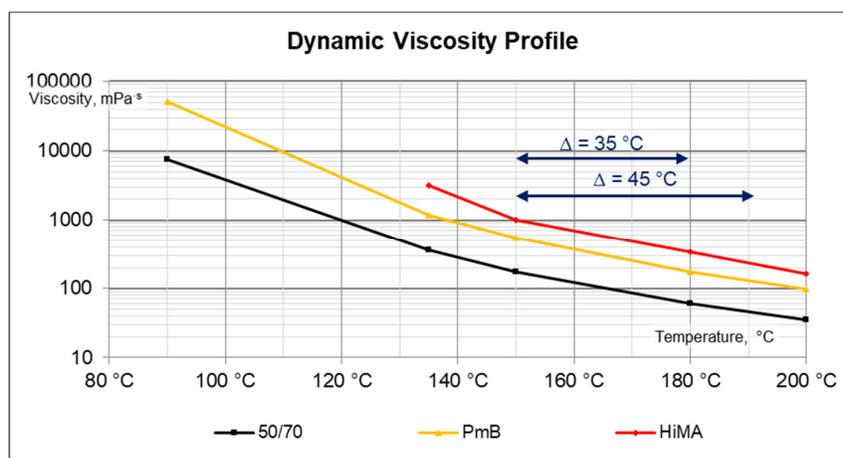


Figure 2. Brookfield dynamic viscosity of the three bitumen

3.2 Fourier Transform Infra-Red spectrometry

In addition to physical properties, the chemical composition of the three binders was characterised using FTIR in ATR mode. This is a quick and easy way to identify and track the presence of SBS polymer. Figure 3 displays the FTIR spectrum in the range of 1800 to 600 cm^{-1} wavelength. For both, the PmB and the HiMA, a peak at 970 cm^{-1} can be observed as typical peak for Butadiene. And for the HiMA, an additional peak at 910 cm^{-1} is visible as for the vinyl group. It is also worth to notice that for the PmB, a specific peak around 1700 cm^{-1} can be observed relevant to the ketone group. The latter is most likely a characteristic peak corresponding to the used base bitumen.

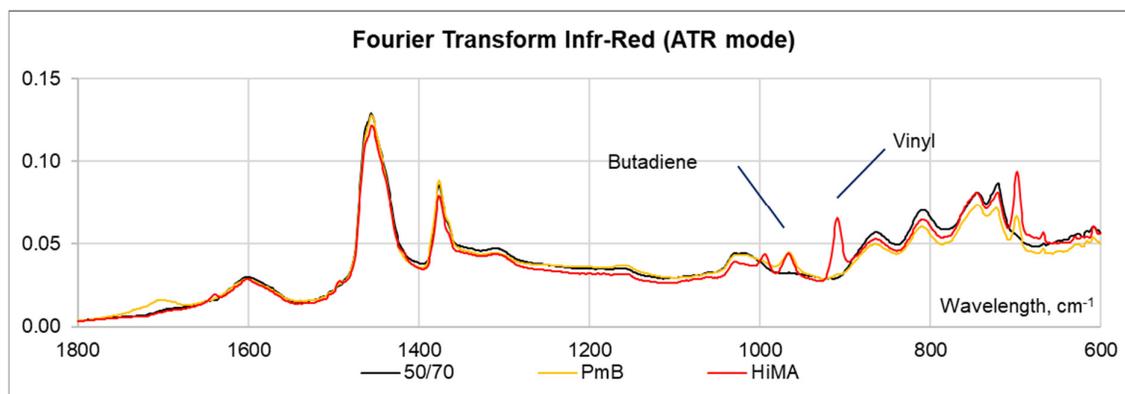


Figure 3. FTIR spectrometry for the three original binders

3.3 Volatile Organic Compounds

For Volatile Organic Compounds, the analysis was made directly from the GC-MS spectrum between 41 and 350 m/z . VOCs were recorded in three families, Alkanes, Monocycloparaffins and Alkyl-benzenes. Knowing the m/z ratio for each species, it is possible to extract them from the total mass chromatogram. The m/z ratio can be found in library and literature [5] [11]. Table 2 shows the different ions peaks considered for each family. Since the peak area is proportional to the number of ions analysed, it enables, by integrating the total peak area, to quantify the emission for the given species. These peak areas are related to the volume of bitumen and the headspace volume. In the case of the experiment, the peak areas were for 3 g of bitumen for a headspace volume of 0.02 L, the us the emitted VOCs are related to peak area $\times 3\text{g}/0.02\text{L}$.

Table 2. Fragments ratios of the recorded VOC

Families	Fragments, m/z (amu)
Alkanes	57+85+71
Monocycloparaffins	67+68+69, 81+82+83, 96+97,
Alkyl-benzenes	91+92, 105+106, 119+120, 133+134, 147+148

The peak area for total and extracted VOC ions were integrated and recorded. The results are presented as the total area for each family. Figure 4 shows the total VOC as integrated for the three families over temperature. To make the reading easier the VOC peak area are reported in logarithmic scale. The errors bars are for the two replicate values. The values

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can be considered as significantly different. As expected, the higher the temperature, the higher the VOC is. The three lines followed similar trend, for every 20 °C the total VOC is increased by a factor of 2 (varying between 1.1 and 2.6 precisely). The PmB had the lowest total VOC in a factor of 10 to 20 times lower as compared to the neat bitumen. For the HiMA binder in a factor of 2 to 3.6 lower than neat bitumen. While the HiMA binder was made from the reference neat bitumen 50/70, the PmB was based on a different bitumen source. This may explain the significantly lower emission. Overall the SBS polymer modified bitumen showed lower emission for VOC as compared to neat bitumen at a given temperature.

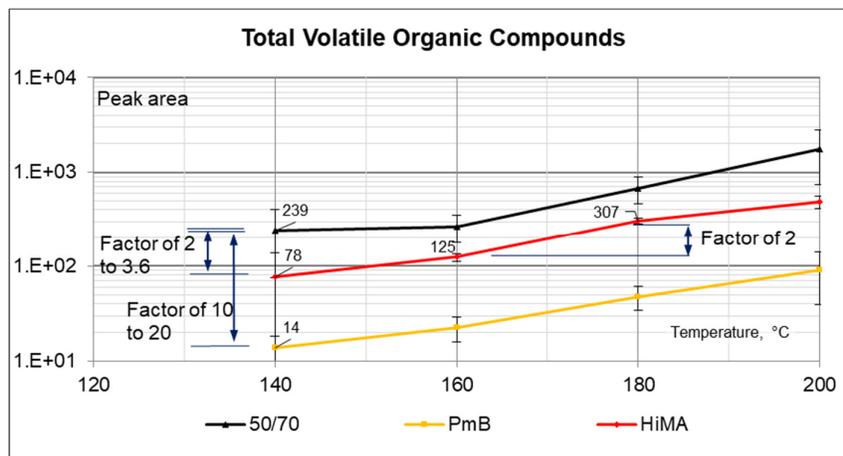


Figure 4. Total VOC peak area vs. temperature for the three bitumen

Figure 5 displays the breakdown of the VOC peak area (in log scale) by families between the Alkanes, the Monocycloparaffins and the Alkyl-benzenes. The three families are equally balanced in terms of peak area except for the PmB which displayed a relative lower Alkyl-benzenes. This may come from the difference of the base bitumen as compared to the HiMA for which the reference 50/70 neat bitumen was used. At comparing like with like between the neat 50/70 bitumen and the HiMA binder, the reduction in intensity for the three families is similar by a factor of 2.5 up to 3.4 for the alkyl-benzenes.

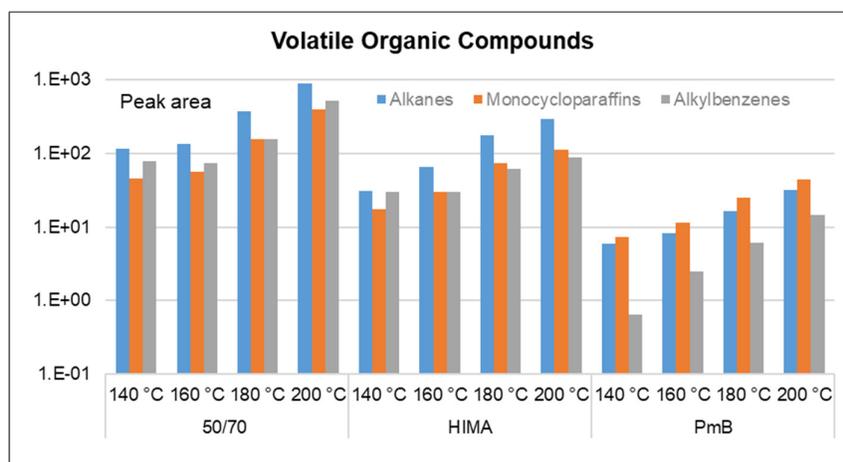


Figure 5. Individual VOC peak area for the three binders at the four temperatures

3.4 Polycyclic Aromatic Hydrocarbons

Polycyclic Aromatic Hydrocarbons were determined using an acquisition mode performed in multiple reaction monitoring (MRM). Two transitions were monitored for each analyte, one for quantification and the other for confirmation. For control and data analysis, GCMS Postrun Analysis was used. The concentration of each PAH was recorded in ng in the head space volume which was 0.02 l. Those concentrations were normalised by the weight of the bitumen sample, which was 3 g, in order to have more absolute values.

Figure 6 reports the total PAH normalised concentration for the three binders vs. temperature as expressed in ng per g of bitumen. To facilitate the reading a logarithmic scale was used. The error bars are for the two replicate values. Considering the two replicate results, the values can be considered as significantly different. Similar to the VOC, the concentration increased with temperature in average by a factor of 2 for every 20 °C. The PmB had the least total PAH in a factor of 8 E&E Congress 2020 – 7th Eurasphalt & Eurobitume Congress – 12-14 May 2020, Madrid Spain
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to 20 times lower as compared to the neat bitumen. For the HiMA binder in a factor of 2 (between 1.7 and 2.7) lower than the neat bitumen. Again the base bitumen used for the PmB was not the 50/70 and thus may explain the difference in total PAH recorded. Overall the SBS polymer modified bitumen showed lower level of detected PAH as compared to neat bitumen.

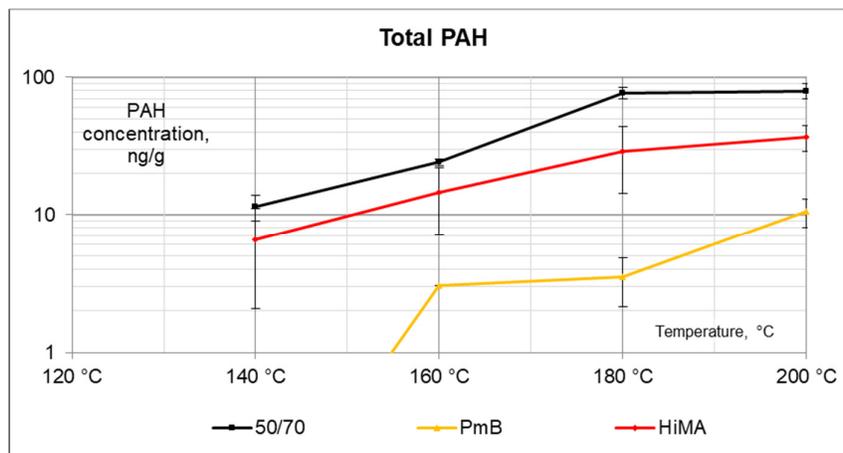


Figure 6. Total PAH concentration vs. temperature for the three bitumen

Figure 7 shows the breakdown of the different PAH recorded during the experiment (in linear scale). From the 16 usual PHAs considered only 7 were detected, the others being below the detection limits of the method. The graph on the left side shows the total PAH detected. The naphthalene was the highest contributor of the total detected PAHs emission for the 50/70 bitumen and the HiMA binder, respectively 93 % to 65 %. However it was almost not detected in the PmB. The graph on right shows the PAHs excluding the naphthalene for the remaining 6 other detected PAHs at a fixed temperature of 180 °C. Most of them were light PAHs and no benzo(a)pyrene was detected. Again the PmB did not exhibit a high level of detected PAH and the HiMA as compared to the neat 50/70 bitumen had lower level.

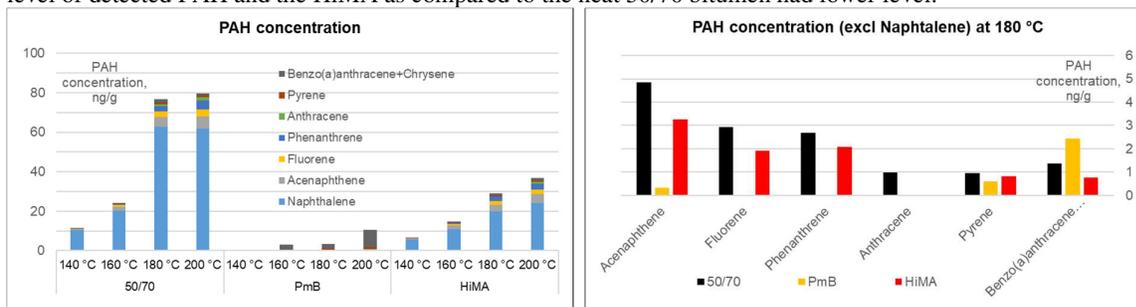


Figure 7. PAH concentration for the three bitumen at four temperatures

4 DISCUSSION

Considering both VOC and PAH, with temperature increase the total recorded emissions increased, by around a factor of 2 every 20 °C. At the same time bitumen physical properties are temperature dependant. The higher the temperature, the lower the viscosity is. During processing of the PmB and later manufacturing asphalt mix with PmB, the temperature is adjusted according to the viscosity. As example, at the asphalt mix plant, the recommended temperature for mixing is defined for a viscosity of about 200 mPas⁻¹ [12]. Thus when comparing fumes emissions of bitumen having different viscosity, it is worth to analyse at an equi-viscosity temperature. Figure 8 displays the total VOC vs. the viscosity for the three binders at the different temperatures, from the lowest, 140 °C on the right side, to the highest 200 °C on the left side. As a result of temperature dependency, the lower the viscosity, the higher the temperature is, and thus the higher the emissions are. However the three bitumen did not show the same level of emission. Overall the neat bitumen 50/70 emitted more than the PmB and the HiMA.

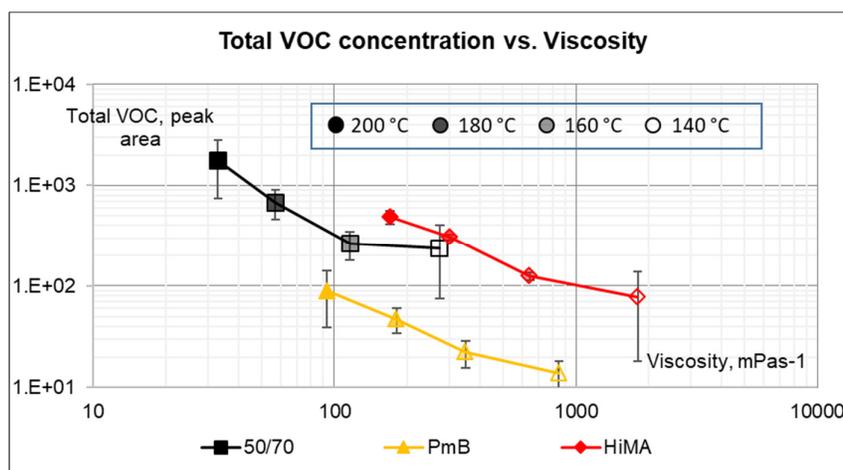


Figure 8. Total VOC peak area vs. viscosity for the three bitumen

As the HiMA binder was based on the 50/70 neat bitumen, it is possible to assess the relative impact of the modification with SBS. For the same temperature, while the viscosity was increased, the emissions, either recorded for the total VOC or total PAH decreased by a factor of 2, reduced by 50%. One possible explanation could be an azeotrope effect. In the case of a blend of two components, the boiling temperature of a component (reference) can be modified by the addition of another component (additive). However this should be further investigated to have a clear understanding on the phenomenon.

For the PmB, the real impact should depend as well from the nature of the base bitumen used to make it. The total emission of bitumen may vary to some extent from bitumen to bitumen, from grade to grade, and from production process to production process.

5 CONCLUSION

The study focused on evaluation of the impact of SBS polymer modification of bitumen on fume emissions. It was conducted in the laboratory on binder, comparing a neat bitumen with two different SBS PmB, a normal one and a highly modified one. A new approach to detect and quantify the Volatile Organic Compounds and the Polycyclic Aromatic Hydrocarbons was used with Thermal Desorption Gas Chromatography Triple Quadrupole Mass Spectrometry after Head Space Stir Bar Sensitive Extraction (HSBSE). The assessment was made at four temperatures from 140 °C to 200 °C, at every 20 °C.

Heavy PAH was not detected during the experiment, either for the neat bitumen or the modified bitumen. Similarly to the VOC the two PmB showed lower detected PAH levels as compared to the neat bitumen for the same temperature. Furthermore comparing the neat bitumen and the modified HiMA, the SBS polymer did not add any known harmful PAH to the binder.

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Even when considering the impact of temperature on the viscosity and indirectly on the level of emissions, the SBS polymer modification did not show significant increase of VOC nor PAH as it may be considered for the processing of the PmB itself or manufacturing and application of asphalt mix.

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Annex

Erratum annex

5. CONCLUSION

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The level of VOC as recorded during the experiment was proportional to the temperature for the three bitumen with a factor of 2 every 20 °C. However, the PmB had the lowest level and the HiMA which was made with the neat reference bitumen was lower than this.

Heavy PAH was not detected during the experiment, either for the neat bitumen or the modified bitumen. Similarly to the VOC the two PmB showed lower detected PAH levels as compared to the neat bitumen for the same temperature. Furthermore comparing the neat bitumen and the modified HiMA, the SBS polymer did not add any known harmful PAH to the binder.

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