Analysis of Bitumen and PmB using Fluorescence Spectroscopy and Microscopy

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Abstract Physicochemical characterization of bitumen and polymer modified bitumen has been a research subject for the last decades. Various microscopic and spectroscopic techniques have been used to unravel the bitumen microstructure and to establish the link to its chemical composition. Over the years, the usage of bitumen has risen. This is particularly true for polymer modified bitumen (PmB) which has primarily been blended with styrene-butadiene-styrene (SBS) polymers. Since there is a demand for homogeneous blending and an overall quality control, suitable methods need to be developed. Fluorescence spectroscopy and fluorescence microscopy were found useful tools to achieve these goals. This paper focuses on the analysis of a 160/220 pen-graded base bitumen and SBS modified bitumen. Complementary analysis of specific surfaces enables a better understanding of chemical composition (spectroscopic information) and microstructure (microscopy).

Keywords bitumen, polymer modified bitumen, fluorescence, spectroscopy, microscopy

1 Introduction

The characterization and chemical analysis of bitumen, a product of the crude oil refinery, is challenging due to its complex composition and microstructure. Polarity chromatography divides the hydrocarbon composition into four fractions (Corbett 1969). These so-called SARA fractions (saturates, aromatics, resins, and asphaltenes) are usually separated according to the ASTM D-4124 standard (Lesueur 2009). The characterization of bitumen and its polymer modified products has involved various microscopic and spectroscopic techniques. Beside FTIR spectroscopy (Hofko, Alavi et al. 2017, Weigel and Stephan 2017, Hofko, Porot et al. 2018), also fluorescence spectroscopy provides molecular information. Previous results from our group show characteristic fluorescence spectra of pure bitumen and those of its four SARA fractions (Handle, Fussl et al. 2016, Grossegger, Grothe et al. 2018). The origin of the fluorescence signals mainly lies within the aromatic and the resin fractions. While fluorescence microscopy is a common technique in bitumen and PmB analysis, fluorescence spectroscopy has not been used to the same extent. Concerning spectroscopy, the following questions arises: How can we obtain consistent results and good reproducibility? What differentiates pure bitumen from polymer modified samples? Which spectroscopic and morphological changes are caused by the addition of the polymer? Will microscopy help to understand these spectroscopic results?

For these aims conventional incident light fluorescence microscopy was chosen. Even at low lateral resolution valuable microstructural features can be resolved which help to interpret the spectra. Previous studies on SBS modified bitumen have already shown promising results regarding the microstructure (Sengoz and Isikyakar 2008).

Here we suggest a preparation and measurement routine for fluorescence spectroscopic analysis on pure bitumen and an approach to analyze the surface of SBS modified bitumen by combining spectroscopy and microscopy.

2 Materials and Methods

2.1 Materials

This study was performed using a 160/220 pen-graded base bitumen, the pure SBS polymer and the resulting SBS modified bitumen (blended with base bitumen and 11% SBS).

2.2 Methods and Procedures

The 160/220 bitumen samples were prepared using a specific preparation procedure that leaves the sample surfaces at a minimum exposure time to air and therefore at a low level of oxidation (s. Fig. 1). A small quantity of bitumen (0.55 – 0.65 g) was heated up to 100°C in a silicone mold (volume: 0,51 cm^3). After heating for a maximum of 10 minutes, the liquid sample was covered with a glass slide and allowed to cool down to room temperature for 20 minutes. Once cooled down, the silicone mold was removed, and the fresh surface was stored under ambient atmosphere for 3 hours before it was used for fluorescence spectroscopic analysis.

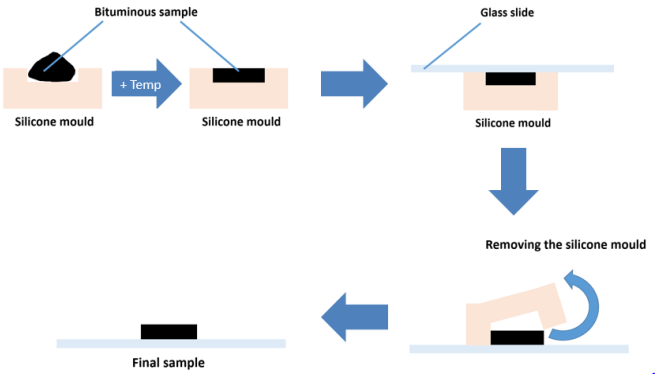

Fig. 1 Scheme of the bituminous sample preparation

The pure SBS pellets were ground using a commercial grinder and liquid nitrogen. The resulting powder was filled in a quartz cuvette and measured directly with the spectrometer.

The SBS modified bitumen samples were heated up to 180°C, homogenized and poured in a siliconized foil template that ran through a rolling machine, creating a 5 mm thick PmB sample. Removing one side of the siliconized foil allowed the application onto a glass slide, removing the second side made analysis possible.

For the fluorescence spectroscopic measurements, an Edinburgh Instruments FPS920 photoluminescence spectroscopy setup was used. This setup contains a XE900 Xenon Arc Lamp (500W) as an illumination source, double Czerny-Turner monochromators (type TMS300) at both excitation and emission arms as well as a S900 single-photon photomultiplier (type R928) as the detector. The setup was used in excitation mode (ex. wavelength 240 – 500 nm, em. wavelength 525 nm).

The fluorescence microscope setup consists of a Nikon Eclipse 50i, a 30 W halogen light source, a color-digital camera (DS-Fl1c) and an epifluorescence unit with a excitation filter at 400-440 nm, an dichroic mirror at 455 nm and a emission filter at 470 nm. Two different objectives with magnification of 10x and 100x were used.

3 Results and Discussion

3.1 Reproducibility of Fluorescence Spectroscopy

The fluorescence spectroscopic analysis on the 160/220 base bitumen showed good reproducibility when using the preparation procedure and parameters presented. To check the repeatability of the device itself, a 160/220 base bitumen was measured consecutively 25 times. The resulting fluorescence excitation scan on the left side of Fig. 2 shows a sufficient repeatability, indicating no changes on the sample surface caused by the device itself (e.g. light beam).

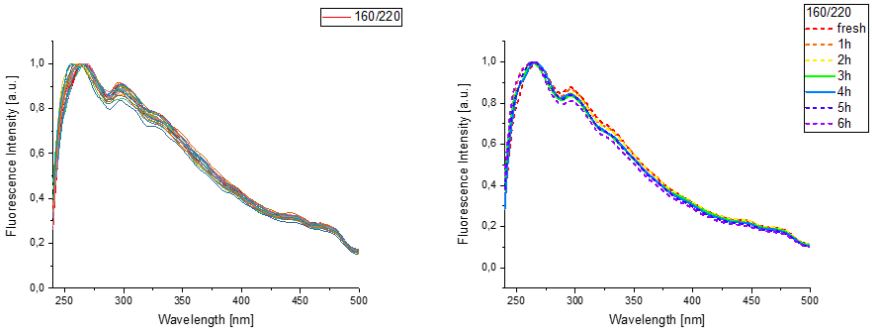

Fig. 2 Fluorescence excitation spectra**:** Repeatability (left) and time dependency (right) of 160/220 bitumen

Applying statistic evaluation on three significant characteristics of the spectrum (s. Tab. 1) one can see that the maximum percentage difference is given at 300 nm with ± 3.9%. This suggests that the maximum at 300 nm should be selected for verification when looking at general measurement repeatability of a 160/220 bitumen.

Tab. 1 Statistic evaluation from 25 repeats at three different wavelengths

Wavelength [nm]	Mean		Confidence interval
264	0,9956	±	0,0090
300	0,8809	±	0,0388
480	0,2531	±	0,0146

Due to low viscosity of the 160/220 bitumen the problem regarding sample stability arises. After a short period, the sample starts to flow in all directions, which changes its surface. Therefore, additional time dependent studies were conducted that revealed that the best reproducibility is obtained when conducting measurements within 3-4 hours after preparation (s. right side of Fig. 2).

3.2 SBS modified bitumen

Fig. 3 shows the fluorescence microscopic observations from the SBS modified bitumen samples. The two different magnifications outline a trend in homogeneity. While sample 1 has a rather fine microstructure, sample 2 and 3 show a coarse-grained microstructure, which can only be observed at higher magnification (100x). Sample 4 shows a significant lower degree of mixing, resulting in a bright continuous area and a dark part that has not been observed in samples 1, 2 and 3. We assume that the bright continuous area is an agglomerated polymer phase.

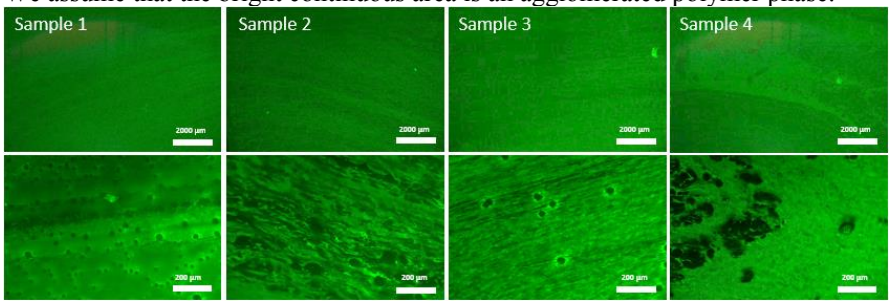

Fig. 3 Surface of the SBS modified bitumen in 10x (upper) and 100x (lower) magnification

These microscopic observations can be correlated with the spectroscopic features on the left side in Fig. 4. The surface of sample 4 contains partially unmixed SBS, which shows a higher fluorescence intensity compared to pure bitumen or a well-blended PmB. This results in a strong signal around 350 nm. The spectrum of sample 1indicates that once a fine microstructure is obtained, the signals from bitumen and SBS contribute almost equally to the final spectrum. As a result of spectroscopy and microscopy from sample 2 and 3, the coarse-grained microstructure has a stronger SBS signal. Hence, we can conclude that the extent of visible microstructures in microscopy correlates with the respective SBS signal in the fluorescence spectra.

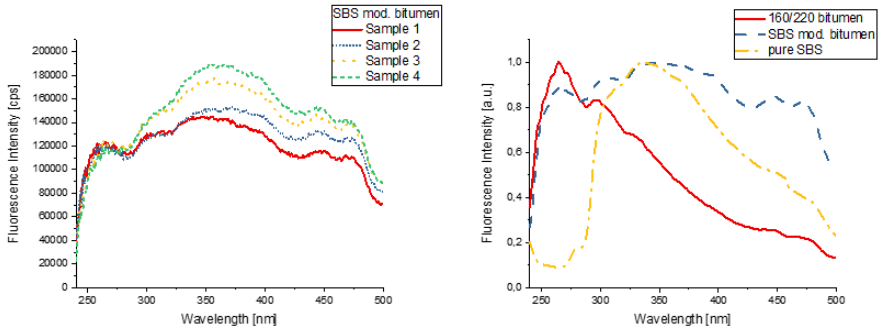

Fig. 4 Fluorescence excitation scans of the SBS modified bitumen samples (left) and the comparison to its 160/220 base bitumen and pure SBS (right)

The right side in Fig. 4 gives evidence that the bitumen exhibits local maxima at 264 and 300 nm and three shoulders at 350, 400 and 480 nm. The pure SBS excels its local maximum at 350 nm. The resulting spectrum of the SBS modified bitumen (sample 1) shows good accordance with the spectra of its pure components.

Hence, the characteristic signals from the two components add up nicely to the resulting PmB spectrum. This gives valuable information about the homogeneity of the sample and the involved blending procedure parameters.

4 Conclusion

The results lead to the conclusion that fluorescence spectroscopy is a viable method for analyzing base bitumen. Sufficient reproducibility is given by using the presented sample preparation technique and the suggested storage time of 3-4 hours before conducting the measurement. For the PmB samples, spectroscopic reproducibility is far more complex, since the resulting information is linked to the SBS concentration on the surface and the homogeneity of the sample. Hence, microscopic monitoring is necessary. The gathered spectroscopic results show good accordance from the comparison to its pure components and will certainly contribute to the task of characterizing polymer modified bitumen.

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