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Morphological investigation of SBS modified bitumen by innovative microscopies: AFM and CLSM

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Highlights

- Morphological characteristics were investigated by AFM and CLSM
- Polymer amount directly effects the morphological characteristics of the PMB
- Topographic and phase properties of the PMB samples were obtained by using AFM
- The dispersion of SBS within the PMB is evaluated by CLSM

Abstract

Styrene-Butadiene-Styrene (SBS) is one of the most commonly used copolymer in the PMB production. SBS modification results in different material characteristics on the neat bitumen depending on the SBS type and of course the amount of the SBS used in the modification. Within the scope of this study, morphological characterisation of SBS modified samples involving different amount of SBS copolymer (4%, 5% and 6%) were examined by using innovative microscopies as AFM and CLSM. The topographic and phase properties of the PMB samples were obtained by using AFM and the dispersion and interaction of SBS copolymer with the bitumen were interpreted based on the images obtained by CLSM. As a result it was concluded that, the amount of the copolymer used in the modification process directly effects the morphological properties of the final product (PMB).

Information

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1. Introduction

Bitumen can be modified by different types of polymer by considering the preferred properties of final product, which is called as Polymer modified bitumen (PMB) [1]. Styrene-Butadiene-Styrene (SBS), Ethylene-Vinyl-Acetate (EVA) or Polypropylene (PP) are among the examples of the polymers that can be used with bitumen. The modification mechanism can be explained as follow: polymer absorbs the oily compounds of bitumen as aromatics and saturates. Beside the type of the polymer used in the modification production conditions of PMB are also effects the characteristics of the sample [2-7].

Widely used polymers is categorized into two groups as plastomers and thermoplastic elastomers, and within the elastomers SBS is the most commonly used copolymer in the industry. SBS modification improves low temperature cracking and rutting resistance of the neat bitumen [8-11]. SBS copolymers are composed of styrene and butadiene triblock chains and it absorbs the maltenes within the bitumen and get swollen. Depending on the similar solubility parameters, PS blocks are swollen by aromatics while the PB blocks are swollen by saturates [12, 13]. The polystyrene (PS) end-block becomes physically cross-linked, forming a three-dimensional network, on the other hand, the polybutadiene (PB) midblock provides the material's elasticity.

SBS modification results in different material characteristics on the neat bitumen depending on the SBS type and of course the amount of the SBS used in the modification. Thermal, rheological, structural, mechanical and physical improvements are yielded by the increase of the SBS amount within the PMB samples. Additionally, morphological changes, which is directly related with the performance of the sample, can be observed depending on the SBS amount used in the modification. Optical microscopy, Scanning electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Atomic Force Microscopy (AFM) and Confocal Laser Scanning Microscopy (CLSM) are some of the microscopies, which

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can be used to evaluate the bitumen morphological characteristics. Within the scope of this study, morphological properties of SBS modified samples involving different amount of SBS copolymer (4, 5 and 6%) were examined by using innovative microscopies as AFM and CLSM.

2. Experimental Studies

2.1. Materials

The neat bitumen with penetration grade within the range 50/70, was used as the neat bitumen, provided by the Turkish Petroleum Refinery Corporation, Aliaga/Izmir terminal. D 1192 SBS copolymer was obtained from Kraton® Polymers/Netherland. Table 1 presents the conventional test results of the neat bitumen used in the study.

Table 1. Properties of the neat bitumen.

Test	Specification	Results	Specification Limits
Penetration (25ºC; 0.1 mm)	ASTM D5-97	61	50–70
Softening Point (ºC)	ASTM D36-95	48.3	46–54
Viscosity at (135ºC), Pa.s	ASTM D4402-06	0.415	-

Within the scope of the study, PMB samples containing 5±1% SBS were examined, as it was aimed to reveal the effect of the change in the SBS ratio within the mixture. PMB samples were produced with bitumen and SBS copolymer in different ratios (4, 5 and 6%) under constant mixing conditions (temperature 175 ± 5°C, mixing time 30 min and mixing speed 2000 rpm).

2.2. Methods

2.2.1. Morphological Investigations by AFM

AFM enables the characterization of the neat bitumen and PMB samples in terms of morphological images. By AFM investigations, topographic features of the bitumen samples can be evaluated at the nanometer-scale. Moreover, bitumen's micro mechanical behavior, as micro friction or phase separation etc. can be studied as well [14]. Stiffness, adhesive behavior etc. are among the different properties of bitumen that depends on the phase separation which can be obtained by AFM [15-17]. Therefore, it can be said that, AFM investigations predict the performance of the bitumen. In addition, one of the most important and efficient advantage of AFM is the sample preparation method, which is comparatively simple than the other microscopies and it allows to operate under ambient conditions.

Bitumen compounds (saturates, aromatics, resins and asphaltene) provides different morphological images under AFM. The characteristic morphology of the neat bitumen involves catana phase, peri-phase, para-phase and bee structures [18]. Basically, bee structure consists of black and white striped stands, describing the areas of higher and lower stiffness than the surrounding area. It can be explained as the result of wrinkling of very thin surface films [19, 20]. In the previous studies, some researchers attributed bee structure to asphaltene [18, 21, 22, 23].

Topography and the phase images of PMB samples were obtained by Nanoscope IIIa, Bruker AFM (Santa Barbara, CA, USA) by using tapping mode attached rectangular V shaped cantilevers (OTR8, Bruker) with a nominal spring constant of 0.57 N/m.

2.2.2. Morphological Investigations by CLSM

CLSM enables to study extremely localized fluorescence emissions and it has many advantages as improved signal strength, narrower focus etc. The scanning technique of CLSM tolerates spatial resolution. Additionally, the sample preparation method for CLSM is trivial [24, 25]. It is possible to examine the compatibility, the dispersion and the network formation of the polymer within the PMB sample by CLSM [24, 26].

The morphology of the SBS modified PMB samples was obtained with a HORIBA Lab Ram (Tokyo, Japan). Spectrometer at 488 nm excitation and a 600 l/mm grating was set for the investigation. All spectrum were collected using a X50 Long working distance objective at 1% and are normalized for acquisition time. The fluorescence intensities were collected between 600-650 nm. DuoScan mirrors were used for collection, at laser power 3.5 % using a X5 objective.

3. Experimental Results

3.1. Morphological results by AFM investigations

Morphological characteristics of PMB samples involving different amount of SBS copolymer were investigated by evaluating the phase and topography images. Figure 1 presents the phase separations of the samples, while Figure 2 depicts the topographical images, where the bee structures can be observed.

The phase images of the PMB sample consists of two main phases as dispersed phase and the continuous phase. The continuous phase, which appears as the dark colour in the AFM phase images, is the light oil composed of aromatic and saturated components of bitumen. As can be seen in Figure 1, the increase on the SBS content within the PMB samples yielded the increase on the dispersed phase and the decrease on the continuous phase. This can be explained with the interaction between the SBS and the oily fractions of the colloidal structure. SBS absorbs the saturates and aromatics of the bitumen, which results in the decreased amount of these compounds. The more

SBS amount during the modification requires more amount of saturates and aromatics to be absorbed. As a result, the sample containing 4% SBS copolymer had the highest continuous phase, while 6% SBS had the lowest one.

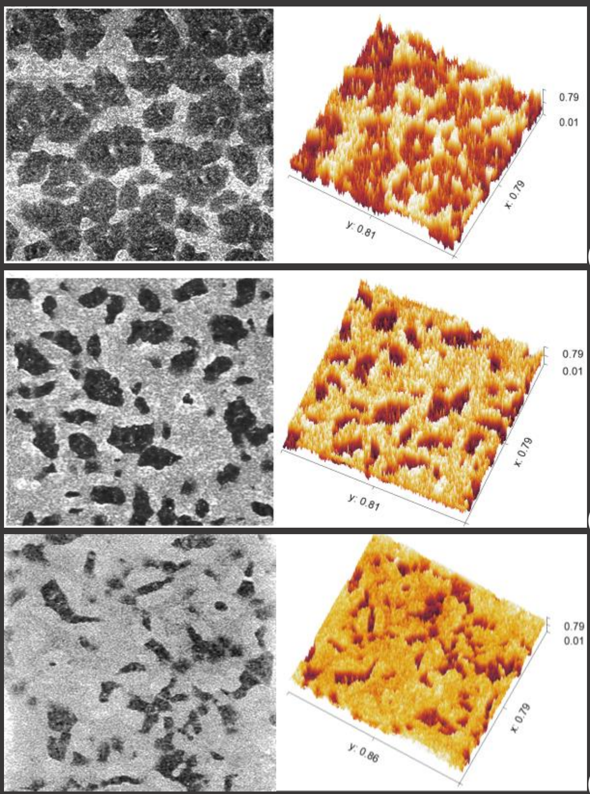

Figure 1. The phase separation images of the PMB samples involving different amount of SBS copolymer; (a) 4% SBS modified bitumen (b) 5% SBS modified bitumen (c) 6% SBS modified bitumen

According to the Figure 2, increasing the SBS content from 4% to 5% caused the increased amount and length of the bee structure. Therefore, it is possible to say that the total area of the bee structure within the sample was increased as well. On the other hand, for the samples having the 6% SBS content had smaller sized bee structures. This can be explained with that, 5% SBS content is the optimum polymer amount for the bitumen used in the study (50/70 penetration grade bitumen). This can be also related with the modification mechanism of SBS copolymer and bitumen. When there is no enough saturates and aromatics amount to be absorbed for the SBS content, the dispersion of the bitumen compounds is directly affected. In this study, it might be said that, 6% SBS modifications affected the components of the bitumen and so does the appearance of the bee structure, which is correlated with the asphaltene compounds. Similar results were found in the study where the effects of different amount (4, 5 and 6%) of SBS modification on the morphological characteristics of the PMB samples were investigated by Scanning electron microscopy (SEM) and optical microscopy [27].

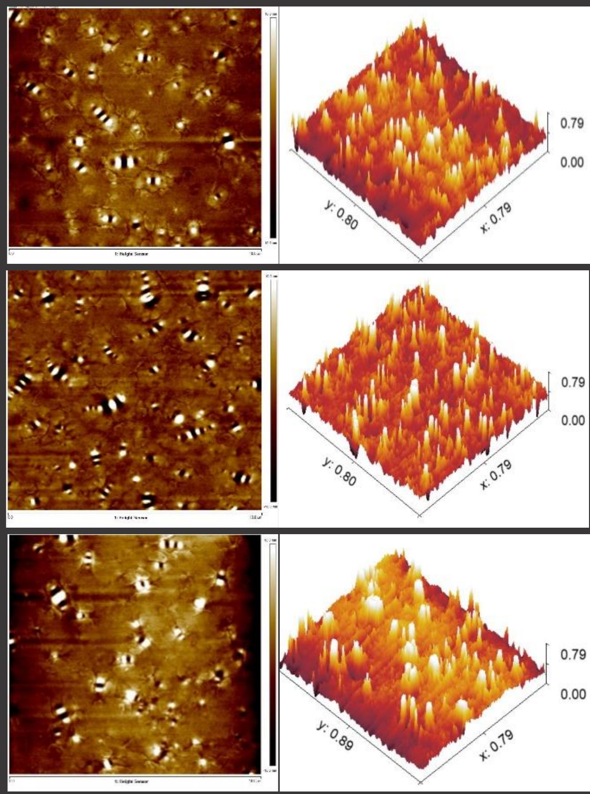

Figure 2. Topographic images of the PMB samples involving different amount of SBS copolymer; (a) 4% SBS modified bitumen (b) 5% SBS modified bitumen (c) 6% SBS modified bitumen

Another evaluation that can be done by Figure 2 is the roughness of the bee structures. By the increase of the SBS content (from 4% to 5%), the roughness of the sample is initially increased however, when the SBS content was chosen as 6%, the roughness of the sample is decreased. This is clearer on the 3D images of the samples.

3.2. Morphological results by CLSM investigations

Another morphological investigation of SBS modified samples was achieved by using CLSM. In Figure 3, morphological images and 3D color maps, which presents the SBS dispersion and the fluorescence intensities of the PMB samples are presented.

Previous studies have shown that, polymer dispersion can be evaluated by morphological images obtained by Transmission electron microscopy (TEM), optical microscopy etc. [26, 28]. In the study of Yan et al., the SBS dispersion were investigated with the fluorescent yellow light emission by the swollen polymer phase. As an innovative technology, the dispersion of the SBS copolymer within the PMB matrix can also be seen under CLSM depending on the fluorescence reflection properties.

The increase on the SBS amount yielded the increased dispersion of the fluorescence reflection (can be seen in blue phase) is obtained in Figure 3. Also, the level of the fluorescence reflection, in other term the intensity of the fluorescence phase, is affected by interaction of the saturate and aromatic compounds of the bitumen. In 3D illustrations of CLSM images, the height of the image is related with the intensities of the fluorescence part. It is worth to mention that, the samples involving 4% and 5% SBS copolymer, the intensities did not bring any significant differences. However, in Figure 3.c, the intensity of the fluorescence phase was decreased. Therefore it is possible to say that, the interaction between the SBS and the bitumen is affected for the PMB sample having 6% SBS. It can be interpreted as the aromatic and saturate amount of the bitumen was not efficient enough for modification with 6% SBS amount as it was for 4% and 5%.

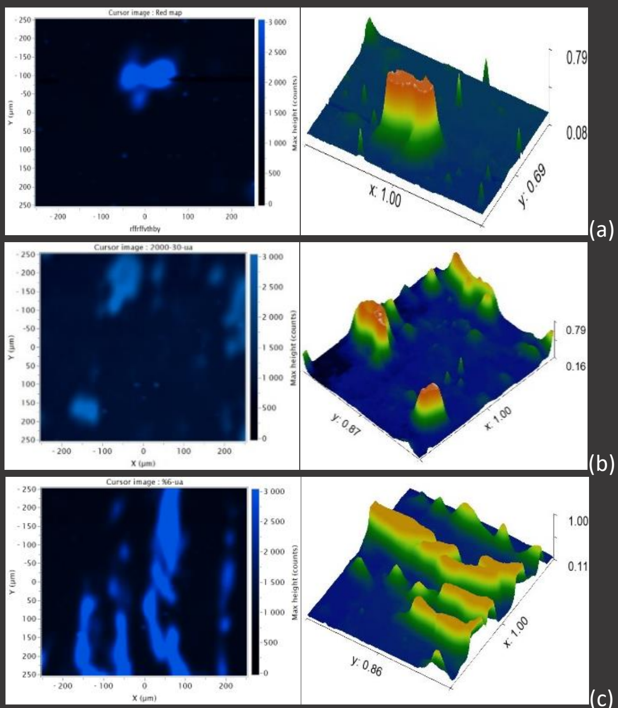

Figure 3. 3D colour maps of PMB samples involving different amount of SBS copolymer; (a) 4% SBS modified bitumen (b) 5% SBS modified bitumen (c) 6% SBS modified bitumen

4. Conclusions and Recommendation

Within the scope of the paper, the effects of different amount of SBS utilization (4, 5 and 6%) for the PMB modification was studied by investigating the morphological characteristics of the produced samples. Morphological properties were evaluated by using innovative microscopies as AFM and CLSM. The topographic and phase properties of the PMB samples were obtained by using AFM and the dispersion and interaction of SBS copolymer with the bitumen were interpreted based on the images obtained by CLSM investigations. The increase on the SBS content within the PMB samples yielded the increase on the dispersed phase and the decrease on the continuous phase. Additionally, increasing SBS content (from 4% to 5%) provided increased amount and length of bee-structure. However, the amount and the length of the bee-structure were decreased when the 6% SBS was utilized for the modification. Increasing the SBS amount yielded better dispersion but decreased intensity levels of the fluorescence reflection.

This study investigates the SBS modification effects on the morphological characteristics of the bitumen, however, the effects on the performance (aging resistance, temperature susceptibility, deformation resistance etc.) of the sample is also very important. For this reason, the effects on the performance, moreover the correlation between the performance and the morphological characteristics of SBS modified samples should be obtained and discussed in the further studies.

Declaration of Interest Statement

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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