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Research Article

EXAMINATION OF STORAGE STABILITY BEHAVIOUR OF POLYMER MODIFIED BITUMEN INVOLVING NANOCLAY

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ABSTRACT
In recent years, the use of nanomaterials has become widespread in the modification of bitumen due to developing nanotechnology. It has been observed that the physical and rheological properties of base and modified bitumens have improved as a result of the use of nanomaterials. In addition, the use of nanomaterials for the solution of the phase separation problem seen for the polymer modified bitumens had a positive effect. In this study, the effect of adding nanoclay into the polymer modified bitumen samples on storage stability was investigated. Styrene-Butadiene-Styrene (SBS), which is a widely used polymer type and Halloysite is a nanoclay type were determined as additives. The additive ratios were determined as 3%, 5% for SBS and 2%, 4% for Halloysite according to the studies in the literature. Modified bitumen samples were produced by high shear mixer. The polymer was added into the base bitumen then Halloysite was added in to the polymer modified bitumen during the production process. After the modified bitumen production, thin section samples were taken from each sample and examined under a microscope and the samples were subjected to the storage stability test. According to the results of the experiments, it was observed that Halloysite additive improves storage stability. However, this improvement is more effective in low polymer percentage. As the percentage of polymer increases, the improvement effect decreases, phase separation increases.

Keywords: *Modified Bitumen, Polymer, Nanoclay, Storage Stability, Phase Separation*

1. INTRODUCTION

Many deformations such as permanent deformations, fatigue cracks and low temperature cracks by the effect of traffic, climate and environmental conditions are occurred on bituminous hot mixtures over time. The bituminous mixture prepared and laid on the road is required to provide properties such as stability, durability, flexibility, fatigue resistance, slip resistance, impermeability and operability (Schaur *et al.*, 2017). The most commonly used method for these deformations is the modification of bituminous binders with additives.

The modification is the process of mixing the various additives in the bitumen in specific ratios and conditions in order to increase the performance of the bitumen or mixture and prevent deformations. The modification process can generally be carried out by adding the admixture to the bitumen prior to the addition of modified bitumen or by adding the additive directly to the mixture in the asphalt plant to obtain a modified mixture (Eskandarsefat *et al.*, 2019). The most common additive type for modification is polymers.The use of polymeric type modifier additives has been used to improve the final performance of the mixture produced with bitumen by improving the temperature sensitivity and physical properties of the bitumen at high and low temperatures (Jahromi *et al.*, 2009). One of the most widely used polymer among these different is Styrene-butadiene-styrene (SBS) from the elastomer group.The polymer-resistant component is polystyrene end blocks, and the middle blocks provide a high degree of flexibility to the material (Vonk *et al.*, 1989). While the quality of the elastomer distribution is affected by a number of factors, the most important of these factors is the amount of cutting (shear force applied) applied by the mixer (Mazurek and Iwański, 2017). When the polymer is added to the hot bitumen, the bitumen rapidly begins to leak into the polymer particles and causes the polymer to dissolve and swelling (Ragni *et al.*, 2018). Polymer modified bituminous mixtures thanks to the modification show high resistance to rutting, thermal cracks, fatigue cracks, aging and temperature sensitivity (Golestani *et al.*, 2012).

However, when the properties of the modified bitumen made with polymer additives were examined, it was seen that negative results were obtained especially in terms of storage stability values and this was related to the incompability resulting from the density difference between bitumen and polymer.Even though performance improvements were made as a result of the modifications, it was seen that especially at high storage temperatures there were separations due to poor bonds between polymer and bitumen(Galooyak *et al.*, 2010; Golestani *et al.*, 2012; Topal *et al.*, 2012).This undesirable situation will be further got worsen by changing climatic conditions and temperatures, ultraviolet lights and aging, due to weakened bonds result of incompatibility (Galooyak *et al.*, 2010).In order to eliminate this density difference, the solution has been started to be used in the modification of nanomaterials with the development of nanotechnology in recent years for the modification of bitumens. Thus, the use of nanomaterials in polymer modified bitumen has been discussed.

Nano materials can be used by themselves as well as using composites together with polymers. Nanocomposites are materials that are formed by dispersing particles of nanometers in a matrix. Nanoclays are also widely used for the production of nano composites, this is because they are easily available and cost-effective.

In this study, Styrene-butadiene-styrene (SBS) as polymer and Halloysite as nanoclay were chosen for modification. Two different ratios were determined for SBS and Halloysite. The morphological structures of modified bitumen samples were examined under fluorescence optical microscope and the phase separation properties were evaluated according to the test results of storage stability test.

2. LABORATORY STUDIES

2.1.Materials

In this study, base bitumen with 50/70 penetration grades bitumen has been obtained from TÜPRAŞ® Aliağa Refinery. In order to characterize original bitumen properties, bitumen test results are presented in Table 1. SBS Kraton® D1101 was chosen as polymer additive. Related to SBS polymer, bulk density is 0.4 kg/dm^3, specific gravity is 0.94 and tensile strength value is 33 MPa. It is a linear block copolymer based on styrene and butadiene with bound styrene of 31% mass (Kraton® 2012). Halloysite was used as nanoclay additive for modification of SBS modified bitumen. A scanning electron microscope (SEM) image of Halloysite is presented in Fig. 1.

Table 1.Original bitumen properties.

Tests	Test Results	Specification limits
Penetration (25°C; 0.1 mm)	65	50-70
Softening point (°C)	54	46-54
Brookfield Viscosity at 135°C (mPa s)	425	-
Brookfield Viscosity at 165°C (mPa s)	113	-

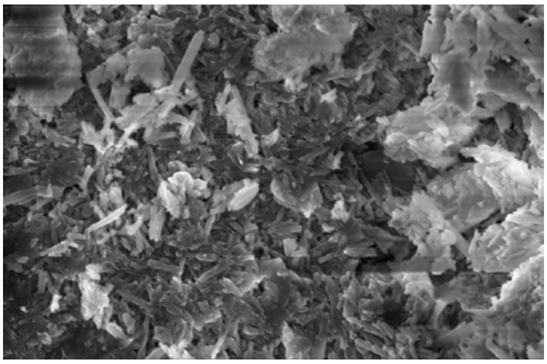

Fig. 1.Sem image of Halloysite nanoclay

The modified bitumen samples were produced with these materials which properties are given above and subjected to morphological structure analysis and storage stability test.

2.1.Preparation of Samples

Base bitumen was heated up to become fluid enough to pour by using of high shear mixer in Fig. 2.

Fig. 2.Modification process byhigh shear mixer

SBS ratios were chosen as 3% and 5%, Halloysite ratios were added as 2% and 4% of the weight of bitumen for experiments. SBS was initially added within the bitumen at 180°C, 2000 rpm 15 minutes. After then Halloysite was mixed with SBS modified bitumen with the same conditions for 45 minutes.

2.3.Analysis of Morphological Structure

Morphological structure analysis helps to evaluate the properties of microstructure between the bitumen and the polymer (Chen*et al.*, 2002).Morphological investigation by fluorescence microscopy is based on the principal of distinctness of base bitumen components with the effect of fluorescent light and accordingly the expansion of polymers (Airey, 2002).

Fig.3.Fluorescence optical microscope

For this analysis, thin section samples were taken and investigated by fluorescence optical microscope in Fig. 3. As a result of this investigation the distribution, quality and morphological structure of additives in base bitumen after production of modified bitumen were determined.

2.4.Storage Stability Test

A modified bitumen sample poured into an aluminum tube is heated vertically to and held at 180°C for 72 hours. The tube is cooled down to room temperature in the upright position and the aluminum tube is divided into three equal parts horizontally. The middle part of the sample is thrown out. The softening point test is conducted for the upper and lower section of the sample. The result of the stability test is assumed to be the difference between softening point values obtained for the upper and lower modified bitumen samples. The softening point difference between the upper and lower parts should not exceed 5°C according to the Modified Bitumen Technical Specifications of General Directorate of Highways (KGM, 2009).

3. RESULTS AND DISCUSSION

After modification process, thin slice samples were taken from all modified bitumen samples. The thin slice samples were investigated under fluorescence optical microscope. Sufficient dispersion should be provided in the samples for obtaining a good image. The samples were kept in the oven at specific temperature and time before microscope investigation to ensure sufficient dispersion. The images taking from samples are illustrated below.

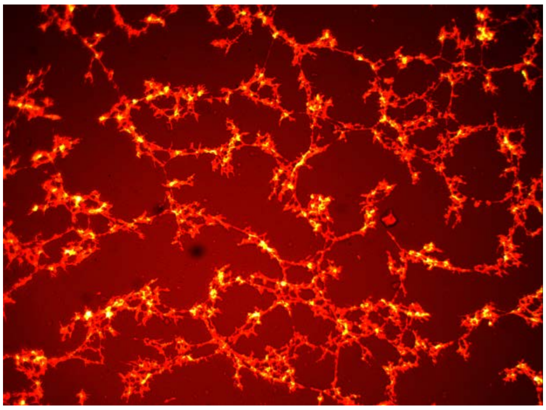

Fig. 4.Microscope image of 3% SBS modified bitumen sample

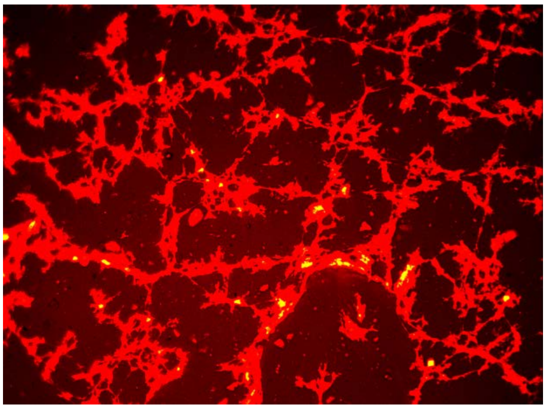

Fig. 5.Microscope image of 3% SBS + 2% Halloysite

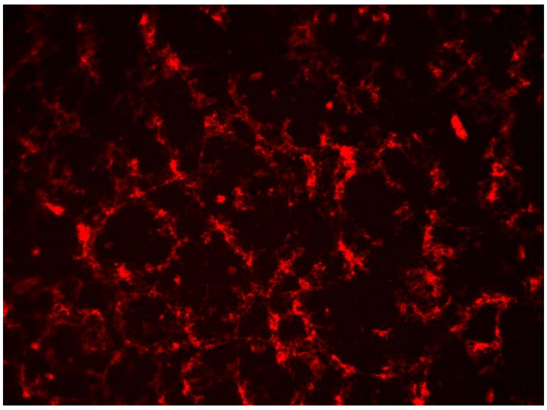

Fig. 6.Microscope image of 3% SBS + 4% Halloysite

According to the image in Fig. 4, polymers were dispersed in the bitumen phase but the bond structures of polymer formed were fine. The bonds were gotten volume and dispersed to larger area in the bitumen phase as a result of Halloysite addition in Fig. 5 and more intense bonds were observedin Fig. 6 with the increase of the nanoclay ratio.

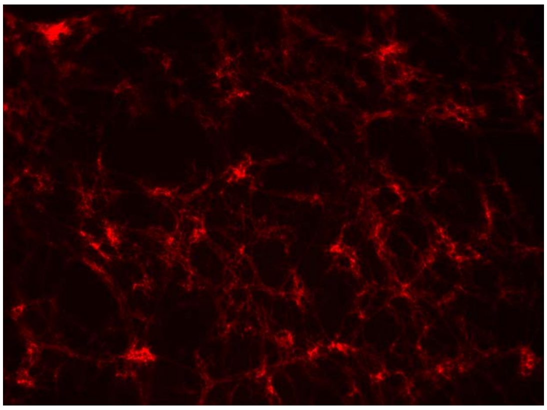

Fig. 7.Microscope image of 5% SBS modified bitumen sample

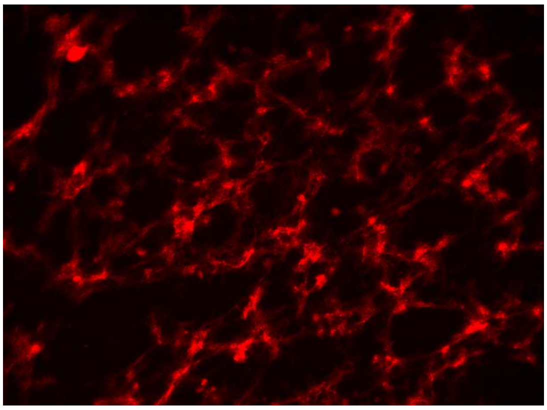

Fig. 8.Microscope image of 5% SBS + 2% Halloysite

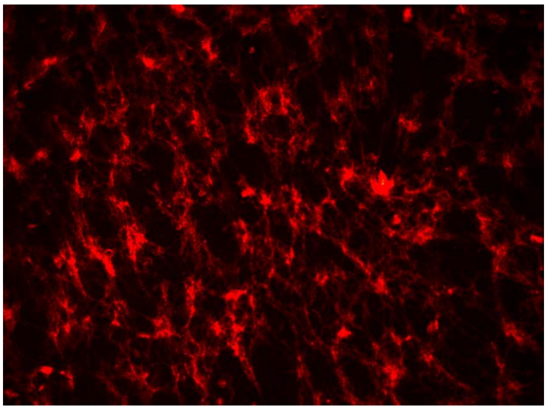

Fig. 9.Microscope image of 5% SBS + 4% Halloysite

The increase in polymer ratio also increased the bonds between them in Fig. 7. Similarly, an increase in the bond density was observed with the increase of the ratio of Halloysite in Fig. 8 and Fig. 9.

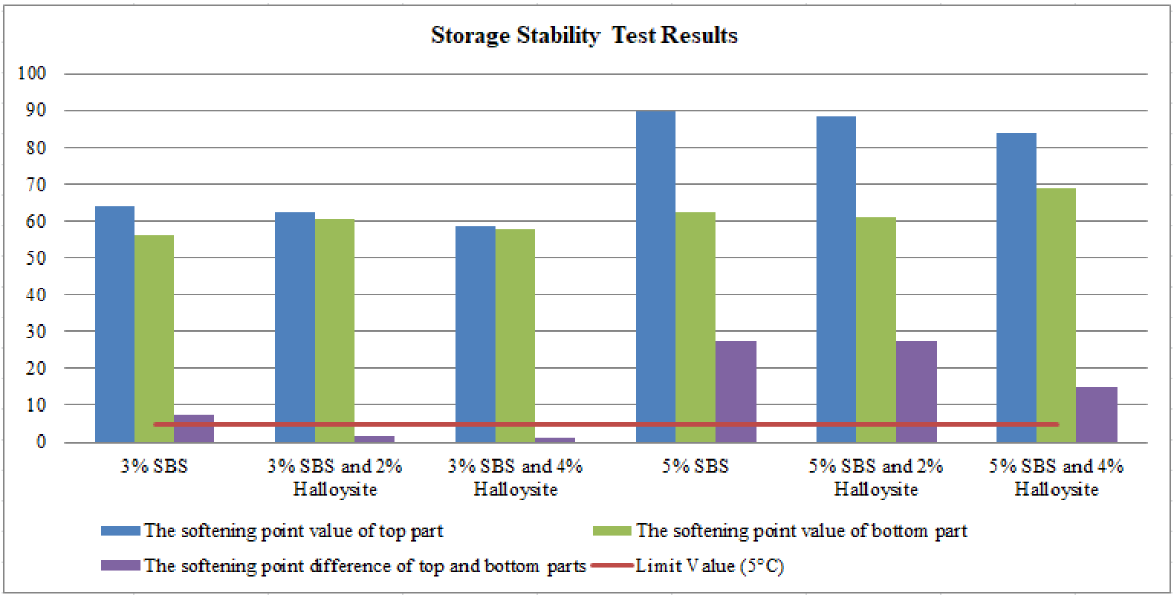

Fig. 10.Storage stability test results of modified bitumen sample

As a result of the storage stability test, lower softening point difference values of top and bottom parts are desired for polymer modified bitumen samples and also the difference does not exceed 5°C. The test result of the modified bitumen samples are seen in Fig. 10, the storage stability values were improved by addition of Halloysite into the polymer modified bitumen. 3% SBS modified bitumen sample has exceeded the limit value. The storage stability values decreased below the limit value as a result of utilization of Halloysite within the bitumen and the decrease of the difference increased with the increment of Halloysite ratio. All the samples haveexceeded the limit value for 5% SBS modified bitumen samples due to the increment of the polymer ratio. The softening point values increased and the storage stability values worsen with the increment of the polymer ratio. Addition of Halloysite was provided lower storage stability values but the values did not fall below the limitation of 5°C.

4. CONCLUSION

The density difference between polymer and bitumen causes to phase separation during the storage period, for this reason the value of storage stability is crucial criterion for modification. In this paper, the images belong to the modified bitumen samples were investigated under fluorescence optical microscope and phase separation was examined according to the storage stability test results of SBS modified bitumen samples involving Halloysite.

The images of modified bitumen samples taken by fluorescence optical microscope were analyzed, the utilization of Halloysite within the bitumen, strengthen the bonds, therefore the values of storage stability decreased. Decrease for storage stability values was observed as a result of the addition of Halloysite and also increase of Halloysite ratios. The samples involving 5% SBS were compared, it is also seen that the storage stability values decrease with addition of Halloysite. But the storage stability value of the 5% SBS modified bitumen is very high and addition of Halloysite decreased the value of storage stability but not below the limit value. Thus, the result is that the increase in the ratio of polymer in modified bitumen effects the storage stability unfavorable.

In this study, modified bitumen samples were investigated under fluorescence optical microscope and subjected to storage stability test. According to the results it is seen that the utilization of Halloysite within the bitumen effects the storage stability values being lower. The results showed that the ratios of additives were very important for modified bitumen samples. Therefore, additive ratios should be determined carefully to ensure desired performance from modified bitumen.

REFERENCES

Airey, G. D. (2002). “Rheological evaluation of EVA polymer modified bitumen.” *Journal of Construction and Building Materials*, Vol. 16, pp. 473-487.

Chen, J., Liao, M. and Shiah, M. (2002).” Asphalt modified by SBS triblock copolymermorphology and model.”*Journal of Materials in Civil Engineering*, Vol. 14, No. 3, pp. 224-229.

Eskandarsefat, S., Dondi, G. and Sangiorgi, C. (2019). “Recycled and rubberized SMA modified mixtures: A comparison between polymer modified bitumen and modified fibres.” *Construction and Building Materials*, Vol. 202, pp. 681-691.

Galooyak, S. S., Dabir, B., Nazarbeygi, A. E. and Moeini, A. (2010).“Rheologicalproperties and storage stability of bitumen/SBS/montmorillonite composites*.”Consturction and Building Materials*, Vol. 24, pp.300-307.

Golestani, B., Nejad, F. M. and Galooyak, S. S. (2012). “Performance evaluation oflinear and nonlinear nanocomposite modified asphalts.”*Consturction and BuildingMaterials*, Vol. 35, pp. 197-203.

Jahromi, S. G. and Khodaii, A. (2009).“Effects of nanoclay on rheological properties of bitumen binder.”*Construction and Building Materials*, Vol. 23, pp. 2894-2904.

KGM, (2009).*Modified bitumen and bituminous binders - modified bitumen storage determination of stability*,Turkish Standard Institute, Ankara, Turkey.

Kraton®. (2012). *Kraton® D1101A Polymer,* Data document.

Mazurek, G. and wanski, M. (2017). “Relaxation modulus of SMA with polymer modified and highly polymer modified bitumen.” *Procedia Engineering*, Vol. 172, pp. 731-738.

Ragni, D., Ferrotti, G., Lu, X. and Canestrari, F. (2018). “Effect of temperature and chemical additives on the short-term ageing o polymer modified bitumen for WMA.” *Materials and Design*, Vol. 160, pp. 514-526.

Schaur, A., Unterberger, S. and Lackner, R. (2017). “Impact of molecular structure of SBS on thermomechanical properties of polymer modified bitumen.” *European Polymer Journal*, Vol. 96, pp. 256-265.

Topal, A., Sureshkumar, M. S., Şengöz, B. and Polacco, G. (2012).“Rheology and microstructure of polymer-modified asphalt nanocomposites.”*International Journal of Materials Research*, Vol. 103, pp. 1271-1276.

Vonk, W. C. and Gooswilligen, G. (1989).“Improvement of paving grade bitumens with SBS polymers.”*Proceeding of the Fourth Eurobitume Symposium*, pp. 289-303.