Visual Abstract

# Fatigue Analysis of Bitumen Modified with Composite of Nano-$SiO_2$ and Styrene Butadiene Styrene Polymer

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**ABSTRACT.** Since fatigue cracking is caused in the middle-temperature conditions due to the stresses from heavy traffic and as the bitumen plays a very important role in controlling this failure, therefore, in recent years, the production of the modified bitumen that can give a good performance in the middle temperatures has always attracted the interest of researchers. One of these bitumen modifiers is the styrene butadiene styrene (SBS) polymer. Due to the phase separation of bitumen and polymer, aging and oxidation, this polymer may not exhibit expected field performance at middle temperatures. Therefore, in this research, it is attempted to analyze the middle-temperature performance using the combination of nano-$SiO_2$ and SBS polymer in the bitumen modification. In this paper, the addition of SBS and nano-$SiO_2$ to the base bitumen resulted in the reduction of the complex modulus, phase angle, storage modulus and loss modulus at middle temperatures, thereby improving the potential of fatigue failure resistance. In general, considering the requirement for the rotational viscosity value up to 3 Pa.s at 135 °C and also, regarding the economic issues in choosing a lower percentage, the combination of 4.5% SBS + 3% nano-$SiO_2$ is selected as the optimal composite.

**KEYWORDS.** Bitumen; Functional analysis; Middle temperature; Nano-$SiO_2$; SBS.

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## INTRODUCTION

Bitumen is usually the byproduct in the crude oil production process, which, therefore, may not have all the specifications required for the production of asphalt mixtures [1]. Asphalt mixtures are subjected to the temperature changes and stresses caused by the passing heavy vehicles, which increase the growth of rutting, fatigue and low-temperature cracking failures. The bitumen plays an important role in the occurrence of these failures. Therefore, in order to achieve the pavements of longer service life, the modification of bitumen is inevitable [2]. Every year, different modifiers are used to improve bitumen properties and behavior. Among these modifiers, in recent decades, the polymers and nano-materials are increasingly used to improve the rheological behavior of bitumen [3-8]. The modification of bitumen with Styrene Butadiene Styrene (SBS) polymer improves the resistance to rutting, fatigue cracking, and low-temperature cracking [9,10], but involves the phase separation and is degraded under the ultraviolet light, as well as oxygen [11,12]. Research results show that modifying the polymer bitumen with nano-materials improves the high- and low-temperature performance, aging, oxidation and phase separation [13,14,3,4,5]. There are some limited studies on the effect of polymer nano-composites; hence, this paper analyzes the middle-temperature performance of the SBS additive and the combined SBS and nano-$SiO_2$ additive in 10, 15, 20, and 25 $^{o}$C to the bitumen PG 64-16 as the most common bitumen in Iran. For this purpose, the bitumen performance, dual composite of bitumen and SBS, and triad composite of bitumen, SBS and nano-$SiO_2$ were evaluated based on the softening point, needle penetration, ductility, rotational viscosity, RTFO mass loss, and dynamic shear rheometer (DSR) tests.

## METHOD

### *Materials*

Bitumen PG 64-16 was prepared from Pasargad Oil Company of Tehran, SBS Polymer (LG 501) was prepared from LG Company, South Korea, and nano-$SiO_2$ was prepared from Degussa Company, Germany. The chemical composition of the base bitumen and the physical and chemical characteristics of SBS and nano-$SiO_2$ are given in Tab. (1), Tab. (2), and, Tab. (3).

| Composition | wt.% |
|---|---|
| Saturates | 8.1 |
| Naphthene-aromatics | 48.9 |
| Polar-aromatics | 30.8 |
| Asphaltenes | 12.2 |

Table 1: Chemical composition of base bitumen.

| Physical and chemical properties | content |
|---|---|
| Molecular structure | Linear |
| Styrene/Butadiene ratio | 31/69 |
| Density (g/cm$^3$) | 0.94 |
| Oil content (phr) | None |
| Melting index (g 10 minutes 200 °C / 5 kg) | < 1 |
| Volatile rate (%) | 0.5 |
| Hardness (Shore A) | 79 |
| Toluene Solution Viscosity | 13.4 |

Table 2: Physical and chemical properties of SBS.

| Physical and chemical properties | content |
|---|---|
| $SiO_2$ | >99% |
| Ti | <120ppm |
| Ca | <70ppm |
| Na | <50ppm |
| Fe | <20ppm |
| APS | 11-13 nm |
| SSA | 180-600 $m^2/gr$ |
| Bulk density | <0.10 $g/cm^3$ |
| True density | 2.4 $g/cm^3$ |

Table 3: Physical and chemical properties of nano-$SiO_2$

### *Preparation of samples*

To prepare the combined bitumen, SBS and nano-$SiO_2$ samples, the high shear mixer was used at 175 °C and 4000 rpm for two hours. On this basis and in order to perform all the tests, 1 kg from each of the samples was prepared including the base bitumen, compound of bitumen and SBS polymer as 2.5, 3, 3.5, 4, 4.5, 5, 5.5 and, 6 wt% of the bitumen and the threefold compound of bitumen, SBS polymer with constant 4.5 wt% of bitumen and nano-$SiO_2$ with 1, 2, 3, 4 and, 5 wt% of bitumen, which resulted in preparation of 1 samples of base bitumen, 8 samples of polymeric bitumen and 5 samples of nano polymeric bitumen.

### *Physical properties tests*

The conventional physical tests including the softening point (ASTM D36), needle penetration at 25 °C (ASTM D5), ductility at 25 °C (ASTM D113), rotational viscosity (ASTM D4402) at 120, 135, 150, and 165 °C, and rolling thin-film oven (RTFO) mass loss (ASTM D2872) tests were performed on the base bitumen and all modified bitumen samples. Moreover, the needle penetration index was calculated according to Equation (1) [12].

$$PI=\frac{1952-500\times\log\left(Pen_{25}\right)-20\times SP}{50\times\log\left(Pen_{25}\right)-SP-120} \tag{1}$$

where the $Pen_{25}$ is the needle penetration at 25 °C (0.1 mm) and SP is the temperature of the softening point of bitumen samples (°C).

### *Dynamic shear rheometer test*

Dynamic shear rheometer (DSR) test (ASTM D7175) was conducted using the controlled stress method at constant frequency (10 rad/s) and 10, 15, 20, and 25 °C for different SBS, nano-$SiO_2$ composites with base bitumen on which the short-term aging process was carried out on an RTFO machine (ASTM D2872). The complex modulus ($G^*$), phase angle ($\delta$), storage modulus ($G'=G^*\times\cos\delta$) and loss modulus ($G''=G^*\times\sin\delta$) were determined for bitumen samples. In order to improve the resistance potential to fatigue, the energy loss should be reduced as much as possible. The energy loss in each loading cycle is directly proportional to $G^*\times\sin\delta$ parameter. For the bitumen to be acceptable in the fatigue test at a given temperature, the value of $G^*\times\sin\delta$ should be less than or equal to 5000 kPa for the aged bitumen with RTFO [15]. This means that it is desirable to reduce the values of $G^*$ and $\delta$.

## RESULTS

### *Physical Properties*

The results of softening point, needle penetration, PI, ductility, rotational viscosity and RTFO mass loss for various composites of SBS and SBS/nano-$SiO_2$ with base bitumen are given in Tab. (4). These tests were selected for the purpose of fatigue analysis of the bitumen modified by SBS polymer and nano-$SiO_2$ among the tests of physical properties of the bitumen. As for investigating the performance at the intermediate temperatures i.e. at temperatures between 10 and 25 Celsius degrees, where failure of the asphalt mixture occurs due to the fatigue, analysis of these tests is appropriate for this purpose.

According to Tab. (4), the addition of SBS and SBS/nano-$SiO_2$ to bitumen generally increases the softening point, PI, and rotational viscosity and decreases the needle penetration. Reducing the needle penetration, increasing the softening point, PI and viscosity will reduce the bitumen's sensitivity to temperature changes and improve its performance at middle temperatures. Considering the effect of SBS polymer, it could be due to the creation of 3D networks in the bituminous environment after creation of long and dispersed chains of SBS polymer. So that the polystyrene and polybutadiene chains would increase the strength and flexibility of the modified bitumen, respectively, which result in reduced fluidity and increased elasticity. Concerning the nano-$SiO_2$ effect, it is due to the interaction between nano-$SiO_2$ material, bitumen and SBS polymer. So that nano-$SiO_2$ by adsorption, establishes intense adhesion with the bitumen and polymer which leads to increased hardness and concentration of bituminous mortar. This in turn reduces the bitumen needle penetration and increases the softening point, PI and RV values. Reduced the needle penetration and increased softening point, PI and RV lead to reduced sensitivity of the bitumen to variation in temperature which is good for it. In the SBS with higher than 4.5 wt%, the reducing trend of the needle penetration and increasing trend of softening point and PI is mitigated which is due to the dominating polymer phase. Also this process is seen in threefold compound consisting of bitumen, SBS polymer and nano-$SiO_2$, where for nano-$SiO_2$ with higher than 4 wt% , the reducing trend of penetration degree and increasing trend of softening point and PI are mitigated which could be due to saturation of the bituminous mortar by nano particles. So that the balanced phase network of bitumen and SBS polymer is disturbed when using too much nano-$SiO_2$.

| Compounds | | Properties | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Softening point (°C) | Penetration at 25°C (dmm) | Ductility at 25°C (cm) | PI | RTFO (Mass loss%) | RV (Pa.s) 120 °C | 135 °C | 150 °C | 165 °C |
| Base bitumen | | 50.3 | 65 | >100 | -0.13 | - | 0.67 | 0.32 | 0.16 | 0.10 |
| SBS (wt% of bitumen) | 2.5% | 57.5 | 54 | >100 | 0.17 | 0.23 | 0.86 | 0.47 | 0.26 | 0.15 |
| | 3% | 59.5 | 54 | >100 | 0.26 | 0.23 | 1.11 | 0.62 | 0.33 | 0.19 |
| | 3.5% | 67 | 49 | >100 | 0.49 | 0.24 | 1.40 | 0.72 | 0.39 | 0.22 |
| | 4% | 79.5 | 48 | >100 | 0.79 | 0.23 | 1.76 | 0.88 | 0.47 | 0.27 |
| | 4.5% | 84.5 | 45 | >100 | 0.86 | 0.22 | 1.93 | 0.97 | 0.52 | 0.32 |
| | 5% | 85 | 43 | 95 | 0.85 | 0.27 | 2.14 | 1.08 | 0.57 | 0.33 |
| | 5.5% | 86.5 | 42 | 99 | 0.87 | 0.25 | 2.47 | 1.25 | 0.64 | 0.37 |
| | 6% | 84.5 | 42 | 94.8 | 0.84 | 0.26 | 2.71 | 1.37 | 0.76 | 0.41 |
| SBS/nano-$SiO_2$ (wt% of bitumen) | 4.5% SBS+1%nano-$SiO_2$ | 85 | 35 | >100 | 0.78 | 0.21 | 2.18 | 1.60 | 0.65 | 0.35 |
| | 4.5% SBS+2%nano-$SiO_2$ | 85.5 | 36 | >100 | 0.80 | 0.21 | 3.39 | 1.72 | 0.87 | 0.52 |
| | 4.5% SBS+3%nano-$SiO_2$ | 86 | 37 | >100 | 0.82 | 0.20 | 4.49 | 2.96 | 1.13 | 0.53 |
| | 4.5% SBS+4%nano-$SiO_2$ | 86.5 | 34 | >100 | 0.80 | 0.21 | 4.86 | 3.63 | 1.62 | 0.74 |
| | 4.5% SBS+5%nano-$SiO_2$ | 85 | 38 | >100 | 0.81 | 0.21 | 5.42 | 3.87 | 1.88 | 0.95 |

Table 4: Physical Properties of base bitumen, bitumen/SBS, and bitumen/SBS/nano-$SiO_2$.

The maximum levels of SBS that can provide the ductility greater than 100 [15] are the composites with the SBS level of 4.5% by weight of bitumen. The appropriate bitumen temperature for mixing and compaction is the temperature equivalent to RV values of $0.17\pm0.2$ and $0.28\pm0.3$, respectively, and the maximum temperature for heating of the bitumen is equal to 176°C [15]. According to Tab. (4), adding SBS polymer to the base bitumen from 2.5 to 6 wt% of bitumen causes continuous increase of RV, but it does not exceed 3 Pa.s at 135°C temperature. In these compounds the maximum RV value at 135°C is equal to 1.37 for a compound of base bitumen and SBS polymer with 6 wt% of the bitumen. Also, addition of nano-$SiO_2$

to the bitumen containing SBS polymer with 4.5 wt% of the bitumen, causes increase in the RV value. This value exceeds the limit of 3 Pa.s for the compounds of 4.5%SBS+4%nano-$SiO_2$ and 4.5% SBS+5% nano-$SiO_2$. Therefore, on this basis the maximum value of nano-$SiO_2$ is equal to 3 wt% of the bitumen in the compound of bitumen modified by SBS polymer with 4.5 wt% of the bitumen. By increase in the temperature, the RV values is reduced. For the compound of bitumen and 4.5% SBS and the threefold compound of bitumen, SBS polymer and nano-$SiO_2$, the mixing and compaction temperatures are both greater than 165 °C which are too close to 176°C and create problems in terms of applicability. Thus, to resolve this problem it is recommended to use admixtures that reduce viscosity such as Fischer-Tropsch Wax. As seen in Tab. (4), adding SBS polymer to bitumen and also adding nano-$SiO_2$ to polymeric bitumen containing SBS polymer with 4.5 wt% of the bitumen, the weight loss is nearly constant and its value in all the compounds is less than 1 wt%.

### *Complex modulus, phase angle, and storage modulus*

The results of complex modulus, phase angle and storage modulus for various composites of SBS, nano-$SiO_2$ with base bitumen are presented in Figs. (1–3), respectively. According to the figures, adding SBS and nano-$SiO_2$ to the base bitumen continuously decreases the complex modulus, phase angle and storage modulus at 10 to 25 °C with the constant frequency of 10 rad/s, indicating the improvement in fatigue resistance potential and middle-temperature performance. Concerning the results of complex modulus at intermediate temperatures (temperatures between 10 and 25 Celsius degrees), as the base bitumen, modified bitumen with 4 wt% of SBS polymer and different threefold combinations of bitumen, nano-$SiO_2$ and 4.5 wt% of SBS polymer, had passed the short term and long term processes of aging prior to the dynamic shear rheometer test, and the aging process of RTFO+PAV could result in further hardness of the bitumen by change in the molecular structure of the bitumen, therefore, the higher the share of bitumen, the higher would be the complex modulus. Thus, adding SBS polymer and also adding nano-$SiO_2$ to the polymeric bitumen with 4.5 wt% SBS polymer at intermediate temperatures could reduce the complex modulus. As the reduction in complex modulus at the intermediate temperatures, leads to increase of resistance to fatigue failure, therefore the performance of modified bitumen at intermediate temperatures is improved. As seen in Fig. (2), it is observed that adding SBS polymer and nano-$SiO_2$ to the SBS polymeric bitumen at temperatures between 10 and 25 Celsius degrees and at constant frequency of 10 radians per second, the phase angle is continuously reduced. This could be due to interaction between nano-$SiO_2$, bitumen and SBS polymer, so that nano-$SiO_2$ particles by adsorption develop enhanced adhesion with the bitumen and polymer compounds which has resulted in reduced phase angle. As stated before, reduction in $\delta$ value reduces loss in viscosity and therefore improves the performance at intermediate temperatures of modified bitumen samples.

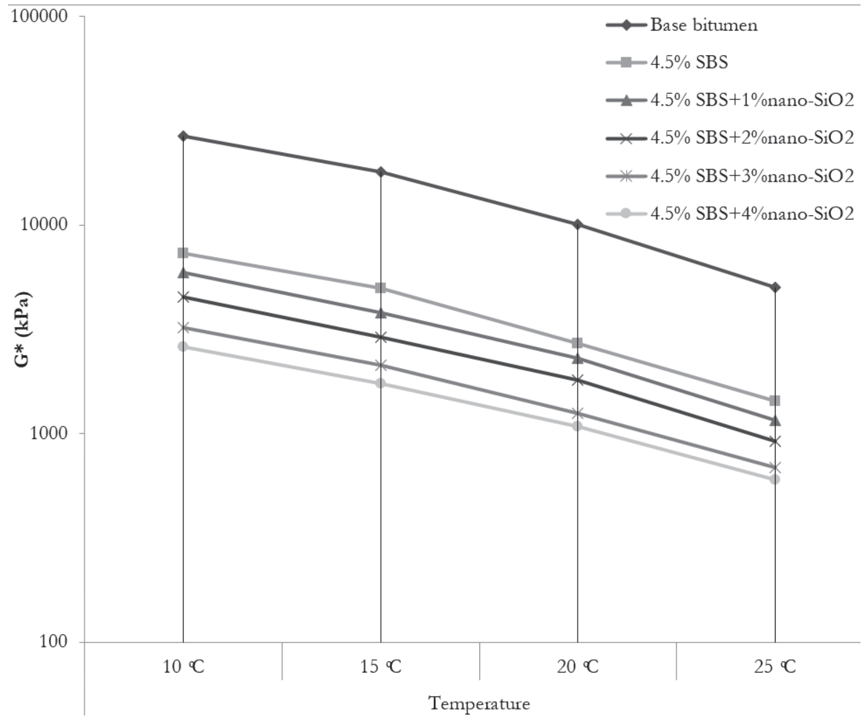

Figure 1: The complex modulus results from DSR test for base bitumen, bitumen/SBS, and bitumen/nano-$SiO_2$/SBS in 10, 15, 20, and 25 $^{o}$C.

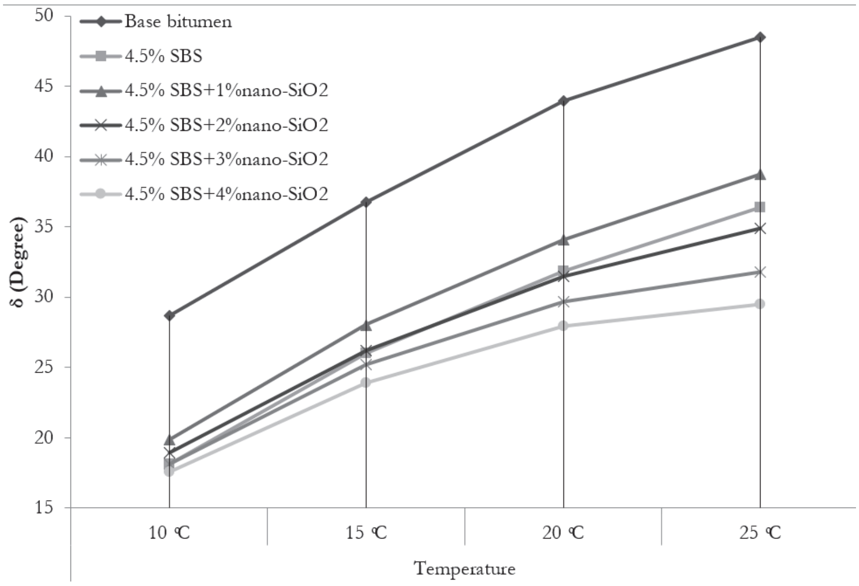

Figure 2: The phase angle results from DSR test for base bitumen, bitumen/SBS, and bitumen/nano-$SiO_2$/SBS in 10, 15, 20, and 25 $^{o}$C.

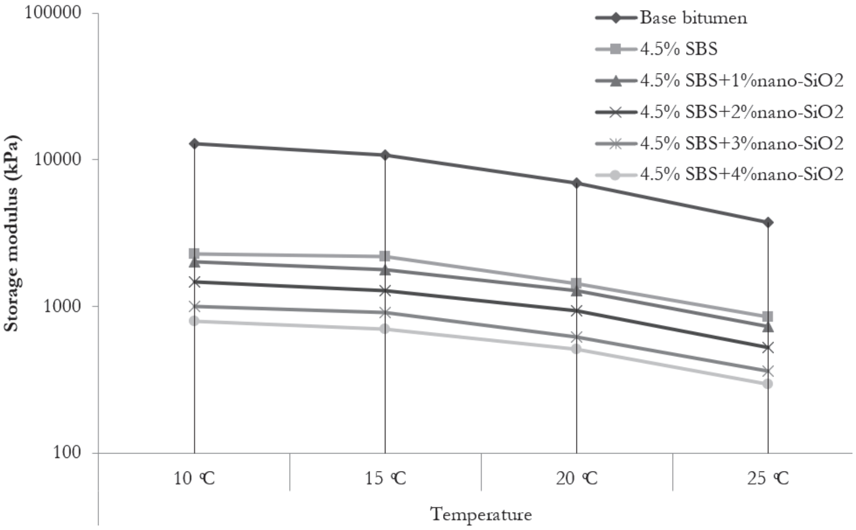

Figure 3: The storage modulus (G') results from DSR test for base bitumen, bitumen/SBS, and bitumen/nano-$SiO_2$/SBS in 10, 15, 20, and 25 $^{o}$C.

### *Loss modulus (fatigue resistance)*

The values of the loss modulus (G"=G*×sinδ) for various composites of SBS, nano-$SiO_2$ with RTFO-aged base bitumen are shown in Fig. (4). As seen in the figure, by adding SBS and nano-$SiO_2$ to the base bitumen, the loss modulus is reduced at 10 to 25 °C with the constant frequency of 10 rad/s, which results in improved fatigue resistance potential and middle-temperature performance of the modified bitumen samples. All different composites of SBS, nano-$SiO_2$ with the base bitumen at temperatures 10 to 25 °C and constant frequency of 10 rad/s have the G*×sinδ values less than 5000 kPa, among which two composites of 4.5% SBS + 3 % nano-SiO2 and 4.5% SBS + 4% nano-$SiO_2$ have the minimum values. As seen in Fig. (4), continuous addition of SBS polymer and nano-$SiO_2$ to the SBS polymer modified bitumen, causes reduction in the parameter values of G*×sinδ, at temperatures of 10-25 Celsius degrees and with constant frequency of 10 radians per seconds, and consequently resistance against fatigue and performance at intermediate temperatures of the modified bituminous samples are both improved. This could be due to the reduced complex modulus and phase angle by addition of nano-$SiO_2$ to the 4.5 wt% SBS polymer modified bitumen at intermediate temperatures which was explained.

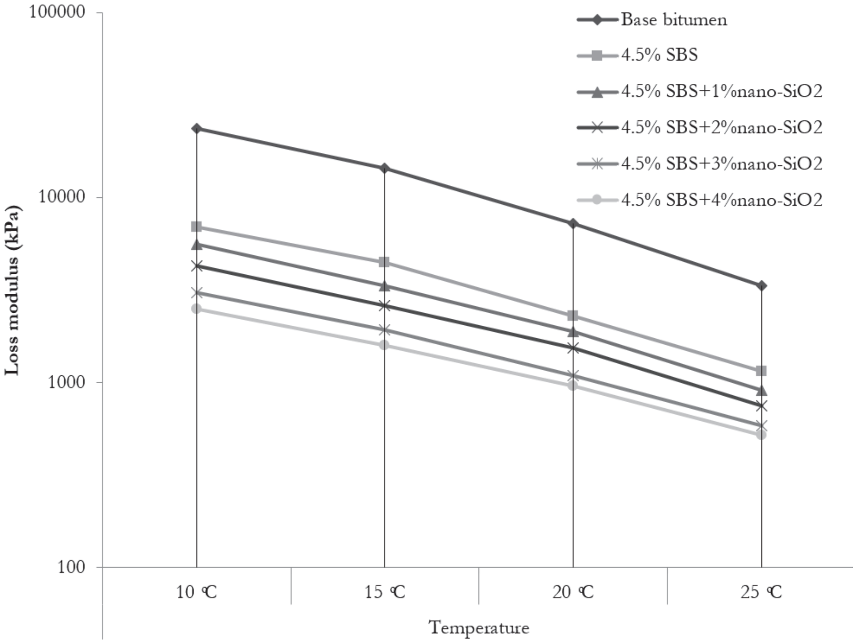

Figure 4: The loss modulus (G”) results from DSR test for base bitumen, bitumen/SBS, and bitumen/nano-$SiO_2$/SBS in 10, 15, 20, and 25 °C.

## CONCLUSION

By adding nano-$SiO_2$ and SBS to the base bitumen, the needle penetration is decreased and the softening point, PI, and rotational viscosity are increased. These results decrease the sensitivity of various composites to temperature changes, reduce the fatigue cracking and improve the performance at the middle temperatures. In all of the various composites of SBS and nano-$SiO_2$ with base bitumen, the ductility at 25 °C was found to be more than 100 cm, indicating the good performance at middle temperatures. The maximum rotational viscosity of bitumen samples at 135 °C is considered equal to 3 Pa.s. All bitumen samples, except for 4.5% SBS + 4% nano-$SiO_2$ satisfied this requirement. All composites were controlling the maximum mass loss in the RTFO test, which is 1%, indicating the resistance to oxidation and short-term aging. By adding nano-silica to the SBS polymer bitumen, the complex modulus, phase angle, storage modulus, and loss modulus at 10 to 25 °C and constant frequency of 10 rad/s were constantly reduced, resulting in the improved fatigue resistance and middle-temperature performance in the bitumen samples. In general, according to the requirement of rotational viscosity up to 3 Pa.s at 135 °C and also, regarding the economic issues in selecting a lower percentage, the combination of 4.5% SBS + 3% nano-$SiO_2$ is selected as the optimal composite.

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