Rheological properties of modified asphalt binder with nanosilica and SBS

A H Abed and A M Oudah

1 Asst. Professor, Civil Engineering Department, Al-Nahrain University, alaah29@yahoo.com, Baghdad, Iraq.
2 Civil Engineering Department, Al-Nahrain University ameer.altemimi90@gmail.com, Iraq.

Abstract. Rheology is the science that deals with the deformation of materials relation with load and time rate of load application. The goal of this study is finding effects of two modifier nanosilica (nSiO₂) and Styrene Butadiene Styrene (SBS) on the chemical bonding and rheological properties of local asphalt binder. In this study, 3% and 5% of nanosilica (nSiO₂) and Styrene Butadiene Styrene (SBS) were added to the asphalt binder. It was found that with the addition of nanosilica to the control asphalt binder lead to slightly increased the viscosity of the control binder, as SBS polymer add the viscosity increased three times than reference viscosity of control asphalt binder. It was noticed the performance grade (PG) of binder not changed with addition of 3% nSiO₂, but PG increased one degree when 5% of SiO₂ is added. PG of control binder increased two and three degrees with additional 3% and 5% SBS respectively. The results show that nSiO2, and SBS slightly effect on the low temperature performance, therefore, low temperature grade not changed. Through FTIR results, it was found that the modified asphalt binder had a positive effect on anti-oxidation as compared with control binder, so, rutting and fatigue cracking performance of modified asphalt binders will be enhanced.

1. Introduction
Polymer usually used as a modifier for asphalt binders to reduce the amount and severity of pavement distresses and to increase service life. The term polymer indicates to multiple “mer” unites, which can be formed by breaking double carbon – carbon bond by rearrange linking with others. The mechanical properties of hot mix asphalt are enhanced due to effect of the physical structure of the polymers chain. The degree of polymerization can be defined from the number of monomers in each chain. Rheological properties of asphalt binder depend on the polymer extent of cross linking, chain lengths, the production process and radial compounds. Since asphalt binder has both viscous and elastic properties, it is considered a viscoelastic material, and can behave as an elastic, viscous or viscoelastic material under prevailing conditions [1] The viscoelastic behavior of asphalt binder is changed according to temperature and loading time, asphalt binder behavior transforms from elastic at low temperature to viscous at moderate and high temperatures [2]. Hydrocarbons are a basic component of asphalt which is a complex aggregation of fairly large molecules. For rearranging microstructure of asphalt binder, polymers are used for developing the rheological properties, Thus, asphalt mixture characteristics to resist damage will be increased. Styrene butadiene styrene (SBS) elastomer polymer and nanosilica was used for this purpose.
2. Objectives
The main objectives of this study are to show effect of the two modifiers nanosilica (nSIO₂) and Styrene Butadiene Styrene (SBS) on the chemical bonding and rheological properties of local asphalt binder using Superpave binder tests.

3. Materials
Asphalt binder produced by Nasiriyah refinery is used as control binder also two types of modifiers are used to increase performance grade of asphalt binder, Elastomers “Styrene Butadiene Styrene (SBS) which widely accepted bitumen-asphalt binder modification agent that used in the whole bitumen industry and Nano SIO₂ that purchased from intelligent materials Pvt. Ltd./NANOSHEL (U.S.A), which have good physical properties by increase specific surface area, extra small size, tunnel effect, easily dispersed in mediums, good suspension and thixotropic material as shown in Figure 1 and Table 1.

![Figure 1. Nano powder SIO2 (15-20 nm)](image)

**Table 1. The characteristics of nSIO₂ (Pvt. Ltd./NANOSHEL, U.S.A).**

| pSio₂ Nano powder | 1.2-1.6, amorphous, Nanoporous |
|-------------------|--------------------------------|
| Purity            | 99.5+ %                        |
| APS               | 15-20nm—Spherical particles    |
| SSA               | 170-200 m²/g                   |
| Color             | White                          |
| Bulk Density      | <0.1 g/cm³                     |
| True Density      | 24 g/cm³                       |
| Ultraviolet Reflectivity | >75%                |
| SiOx              | 10 ppm                         |
| Al                | 10 ppm                         |
| Fe                | 50 ppm                         |
| Sr                | 40 ppm                         |
| Ca                | 20 ppm                         |
| Mg                | 20 ppm                         |
| Cl                | 10 ppm                         |
3.1 Preparation of Polymer-Asphalt Mixes
Mixing asphalt binder with SBS polymer is required special conditions, it should be mixed with a specific temperature and rotational energy (mixing speed), so a special device for mixing asphalt with the modifiers had been manufactured to mix at any temperature, mix at any speed revolution and to prevent asphalt binder from oxidation through mixing. For getting compatibility and stability SBS polymer with asphalt binder, initial mixing rate start is 250 rpm then could be increased gradually every ten minutes until reached the maximum rate of 2,000 rpm for four hours at 180 °c. The polymer is adding to the asphalt binder gradually each 0.5 hour, then, the temperature of the mixture is dropping immediately when the polymer is adding, therefore, need raising temperature to 180°C, as mixing is completed as the modifier used no longer climbed on the mixer shaft. Two concentrations of SBS were made 3% and 5% by weight of controller asphalt binder. Then, the Nanosilica is gradually added to the modified asphalt binder. Which mixed by mixer device at 2000 rpm for four hours at 130 °c, also, two concentrations of Nanosilica was used 3% and 5% by weight of modified asphalt binder. Figure 2 shows local manufactured mixing equipment which is mix at any temperature, mix at any speed revolution and save asphalt binder from oxidation through mixing.

4. Microstructure of Modified Asphalt Binder
Scanning Electron Microscopy (SEM) is used to show dispersions and reactions of SBS and Nanosilica particles in asphalt binder which changing micro-structures of asphalt binder, that may be increased resistance to high temperature distress. Figure 3 shows plot of SEM device that used in this study.

Figure 2. Manufactured mixing device

Figure 3. SEM device
5. Chemical Bonding and Aging of the Modified Asphalt Binder

Fourier Transform Infrared Spectroscopy (FTIR) demonstrates the developing of asphalt binder properties against aging, through measured chemical bonding changes between original and modified asphalt binder. Figure 4 shows a plot of FTIR device. The FTIR test was used to evaluates the chemical bonding changes of control and modified asphalt binder, and the results are shown in Figures 5, 6 and 7. Figure 8 explains the main peaks of FTIR test for asphalt binder. It can be seen that the strong peaks around 2850 cm⁻¹ and 2920 cm⁻¹ is typical C-H stretching vibrations in aliphatic chains. The peak at around 966 cm⁻¹ is attributed to bending C-H trans-substituted – CH = CH = of butadiene block (ethylene band). The aliphatic branched band (bending C-H of CH3) and aliphatic index band (bending C-H of – (CH2)n) are observed at 1376 cm⁻¹ and 1460 cm⁻¹ respectively. The band at around 1030 cm⁻¹ is assigned to stretching sulfoxide [3]. The 1600 cm⁻¹ and 1700 cm⁻¹ bands correspond to the aromatic and carbonyl band respectively. It is obvious that the FTIR figures trend of control and modified asphalt binder are different, this proves that the microstructure of modified asphalt binder was changed relative to the neat asphalt binder. Based on [4], the carbonyl index (C=O) and sulfoxide index (S=O) are chosen as an aging index. Figures 9 and 10 show carbonyl index and sulfoxide index of control asphalt binder, it can be noticed that these values increased as adding modifiers. So, the aging process of binders become less and delayed.
Figure 6. FTIR test of nano silica modified binder

Figure 7. FTIR test of SBS modified binder

Figure 8. The main peaks of asphalt binder at FTIR test
Figure 9. FTIR Absorbance of control and modified binder at 1700 cm\(^{-1}\) (Carbonyl)

Figure 10. FTIR Absorbance of control and modified binder at 1030 cm\(^{-1}\) (Sulfoxide)
6. Rheological Properties of Control (Neat) Asphalt Binder

The purpose of the asphalt inspection equipment according to the Superpave system are to measure the rheological properties which are directly related to field performance based on engineering [5], results of rutting parameters (G*/sinδ) (at original and rolling thin film oven) fatigue parameter (G*. sin δ) and low temperature crack (Stiffness, m value) for control binder was tabulated in the Table 2, according to [6] the performance of control asphalt can be classified to PG 64-16.

**Table 2.** Rheological properties of control (neat) asphalt binder

| Standard Specification | Performance Grade of control (Neat) Asphalt |
|------------------------|---------------------------------------------|
|                        | Temperature Measured | Parameter Measured | Requirements |
| RV, Pa.sec             | AASHTO T 316 @135 ºC | 0.538<sup>a</sup> | 3 Pa.s, Max |
|                        | AASHTO T 316 @165 ºC | 0.138<sup>a</sup> | |
| G*/sin δ, kPa          | AASHTO T 315 @64 ºC | 1.12<sup>a</sup> | 1 kPa, Min |
| G*/sin δ, kPa          | AASHTO T 315 @64 ºC | 2.57<sup>b</sup> | 2.2 kPa, Min |
|                        | AASHTO T 240 @64 ºC | 2.57<sup>b</sup> | |
| Mass Loss %            | AASHTO T 240         | 0.51<sup>b</sup> | 1, Max |
| G*. sin δ, kPa         | AASHTO T 315 @28 ºC | 4430<sup>c</sup> | 5000 kPa, Max |
|                        | AASHTO T 49 @ -16ºC | 188<sup>c</sup> | 300 MPa, Max |
| m-value                | AASHTO T 313 @ -16 ºC | 0.381<sup>c</sup> | 0.3, Min |

<sup>a</sup> Original binder  
<sup>b</sup> Rolling Thin Film Oven (RTFO) Residue  
<sup>c</sup> Pressure Aging Vessel (Pav-110 C) Residue

7. Rheological Properties of Modified Asphalt Binder with nanosilica

Tables 3 and 4 are demonstrated results of modified asphalt binder with 3% and 5% of nanosilica. It can be seen that rutting parameter (G*/sinδ) increases by an average of 15% and 20% with the addition of 3% and 5% of nanosilica respectively. Furthermore, the Performance grade (PG) of 3% nanosilica modified asphalt binder is the same as compared with control asphalt binder (PG 64-16), while it was increased one degree when adding 5% of nanosilica (PG 64-16 to PG 70-16). Fatigue parameter (G*. sinδ) of 3% and 5% nanosilica modified binder enhanced by an average of 8% and 10% respectively.
Table 3 Rheological properties of modified asphalt binder with 3% nanosilica

| Standard Specification | Performance Grade of Modified Asphalt with 3% nSIO2 |
|------------------------|---------------------------------------------------|
| RV, Pa.sec             | AASHTO T 316                                      |
| @135 °C               | 0.55a                                             |
| @165 °C               | 0.15a                                             |
| @64 °C                | 1.73b                                             |
| @70 °C                | 1.2b                                              |
| G*/sin δ, kPa          | AASHTO T 315                                      |
| @64 °C                | 2.95b                                             |
| @70 °C                | 1.92b                                             |
| G*/sin δ, kPa          | AASHTO T 315                                      |
| Mass Loss, %           | AASHTO T 240                                      |
| @28 °C                | 4075c                                             |
| 0.51b                  | 1, Max                                            |
| G*, sin δ, kPa         | AASHTO T 315                                      |
| @28 °C                | 223c                                              |
| S, MPa                 | AASHTO T 49                                       |
| @ -16 °C              | 0.349c                                            |
| m-value                | AASHTO T 313                                      |
| a Original binder      |                                                   |
| b Rolling Thin Film Oven (RTFO) Residue |                       |
| c Pressure Aging Vessel (Pav-110 C) Residue |                  |

Table 4 Rheological properties of modified asphalt binder with 5% nanosilica

| Standard Specification | Performance Grade of Modified Asphalt with 5% nSIO2 |
|------------------------|---------------------------------------------------|
| RV, Pa.sec             | AASHTO T 316                                      |
| @135 °C               | 0.563a                                            |
| @165 °C               | 0.163a                                            |
| @64 °C                | 1.88a                                             |
| @70 °C                | 1.52a                                             |
| @76 °C                | 1.08                                              |
| @64 °C                | 3.09b                                             |
| G*/sin δ, kPa          | AASHTO T 315                                      |
| @70 °C                | 2.44b                                             |
| @76 °C                | 1.88b                                             |
| G*/sin δ, kPa          | AASHTO T 315                                      |
| Mass Loss, %           | AASHTO T 240                                      |
| @28 °C                | 3987c                                             |
| 0.54b                  | 1, Max                                            |
| G*, sin δ, kPa         | AASHTO T 315                                      |
| @28 °C                | 244c                                              |
| S, MPa                 | AASHTO T 49                                       |
| @ -16 °C              | 0.305c                                            |
| m-value                | AASHTO T 313                                      |
| a Original binder      |                                                   |
| b Rolling Thin Film Oven (RTFO) Residue |                       |
| c Pressure Aging Vessel (Pav-110 C) Residue |                  |
8. Rheological Properties Modified Asphalt Binder with SBS

Tables 5 and 6 show that the SBS modified asphalt binder has higher rutting parameter \( (G*/\sin\delta) \) than that of control binder. The Performance grade (PG) of 3% SBS modified binder increased two degrees (PG 76-16), as increasing modifier to 5% the performance grade three degrees to become (PG 82-16). Fatigue parameter \( (G*, \sin\delta) \) of 3% and 5% SBS modified binder developed and pass the specifications of Superpave at 31 C°. it can be seen that low temperatures cracks were not affected for all results.

Table 5 Rheological properties of modified asphalt binder with 3% SBS

| Standard Specification | Performance Grade of Modified Asphalt with 3% SBS |
|------------------------|--------------------------------------------------|
|                        | Temperature Measured | Parameter Measured | Requirements |
| RV, Pa.sec             | AASHTO T 316         | @135 °C 1.525\(^{a}\) | 3 Pa.s, Max |
|                        | AASHTO T 316         | @165 °C 0.375\(^{a}\) |                             |
| G*/sin \(\delta\), kPa | AASHTO T 315         | @76 °C 2.61\(^{b}\) | 1 kPa, Min |
|                        | AASHTO T 315         | @82 °C 0.87\(^{b}\) |                             |
| G*/sin \(\delta\), kPa | AASHTO T 240         | @76 °C 3.08\(^{b}\) | 2.2 kPa, Min |
|                        | AASHTO T 240         | @82 °C 1.76\(^{b}\) |                             |
| Mass Loss ,\%          | AASHTO T 240         | @31 °C 0.45\(^{b}\) | 1, Max                   |
| G*, sin \(\delta\), kPa| AASHTO T 315         | @31 °C 4638\(^{c}\) | 5000 kPa, Max            |
|                        | AASHTO T 49          | @ -16 °C 212\(^{c}\) | 300 MPa, Max             |
| S, MPa                 | AASHTO T 313         | @ -16 °C 0.376\(^{c}\) | 0.3, Min |

\(^{a}\) Original binder  
\(^{b}\) Rolling Thin Film Oven (RTFO) Residue  
\(^{c}\) Pressure Aging Vessel (Pav-110 C) Residue

9. Viscosity of Modified Asphalt Binder

Through Tables 2 to 6 show the viscosities of modified asphalt binder, it was found that the viscosity of modified asphalt binder by nanosilica increases slightly by an average of 2%. The viscosity of SBS modified asphalt binder much increases by an average of 180% and 280% with the addition 3% and 5% of SBS respectively, therefore, the workability of asphalt binder will be difficult and it will need higher temperature for mixing and compaction.
Table 6 Rheological properties of modified asphalt binder with 5% SBS

| Standard Specification | Performance Grade of Modified Asphalt with 5% SBS |
|------------------------|--------------------------------------------------|
|                        | Temperature Measured | Parameter Measured | Requirements |
| RV, Pa.sec             | AASHTO T 316         | @ 135 °C           | 2.075\textsuperscript{a} | 3 Pa.s, Max |
|                        |                     | @ 165 °C           | 0.575\textsuperscript{a} |            |
| G*/sin δ, kPa          | AASHTO T 315         | @ 82 °C            | 1.12\textsuperscript{a} |            |
|                        |                     | @ 88 °C            | 0.65\textsuperscript{a} | 1 kPa, Min |
| G*/sin δ, kPa          | AASHTO T 240         | @ 82 °C            | 2.72\textsuperscript{b} | 2.2 kPa, Min |
|                        |                     | @ 88 °C            | 1.86\textsuperscript{b} |            |
| Mass Loss, %           | AASHTO T 240         |                     | 0.53\textsuperscript{b} | 1, Max     |
| G*, sin δ, kPa         | AASHTO T 315         | @ 31 °C            | 4354\textsuperscript{c} | 5000 kPa, Max |
| S, MPa                 | AASHTO T 49          | @ -16 °C           | 221\textsuperscript{c} | 300 MPa, Max |
| m-value                | AASHTO T 313         | @ -16 °C           | 0.352\textsuperscript{c} | 0.3, Min   |

\textsuperscript{a} Original binder
\textsuperscript{b} Rolling Thin Film Oven (RTFO) Residue
\textsuperscript{c} Pressure Aging Vessel (Pav-110 C) Residue

9.1 Compaction and Mixing Temperatures of the Modified Asphalt Binder

Superpave system limited viscosity for mixing as (0.17 ± 0.2) Pa.sec and for compaction (0.28 ± 0.3) Pa.sec, through relationship between viscosity and temperature, mixing and compaction temperatures were found. Table 7 illustrated mixing and compaction temperatures of control, nSIO2, and SBS modified asphalt binder. It can be found that mixing and compaction temperatures of the modified asphalt binder with nanosilica slightly increased as compared with control binder, but evident increasing can be seen in the mixing and compaction temperatures with SBS modified asphalt binder.

Table 7 Mixing and compaction temperatures of control and modified asphalt binder

|                     | Mixing Temperature, C° | Compaction Temperature, C° |
|---------------------|------------------------|-----------------------------|
|                     | Min        | Max        | Min        | Max        |
| Control Binder      | 158        | 163        | 147        | 152        |
| 3% nSIO2            | 160        | 165        | 148        | 153        |
| 5% nSIO2            | 162        | 167        | 149        | 154        |
| 3% SBS              | 179        | 185        | 169        | 173        |
| 5% SBS              | 191        | 196        | 179        | 184        |
10. Comparison Rheological Properties of Control and Modified Asphalt Binder

Figures 11 and 12 show the performance grade (PG) of control, nSIO2, and SBS modified asphalt binder with content of 3% and 5% respectively. SBS modified binder has higher performance grade (PG) comparing with neat asphalt binder and nanosilica modified asphalt binder. The mean problem of adding SBS to the asphalt binder is increasing viscosity too much, so, mixing temperature will be higher and reach to 185 °C, which lead to increase oxidation of the asphalt binder, then cracks will be formed after few time, rather than less workability in mixing. Figures 13 and 14 show the mixing and compaction temperatures of control and modified binder. Figure 15 shows the stiffness at low temperatures of all types of asphalt binder that used in this study. It can be seen that low temperature not effected, increasing stiffness at low temperature leads to increase sensibility to low temperature cracks.

![Figure 11. PG of binder with 3% content of different modifiers](image1)

![Figure 12. PG of binder with 5% content of different modifiers](image2)
Figure 13. Mixing temperatures of control and modified binder

Figure 14. Compaction temperatures of control and modified binder
11. Conclusions
Two types of modifiers were used in this study Elastomer polymer “Styrene Butadiene Styrene (SBS)” and Nanosilica at different percentages the following conclusions can be gotten:
- Through classification of Superpave system, the performance grade of control asphalt binder was PG 64-16
- As adding 3% of nanosilica as modifier to the asphalt binder, the performance grade of modified asphalt binder not effected. It was found that (PG) increased one degree and become (PG 70-16) when 5% of nanosilica was added to control asphalt binder.
- With addition of 3% and 5% of SBS, the performance grade of base binder (PG 64-16) increases two and three degrees (PG 76-16), (PG 82-16) respectively.
- the viscosity of nanosilica modified asphalt binder not effected, therefore, lower viscosity of the binder shows that a lower mixing and compaction temperature or lower energy consuming of the construction process will be attained, so nanomaterials was considered as good modifiers for asphalt binder due to low viscosity, but viscosity values increase about three times as adding SBS polymer.
- Nanotechnology is a good solution for avoiding increasing viscosity values of asphalt binder.
- The scanning electron microscopy (SEM) images shows that the microstructure of modified asphalt binders was changed relative to the control asphalt binder. It was observed a good dispersion of particles in the modified asphalt binder.
- Through bending beam rheometer (BBR) results, it was illustrated that the nanosilica, and SBS polymer have no effect on the low temperature grade, so, the stress relaxation capacity not changed.
- FTIR results show that modified asphalt binder with nanosilica will reduce the aging process, oxidant reactions and delayed.

Figure 15. Stiffness of control and modified asphalt binder at 60 second
12. References

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