Rehabilitation of Asphalt Binder to Improve Rutting, Fatigue and Thermal Cracking Behavior using Nano-Silica and Synthesized Polyurethane

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ABSTRACT
The aim of this study was to investigate the behaviour of the binders modified by nano-silica and synthesized polyurethane. To do so, firstly, the binder was modified by three different percentages of nano-silica and poly-urethane. Then, the asphalt binders were aged in different levels based on the test conditions. The high- and low-temperature performance were evaluated using Multiple Stress Creep Recovery (MSCR) and the Bending Beam Rheometer (BBR) tests, respectively. For investigation the fatigue performance in intermediate temperature, Time Sweep (TS) test was performed. The results indicate that the nano-silica improved the performance of the asphalt binder at high temperatures and lowered the efficiency at low temperatures. The synthesized polyurethane had no effect on the high-temperature performance grade of the asphalt binder. However, it improved the low-temperature performance grade. The results of fatigue test indicate that the effect of polyurethane was better than the nano-silica. Fourier transform infrared spectroscopy test was utilized to investigate chemical properties. Obtained results affirmed the presence of nano-silica and polyurethane bonds. Chemical bonds at low and intermediate temperatures, as well as physical properties and stiffness at high temperatures, play a more important role in the performance of the asphalt binder.

1. Introduction
Annually, damages to the pavement incur large costs in the transportation system of countries. Asphalt binder plays a determining role in these damages [1]. One method to extend the lifetime of the pavement is to modify the asphalt binder.
Various studies have been conducted on the modification of the asphalt binder with the nano-materials [2]. The research on the strain recovery of asphalt binder modified by nano-silica showed that the addition of nano-silica had a positive effect on the recovery [3]. The use of nano-silica increased elastic properties, decreased the phase angle and enhanced the complex modulus in the asphalt binder. The $G^* \cdot \sin \delta$ parameter increased and therefore, the fatigue resistance reduced. In low temperature, asphalt binder modified by nano-materials, increased stiffness and decreased $m$-value [4]. The fatigue life of the asphalt binder modified by the nano-silica increased more in comparison to the asphalt binder modified by nano-TiO2 and nano-CaCO3 [5].

Mixing of polymers with the asphalt binder is a time-consuming and high-temperature process [6,7]. Reactive polymers is more environmentally suitable and, unlike most additives, there is no need to increase the mixing temperature when making a modified asphalt sample. Polyurethane is the general designation for the polymers with urethane bonds. Urethane bonds are formed by the reaction of the isocyanate group with polyol.

Some groups such as hydroxyl (OH), with active hydrogen, react with an isocyanate group to create urethane bonds [8]. In terms of polyurethanes, most studies were performed at high temperatures by examining the Superpave parameters. Another study investigated the binders with modified polyurethane and the $G^*/\sin \delta$ parameter. The results showed a reasonable resistance in the binder to the permanent deformation of rutting [9, 10].

In the synthesized polyurethane (MDI1-PPG2), a decrease in the phase angle was observed in addition to the increase in the complex modulus. The asphalt binder modified by polyurethane foam showed an increase in the viscosity and the $G^*/\sin \delta$ parameter [11]. The increase in the $G^*/\sin \delta$ parameter has been used as an indicator of rutting resistance in asphalt binder [12]. Recent studies have shown that this parameter cannot predict well the in-situ rutting [13]. To study the fatigue of asphalt binder, firstly, $G^*/\sin \delta$ parameter was introduced by SHRP institution. Bahia et al. [14] showed that there is no correlation between fatigue life of the mixture and this parameter. The MSCR and TS test were extended to calculate the rutting and fatigue life of the asphalt binder.

To study the molecular structure, the Fourier Transform Infrared Spectroscopy (FTIR) test was used. There are three distinct groups for nano-silica, which are not found in the basic asphalt binders. The results indicated that the three peaks of 450, 850, and 1050 confirmed the nano-silica tensile bonding [15,16].

The results for asphalt binder modified synthesized polyurethane indicated the presence of the NCO bond in the isocyanate with the wave-number of 2268.88 ($cm^{-1}$) and OH bond in the polyol with the wave-number of 3473.136 ($cm^{-1}$). Having a combination of polyol and isocyanate and polyurethane synthesis, Urethane bonds with a wave number of 1762.33 ($cm^{-1}$) were observed [8]. In this study, the effect of the nano-silica and synthesized polyurethane on rheological parameters of the asphalt binder at high temperatures was studied. Also, fatigue and

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1 diphenylmethane diisocyanate  
2 Polypropylene glycol
rutting behavior of the asphalt binder was investigated using TS and MSCR tests. Besides, the BBR tests were carried out at low temperatures to investigate the thermal cracking resistance. Another purpose of this research was to synthesis of polyurethane and the development of asphalt binder modified by polyurethane.

2. Materials

In this study, the asphalt binder from the Jay Oil Refinery Co. with penetration grade of 85-100 was used. The properties of base asphalt binder are listed in Table 1.

<table>
<thead>
<tr>
<th>Test</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Softening point (°C)</td>
<td>46.6</td>
</tr>
<tr>
<td>Viscosity @ 135°C (Pa.s)</td>
<td>0.25</td>
</tr>
<tr>
<td>Penetration @ 25°C (0.1 mm)</td>
<td>88</td>
</tr>
<tr>
<td>Flash point temperature (°C)</td>
<td>332</td>
</tr>
</tbody>
</table>

The specifications of nano-silica and polyurethane used in this study are presented in Table 2.

<table>
<thead>
<tr>
<th>Additives</th>
<th>Nano-silica</th>
<th>Synthesized polyurethane</th>
</tr>
</thead>
<tbody>
<tr>
<td>the amount of</td>
<td>3, 5 and 7 wt. % of asphalt binder</td>
<td>3, 5 and 7 wt. % of asphalt binder</td>
</tr>
<tr>
<td>Temperature</td>
<td>160°C</td>
<td>90°C</td>
</tr>
<tr>
<td>Speed</td>
<td>4000 rpm</td>
<td>1050 rpm</td>
</tr>
<tr>
<td>Time</td>
<td>45 minutes to 1 hour</td>
<td></td>
</tr>
</tbody>
</table>

3. Methodology for Laboratory

3.1. Sample preparation for laboratory

This polymer was synthesized by reaction of a polyether polyol and a polymeric MDI at 30-40 °C, for 48 h, in nitrogen atmosphere and under agitation [11].

In this study, a high-shear machine was used to add nano-silica and polyurethane to the asphalt binder according to the previous research [15, 17]. This parameters was used, according to previous studies. Sample preparation details are listed in Table 3.

3.2. Sample preparation for FTIR

The Fourier transform infrared spectroscopy (FTIR) was used to study the molecular structure. The IR spectrum reaching the sample, some parts were absorbed by the sample and some other parts were transmitted through it. The resultant spectrum shows the molecular absorption and the transmission, and generates the molecular fingerprint. Similar to such fingerprint, the molecular structure of materials is also exclusive.

4. Laboratory testing

Fatigue and rutting behavior of the asphalt binder was investigated using TS and MSCR tests. The BBR tests were carried out at low temperatures to investigate the thermal
cracking resistance. For each test, two replicates were performed and the average results were presented.

4.1. MSCR Test

The MSCR test is performed with 1s loading and 9s unloading at strain levels of 0.1 and 3.2 kPa in 10 cycles for each stress level [18]. The non-recoverable creep compliance (Jnr) and recovery percentage (R) in each cycle are obtained to determine the performance of asphalt binder. Tests were performed at temperatures of 58°C, 64°C, 70°C and 76°C [19]. Since rutting, as opposed to fatigue, occurs within few years of operation, rolling thin film oven (RTFO) is applied to the sample. In RTFO, aging of the asphalt binder was performed at 163°C for 85 min [20,21].

4.2. BBR Test

The BBR test was performed to determine the performance of the asphalt binder at low temperature (-6°C, -12°C and -18°C). After applying the short-term ageing process of RTFO, Pressure Aging Vessel (PAV) is applied on the asphalt binder and the sample is pressurised to 2.1 MPa at 90°C for 20 hours. The results of this experiment on the samples are two creep stiffness parameters and the variations of the asphalt binder stiffness with time during loading (m).

4.3. TS Test

This test was used to evaluate fatigue life of asphalt binder at intermediate temperature, and to measure fatigue life with loading cycle in fixed domain. Loading was done at strain level of 2.5% and 5%, at 20 °C. Fatigue test was carried out on asphalt binder embedded between plates with a diameter of 8 mm and a thickness of 2 mm. The frequency in the TS test was 10 Hz [24]. In the TS test, a 50% reduction in shear modulus is considered as fatigue life.

5. Results and Discussion

5.1. Rutting Test Results

The effect of nano-silica and synthesized polyurethane on the high-temperature rheological properties of the asphalt binder is shown in Figure 1. To study the behavior of samples at high temperature, the G*/sinδ parameter was studied without aging and after RTFO.

![Fig. 1. G*/ Sinδ parameter of asphalt binder: before RTFO (a), after RTFO (b).](image)

The results indicate that with an increase in the amount of nano-silica, the G*/Sinδ parameter increased and the rheological behavior of the asphalt binder was significantly improved at the high temperature. For the polyurethane, low percentages, i.e. 3% and 5%, were not influential. For 7% polyurethane, G*/Sinδ parameter showed slightly increase.

To test the high-temperature performance, the MSCR test was carried out at various temperatures, so that a wide range of high temperatures is considered. The results of this experiment are presented in Figure 2.
Fig. 2. Jnr Parameters at 0.1 kPa (a), 3.2 kPa (b).

Jnr is considered as a parameter for rutting resistance [25]. The Jnr could be a measure of the material resistance to rutting. Nanosilica reduces the Jnr parameter and has an acceptable degree of effectiveness for asphalt binder rutting performance at high temperatures and strains. This indicates a lesser rutting of asphalt binders modified by nanosilica. It also shows the resistance of nanosilica at high temperatures against rutting. Test results indicated a slight increase in the Jnr of 3% and 5% polyurethane binders. Asphalt binder with 7% polyurethane slightly improved the property of rutting resistance. The results of R (%) are presented in Figure 3.

Fig. 3. Recovery parameters at 0.1 kPa (a), 3.2 kPa (b).

The results reveal that the recovery in the two stress levels has increased with an increase in the amount of nanosilica. Nanosilica also has a reasonable elasticity in the asphalt binder samples. The asphalt binder modified by 3% or 5% nano-silica in stress level of 0.1 kPa has considerable recovery in various temperatures. In the 3.2 kPa stress level, it had no significant recovery when compared to the base asphalt binder. Adding 7% of nanosilica to the asphalt binder leads to a considerable recovery in the two stress levels. There is a negative recovery at high temperatures (outside the range of high PG), low percentages of additive and high stress levels.

For the synthesized polyurethane, low percentages, i.e. 3% and 5%, had no effect on recovery. Asphalt binder modified by 7% polyurethane slightly improved the recovery of asphalt binder. The different of Jnr in two stress levels of 0.1 and 3.2 kPa represents the sensitivity of asphalt binder to the stress level. The results of different percentages of non-recoverable strain and recovery are presented in Figure 4.

Fig. 4. Jnr, diff Parameter.

Compared to the base asphalt binder, the asphalt binder containing 3% or 5% of nanosilica was more sensitive to the stress level. Increasing nanosilica resulted in a decrease in the asphalt binder's sensitivity to the stress level. This sensitivity was reduced for 7 percent of nanosilica. The procedure was the same for the synthesized polyurethane. Compared to the base asphalt binder, the asphalt binder containing 3% or 5%
polyurethane showed a higher sensitivity, but the sensitivity to the stress level was reduced for 7 percent of polyurethane. The relation between the parameters Jnr and R (%) is shown in Fig. 5.

As parameter Jnr increases, R (%) decreases. However, there was no significant relationship between these two parameters.

5.2. Low-Temperature Performance Based on BBR Test Results

In order to investigate the behavior of the asphalt binder at low temperatures, the stiffness and m-value were investigated. The sample is under the PAV. Figure 6 shows the changes in the stiffness and Figure 7 shows the variation of the m-value parameter. Tests were carried out at temperatures -6, -12 and -18°C.

Adding nano-silica increases the stiffness, decreases the m-value parameter, and thus reduces thermal cracking resistance. For asphalt binders modified by Nano-silica increased stiffness and decreased m-value parameter were observed as same as the temperature of -6°C, at -12°C.

At the temperature of -6°C, a change in the stiffness was observed in the synthesized polyurethane. For polyurethane synthesized at the temperature of -6°C, an increase in the stiffness parameter resulted in an increase in the m-value, and therefore, an increase in the thermal cracking resistance. The results indicate that the stiffness of the asphalt binder cannot be a measure of its resistance to cracking at low temperature, and the resistance and softness of the additive are important, too. Polyurethane increases the asphalt binder stiffness. Polyurethane improves the low-temperature performance of asphalt binder compared to basic asphalt binder.

At -12°C, the synthesized polyurethane showed reduced stiffness and increased value of m-value parameter. At -18°C, for 7% polyurethane, the m-value parameter was in the permissible range. Other samples were not tested at -18 °C. Because they did not pass the standard at -12 °C or passed through the boundary.
The synthesized polyurethane performs well in this field and increases the resistance to thermal cracking. It also appears that at lower temperatures, this material creates higher flexibility with an increase in the weight percentage in the asphalt binder. With asphalt aging, the amount of resin increases, which make the asphalt binder stiff and brittle. Adding materials with flexible bonding can help low-temperature performance. The synthesized polyurethane has a suitable resilience at low temperatures, but is not flexible enough for nano-silica bonds. The BBR test shows that rigidity or flexibility alone is not a criterion for the performance of the modified asphalt binders at low temperatures, and bonding properties and additive behavior are also important. For any type of additive, it is possible to have different behavior at different temperatures.

5.3. Determination of Performance Grade

The performance grade of considered asphalt binders in this study is presented in Table 4.

Table 4. Performance grade of asphalt binder at PG and MSCR system.

<table>
<thead>
<tr>
<th>Binder type</th>
<th>PG system (°C)</th>
<th>MSCR system based on traffic levels</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Standard (S)</td>
<td>Heavy (H)</td>
</tr>
<tr>
<td>Base binder</td>
<td>58-22</td>
<td>58V-16</td>
</tr>
<tr>
<td>binder with 3% nano-silica</td>
<td>58-16</td>
<td>58H-16</td>
</tr>
<tr>
<td>binder with 5% nano-silica</td>
<td>64-16</td>
<td>64S-16</td>
</tr>
<tr>
<td>binder with 7% nano-silica</td>
<td>70-16</td>
<td>70H-16</td>
</tr>
<tr>
<td>binder with 3% polyurethane</td>
<td>58-22</td>
<td>58V-16</td>
</tr>
<tr>
<td>binder with 5% polyurethane</td>
<td>58-22</td>
<td>58V-16</td>
</tr>
<tr>
<td>binder with 7% polyurethane</td>
<td>58-28</td>
<td>58V-16</td>
</tr>
</tbody>
</table>

5.4. Fatigue Performance Based on TS Test Results

Figure 8 provides fatigue life samples of TS test at strain level of 2.5% and 5%. The results show that fatigue life increased with an increase of nano-silica and polyurethane content.

The performance grades of asphalt binders used in this study were classified in two ways. The results showed that the behavior of the asphalt binder modified by nano-silica improved at high temperature. Modification by nano-silica resulted in better performance of asphalt binder. The best performance was obtained with 7% nano-silica at high temperatures. However, nano-silica had poor performance at low temperatures and deteriorated the performance of the base binder. Polyurethane gave rise to a better high-temperature performance but was not sufficient to enhance performance grade. Moreover, a mixture of 7% Polyurethane improved the low-temperature performance grade by one degree.
fatigue life of the asphalt binder modified by nano-silica and polyurethane increased 3.7 and 4 times, respectively. The results showed that the fatigue life for different matters is dependent on strain level and additive percentage. The polyurethane had better performance in low strain, while there is the same performance between the two additives in high strain. The result show that 7% additive is the highest amount that produce the highest results compared to other percentages for both additives.

5.5. SEM Test

The scanning electron microscopy (SEM) was also used to measure, identify and analyze the modified asphalt binder.

The SEM result show that the mix of nano-silica and asphalt binder has a homogeneous structure.

5.6. FTIR Test Result

The FTIR test was used to identify the compounds in base and modified samples in un-aged conditions. The bonds in the asphalt binders are shown in Figure 10.

Fig. 10. FTIR test of base and modified asphalt binder.

The absorption band of the region 1115 (cm$^{-1}$) confirms the existence of the Si-O-Si group in asphalt binder modified nano-silica. The symmetric tensile fluctuations of the group appear in the region 744 (cm$^{-1}$) and 471 (cm$^{-1}$). As results show, in the spectrum of the modified asphalt binder, a peak point is observed for urethane bonds with a wave-number of 1726.96 (cm$^{-1}$), indicating the presence of urethane bonds in this sample. This wave number, which is related to urethane bonds, is not observed in the basic asphalt binder.

The results indicated that the chemical bonds is important for modified asphalt binder, in addition to the physical property. It seems rutting parameters is dependent on the physical properties. For thermal cracking, chemical bonds play a more important role. In general, the chemical bonds are highly affected on the behavior of asphalt binder at lower temperatures. The physical properties and stiffness are determinants of asphalt binder behavior at higher temperatures.

Optimal content for additives in this research for asphalt binder with respect to different properties are shown in Table 5.
Table 5. Percentage of use of the additive to achieve the best performance in this study.

<table>
<thead>
<tr>
<th>Test</th>
<th>Nano-silica</th>
<th>Polyurethane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rutting</td>
<td>7%</td>
<td>7%</td>
</tr>
<tr>
<td>Fatigue</td>
<td>7%</td>
<td>7%</td>
</tr>
<tr>
<td>Thermal cracking</td>
<td>7%</td>
<td></td>
</tr>
</tbody>
</table>

6. Summary and Conclusions

In this research, the properties of rutting, fatigue and low-temperature performance of asphalt binder modified by nano-silica and synthesized polyurethane were investigated. Based on the data analysis, the following conclusions:

- Superpave rutting parameter and MSCR test results show that nano-silica decrease Jnr value and increase recovery and G*/Sinδ parameter. At high temperatures, synthesized polyurethane showed a slight increase in the rutting resistance.

- Nano-silica took the high-temperature performance to three grades higher. The low-temperature performance reduced one grade. Synthesized polyurethane had no effect on the high-temperature performance of the binder, but had a positive effect on the low-temperature performance. For 7% polyurethane, an improvement of one grade was observed for the low-temperature performance of the binder.

- TS test results showed that nano-silica and synthesized polyurethane increased the fatigue life of asphalt binder. The polyurethane had better performance in low strain, while there was the same performance between the two additives in high strain. Optimum amount of the both additives was 7% of asphalt binder weight.

- FTIR test was performed to ensure appropriate modification of the binder by nano-materials and the synthesized polyurethane. This form of the spectrum is indicative of the presence of silica and urethane bonds in the binder.

- Chemical bonds at low temperatures, and physical properties and stiffness at high temperatures, play a more important role in performance of asphalt binder.

REFERENCES


