Impact of Nano Materials on the Properties of Asphalt Cement

Salar Khudhr Hussein¹ & Taman Ahmed Hussein² & Ganjeena Jalal Khoshnaw³

¹Civil Engineering Department, Technical College, Erbil Polytechnic University, Erbil, Iraq
²&³Civil Engineering Department, Faculty of Engineering, Tishk International University, Erbil, Iraq
³Road Const. Department, Erbil Technology College, Erbil Polytechnic University, Erbil, Iraq
Correspondence: Ganjeena Jalal Khoshnaw, Erbil Polytechnic University, Erbil, Iraq.
Email: ganjeena.khoshnaw@tiu.edu.iq

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Abstract: Traditional pavement materials are difficult to meet the realistic specifications of current and future highway pavement design requirements. Crude oil refineries with different sizes and efficiencies produce Asphalt cements (rheological and physical) which sometimes need modifications according to the pavement type, environment condition and site requirements. The interest of researchers in nanotechnology applications, particularly in the field of pavement materials, has increased over the last decade. In the present research Aluminum Oxide (Al2O3) and Silica Oxide (Si2O3) were used as Nano material modifiers to investigate their effects on Asphalt cement properties. Three percentages (3, 5, and 7%) by weight from both of them were mixed with asphalt type 40/50 penetration grade obtained from Lanas/Erbil refinery. Rheological and physical properties were investigated for all samples in the laboratory. Results showed that both Nano (silica and alumina) decreased the penetration value by (5) percent and increase the ductility value and softening point temperature. Furthermore, rotational viscosity and stiffness of the modified Asphalt cement found to be increasing gradually with adding more percentages of Nano materials, while temperature sensitivity decreases. Results also recommended that adding (5%) by weight for both Nano materials considered as optimum amount. Low productivity obtained at low and intermediate temperatures mixing Nanoparticles to the asphalt binder.

Keywords: Nano Technology, Nano Silica, Nano Alumina, Rheological and Physical Properties, Modified Asphalt, Viscosity

1. Introduction

Traditional pavement materials are difficult to meet the realistic specifications of current and future highway pavement design requirements. Bitumen efficiency is indeed not typically optimal to withstand various conditions produced by the asphalt mixture. Depending on this inefficiency, it is proven by several studies that the conventional asphalt needs to be improved by exercising additives to better performance of HAM. The demand for superior asphalt binder performance has resulted in the increased use of modifiers such as polymers, synthetic waxes, and nanoparticles in recent years (Bayekolaei et al., 2016). Polymer modified asphalt binder is enhancing the thermal cracking resistance (Isacsson & Zeng, 1988). One of the problems which polymers suffer from is asphalt cement compatibility and storage stability (Yusoff et al., 2014). This problem prompted researchers to strengthen the asphalt cement binder by studying the effect of several alternative modifiers. In modified asphalt, nanotechnology has been used more and more with different sorts of nanomaterials...
used as binder modifiers. The use of artificial Nano materials is used to change the asphalt binder's efficiency and increase its paving life. At the molecular level, after all, on the nanoscale, the manufacture of advanced techniques cause phenomena associated with atomic and molecular interaction to have a strong effect on the macroscopic property of the material (Chong, 2004).

The modification of asphalt binders using nanoparticles has gained attraction due to their unique features such as quantum effects and high surface area-to-volume ratio. Nanoscale modification improves some characteristics of asphalt binder and asphalt mixtures, such as rutting and fatigue problems, but more investigations are required before it can be applied on a large scale (Ghile, 2006, Khattak et al., 2012). Asphalt cohesion and viscosity can increase with the addition of nanoparticles, which are good for high temperature conditions. (Ping & Yunlong, 2014).

2. Previous Researches

Literature studies have shown that the impact of Nano modifiers on asphalt binders varies depending on the type of materials; various nanomaterials can be used to modify asphalt cement such as Nano silica, Nano plastic, Nano clay, Nano hydrated lime, Nano titanium, powders or Nano fibers, and Nano tubes (Yusoff et al., 2004; Khattak et al., 2012; Shafabakhsh al., 2014; Ani & Shafabakhsh, 2015). Alumina nanomaterials used in the modification of asphalt, have improved the performance of asphalt binders regarding their resistance to both high-temperature thermal rutting and low-temperature fatigue cracking. In addition to this, small quantities of Nano alumina applied to asphalt have a noticeable effect on the physical properties of the binder composite (Jahromi & Khodaii, 2009). In this regard, Nano alumina can modify asphalt by reducing penetration and increasing kinematic viscosity (Morshed et al., 2019).

Silica, which is a major compound used worldwide, is another type of Nano material that is actively used in the manufacture of silica gels, colloidal silica, and fumed silica industries (Yang & Tighe, 2013). For the processing of preparation of Nano silica, vapor phase, sol-gel and other techniques are used (Yu et al., 2007). Nano silica is one of the nanomaterials that have been shown to be effective in improving the mechanical properties of asphalt binder performance; low manufacturing costs and high-performance properties are the benefits of Nano Silica (Lazzara & Milioto, 2010). Nano silica has many characteristics, such as excellent stability, high chemical purity, large specific surface area, good adsorption, and excellent dispersion capability (Yao et al., 2013). The use of Nano silica powder has been shown to minimize the rut depth by about half of the asphalt cement when adding 2-4 percent of Nano silica by weight to asphalt binder. Furthermore, Nano silica could enhance aging resistance and slow the asphalt binder aging process (Yao et al., 2013 & Yao et al., 2011). In this research, Nano-alumina (Al2O3) and Nano silica (Si2Os) were used to modify the 40-50 grade bitumen. Based on the penetration value, softening point temperature, temperature sensitivity (penetration index), rotational viscosity, Thin Film Oven Test (TFOT) and ductility measure, the research aimed to study the rheological and physical characteristics of Nano alumina and Nano silica modified asphalt binder.

3. Materials Used and Methodology

3.1 Binder

Asphalt 40-50 penetration graded bitumen was used in testing virgin Asphalt binder regarding its physical properties. The asphalt obtained from the Lanas/Erbil refinery. Table-1 shows the physical properties of the base asphalt.
Table 1: Physical properties of virgin asphalt binder type 40-50

<table>
<thead>
<tr>
<th>Tests</th>
<th>Result</th>
<th>Test method</th>
<th>Limits</th>
</tr>
</thead>
<tbody>
<tr>
<td>Penetration (0.1 mm)</td>
<td>43</td>
<td>ASTM–D5</td>
<td>40-50</td>
</tr>
<tr>
<td>Softening Point R&amp;B</td>
<td>55.3</td>
<td>ASTM-D36</td>
<td>52-60</td>
</tr>
<tr>
<td>Ductility 25 C</td>
<td>117</td>
<td>ASTM-D113</td>
<td>&gt;100</td>
</tr>
<tr>
<td>Kinematic viscosity(cSt)</td>
<td>480</td>
<td>ASTM-D2170</td>
<td>-</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>1.03</td>
<td>ASTM-D70</td>
<td>1.01-1.05</td>
</tr>
<tr>
<td>Flash point</td>
<td>290</td>
<td>ASTM-D92</td>
<td>&gt;250</td>
</tr>
<tr>
<td>Los on heating %</td>
<td>0.4</td>
<td>ASTM-D6</td>
<td>&lt;0.5</td>
</tr>
</tbody>
</table>

3.2 Nano Particles

Two separate types of synthetic Nano materials were used as modifier namely, Nano alumina and Nano silica, with a mean particle size of 20 nm and 20-30 nm respectively. The materials obtained from US Research center of Nano materials, Inc. The physical and chemical characteristics of both Nano materials are shown in Table 2 below.

Table 2: The properties of Nano Alumina

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Aluminum Nanomaterial</th>
<th>Silica Nanomaterial</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical composition</td>
<td>Al₂O₃</td>
<td>SiO₂</td>
</tr>
<tr>
<td>Particle size</td>
<td>20 nm</td>
<td>20-30 nm</td>
</tr>
<tr>
<td>Appearance</td>
<td>White powder</td>
<td>White powder</td>
</tr>
<tr>
<td>Specific surface area (SSA)</td>
<td>&gt;138 m²/g</td>
<td>180-600m²/g</td>
</tr>
<tr>
<td>Purity</td>
<td>&lt; 99 %</td>
<td>&lt; 99.5 %</td>
</tr>
<tr>
<td>Density</td>
<td>3890 Kg/m³</td>
<td>2400 Kg/m³</td>
</tr>
<tr>
<td>Stability</td>
<td>Completely stable</td>
<td>Completely stable</td>
</tr>
</tbody>
</table>

3.3 Mixing Design Procedure

The asphalt modification is done by adding the Nano silica and Nano alumina materials directly to asphalt by using 3%, 5%, and 7% by weight for each type. The asphalt is heated to 145°C. After mixing the materials, the samples were prepared for testing for each type of the modifier according to the specifications and standard testing procedure.

3.4 Sample Preparation

The asphalt binder mixing method was produced by heating the asphalt binder to 145°C. The nanomaterial powder was eventually added to the Asphalt binder. The mixture was prepared by blending the materials with a mechanical mixer for 60 minutes at a speed of 1500 rpm to achieve a homogeneous material. The modified Asphalt binder tests included penetration grade, softening point temperature, penetration index, Brookfield rotational viscosity, ductility, and TFOT test.

3.5 Temperature Susceptibility

Asphalt is the thermoplastic material. Therefore, with temperature, its properties will be exposed to physical changes. Susceptibility to temperature is a very important property of asphalt and
characterized as the temperature at which asphalt consistency changes as the temperature changes. A penetration index property of Asphalt binder was found using the following equation:

\[
PI = \frac{20 - 500A}{1 + 50A}
\]

\[
A = \frac{\log 800 - \log(\text{Penat}25\degree\text{C})}{T_{R&B} - 25\degree\text{C}}
\]

Where: \( PI \) = Penetration Index. And \( T_{R&B} \): Softening temperature in degrees Celsius (°C).

4.6 Laboratory Tests

The following empirical tests (penetration test, softening point, penetration index, kinematic viscosity, basic gravity, TFOT and ductility) were performed on control and modified asphalts with 3, 5, 7 percentages of Nano alumina and Nano silica to investigate the effects of these modifiers on the asphalt binder material properties. Tests have been conducted in accordance with the ASTM test procedures of the American standards shown in Table 1. Although the penetration test (ASTM –D5) is an old test, many agencies around the world still use it to evaluate the stiffness of the asphalt binder material under standard conditions. The softening point test (ASTM-D36) is an indicator of flow of asphalt binder material. The kinematic viscometer (ASTM-D2170) is now widely used to test the viscosity of asphalt cement. The sensitivity of asphalt binder material to temperature (penetration index) (ASTM-D6) was evaluated by the relationship between the penetration value and the results of the softening point temperature (SP/pen) (Enieb & Diab, 2017). To define the loss by heating the Asphalt, TFOT was performed. The cohesion of the asphalt binder material is indicated by ductility test conducted according to (ASTM-D113).

4. Results and Discussion

Rheological test on virgin and modified bitumen with different Nano additives content are conducted to investigate the influence of addition of each type of nanomaterial of the unmodified bitumen on different properties of the mix. Figure (1) exhibits the influence of the asphalt cement binder after addition both nanomaterial types with different percentages on the penetration value. The figure shows that the penetration value of the binder decreases after adding 3% and 5% of Nano alumina and Nano silica for both materials producing the best binder stiffness. While adding 7% of Nano Materials resulted slight increase in penetration value occurred due to the uneven dispersion of asphalt nanoparticles when there is agglomeration. In general, it can conclude that both Nano materials affecting in same manner. The decrease in the penetration value of asphalt is an indication for better hardness and stiffness at moderate temperatures.

Figure 1: penetration of base with Al2O3 and Si2O3-modified asphalt binders
The penetration index (PI) is a term often used to describe the temperature sensitivity of the asphalt binder. The higher the penetration index value, the lower the sensitivity to temperature and the higher the stiffness. Lower temperature sensitivity is an indication of greater resistance during the summer seasons versus low-temperature cracking and rutting deformation (Marandi & Ghasemi, 2013). The control sample (0% of Nano modifier) recorded PI value=-0.307. The results showed that for addition of Nano silica and Nano alumina modifier to asphalt binders of 3%, 5% and 7% results give the PI values -0.352, -0.529 and -0.07 for silica and -0.247, -0.189 and -0.330 for alumina respectively as shown in Figure 2.

![Figure 2: Penetration index of base with Al2O3 and Si2O3 -modified asphalt binders](image)

It can be shown also that the adjusted asphalt PI value is reducing in incompatible manner with the increase in the percentages of Nano-silica and Nano-alumina values. However, the inclusion of these Nano materials has a negative effect on the asphalt cement binder's temperature sensitivity, but the PI values are still within the range of (+2.0 to -2.0) which is good indication that the modified asphalt can be used for highway paving (Enieb & Diab, 2017).

Moreover, based on Figure 3 below, it was noted that adding Nano alumina and Nano silica to the asphalt binder contributes up to 5 percent improvement in the softening point of the modified asphalt binders. But for the Nano silica, the softening point stays the same for 7 percent and reports a decrease in the same Nano alumina ratio. This is due to the solid phase of Nano material process, which improves the hardness of modified asphalt cement.

![Figure 3: Softening of base with Al2O3 and Si2O3 -modified asphalt binders](image)
The viscosity of the base binder becomes greater after addition of both nanomaterials at the test temperature of (135°C). However, compared with the base asphalt binder, the modified asphalt cement sample showed a substantial change, as shown in Figure 4. The increase in viscosity is a result of the hardening effect of nanomaterials. The increased viscosity of the modified asphalt binders could be due to better dispersion of the added Nano material layers in the base binder, which contributes to an increase in the bonding strength by restricting the flow of asphalt. This makes it harder and increases the physical properties of the asphalt, this is good indication for the improvement in the properties of asphalt cement binder.

![Figure 4: Viscosity of base with Al2O3 and Si2O3-modified asphalt binders](image)

The main mechanisms of aging of bitumen are oxidation and loss volatiles for the virgin and modified binder can be found with TFTO test as shown in table 3 for finding the loss on heating. The results showed that the base binder loss on heat is 0.4% while the loss on heat for all the percentages of Nano alumina and silica were zero.

<table>
<thead>
<tr>
<th>Nano Particles %</th>
<th>Loss on Heating</th>
</tr>
</thead>
<tbody>
<tr>
<td>0% Control</td>
<td>0.4%</td>
</tr>
<tr>
<td>3% Si2O3</td>
<td>0</td>
</tr>
<tr>
<td>5% Si2O3</td>
<td>0</td>
</tr>
<tr>
<td>7% Si2O3</td>
<td>0</td>
</tr>
<tr>
<td>3% Al2O3</td>
<td>0</td>
</tr>
<tr>
<td>5% Al2O3</td>
<td>0</td>
</tr>
<tr>
<td>7% Al2O3</td>
<td>0</td>
</tr>
</tbody>
</table>

The property of ductility is used to show the asphalt cement binder's cohesion. The relationship between the ductility values of the Nano alumina asphalt material and the Nano silica material contents are shown in Figure 4. It can be noted from the figure that the ductility value decreases with the increase in the percentage of nanomaterials, confirming that the outcome of previous research (Zghair et al., 2019). But for the Nano alumina adding of 7% to the binder, the ductility values started to increase in
a remarkable rate which confirms the results of the previous studies (Ali et al., 2016 & Ali et al., 2017). That is in line with the increased stiffness of the modified binders. Therefore, Nano silica powder diffusion and adsorption in the asphalt cement binder contributes to the absorption of light volatiles (oily material) in the molten component and increases the asphalting part of the bitumen binder. However, rising asphalt stiffness resulting from the alteration of Nano silica contributes to a decrease in ductility.

![Figure 4: Ductility of base with Al2O3 and Si2O3-modified asphalt binders](image)

**5. Conclusion**

From the tests conducted in this study and methodology followed, it was found that adding nanomaterial such as Nano Alumina and Nano Silica to Asphalt Cement have a noticeable effect on the radiological and physical properties of Asphalt Cement binder. The additives by weight at rate of 3%, 5% and 7% produced a modified Asphalt cement binder that can be used in paving the highways to produce better performance and longer service lives. The following can be concluded:

1. Penetration value for Asphalt cement binder material decreased with increasing Nano silica and Nano alumina percentages by about 49% when 5% modifier had added. It is an indicator for better Asphalt hardness and stiffness at moderate temperatures.
2. Better resistance to the oxidation process and aging obtained when Nano Silica and Nano Alumina added to the base Asphalt, the ductility decreases by up to 7% meaning that its stiffness increases with an increase in Nano materials.
3. The Asphalt binder material penetration index decreases in an incompatible way with the rise in the percentage of both Nano materials.
4. In hot weather conditions, the modified asphalt cement binder was more sustainable. Lower penetration value, high softening point temperature and high viscosity are observed based on the research results.
5. Finally, in this research, the modified asphalt binder showed the best properties when 5% percent Al2O3 and Si2O3 nanoparticles are utilized and considered as optimal value.

**References**


