Investigating the preparation and characterization of nanoclay modified asphalts

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Abstract: In order to extend the lifespan of flexible pavements materials, a binder quality requests to be modified. The aim of the present research is to assess the physical features of original and modified asphalts with nanoclay materials. These features including; softening point values, penetration grades, viscosity values, penetration index values, and ductility. Three percentages of nanoclay contents (3, 5, and 7) % by of the asphalt weight were blended by a shear blender set at (4000) rpm., and mixing time set about 45 min. at 140 °C. Physical tests results showed that adding nanoclay material as a modifier was beneficial in enhancing the asphalts features. For example, viscosity values and softening point values increase when increase in the nanoclay content. Consequently, the mixing temperatures and compaction temperatures of the modified asphalts increase with increase the nanoclay content to reach (170 °C). While the penetration and ductility values decrease when increase the modifier content. Regarding the penetration index of the modified asphalts, it is enhanced by increase in the nanoclay proportions. Hence, the modified asphalt with 7% of nanoclay produces the greater value of penetration index accordingly, it has a positive influence on the rutting resistance.

Keyword: Nanoclay, Asphalt Properties, Modification method. Physical tests, Mixing and compaction temperatures

1. Introduction

Asphalt is an organic material that is normally used in flexible pavement materials, due to better viscoelastic behaviors. Unfortunately, asphalt alters brittle at lower temperatures and elastic at greater temperatures. This can lead to high temperature rutting failure and low temperature cracking failure of asphalt concrete pavements. Its uses are limited by theses sensitivities of temperature [1]. To develop the performance of asphalts and mixes, the addition of additives such as polymer [2], limestone [3], rubber [4], and waste material powders [5-8] have become common in recent decades.

Nanotechnology technique could make benefits by two behaviors. Firstly, by developing more economic, durable, and efficient procedure and materials, and secondly by forming wholly new products. The greatest type used of clay is layered silicates is montmorillonite clay (MMT) type, that has a (2:1) layered structure with two of silica tetrahedron sandwiching an alumina octahedron [9]. Nano-modification of asphalts has the probable to expose wholly innovative practices and categories of asphalts with extensive significances for the transportation substructure. The ability clay to aim the modification at the nano structural level, potentials to deliver the optimization of binder properties and performance needed to meaningfully evolution performance, durability, and sustainability [10].

Nano-materials are alternative types of modifiers, which have exposed encouraging consequences in improving the rheological and physical characteristics of asphalts [11]. Numerous types of the nano powders, Nano-clay powders have significant influences on developing the performance properties of both asphalt binder and mix [12-17].

Many studies investigated the modified polymers with Nano-clay. Nevertheless, restricted researches are existing around nanoclay modified asphalts. Variables of material which can be studied and their effect on the properties and behavior of the final nano-composite binder’s materials can be investigate; consist of clay category, choice of clay pre-treatment, and the technique in which the polymer is combined into the Nano-composite material [18]. The clay pureness can distress the final nano-composite properties. Several clay forms are alumina silicates, that take a layered structure, and involve
silica tetrahedron (SiO$_4$) combined to alumina octahedron (AlO$_6$) in a variation of methods. A (2-1) proportion of the tetrahedron to the octahedron significances into minerals of clay, with montmorillonite (MMT) is the furthermost common. The aspect ratios of the montmorillonite are high, typically 100–1500 and thickness layers (platelets) is 1 nm [19].

The modifying asphalt with nanoclay causes enhancement of the lifespan of flexible pavement and the stability of asphalt mix (20&21, 34& 35).

The key aim of this research is to investigate physical and rheological features of the modified asphalts with selected three contents (3%, 5%, and 7) % of nanoclay by asphalt weight. The considered physical tests in this study are the softening point temperature values, ductility values, penetration grades, viscosity values, and susceptibility of temperature (penetration index) P.I. In addition, the mixing and compaction temperatures (workability) of the modified asphalts will be investigated.

2. Methodology and experimental procedure

2.1 Asphalt binder

The original asphalt used in this research is (60-70) penetration, which was brought from the Dora Refinery at Iraq. Table 1 displays the features of the used original asphalt.

| Test                  | Penetration  | Rotational Viscosity | Softening point | Penetration index | Flashpoint | Fire point | Ductility value |
|-----------------------|--------------|----------------------|-----------------|------------------|------------|------------|----------------|
| Standard              | ASTM D5[22]  | ASTM D4402 [23]      | ASTM D36 [24]   | ASTM D36 [24]    | ASTM D92 [25] | Flashpoint | Fire point    |
| Results               | 66           | 430 @ 135 °C         | 49.5            | -0.665           | 302°C      | Fire point | 130            |
| Limits of Iraqi      | 60-70        | ----                 | ----            | ----             | > 323 °C   | >100       |
| Specification [27]    |              | 128 @ 165 °C         |                 |                  | 310°C      |            |

2.2 Nonclay material (nC)

The used nanoclay is a hydrophilic high purity Montmorillonite powder. It was bought from Nanocor © Inc., USA, and used as conventional powder as shown in plate (1). The Montmorillonite powder consists of minerals of aluminosilicate. The physical characteristics and chemical compositions of the nanoclay powder are exposed in Tables 2 and 3. Montmorillonite powder has a sheet layered structure, even though their sizes in length and width directions are 100 nm and the plate thickness is 1 nm.

Accordingly, an individual sheet has aspect ratio about (200 to 1000), with a common of platelets at the (200 to 400) variety after cleansing process. Theoretical formulation of the montmorillonite (MMT.) as: (Na, Ca) - (Al, Mg) 2 (SiO10) (OH) 2 nH$_2$O
Table 2. The Chemical analysis of the used nanoclay powder *.

| Oxide Composition | SiO₂ (%) | Al₂O₃ (%) | Fe₂O₃ (%) | CaO (%) | MgO (%) | L.S.F. (%) | Insoluble residue, (%) | L.O.I. (%) | So₃ (%) |
|-------------------|----------|-----------|-----------|---------|---------|-----------|------------------------|------------|--------|
| Oxide (%)         |          |           |           |         |         |           |                        |            |        |
| 58.7              | 81       | 31        | 34        | 16      | 0.02    | 55.24     | 40.62                  |            | 0.06   |

Table 3. Physical features of the nanoclay powder *.

| Feature                      | Value          |
|------------------------------|----------------|
| Surface modifier            | Dimethyl; di-hydrogenated tallow ammonium |
| Particle size                | 14–19 µm       |
| Color                        | White          |
| Specific gravity             | 1.8            |
| Bulk density (kg/m³)         | 250–300        |
| Surface modifier concentration % wt. | 33–37         |

*physical features & chemical analysis were performed consistent with data sheet of manufacture.

2.3 Preparation method of Asphalts modified with nanoclay powder

About 300 g of Nanoclay (nC) modified asphalt specimens and the original asphalt were pre-heated to (140 +/- 5) ºC. The shear blender can be fixed at a rotational speed (4,000) rpm. and mixing time fixed at 45 min. Nanoclay was added with percentage of content 3%, 5% and 7% of asphalt weight, in closed steel container and put inside an electronic oven for 45 min.

2.4 Physical Tests of the modified asphalts

Physical tests were carried out to investigate the properties of the modified asphalts with three selected contents (3, 5 and 7) % of nanoclay by weight of asphalt. These tests are penetration grade, viscosity values, penetration index (PI.), softening point, and ductility value. The examinations were attained based on the standard specification.

3. Results and Discussions

Figure 1, shows that the penetration grades have been reduced when the percentage of the nanoclay content increases. The reduction of the penetration value is an indication of enhancing the stiffness of the modified asphalt at moderate temperature (25) ºC. The consequence is attributed to the diffusion of nanoclay particles into the asphalt, causes evaporation of light volatiles materials in maltene part and convert to asphaltene part of modified asphalts [28 & 35]. Accordingly, the stiffness of nanoclay particles is greater than the stiffness of asphalt. This produces the stiffness of the nC modified asphalts.
superior reduction in the penetration grades was noted at 7% of nanoclay content for the modified asphalts in compared with the original asphalt; subsequently there is no important alteration between 5% and 7% nanoclay percent, as agreed with M. El-Shafie,2013 [29].

Figure 2, shows the results of the softening point values of the modified binders with nanoclay contents. It can be noticed that the softening point rises because of adding nanoclay material. It indicates that the modified asphalts are less sensitive to great temperature variations, and it has resistance to rutting failure in compared to original asphalt. The result is attributed to depletion of the light volatiles material in the maltene portion then amend to the asphaltenes portion [28]. This performance is due to the consequence of chemical reaction, also alteration in the chemical microstructure of modified asphalts, the same was mentioned by Ghile.2005 [30].

Figure 3 presents the penetration index (P.I.) of the modified asphalts versus nanoclay proportions. It can be detected that the penetration index (P.I.) values increases with the addition of the nanoclay material. Nevertheless, the addition of nanoclay has a role in improving the behavior on the temperature susceptibility. The modified binder with 7% of nanoclay content presents the max PI. value in compared with the original; were within the range of PI values (+2.0 to -2.0), and all the modified asphalts can be used in construction of flexible pavements [31, 34, 35].

The rotational viscosity test is used to estimate the workability of asphalts at great temperatures, which is supposed to be one of the supreme important properties of asphalts. Figures 4 and 5 show the viscosity values resulted from modifying asphalts with nanoclay. It can be observed that there is an enhancement in viscosity of nC modified asphalts. These enhancements are related with the addition of nanoclay proportions into asphalts. The modified asphalt with 7% of nanoclay content exhibited the superior value of viscosity in compared with original asphalt, which were within the allowable max viscosity about (3) Pa. sec. at 135 °C, conferring with the limits of standards specifications. The main reason is the creation of the exfoliated microstructure which causes to have thicker film, because of agglomeration of nanoclay particle. This may block the dislocation of modified asphalt molecules chains [32]. Also, to the influence be supposed that if the nanoclay is more usually separate they must to add more strength to rise the resistance to shear flow of molecular [33].

Figure 6 shows the relationship of temperatures mixing and compaction for original and modified asphalts, according to the estimation the viscosity values at temperatures values approximately (135 &165) °C. Based on the results of figure 6, it can be noticed that there is an increase in the mixing temperatures and compaction temperatures for modified asphalts. This rise is correlated with the increase of viscosity of modified asphalts by adding the nanoclay content, hence the modified asphalts do not melt satisfactory at typical mixing temperatures (160°C) used for the base asphalt. The modified asphalt with 7% nanoclay content exhibited the greater value of temperatures mixing and compaction in compared with the original asphalt.

Figure 7 shows the results of the ductility test of modified asphalts against nanoclay proportions. It can be noticed that the ductility values are reduced by the addition of the nanoclay. It is an indication of depletion of light volatiles materials into the maltene segment and progresses to the asphaltenes segment of the modified asphalts. In addition, the maximum decrease in the ductility value was noted with 7% nanoclay content, as a result of the fact that the non-homogenous dispersion of nanoclay particles.
Figure 1. Penetration grades for the unmodified and the nC modified asphalts with nanoclay contents.

Figure 2. Softening point temperatures for the unmodified and the nC modified asphalts with nanoclay contents.
Figure 3. Penetration index for the unmodified and the nC modified asphalts with nanoclay contents.

Figure 4. Rotational viscosity values for the unmodified and the nC modified asphalts with nanoclay contents at 135 °C.
Figure 5. Rotational viscosity values for the unmodified and the nC modified asphalts with nanoclay contents at 165°C.

Figure 6. Relationships of temperatures mixing & compaction for the unmodified and the nC modified asphalts.
Figure 7. Ductility value for the unmodified and the nC modified asphalts with nanoclay contents.

4. Conclusions
The current research was conducted to estimate the influences of nanoclay powder on the asphalt properties according to physical tests. According to the results of this research, the subsequent conclusions could be drawn:

1. Using nanoclay reduces the penetration grades, while it improves the softening point temperatures of the modified asphalts. The greater drop in the penetration value, correspondingly rise in the softening point were seen at 7% nanoclay proportion for all types of modified asphalts in compared with the original asphalt. There is no important alteration between 5% and 7% nanoclay proportion.

2. Regarding to the susceptibility of temperature (penetration index PI.) values, the PI. values for the modified asphalts are enhanced by the addition of the nanoclay contents. The modified asphalt with 7% nanoclay content has the maximum PI. value and resulted in improvement in the susceptibility of temperature.

3. The use of nanoclay particles improved the rotational viscosity value when compared with the original asphalt. The modified asphalt with 7% nanoclay content showed the superior value of viscosity in compared with all types of modified asphalts.

4. Ductility values of all types of the modified asphalts reduce by adding the nanoclay contents. This can be explained by increase its stiffness with alteration of chemical microstructure of modified asphalts. In addition, the maximum decrease in the ductility value was noted with 7% nanoclay content, as a result of the fact that the non-homogenous dispersion of nanoclay particles.

5. According to the physical features of the tested samples of nC modified asphalts; such as superior penetration index (P.I.) value, greater viscosity value, greater softening point value, lower penetration grade, and ductility value with satisfactory limits; the 7% of nanoclay content was reasonable to improve these properties.

6. The shear blender set at 4000 rpm. used for 45 mins. and mixing temperature set at (140 +/- 5) °C were acceptable to gain a good spreading of nanoclay material into the asphalt binder. Moreover,
it can be practical that the extended mixing duration may result in a slight improvement of the dispersion of nanoclay. However, this may lead to extra waste of energy and cost.

7. The mixing temperatures and compaction temperatures of the modified asphalts increased with the addition the nanoclay proportions. It indicates to the rise of the viscosity of nC modified asphalts. That is the added material cannot melt at the typical mixing temperature (160°C) used of the base asphalt. So, a great mixing temperature and compaction temperature which are essential for the manufacture process of the modified asphalts mixes were raised to (170 °C).

5. References

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