Assessment of the Influence of Nano Metakaolin filler on Asphalt Binder Rheological Properties

Hussein H. Zghair 1, *, Hasan H. Joni 1 & Ali Ahmed Mohammed2

1Civil Engineering Department, University of Technology, Baghdad, Iraq.
2Faculty of Civil & Environmental Eng., Universiti Tun Hussein Onn Malaysia, Malaysia.
*E-mail address: 11539@uotechnology.edu.iq

Abstract. This paper investigates the effects of using nano metakaolin filler on the rheological properties of asphalt binder. In this work, asphalt binder of penetration grade 60 to 70 was prepared at three percentages (1%, 3%, and 5%) of asphalt weight using a high shear mixer fixed at 4,000 rpm for 60 min. Evaluations were then made of the properties of the modified asphalt binder such as the rotational viscosity, penetration grade, softening point temperature, temperature susceptibility, and ductility. The results of this work showed that the use of nano metakaolin filler as a modifier was helpful in improving asphalt binder properties. In general, it was found that the viscosity and softening point values increased, while the penetration value and temperature susceptibility (P.I.) values were reduced. The high shear mixing allowed good diffusion of nMK fillers into the asphalt binder, producing a homogenous composite binder. Additionally, the results showed that 5% nano metakaolin by asphalt weight was a reasonable additive to develop the rheological properties, increasing the softening point and viscosity values by about 14 and 77%, respectively while developing higher percentages of reduction in penetration value and ductility value of about 30 and 18%, respectively, making this more applicable to the construction of highway pavements in hot weather conditions.

Keyword: Asphalt Binder, Nano Metakaolin, Modification Method

1. Introduction

Recently, flexible pavement construction has been quickly developing all over the world due to a dramatic increase in traffic loads and harsh environmental circumstances. These circumstances, however, also promote quick deterioration of traditional materials used for flexible pavements, making it hard to meet the practical demands for construction of highway pavement. Consequently, higher quality and more eco-friendly pavement materials with longer lifetimes are urgently demanded [1]. The lifespan of pavement material is the most significant issues to be taken into account when considering economy and other design factors. Distress to asphalt binders decreases flexible pavement durability, and thus, to sustain the lifetime of pavement materials, this must be directly addressed. Common flexible pavement modes of failure include rutting, which usually occurs in the form of permanent deformation [2]. Thus, flexible pavements require asphalt binders characterised by superior performance in the face of such issues, generally in the form of a modified asphalt binder [3]. Using technology and production processes to develop new materials based on increases in the understanding of the characteristics of asphalt binder make it easier to evaluate the benefits of new modifiers and additives in asphalt binders and mixes.
Additives exist in several forms, including by-product materials from manufacturing processes [4-7]. The most common type of modifiers used in the modification process for asphalt binders and the mixes is polymers, which are thermosetting and thermoplastic. Most have now been assessed in hot asphalt mixes, and they affect many properties such as Marshall stability, moisture resistance, and rutting and fatigue resistance [8]. Nanotechnology science has recently been adopted as an innovative method in the manufacturing of such materials, with nano scale now commonly used in several fields. [9]. Many researchers have studied the possibility of using nano-materials to modify concrete; however, the study of nano-material to modify asphalt binder is relatively new. Common nano materials include nano clay, nano-silica, nano titanium, nano polymer, nano hydrated lime, and carbon nanotube [10 & 11]. Nano metakaolin (nMK) is a cementitious material that conforms to the requirements of the standard specifications [12]. Metakaolin (Al2O3; 2SiO2) filler is unique, as it is not manufactured from by-product materials or industrial processes, but instead extracted from the naturally occurring minerals, then used specifically industrially in the products of concrete. It is produced for particular aims in controlled circumstances, thus allowing specification of colour, removal of impurities, and reduction of particle size. Nano metakaolin is manufactured by the calcination method (thermal treatment) at temperatures of about 600 to 800 °C for two hours. The de-hydroxylation and disorder processes present pozzolanic characteristics, allowing the material to be used as a nanofiller [13]. Many studies have investigated the use of nano metakaolin to modify concrete and its influences on concrete characteristics, as well as presenting the material as an effective pozzolanic material [14].

Until now, limited research has been done on the characteristics of asphalt binder modified with nano metakaolin filler, however. This research thus aims to assess the influences of nano metakaolin filler on the characteristics of asphalt binder such as rotational viscosity, penetration value, softening point temperature, temperature susceptibility, and ductility at three percentages (1%, 3%, and 5% of asphalt weight) as mixed using a high shear mixer fixed at 4,000 rpm for 60 minutes to obtain a homogeneous composite.

2. Properties of Materials Used

2.1 Asphalt binder

The control asphalt binder is of 60 to 70 penetration grade, provided by the Dora refinery in Iraq. The characteristics of the control asphalt binder are as shown in a table 1.

| Test                        | ASTM     | Results                  | Iraqi Specification Limits, [21] |
|-----------------------------|----------|--------------------------|----------------------------------|
| Rotational viscosity        | D-4402, [15] | @ 135 °C 430 @ 165 °C 128 | ---                              |
| Ductility                   | D-113, [16] | 130                      | >100                             |
| Penetration                 | D-5, [17]  | 66                       | 60-70                            |
| Softening Point             | D-36, [18] | 49.5                     | ---                              |
| Penetration Index           | D-36, [18] | -0.665                   | ---                              |
| Flash Point, Fire Point     | D-92, [19] | Flash point 307°C        | > 232 °C                         |
|                             |          | Fire point 310°C         | ---                              |
| Thin Film Oven Test         | D-1754M, [20] | Pen. 89.9               | >52                              |
|                             |          | Mass loss 0.222          | <1                               |
|                             |          | Duc. 120                | >50                              |
2.2 Nano Metakaolin filler (nMK)

Nano metakaolin is an amorphous and light grey filler, as presented in Figure 1. The filler used in this research was bought from Nanocor Inc, a company located in the USA, as nano clay filler and used after thermal treatment at 750˚C for two hours, as mentioned in [22]. The chemical compositions of nMK filler are shown in table 2, while the physical properties are exhibited in table 3.

![Image of Nano Size of Metakaolin filler.](image)

Table 2. Chemical compositions of used nMK filler

| Chemical content (%) | Al₂O₃ | SiO₂ | Fe₂O₃ | CaO | L.S.F | MgO | SO₃ | Loss on Ignition | Insoluble residue |
|----------------------|-------|------|-------|-----|-------|-----|-----|------------------|------------------|
| nMK                  | 1.41  | 74.92| 1.17  | 0.01 | 0.34  | 0.07| 0.72| 57.65            |

Table 3. Physical properties of used nMK filler

| The surface modifier | Colour            | Particle size (micron) | Surface modifier concentration | Bulk density (kg/m³) | Specific gravity | Specific surface area, cm²/g. |
|----------------------|-------------------|------------------------|--------------------------------|----------------------|------------------|-----------------------------|
| Dimethyl, di-hydrogenated tallow ammonium | Light grey | 14–19 | 33–36 wt. % | 250–300 | 1.8 | 48000 |

*a chemical analysis and physical properties were performed according to the manufacturer data, and the National Center for Construction laboratories.

3. Modification Technique of Asphalt Binder

A high shear mixer was used to modify the asphalt binder with nano metakaolin filler. This mixer was fixed at 4,000 rpm, for 60 minutes at a mixing temperature of 140˚C, based on the viscosity of the control asphalt binder. Gradual addition of nMK filler to the asphalt binder at 1%, 3%, and 5% by weight was done to achieve homogeneous composite binder samples, as seen in Figure 2. Finally, the nMK modified asphalt binders were tested to assess their properties.
4. Laboratory Tests of Asphalt Binder Modified with nMK filler

To evaluate the influence of nano Metakaolin filler on asphalt binder based on rheological tests, rotational viscosity, penetration, softening point, penetration index, and ductility tests were carried out on the control asphalt binder and those modified with nano Metakaolin filler at various percentages. All tests were undertaken according to the standard specifications (ASTM). The penetration test is an old test, but it is still used across the world to assess the stiffness of asphalt, while softening point temperature is an indication of the flow of asphalt binder. The Brookfield rotational viscometer is now generally used to evaluate the viscosity of asphalt binder, and the penetration index value is an indication of the temperature susceptibility of asphalt binder, which can be calculated based on the relationship between penetration value and softening point value (SP/pen) [23]. The ductility test was used to evaluate the cohesion and homogeneity of the composite asphalt binder.

5. Results and Discussions

The main investigations used to estimate the rheological characteristics of the asphalt binders were the penetration grade and softening point temperature tests at moderate temperatures, carried out on all binder types. Figure 3 a and 3 b present the results of penetration and softening point tests for control and nMK modified asphalt binders. The penetration values of the nMK modified asphalt binders are reduced as the softening point is increased by the addition of the nano metakaolin filler. This may be due to enhancement of the stiffness of modified binder due to adsorption and dispersion of nano metakaolin filler into the asphalt binder, as well as a decrease in the quantity of light volatiles in the maltene phase and resin in the asphaltene phase. The nano metakaolin fillers are certainly clearly stiffer than the control asphalt binder [24]. The great reduction in penetration values and high improvement in softening point values detected within asphalt binder modified with nMK filler at 5% also agreed with the results in [25].
Figure 3. (a) Penetration values and (b) softening point values of control and modified asphalt binder with nano metakaolin fillers.

Figure 4 shows that the penetration index (P.I.) values for various percentages of nano metakaolin filler increased as the nano metakaolin filler content increased. The literature has shown a range of the P.I. values for asphalt binder ranging from -2, very temperature susceptible to +7, not influenced by temperature at all [23]. Generally, however, adding of nMK filler has a helpful effect on temperature susceptibility, increasing resistance to permanent deformations compared with the control asphalt binder. The asphalt binder modified with nMK filler at 5% exhibited the best penetration index, though all the penetration index (P.I.) values for asphalt binders modified with nMK content were within the standard specifications (+2.0 to -2.0), and thus could be used to construct highway pavements [26].

Figure 4. Penetration index values of control and modified asphalt binders with nano metakaolin fillers.
The rotational viscosity test was used to estimate the appropriate temperatures for mixing and compaction procedures of the hot asphalt mixes, taking into account the significant rheological characteristics of the asphalt binder. Figures 5 a and b show the relationship of rotational viscosity values with the percentage contents of nMK filler at 135 to 165 °C for the control and modified asphalt binders. From the test results, the viscosity values improve with the addition of nano metakaolin filler. These improvements can be attributed to increased stiffness of modified asphalt binder due to adsorption and dispersion of nano metakaolin filler into the asphalt binder which decreases the light volatiles in the maltene phase and alters the resin in the asphaltene phase in modified asphalt. The nano metakaolin fillers are stiffer than the control asphalt binder, and asphalt binder modified with nMK filler at 5% exhibited a higher value compared with other asphalt types, this being under the allowable maximum rotational viscosity value of 3 Pa*second at 135 °C given in the standard specifications. The huge surface area and reactivity of nMK filler forms an exfoliated structure, resulting in a thicker film on nMK modified asphalt binder. This may be the result of chemical reactions and modification of chemical structures in modified asphalt binder, as mentioned in [27 and 28].

![Figure 5](image-url)

**Figure 5.** (a) Rotational viscosity values at 135 °C and (b) Rotational viscosity values at 165 °C of control and modified asphalt binder with nano metakaolin fillers.

The ductility test was used to indicate the cohesion, elasticity, and homogeneity of the control and modified asphalt binders, indicating cracking resistance at low temperatures. Figure 6 shows these ductility values against nMK content. The ductility value decreased as nMK filler percentage increased, offering an indication of the loss of light volatiles in the maltene phase and changes to the resin in the asphaltene phase of the modified asphalt. The lowest value of ductility was observed at 5% nMK filler, but this was within the allowable range of standard specifications at >100 cm. This can be attributed to the larger surface area of nMK filler, as well as it being stiffer than the other types of asphalt binders. In addition, this impact may be the result of chemical reactions and modification of chemical structures caused by the dispersion of nanofiller into the modified asphalt binder, as mentioned by [27 and 28].
Conclusions

The main purpose of this research was to show the rheological properties of asphalt binder modified with nano metakaolin filler. Based on the results, the following conclusions have been drawn:

1. The penetration values of the nMK modified asphalt were reduced, whilst the softening point values were increased. This is an indication of the increased stiffness of the nMK modified asphalt binder at moderate temperatures. The reduction in penetration values and increase in softening point values were about 30% and 14%, respectively.

2. Regarding the temperature susceptibility (P.I.) values of the modified asphalt binder, these are improved by adding the nano metakaolin filler, an indication of increased resistance to rutting.

3. The rotational viscosity is improved with the addition of nano metakaolin filler content, which can be attributed to enhancement in the stiffness of modified asphalt binder at higher temperatures. The highest percentage increase in viscosity value was about 77%.

4. Ductility values of the nMK modified asphalt binder decreased with the addition of nano metakaolin filler content, indicating that its stiffness is improved by modification of the chemical structure and the agglomeration of nMK fillers into modified asphalt binder. The highest percentage reduction in ductility value was about 18%.

5. The shear mixing fixed at 4,000 rpm. for 60 min. at 140°C was satisfactory in terms of achieving a good diffusion of nMK fillers into the asphalt binder and gaining a homogenous composite binder.

6. Based on the rheological characteristics of the nMK modified binder, such as the lower value of penetration, greater value of softening point, greater value of viscosity, and ductility values within the allowable range, the 5% nMK filler is a reasonable selection to improve the rheological characteristics of highway pavements in hot climates.

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