Determining the Effect of Ageing of Nano-Clay Modified Bitumen Using Atomic Force Microscopy

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Abstract

This study investigates the effects of ageing simulation on the physical properties of nano-clay modified bitumens (NCMBs). Bitumen with penetration grade 60/70 is modified with 0, 2 and 4% nano-clay, and the consistency of the samples is characterized using the penetration, softening point, and viscosity tests before and after aging. Atomic force microscopy (AFM) is used to evaluate the surface roughness and tip deflection of the modified bitumens. The results of the consistency tests revealed that the incorporation of nano-clay up to 4% NC resulted in increased hardness of the modified bitumen, and all modified bitumens were affected by ageing; the results for surface roughness and tip deflection showed a similar trend and 2NCMB exhibited the lowest roughness and highest tip deflection. However, the results of consistency tests and AFM for ageing sensitivity of the bitumens are different, indicating that the addition of nano-clay has an effect on the modified bitumen but not on the unmodified bitumen. There is a high correlation between the results of consistency tests, surface roughness and tip deflection, which implies that AFM is able to identify any changes in the fluidity of the bitumen. However, the correlation between tip deflection and penetration is very weak.

Key words: Bitumen; nano-clay; ageing; Consistency Tests; Atomic Force Microscope.

1. Introduction

Bitumen is used primarily in civil engineering and is produced through distillation of crude oil. It is most frequently used as a binder in road construction, where the binder is combined with graded aggregate to obtain asphalt mixture [1]. Bitumen is very sensitive and can be affected by sunlight, changes in temperature, moisture, oxygen, etc. This sensitivity could cause changes in the physical characteristics of the bitumen which are reflected in the mechanical properties of the asphalt mixture. Weaknesses in the mechanical properties of bitumen are the cause of most problems
occurring in pavements [2]. One of the primary determinants of the properties of bitumen is ageing, which in turn influence the mechanical properties of asphalt mixtures via certain mechanisms [3].

One of the common mechanisms that occur in bitumen is oxidation [4]. Oxidation occurs when diffused oxygen reacts with bitumen, especially in hot weather. The rate of oxidation is for the most part determined by the increase in temperature; the type of bitumen and its thickness; and the type of aggregate and its gradation [5]. Increased oxidation rate of bitumen could be a result of a dramatic increase in temperature and this could occur during the mixing and compaction stages. This phenomenon is called short-term ageing. The surface of a pavement is exposed to sunlight during its service life, and the bitumen softens as the temperature increased. This allows oxygen to diffuse much more readily inside the pavement structure. The diffusion and reaction of oxygen in bitumen resulted in increased viscosity, which in consequence increase the bitumen’s stiffness. This may cause cracking, particularly in the low temperature region [3].

Due to the natural properties of bitumen, that cannot stand for long-term heavy traffic and adverse weather conditions [6]; however, modification can cause a change to improve the properties of the bitumen [7]. One of the methods for bitumen modifications is through the addition of additives such as polymer modifiers (elastomers, thermoplastic elastomers and reactive polymers) that enhance the stiffness, elasticity, cohesion and adhesion properties of bitumen [6, 7]. It was also reported that bitumen is one of the multi-phase composites materials in its mesoscale, which its mechanical properties such as the elastic properties, directly affect the performance and consider one of the important design parameters for achieving the desired practical performance [8, 9]. In general, it can be stated that modification of bitumen with additives has a direct effect on the physical, rheological, aging and adhesion properties of the bitumen [10-12]. Recently, nano-materials have been added to the list of the additives that may be beneficial to bitumen and asphalt mixture [13]. This material has been shown to alter the physical properties of bitumen. Studies have confirmed a reduction in the ageing effect of asphalt mixtures when nano-clay was added to the bitumen [14, 15]. In these studies, several tests were conducted, including consistency tests to investigate ageing, compacted-mixture test, and chemical tests. The studies differ with respect to the materials used and the applied wet condition, but the results of all studies indicate that the
addition of nano-clay improved the properties of the bitumen and that improvement is reflected in the properties of the asphalt mixtures.

Recently, researchers have been focusing more attention on using the Atomic Force Microscope (AFM) technique to evaluate the properties of bituminous binders. The general information on material properties can be obtained by using AFM, such as surface topography image of the material and force-distance curve. Also, different types of forces such as mechanical contact force, friction, van der Waals forces, capillary forces, chemical bonding and electrostatic and magnetic forces can be measured. The force-distance curve (or force curve) is used to determine elasticity, hardness, Hamaker constant, adhesion and surface charge densities [16]. AFM is a flexible high-resolution scanning probe microscopy technique that uses a laser-tracked cantilever with a sharp underside tip to raster over the sample while interacting with the surface. The sample is scanned using a tip mounted on a cantilever spring, as illustrated in Figure 1. During scanning the force between the tip and the sample is measured by monitoring the deflection of the cantilever. A topographic image of the sample is produced by plotting the deflection of the cantilever against its position on the sample [16].

The contrast in the image is due to the force between the tip and the sample, which is the result of the separation of the tip from the sample as well as the material properties of the tip and the sample. Thus far the image contrast in the majority of applications in produced through a very short-range repulsion which occurs when the electron orbitals of the tip overlaps with that of the sample (Born repulsion). Nonetheless, a more detailed interaction between the tip and sample can be used to determine the properties of the sample, the tip, or the medium between them. These measurements are referred to as ‘‘force measurements’’. In an AFM force measurement, the tip attached to a cantilever spring is moved towards the sample in a normal direction. The vertical position of the tip and the deflection of the cantilever are measured and transformed into force-distance curves known as ‘‘force curves’’ [16].

AFM techniques have been recently used as a nano-scale test to investigate the general changes in bitumen due to the variation in its penetration grade, performance grade, modification, ageing, moisture damage, etc. [17-22]. In a study conducted by Xu et al. [23] to investigate the adhesive
surface characteristics of bitumen, the micro-phase separated topographic morphologies were visualized by AFM, where measurement of topography, adhesion and elastic modulus were made. The investigation involved seven bitumen samples obtained from different suppliers. AFM is very good tool for characterizing the seven types of bitumens which have the same penetration grade but different structures with respect to their bee structure, Young’s modulus and adhesive forces [23]. Another study employed AFM to investigate the effect of ageing on bitumen modified with organo-montmorillonite. The morphology of the bitumens was analysed and compared with those of unmodified and organo-montmorillonite modified bitumens before and after ageing. Analysis of the results revealed the ability of AFM to characterize the modification of the bitumens and the effect of ageing process [24].

This study aims to examine the effects of adding nano-clay to bitumen and the effect of ageing on the physical properties of the modified bitumens. Ageing procedures were conducted to simulate the effect of short-term ageing (STA) and long-term ageing (LTA) on the nano-clay modified bitumens. The ageing effects were then evaluated through consistency tests, and following this AFM was used to investigate surface topography and tip deflection. Statistical analysis was conducted to determine if there is a relationship between the results of the consistency tests and the results of AFM. It is hypothesized that any variation in surface roughness and tip deflection measured by surface topography is correlated with the hardness of the material, which means that soft materials have high surface roughness while hard materials have low surface roughness.

2. Experimental Design

2.1 Materials and sample preparation

This study used 60/70 penetration grade bitumen having a penetration value of 69 (0.1 mm), softening point of 45 (°C), and a viscosity of 499 (mPa.s). The nano-clay used in this study is a halloysite nano-tube composed of double layers of alumina, silicon, hydrogen, and oxygen and its chemical formula is \( \text{Al}_4\text{Si}_4\text{O}_{10}\text{(OH)}_8\cdot 4\text{H}_2\text{O} \). The outer surface of the halloysite nano-tubes have electro-chemical properties that are similar to those of silicon dioxide (SiO₂) with the negative charge at pH 6.5–6.9, as reported by the supplier. While silica is mainly located on the outer surface
of the nano-tube, the positively-charge alumina is located on its inner surface and its edges [25]. The surface area of this kind of nano-tube is approximately 57 m²/g [25, 26]. This nano tube has an outer diameter of 30-70 nm and a length of between 200–600 nm [26, 27]. Figure 2 displays an image of nano-clay which was captured using a Field Emission Scanning Electron Microscope (FESEM).

The modified bitumen samples were prepared by adding different percentages of nano-clay, viz., 0%, 2%, 4%, and 6% by mass of bitumen. Bitumen in the amount of 200 ± 10 g was poured into a can and heated to 150 °C for one hour until it reached a fluid state; the additive was heated at 100 °C for four hours to remove all traces of moisture, and was then gradually added into the liquid bitumen and mixed in a mechanical shear mixer at a rate of 500 rpm until the additive particles were no longer visible; this usually took between 3–5 minutes. The rotational rate of mixing was then increased to 2000 rpm and mixing was continued for another two hours. The selected mixing duration of two hours was to ensure a better storage stability of the modified bitumen, as recommended by Omar et al. [10]. For reference purpose, the samples were designated as follows: the sample with 0% nano-clay is named 0NCMB, that with 2% nano-clay is 2NCMB, that with 4% nano-clay is 4NCMB, and with 6% nano-clay is 6NCMB.

2.2 Ageing procedure

The bitumens were first aged by rolling thin film oven test (RTFOT) to simulate short-term ageing (STA) in accordance with the ASTM D2872 procedure. Modified bitumen in the amount of 35g was poured into a standard glass bottle, after which the bottle was placed in the oven’s carriage. The oven was kept at 163 °C while the carriage rotates at a rate of 15rpm for 85 min. Simulation of long-term ageing (LTA) was done using a pressure ageing vessel (PAV) oven in accordance with the ASTM D6521 procedure. The LTA procedure was performed immediately after completing the STA simulation. Modified bitumen in the amount of 50 g was poured into a standard pan and placed in the PAV oven. The temperature was set at 109 °C and the air pressure was 2.1 ± 0.1 MPa. The ageing procedure was carried out for 20 h.
2.3 Consistency and storage stability tests

Consistency tests were performed to evaluate the physical properties of the unmodified and modified bitumens [28]. These tests were used to determine any changes that may occur in the bitumen after modification and after the ageing procedures. In this study the penetration and softening point tests were used to evaluate the changes in the physical properties of both the unaged and aged bitumens. The penetration, softening point and viscosity tests were performed in accordance with ASTM D5, ASTM D36 and ASTM D4402, respectively.

Storage stability test was carried out in accordance with ASTM D7173-14 to determine a modified bitumen’s stability when stored at high temperature. The hot modified bitumen is poured into an aluminum tube with a diameter of 25 mm and a length of 140 mm, and was then placed in a 163 °C oven for 48 hours. The tube was allowed to cool, after which it was cut into three parts. The top and bottom section of the tube were tested using the softening point test. To pass this test the difference in the softening points of the two sections should be less than or equal to 2.5 °C. It should be noted that the percentage of added nano-clay was based on the results of the storage stability test.

2.4 Sample preparation for AFM testing

The samples used in AFM testing must be very thin, and thus special attention was given to obtain a thin and uniform surface. The two methods that can be used to prepare the samples have been described by Yu et al. [29]; the first method is the solution-cast method where the bitumen is dissolved with toluene. The liquid bitumen is then placed on a glass slide and the excess bitumen are be removed. This method, however, was not used because of the possibility of the nano-clay particles absorbing the toluene which cannot be easily removed. The second method, heat-cast, was used in this investigation. To prepare the unaged bitumen sample for the AFM test, a high temperature resistance tap was wrapped on each side of a glass slide and the glass slide was then placed on a 150 °C plate heater. The temperature for modified bitumens is 160 °C in the case of STA and 170 °C in the case of LTA to allow the sample to become more liquid. Next a small drop of hot bitumen was taken from a 150 °C oven and was placed on the glass slide, and the slide was
immediately moved around to spread the bitumen and obtain a smooth thin surface, after which any excess bitumen was removed. The tapes were then removed from the glass slide and the sample was ready for AFM testing. The aforementioned procedures were carried out as described by Arifuzzaman [30].

2.5 Atomic Force Microscopy (AFM)

Atomic force microscopy (AFM) was performed at the Quasi-S Sdn Bhd Company, Singapore. AFM technique provides 2D and 3D profiles of the bitumen surface on a nano scale by measuring the forces between the sharp tip and the bitumen surface. The contact mode, intermittent-contact mode, and non-contact mode can be used in this test depending on factors such as the type of material. However, the non-contact mode was used in this study since it is more suitable for soft material such as bitumen. In the non-contact mode, the tip does not come into contact with the sample surface. The cantilever oscillates at or near its resonance frequency [31]. The AFM test, which uses a sharp tip to probe the surface features by raster scanning, can perfectly image the surface topography. The tip with a radius of 2 nm is supported on a flexible cantilever in the AFM machine. The AFM cantilever “gently” scans the surface and records the small frequency between the tip and the bitumen surface. The deflection between the tip and bitumen surface is dependent on the spring constant (stiffness of the cantilever and the distance between the tip and bitumen surface). To measure the tip deflection for the bitumen, a force distance curve was used to determine the interaction force between a cluster of atoms in the AFM cantilever tip and the sample surface.

In the test, the surface of an asphalt or aggregate sample was probed with a sharp tip located at the free end of the cantilever. The attractive or repulsive force between the tip and the sample surface caused the cantilever to bend or deflect. A laser beam reflection measures the cantilever deflection as the tip was brought vertically towards the sample surface and then away from it. The tips used in this test are made from silicon nitride (Si3N4). These tips are high resolution silicon AFM cantilevers; a tip known as NSG01 bare was used for topography while another tip, CSG01 bare, was used for force curve. The test was conducted in a non-contact mode. The scan rate of the test is 3 Hz with a scanning area of 50 µm x 50 µm for all samples [30]. At the end of the test, the
Image Analysis P9 program was used to analyze the scanned area, and the results of the surface topography and tip deflection were obtained.

3. Results and Discussion

3.1 Consistency Tests

The results of the consistency tests for nano-clay modified bitumen samples are given in Table 1. As expected, as the penetration value decreased, the values for softening point and viscosity increased; this indicates that the addition of the nano-clay increased the bitumen’s stiffness. Even though the addition of 6% nano-clay had a different effect on the bitumen, the results from the consistency tests are in good agreement in terms of the increase or decrease of bitumen hardness. This finding is in good agreement with the findings of previous studies [32, 33].

The results for bitumen storage stability are presented in Table 2. The good dispersion of nano-clay has the effect of enhancing the storage stability of 2NCMB and 4NCMB, although 6NCMB has a better storage stability with a value greater than 2.5 °C, indicating that the agglomeration of particles is responsible for the improved storage stability. This demonstrates that the mixing speed has to be increased with the addition of higher percentages of NC. Based on the results of the storage stability test, 2NCMB and 4NCMB were chosen for this investigation.

Table 1 presents the results of the penetration, softening point, and viscosity tests for both the unaged and aged bitumen. The 6NCMB sample was not aged since it was not included in the investigation. The result for modified bitumen shows that viscosity increased when nano-clay particles were added, and that viscosity continued to increase when the bitumens were subjected to ageing procedures. The following section discusses the evaluation of the modified bitumens.

Ageing effect was evaluated using consistency tests, viz., penetration, softening point, and viscosity tests. Table 1 presents the results of consistency tests for the unaged and aged bitumens. While subjecting the bitumens to STA and LTA resulted in increased viscosity of all bitumens, the rate of increase varies between bitumen. For this reason, each test was evaluated to highlight the
increase in viscosity and to determine whether nano-clay reduces ageing effects after each ageing stage.

The increase in hardness due to ageing was determined using the penetration test. The retained penetration was determined using Equation 1.

\[
\text{Retained Penetration} \% = \left( \frac{\text{Pen}_{\text{aged}}}{\text{Pen}_{\text{unaged}}} \right) \times 100
\]  

(1)

where \( \text{Pen}_{\text{aged}} \) is the penetration during the ageing stage, and \( \text{Pen}_{\text{unaged}} \) is penetration for unaged bitumen.

The effect of ageing was also evaluated using a softening point test. The increase in the rate of the ageing was determined using Equation 2.

\[
\text{SPR} = \left( \frac{\text{SP}_{\text{aged}} - \text{SP}_{\text{unaged}}}{\text{SP}_{\text{unaged}}} \right) \times 100
\]

(2)

where SPR is the softening point ratio for STA or LTA, \( \text{SP}_{\text{aged}} \) is the bitumen’s softening point in STA or LTA, and \( \text{SP}_{\text{unaged}} \) is the softening point of unaged bitumen.

Ageing effect was also investigated using viscosity test. The ageing index for the viscosity test was determined using Equation 3.

\[
\text{Ageing Index} = \frac{\text{vis}_{\text{aged}}}{\text{vis}_{\text{unaged}}}
\]

(3)

where \( \text{vis}_{\text{aged}} \) is the viscosity value after ageing and \( \text{vis}_{\text{unaged}} \) is the viscosity value for unaged bitumen.
The results of the bitumens’ retained penetration are listed in Table 3. The results show that all modified bitumens were affected by ageing, but there was a reduction in the ageing effect of both 2NCMB and 4NCMB. The increase in retained penetration for 2NCMB and 4NCMB after STA and LTA is an indication of reduced ageing sensitivity, while 0NCMB was more affected. The values of softening point ratio (SPR) for aged bitumens are listed in Table 3. The results show that ageing ratio decreased for 2NCMB and 4NCMB and for both STA and LTA. This result is in good agreement with the results of retained penetration. Just as in the previous tests, the results of viscosity test indicate the changes that occurred in bitumen viscosity due to ageing effects. The results in Table 3 show a lower ageing index for 2NCMB and 4NCMB compared to that of 0NCMB.

The addition of nano-clay resulted in reduced ageing sensitivity due to the nano-clay’s unique heat absorption property [26, 27]. Similar investigations have proven that ageing resistance improved when nano-materials were added [34-36]. The improvement in oxidation ageing resistance may be related to the unique feature of nano-clay, namely, its heat absorption property [26, 27]. The nano-clay particles dispersed within the bitumen absorb heat during the ageing process and therefore lower the effect of oxidation. The reduction of ageing effects could be explained as follows: when bitumen was heated and mixed with nano-clay, some amount of maltenes may enter the nano-tube; however, since the size of asphaltene is almost the same as the inner diameter of the tube, they were not able enter the nano-clay particles. An increase in asphaltene content resulted in increased viscosity of the unaged modified bitumen. During the ageing process, the nano-clay particles protect the maltenes inside the tube structure and hence protect the bitumen from oxidation by absorbing heat.

### 3.2 Atomic force microscopy

Atomic force microscopy (AFM) is a nano-scale test in which a structure is imaged by scanning the bitumen surface with a tiny tip [31, 37]. In this section, AFM was used to evaluate the effect of ageing simulation on the bitumen structure by measuring surface roughness by means of topography imaging, and determining tip deflection which was used to identify the changes on bitumen surface after exposing the bitumen to STA and LTA.
3.2.1 Surface topography

Surface topography images were taken for all bitumens that have been subjected to STA and LTA simulation. Figure 3 shows the surface topography images for unaged modified bitumens with a scanned area of 10 µm x 10 µm. The surface topography of all bitumens has been altered due to the effect of ageing. To determine the nature of change on the surface, the surface roughness of all unaged and aged samples were evaluated. The area scanned to determine the surface topography of all samples is 50 µm x 50 µm. Surface roughness is a parameter used to quantify the surface texture of a sample. A small roughness value indicates a smooth surface while a high roughness value indicates a rough surface [38].

Figure 4 shows a typical example of a bitumen surface obtained through topography imaging and a 2D roughness profile. The green line (the primary profile) shows the measured distance of the bitumen roughness in Figure 3. The roughness of all bitumens was measured before and after ageing. The values were recorded and analyzed using the Image Analysis P9 program to obtain the average roughness.

As have been stated previously, the higher surface roughness of soft bitumen is related to low viscosity (high fluidity), while the low surface roughness of hard bitumen is related to high viscosity (low fluidity) [38]. The three bitumen samples modified with nano-clay in the amount of 0, 2 and 4% bitumen mass were subjected to the same mixing process. Any change in their surface roughness before STA would be due to the dispersion of nano-clay particles. The results for surface roughness of the modified bitumens are presented in Figure 5. It can be seen that the addition of nano-clay particles to the bitumen resulted in reduced surface roughness of the 2NCMB and 4NCMB. It can be concluded that nano-clay has a considerable effect on the stiffness property of the modified bitumens. However, Figure 5 shows that there is a slight increase in the surface roughness of 4NCMB compared to 2NCMB; this may be because the addition of 4% nano-clay requires a stronger mixing power in order to ensure a better dispersion of nano-clay in the bitumen.
This means that 2NCMB is slightly harder than 4NCMB. The absorption of maltenes fraction by the nano-clay increased the asphaltene component of 2NCMB.

STA also reduced the surface roughness of all aged modified bitumens, which is an indication of increased hardness of the bitumens. In order to evaluate the effect of STA on modified bitumens and to determine the difference in their response to the effect of STA, the ageing index was calculated using Equation 3. The ageing index of the surface roughness are 0.82, 0.87 and 0.87 for 0NCMB, 2NCMB and 4NCMB, respectively (Table 4). It can be concluded that 0NCMB is more sensitive than 2NCMB and 4NCMB. As previously mentioned, nano-clay particles protect the maltenes inside the tube structure and this resulted in enhanced hardness of the bitumens; the dispersed nano-clay particles protect the modified bitumen from oxidation by absorbing heat, thereby reducing its temperature sensitivity.

Subjecting the bitumen sample to LTA may result in reduced surface roughness due to the increase in bitumen hardness. To evaluate the effect of LTA on modified bitumens and to determine the difference in their response to the effect of LTA, the ageing index was calculated using Equation 3 and the result is presented in Table 4. It shows that 0NCMB is the most sensitive modified bitumen with an ageing index of 0.46; this indicates that the value of surface roughness was reduced by more than half of the surface roughness of unaged bitumen. The ageing index for 2NCMB and 4NCMB are 0.60 and 0.53, respectively. 2NCMB showed a better resistance to LTA than 4NCMB. This may be related to the better dispersion of nano-clay particles in 2NCMB; it may be due to the agglomeration of nano-clay particles formed in the 4NCMB sample which reduce its ability to resist ageing. It is also possible that 4NCMB requires a higher mixing power than the one used in this study.

3.2.2 Tip deflection

Tip deflection is a useful parameter and can be examined using the AFM technique. A force-distance curve can be used to determine the interaction force between a cluster of atoms at the AFM cantilever tip and the sample surface [39]. This parameter can be obtained by determining the slope of the force-distance curve. An example of a typical force-distance curve is shown in
Figure 6. In this test, the sample is probed with a sharp tip located at the free end of a cantilever. The attractive or retraction force between the tip and the sample surface causes the cantilever to bend or deflect. Where the tip deflection value is one of this paper aims, for this reason the attraction force was neglected. A laser beam reflection technique, which is built into the AFM system, measures the cantilever deflection as the tip is brought vertically towards the sample surface and then away from it. In the figure, the y-axis represents the retraction force, and the x-axis represents the distance between the tip and the surface of bitumen.

The results for tip deflection at the bitumen surface generated by the program are presented in Figure 7. The unaged and aged modified bitumens were evaluated using a silicon nitride tip, where tip deflection is an indication of the material’s solidity. Harder materials produce low tip deflection values while softer materials produce high tip deflection value [16].

Figure 7 shows that the addition of nano-clay particles to bitumen did not cause any change in 2NCMB; nonetheless a reduction in the tip deflection of 4NCMB was observed, indicating an increase in the binder’s hardness. This result is totally different from that of the surface roughness. It can be concluded that the addition of 2% of nano-clay did not have any discernable effect on the bitumen when tip deflection was measured. However, the slight reduction in the tip deflection of 4NCMB compared to that of 2NCMB may be attributed to the 4% of nano-clay increasing the hardness of the modified bitumen. Previous studies have shown that although the AFM method was used to characterize a material, the results of force measurement varied, and in some cases, they did not correlate with each other [16].

STA has the effect of reducing the tip deflection of all modified bitumens, as can be seen in Figure 6; this is an indication of enhanced hardness of the modified bitumen. In order to evaluate the effect of STA on modified bitumens and to determine the difference in their response to the effect of STA, the ageing index was calculated using Equation 3. The ageing index for tip deflection are 0.63, 0.89 and 0.89 for 0NCMB, 2NCMB and 4NCMB, respectively (Table 5). This indicates a higher ageing sensitivity of 0NCMB in comparison to those of 2NCMB and 4NCMB. The LTA process was expected to increase the hardness of aged bitumens whilst reducing the tip deflection. In order to evaluate the effect of LTA on modified bitumens and to determine the difference in
their response to the effect of STA, the ageing index was calculated using Equation 3. Result shows that 0NCMB is the most sensitive modified bitumen with an ageing index value of 0.56; this indicates that the value of tip deflection was reduced to almost half the value of the tip deflection of the unaged bitumen. The ageing index for 2NCMB and 4NCMB are 0.62 and 0.58, respectively. 2NCMB and 4NCMB showed a better resistance to ageing in the LTA stage. As stated before, nano-clay particles protect the maltenes in the tube structure and this has the effect of increasing the hardness of the modified bitumen. The dispersed nano-clay protect the modified bitumen from oxidation by absorbing heat, thereby reducing its temperature sensitivity. However, the ageing index for tip deflection showed a similar trend to that of the ageing index for surface roughness. Both results confirmed that the rank of modified bitumens in terms of better ageing resistance is 2NCMB, followed by 4NCMB and 0NCMB.

4. Correlation between Consistency Tests and AFM Method

This section presents the correlation for the results of the consistency tests and AFM method. This paper hypothesized that any variation in surface roughness and tip deflection measured by surface topography is correlated with the hardness of the material. The Pearson product-moment correlation coefficient is a measure of the linear relationship between two different variables, that has a value between +1 and -1 [40]. The value close to +1 indicates the strong linear proportional correlation between the dependent and independent variables, while the value close to -1 indicates the strong inverse proportional correlation between the dependent and independent variables. It is commonly used in the engineering to measure the strength of the relationship between two variables. The Pearson product-moment correlation coefficient was used in this study to investigate the correlation between the average results of consistency tests and that of the AFM method. The results are presented in Table 6. The Pearson product-moment correlation coefficient hypothesized that there is a good correlation between the surface roughness and the consistency test which ranged between -0.834 for the viscosity test and -0.927 for the softening point test. The negative sign indicates a decrease in one variable, namely surface roughness, whilst the softening point and viscosity showed an increase.
Tip deflection has a different correlation with the results of consistency tests compared to the correlation between surface roughness and consistency tests. The correlation range between 0.325 and -0.853. The average result for tip deflection shows a correlation of 0.325 with the result for penetration, which is a poor relationship. The correlation with the result for softening point is -0.558, and the strongest correlation of -0.853 is with the result for viscosity. The proposed hypothesis is in good agreement with the general results, and this shows that there is a strong relationship between the results of consistency tests and that of the AFM test. This confirms that the AFM method is a useful tool for characterizing the modified bitumens and for evaluating ageing effect.

5. Conclusion

An investigation was conducted to evaluate the effect of ageing simulation on modified bitumens. Bitumen with 60/70 penetration grade was modified with nano-clay in the amount of 0, 2 and 4% by mass of bitumen. The effects of STA and LTA were evaluated using the commonly used tests, namely penetration test, softening point test and viscosity test. Following this, the surface roughness and tip deflection were determined using AFM. This paper hypothesized that if the solidity of a material can be determined by surface roughness and tip deflection, and then there exists a degree of reasonable correlation between the two parameters and the consistency tests. The following conclusions are made based on the results obtained in this experimental study.

a) The addition of nano-clay to bitumen resulted in reduced penetration and higher softening point and viscosity values. The increase in the hardness for 2NCMB and 4NCMB are higher than those for 0NCMB. Besides, storage stability results showed adequate stability for modified bitumens with NC particles up to 4% NC.

b) The effects of STA and LTA were observed for all modified bitumens when the results of consistency test were taken into account. However, the retained penetration, SPR and viscosity ageing index were calculated to determine the bitumens’ sensitivity to ageing. Both retained penetration and SPR values confirmed that 4NCMB has the best ageing resistance, while the ageing index value for viscosity showed that 2NCMB has a better ageing resistance.

c) The result for surface roughness confirmed that the incorporation of nano-clay particles affect the solidity of 2NCMB and 4NCMB. The hardness of 2NCMB is slightly higher than that of
4NCMB. The result for tip deflection test showed that 0NCMB and 2NCMB have the same tip deflection, while 4NCMB has a smaller tip deflection. This indicates that the hardness of 4NCMB has increased.

d) The ageing index for surface roughness and tip deflection were determined. It showed that 2NCMB and 4NCMB have a better resistance towards ageing compared to 0NCMB. However, in the case of LTA, the 2NCMB was less affected than all the other samples.

e) The results of consistency tests proved that the addition of nano-clay particles delayed the ageing effect, and this finding is supported by the results of AFM. This is an indication of enhanced ageing resistance.

f) The correlation between the results of consistency tests and AFM method varies but are in good agreement, with the exception of the correlation between tip deflection and penetration. It showed that the changes identified by the results of consistency tests were also observed and confirmed by the results of AFM. The reduction in fluidity brought about by the addition on nano-clay and the effect of ageing simulation was anticipated as stated in the hypothesis. This confirmed that AFM is a good tool for evaluating ageing effect.

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Figure 1 Schematic of an atomic force microscope [16]

Figure 2 FESEM for nano-clay particles
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Table 1 Physical properties of the modified bitumen

| Test                      | Ageing stage | Standard test | 0NCMB | 2NCMB | 4NCMB | 6NCMB |
|---------------------------|--------------|---------------|-------|-------|-------|-------|
| Penetration (0.1 mm)      | Unaged       | ASTM D5       | 66    | 37    | 28    | 31    |
| at 25°C                   | STA          | 57            | 34    | 29    | 23    | -     |
|                           | LTA          | 57            | 34    | 29    | 23    | -     |
| Softening point (°C)      | Unaged       | ASTM D36      | 47    | 55    | 59    | 58    |
|                           | STA          | 52            | 58    | 62    | -     | -     |
|                           | LTA          | 60            | 62    | 64    | -     | -     |
| Viscosity (mPa. s)        | Unaged       | ASTM D4402    | 551   | 705   | 775   | 732   |
| at 135°C                  | STA          | 794           | 821   | 906   | -     | -     |
|                           | LTA          | 1123          | 915   | 1134  | -     | -     |

STA = short-term ageing, LTA = long-term ageing

Table 2 Results for storage stability test

| Bitumen | Top (°C) | Bottom (°C) | Different (°C) |
|---------|----------|-------------|----------------|
| 2NCMB   | 53.4     | 55.3        | 1.9            |
| 4NCMB   | 57.1     | 59.5        | 2.4            |
| 6NCMB   | 56.3     | 60.0        | 3.7            |

Table 3 Physical properties of nano-clay modified bitumen after ageing

| Sample | Retained penetration | SPR | Viscosity | Ageing index |
|--------|----------------------|-----|-----------|--------------|
|        | STA | LTA | STA (%) | LTA (%) | STA | LTA |
| 0NCMB  | 0.86 | 0.53 | 13      | 30.4    | 1.44 | 2.04 |
| 2NCMB  | 0.92 | 0.78 | 5.5     | 9.1     | 1.16 | 1.30 |
| 4NCMB  | 0.93 | 0.82 | 5.1     | 8.5     | 1.17 | 1.46 |

Table 4 Ageing index for surface roughness

| Sample | STA | LTA |
|--------|-----|-----|
| 0NCMB  | 0.82 | 0.46 |
| 2NCMB  | 0.87 | 0.60 |
| 4NCMB  | 0.87 | 0.53 |
Table 5 Ageing index for tip deflection

| Sample | STA | LTA |
|--------|-----|-----|
| 0NCMB  | 0.63| 0.56|
| 2NCMB  | 0.89| 0.62|
| 4NCMB  | 0.89| 0.58|

Table 6 Correlation between the results of Consistency tests and AFM method

| Test | Surface roughness | Tip deflection | Penetration (0.1 mm) | Softening Point (°C) | Viscosity (mPa.s) |
|------|-------------------|----------------|----------------------|----------------------|-----------------|
|      | Pearson Correlation | 1 | 0.612 | 0.875 | - 0.927 | - 0.834 |
|      | Sig. (2-tailed) | - | 0.080 | 0.002 | 0.000 | 0.005 |
|      | N | 9 | 9 | 9 | 9 | 9 |
|      | Pearson Correlation | 0.612 | 1 | 0.325 | - 0.558 | - 0.853 |
|      | Sig. (2-tailed) | 0.080 | - | 0.394 | 0.119 | 0.003 |
|      | N | 9 | 9 | 9 | 9 | 9 |

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