applied sciences

MDPI

Article

The Effect of Ageing on Chemical and Strength Characteristics of Nanoclay-Modified Bitumen and Asphalt Mixture

Hend Ali Omar [1,*], Herda Yati Katman [2,*], Munder Bilema [3], Mohamed Khalifa Ali Ahmed [1], Abdalrhman Milad [4] and Nur Izzi Md Yusoff [4]

[1] Department of Civil Engineering, University of Tripoli, Tripoli 13275, Libya; mo.ahmed@uot.edu.ly
[2] Department of Civil Engineering, Universiti Tenaga Nasional (UNITEN), Kajang 43000, Selangor, Malaysia
[3] Faculty of Civil Engineering and Built Environment, Universiti Tun Hussein Onn Malaysia, Batu Pahat 86400, Johor, Malaysia; mondo199131@gmail.com
[4] Department of Civil Engineering, Universiti Kebangsaan Malaysia, Bangi 43600, Selangor, Malaysia; miladabdalrhman@siswa.ukm.edu.my (A.M.); izzi@ukm.edu.my (N.I.M.Y.)
* Correspondence: hend.omar@uot.edu.ly (H.A.O.); Herda@uniten.edu.my (H.Y.K.)

Abstract: This study was conducted to investigate the effect of ageing on bitumen, before and after modification. Nano-clay modified bitumen (NCMB) was produced by adding nano-clay (NC) to 60/70 penetration grade bitumen; then, the binder was tested using conventional tests for properties such as penetration, softening point and viscosity. These tests were carried out on the modified binder before and after ageing. A rolling thin film oven (RTFO) was used to simulate short-term ageing (STA), and a pressure ageing vessel (PAV) was used to simulate long-term ageing (LTA) for the modified binder. After initial results showed an improvement for the modified bitumen regarding the effect of ageing, the investigation continued using Fourier transform infrared spectroscopy (FTIR), where the microstructure distribution of the modified binder before and after ageing was observed. Finally, there was no doubt that the effect of ageing on mixtures should be investigated. For this step, the indirect tensile strength (ITS) test, which highlights the strength changes that occur for the mixtures after ageing, was selected. The results indicated that the tensile strength of mixtures made with modified bitumen showed better resistance against ageing when NC was added, which is in good agreement with the results of previous binder tests. The results of this study show that the modification of bitumen using nano-clay as an additive improves the ageing resistance of the binder, which is consequently reflected in the strength of the asphalt mixture.

Keywords: bitumen; nano-clay; ageing; consistency test; Fourier transform infrared spectroscopy (FTIR); indirect tensile strength test (ITS)

Citation: Omar, H.A.; Katman, H.Y.; Bilema, M.; Ahmed, M.K.A.; Milad, A.; Md Yusoff, N.I. The Effect of Ageing on Chemical and Strength Characteristics of Nanoclay-Modified Bitumen and Asphalt Mixture. *Appl. Sci.* **2021**, *11*, 6709. https://doi.org/10.3390/app11156709

Academic Editor: Francesco Enrichi

Received: 21 June 2021
Accepted: 13 July 2021
Published: 22 July 2021

1. Introduction

The durability of flexible pavement is affected by several factors over its service life. Much research has been carried out to investigate the ageing of asphalt mixture in the laboratory by simulating ageing and factors such as heat, oxidation, time, and sunlight. At least fifteen mechanisms have been identified; however, the most common are the following four: oxidation (in darkness or direct light), loss of volatiles by evaporation, loss of volatiles by exudation, and steric or physical hardening [1]. It is stated that volatilization is the main ageing mechanism for bitumen during mixing and construction, while oxidation and some steric hardening are the main reasons for ageing during service life [2]. Oxidation is considered the main cause of hardening of bitumen, and it is considered one of the ageing mechanisms that has a serious influence on bitumen properties [1,3–5]. Although bitumen is the main material in asphalt mixtures affected by ageing, with demonstrated chemical changes that are reflected in its physical properties [6,7], the aggregate and the designation of the asphalt mixture with high void content also play a significant role in accelerating pavement ageing [1,4]. Furthermore, one study showed that asphaltene-rich bitumen tends to age faster than bitumen with low asphaltene content [1].

Elevated temperatures in very hot and dry places, such as desert regions, lead to an increase in pavement temperature resulting in chemical changes to bitumen bulk, leading to hardening, especially on the surface. The hardening rate increases due to increased temperature and also due to exposure to sunlight during the summer [4,7]. These two factors are considered the main reasons for early ageing of the surface layer of pavement, even if there is no traffic load in the desert region.

Like any organic material, bitumen changes physically after a change in its chemical composition. Oxidation changes the functional groups inside the bitumen, where new polar groups containing oxygen are formed, such as carbonyl, and results in an increase in sulfoxide groups. As reported previously, the reaction of oxygen with bitumen molecules results in larger and more complex molecules that make the bitumen harder and less flexible. Where there is an increased content of asphaltene, this leads to increased viscosity and stiffness, which are considered to be the main reasons for fatigue and thermal cracking [1,4,7–11].

As ageing pushes pavement to the end of its service life, especially in hot regions such as southern Libya, many studies have been carried out regarding delaying ageing. Various types of additives are used to modify bitumen, such as thermoplastic elastomers like polyurethane, polyether–polyester copolymers and olefinic [12], and high- and low-density polyethylene [13], polyvinyl chloride, polystyrene, polypropylene and ethylene–vinyl acetate [14], which are considered plastomers, natural rubber, crumb rubber and more [1,12,14–16].

Recently, nanomaterials have attracted the interest of pavement researchers due to their unique properties and incredible features, which make it possible for them to be used as an additive in asphalt mixtures [17]. The presence of nanomaterials could improve asphalt material properties such as viscoelasticity and high temperature properties as well as resistance to fatigue, ageing and moisture damage [17–19]. Many types of nanomaterial have been introduced in previous studies, such as nano-clay, nano-carbon, nano-zinc and more [17,18,20]. However, fewer studies have been based on nano-modified asphalt mixtures than on nano-modified binders. Furthermore, factors such as environmental effects, cost, and the economic and ecological assessments of nano-modified asphalt also need to be considered [4,7,17,18,21].

The internal strength of an asphalt mixture for flexible pavement can be affected by many factors, such as water infiltration, ageing conditions and traffic load over its service time, resulting in the appearance of permanent deformation (rutting) and fatigue cracking [22,23]. The indirect tensile strength (ITS) test has been used effectively in evaluating the effect of ageing on the strength of a mixture [24,25]. Islam et al. [25] stated that the ITS of the oven loose mixture STA, laboratory LTA and field-aged samples increased, while the flow number showed a reduction with the conditioning period, where the bitumen film or mastic became too oxidized.

In this research, nano-clay (NC), known as halloysite nanotubes, was used as a modifier for bitumen. The selection of halloysite nanotubes was based on its unique feature of thermal resistance through the absorption of heat [26,27]. To examine the effectiveness of this feature, NC was added to bitumen, and then the modified bitumen was evaluated before and after exposure to ageing conditions. The physical and chemical properties for unmodified and modified binders were evaluated, and then the mechanical properties for modified asphalt mixtures were also examined. Short-term ageing (STA) and long-term ageing (LTA) simulations were imposed to modified bitumen to study the changes in physical and chemical properties before and after ageing. The physical properties were evaluated using consistency tests for penetration, softening point and viscosity. The main reason for choosing these tests was their simplicity, speed and usefulness as an indicator for ageing measurements. The changes in chemical properties were evaluated using the FTIR method, where the chemical reaction between the bituminous binder and the NC was first assessed, and then the effect of ageing was evaluated for all binders. The ITS test was carried out on asphalt mixtures prepared with modified bitumen, before and after ageing simulations, to study the effect of the addition of NC on the strength of the asphalt mixture.

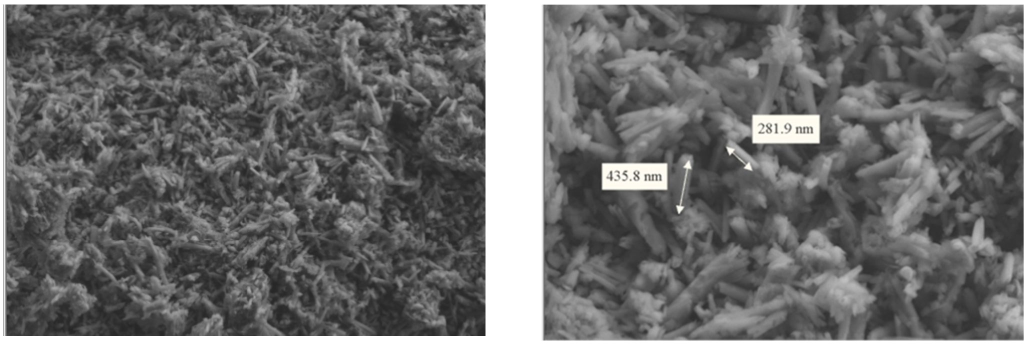
2. Materials and Methods

2.1. Materials and Sample Preparation

2.1.1. Bituminous Binders

A 60/70 penetration grade bitumen with a penetration of 68 deci-millimeter (dmm) at 25 °C (ASTM D5), softening point of 46 °C (ASTM D36) and viscosity of 551 mPa·s at 135 °C (ASTM D4402) was used in this investigation. It was supplied in sealed cans by Cenco Sains, Kuala Lumpur, Malaysia, and stored in a dark place.

The nano-clay was supplied by the same company. Known as Halloysite nanotubes, it is a type of alumino-silicate clay ($Al_2Si_2O_5$ $(OH)_4$.2 H_2O with 1:1 layer) with a cylindrical shape. The cylindrical particles have an outer diameter of 30 to 70 nm and a length of 200 to 650 nm. Its surface area is approximately 57 m^2/g, and its color is white to tan, as reported by the supplier. It is composed of double layers of alumina, silicon, oxygen and hydrogen. Silica, with a negative charge, is located mainly on the outer surface of the nano-tube, and alumina, with a positive charge, is located on the inner surface and on the edges of the nano-tube [25]. Figure 1 shows an image of the nano-clay obtained using field emission scanning electron microscopy (FESEM). Images were captured to show the particles at 30.00 and 10.00 magnifications. The images show that the particles of halloysite nanotubes are tubular and their length ranges from 600 to 250 nm, which is the same as reported by the supplier.



(**a**) (**b**)

Figure 1. Field emission scanning electron microscopy (FESEM) for nano-clay, (**a**) Mag = 30.00 kX and (**b**) Mag = 10.00 kX.

The nano-clay was left in the oven at 100 °C for six hours to ensure that any humidity would be removed. Binder (200 ± 10 g) was poured into a can and then heated in the oven to 155 °C for less than one hour, until it reached a fluid state. The can was put in an oil bath at 150 ± 5 °C, and the nano-clay (0, 2 and 4% by mass of bitumen) was added. The main reason for not proceeding with the addition of 6% nano-clay was due to its poor storage stability when the temperature exceeds 2.5 °C, which occurred when the softening point test was conducted. The mixing procedure was performed by a mechanical mixer, commencing at 500 rpm when the nano-clay was added, to prevent any scattering of nano-clay particles. After five minutes, the mixing speed was increased to 2800 rpm for one hour. Mixing was performed for unmodified and modified bitumen to ensure the same applied conditions.

The names of the binders were 0 NCMB, 2 NCMB and 4 NCMB, where the number indicates the percentage of nano-clay by mass of bitumen and NCMB indicates nano-clay modified bitumen. STA binders were prepared by RTFO, in accordance with specification ASTM D2872, where the test was performed at 163 °C for 85 min. LTA binders were prepared using the PAV oven, in accordance with specification ASTM D6521, where the test was performed in an oven under a pressure of 2.1 MPa at 100 °C for 20 h.

2.1.2. Asphalt Mixture

Cylindrical samples (diameter 101.6 mm and height 64 mm) of asphalt mixture were prepared using a Servopac gyratory compactor following AASHTO specification T 312-07. The number of gyrations for an equivalent single axial load (ESAL) for the study ranged from 10 to 30 × 10^6, corresponding with N_{design} of 100 gyrations. Three samples for each mixture were prepared using five modified binder contents (4.5%, 5.0%, 5.5%, 6.0% and 6.5% of the total asphalt mixture weight) to determine the optimum binder content (OBC).

The aggregate used in this research was granite with a maximum particle size of 19.0 mm. The aggregate gradation is illustrated in Figure 2. Air voidage of 4% was selected for all mixtures of the OBC. Mixing and compaction temperatures were determined based on the results of rotational viscosity. The mixing temperature was chosen as the range corresponding to 0.17 ± 0.02 Pa.s, while the compaction temperature was chosen as the range corresponding to 0.28 ± 0.03 Pa.s. The selected mixing temperatures were 155 °C, 160 °C and 163 °C for 0 NCMB, 2 NCMB and 4 NCMB, respectively, while the selected compaction temperatures were 146 °C, 150 °C and 152 °C for 0 NCMB, 2 NCMB and 4 NCMB, respectively. The OBC for 0 NCMB, 2 NCMB and 4 NCMB was 5.2%, 5.5% and 5.8%, respectively. In this study, after determining the OBC, the mixtures were prepared at air voids of 7 ± 0.5%. It is well-known that one of the factors leading to increased rate of ageing is higher air voidage. More air voidage allows oxygen to enter the mixture and results in more chemical change during STA and LTA, influencing the strength of the asphalt mixture.

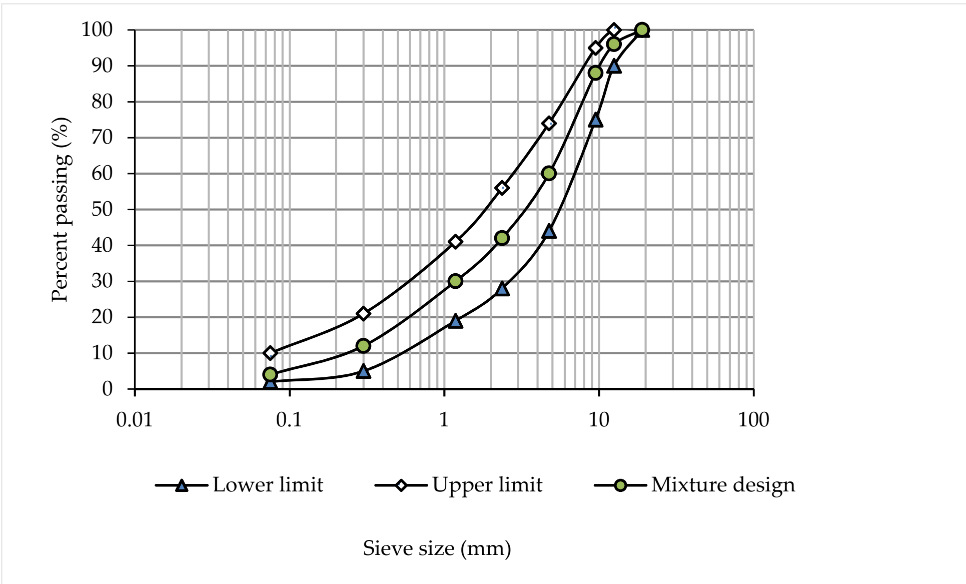


Figure 2. Aggregate gradation.

To simulate ageing of the mixture, the AASHTO R 30 standard process was followed. The asphalt mixture was subjected to STA, which simulates the mixing and compaction phase of the construction. After mixing in the mechanical mixer, the mixture was placed in the oven at compaction temperature for four hours, stirring hourly to ensure that all coated aggregate particles were exposed to the air inside the oven, and compacted prior to testing. The LTA simulates the ageing that occurs over the service life. It was performed, after the application of STA simulation, by subjecting the compacted mixture to a temperature of 85 °C for five days.

2.2. Consistency Tests

Consistency tests for penetration (ASTM D5), softening point (ASTM D36) and viscosity (ASTM D4402) were conducted in accordance with their relative standard to evaluate the effect of ageing on the unmodified and modified binders. The penetration test was carried out with the following procedure: a needle of specified dimensions was allowed to penetrate a sample of bitumen under a known load at a fixed temperature for a known time. Ageing reduces the penetration of the needle through bitumen after the rolling thin film oven test (RTFOT). The reduction in penetration will be more when the PAV procedure is applied. The penetration ageing index is used to characterize the increase in bitumen hardness after ageing. It is calculated according to Equation (1):

$$\text{Ageing Index for a test} = \frac{\text{Aged result test value}}{\text{Unaged result test value}} \quad (1)$$

The softening point test is a good indicator of the sensitivity of the bitumen. The softening point temperature is the temperature where bitumen softens and eventually deforms until it touches the bottom plate, 25 mm below the ring in the test. After ageing, the softening point temperature increases, indicating an increase in the hardness of the bitumen. The ageing index was calculated using Equation (1), with an increase in the ageing index indicating an increase in the softening point after ageing.

The increase in softening point and the reduction in penetration for bitumen at various ageing stages are used to determine the changes in the consistency parameter as a function of temperature, defined as temperature susceptibility. To observe the temperature susceptibility of the modified binders, the penetration index (PI) should be calculated using Equation (2):

$$\text{PI} = \frac{1952 - 500 * \log(\text{Pen}_{25}) - 20 \times \text{SP}}{50 \times \log(\text{Pen}_{25}) - \text{SP} - 120} \quad (2)$$

The PI can be used to give a good approximation of the behavior to be expected. The PI calculated from one penetration and one softening point may vary from the values calculated from two penetration values, and for this reason, confirmation using stiffness or viscosity measurements is desirable [1].

The Brookfield viscometer was used to measure the resistance of the bitumen to flow. Ageing causes a change in viscosity. The change in viscosity is selected for the evaluation of the ageing effect on modified bitumen. The ageing index is the ratio of the bitumen viscosity after ageing to that before ageing. It is commonly used to normalize the ageing behavior of samples with different viscosities, such as modified bitumen. The viscosity ageing index is calculated according to Equation (1).

2.3. The Fourier Transform Infrared (FTIR) Test

The Fourier Transform Infrared (FTIR, test was performed at the Quasi-S Sdn Bhd Company, Singapore. The Bruker Tensor II FT-IR Spectrometer was used with a resolution (cm^{-1}) of 4, a mode of attenuated total reflectance (ATR), and a scan range of 4000–650 cm^{-1}, which is considered a mid-infrared spectrum. Infrared (IR) radiation was passed through the binder, where some of the infrared radiation was absorbed by the components of the binder. The resulting spectrum represents molecular absorption, which creates a molecular fingerprint of the bitumen's components [28].

The unaged samples subjected to the FTIR test were prepared immediately after mixing the preparation and after ageing for aged samples, for both STA and LTA. A drop of bitumen sample was put on a glass slide and placed on a heater plate at 150 °C for around one minute to obtain a thin layer and smooth surface. The prepared samples were then stored in a dark, cold place prior to testing. Investigation of the ageing effect on the modified binders was performed by recording the absorbance for selected bands and checking the variation between the binders at ageing stages.

2.4. Indirect Tensile Strength (ITS) Test

The indirect tensile strength (ITS) test was used to investigate changes in the strength of the mixture due to water. The test was carried out to evaluate the effect of STA and LTA on the strength of the modified mixtures. Samples were prepared, unaged, for both STA and LTA for all mixtures, and then tested using the universal testing machine. The applied load of 50 mm per minute was in a vertical diametric plane, and the maximum load when failure occurred was recorded. The test was applied at 20 °C. The ITS was calculated using Equation (3).

$$ITS = 2000F/\pi TD \tag{3}$$

where ITS is the indirect tensile strength (kPa), F is the maximum value of the applied vertical load (N), T is the thickness of the sample (mm), and D is the sample diameter (mm).

3. Results and Discussion

3.1. Consistency Tests

Various physical properties—penetration, penetration ageing index, softening point, softening point index and penetration index (PI) of the unaged and aged modified binders are detailed in Table 1. Based on the results obtained for modified binders, it can be concluded that NC had a considerable effect on the stiffness of the modified binders before ageing.

Table 1. Penetration, penetration ageing index, softening point, softening point index and penetration index (PI).

Sample	Ageing	Penetration (0.1 mm)	Penetration Ageing Index	Softening Point (°C)	Softening Point Index	PI
0 NCMB	unaged	64.6	-	47.5	-	−1.3
	STA	52.3	0.81	52.2	1.10	−0.6
	LTA	42.1	0.65	58.1	1.22	0.2
2 NCMB	unaged	54.0	-	53.4	-	−0.2
	STA	48.3	0.89	59.0	1.10	0.7
	LTA	39.8	0.74	62.3	1.16	0.9
4 NCMB	unaged	49.2	-	59.0	-	0.8
	STA	43.2	0.88	61.6	1.04	1.0
	LTA	38.9	0.79	64.7	1.09	1.3

It was notable that mixing had little influence on the stiffness of the modified binder with no NC particles, where the penetration reduced from 68 (0.1 dmm) for the unmodified bitumen 60/70 penetration grade to 64.6 (0.1 dmm) for 0 NCMB (still in the same penetration grade). However, the addition of NC for 2 NCMB and 4 NCMB led to an increase in stiffness of the modified bitumen. The penetration values decreased, while the softening point increased, indicating the effect of NC particles on the bulk of the modified bitumen. The increase in the stiffness was expected and could be explained by the absorption of the maltenes phase by NC, leading to an increase in asphaltene content. Applying STA and LTA led to an increase in stiffness of the modified bitumen. To check which binder was more sensitive, penetration ageing index and softening point index were determined. Based on the results in Table 1, the 0 NCMB was more sensitive for both STA and LTA compared to 2 NCMB and 4 NCMB. The sensitivity of the 0 NCMB indicates that its temperature susceptibility that makes it more susceptible to thermal cracking. NC reduced the sensitivity of 2 NCMB and 4 NCMB to ageing; these particles absorb the heat, preventing the increase of the asphaltene formation by absorbing some of the maltenes [28].

The change in the consistency parameter as a function of temperature is a sign of the temperature susceptibility and can be obtained by determination of the PI. The PI values for the binders increased after the addition of NC. In addition, the increase in PI extended after STA and LTA for all modified binders, as can be seen in Table 1. Comparing PI values between modified binders, it can be seen that for all ageing stages (unaged, STA and LTA) the PI was highest for 4 NCMB and lowest for 0 NCMB. This result is in good agreement with the penetration ageing index and softening point index data. The higher PI values for 2 NCMB and 4 NCMB indicate that these binders are less susceptible to temperature and more elastic [14]. Table 2 details the viscosity ageing index (VAI) data. All NCMB was mixed and prepared in the same condition.

Table 2. Viscosity ageing index.

	Viscosity (Pa.s) at 135 °C			VAI	
NC %	**Unaged**	**STA**	**LTA**	**STA**	**LTA**
0%	606	820	1068	1.35	1.76
2%	702	790	886	1.13	1.26
4%	770	859	992	1.12	1.29

The viscosity at 135 °C was evaluated for unaged and aged modified bitumen. Ageing increases the viscosity for modified bitumen, but responses were varied. All samples showed an increase in viscosity after both STA and LTA.

After STA, VAI was highest for 0 NCMB and less, and almost the same for 2 NCMB and 4 NCMB. After LTA, VAI was highest for 0 NCMB and reduced for 2 NCMB and 4 NCMB. When VAI reduces from 0 NCMB to 2 NCMB and 4 NCMB, this means that the sensitivity is reduced. The addition of NC reduced the effect of temperature and improved the ageing resistance. The heat absorption of NC resists the effect of the ageing temperature [29]. The additional of NC in 2 NCMB and 4 NCMB absorbs the heat and therefore reduces the effect of temperature on bitumen structure and protects it from oxidation [28].

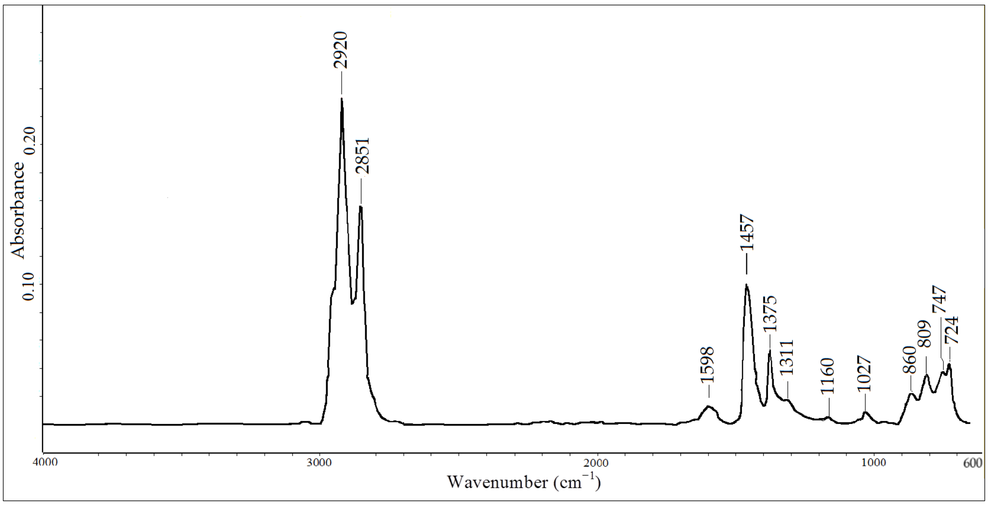
3.2. The Fourier Transform Infrared (FTIR) Test

Table 3 shows the functional groups of the binders and the peak position obtained from the FTIR test for modified bitumen before and after ageing. The investigated range, which was mid-infrared spectrum (4000–600 cm^{-1}), showed many groups before and after ageing. The FTIR test demonstrated that there are no new bands created after adding nano-clay particles for unaged 0 NCMB, 2 NCMB and 4 NCMB, as can be seen in Figure 3a–c. This means that there is no chemical activity between nano-clay and bitumen. Mixing did not create any new groups for unaged modified bitumen.

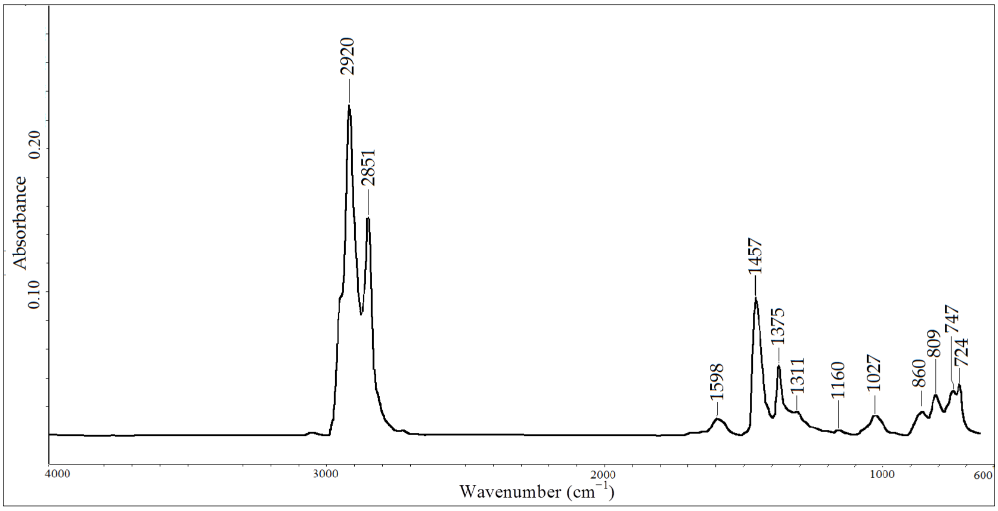
Table 3. Functional groups and their peak position.

Functional Group	Peak Position (cm^{-1})
C–H asymmetric stretching	2920
C–H symmetric stretching	2851
C=O stretching	1694
C=C stretching	1597
CH_2 deformation	1457
CH_3 deformation	1375
S=O stretch	1027
CH out-of-plane deformation	900–690

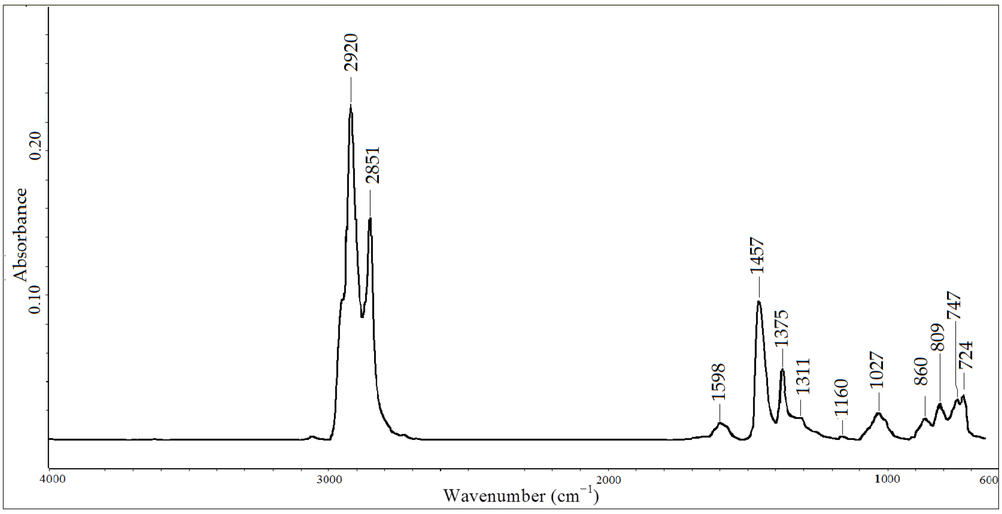
In this paper, attention was given to groups believed to help the detection of changes that occur during ageing of the samples. The selected groups, based on their compounds, were (1) oxygen-containing compounds, (2) aliphatic hydrocarbons, (3) aromatic compounds and (4) sulfur compounds.



(**a**)



(**b**)



(**c**)

Figure 3. FTIR spectrum results for (**a**) 0 NCMB, (**b**) 2 NCMB and (**c**) 4 NCMB.

3.2.1. Oxygen-Containing Compounds

The oxygen-containing compounds are alcohols and phenols, ethers, aliphatic and aromatic ketones, esters and carboxylic acids and anhydrides [30]. Carbonyl stretching is one of the popular known bands used to evaluate the ageing of bitumen [6,31,32]. It is well known that development and increase in the carbonyl groups indicates an increase in the number of large molecules in the bituminous binder, resulting in higher stiffness and more solid-like behavior as a result of ageing [6]. It is usually the most intense band in the spectrum, and depending on the type of C=O bond, it occurs in the 1830–1650 cm^{-1} region. It may be absorbed above 2000 cm^{-1}, under consideration at 2923 cm^{-1} and 2856 cm^{-1} [33,34]. Aliphatic and aromatic ketones show carbonyl bands at 1730–1700 and 1700–1680 cm^{-1}, respectively, while aromatic aldehydes produce carbonyl bands in the range of 1720–1680 cm^{-1} [30].

The carboxylic acid observed at a wave number of 1694 cm^{-1}, representing the formation of C=O, is responsible for increasing bitumen hardening; researchers have stated that the formation of the carbonyl group is correlated to an increase in the asphaltene after ageing [6,9,35]. Oxidation creates carbonyl compounds by oxidizing aromatic compounds. The formation of carbonyl groups results in an increased asphaltene fraction, which has been proven to be the one of main reasons for an increase in the binder viscosity [6,35].

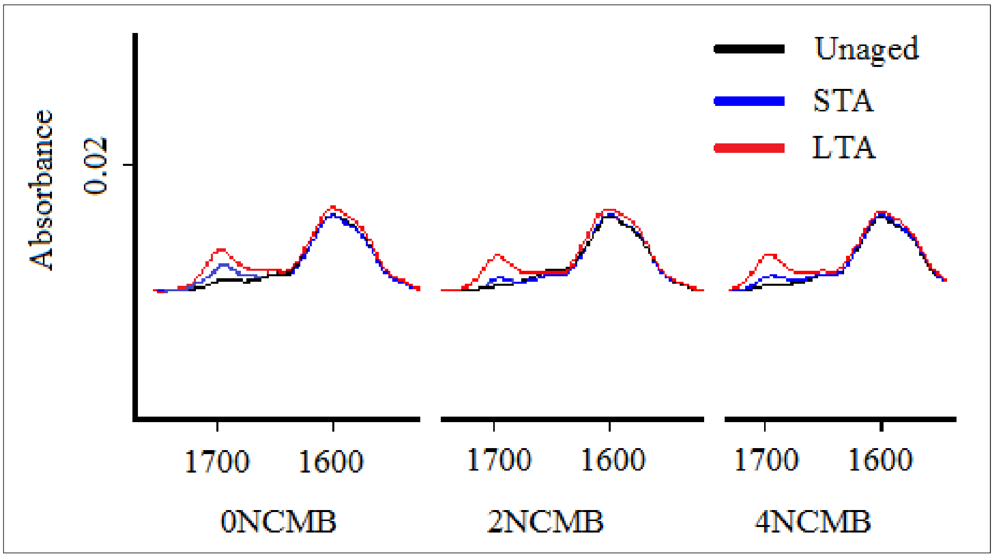
The absorbance peak at the wave number of 1694 cm^{-1} represents the carbonyl acid absorbance value for the modified binders before and after ageing and is presented in Figure 4, where Figure 4a,b show the FTIR spectrum results of the band and its absorbance values, respectively. It is notable that an ageing effect was observed for all the modified binders, where the band of carboxylic acid was formed. However, the formation of this band varied between STA and LTA for the binders, showing that the most sensitive binder was 0 NCMB, where the value of the absorbance peak was higher than 2 NCMB and 4 NCMB after STA, by 39.02% and 29.27%, respectively. This means that an improvement against ageing occurred after adding NC particles. In addition, after LTA, the absorbance peak for 0 NCMB was higher than for the rest of the modified binders, but not as much as after STA, where the increase of absorbance for 0 NCMB was higher than 2 NCMB and 4 NCMB by 6.45% and 9.68%, respectively. The formation of carboxylic acid at a wave number of 1694 cm^{-1} was varied due to the addition of NC particles and ageing. The improvement in oxidation ageing resistance for 2 NCMB and 4 NCMB might be related to a unique property of NC, namely heat absorption. NC particles absorb heat and therefore reduce the effect of temperature on the bitumen structure during ageing and protect it from oxidation. This fact has been observed in previous studies where NC has been investigated [28,29,36].

3.2.2. Aliphatic Hydrocarbons

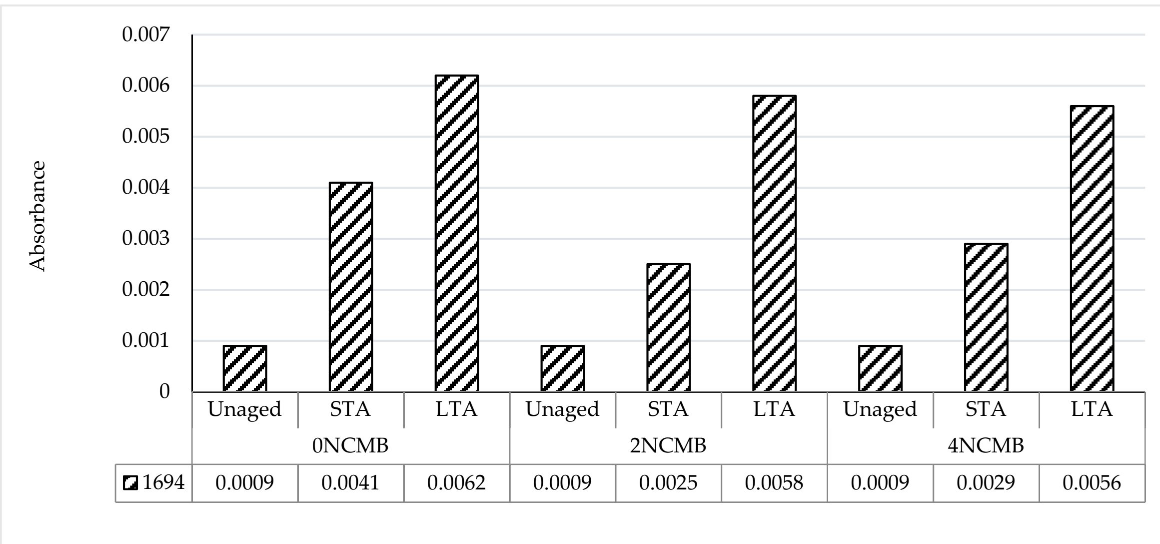
Aliphatic hydrocarbons arise within C–H stretching bands and can occur in the range of 3055–2730 cm^{-1}. Methylene symmetric C–H stretching occurred at 2920 and 2851 cm^{-1}. These bands are considered part of the saturates fraction, where both bands are assigned to the alkyl functional group [6,37]. Figure 5a shows the FTIR spectrum results of bands. The absorbance peaks at wave numbers 2920 and 2851 cm^{-1} were recorded for all samples before and after ageing and are illustrated in Figure 5b. Before ageing, the recorded absorbance at both wave numbers was almost the same for all binders. No changes were recorded due to adding NC particles or mixing factors (temperature and duration). However, ageing influences the absorbance at both wave numbers; a slight reduction was detected after STA and LTA, as shown in Figure 5b.

After STA, the absorbance at 2920 cm^{-1} for 0 NCMB, 2 NCMB and 4 NCMB was 0.225, 0.227 and 0.226, respectively, as presented in Figure 5b. The absorbance at 2851 cm^{-1} for 0 NCMB, 2 NCMB and 4 NCMB was 0.149, 0.156 and 0.153, respectively. It is clear that the STA procedure has little effect on these bands. After LTA, the reduction in absorbance peak value for both wave numbers continued, and variation in their absorbance was detected clearly between the modified binders. The 0 NCMB was more sensitive, where the highest reduction was recorded compared to 2 NCMB and 4 NCMB. The absorbance at 2920 cm^{-1} for 0 NCMB, 2 NCMB and 4 NCMB was 0.194, 0.199 and 0.208, respectively, and the absorbance at 2851 cm^{-1} for 0 NCMB, 2 NCMB and 4 NCMB was 0.130, 0.134 and 0.138, respectively.

The reduction in absorbance reflects the reduction in the concentration (density of a material) of the C-H band, which may lead to reduction of its mass. However, no changes were detected on its wave numbers, which mean that both bands are inert bands. The variation in absorbance reduction may be used to rank the sensitivity of the bitumen; 0 NCMB was more sensitive compared to 2 NCMB and 4 NCMB, which highlights the benefit of the addition of NC. As per previous studies, the same conclusion was stated, as the bands at 2920 and 2851 cm^{-1} decreased slightly after the ageing procedure. The reduction was in mass, but no changes were detected after ageing due to chemical inertness, as was stated previously [31,32,37].

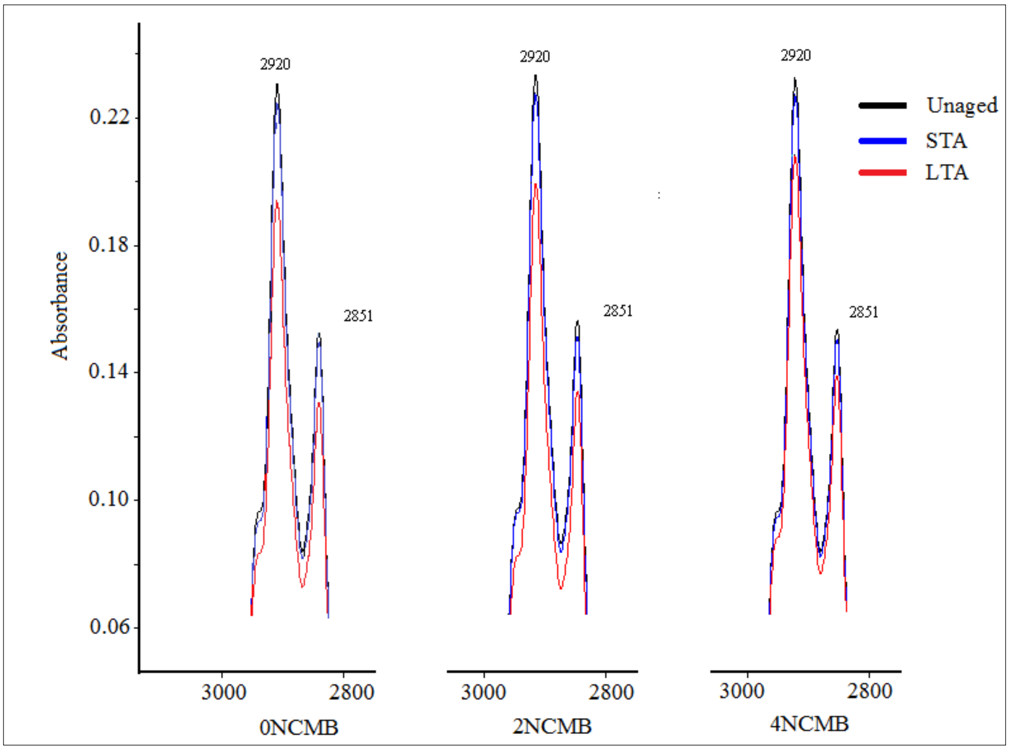


(**a**)

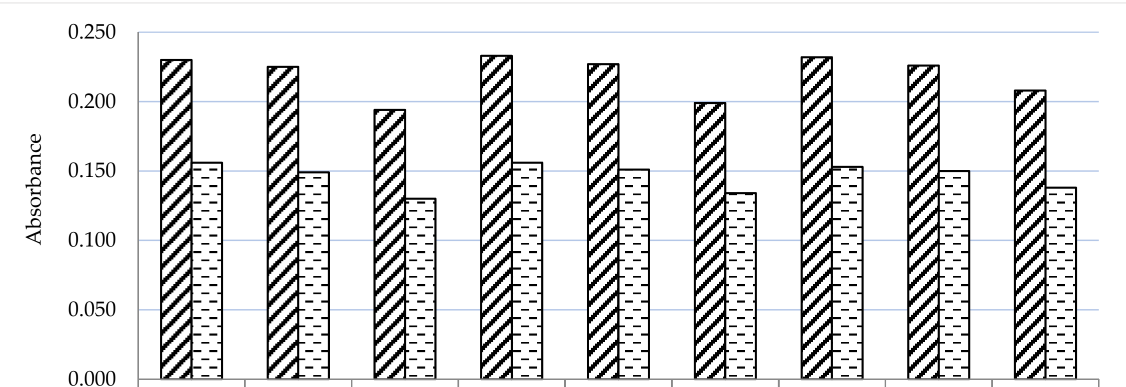


(**b**)

Figure 4. (**a**) FTIR spectrum results of band at wave number 1694 cm^{-1}; (**b**) absorbance value for carboxylic acid at wave number 1694 cm^{-1}.



(**a**)



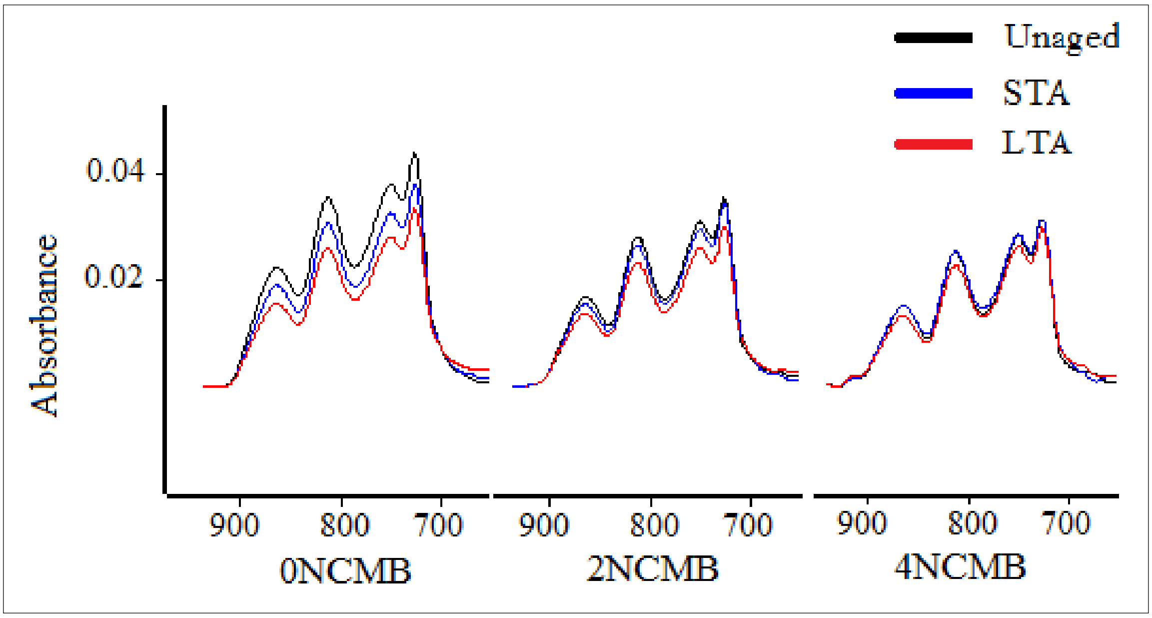
	Unaged	STA	LTA	Unaged	STA	LTA	Unaged	STA	LTA
	0NCMB			2NCMB			4NCMB		
2920	0.230	0.225	0.194	0.233	0.227	0.199	0.232	0.226	0.208
2851	0.156	0.149	0.130	0.156	0.151	0.134	0.153	0.150	0.138

(**b**)

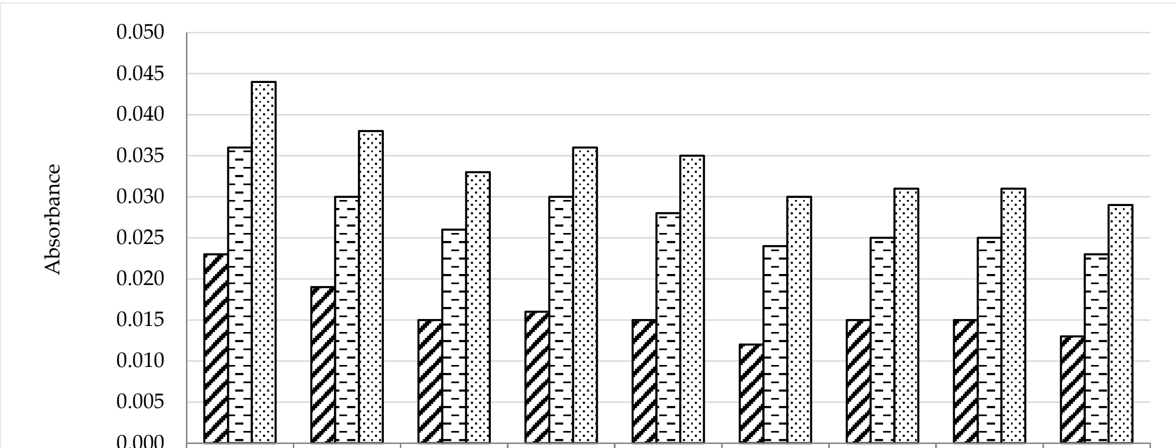
Figure 5. (**a**) FTIR spectrum results of bands at wave numbers 2920 and 2851 cm^{-1}; (**b**) absorbance value for carboxylic acid at wave numbers 2920 and 2851 cm^{-1}.

3.2.3. Aromatic Compounds

Aromatic compounds can be observed in five regions: 3100–3000 cm^{-1}, 2000–1700 cm^{-1}, 1650–1430 cm^{-1}, 1275–1000 cm^{-1} and 900–690 cm^{-1} [30]. However, the last region is under evaluation; FTIR spectrum results of bands are presented in Figure 6a. Many vibrations may vary by hundreds of wave numbers, as per the bands in the region 900–700 cm^{-1}; the variation in these bands showed differences in the absorbance for all modified bitumen after ageing, as can be seen in Figure 6b. These bands are called out-of-plane bending. The bands of the out-of-plane bending vibrations for compounds responsible for aromatics were strong and could be observed easily. For 0 NCMB, the variation in the bands before and after STA and LTA was very clear. Reduction in the absorbance value for the bands after ageing was observed. The absorbance of C-H out-of-plane stretching was reduced due to the effect of ageing, and the reduction was increased when ageing was more severe (LTA compared to unaged). The variations in the bands for 2 NCMB before and after ageing were different compared to 0 NCMB. The bands were more closed, and the effect of ageing was less as compared to 0 NCMB. In addition, the variations in the bands for 4 NCMB before and after ageing were more closed and similar. The results for unaged and STA were almost same. The results for LTA showed a slightly smaller reduction in the absorbance.



(**a**)



	Unaged	STA	LTA	Unaged	STA	LTA	Unaged	STA	LTA
	0NCMB			2NCMB			4NCMB		
860	0.023	0.019	0.015	0.016	0.015	0.012	0.015	0.015	0.013
809	0.036	0.030	0.026	0.030	0.028	0.024	0.025	0.025	0.023
724	0.044	0.038	0.033	0.036	0.035	0.03	0.031	0.031	0.029

(**b**)

Figure 6. (**a**) FTIR spectrum results of bands at wave numbers 860,809 and 724 cm^{-1}; (**b**) absorbance values for carboxylic acid at wave numbers 860,809 and 724 cm^{-1}.

It can be concluded that the band of C–H out-of-plane stretching, which reflects the existence of aromatics, was affected by ageing for all the samples. The reduction in this band was expected, as the ageing effect reduces the aromatic in the bitumen binder [1,6,14,31,38]. It was stated and accepted by researchers that the aromatics generate resins, which in turn generate asphaltenes [1,7,11,39]. The most sensitive to ageing was 0 NCMB, followed by 2 NCMB. The 4 NCMB showed less sensitivity, confirming that hard bitumen shows less sensitivity to ageing [1].

3.2.4. Sulfur Compounds

The SO_2 and SO groups of sulfur compounds for any organic material produce strong infrared bands in the range of 1400–1000 cm^{-1} [30]. In most of the studies regarding bitumen ageing, the sulfoxide band at wave number 1027 cm^{-1} was given special attention. It is well known that sulfur is an element that can be found in bitumen in the range of 0–6% [1]. Most of the studies confirmed that, during ageing, sulfoxides are formed due to an oxidation reaction within the molecules and lead to an increase in polarity [1,4,31,32,40]. After ageing, they are found in the resins or asphaltenes [31].

Based on the results presented in Figure 7a, sulfoxides are originally found in all modified bitumen. The S=O stretching shows stretching bands at 1060–1015 cm^{-1}, but its absorbance peak may differ from the modified bitumen due to the addition of NC particles and ageing.

As can be seen in Figure 7b, the recorded absorbance at wave number 1027 cm^{-1} is similar for all modified binders before ageing. No changes are recorded due to adding NC particles. The absorbance values at wave number 1027 cm^{-1} are 0.009, 0.008 and 0.009 for 0 NCMB, 2 NCMB and 4 NCMB, respectively. The same observation has been noted after applying STA, where there are no clear changes for the absorbance of the binders. LTA showed a different trend. An increase was recorded for the sulfoxide band for all the binders. This increase in the peak of the band is an indicator of an increase in the concentration of the sulfoxide. However, as in previous ageing stages, no large changes were recorded for the absorbance values between the binders. For all the binders tested, there was a small difference between unaged and STA with regard to the formation of the sulfoxide band, while LTA had a clear effect.

3.2.5. Quantification of Ageing Index

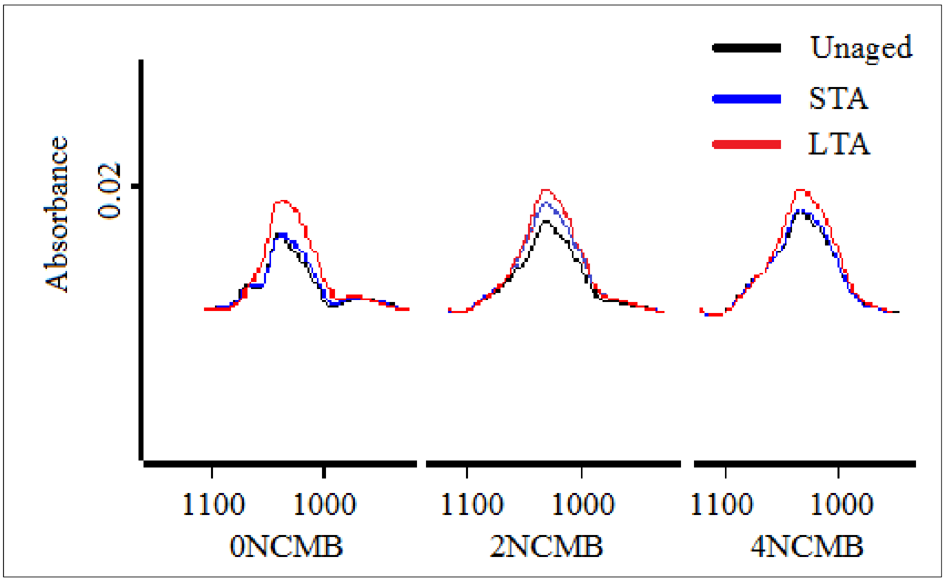
Infrared spectroscopy was used to study the most interesting groups containing C–H, C=O and S=O, where determining the area of the peaks is very important for investigating the ageing effect. The area of the carbonyl (C=O) absorption was calculated in the range of 1752–1653 cm^{-1}, to cover the region that contained carboxylic acids, ketones and anhydrides. Petersen [8] stated that the reason behind considering the total carbonyl area is that the infrared spectra in the carbonyl region becomes more complicated for aged binders due to the intense ketone band appearance. Determining the anhydrides is also difficult because their absorption bands are overlapped by the strong ketone. Carboxylic acids are naturally present in bitumen and form extremely strong hydrogen bonds.

Sulfoxide is important with regard to the determination of changes within functional groups due to ageing. The intense peak at 1027 cm^{-1}, assigned to the stretching vibration of sulfoxide (S=O), was also investigated. This is considered the functional group that is most formed in bitumen after the oxidation of sulfide moieties. The area of this band is determined to be in the range of 1065–1007 cm^{-1} and is used for ageing investigation, as in the previous group.

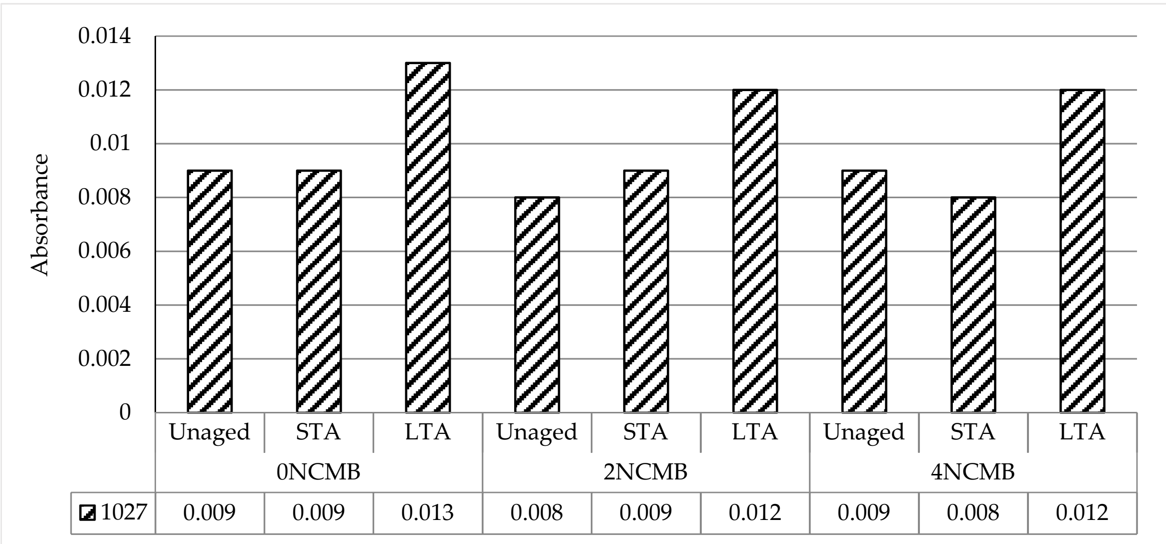
The changes in chemical bonding for the binders due to ageing can be determined by calculating the ratio changes of the chemical bonding. The ratio changes in the carbonyl band ($I_{c=o}$) and the sulfoxide band ($I_{s=o}$) for all the binders, before and after STA and LTA, are calculated using Equations (4) and (5) and are shown in Figures 8 and 9.

$$I_{C=O} = \frac{\text{Area of the carbonyl band centered around 1694 cm}^{-1}}{\Sigma\text{Area of the spectral bands between 2000 and 600 cm}^{-1}} \quad (4)$$

$$I_{S=O} = \frac{\text{Area of the sulfoxide band centered around 1027 cm}^{-1}}{\Sigma\text{Area of the spectral bands between 2000 and 600 cm}^{-1}} \quad (5)$$



(**a**)



(**b**)

Figure 7. (**a**) FTIR spectrum results of bands at wave number 1027 cm^{-1}; (**b**) absorbance value for sulfoxide at wave number 1027 cm^{-1}.

Based on previous studies [4,8,9,31,32,41,42], the formation and increase in the carbonyl index is observed after both STA and LTA for all binders. Formation of the carbonyl band centered around 1694 cm $^{-1}$ is calculated, and as can be seen in Figure 8, the oxidation due to STA and LTA leads to an increase in the functional carbonyl group. As stated previously, carboxylic acids and ketones are the main oxidation products for the carbonyl group, and they are responsible for the increase of asphaltenes that leads to bitumen hardness [4]. However, the values of the ratio of the carbonyl band showed that the formation of this band for the unaged binders was higher for 0 NCMB compared to 2 NCMB and 4 NCMB, while after STA, the ratio decreased after the addition of the NC particles. An unexpected result was noted after LTA, where the ratio of the carbonyl band showed a slight increase for 2 NCMB compared to 0 NCMB (4%), while 4 NCMB revealed the best result. Generally, it can be concluded that NC particles enhance resistance to ageing; this result is consistent with previous studies [18–20,28,40].

The ratio of the sulfoxide band was also calculated before and after ageing. Variation in the values of the ratio for unaged and STA did not give any clear information about whether NC particles improved resistance to ageing. The values showed that, when unaged, reduction in the ratio was noted for 2 NCMB and 4 NCMB compared with 0 NCMB, while after STA, the values were almost the same for all binders. The improvement in ageing resistance was only clear at the last stage of ageing, as can be seen in Figure 9, where 4 NCMB showed the least sensitivity to ageing, followed by 2 NC. Regarding the variation of the results for the ratio of the sulfoxide band for unaged and STA, the sulfoxide is thermally unstable [6], which is why the sulfoxide index was not considered as an ageing index in a previous study [43]. After LTA, a steady-state level may be attained, and at this level of ageing, the ratio of the sulfoxide band may be used to rank the sensitivity of the binders to ageing, where 4 NCMB shows less ageing sensitivity. Although the sulfoxide was thermally unstable, it showed an improvement in ageing resistance after LTA. This finding is in good agreement with a previous study done by Wang et al. [44].

3.3. Indirect Tensile Strength (ITS) Test

The ITS test was conducted on modified asphalt mixtures at unaged, STA and LTA conditions. Figure 10 shows the strength of asphalt mixtures at failure increasing with ageing. This result was expected, based on previous studies about the effect of ageing on asphalt mixture performance [20,24,25]. The ITS for all aged samples increased. The ITS for unaged 2 NCMB and 4 NCMB showed an improvement compared with 0 NCMB. ITS increased 13% and 8% for 2 NCMB and 4 NCMB, respectively. The increase in viscosity of modified bitumen, due to adding NC particles, was reflected in an increase in the strength of the mixtures. However, the same trend was observed in mixtures after STA.

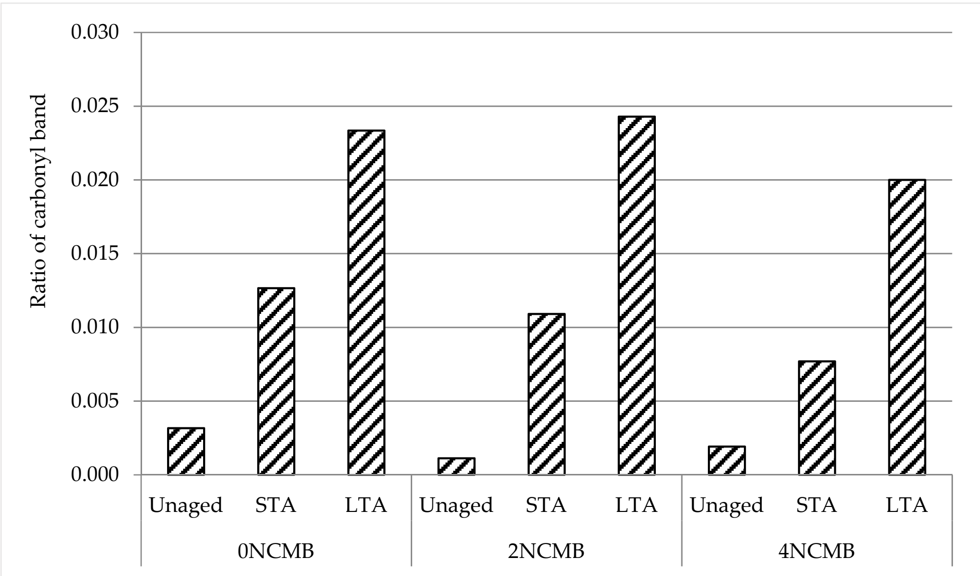


Figure 8. The ratio of the carbonyl band.

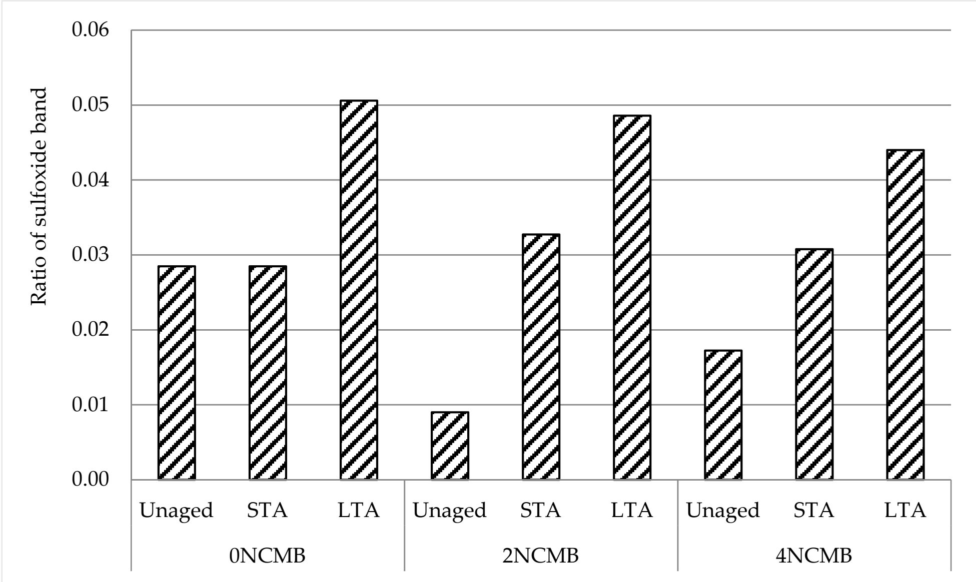


Figure 9. The ratio of the sulfoxide band.

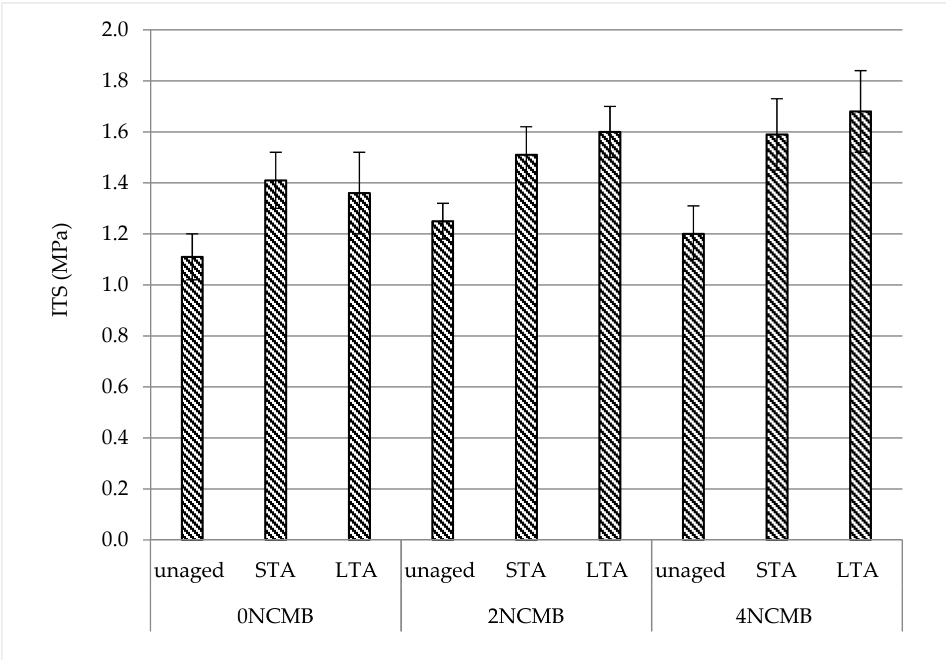


Figure 10. Indirect tensile strength (ITS) results.

After the application of STA on the mixtures based on their own mixing and compaction temperature, the ITS test was conducted at 20 °C. The results showed an improvement for all mixtures, as can be observed in Figure 9. This is a good result, which highlights the importance of STA in the paving stage.

The ITS result showed a considerable increase for both 2 NCMB and 4 NCMB, compared with 0 NCMB. The increase was recorded as 7% and 13% for 2 NCMB and 4 NCMB, respectively. During production and compaction in the field, which is simulated by STA in the lab, the loss of volatile components and oxidation of the bitumen occurred. Oxidation and volatile loss (which first results from evaporation of volatile components, and then by penetration of the oil component of the bitumen into aggregate particles) leads to an increase in mixture hardness. Increasing the mixture hardness, specifically in STA, plays a significant role in improving the load-bearing capacity and resistance to permanent deformation (rutting) of the asphalt mixture in its early service life; a stiffer mixture is produced, leading to a reduction in the mixture flexibility [1,10,45]. NC particles improve the strength of the mixture for STA, and it is believed to play an important role in LTA. The result obtained is in good agreement with previous studies, where nano-clay increased the viscosity of the modified binder and subsequently improved the strength of the mixtures [36].

The ITS was reduced for 0 NCMB after LTA, while the increase in ITS for 2 NCMB and 4 NCMB extended into LTA. The ITS was reduced from 1.41 MPa for STA to 1.36 MPa for LTA for 0 NCMB. The progressive oxidation during LTA leads to an increase in binder viscosity, which results in a strength reduction of the 0 NCMB mixture. The increase in viscosity is related to the increase in asphaltene content; the flexibility is reduced, making the bitumen more brittle and hence more easily broken. The ITS increased from 1.51 MPa for STA to 1.61 MPa for LTA for 2 NCMB, while the ITS for 4 NCMB increased from 1.59 MPa for STA to 1.68 MPa for LTA. This indicates improvement of the mixture strength after ageing as a result of the addition of NC particles. The ITS values of the 2 NCMB and 4 NCMB mixtures indicate improvement of the cohesion of the aged bitumen in the mixture, which could reflect improved resistance against cracking. The improvement in ageing resistance for the mixtures using halloysite nanotube modified bitumen is in good agreement with previous studies done by López-Montero et al. [20] and Wang et al. [44].

4. Conclusions

Nano-clay, also known as Halloysite nanotubes, which is a type of alumino-silicate clay, was added to bitumen at 0%, 2% and 4% by weight of bitumen for this study. The modified bitumen was aged, using STA and LTA, and then tested using consistency tests (to monitor the change in physical properties) and the FTIR method (to detect any chemical changes). Mixtures were also investigated using the ITS test, and any improvement in the modified bitumen after ageing was determined.

The conclusion is that the physical and chemical properties of all the modified binders and the strength of their mixtures were affected by ageing. Ageing was dependent on NC percentage. However, the modified binders, including NC particles, showed a reduction in ageing sensitivity due to the absorption of heat from the NC. The conclusions may be summarized as follows:

- Reduction in fluidity caused by mixing was observed in 0 NCMB. However, the penetration grade was still in the range of 60–70, which means only a slight impact from mixing.
- The addition of nano-clay particles caused an increase in the viscosity of the unaged 2 NCMB and 4 NCMB, which means an increase in stiffness and a reduction in temperature susceptibility.
- All modified nano-clay bitumens were affected by ageing. However, the results of the consistency tests and their ageing index showed that 2 NCMB and 4 NCMB had better resistance against ageing than 0 NCMB. The increase in PI for 2 NCMB and 4 NCMB indicates an improvement in temperature susceptibility.
- The FTIR test demonstrated that there are no newly created bands after adding nano-clay particles for unaged 0 NCMB, 2 NCMB and 4 NCMB. This suggests that there is no chemical activity between nano-clay and bitumen.
- The FTIR results showed that the absorbance peak was affected by ageing for all selected functional groups in this study. The selected groups were oxygen-containing compounds, aliphatic hydrocarbons, aromatic compounds, and sulfur compounds. Based on the absorbance peak, 2 NCMB and 4 NCMB were less sensitive to ageing.
- Quantification of the changes in chemical bonding for the carbonyl band and the sulfoxide band were calculated. The increase in the ratio of these bands indicates an increase in asphaltene content. Based on the results, 4 NCMB was the best modified binder, showing less ageing sensitivity.

- The results of the ITS test were in line with previous results; STA and LTA resulted in increased ITS due to increased stiffness. The increase in the ITS of 2 NCMB and 4 NCMB indicates improved cohesion of the aged bitumen in the mixture, which could reflect improved resistance against cracking, leading to increased pavement durability.

Author Contributions: H.A.O.: Conceptualization, Writing—original draft, Methodology, Investigation, Formal analysis. H.Y.K.: Data curation, Funding acquisition. M.B.: Reviewing and Editing, Software. M.K.A.A.: Visualization, Data curation. A.M.: Reviewing and Editing, Validation. N.I.M.Y.: Supervision, Reviewing and Editing, Funding acquisition. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Universiti Kebangsaan Malaysia (Grant number DIP-2020-003) and Universiti Tenaga Nasional (J5100D4103-BOLDREFRESH2025-CENTRE OF EXCELLENCE)).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: All data used in this research can be provided upon request.

Acknowledgments: The authors would like to thank Universiti Tenaga Nasional for their financial support.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Hunter, R.N.; Self, A.; Read, J.; Hobson, E. *The Shell Bitumen Handbook*; ICE Publishing: London, UK, 2015.
2. Airey, G.D. State of the art report on ageing test methods for bituminous pavement materials. *Int. J. Pavement Eng.* **2003**, *4*, 165–176. [CrossRef]
3. Sirin, O.; Paul, D.K.; Kassem, E. State of the art study on aging of asphalt mixtures and use of antioxidant additives. *Adv. Civ. Eng.* **2018**, 3428961. [CrossRef]
4. Tauste, R.; Moreno-Navarro, F.; Sol-Sánchez, M.; Rubio-Gámez, M. Understanding the bitumen ageing phenomenon: A review. *Constr. Build. Mater.* **2018**, *192*, 593–609. [CrossRef]
5. Mousavi, M.; Pahlavan, F.; Oldham, D.; Hosseinnezhad, S.; Fini, E.H. Multiscale investigation of oxidative aging in biomodified asphalt binder. *J. Phys. Chem. C* **2016**, *120*, 17224–17233. [CrossRef]
6. Lesueur, D. The colloidal structure of bitumen: Consequences on the rheology and on the mechanisms of bitumen modification. *Adv. Colloid Interface Sci.* **2009**, *145*, 42–82. [CrossRef] [PubMed]
7. Fernández-Gómez, W.D.; Quintana, H.A.R.; Lizcano, F.R. A review of asphalt and asphalt mixture aging. *Ing. E Investig.* **2013**, *33*, 5–12.
8. Petersen, J.C. Quantitative functional group analysis of asphalts using differential infrared spectrometry and selective chemical reactions–theory and application. *Transp. Res. Rec.* **1986**, *1096*, 1–11.
9. Petersen, J.C.; Branthaver, J.F.; Robertson, R.E.; Harnsberger, P.M.; Duvall, J.J.; Ensley, E.K. Effects of physicochemical factors on asphalt oxidation kinetics. *Transp. Res. Rec.* **1993**, *1391*, 1–10.
10. Scholz, T.V. *Durability of Bituminous Paving Mixtures*; University of Nottingham: Nottingham, UK, 1995.
11. Siddiqui, M.N.; Ali, M.F. Studies on the aging behavior of the Arabian asphalts. *Fuel* **1999**, *78*, 1005–1015. [CrossRef]
12. Subhy, A. Advanced analytical techniques in fatigue and rutting related characterisations of modified bitumen: Literature review. *Constr. Build. Mater.* **2017**, *156*, 28–45. [CrossRef]
13. Olabemiwo, O.M.; Akintomiwa, O.; Bakare, H. Preliminary investigation on modification of Agbabu natural bitumen with some polymeric materials. *Int. J. Sci. Eng. Res* **2015**, *6*, 1342.
14. Dehouche, N.; Kaci, M.; Mokhtar, K.A. Influence of thermo-oxidative aging on chemical composition and physical properties of polymer modified bitumens. *Constr. Build. Mater.* **2012**, *26*, 350–356. [CrossRef]
15. Zhu, J.; Balieu, R.; Wang, H. The use of solubility parameters and free energy theory for phase behaviour of polymer-modified bitumen: A review. *Road Mater. Pavement Des.* **2021**, *22*, 757–778. [CrossRef]
16. Pyshyev, S.; Gunka, V.; Grytsenko, Y.; Bratychak, M. Polymer modified bitumen. *Chem. Chem. Technol.* **2016**, *10*, 631–636. [CrossRef]
17. Crucho, J.; Picado-Santos, L.; Neves, J.; Capitão, S. A review of nanomaterials' effect on mechanical performance and aging of asphalt mixtures. *Appl. Sci.* **2019**, *9*, 3657. [CrossRef]
18. Martinho, F.C.; Farinha, J.P.S. An overview of the use of nanoclay modified bitumen in asphalt mixtures for enhanced flexible pavement performances. *Road Mater. Pavement Des.* **2019**, *20*, 671–701. [CrossRef]
19. Ali Omar, H.; Mubaraki, M.; Abdullah, N.H.; Al-Sabaeei, A.; Memon, A.M.; Khan, M.I.; Sutanto, M.H.; Md Yusoff, N.I. Determining the Effect of Ageing of Nano-Clay Modified Bitumen Using Atomic Force Microscopy. *Sci. Iran.* **2021**, 28. [CrossRef]
20. López-Montero, T.; Crucho, J.; Picado-Santos, L.; Miró, R. Effect of nanomaterials on ageing and moisture damage using the indirect tensile strength test. *Constr. Build. Mater.* **2018**, *168*, 31–40. [CrossRef]

21. Li, R.; Xiao, F.; Amirkhanian, S.; You, Z.; Huang, J. Developments of nano materials and technologies on asphalt materials–A review. *Constr. Build. Mater.* **2017**, *143*, 633–648. [CrossRef]
22. Nejad, F.M.; Azarhoosh, A.; Hamedi, G.H.; Azarhoosh, M. Influence of using nonmaterial to reduce the moisture susceptibility of hot mix asphalt. *Constr. Build. Mater.* **2012**, *31*, 384–388. [CrossRef]
23. Copeland, A.R. *Influence of Moisture on Bond Strength of Asphalt-Aggregate Systems*; Vanderbilt University: Nashville, TN, USA, 2007.
24. Gao, Y.; Geng, D.; Huang, X.; Li, G. Degradation evaluation index of asphalt pavement based on mechanical performance of asphalt mixture. *Constr. Build. Mater.* **2017**, *140*, 75–81. [CrossRef]
25. Islam, M.R.; Hossain, M.I.; Tarefder, R.A. A study of asphalt aging using Indirect Tensile Strength test. *Constr. Build. Mater.* **2015**, *95*, 218–223. [CrossRef]
26. Rawtani, D.; Agrawal, Y. Multifarious applications of halloysite nanotubes: A review. *Rev. Adv. Mater. Sci.* **2012**, *30*, 282–295.
27. Deng, S.; Zhang, J.; Ye, L. Effects of chemical treatment and mixing methods on fracture behaviour of halloysite-epoxy nanocomposites. In Proceedings of the 17th Internatioanl Conference on Composite Materials, Edinburgh, UK, 27–31 July 2009.
28. Omar, H.A.; Yusoff, N.I.M.; Sajuri, Z.; Ceylan, H.; Jakarni, F.M.; Ismail, A. Determining the effects of aging on halloysite nano-tube modified binders through the pull-off test method. *Constr. Build. Mater.* **2016**, *126*, 245–252. [CrossRef]
29. Lau, K.-t.; Gu, C.; Hui, D. A critical review on nanotube and nanotube/nanoclay related polymer composite materials. *Compos. Part B: Eng.* **2006**, *37*, 425–436. [CrossRef]
30. Stuart, B.H. *Infrared Spectroscopy: Fundamental and Applications*; John Wiley & Sons: Hoboken, NJ, USA, 2004.
31. Mirwald, J.; Werkovits, S.; Camargo, I.; Maschauer, D.; Hofko, B.; Grothe, H. Understanding bitumen ageing by investigation of its polarity fractions. *Constr. Build. Mater.* **2020**, *250*, 118809. [CrossRef]
32. Mirwald, J.; Maschauer, D.; Hofko, B.; Grothe, H. Impact of reactive oxygen species on bitumen aging–The Viennese binder aging method. *Constr. Build. Mater.* **2020**, *257*, 119495. [CrossRef]
33. Zhang, D.; Zhang, H.; Shi, C. Investigation of aging performance of SBS modified asphalt with various aging methods. *Constr. Build. Mater.* **2017**, *145*, 445–451. [CrossRef]
34. Zhang, D.; Zhang, H.; Zhu, C.; Shi, C. Synergetic effect of multi-dimensional nanomaterials for anti-aging properties of SBS modified bitumen. *Constr. Build. Mater.* **2017**, *144*, 423–431. [CrossRef]
35. Petersen, J.C. A review of the fundamentals of asphalt oxidation: Chemical, physicochemical, physical property, and durability relationships. *Transp. Res. Circ.* **2009**. [CrossRef]
36. Omar, H.A.; Yusoff, N.I.M.; Ceylan, H.; Rahman, I.A.; Sajuri, Z.; Jakarni, F.M.; Ismail, A. Determining the water damage resistance of nano-clay modified bitumens using the indirect tensile strength and surface free energy methods. *Constr. Build. Mater.* **2018**, *167*, 391–402. [CrossRef]
37. Handle, F.; Harir, M.; Füssl, J.; Koyun, A.e.N.; Grossegger, D.; Hertkorn, N.; Eberhardsteiner, L.; Hofko, B.; Hospodka, M.; Blab, R. Tracking aging of bitumen and its saturate, aromatic, resin, and asphaltene fractions using high-field Fourier transform ion cyclotron resonance mass spectrometry. *Energy Fuels* **2017**, *31*, 4771–4779. [CrossRef]
38. Lu, X.; Isacsson, U. Effect of ageing on bitumen chemistry and rheology. *Constr. Build. Mater.* **2002**, *16*, 15–22. [CrossRef]
39. Moschopedis, S.E.; Speight, J.G. Influence of metal salts on bitumen oxidation. *Fuel* **1978**, *57*, 235–240. [CrossRef]
40. Yao, H.; Dai, Q.; You, Z. Fourier Transform Infrared Spectroscopy characterization of aging-related properties of original and nano-modified asphalt binders. *Constr. Build. Mater.* **2015**, *101*, 1078–1087. [CrossRef]
41. Yang, Z.; Zhang, X.; Zhang, Z.; Zou, B.; Zhu, Z.; Lu, G.; Xu, W.; Yu, J.; Yu, H. Effect of aging on chemical and rheological properties of bitumen. *Polymers* **2018**, *10*, 1345. [CrossRef]
42. Guduru, G.; Goli, A.K.; Matolia, S.; Kuna, K.K. Chemical and Performance Characteristics of Rejuvenated Bituminous Materials with High Reclaimed Asphalt Content. *J. Mater. Civ. Eng.* **2021**, *33*, 04020434. [CrossRef]
43. Yao, H.; You, Z.; Li, L.; Goh, S.W.; Lee, C.H.; Yap, Y.K.; Shi, X. Rheological properties and chemical analysis of nanoclay and carbon microfiber modified asphalt with Fourier transform infrared spectroscopy. *Constr. Build. Mater.* **2013**, *38*, 327–337. [CrossRef]
44. Wang, D.; Liu, Q.; Yang, Q.; Tovar, C.; Tan, Y.; Oeser, M. Thermal oxidative and ultraviolet ageing behaviour of nano-montmorillonite modified bitumen. *Road Mater. Pavement Des.* **2021**, *22*, 121–139. [CrossRef]
45. Vallerga, B. Pavement deficiencies related to asphalt durability. In Proceedings of the Association of Asphalt Paving Technologists Proceedings, San Diego, CA, USA, 16–18 February 1981; Volume 50, pp. 481–491.