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Rheological properties and chemical analysis of nanoclay and carbon microfiber modified asphalt with Fourier transform infrared spectroscopy

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HIGHLIGHTS

- ▶ Asphalt binders blended with four nano/micro-modifiers were used.
- ▶ The complex shear modulus was measured with DSR.
- ▶ The chemical bonding of asphalt binders was analyzed through FTIR.
- ▶ The addition of four modifiers can delay the aging and oxidation effect.

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ABSTRACT

This work aims to improve the rutting and fatigue cracking resistance of asphalt binders using selected nano- or micro-sized materials and to shed light on the microstructure changes induced by such modification to asphalt binders. The four modifiers (Nanomer I.44P, carbon microfiber, non-modified nanoclay and polymer modified nanoclay) were added into the control asphalt binder (PG 58-34). The Superpave™ tests and Fourier transform infrared spectroscopy (FTIR) measurements were conducted for obtaining the complex shear modulus G^* and microstructure distribution of modified asphalt binders. Meanwhile, the short-term and long-term aging processes of asphalt binders are simulated by rolling thin film oven (RTFO) and pressure aging vessel (PAV) tests. From the dynamic shear rheometer (DSR) and FTIR tests results, the complex shear modulus G^* values of nano- or micro-materials (Nanomer I.44P, non-modified nanoclay and carbon microfiber) modified asphalt binders increase, and the performance of resistance to rutting is improved compared to the control asphalt binder. The addition of polymer modified nanoclay (PMN) into the control asphalt binder decreases the complex shear modulus, and enhances the resistance to fatigue cracking. Moreover, the addition of four modifiers into the control asphalt binder can delay and weaken the aging and oxidation effect.

1. Introduction

Asphalt materials are obtained from crude petroleum as byproducts. About 90–95% by weight of asphalt consist of hydrogen and carbon, and two types' atoms (heteroatoms and metals) are in the remaining portion of asphalt. The heteroatoms contain the nitrogen, oxygen and sulfur, which replace the carbon by heat or shear stress. These contribute to the physical and chemical performance by causing much of the interaction between molecules. Metal atoms, such as vanadium, nickel and iron, are represented in trace quantities, typically far less than 1% [1,2]. Asphalt compositions are so complicated and composed of organic molecules, which can react with oxygen from the environment air. Also, the molecules in asphalt binders can affect the aging and oxidation extent and molecular reactions depend on temperature, modifier type and concentration. The oxidation also changes the structure and composition of asphalt. Generally speaking, the oxidation makes the asphalt stiffer and brittle [3–5]. So, in asphalt pavement service years, when the rutting and fatigue cracking appear, it depends on the oxidation rate [6,7].

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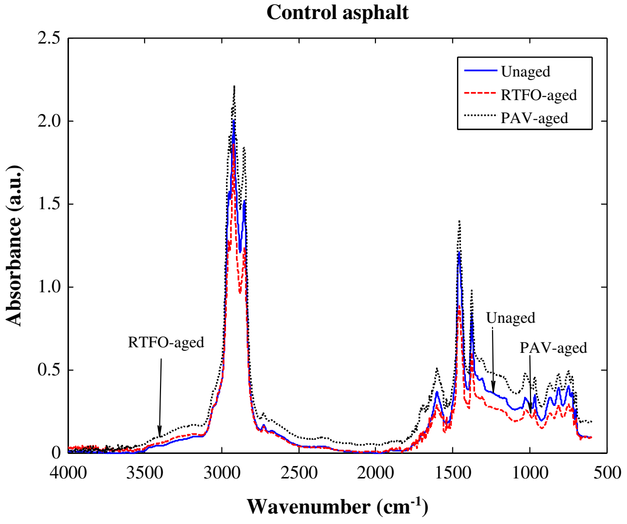
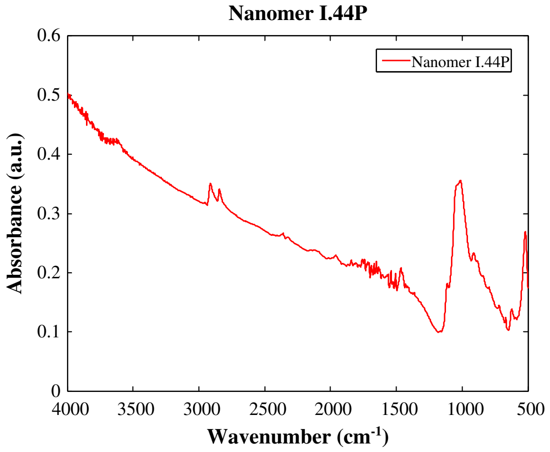
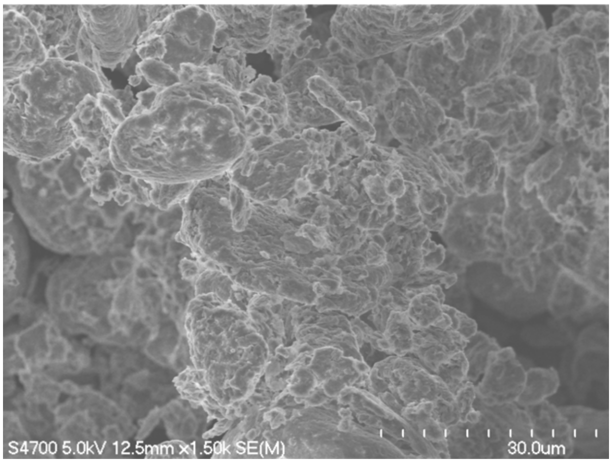


Fig. 1. FTIR spectra of control asphalt binder.

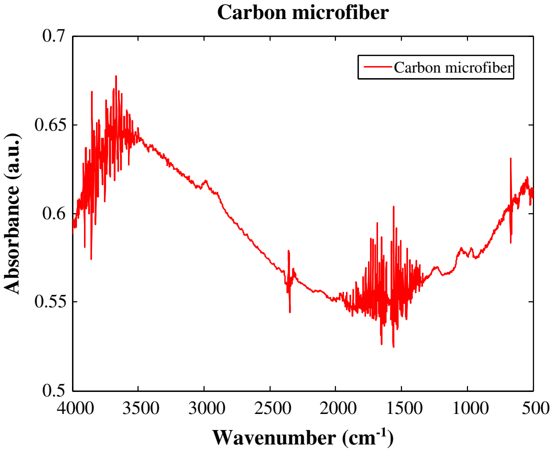


(a) FTIR spectra of NI.44P

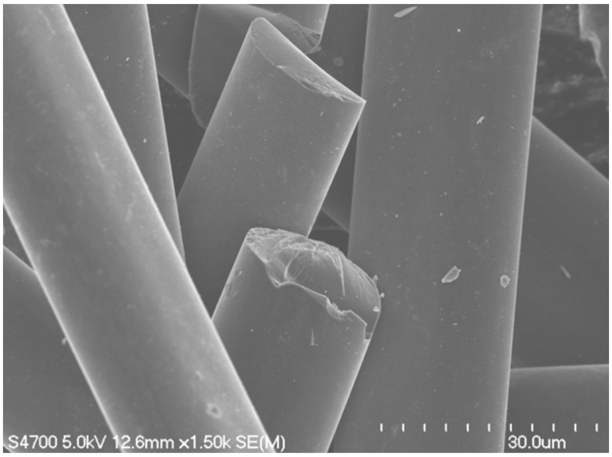


(b) SEM image of NI.44P

Fig. 2. The SEM image and FTIR spectra of Nanomer I.44P.



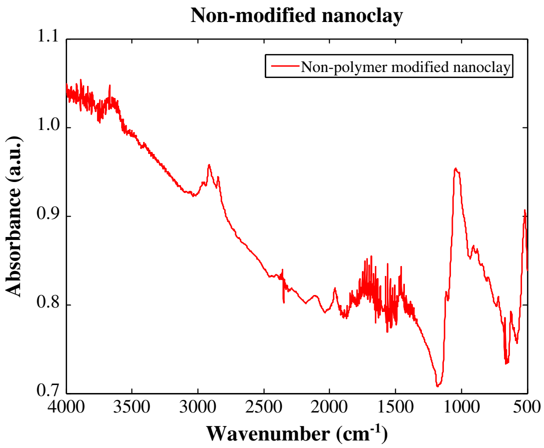
(a) FTIR spectra of MCF



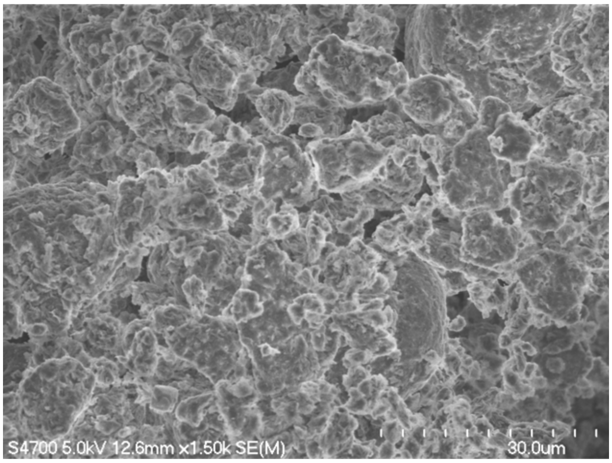
(b) SEM image of MCF

Fig. 3. The SEM image and FTIR spectra of carbon microfiber.

Asphalt binder is widely used for road pavement construction. Due to the limitation of temperature susceptibility, the low-temperature and high-temperature performance of asphalt binders need to be improved. Therefore, the asphalt modification research emerges as the times require, and develop prosperously. In general, the fibers and polymers, such as carbon fibers, styrene–butadiene–styrene (SBS), styrene–butadiene–rubber (SBR), ethylene glycidyl acrylate (EGA) terpolymer, crumb rubber, and are used broadly in the construction [8–19]. Research showed the fiber-reinforced asphalt materials (FRAM) improved the resistance to aging, fatigue cracking and moisture damage. Polypropylene fibers, polyester fibers, asbestos fibers, cellulose fibers, carbon fibers, glass fibers and nylon fibers have been used to enhance the performance of asphalt concrete [20–22]. It is obvious that the SBS material has been using in the entire world, and the properties and aging influence of SBS modified asphalt binder were investigated by dynamic shear rheometer (DSR), Fourier transform infrared spectroscopy (FTIR), atomic force microscopy (AFM), rolling thin film oven (RTFO), pressure aging vessel (PAV) tests. These results showed that SBS could significantly improve the low-temperature performance of asphalt concrete [12,13,23,24]. SBR is an important asphalt modifier in the pavement construction. Through the SBR modification in the asphalt binders, the low-temperature ductility and elastic recovery were enhanced; also, the viscosity was increased [14,15,25]. In addition, EGA has been used for roads since 1991, and EGA modifier solved the separation problem of asphalt storing and transportation. It is shown that the moisture damage of EGA modified asphalt mixture also decreased in the research [14]. In recent years, crumb rubber modifier (CRM) has been increasingly used in re-

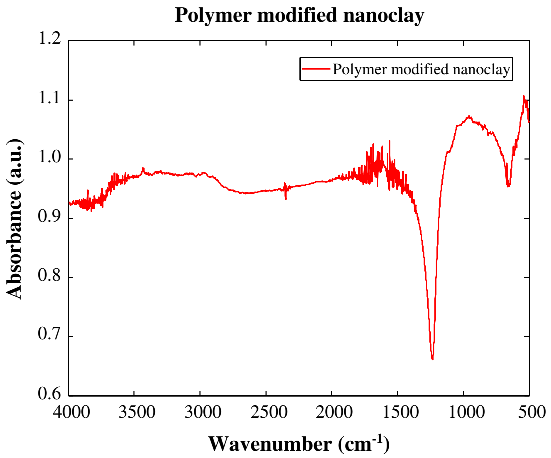


(a) FTIR spectra of NMN

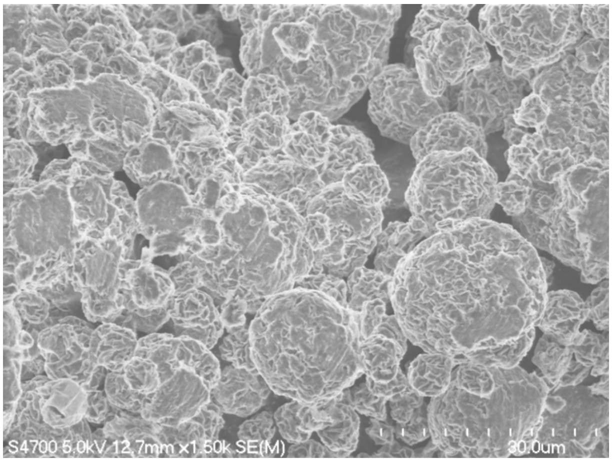


(b) SEM image of NMN [46]

Fig. 4. The SEM image and FTIR spectra of non-modified nanoclay [46].



(a) FTIR spectra of PMN



(b) SEM image of PMN [46]

Fig. 5. The SEM image and FTIR spectra of polymer modified nanoclay [46].

search projects and construction. The crumb rubber could improve the viscosity, rheological properties, rutting resistance and thermal cracking of asphalt binders. The performance of crumb rubber modified asphalt depended on the CRM type, binder and mixing condition [17,18,26–30].

In the last decade or so, nanotechnology has emerged as the potential solution to greatly enhance the performance and durability of construction materials. Nanomaterials are defined as materials with at least one dimension that falls in the length scale of 1–100 nm. Due to the small size and high surface area, the property of nanomaterials is much different from normal size materials. Therefore, research engineers tried to apply the nanomaterials into the pavement engineering. Some research showed that the rutting and fatigue cracking resistance of asphalt binders and mixtures improved with the addition of nanomaterials. Nanoclay and carbon nano-fiber were used as additives to modify the asphalt binder. The complex shear modulus of nano-modified asphalt binders increased relative to the control asphalt binder, as well as the failure temperature and high temperature performance grade. The rutting resistance performance of nanoclay and carbon fiber modified asphalt mixtures would be enhanced [31–36]. Recently, the nano-sized hydrated lime was selected as the additive to blend with warm-mix-asphalt (WMA) mixture. The moisture susceptibility of WMA mixture was investigated in the study [37]. In addition, the combination of Nano-SiO_2 and SBS were used to mix with stone matrix asphalt, and the physical and mechanical properties of asphalt binders and mixtures were improved [38].

FTIR methodology, or a simple failure analysis technique, can detect molecular vibrations that may be in the form of two atoms in a diatomic molecule experiencing a simple coupled motion to each individual atom in a large polyfunctional molecule undergoing motion. From the infrared spectra of test, the material information about chemical bonding and materials structure would be obtained [39]. In this study, the ethylene band, sulfoxide band, aliphatic branched band, aliphatic index band, aromatic band and carbonyl band in the infrared spectra related to the performance of asphalt binders were investigated. Based on a review of the literature, the four nano- or micro-materials (Nanomer I.44P, carbon microfiber, non-modified nanoclay and polymer modified nanoclay) were applied to modify the control asphalt binder (PG 58-34), and the DSR and FTIR tests were employed to evaluate the macro- and micro-properties of modified asphalt binders. The Hitachi S-4700 field emission scanning electron microscope (SEM) was employed to test the microstructures of nanomaterials. The results of these tests show the addition of ultrafine materials can enhance the properties of asphalt binders.

2. Objectives and scopes

The selected ultrafine materials (Nanomer I.44P, carbon microfiber, non-modified nanoclay and polymer modified nanoclay) were added into the control asphalt to modify and enhance the

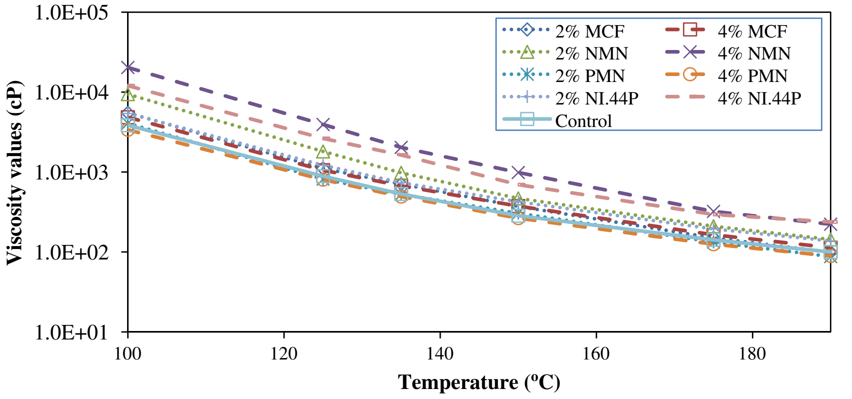


Fig. 6. Viscosity results of control and modified asphalt binders.

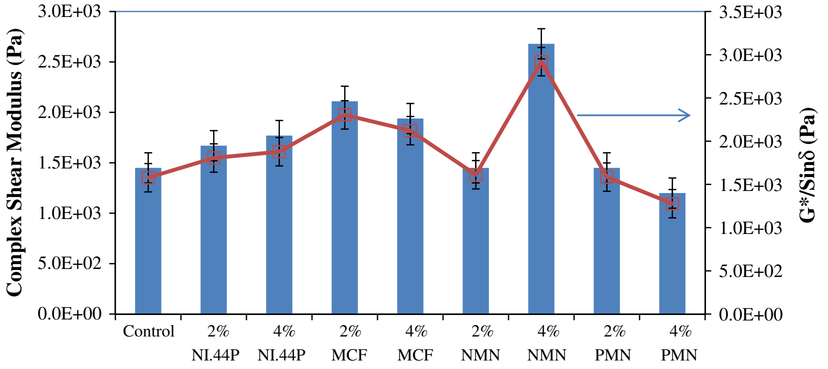


Fig. 7. Complex shear modulus and rutting factor of unaged control and modified asphalt binders (with standard error bars).

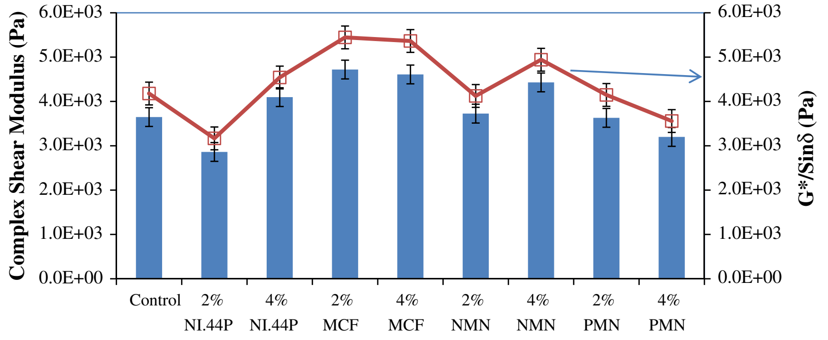


Fig. 8. Complex shear modulus and rutting factor of RTFO-aged control and modified asphalt binders (with standard error bars).

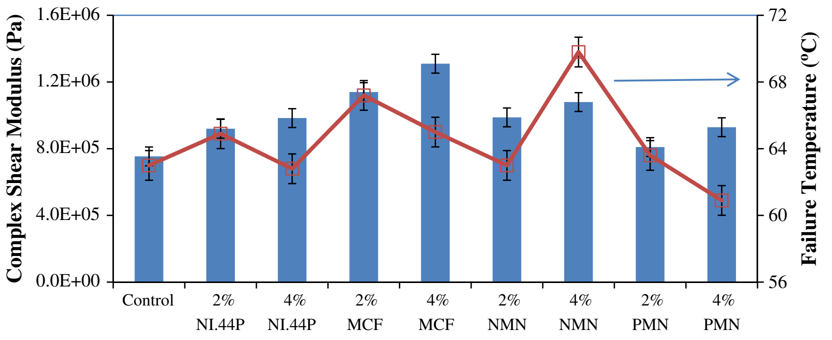


Fig. 9. Complex shear modulus and failure temperatures of PAV-aged control and modified asphalt binders (with standard error bars).

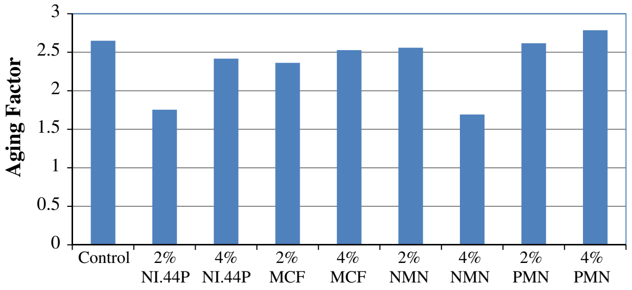


Fig. 10. Aging factor of control and modified asphalt binders.

Table 1
Assignations of the main bands of the FT-IR spectra[13].

Wavenumber (cm^{-1})	Assignations[a]
3594, 3735	νO—H
2924, 2853	νC—H aliphatic
1735	νC═O
1700	νC═O conjugated
1600	νC═C aromatic
1460	δC—H of —(CH$_2$)$_n$— (aliphatic index)
1376	δC—H of CH$_3$ (aliphatic branched)
1030	νS═O sulfoxide
966	δC—H trans disubstituted —CH═CH— (butadiene block)
748, 690	δC—H aromatic monosubstitued (styrene block)

[a] ν = Stretching, δ = bending.

properties of asphalt binders. The objective of this paper is to investigate the rutting and fatigue resistance performance and micro-structure changing of modified asphalt binders through the DSR and FTIR tests. The chemical bonding and its combined types in the asphalt binders fundamentally affect the performance of asphalt binders. And the changed ratios of element bonding indicate that macro-properties of asphalt binders change. Therefore, the microstructure analysis of modified asphalt binders was conducted to explain the test results, and the addition of ultrafine materials into the control asphalt binder could improve the overall performance of binders.

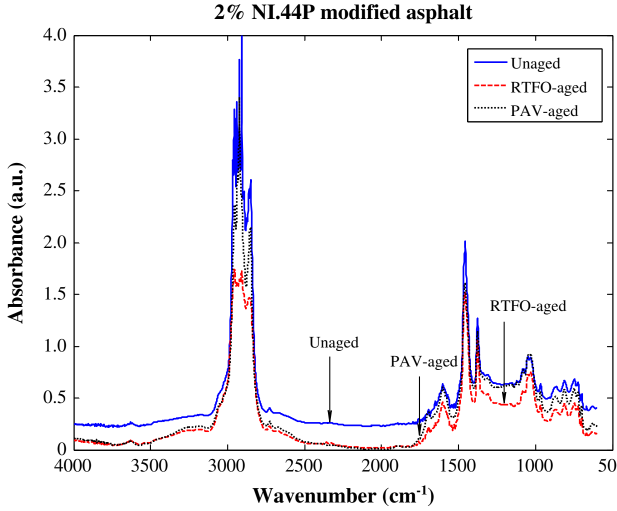
3. Materials preparation

3.1. Control asphalt PG 58-34

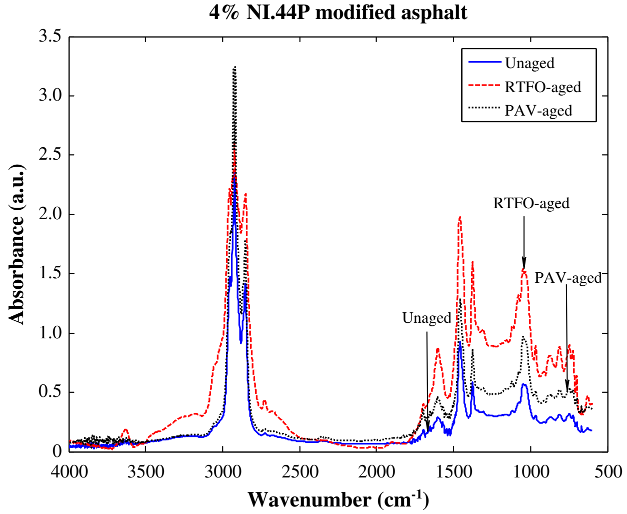
The control asphalt binder PG58-34 was obtained from Gladstone, Michigan. It is noted that the control asphalt was modified with acrylonitrile butadiene styrene (ABS) to strength the lower temperature grade. The addition of ultrafine materials into the control asphalt binder is mainly to improve the high-temperature performance of the asphalt binder. Fig. 1 shows the FTIR spectra of unaged, RTFO-aged and PAV-aged control asphalt binder. It is noted that there is a peak at 1690 cm^{-1} (bending C═O conjugated) and the area is increased intensively in the PAV-aged control asphalt binder relative to the unaged control asphalt binder and it indicates violent oxidation reactions of control asphalt happened during the PAV aging process. It means carbonyl index is an aging index [40,41].

3.2. Nanomer (NI.44P)

Nanomer nanoclays are high purity and compatible with montmorillonites. The NI.44P nanoclay samples were used in this study, which is processed by quaternary ammonium chemistry, and it has good heat stability and electrochemical property. Fig. 2 shows the FTIR spectra of NI.44P. The hydrogen bonds are observed at 2887–2919 cm^{-1} and 992–999 cm^{-1}. The peaks centered at 2924 cm^{-1} and 2853 cm^{-1} indicates the stretching C—H aliphatic bonds. The peaks at 3594 cm^{-1} and 3735 cm^{-1} present the stretching O—H bonds [13]. From the SEM image (Fig. 2), the agglomeration phenomena happened in the nano-scale NI.44P materials when it was exposed to air, and NI.44P materials of different sizes were gluing together. However, some of the nanomaterials would stay at the nanometer size.



(a) 2% NI.44P modified asphalt binder



(b) 4% NI.44P modified asphalt binder

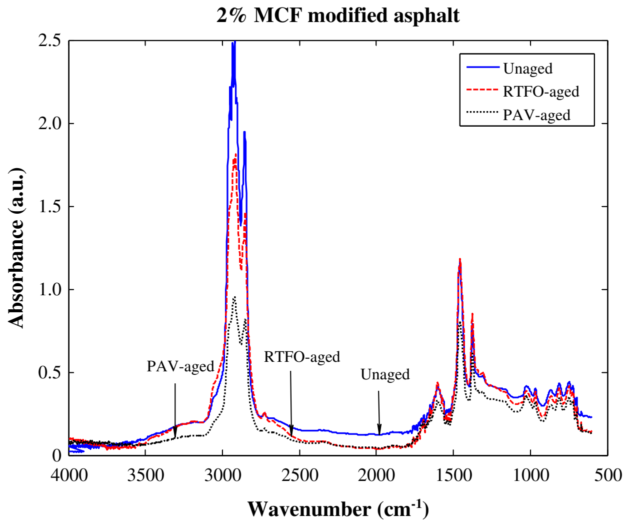
Fig. 11. FTIR spectra of NI.44P modified asphalt binder.

3.3. Carbon microfibers (MCF)

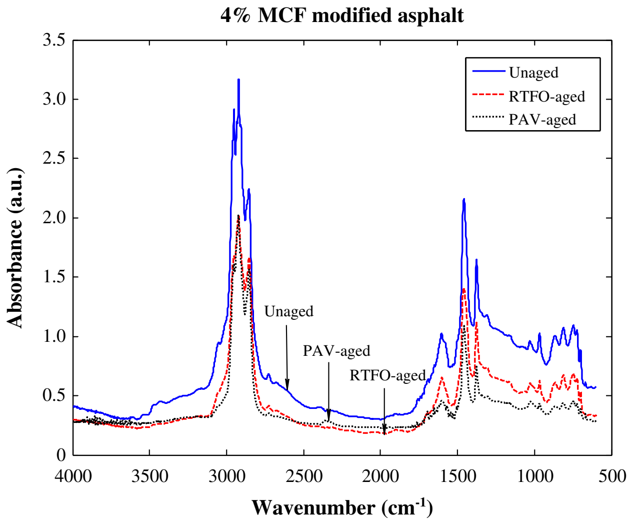
MCFs are always used as reinforcement materials. It usually can improve the crack resistance, enhance the electrical conductivity and lower the activation energy. Its tensile strength is 670 MPa; tensile elastic modulus is 30 GPa; elongation is 2.2%; specific gravity is 1.63; thermal conductivity is 5–10 W/m/K; oxidation onset temperature is 310 °C. The carbon microfibers [42,43] were KRECA chop C-103T, 3 mm in length with a filament diameter of 18 μm and obtained from Japan. The FTIR spectra of MCF are shown in Fig. 3. In this study, silicon substrate with 350 μm thickness was used. The substrate may affect the FTIR data of MCF, and it has some noises. Several peaks appeared around 1000 cm^{-1}, and it was supposed to have peaks around 1600 cm^{-1}. From the SEM image of MCF (Fig. 3), the tube shape and cross section of MCF are observed and the size of the material is still in the micro-scale. This structure may be helpful for improving the rutting resistance performance of asphalt binders.

3.4. Non-modified nanoclays (NMN) and polymer modified nanoclays (PMN)

Non-modified nanoclay raw material is montmorillonite, and has a platelet structure. The individual platelet thickness is only one nanometer, but it has the high aspect ratio. The non-modified nanoclay is hydrophilic, and the polymer modified nanoclay is hydrophobic. PMN is modified by polysiloxane, and it can be readily dispersed in polymers. PMN has better barrier properties, tear and compression strength compared with NMN [33,44,45]. Figs. 4 and 5 display the FTIR spectra of NMN and PMN. FTIR spectra of NMN show that it mainly contains the Si—O (Si) asymmetric stretching bands (1085 cm^{-1}); asymmetric vibration of Si—O (H) is near 975 cm^{-1}; O—H stretching bonds (3594 cm^{-1} and 3735 cm^{-1}); However, from

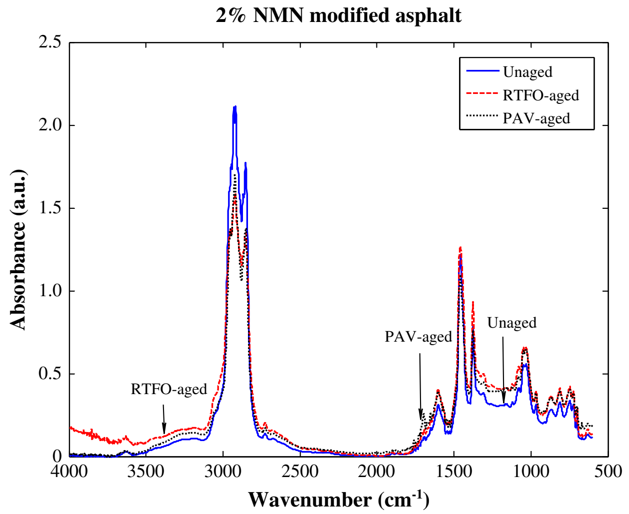


(a) 2% MCF modified asphalt binder

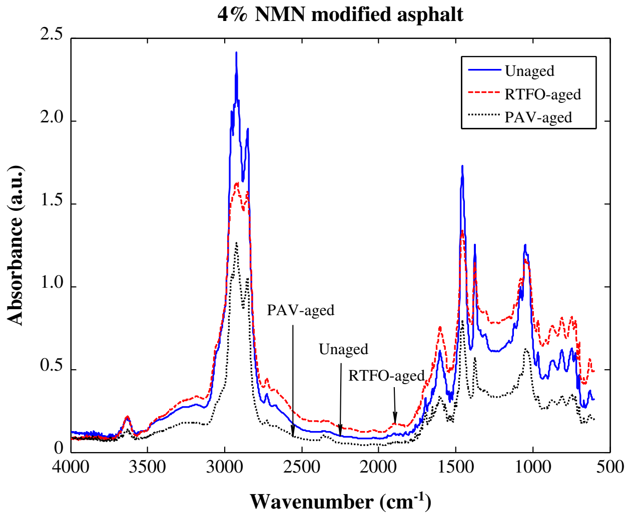


(b) 4% MCF modified asphalt binder

Fig. 12. FTIR spectra of MCF modified asphalt binder.



(a) 2% NMN modified asphalt binder



(b) 4% NMN modified asphalt binder

Fig. 13. FTIR spectra of NMN modified asphalt binder.

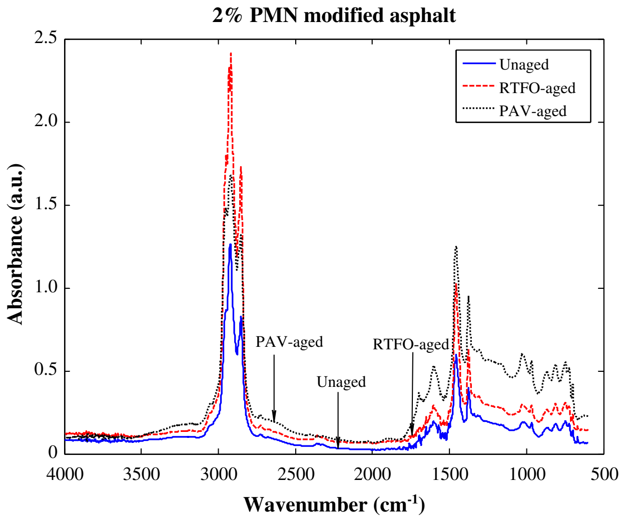
Fig. 5, The bands located across 953–1180 cm^{-1} is considered as the stretching C—C and C—O, and the bending C—H bonds, and the peak area of PMN is more than NMN. From the micro-images of NMN and PMN (Figs. 4 and 5), it is apparent that the agglomeration of materials occurred, and most of the nanomaterials would stay at the nanometer size. After the agglomeration of nanomaterials, the piece-shaped NMN and circle-shaped PMN particles are observed by SEM. Note while the SEM micrographs show particles of micron size; these nanoclay platelets (average spacing between platelets) still feature one of its dimensions at nanometer level.

4. Samples preparation and experiments arrangement

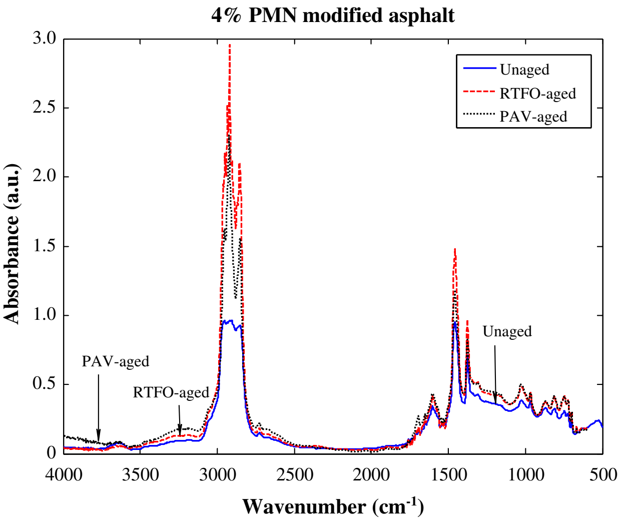
These modifiers were added into the control PG 58-34 asphalt binder at 2% and 4% concentrations by the weight of control asphalt binder. The modified asphalt binders were prepared in the high shear mixing machine under the conditions of around 130 °C temperature and 4000 rpm (rpm). During the mixing process, some bubbles floated from the surface of asphalt binders, indicating likely chemical reactions between the modifiers and the asphalt binder. After mixing for around 2 h, the modified asphalt binders were ready for testing. In this study, FTIR spectra and complex shear modulus were recorded by Jasco IRT 3000 FTIR spectrometer and a dynamic shear rheometer (DSR), respectively. In the FTIR test, silicon substrate (100 Ω cm) with 350 μm thickness was used. According to the Superpave™ specification, the DSR was conducted to evaluate the permanent deformation and fatigue cracking properties of modified asphalt binders, and FTIR tests were carried out for microstructure performance of modified asphalt binders.

The DSR is generally used to characterize the elastic and viscous behavior of asphalt binders. The thin binder samples sandwiched between the upper and lower plates were tested with the DSR, where the 25 mm plate is for unaged and RTFO samples and 8 mm plate is for PAV samples. The upper plate oscillates back and forth at a certain frequency to create a shearing force. The data was recorded by software according to the different frequencies and temperatures.

As is well known, the complex mixtures of organic molecules are in those binders, and asphalt binder aging process partially is the process of oxidation reactions in asphalt binders [40,47,48]. Simultaneously, the aging process not only produces the structural modification in chemical compositions, but also the changes in the component distribution. After the oxidation, the bonding between chemical elements is changed and the interactions between molecules also are altered. Interactions include: π–π interactions be-



(a) 2% PMN modified asphalt binder



(b) 4% PMN modified asphalt binder

Fig. 14. FTIR spectra of PMN modified asphalt binder.

tween aromatic rings, Van der Waals interactions between aliphatic chains, and polar interactions (hydrogen bonding, carbon bonding, ionic, etc.) involving heteroatom. These interactions generate the bonding force and inter-molecular associations [13,49]. Microstructure and bonding of the asphalt binders have the relationship with the performance of asphalt binders. Therefore, the microstructure analysis of asphalt binders was carried out by FTIR instrument.

5. Viscosity results and discussion

Fig. 6 shows that the viscosity values of control and modified asphalt binders. The viscosity values of MCF, NI.44P and NMN modified asphalt binders are higher than the control asphalt binder. The more NI.44P and NMN are added into the control asphalt binder, the higher viscosity values are displayed from the trend. However, the PMN modified asphalt binder has lower viscosity values than control asphalt, and viscosity of 4% PMN modified asphalt binder is lower than 2% PMN modified asphalt binder. All viscosity data of control and modified asphalt binders are lower than 3 Pa s, and pass the specification standard of Superpave™. The polymer modification of PMN probably results in lower viscosity of PMN modified asphalt binder, but MCF, NMN and NI.44P modified asphalt binders seem to have more potential to resist the deformation.

6. Complex shear modulus and FE-SEM results and discussions

The DSR test was conducted at the conditions of 58 °C temperature and 10 rad/s (1.59 Hz) frequency, and the DSR test condition of asphalt samples after PAV aging process is 25 °C and 10 rad/s. The results of unaged, RTFO-aged and PAV-aged asphalt binders are shown from Figs. 7 to 9.

Fig. 7 shows the complex shear modulus of modified asphalt binders at unaged condition. In Fig. 7, the complex shear modulus of control asphalt binder is higher than that of PMN modified asphalt binders, and the modulus of control asphalt binder is lower than those of NI.44P, MCF and NMN modified asphalt binders. The complex shear modulus of modified asphalt binders after RTFO aging is described in Fig. 8. Form Fig. 8, the complex shear modulus trends of control asphalt and modified asphalt binders are similar with the trend of unaged asphalt binders. However, it can be shown from Fig. 9 that the complex shear modulus of modified asphalt binders is higher than that of control asphalt binder after PAV aging.

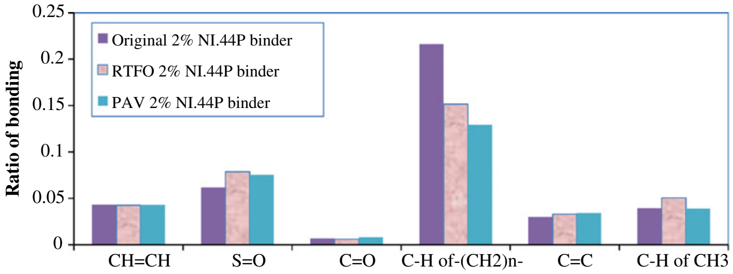
From the rutting factor ($G^*/\sin\delta$) results in Figs. 7 and 8, NI.44P, MCF and NMN modified asphalt binders have higher values of rutting factor. According to the specification, these modified binders reduce the rutting susceptibility, and also have the improvement on permanent deformation resistance at high temperature compared to the control binder. However, PMN modified binder has lower values of rutting factor. The original and RTFO binders have the similar trend of rutting factor.

From Fig. 9, the failure temperatures of NI.44P, MCF and NMN modified asphalt binders are higher than control asphalt binder, and PMN modified binder has lower failure temperature than control binder. Aging factor results in Fig. 10 show that the aging factor of control asphalt binder is higher than those of NI.44P, MCF and NMN modified asphalt binders, and lower than PMN modified asphalt binder. The results are consistent with the data of Figs. 7 and 8. From the complex shear modulus and rutting factor results of control and modified asphalt binders, the addition of micro- and nano-powders (NI.44P, MCF and NMN) in the asphalt makes the control asphalt binder stiffer than before. High complex shear modulus and rutting factor of these modified asphalt binders reveal that the asphalt binder can reflect more energy when loading is applied, and also indicate that the modified asphalt binders have more resistant ability to rutting and fatigue cracking under high and intermediate temperatures. But the recovery ability of these modified asphalt binders at low temperatures may be reduced. Meanwhile, with the addition of PMN into the control asphalt binder, the complex shear modulus and rutting factor of PMN modified asphalt binder decrease. The recovery ability of modified asphalt binder at low temperatures may be improved when loading is applied.

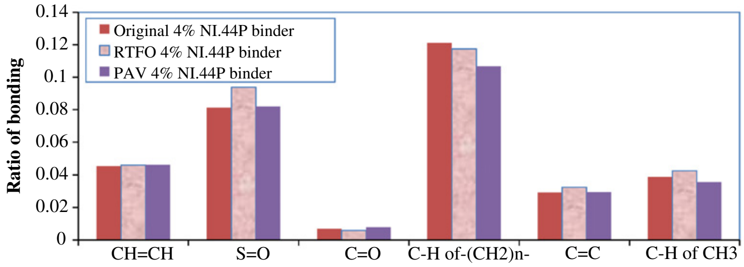
7. FTIR results and discussions

FTIR is a technique, which can get the infrared absorbance spectrum of the solid, liquid or gas. In this approach, the bonding in the test material will be known according to the assignations of FTIR spectra main bands. The main bands wavenumber are shown in Table 1 and the FTIR spectra of modified asphalt binders are shown from Figs. 11–14.

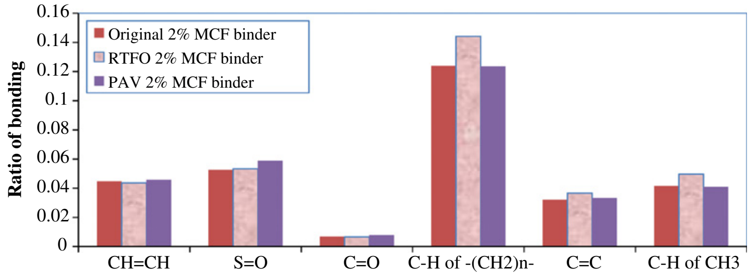
Figs. 11–14 show the infrared spectra (IR) analysis images of modified asphalt binders (NI.44P, MCF, NMN and PMN modified



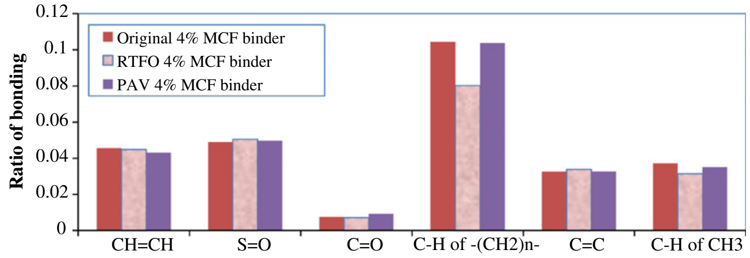
(a) Ratio of bonding in the 2% NI.44P modified asphalt binder



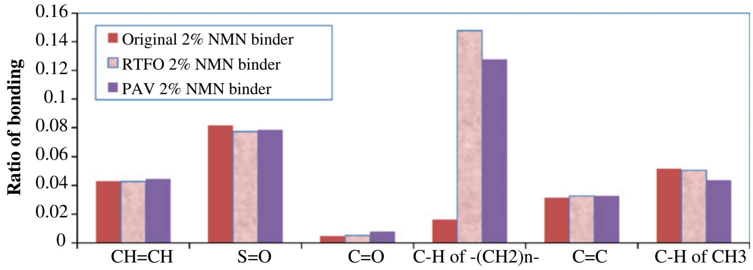
(b) Ratio of bonding in the 4% NI.44P modified asphalt binder



(c) Ratio of bonding in the 2% MCF modified asphalt binder



(d) Ratio of bonding in the 4% MCF modified asphalt binder

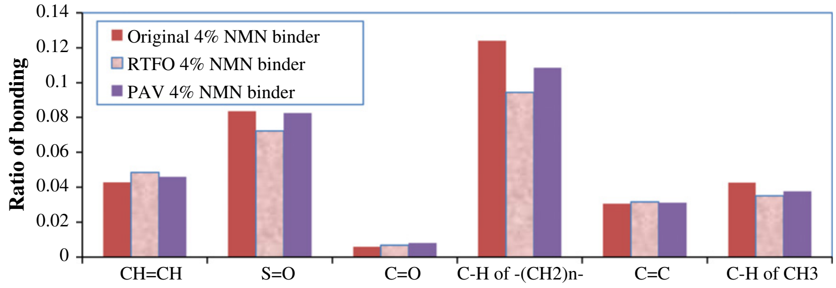


(e) Ratio of bonding in the 2% NMN modified asphalt binder

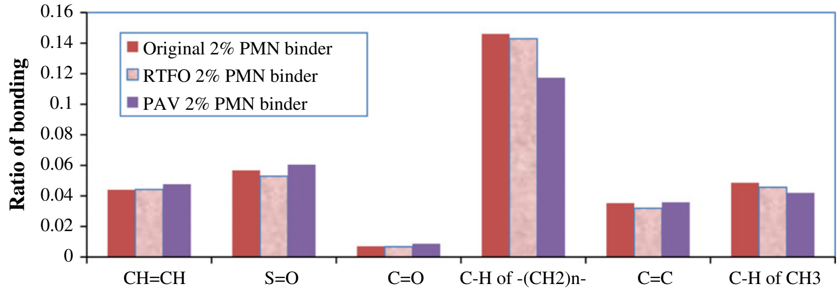
Fig. 15. Ratio of bonding in the control and modified asphalt binders.

asphalt binders). It can be seen that the chemical bonding was changed in the asphalt binder before and after RTFO and PAV aging. According to the bands of bonding in Table 1, the ratio changes of chemical bonding will be calculated for the sake of avoiding the samples thickness effect [50]. Based on Eqs. (1)–(6), the ratio changes in the modified asphalt binders before and after RTFO and PAV aging are shown in Fig. 15.

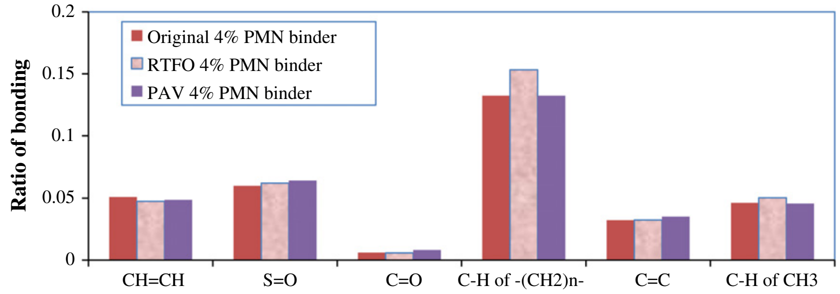
$$I_{CH=CH} = \frac{\text{Area of the ethylene band centered around } 966\,\text{cm}^{-1}}{\sum \text{Area of the spectral bands between } 2000\,\text{cm}^{-1} \text{ and } 600\,\text{cm}^{-1}} \quad (1)$$



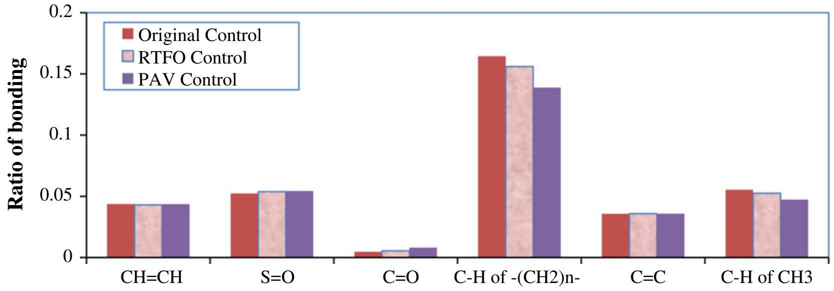
(f) Ratio of bonding in the 4% NMN modified asphalt binder



(g) Ratio of bonding in the 2% PMN modified asphalt binder



(h) Ratio of bonding in the 4% PMN modified asphalt binder



(i) Ratio of bonding in the control asphalt binder

Fig. 15. (*continued*)

$$I_{S=O} = \frac{\text{Area of the sulfoxide band centered around } 1030\ \text{cm}^{-1}}{\sum \text{Area of the spectral bands between } 2000\ \text{cm}^{-1} \text{ and } 600\ \text{cm}^{-1}} \tag{2}$$

$$I_{C-H\ \text{of}\ CH_3} = \frac{\text{Area of the aliphatic branched band centered around } 1376\ \text{cm}^{-1}}{\sum \text{Area of the spectral bands between } 2000\ \text{cm}^{-1} \text{ and } 600\ \text{cm}^{-1}} \tag{3}$$

$$I_{C-H\ \text{of}-(CH_2)_n-} = \frac{\text{Area of the aliphatic index band centered around } 1460\ \text{cm}^{-1}}{\sum \text{Area of the spectral bands between } 2000\ \text{cm}^{-1} \text{ and } 600\ \text{cm}^{-1}} \tag{4}$$

$$I_{C=C} = \frac{\text{Area of the aromatic band centered around } 1600\ \text{cm}^{-1}}{\sum \text{Area of the spectral bands between } 2000\ \text{cm}^{-1} \text{ and } 600\ \text{cm}^{-1}} \tag{5}$$

$$I_{C=O} = \frac{\text{Area of the carbonyl band centered around } 1690\ \text{cm}^{-1}}{\sum \text{Area of the spectral bands between } 2000\ \text{cm}^{-1} \text{ and } 600\ \text{cm}^{-1}} \tag{6}$$

Fig. 15 shows that the ratio changes of chemical bonding in the control and modified asphalt binders before and after RTFO and PAV aging process. Based on the literature review [13,40,41,49–

52], the carbonyl index indicates the degree of oxidation in the asphalt binder. From Fig. 15, the carbonyl index (C=O) in the modified asphalt binders decreases slightly after RTFO aging process, and increases significantly after PAV aging process compared with the ratios of unaged asphalt binders. Potentially, the addition of nano-powders into the asphalt binder can delay and weaken the oxidation reaction. Meanwhile, the sulfoxide index (S=O) in the control and modified asphalt binders after RTFO and PAV aging shows a different trend with the carbonyl index. From previous research results [50], the sulfoxide index (S=O) ratio may decrease in the asphalt binder after RTFO and PAV aging process. The results in this study coincide with it. For this reason, the sulfoxide index is not considered as an aging index in the asphalt binder.

It is well known that the aging process of asphalt binder actually is an oxidation reaction process between oxygen and asphalt [41,50–52]. Asphalt is composed of hydrocarbons and many small amounts of metals. In the atmospheric condition, the oxygen attacks the weak bonding of molecules in the asphalt, and transforms into carbon dioxide and water from complete oxidation reactions. Also, the nitrogen and sulfur elements may become nitrogen oxides and sulfur dioxide that escape from asphalt binder [3–5,53]. During the aging process of asphalt binder, the natural resins and asphaltenes (asphaltenes are soluble in aromatics) react with oxygen and generate the aromatic or aromatic hydrocarbons. Then, after aging reactions, the ratios of aromatic index will be increased. That reflects the aromatic ratio changing results from Fig. 15. However, with the addition of carbon microfiber in the asphalt, the aromatic increases significantly in the modified asphalt binder after RTFO aging. Probably, the carbon microfiber increases the aromatic (C=C) ratio in the modified asphalt binder, and the aromatic ratio in the modified asphalt binder after PAV aging decreases for the anti-oxidation property and consuming of carbon microfiber.

Aromatic is a hydrocarbon with planar structure and characterized by double or single bonds betweens carbon rings, and they can be stacked over each other. However, aliphatic is non-planar structure with single carbon bonds, and do not stack over. These different chemical structures lead to different properties of aromatic and aliphatic [4,54–56]. During the aging reactions in the asphalt binder, aromatic index ratio increases and aliphatic index ratio decreases in the modified asphalt binder relative to the control asphalt binder. That case coincides with the results shown in Fig. 15. As the presence of sunlight and heat in the air, the maltene factions solubilized in the aliphatic hydrocarbons will react with the oxygen to form the asphaltenes, and the asphaltenes in the asphalt will be hydrogenated into the aromatic.

The control asphalt was modified by acrylonitrile butadiene styrene (ABS), so the butadiene index was observed from FTIR tests. From the research results of Cortizo et al. [13,49], during the aging process in the asphalt binder, the terminal vinyl (bands 910 cm^{-1} and 995 cm^{-1}) is reacted preferentially to the trans-double bonding (bending C—H of trans-disubstituted —CH=CH—, band 996 cm^{-1}). In addition, due to the addition and reactions of ultrafine materials, these two reasons may lead to the increase of bending C—H of trans-disubstituted —CH=CH—. However, as the aging reaction is occurring, the ratio of band 996 cm^{-1} will start to decrease. The trends of bending C—H of trans-disubstituted —CH=CH— in the control and modified asphalt binders are shown in Fig. 15.

In general, the line trend of FTIR in the control asphalt is different from the trends of modified asphalt binders. It represents that there may have been reactions between nano-powders and control asphalt binder. The new and dense microstructures were formed in the modified asphalt binder. From the DSR and FTIR test data, the addition of materials (NI.44P, MCF and NMN) into the control asphalt can improve the resistance to permanent deformation and PMN modified asphalt binder can enhance the prevention of fatigue cracking. Simultaneously, the addition of nano- or micro-materials in the asphalt could have the positive effect on anti-oxidation.

8. Conclusions

In this study, the ultrafine materials (NI.44P, MCF, NMN and PMN) were added into the control asphalt to improve the properties of the asphalt binder. Based on the DSR and FTIR tests, the main findings are provided as follows.

From the mixing and preparation of nano- and micro-modified asphalt binders, it is deduced that the nano- or micro-materials may have chemical reactions and physical dispersion with the control asphalt. From the DSR results, the addition of NI.44P, MCF and NMN materials can increase the complex shear modulus of these modified asphalt binders relative to the control asphalt binder, and improve the resistance to rutting, however, the complex shear modulus of PMN modified asphalt binder decreases and the recovery ability of PMN modified asphalt binder may be enhanced. FTIR spectroscopy shows the addition of nano- or micro-materials in the asphalt binder, the oxidation reaction may be weakened in the modified asphalt binder when it is exposed to sunlight and heat.

In summary, the effect of modified asphalt binder on anti-oxidation is improved when the selected nano- or micro-materials were added in the control asphalt. For future work, the asphalt mixture tests and model simulation are planned for evaluating the macro-scale properties of modified asphalt mixtures.

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