



Article Rheological Characteristics Evaluation of Bitumen Composites Containing Rock Asphalt and Diatomite

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Abstract: Previous studies have showed that rock asphalt (RA) or diatomite were used to modify the petroleum bitumen. This paper presents the findings from a study conducted to evaluate the potential impact of RA and diatomite on the rheological characteristics of bitumen composites. RA and diatomite with three different dosages were added into the petroleum bitumen: 18% RA, 13% RA+7% diatomite, and 16% RA+9% diatomite by weight. The rheological characteristics of the RA and diatomite modified bitumens were evaluated in this study. The tests conducted included temperature sweep and frequency sweep tests with a dynamic shear rheometer (DSR), a Brookfield rotation viscosity test, and a scanning electron microscope test. The research showed that the addition of RA and diatomite to petroleum bitumen considerably increased the apparent viscosity, dynamic shear modulus, and rutting resistance in bitumen specimens. However, the DSR test indicated a slight reduction in the fatigue performance of composites made of RA and diatomite modified bitumens. Overall, RA and diatomite are good modifiers for petroleum bitumen for a performance improvement.

Keywords: rock asphalt; diatomite; rheological characteristics; high temperature performance; fatigue performance; low temperature performance

1. Introduction

The types of asphalt pavement damage mainly include ruts, pits, cracks, potholes, and surface shedding [1]. After several years of service, some asphalt pavements are faced with early damage. The use of high-quality bitumen materials can solve or alleviate the early problems of highway pavement [2–4]. Therefore, modified asphalt has been widely used in asphalt pavements in the past ten years. SBS-modified (Styrene-Butadiene-Styrene Block Copolymer) asphalt is the most widely used, but the production equipment of SBS-modified asphalt is very expensive and the production and transportation costs are high [5]. As a result, it is urgent to find some modified asphalt with excellent road performance, simple construction, and low costs. Rock asphalt and diatomite are good choices among many asphalt modifiers [6,7].

Rock asphalt is a natural bitumen. Its color is dark brown in micronized powder. Rock asphalt is mined in underground shafts. Rock asphalt was added into mixtures as a modifier additive [8]. Rock asphalt is made up of very high molecular weight, oligomeric, polar polynuclear hydrocarbons [9,10]. Rock asphalt

has stable and durable properties. It can change the ratio of asphaltic oil and asphaltenes [11,12]; can increase the high-temperature hardness of petroleum bitumen; and can help delay the occurrence of early defects such as potholes, ruts, and cracks on asphalt pavements [13,14].

Therefore, the fatigue performance of rock asphalt-modified bitumens was studied [15–17]. The results showed that the reduced dissipated energy ratio was a good evaluation index and that the fatigue performance of rock asphalt-modified bitumen depended on the loading mode of the test. Further, researchers studied the influence of Buton rock asphalt on the high-temperature rheological properties of asphalt and mineral filler mortar and concluded that the Buton rock asphalt could significantly improve the high temperature rheological properties of the mortar. The Buton rock asphalt mortar at an additional 20% concentration had the same anti-rutting performance as SBS-modified bitumen mortar [18–21]. Gilsonite could improve the Marshall stability and elastic modulus parameters of the mixture, but its flexibility was significantly reduced by using two gradations of Gilsonite-modified bitumen. The Marshall stability, dynamic creep, and elastic modulus parameters of the mixture could improve the Marshall stability and elastic modulus parameters of the rutting resistance, but the flexibility of the mixture was significantly reduced [22,23].

Moreover, a laboratory evaluation on the performance of compound-modified asphalt for rock asphalt/SBR, rock asphalt/Nano-CaCO₃, rock asphalt/Nano-silica, and Nano-silica/rock asphalt/SBS have also been studied by researchers. The anti-rutting performance of 10% BRA/Nano-CaCO₃ compound-modified asphalt was the best. The thermal cracking performance of 5% BRA/SBR-modified asphalt has been effectively improved, and that of nano-CaCO₃ was not obvious. Compound-modified asphalt mixtures have higher temperature stability, low-temperature cracking resistance, moisture susceptibility, and durability than 5% SBS modified asphalt [24–26].

Diatomite is a biogenic siliceous sedimentary rock and a type of nonmetallic mineral, which is mainly composed of diatom remains and soft mud, and its main chemical composition is silica (SiO₂). Diatomite has the characteristics of a high porosity, a low density, a large specific surface area, a strong adsorption capacity, stable chemical properties, and a high melting point [27,28]. Li et al. carried out a dynamic temperature scanning test of diatomite modified bitumen mortar. They compared the performance of modified bitumen mortar by adding spherical and rod-shaped diatomite [29]. The results showed that the high temperature performance of the rod-shaped diatomite bitumen mortar was better than that of the spherical diatomite. Although, diatomite can reduce the fatigue performance of modified bitumen mortar, it can significantly improve the high-temperature performance and moisture stability of the bitumen mixture. The properties of a diatomite and basalt fiber composite-modified bitumen mortar were studied [30]; the results showed that the high-temperature and low-temperature performance of the bitumen were improved. Davar et al. studied the 20 °C four-point bending fatigue life test and 5 °C indirect tensile test of a composite modified bitumen with diatomite and basalt fiber [31] and concluded that the fatigue life of the diatomite and basalt fiber modified bitumen increased and that the simultaneous use of diatomite and basalt fiber could make up for the weakness of the bitumen mixture at low temperatures.

Diatomite can play an active and effective role in bitumens and bitumen mixtures. The addition of diatomite to asphalt can increase the softening point and viscosity of bitumen and can decrease the needle penetration. Diatomite-modified bitumen has good thermal stability and adhesion. The high-temperature performance and moisture damage resistance of a diatomite-modified bitumen mixture were improved significantly but not the low-temperature performance [32,33]. Li et al. evaluated the pavement performance of a rock asphalt and diatomite-modified bitumen mixture and reported that the dynamic stability of bitumen mixture was improved the most; moisture stability is superior when the mixed diatomite content is 20% [34].

The research of bitumen mixture-modified by rock asphalt or single diatomite shows that the two types of materials are effective for improving the pavement performance of bitumen concrete, but there are still many shortcomings in improving bitumen concrete by a single material. Combining

the two types of materials can overcome their shortcomings and makes full use of the adsorption function of diatomite and the high-temperature performance of rock asphalt. Previous studies focus on the middle- and high-temperature rheological properties of bitumen, but a few of them focus on the low-temperature rheological characteristics, particularly the low-temperature fatigue properties of bitumen. Therefore, the high- and low-temperature rheological characteristics of North American rock asphalt composite diatomite-modified bitumen are investigated in this study.

2. Materials and Preparation

2.1. Materials

The petroleum bitumen used in the study was produced in Foshan, Guangdong Province, China. The petroleum bitumen was in accordance of the penetration grading of bitumen. Some physical properties of the petroleum bitumen are shown in Table 1. The RA used in this study was sourced from Utah, USA. Some physical properties of the rock asphalt are shown in Table 2. It can be speculated from Table 2 that the asphalt content of rock asphalt was about 90% and that the main component of the rest was ash. The diatomite used in this study was sourced from Xundian, Yunnan Province, China. Some physical properties of the diatomite are shown in Table 3. Diatomite's main chemical composition is SiO₂. The mineral filler used in this study was sourced from Foshan, Guangdong Province, China. Some physical properties of the mineral filler are shown in Table 4. The physical properties of petroleum bitumen, rock asphalt, diatomite, and mineral filler were normal.

Table 1. The physical properties of petroleum bitumen; RTFOT: Rolling Thin Film Oven Test.

	Virgin Bitumen				RTFOT Residue			
Properties	Penetration Grade at 25 °C (0.1 mm)	Softening Point (°C)	Ductility at 10 °C (cm)	Viscosity at 60 °C (Pa•s)	Mass Change (%)	Residual Penetration Ratio at 25 °C (%)	Residual Ductility at 10 °C (cm)	Softening Point (°C)
Requirement	60-80	≥ 46	≥ 15	≥ 180	± 0.8	≥ 61	≥ 6	_
Results	71	47	33	210	-0.2	72	9	53

Table 2. The physical properties of rock asphalt.

Properties	Solubility in C ₂ HCl ₃ (%)	Specific Gravity at 25 °C (kg/m ³)	Flash Point (°C)	Moisture (%)	ASH (%)	1.18 mm Percentage Passing Sieves (%)
Results	91	1153	298	0.6	7.0	100

Table 3. The physical properties of diatomite.

Properties	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	TiO ₂	K ₂ O	Loss on Ignition (%)
Requirement	\geq 75	—	—	—	—	—	—	—
Results	85.2	3.6	2.3	0.6	1.6	0.2	0.4	5.2

Table 4. The physical properties of mineral filler.

Properties	Specific Gravity at	Hydrophilic	Size Range (%)			
Topetties	²⁵ °C (g/cm ³)	Coefficient	<0.6 mm	<0.15 mm	<0.075 mm	
Requirement	≥2.50	<1	100	90–100	75–100	
Results	2.723	0.57	100	95.3	80.9	

2.2. Sample Preparation

Four different dosages of modifiers were added into the petroleum bitumen: 10% mineral filler, 18% RA, 13% RA+7% diatomite, and 16% RA+9% diatomite by weight. The control bitumen binder

without modifier was also investigated for a comparison. The modified bitumens were prepared by blending a certain amount of mineral filler, RA, and RA and diatomite into the petroleum bitumen. In detail, the petroleum bitumen was preheated to 150 °C. The mineral, RA, and RA and diatomite were added into the petroleum bitumen at room temperature. The mixture was heated and maintained at a temperature of 175 °C for one hour. Afterward, the mixture was blended with a high shear mixer for 30 min at 3000 rpm.

3. Experimental Methods

3.1. SEM Tests

The SEM tests applied explored the surface morphology and microstructure of bitumen binders. The SEM tests were conducted with a Zeiss field emission scanning electron microscope (SEM) produced by Carl Zeiss AG, Oberkochen, Germany. The RA and diatomite had particle sizes of 500 mesh. In this study, the SEM tests were conducted at 5000× magnification.

3.2. Rotation Viscosity Test

The apparent viscosities of the petroleum bitumen and composite modified asphalt were measured by a DV-II rotary viscometer made by the Brookfield Company, Middleboro, MA, America. The temperatures for rotational viscosity measurements were 135 °C and 175 °C. Three different dosages of modifiers were added into the petroleum bitumen: 18% RA, 13% RA+7% diatomite, and 16% RA+9% diatomite by weight.

3.3. Dynamic Shear Rheometer (DSR) Test

The temperature and frequency sweep tests were conducted to evaluate the linear rheological characteristics of composite-modified asphalt with different RA and diatomite. The commonly obtained rheological indices from the DSR test were the dynamic shear modulus (G*), phase angle (δ), and loss tangent (tan δ). These indices were used to evaluate the viscosity and elasticity of the composite modified asphalt. The rutting factor (G*/sin δ) was used to evaluate the anti-rutting ability of composite-modified asphalt as a high-temperature performance index, and the fatigue factor (G*.sin δ) was used to evaluate the anti-fatigue performance. The asphalt samples were 25 mm in diameter and 1 mm in thinkness.

3.3.1. Temperature Sweep Tests

In this study, the temperature sweep tests were conducted at nine different temperatures: 30, 35, 40, 45, 50, 55, 60, 65, and 70 °C. The strain was controlled at 5%, and the angular velocity was 10 rad/s. Five different dosages of modifiers were added into the petroleum bitumen to evaluate the viscoelastic property of bitumen binders: 0%, 10% mineral filler, 18% RA, 13% RA+7% diatomite, and 16% RA+9% diatomite by weight. Among them, the mineral content in 16% RA+9% diatomite was equivalent to that in 10% mineral filler.

3.3.2. Frequency Sweep Tests

Under traffic loads, the asphalt pavement structure showed a dynamic loading effect, and the bitumen material exhibited different viscoelastic properties under different load frequencies. The frequency sweep test can simulate the speed of a vehicle running on the road. The loading frequency of 10 Hz simulates the speed of 60 km/h, and the loading frequency of 15 Hz simulates the speed of 90 km/h. The frequency sweep tests were conducted while changing the load frequency from 1 Hz to 25 Hz. The test temperature was 60 °C. In this study, three different dosages of modifiers were added into the petroleum bitumen to evaluate the viscoelastic property of the bitumen binders: 0%, 13% RA+7% diatomite, and 16% RA+9% diatomite by weight.

3.4. Bending Beam Rheometer (BBR) Test

The BBR test was used to evaluate the low-temperature performance of bitumen binders. The creep stiffness and m-value could be obtained from the BBR test at 60 s under three different temperatures (-6, -12, and -18 °C). The Superpave binder specification sets a maximum value of 300 MPa for the creep stiffness and a minimum value of 0.3 for m-value [11]. The m-value indicated a bitumen stiffness sensitivity with time and stress relaxation ability. The BBR tests were carried out at -6, -12, and -18 °C. Three different dosages of modifiers were added into the petroleum bitumen to obtain the creep stiffness and m-value of the bitumen binders: 0%, 13% RA+7% diatomite, and 16% RA+9% diatomite by weight. All samples were subjected to RTFOT (Rolling Thin Film Oven Test) aging and PAV (Pressure Ageing Vessel) aging.

4. Results and Discussion

4.1. SEM Tests

Figure 1 shows the SEM test result of RA. It can be seen from Figure 1 that the surface of the large particles is smooth, clear, and dispersed in all directions and that the fine particles are adhered to the larger particles. Previous studies have reported that RA contained highly polar functional groups with high free energy and strong absorbability [15]. Under high temperature conditions, the RA particles reach a molten state and rapidly fuse with the petroleum bitumen, improving the anti-stripping capability of the aggregate and improving the water stability of the asphalt mixture.

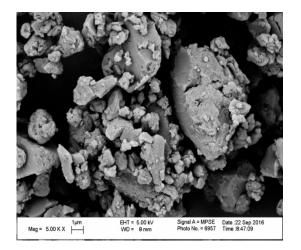


Figure 1. A SEM image of rock asphalt (RA).

As shown in Figure 2, the diatomite has a unique porous structure, a high porosity, a large specific surface area, and an active surface on both the inner and outer surfaces, presenting great adhesion ability and adhesion strength. Since the diatomite is mixed with the petroleum bitumen, the petroleum bitumen is absorbed on the surface of diatomite particles, and the light oil in the petroleum bitumen is also drawn into the pores of the micro-cavity to form a mechanical locking force. The surface of the diatomite shows a strong polar asphaltene layer, which greatly improves the cohesive force with the aggregate and improves the water stability of the asphalt mixture.

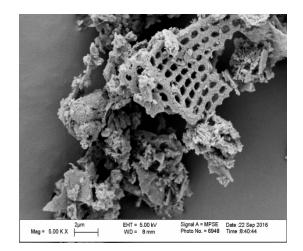


Figure 2. A SEM image of diatomite.

4.2. Rotational Viscosity Test

Table 5 displays the rotational viscosity test for the control (0% RA+0% diatomite) and the modified bitumen of RA and diatomite. With an increase of RA and diatomite dosage, the apparent viscosity increases significantly at the two tested temperatures. Obviously, the RA and diatomite are also beneficial for the high-temperature performance of the bitumen. The apparent viscosity with the same dosage of RA and diatomite increases more at the lower tested temperatures. When the test temperature was 135 °C, the apparent viscosity of 16% RA+9% diatomite composite-modified asphalt reached 3.78 Pa·S, which exceeded the specification that the apparent viscosity of modified asphalt should not be greater than 3 Pa·S. Therefore, the dosage of diatomite should not exceed 9% when RA is 16% added into the petroleum bitumen by weight. Similarly, the dosage of RA should not exceed 16% when diatomite is 9%.

Component	Apparent Viscosity (Pa·S)			
Component	135 °C	175 °C		
control	0.41	0.08		
18% RA+0% diatomite	2.55	0.18		
13% RA+7% diatomite	1.84	0.25		
16% RA+9% diatomite	3.78	0.41		

Table 5. The rotation viscosity test.

4.3. Dynamic Shear Rheometer (DSR) Test

4.3.1. Temperature Sweep Tests

The temperature sweep test results are summarized in Figure 3. As expected and seen in Figure 3a, all of the modified bitumens showed higher values of dynamic shear modulus G* as compared to the control bitumen, showing the trend of elastic enhancement as well as the significant improvement in its high-temperature performance. By comparison, the dynamic shear modulus G* was 16% RA+9% diatomite > 13% RA+7% diatomite > 18% RA > 10% mineral filler > petroleum bitumen. For example, at a temperature of 60 °C, the dynamic shear modulus of 10% mineral filler, 18% RA, 13% RA+7% diatomite, and 16% RA+9% diatomite modified bitumen increased 71.9%, 439.0%, 554.5%, and 2278.6% more than that of the control bitumen, respectively. The dynamic shear modulus G* of the 16% RA+9% diatomite composite-modified bitumen was the largest, and the curve was flatter, indicating that the higher the content of RA and diatomite, the better the sensitivity of modified bitumen. The dynamic shear modulus G* of 13% RA+7% diatomite modified bitumen was similar to that of 18% RA-modified bitumen, which meant that the 13% RA+7% diatomite-modified bitumen reached the dynamic shear

modulus of 18% RA modified bitumen, both of which have similar high-temperature performances. These results indicate that RA and diatomite could significantly increase the stiffness of the bitumen.

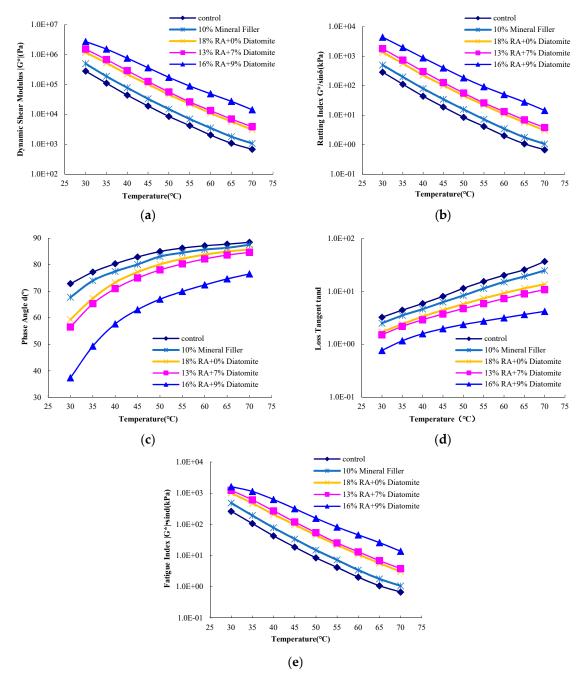


Figure 3. The temperature sweep results: (**a**) dynamic shear modulus; (**b**) rutting index; (**c**) phase angle; (**d**) loss tangent; and (**e**) fatigue index.

Figure 3b presents the rutting index $G^*/\sin\delta$ of petroleum bitumen and four modified bitumens. The trend of the rutting index $G^*/\sin\delta$ is overall similar to that of the dynamic modulus. In this study, the rutting index $G^*/\sin\delta$ of the 18% RA-modified bitumen and 13% RA+7% diatomite-modified bitumen were extremely close. The rutting index $G^*/\sin\delta$ of the 16% RA + 9% diatomite composite-modified bitumen was approximately four times that of the 18% RA-modified bitumen. The rutting index $G^*/\sin\delta$ of the 16% RA+9% diatomite-modified bitumen was approximately 10 times that of 10% mineral filler-modified bitumen. The rutting index $G^*/\sin\delta$ of the 16% RA+9% diatomite-modified bitumen was approximately 20 times that of the petroleum bitumen, which indicated that both RA and diatomite could significantly increase the rutting performance. Further, the rutting performance improved with a higher RA and diatomite dosage.

Phase angle δ is the lag of the strain with respect to the stress. The phase angle δ for a pure elastic material is 0°, while for a pure plastic material is 90° [11]. Bitumen is a typical viscoelastic material, so the phase angle δ should be between 0° and 90°. Under periodic loading, the peak strain falls behind the peak stress significantly, forming the phase angle δ . Figure 3c shows the phase angle test results of petroleum bitumen and four modified bitumens. According to Figure 3c, the phase angle of the bitumen vary from 37° to 89°, within the theoretical range (0–90°). Figure 3c shows that a higher temperature results in a longer strain hysteresis, a higher phase angle, and a higher viscosity of bitumen. The phase angle of the petroleum bitumen is significantly larger than that of the modified bitumen, which indicates that the modifier constrains the movement of the bitumen molecule, enhances the elastic part of the bitumen, and improves the stability and resistance to the deformation of the modified asphalt.

Figure 3d illustrates the loss tangent $\tan \delta$ of petroleum bitumen and four modified bitumens. The order of the magnitude of the loss tangent is the same as that of the phase angle, and the phase angle of different bitumens is getting increasingly closer with a higher temperature and tends to be the same. By contrast, the loss tangent of different bitumens is increasingly diverging with higher temperature, and the difference is becoming greater.

The fatigue index $|G^*| \cdot \sin \delta$ test results of the petroleum bitumen and four modified bitumens are showed in Figure 3e. It can be obviously seen that the trend of the fatigue index $|G^*| \cdot \sin \delta$ is overall similar to that of the dynamic shear modulus. The amount of work consumed by bitumen under constant strain per load cycle is proportional to the fatigue index $|G^*| \cdot \sin \delta$. The smaller the fatigue index $|G^*| \cdot \sin \delta$ value, the lesser the energy consumed. The more elastic the bitumen binder, the greater the capability to restore the deformation after multiple loadings and the lower the likelihood of fatigue cracking. At different temperatures, the fatigue factor $|G^*| \cdot \sin \delta$ of petroleum bitumen is lower than that of the modified bitumens, which indicates that the fatigue performance of the petroleum bitumen is better compared to that of the modified bitumens. The petroleum bitumen shows a better fatigue resistance because the modified bitumens contain minerals, which reduce the fatigue performance of the bitumen mortar.

The RA and diatomite-modified bitumen shows an excellent high-temperature stability and rutting performance. Further, a higher RA and diatomite dosage brings a better high-temperature performance, indicating RA and diatomite can enhance the high resistance against the permanent deformation of petroleum bitumen.

4.3.2. Frequency Sweep Tests

The frequency sweep test results are summarized in Figure 4. Figure 4a illustrates the dynamic shear modulus G* of petroleum bitumen and two modified bitumens at a frequency from 1 Hz to 25 Hz. At the same frequency, two modified bitumens show higher values of dynamic shear modulus G* as compared to the control bitumen, indicating that RA and diatomite can significantly increase the high-temperature performance of the bitumen. Further, a higher dosage of the composite modifier of RA and diatomite results in a higher value of dynamic shear modulus G*. As shown in Figure 4b, the rutting index G*/sin δ increases gradually with frequency. The rutting index G*/sin δ increases faster when the sweep frequency is lower than 5 Hz. Contrastively, the rutting index G*/sin δ increases slowly and gradually and tends to be stable when the sweep frequency is higher than 5 Hz. Moreover, a higher dosage of RA and diatomite results in a better anti-rutting performance of the modified bitumen. The results show that the dynamic shear modulus G* and rutting factor G*/sin δ of petroleum bitumen are improved by incorporating RA and diatomite, which significantly improves the deformation resistance. In addition, the anti-rutting performance is improved gradually with the higher dosage of RA and diatomite.

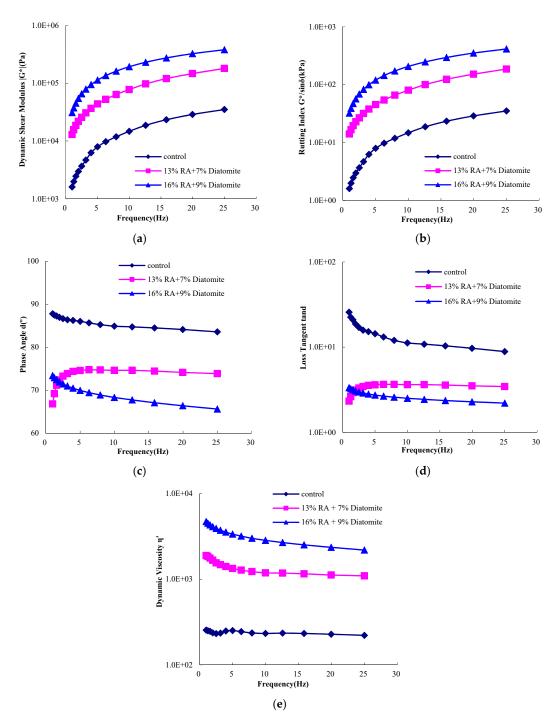


Figure 4. The frequency sweep results: (**a**) dynamic shear modulus; (**b**) rutting index; (**c**) phase angle; (**d**) loss tangent; and (**e**) fatigue index.

Figure 4c presents the phase angle δ of petroleum bitumen and two modified bitumens. It can be seen that the phase angle δ overall decreases with an increase in the RA and diatomite dosage. In detail, the phase angle δ for the control, 13% RA+7% diatomite-, and 16% RA+9% diatomite-modified bitumens are 84.9°, 74.6°, and 68.3°, respectively at 10 Hz. However, the phase angle δ of 13% RA+7% diatomite-modified asphalt shows different characteristics. The phase angle δ rises sharply when the frequency is less than 6 Hz, and it decreases gradually after 6 Hz. This indicates that the phase angle δ of RA and diatomite-modified asphalt shows a completely different behavior at low frequency and high frequency with a low dosage of RA and diatomite. Therefore, it is suggested that a higher dosage of compound RA and diatomite be used. By comparison, the phase angle δ of the petroleum bitumen

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is close to 90°, indicating that the petroleum bitumen is going to lose its elasticity and enter into viscous flow. The phase angle δ of two modified bitumens are no more than 75°, indicating that RA and diatomite constrain the free movement of bitumen molecules, ensuring the bitumen maintains a good overall structure, and performing a resistance to permanent deformation. As shown in Figure 4d, the change rule of the loss tangent tan δ is the same as that of the phase angle δ .

The fatigue index $|G^*| \cdot \sin \delta$ of each bitumen increases with an increase in frequency, as shown in Figure 4e. The fatigue index $|G^*| \cdot \sin \delta$ increases sharply when the frequency is less than 5 Hz. Correspondingly, the fatigue factor $|G^*| \cdot \sin \delta$ increases gradually when the frequency exceeds 5 Hz. In detail, the fatigue index $|G^*| \cdot \sin \delta$ of two modified bitumens is larger than that of control bitumen at the same frequency. According to this, the modified bitumen mortar with RA and diatomite contains a certain amount of minerals and reduces its fatigue performance.

4.4. BBR Test

Figure 5 presents the creep stiffness and m-value for all bitumen binders at 60 s under -6, -12, and -18 °C. Obviously, with a decrease in temperature from -6 to -18 °C, the creep stiffness increases and the m-value decreases for all bitumen binders. The creep stiffness of the RA+diatomite bitumens was obviously higher than that of the control bitumen, while the m-value of the RA+diatomite bitumens was slightly lower than that of the control bitumen. In detail, we failed to obtain the test results of the 16% RA+9% diatomite-modified bitumen at -18 °C, but the 13% RA+7% diatomite-modified bitumen had a high creep stiffness of 573 MPa, so we could predict a higher value of the 16% RA+9% diatomite-modified bitumen. A higher stiffness corresponds to a smaller creep compliance; a greater stress was required to produce a unit strain of bitumen binder. A higher m-value indicated a better stress relaxation ability and a better cracking resistance. Therefore, the addition of RA and diatomite can weaken the low temperature performance of petroleum bitumen.

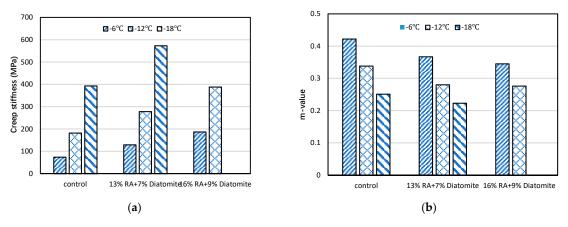


Figure 5. The BBR test results: (a) creep stiffness and (b) m-value.

5. Conclusions

In this study, a series of tests were conducted in order to evaluate the rheological characteristics of petroleum bitumen modified by rock asphalt (RA) and diatomite. Based on the results and discussion, some conclusion can be drawn as follows.

(1) The addition of RA and diatomite significantly improved the apparent viscosity of petroleum bitumen binders. When the test temperature was 175 $^{\circ}$ C, the apparent viscosity of 13% RA+7% diatomite composite-modified asphalt was 212.5% higher than that of petroleum bitumen.

(2) The master curves indicated that the addition of RA and diatomite significantly increased the dynamic shear modulus of petroleum bitumen binders. Further, a higher dosage of RA and diatomite resulted in a higher dynamic shear modulus. This increase was desirable for an improved

high-temperature performance of bitumen. The dynamic shear modulus of the 13% RA+7% diatomite composite-modified asphalt was 427.0% higher than that of petroleum bitumen at 60 °C and 10 Hz.

(3) The master curves indicated that the addition of RA and diatomite effectively enhanced the rutting performance and deformation resistance of petroleum bitumen binders. The rutting index $G^*/\sin\delta$ of the 16% RA+9% diatomite-modified asphalt was approximately 20 times that of the petroleum bitumen in the temperature sweep tests.

(4) At different temperatures, the fatigue factor $|G^*| \cdot \sin \delta$ of petroleum bitumen was 5 times lower than that of the modified bitumens, which indicated that the fatigue performance of bitumen binders decreased with the addition of RA and diatomite.

(5) At -12 °C, the m-value of the 13% RA+7% diatomite composite-modified asphalt was 20.7% lower than that of petroleum bitumen. The low-temperature performance of bitumen binders weakened with the addition of RA and diatomite.

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

References

- 1. Widyatmoko, I.; Elliott, R. Characteristics of elastomeric and plastomeric binders in contact with natural asphalts. *Constr. Build. Mater.* **2008**, *22*, 239–249. [CrossRef]
- Liao, M.; Chen, J.; Airey, G.D.; Wang, S. Rheological behavior of bitumen mixed with Trinidad lake asphalt. *Constr. Build. Mater.* 2014, 66, 361–367. [CrossRef]
- 3. Xin, C.; Lu, Q.; Ai, C.; Rahman, A.; Qiu, Y. Optimization of hard modified asphalt formula for gussasphalt based on uniform experimental design. *Constr. Build. Mater.* **2017**, *136*, 556–564. [CrossRef]
- 4. Xu, G.; Wang, H.; Zhu, H. Rheological properties and anti-aging performance of asphalt binder modified with wood lignin. *Constr. Build. Mater.* **2017**, *151*, 801–808. [CrossRef]
- 5. Kök, B.V.; Yilmaz, M.; Guler, M. Evaluation of high temperature performance of SBS + Gilsonite modified binder. *Fuel* **2011**, *90*, 3093–3099. [CrossRef]
- 6. Huang, W.; Xu, G. Experimental investigation on the pavement performance of Buton rock asphalt mixtures. *J. South China Univ. Technol. (Nat. Sci. Ed.)* **2012**, *40*, 87–91.
- Galzerano, B.; Capasso, I.; Verdolotti, L.; Lavorgna, M.; Vollaro, P.; Caputo, D.; Iannace, S.; Liguori, B. Design of sustainable porous materials based on 3D-structured silica exoskeletons, *Diatomite*: Chemico-physical and functional properties. *Mater. Des.* 2018, 145, 196–204. [CrossRef]
- 8. Jahanian, H.R.; Shafabakhsh, G.H.; Divandari, H. Performance evaluation of hot mix asphalt (HMA) containing bitumen modified with Gilsonite. *Constr. Build. Mater.* **2017**, *131*, 156–164. [CrossRef]
- 9. Li, K.; Vasiliu, M.; McAlpin, C.R.; Yang, Y.; Dixon, D.A.; Voorhees, K.J.; Batzle, M.; Liberatore, M.W.; Herring, A.M. Further insights into the structure and chemistry of the Gilsonite asphaltene from a combined theoretical and experimental approach. *Fuel* **2015**, *157*, 16–20. [CrossRef]
- 10. Sun, D. A study on xinjiang asphaltite as an asphalt modifier. Part I: Composition, structure, and thermal behavior. *Pet. Sci. Technol.* **2012**, *30*, 307–315. [CrossRef]

- Helms, J.R.; Kong, X.; Salmon, E.; Hatcher, P.G.; Schmidt-Rohr, K. Structural characterization of gilsonite bitumen by advanced nuclear magnetic resonance spectroscopy and ultrahigh resolution mass spectrometry revealing pyrrolic and aromatic rings substituted with aliphatic chains. *Org. Geochem.* 2012, 44, 21–36. [CrossRef]
- 12. Zhong, K.; Yang, X.; Luo, S. Performance evaluation of petroleum bitumen binders and mixtures modified by natural rock asphalt from Xinjiang China. *Constr. Build. Mater.* **2017**, *154*, 623–631. [CrossRef]
- 13. Huang, W.; Xu, G.; Liu, Y.; Wang, D. Study on modification mechanism of North American rock asphalt based on microstructure. *Funct. Mater.* **2015**, *46*, 12082–12086. (In Chinese)
- Zhang, C.; Li, Y.; Cheng, X.; Liang, S.; Guo, X.; Zhao, H. Effects of plasma-treated rock asphalt on the mechanical properties and microstructure of oil-well cement. *Constr. Build. Mater.* 2018, 186, 163–173. [CrossRef]
- 15. Wang, M.; Lin, F.; Liu, L. Dynamic rheological properties and microscopic characteristics of ash mastics. *J. Tongji Univ. (Nat. Sci. Ed.)* **2016**, *44*, 567–571.
- 16. AASHTO. Standard Method of Test for Determining the Rheological Properties of Asphalt Binder Using a Dynamic Shear Rheometer (DSR); American Association of State Highway and Transportation Officials: Washington, DC, USA, 2009.
- 17. Li, Y.; Chen, J.; Yan, J.; Guo, M. Influence of Buton rock asphalt on the physical and mechanical properties of asphalt binder and asphalt mixture. *Adv. Mater. Sci. Eng.* **2018**, 1–7. [CrossRef]
- 18. Yin, Y.; Zhang, X. Effect of Buton rock asphalt on rheological properties of asphalt mortar at high temperature. *J. Wuhan Univ. Technol.* **2010**, *32*, 85–89.
- 19. Li, R.; Karki, P.; Hao, P.; Bhasin, A. Rheological and low temperature properties of asphalt composites containing rock asphalts. *Constr. Build. Mater.* **2015**, *96*, 47–54. [CrossRef]
- 20. Lv, S.; Fan, X.; Yao, H.; You, L.; You, Z.; Fan, G. Analysis of performance and mechanism of Buton rock asphalt modified asphalt. *J. Appl. Polym. Sci.* **2018**, 1–8. [CrossRef]
- 21. Mahyuddin, A.; Tjaronge, M.W.; Ali, N.; Ramli, M.I. Experimental analysis on stability and indirect tensile strength in asphalt emulsion mixture containing Buton granular asphalt. *Int. J. Appl. Eng. Res.* **2017**, *12*, 3162–3169.
- 22. Wang, C.; Wang, H.; Zhao, L.; Cao, D. Experimental study on rheological characteristics and performance of high modulus asphalt binder with different modifiers. *Constr. Build. Mater.* **2017**, *155*, 26–36. [CrossRef]
- 23. AASHTO. Standard Method of Test for Determining the Flexural Creep Stiffness of Asphalt Binder Using the Bending Beam Rheometer (BBR); American Association of State Highway and Transportation Officials: Washington, DC, USA, 2016.
- 24. Shi, X.; Cai, L.; Xu, W.; Fan, J.; Wang, X. Effects of nano-silica and rock asphalt on rheological properties of modified bitumen. *Constr. Build. Mater.* **2018**, *161*, 705–714. [CrossRef]
- 25. Lv, S.; Wang, S.; Guo, T.; Xia, C.; Li, J.; Hou, G. Laboratory evaluation on performance of compound-modified asphalt for rock asphalt/SBR and rock asphalt/Nano-CaCO. *Appl. Sci.* **2018**, *8*, 1009. [CrossRef]
- 26. Cai, L.; Shi, X.; Xue, J. Laboratory evaluation of composed modified asphalt binder and mixture containing nano-silica/rock asphalt/SBS. *Constr. Build. Mater.* **2018**, 172, 204–211. [CrossRef]
- 27. Acurio, K.; Chico-Proano, A.; Martinez-Gomez, J.; Avila, C.F.; Avila, A.; Orozco, M. Thermal performance enhancement of organic phase change materials using spent diatomite from the palm oil bleaching process as support. *Constr. Build. Mater.* **2018**, *192*, 633–642. [CrossRef]
- 28. Yin, H. Study on the Mechanism of Diatomite Modification and Its Application in Dry Mixing of Asphalt Mixture. Master's Thesis, Chongqing Jiaotong University, Chongqing, China, 2012. Unpublished.
- 29. Li, X.; Zhang, X.; Li, Z. Dynamic viscoelastic characteristics of diatomite modified asphalt mortar. *Highway* **2006**, *10*, 145–148.
- 30. Cheng, Y.; Zhu, C.; Tan, G.; Lv, Z.; Yang, J.; Ma, J. Laboratory study on properties of diatomite and basalt fiber compound modified asphalt mastic. *Adv. Mater. Sci. Eng.* **2017**, 2017, 4175167. [CrossRef]
- 31. Davar, A.; Tanzadeh, J.; Fadaee, O. Experimental evaluation of the basalt fibers and diatomite powder compound on enhanced fatigue life and tensile strength of hot mix asphalt at low temperatures. *Constr. Build. Mater.* **2017**, *153*, 238–246. [CrossRef]
- 32. Guo, Q.; Li, L.; Cheng, Y.; Jiao, Y.; Xu, C. Laboratory evaluation on performance of diatomite and glass fiber compound modified asphalt mixture. *Mater. Des.* **2015**, *66*, 51–59. [CrossRef]

- 33. Wei, H.; He, Q.; Jiao, Y.; Chen, J.; Hu, M. Evaluation of anti-icing performance for crumb rubber and diatomite compound modified asphalt mixture. *Constr. Build. Mater.* **2016**, *107*, 109–116. [CrossRef]
- 34. Li, J.; Zhao, X. Study on test performance of rock asphalt composite diatomite modified asphalt mixture. *Road Traffic Technol. (Appl. Technol. Ed.)* **2016**, *4*, 66–68.



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