Mechanism of HCB-Modified Asphalt and Dynamic Properties of Mixtures

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Abstract: Hydroxymethyl carbon black (HCB) was prepared as an asphalt modifier with a high oxygen content and active surface chemical properties. The microstructure of HCB was analyzed by scanning electron microscopy, energy-dispersive X-ray spectroscopy, and Fourier-transform infrared spectroscopy. The improvement effect of HCB on asphalt's physical, dynamic shear, rheological, and aging properties was evaluated. To analyze the dynamic properties of the HCB-modified asphalt mixtures, a simple performance test (SPT) was conducted, and then the change laws of the dynamic modulus and phase angle for the HCB mixtures were clarified. The results showed that the surface of HCB is smooth and that the oxygen content increases with the generation of hydroxyl functional groups. Polar oxygen-containing functional groups and hydrogen bonds are helpful in improving the resistance to cracking and aging. The surface activity of HCB is susceptible to temperature and frequency, causing a slight influence of HCB on the viscoelasticity of asphalt mixtures at high and low frequencies. At low temperatures and high frequencies, the HCB enhanced the elasticity characteristics and weakened the viscosity characteristics of asphalt mixtures.

Keywords: hydroxymethyl carbon black; modified asphalt; asphalt mixture; microscopic analysis; rheological properties; dynamic response

1. Introduction

Processing waste materials into asphalt modifiers can not only effectively improve the performance of asphalt and its mixtures, but also achieve sustainable utilization of waste materials [1,2]. Waste rubber tires have increased massively and sharply with the development of the automotive industry, which has become a global source of pollution. Carbon black (CB) is one of the products of waste rubber under high temperature [3]. CB has wide application prospects in the field of materials, with fine particles, closely packed mesh chains, and a large specific surface area [4,5]. The addition of CB can improve the aging properties, electrical conductivity, and thermal conductivity of asphalt [6–8], and it can also optimize some performance aspects of asphalt mixtures, such as resistance to cracking and rutting [9–13].

However, CB has limited ability to improve asphalt performance. Some scholars have tried to modify CB or to compound CB with other modifiers. Chen et al. [14] ascertained the temperature susceptibility of styrene–butadiene–styrene (SBS) modified asphalt with white carbon black. Li et al. [15] used pyrolysis carbon-black nanoparticles as a modifier and adopted aromatic
hydrocarbon oil as the softening agent for asphalt binders. The anti-rutting performance and low-temperature performance were improved.

An asphalt mixture counts as a typical multiphase granular material, of which the viscoelastic dynamic response is bound by the rutting, cracking, and fatigue of asphalt pavement [16–18]. Delving into the viscoelastic response of CB-modified asphalt mixtures will be conducive to deeply understand their dynamic responses under environmental factors and vehicle load. Li [19] comparatively analyzed the effects of CB and SBS on the dynamic moduli of asphalt mixtures, but he did not explain the difference.

Based on the above problems, this investigation hydroxylated carbon black to improve the performance of asphalt and its mixtures. A series of microscopic experiments were conducted to study the structure of HCB. The physical and rheological properties of HCB-modified asphalt were analyzed and the modification mechanism of hydroxymethyl carbon black (HCB) was revealed.

2. Materials

2.1. Base Asphalt

SK90# asphalt was used as the base asphalt for preparing modified asphalt and its mixtures. The physical indicators of the asphalt are presented in Table 1.

| Test Indicators                          | Base Asphalt | Test Methods |
|-----------------------------------------|--------------|--------------|
| Penetration (25 °C, 5 s, 100 g)/(1/10 mm) | 83           | ASTM D5      |
| Softening point (R&B)/°C                | 44.5         | ASTM D36     |
| Ductility (5 °C, 5 cm/min)/cm           | 7.4          | ASTM D113    |
| Viscosity (135 °C)/pa.s                 | 0.370        | ASTM D 4402  |

2.2. Preparation of HCB

CB with a weight of 10 g and nitric acid solution with a concentration of 8 mol/L were added into a three-necked flask, and then the oxidation reaction of CB by nitric acid proceeded for 8 h at 80 °C. The solution was constantly stirred during the reaction. The reaction product was repeatedly washed and filtered to neutrality with a Buchner funnel, and then the filtered CB was dried in an electrothermocstatic blast oven at 50 °C. In this way, oxygenated carbon black was obtained. The oxidation reaction with nitric acid converted the non-polar surface of CB into a local polar surface and increased the number of oxygen-containing functional groups (–OH, –COOH) on the surface of CB. The action decreased the adsorption force between CB particles and strengthened the interaction of carbon black particles with asphalt.

Five grams of oxygenated CB, 50 mL formaldehyde, and 5 mL NaOH with a mass fraction of 20% were added to a three-necked flask, and then the hydroxymethyl reaction proceeded under a nitrogen atmosphere for 5 h at 50 °C. The subsequent steps were the same as those above. In this way, HCB was obtained.

2.3. Preparation of HCB-Modified Asphalt

The asphalt was heated to 85 °C, and CB or HCB, which accounted for 5% of the asphalt mass, was slowly poured into the asphalt. The CB–asphalt and HCB–asphalt were sheared at the rate of 500 r/min at 130 °C for 10 min, and then shearing was performed at the rate of 2000 r/min at 150 °C for 20 min.

2.4. Preparation of HCB-Modified Asphalt Mixture

Amphibolite rock was adopted as both coarse and fine aggregates, and limestone was applied as filler. The base asphalt mixture (BAM) and hydroxymethyl carbon black modified asphalt mixture (HAM) were mixed to produce an AC-13 mixture; the gradation is presented in Table 2. The optimal
Asphalt content (OAC) was determined via the Marshall design method. The OACs of BAM and HAM were 4.5%, and the content of HCB was 5% of OAC. The parameters of asphalt mixture for the Marshall design method are shown in Table 3.

### Table 2. Mixture gradation.

| Mixture   | 16 mm | 13.2 mm | 9.5 mm | 4.75 mm | 2.36 mm | 1.18 mm | 0.6 mm | 0.3 mm | 0.15 mm | 0.075 mm |
|-----------|-------|---------|--------|--------|---------|---------|-------|--------|---------|----------|
| AC-13     | 100   | 95.6    | 72.7   | 40.4   | 30      | 19.4    | 14.5  | 10.3   | 8.1     | 5.1      |

### Table 3. Parameters of asphalt mixture for the Marshall design method.

| Asphalt Mixture | Optimal Asphalt Content (%) | Volume of Air Voids (%) | Voids in Mineral Aggregate (%) | Voids Filled with Asphalt (%) | Marshall Stability (kN) | Flow Value (mm) |
|-----------------|----------------------------|-------------------------|--------------------------------|-------------------------------|-------------------------|-----------------|
| BAM             | 4.5                        | 3.95                    | 14.5                           | 72.8                          | 12.5                    | 3.1             |
| HAM             | 4.5                        | 4.18                    | 14.4                           | 72.3                          | 13.4                    | 2.5             |

### 3. Test Methods

#### 3.1. Microscopic Tests of HCB

1. Scanning Electron Microscopy (SEM)
   
   The morphology of CB and HCB was assessed using a Quanta200 SEM produced by the American FEI Company. The electron beam emitted by the electron emission system scans the surface of specimen materials, and its signal intensity depends on the surface structure and composition of the specimen material. In order to improve the conductive effect, the specimen materials were sprayed with gold using a carbon coater.

2. Energy-Dispersive X-Ray Spectroscopy (EDS)
   
   The elemental compositions of CB and HCB were determined using a GENESIS XM EDS produced by the American EDAX Inc. SEM and EDS are often used in combination to observe morphology and explore the elements of specimen materials. The element types can be determined by analyzing characteristic X-rays with different energies. The content of the elements can be calculated based on the intensity of the characteristic X-rays.

3. Fourier-Transform Infrared Spectroscopy (FTIR)
   
   We used a Vector-22 FTIR produced by the German Bruker company to measure the functional groups of CB and HCB. The specimen materials were prepared using the KBr disc technique.

#### 3.2. Property Tests of HCB-Modified Asphalt

In order to evaluate the modification effect of HCB on asphalt, basic indicators such as penetration, softening point, ductility, and Brookfield viscosity were measured according to the requirements of the Test Procedure for Highway Engineering Asphalt and Asphalt Mixture (JTG E20–2011). A dynamic shear rheometer (DSR) was used to measure the complex shear modulus ($G^*$), phase angle ($\delta$), and rutting factor ($G^*/\sin \delta$) to evaluate the rheological properties of the modified asphalt.

#### 3.3. SPT of HCB-Modified Asphalt Mixture

In this experiment, $\varphi 150$ mm $\times$ H 150 mm cylinders prepared in the Troxler 4140 gyratory compactor were cored and cut to obtain $\varphi 100$ mm $\times$ H 110 mm specimens. Dynamic moduli and phase angle tests are measured by Simple Performance Test (SPT). The stress corresponding to 50–150 microstrain was taken by sine wave. Three parallel tests were conducted to reduce discrepancy. Referring to test conditions of previous research, the test temperatures were 4.4 °C, 21.1 °C, 37.8 °C, and 54.4 °C with the respective load frequencies of 0.1 Hz, 0.5 Hz, 1 Hz, 5 Hz, 10 Hz, and 25 Hz. SPT equipment and specimen are exhibited in Figures 1 and 2, respectively.
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Figure 1. SPT equipment.

Figure 2. The specimens.

4. Microstructural Analysis of HCB

SEM, XRD, and FTIR tests were carried out on CB and HCB, as shown in Figures 3–5, respectively. The chemical properties of CB and HCB and their influence on the properties of asphalt were analyzed via the microstructure, characteristic functional groups, and oxygen content.

Figure 3. The microstructures of (a) CB and (b) HCB.
while the surface of HCB was smoother than that of CB. In addition, its shape was irregular and the properties of asphalt.

The infrared spectrum of HCB. The peak was sharp and there was no interference from other absorption bands, indicating the generation of the hydroxyl group. The hydroxyl groups on the surface of HCB combined with the carbonyl group in the asphalt to form hydrogen bonds, which can affect the properties of asphalt. Therefore, HCB effectively strengthened the resistance to shear–slip deformation of asphalt, and HCB-modified asphalt is better than that of CB.

As illustrated in Figure 4, the infrared spectra of CB and HCB had some similar characteristics. The absorption bands of C–H overtone absorption and C=C in-plane deformation vibration appeared at approximately 1654 cm$^{-1}$, but the absorption intensity was weak; the Si–O absorbance band appeared at 1375 cm$^{-1}$, and the C–O absorbance bands appeared at 1063 cm$^{-1}$, 1013 cm$^{-1}$, and 975 cm$^{-1}$. The infrared spectrum of CB showed no absorption peak near 3500 cm$^{-1}$. However, the broad and strong characteristic absorption peak at 3446 cm$^{-1}$ corresponded to the stretching vibration of O–H in the infrared spectrum of HCB. The peak was sharp and there was no interference from other absorption peaks, indicating the generation of the hydroxyl group. The hydroxyl groups on the surface of HCB combined with the carbonyl group in the asphalt to form hydrogen bonds, which can affect the properties of asphalt.

Based on Figure 5, CB and HCB contain C, Si, O, and Au elements. The Si element was an impurity contained in the specimen materials, and the Au element was introduced when the specimen materials were sprayed with gold. This investigation chose Au as the internal reference element to calculate the oxygen content.

Figure 3 shows that CB particles were mostly ellipsoidal aggregates and the surface was rough, while the surface of HCB was smoother than that of CB. In addition, its shape was irregular and the floc was apparently reduced. Due to the different degree of polymerization, the particle size of the HCB varied, and the average particle size was between 5 and 100 μm. These characteristics gave HCB higher surface energy and larger intermolecular forces, and the interaction between particles and asphalt was stronger.

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were sprayed with gold. This investigation chose Au as the internal reference element to calculate the oxygen content.

The oxygen content of CB was 13.62%, and the oxygen content of HCB was higher than that of CB, reaching 24.78%. It is generally believed that the higher the oxygen content, the more active the surface chemical properties of carbon black. HCB contains CH, C= C, Si–O, and CO, and has a high oxygen content, so HCB can react with cycloalkanes and paraffins in asphalt to form chemical bonds. These chemical bonds are greater than van der Waals forces (VDW), which have a positive modification effect on asphalt.

5. Analysis of HCB-Modified Asphalt Properties

5.1. Basic Properties

To evaluate the modification effect of HCB on asphalt, basic properties such as penetration, softening point, ductility, and viscosity of CB- and HCB-modified asphalts were measured, with the result exhibited in Table 4.

| Test Indicators                      | Base Asphalt | CB-Modified Asphalt | HCB-Modified Asphalt |
|--------------------------------------|--------------|---------------------|----------------------|
| Penetration (25 °C, 5 s, 100 g)/(1/10 mm) | 83           | 81                  | 73                   |
| Softening point (R&B)/°C             | 44.5         | 46.2                | 47.4                 |
| Ductility (5 °C, 5 cm/min)/cm         | 7.4          | 7.3                 | 8.1                  |
| Viscosity (135 °C)/pa.s              | 0.370        | 0.390               | 0.425                |

HCB reduced the penetration of asphalt by 10 mm, the softening point increased by 3 °C, the ductility increased by 0.7 cm, and the viscosity increased by 0.05 pa.s. However, CB had a slight effect on asphalt. Therefore, HCB effectively strengthened the resistance to shear–slip deformation of asphalt, and its modification effect on asphalt was better than that of CB.

5.2. Rheological Properties

Asphalt is a typical viscoelastic material with significant rheological properties. Asphalt binder has more viscous components at high temperatures, enhancing resistance to rutting, and it has more elastic components at low temperatures, enhancing resistance to cracking. The complex shear modulus (G*), phase angle (δ), and rut factor (G*/sin) values of base asphalt (BA), CB-modified asphalt, and HCB-modified asphalt are shown in Figures 6–8.

![Figure 6. Effect of CB and HCB on complex shear modulus of asphalt.](image-url)
A similar tendency was observed for modified asphalt and BA to that shown in Figure 6, indicating that three asphalt binders exhibited simple linear viscoelastic behavior. At temperatures below 40 °C, the G* values of the two modified asphalts were larger than that of the BA, with a slightly larger G* for the HCB-modified asphalt. The G* of asphalt can be used to evaluate the softness and hardness of asphalt. The larger the G*, the harder the asphalt. Therefore, CB and HCB can stiffen asphalt, but the effect was not obvious. When the temperature exceeded 40 °C, the curves of G* of CB- and HCB-modified asphalt approximately coincided with that of BA, indicating a small effect of CB and HCB on asphalt at higher temperatures.

As depicted in Figure 7, the phase angles of the three asphalt binders gradually increased with increasing temperature. When the temperature was less than 40 °C, the order produced by phase angles was BA > CB-modified asphalt > HCB-modified asphalt. Thus, CB and HCB weakened the viscosity and enhanced the elasticity of asphalt; in particular, HCB had a better effect on improving the resistance to shear deformation of asphalt. For temperatures exceeding 40 °C, the phase angle curves of the modified asphalt were close to that of the BA. Therefore, the CB and HCB had slight effects on the antideformation capability of asphalt at high temperature.

The rutting factor (G*/sin δ) can be used to evaluate resistance to rutting deformation. A large G*/sin δ means a greater capacity of the asphalt to resist rutting deformation. From Figure 8, the improvement effect of HCB on G*/sin δ of asphalt was more obvious than that of CB, so HCB-modified
asphalt had better resistance to rutting deformation. However, the difference of $G^*/\sin \delta$ between the modified asphalt and BA was small with increasing temperature. Oxygen-containing functional groups such as $-\text{OH}$ are formed on the surface of HCB, increasing the polarity of the carbon black surface. As a result, the adsorption between HCB particles is weakened, and the dispersion capability in asphalt is improved. The interaction effect between HCB and asphalt and the particle effect were enhanced, which increased the viscosity and strengthened the resistance to cracking and shear–slip deformation of HCB-modified asphalt at low temperatures.

5.3. Aging Properties

The thin-film oven test (TFOT) method was used to simulate the aging process of three asphalt binders. The aging temperature was $(163 \pm 1)^\circ C$ with an aging time of 5 h. To analyze the effects of CB and HCB on the aging properties of asphalt, the penetration ratio and softening point increases were also measured.

It can be seen from Table 5 that the penetration and ductility of the three asphalt binders after aging were reduced, while the softening point was increased. In particular, the ductility values of the BA and CB-modified asphalt were reduced to 0. The ductility of the HCB-modified asphalt was reduced to 4.5 cm, indicating good anti-aging capacity. The penetration ratios of CB- and HCB-modified asphalts were 62.7% and 64.7%, respectively, which were higher than the 56.4% of BA; the softening point increases were 6.2 °C and 5.4 °C, which were lower than the 7.0 °C of asphalt. There are a certain number of hydrogen bonds in HCB-modified asphalt, which will break after absorbing enough energy. TFOT can provide enough thermal energy for the hydrogen bonds, preventing the aging of asphalt. Polyecondensation and oxidation reactions happen in asphalt during the aging process, increasing the number of carbonyl functional groups. These reactions increased the number of hydrogen bonds in the HCB-modified asphalt. Therefore, the resistance to aging of HCB-modified asphalt was the best.

| Test Indicators               | BA Before Aging | BA After Aging | CB-Modified Asphalt Before Aging | CB-Modified Asphalt After Aging | HCB-Modified Asphalt Before Aging | HCB-Modified Asphalt After Aging |
|------------------------------|----------------|---------------|---------------------------------|--------------------------------|----------------------------------|----------------------------------|
| Penetration (25 °C)/(1/10 mm) | 83             | 46            | 81                              | 48                             | 73                               | 47                               |
| Ductility (5 °C)/cm           | 7.4            | 0             | 7.3                             | 0                              | 8.1                              | 4.5                              |
| Softening point (R&B)/°C      | 44.5           | 51.5          | 46.2                            | 52.4                           | 47.4                             | 52.8                             |
| Penetration ratio (%)         | -              | 56.4          | -                               | 62.7                           | -                                | 64.7                             |
| Softening point increase (°C) | -              | 7.0           | -                               | 6.2                            | -                                | 5.4                              |

6. Dynamic Properties of HAM

HCB-modified asphalt had better capacity to resist shear deformation and aging than the CB-modified asphalt, which indicated a better modification effect of HCB. To analyze the dynamic properties of the hydroxymethyl carbon black modified asphalt mixture (HAM) and reveal the changing mechanism of dynamic properties, SPT tests were conducted on HAM and the base asphalt mixture (BAM).

6.1. Dynamic Response Parameter Analysis

Dynamic modulus and phase angle are considered the important parameters to characterize the viscoelasticity of asphalt mixtures, which can reflect the actual force and dynamic response of asphalt pavement [20,21]. Under different temperatures, the dynamic moduli and phase angle of HAM and BAM with the variation of loading frequencies are exhibited in Figures 9 and 10.
As shown in Figure 9, the variation tendency of the dynamic modulus for two mixtures remained the same, i.e., both of the dynamic moduli slid progressively with the increase of temperature. The dynamic modulus of HAM was evidently larger than that of BAM at lower temperatures (4.4 °C and 21.1 °C), which suggests that adding HCB can increase the nondeformability of an asphalt mixture; polar oxygen-containing functional groups enhance the elasticity of asphalt. The difference of dynamic moduli for the two mixtures slid progressively with the increase of temperature; in particular, both of the dynamic moduli were almost the same at 54.4 °C, which suggests that the viscoelasticities of the mixtures were similar at higher temperature. In addition, the dynamic moduli increased progressively with the growth of loading frequency, whereas the increase was different in different frequency ranges (0.1–1 Hz). The dynamic moduli increased sharply at a lower frequency range (0.1–1 Hz), and it was smaller and smaller at higher loading frequencies (5–25 Hz). The higher the frequency, the shorter the duration of the load, and the smaller the creep deformation of the asphalt mixture.

As shown in Figure 10, the variation tendency of phase angles for two mixtures remained the same. As the loading frequency decreased, the phase angle increased progressively at the lower temperature of 4.4 °C, and at 21.1 °C, and the increase of phase angle of the HAM asphalt mixture was relatively small. HCB can enhance the elasticity of asphalt mixtures, while there was no apparent difference in phase angle between the two asphalt mixtures at higher temperatures.
6.2. The Master Curve Analysis of Dynamic Response Parameters

The master curve of a dynamic modulus is explained by the sigmoidal model [18], i.e., the horizontal translation of the shift factor is realized by adopting nonlinear least-squares fitting, as exhibited in Equation (1).

\[ \log |E^*| = \delta + \frac{\alpha - \delta}{1 + e^{\beta + \gamma \log f_r}} \]  

where \( E^* \) is dynamic modulus; \( f_r \) is the reduced frequency; \( \delta \) is the minimum value of the dynamic modulus; \( \alpha \) is the maximum value of the dynamic modulus; and \( \beta \) and \( \gamma \) are regression parameters, which are determined by the properties of the binder.

For a given reference temperature, the horizontal movement number value of frequency is a shift factor. The relationship between the reduced frequency \( f_r \) and shift factor \( \alpha(T) \) is exhibited in Equation (2).

\[ f_r = f \cdot a(T) \]  

where \( f \) is the loading frequency in Hz; \( f_r \) is the reduced frequency in Hz; and \( \alpha(T) \) is the shift factor.

When the master curve is determined, the shift factor of the dynamic modulus can be acquired via Equation (3).

\[ \log[a(T)] = \frac{\Delta E_a}{19.14714} \left( \frac{1}{T + 273.15} - \frac{1}{T_r + 273.15} \right) \]  

where \( \Delta E_a \) is activation energy in J/mol; \( T_r \) and \( T \) are reference temperature and test temperature in °C; and the shift factor \( \alpha(T) = 1 \) a the reference temperature.

The reduction frequency can be acquired via Equation (4), adopting the Arrhenius equation.

\[ \log f_r = \log f - \frac{\Delta E_a}{19.14714} \left( \frac{1}{T + 273.15} - \frac{1}{T_r + 273.15} \right) \]  

where \( f \) is the test frequency in Hz.

The master curve is exhibited in Equation (5).

\[ \log \log |E^*| = \delta + \frac{\alpha - \delta}{1 + e^{\beta + \gamma \log f_r - \Delta E_a/T_r} \left( \frac{1}{T + 273.15} - \frac{1}{T_r + 273.15} \right) \} } \]  

Dynamic modulus test results were ascertained via sigmoidal function, using the numerical analysis software Origin and adopting 21.1 °C as the reference temperature. The initial values of the parameters were: \( \beta = -1.0, \gamma = -0.5, \delta = 0.5, \Delta E_a = 200,000 \). The activation energy \( \Delta E_a \) and shift factor \( \alpha(T) \) of mixtures are exhibited in Table 6, and the fitting parameter of the master curve for the dynamic modulus is exhibited in Table 7.

| Mixtures                     | Transition Temperature (°C) | Activation Energy \( \Delta E_a \) (J) | Shift Factor \( \log[a(T)] \) |
|------------------------------|----------------------------|--------------------------------------|-------------------------------|
| BAM                          | 4.4                        | 216631.4                             | 2.314                         |
|                              | 21.1                       | 0                                    | 0                             |
|                              | 37.8                       | 230131.7                             | -2.194                        |
|                              | 54.4                       | 221084.2                             | -3.989                        |
| HAM modified asphalt mixture | 4.4                        | 208657.3                             | 2.228                         |
|                              | 21.1                       | 0                                    | 0                             |
|                              | 37.8                       | 231061.2                             | -2.203                        |
|                              | 54.4                       | 225021.7                             | -4.060                        |

| Mixtures                     | \( \alpha \)               | \( \beta \)                         | \( \gamma \)                 | \( \delta \) | \( R^2 \) |
|------------------------------|----------------------------|-------------------------------------|------------------------------|--------------|----------|
| BAM                          | 4.32205                    | 2.07160                             | -1.10936                     | -0.53270    | 0.99470  |
| HAM modified asphalt mixture | 4.37454                    | 2.18026                             | -1.15643                     | -0.62096    | 0.99865  |
The master curve of the dynamic modulus was obtained by moving the data horizontally along the logarithmic frequency axis. As a function of the loading frequency and temperature, the dynamic modulus was reduced to a function of frequency. Activation energy indicates the energy barrier that must be surmounted when the curve is moved with reference temperature, and the larger the activation energy, the more difficult it is to move the curve. In addition, activation energy is consistent with shift factor. When the test temperature is lower than the reference temperature, \( \log[a(T)] > 0 \); when the test temperature is higher than the reference temperature, \( \log[a(T)] < 0 \); when the test temperature is equal to the reference temperature, \( \log[a(T)] = 0 \). The activation energy and shift factor of BAM were higher than that of HAM when the test temperature was lower than the reference temperature; the activation energy and the absolute value of shift factor of HAM were higher than those of BAM when the test temperature was higher than the reference temperature.

The master curves demonstrated the relationship between dynamic response and loading frequency. In line with the master curves of dynamic response, the mechanical properties at very high or low frequencies could be calculated. The master curves of dynamic modulus and shift factor for mixtures are respectively exhibited in Figures 11 and 12.

As shown in Figure 11, the master curve of the dynamic modulus was basically flat following the “S” curve, and the dynamic modulus grew with the increase of loading frequency and temperature. When mixtures were at high temperature, the surface activation energy of aggregates of HCB increased, and aggregates of HCB usually combine with each other to form agglomerates, causing stiffer asphalt binder, stronger viscoelasticity, and better resistance to shear deformation. The phase angle grew first and then slides with the increase of loading frequency, while the difference between BAM and HAM was not slight. High temperature and low frequency were equivalent, as were low temperature and high frequency.

As shown in Figure 13, the dynamic modulus of HAM was slightly higher than that of BAM in the higher frequency range; conversely the phase angle of BAM is larger. The differences of dynamic
modulus and phase angle between the two mixtures were not evident in the lower frequency range. The aggregates of HCB tended to exist stably with low-frequency vibration. When the frequency was relatively low, the effect of carbon black on asphalt was not obvious. When the frequency was greater than 0.01 Hz, the phase angle of the HAM was smaller than that of the BAM. When the frequency was less than 0.01 Hz, the phase angles of the two mixtures were not much different. As mentioned above, the loading frequency and temperature conditions were equivalent for viscoelastic materials, inclusive of asphalt mixture. Therefore, at temperatures below 37.8 °C, HAM had a higher dynamic modulus and had strong non-deformability. As the temperature rose to over 37.8 °C, the viscoelastic responses of the two mixtures were slightly different from each other, i.e., the modified effect of carbon black was not evident in the case of high temperatures.

Figure 11. Dynamic modulus master curve: (a) BAM, (b) HAM.

Figure 12. Phase angle master curves: (a) BAM, (b) HAM.

Figure 13. Comparison of dynamic modulus and phase angle master curves: (a) dynamic modulus, (b) phase angle.
7. Conclusions

(1) Compared with CB, the surface of HCB was smoother, the floc was significantly reduced, and the oxygen content was increased. Oxygen-containing functional groups increased the polarity of carbon black surface, causing greater viscous force between HCB and asphalt. The created hydroxyl functional groups were combined with the carbonyl group of asphalt to form hydrogen bonds, improving the resistance to aging of asphalt. HCB was better than CB at improving the low-temperature resistance to cracking and aging of asphalt.

(2) The surface activity of aggregates of HCB was susceptible to temperature and frequency. The effect of HCB on the viscoelasticity of asphalt mixtures was not obvious at high temperature and low frequency. At low temperature and high frequency, HCB significantly increased the dynamic modulus of the asphalt mixture and reduced the phase angle, so it enhanced the elasticity and weakened the viscosity.

(3) Based on the dynamic modulus and phase angle master curves of the two asphalt mixtures, it can be predicted that when the frequency is greater than 0.01 Hz, the phase angle of the HAM will be smaller than that of the BAM, and when the frequency is less than 0.01 Hz, the difference in phase angle between the two asphalt mixtures will be relatively small. The activation energy (\(\Delta E_a\)) and shift factor (log\([\alpha(T)\]) of HAM were smaller than those of BAM below reference temperature, while they outstripped the BAM when the temperature was higher than reference temperature.

This paper only investigated the physical and rheological properties of HCB-modified asphalt and dynamic properties of its mixture, and did not make comparisons with other modified asphalts. In subsequent research, rubber- and SBS-modified asphalt will be studied, and the modified effects of these modified asphalts will be compared.

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