Study of the Molecular Components and Rheological Properties of Asphalt after Long-Term Aging under the Action of Moisture

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Abstract: This study aimed to investigate variations and relationships between molecular components and rheological properties during the long-term aging of SBS-modified asphalt by the action of moisture. The chemical components and changes in molecular weight during aqueous PAV aging were observed using a four-component test and GPC test, and these morphological changes were quantified. Viscosity tests, time-scan tests and damage-healing tests were carried out to investigate the rheological properties during the aging process. Finally, the mechanism of asphalt aging under the influence of moisture was discussed. The results showed that moisture facilitated the long-term aging of asphalt and complicated the aging behavior under pressure-aging conditions. The dissolution of certain hydrophilic groups may be responsible for the decrease in resin content. The fatigue and self-healing properties of asphalt were weakened by moisture during the aging process. This was mainly attributed to a decrease in the composition of the asphalt colloidal dispersion medium, which resulted in earlier and faster development of microcracks under repeated loading as well as retardation in the rate of asphalt surface approach, wetting and spreading. Under long-term aging in the presence of moisture, the molecular components of the asphalt showed significant correlations with the rheological properties. The results of this study can contribute to further explaining the influence of moisture on the thermal-oxidative aging of asphalt.

Keywords: asphalt aging; moisture effect; molecular components; rheological properties; correlation

1. Introduction

Moisture is an environmental factor that usually affects asphalt pavement material [1], whether during the mixing, construction, operation or maintenance. Extensive studies are used to explain the mechanisms by which moisture affects the attenuation of the bond between asphalt and aggregate [2,3]. It is found that the cohesion of the asphalt and its bond with the aggregate are weakened due to moisture penetrating asphalt [4], thereby shortening the service life of asphalt pavement. Oxygen and heat are ubiquitous, as with moisture, which results in constant asphalt oxidation and a gradual deterioration of the asphalt binder properties. Hence, it is of vital importance to study the interaction between moisture and oxidation and its effect on the properties of asphalt and asphalt mixtures.

Some studies focusing on the effect of moisture on asphalt aging have been reported so far. Huang et al. [5] studied the chemical components and microscopic morphology of asphalt under the action of high temperature and water immersion. It was found that moisture could trigger complex chemical reactions with waxes and surfactants in asphalt, contributing to increasing polar components on the asphalt surface. Noguera et al. [6] studied the interaction mechanism among asphalt, moisture, and oxygen by immersing asphalt in an aqueous solution at room temperature. It was found that AC 80–100 and AC 60–70 (AC 80–100 and AC 60–70 refer to asphalt cements with penetration test values
between 80 and 100 tenths of a millimeter and between 60 and 70 tenths of a millimeter, respectively) experienced an increase in their stiffness and viscosity after 12 months of immersion, followed by significant variations in chemical components. These changes were considered to be brought by interactions between asphalt and water-oxygen molecules. Similarly, Pang et al. [7] simulated the effect of moisture on asphalt through immersion under room temperature and considered the effect of the pH value of the solution as well as the salt concentration. It was concluded that moisture influenced the chemical components and structural changes in asphalt, and that these changes could be further exacerbated if aqueous solute components were added. As the immersion method is time-consuming, and does not reflect the thermal and oxidative aging effects of asphalt very well, a new test method has been developed in which moisture is subtly added to the pressure-aging apparatus, allowing it to participate in the thermal and oxidative aging process. Compared to the immersion method, the aging environment is much closer to the real-life scenario and the test time is significantly reduced. Thomas [8] simulated the long-term effects of moisture, oxygen, and heat on the asphalt by adding a certain mass of water to a pressure aging vessel (PAV) at 60 °C and 80 °C. It was concluded that the colloidal structure of asphalt was prominently disrupted by moisture and temperature, which intensifies the chemical aging. Ma et al. [9] also investigated the aging characteristics of asphalt binders by adding a moisture factor to PAV. The result showed that the addition of moisture significantly reduced the service life of the asphalt. Huang [10] et al. also conducted PAV aging tests on bitumen, with and without water, and found that the effect of moisture on the aging characteristics of bitumen was related to the source of the bitumen. Moisture had little effect on the low-temperature properties of the bitumen, but the high-temperature properties were severely degraded. Xiao [11] et al. investigated the effect of the pH value and the action time of water on the PAV aging performance of asphalt and found that the acidity of the aqueous solution and the chloride salt solubility were positively related to the degree of asphalt aging. Since humidity varies from region to region, Yu [12] et al. analyzed the effect of humidity on the PAV aging process of asphalt by controlling the mass of water added to change the relative humidity of the pressure vessel. The results obtained concluded that the threshold of humidity failure for high-temperature performance of asphalt was 80%. Li [13] et al. showed that the longer the time of moisture action the greater the effect on the PAV aging properties of asphalt. The aforementioned findings suggested that moisture interacted with the asphalt binder and increased its oxidation, thereby interfering with the asphalt structure, altering its physical and chemical properties, and causing the asphalt to be sticky and stiff. However, an opposite conclusion was drawn in another study, namely, that the asphalt hardening could be retarded under moist conditions [14]. Some studies further concluded that moisture rarely affected the oxidation rate of asphalt at 60 °C, with little variation in the rheological properties of the asphalt binder [15]. It can be noted that the interaction between moisture and oxidation was relatively complex, and a definitive conclusion has not yet been reached. The contradiction may boil down to different evaluation indicators, types of asphalt binders, and test conditions [16]. Therefore, in order to clarify the effect of moisture and oxidation on asphalt, in-depth studies are needed to comprehensively evaluate different types of asphalt, simulation methods, and property characterization from various angles.

With reference to previous research results, this study simulated the effect of moisture on the long-term aging of SBS-modified asphalt through an aqueous PAV test. Considering the different time of moisture effect in different regions, different gradients of moisture duration (0 h, 5 h, 10 h, 15 h and 20 h) were used in the 20 h PAV aging test. The four-component test and gel permeation chromatography (GPC) were used to qualitatively and quantitatively assess the molecular components of asphalt during long-term aging under the influence of moisture. The viscosity test, time-scan test and damage-healing test were also used to investigate the changes in mobility, fatigue and self-healing properties of asphalt.
2. Materials and Methods

2.1. Materials

The test materials in this study were the Kunlun styrene-butadiene-styrene (SBS) modified asphalts. The SBS modifier was 5% of the asphalt mass. The basic performance parameters of SBS-modified asphalt were shown in Table 1.

Table 1. Basic performance parameters of SBS-modified asphalt.

<table>
<thead>
<tr>
<th>Test Item</th>
<th>Technical Indicator [17]</th>
<th>Test Result</th>
<th>Test Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Penetration (25 °C) /0.1 mm</td>
<td>40~60</td>
<td>50</td>
<td>T0604-2011</td>
</tr>
<tr>
<td>Softening/°C</td>
<td>≥60</td>
<td>69.2</td>
<td>T0605-2011</td>
</tr>
<tr>
<td>5 °C ductility (5 cm/5 min)/cm</td>
<td>≥20</td>
<td>40</td>
<td>T0606-2011</td>
</tr>
<tr>
<td>Recovery of elasticity 25 °C/%</td>
<td>≥75</td>
<td>97</td>
<td>T0662-2011</td>
</tr>
<tr>
<td>135 °C dynamic viscosity/Pa·s</td>
<td>≤3</td>
<td>1.94</td>
<td>T0620-2011</td>
</tr>
<tr>
<td>Rolling thin film oven (RTFO) test</td>
<td>Mass loss/%</td>
<td>±1</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>Ratio of penetration</td>
<td>≥65</td>
<td>71</td>
</tr>
<tr>
<td></td>
<td>(25 °C)/%</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5 °C ductility/cm</td>
<td>≥15</td>
<td>25</td>
</tr>
</tbody>
</table>

2.2. Specimen Preparation

The standard anhydrous PAV test was conducted concerning AASHTO R28, with an aging time of 20 h, a temperature setting of 100 °C and a pressure of 2.1 MPa. The aqueous PAV aging test was conducted based on parameters of the standard anhydrous PAV test. The preparation procedures are as follows:

(i) Spraying water on the asphalt surface. A total of 50 g of asphalt aged after rolling thin-film oven (RTFO) was poured evenly onto the aging tray. According to the literature [12], the moisture in the PAV can reach 100% when the mass of water was 5.9 g. Thus, the mass of water sprayed on the asphalt was chosen to be 5.9 g. The evaporation of water during this process was ignored due to the short spraying process.

(ii) The m h aqueous PAV test was performed. The specimens with water were treated for m h pressure aging under the standard anhydrous PAV test.

(iii) Specimen dehydration and vessel drying were carried out. Asphalt samples that have undergone m h aqueous PAV aging were dehydrated in an oven at 120 °C for 30 min to eliminate moisture that may have seeped inside the asphalt and to wipe out residual moisture from PAV inside.

(iv) The standard anhydrous PAV with n (n = 20 – m) h was performed.

All specimens were labeled as PAm-n. The control group was PA0-20, which had a moisture action time of 0 h, and a standard anhydrous PAV test time of 20 h, which was placed in an oven at 120 °C for 30 min at the end of the test to eliminate the effect of dehydration time on the asphalt properties. The asphalt preparation process is shown in Figure 1.

2.3. Asphalt Molecular Tests

2.3.1. Four-Component Test

The four-component test was used to analyze the changes in the asphaltenes, resins, saturates and aromatics of asphalt. With a reference to the chemical component test of asphalt (four-component method) in JTG E20-2011, this study analyzed the four-component compositions of asphalt during aging using solvent precipitation and column chromatography. The asphalt sample (1.0 ± 0.1) g is dissolved in n-heptane, filtered through filter paper, the insoluble fraction is refluxed with toluene to obtain the asphaltenes solution, the soluble fraction is poured into the adsorption column, rinsed with n-heptane to obtain the saturates fraction solution, toluene to obtain the aromatics fraction solution and toluene-ethanol to obtain the resin solution. The solutions are dried in a vacuum oven (105 °C, 93 kPa) and weighed to obtain the mass of each component.
2.3.2. GPC Test

The GPC test was used to obtain the distribution of asphalt molecules at different sizes before and after aging. During the aging process, the type and content of asphalt molecules were constantly changing, accompanied by a variety of physical and chemical reactions such as volatilization, oxidation, and polymerization [18]. Understanding the changing pattern of the molecular weight can contribute to explaining the aging effect of asphalt. Tetrahydrofuran was used in this test to dissolve the asphalt. A sample solution was prepared with a concentration of 1.0 mg/mL. The sample was then injected at a rate of 0.7 mL/min.

2.4. Asphalt Rheology Tests

2.4.1. Viscosity Test

Viscosity was a characterization of asphalt mobility. In this study, asphalt was tested for Brookfield viscosity at five different temperatures, 95 °C, 115 °C, 135 °C, 155 °C and 175 °C, regarding ASTM D4402. The viscous activation energy was calculated to assess its temperature sensitivity.

2.4.2. Time-Scan Test

The time-scan test was used to simulate the repeated action of vehicle loads on the pavement. The number of shears corresponding to a decrease in the complex modulus of asphalt G* to 50% of the initial value can be used as an indicator for assessing the fatigue life of asphalt [19]. The time-scan test was informed by the results of the NCHRP 9-10 project [20]. In order to avoid the phenomenon of test failure occurring at the asphalt-fixture interface at lower temperatures, and with reference to the literature [21–23], the time scan test temperature was chosen to be 30 °C. The other specific parameters of the time-scan test used in this study were 10 Hz test frequency, selection of parallel plates with a diameter of 8 mm and 2 mm spacing. The strain pattern was adopted, with a strain level of 5%. The damage mode of asphalt was checked at the end of each test. If the damage occurred at the interface between the asphalt and the parallel plate, the test data should be invalidated and retested.
2.4.3. Damage-Healing Test

Owing to the intermittent effect of the vehicle on the road, the adoption of a damage-healing test was in line with the actual loading of the road. When the temperature is low, the asphalt self-healing phenomenon is not obvious. To better observe and compare the difference in self-healing performance between different asphalts, the test temperature for the damage-healing test was also 30°C. The other parameters of the test were similar to those of the time-scan test, but an interval was added. The test was stopped when the complex modulus of the asphalt dropped to 50% of the initial modulus value, and after a 10 min interval, the test was loaded again until the complex modulus re-dropped to 50% before healing.

3. Test Results and Analysis

3.1. Asphalt Molecular Components

3.1.1. Four-Component Test

It is generally considered that asphalt can be divided into four components: saturates, aromatics, asphaltenes and resins. The saturates had a lubricating and softening effect. The aromatics were the dispersing medium for asphalt. The resins had a significant influence on the adhesion of asphalt. The asphaltenes were the thickeners for asphalt. A proper content of components was the prerequisite to forming a stable colloidal dispersion system and ensuring favorable rheological properties. The component analysis was performed on the original SBS-modified asphalt and the long-term aging asphalt that underwent a different time of moisture effect. The results are shown in Figure 2. It can be seen that, compared to the unaged SBS-modified asphalt, the saturates and aromatics of PA0-20 asphalt exhibited a decrease in mass ratio. However, there were increases in the asphaltenes and resins, with their amplitude of variation larger than that of the other two components. It was primarily because, under the joint action of heat and oxygen, the saturates and aromatics in the asphalt phase caused certain mass loss due to their light weight and can be partially converted into asphaltenes during the oxidative process. However, different from the PA0-20 asphalt, the resins of the PAV aged asphalt under the influence of water did not increase, but instead gradually decreased. The same was found in the literature [6,7] by testing the asphalt components after water immersion. This change was jointly caused by the aging due to oxygen absorption of asphalt and dissolution of hydrophilic groups and water-soluble substances in the asphalt. The resins and aromatics were more prone to oxidation than asphaltenes and saturates, leading to greater mass damage to the former, especially under the influence of moisture, and the aging of asphalt may become more complex, which possibly leads to the transformation of resins into other substances. In addition, the addition of moisture created a moist environment in the aging vessel, where the polar or hydrophilic groups contained in the resins were easily dissolved [24,25], resulting in a reduction in resins content. The mass ratio of the asphalt four-component continued to change as the time of moisture effect increased. For example, when the time was 20 h, the contents of asphaltenes and resins in the asphalt were 22.7% and 27.7%, respectively, representing a change of 9% and 4.4% compared to PA0-20 asphalt. It indicated that the asphalt aging process was promoted in the presence of moisture.

Studies have shown that the chemical components of asphalt were closely related to rheological properties and road performance [26,27]. Figure 2 shows that the contents of asphalt resins, saturates and aromatics decreased and the asphaltenes increased after the aging of aqueous PAV. The colloid instability index (CII) can better reflect the variation in the peptization ability of the asphalt during aging. The asphalt was prone to be gel-like, and the asphalt colloid became unstable with larger CII. The instability index of asphalt colloids was defined as:

\[
CII = \frac{Asphaltenes + Saturates}{Resins + Aromatics}
\]  

(1)

The data from the components test in Figure 2 were substituted into Equation (1) to calculate CII. The calculated results were shown in Table 2. It can be seen that the instability
index of asphalt colloids increased under thermal-oxidative aging, and the CII was prone to increase with the extended time of moisture effect. In other words, the asphalt had an increasingly unstable colloidal structure when the time of moisture effect increased, and its colloid was closer to gel-type. In the absence of moisture, the CII value of PAV-aged asphalt was 0.36. When the time of moisture effect was 20 h, the CII value of PA20-0 asphalt increased to 0.50. It demonstrated that the asphalt aging was intensified owing to moisture.

Figure 2. Results of four-component test under different working conditions.

Table 2. Calculated results of instability index of asphalt.

<table>
<thead>
<tr>
<th>Asphalt</th>
<th>OA</th>
<th>PA0-20</th>
<th>PA5-15</th>
<th>PA10-10</th>
<th>PA15-5</th>
<th>PA20-0</th>
</tr>
</thead>
<tbody>
<tr>
<td>CII</td>
<td>0.31</td>
<td>0.36</td>
<td>0.38</td>
<td>0.43</td>
<td>0.46</td>
<td>0.50</td>
</tr>
</tbody>
</table>

3.1.2. GPC Test

Figure 3 shows the GPC curves of the asphalt under different working conditions. As can be seen, the GPC curves of SBS-modified asphalt under different working conditions were basically the same. All curves had only two peaks that appear in a relatively similar position. During the leaching between 22 min and 25 min, the characteristic peaks of the asphalt under different working conditions were significantly different, mainly reflected in the gradual upward shift of the curve in this area as the time of moisture effect increased. Based on the GPC test principles, molecules with large sizes were leached first. In other words, macromolecules in the asphalt were leached between 22 min to 25 min. It indicated that the aqueous PAV test led to the rising content of large molecules in the asphalt. This was consistent with the previous conclusion that moisture increased the asphalt aging, resulted in volatilization of the light components, and contributed to increasing asphaltene (heavy components) content, which in turn increased the content of asphalt macromolecules.
Zhao et al. [28] carried out a macromolecular microstructure study of two lab-aged and seven recycled asphalt binders. In the study, a good correlation was found between the rheological properties of aged asphalt and the proportion of large molecule size \((LMS)\) content. To further quantify the changes in the asphalt molecular weight during aging, three parameters, namely \(LMS\), medium molecular size \((MMS)\) and small molecular size \((SMS)\), were introduced to assess the distribution of asphalt molecules at different sizes. \(LMS\), \(MMS\) and \(SMS\) are divided by dividing the chromatogram equally into 13 slices, where slices 1 to 5 are \(LMS\), slices 6 to 9 are \(MMS\) and slices 10 to 13 are \(SMS\). The three parameters are calculated as follows:

\[
LMS = \frac{S_{LMS}}{S_a} \times 100\% 
\]

\[
MMS = \frac{S_{MMS}}{S_a} \times 100\% 
\]

\[
SMS = \frac{S_{SMS}}{S_a} \times 100\% 
\]

where, \(S_{LMS}\), \(S_{MMS}\), \(S_{SMS}\) are the integral areas of \(LMS\), \(MMS\), and \(SMS\), respectively (shown in Figure 3) and \(S_a\) is the sum of integral areas of three areas.

As shown in Figure 4, the distribution of asphalt molecules at different sizes was calculated by combining Figure 3 and Equations (2)–(4). It can be seen that, as the time of moisture effect is extended, the \(LMS\) of PAV-aged asphalt gradually increased, \(SMS\) decreases gradually, and \(MMS\) shows a slight upward and downward fluctuation trend. This is consistent with the previous analysis.
3.2. Asphalt Rheological Properties

3.2.1. Viscosity-Temperature Characteristics

It was shown by extensive studies that the dependence of asphalt viscosity on temperature can be expressed using the Arrhenius equation \[\eta = A e^{\frac{E}{B T}}\] (5)

By taking the logarithm of both sides of the equation above, it is obtained that

\[\ln(\eta) = \ln(A) + \frac{E}{B T}\] (6)

where, \(\eta\) is the asphalt viscosity, Pa·s; \(m\) and \(n\) are the fitting parameters; \(E\) is the viscous activation energy, kJ/mol; and \(T\) is the thermodynamic temperature, K.

The viscosity-temperature properties of asphalt were fitted based on Equation (6). The viscosity-temperature properties of SBS-modified asphalt under different working conditions are shown in Figure 5. It can be found that the asphalt viscosity increased after thermal-oxidative aging. With an extended time of moisture effect, the value of asphalt viscosity was found to exhibit linear growth. That is due to changes in colloidal structure caused by volatilization, oxidation and dissolution of asphalt molecules. Then, with decreasing light components and rising heavy components, the number of asphalt macromolecules increased and consistency enhanced, which greatly weakened the motility.

In addition, it can be obtained from the fitting results in Figure 5 that the viscous activation energy \(E\) for OA, PA0-20, PA5-15, PA10-10, PA15-5 and PA20-0 asphalts were 64.8, 66.3, 69.0, 69.7, 71.3 and 72.2 kJ/mol, respectively. Colloidal materials such as asphalt are needed to absorb energy during flow to overcome the barrier among fluids. Then, fluids can move from the previous position to the surrounding “hole” in order to achieve viscous flow. The minimum energy required to overcome the barrier was called the viscous activation energy [30]. The higher the viscous activation energy was, the more energy would be required and the inferior the fluidity would be. The activation energy of PAV-aged asphalt

![Figure 4. Distribution of asphalt molecules under different working conditions.](image-url)
increased due to the impact of moisture, and the longer the time of moisture effect was, the
greater the activation energy would be. It indicated that moisture intensified the physical
and chemical reactions such as volatilization, oxidation and vulcanization of the asphalt
aging process, breaking the equilibrium of its colloidal structure, and thus affecting its
viscosity-temperature properties.

Figure 5. Relationship between viscosity and temperature properties of asphalt under different
working conditions.

3.2.2. Fatigue Property

Figure 6 shows the fatigue life of asphalt under different conditions. It can be found
that the number of times for the asphalt to withstand the shear stress decreased with
a longer time of moisture effect. For instance, the fatigue life of PA0-20 asphalt was
32,275 times. Under the condition that the time of moisture effect increased by 20 h, the
fatigue life dropped down to 27,509 times, accounting for a decrease of 14.5%. It indicated
that the moisture effect time served as a vital factor in the deterioration of the asphalt
fatigue performance after long-term aging. When analyzed from the colloid theory, it
was because asphalt can be considered as a colloidal structure with asphaltenes (macro-
molecular substances) as the core and saturates, aromatics and resins as the dispersing
medium [31]. Under the coupling of moisture, oxygen and heat, the dispersion medium
underwent reactions such as volatilization, transformation and dissolution, resulting in a
decrease in content. At the same time, substances with a larger molecular weight such as
asphaltenes, oxygen-containing functional groups and sulfur-containing functional groups
were generated. Asphalt became brittle and was prone to microcracking, with rapid crack
growth under repeated loading [32,33], thereby shortening the fatigue life. It can also be
observed from Figure 6 that the fatigue life still exhibited a downward trend despite the
decreasing speed leveling off at 20 h, and it may be further reduced as the time was extended.
Thus, in order to optimize the selection of asphalt materials, the effect of moisture on
asphalt durability should be taken into account in the construction of asphalt roads in areas
with abundant rainfall, or coastal regions.
3.2.3. Self-Healing Properties

Figure 7 shows the normalized complex modulus values of asphalt as a function of time under different working conditions. The complex moduli of different asphalts were normalized using the initial modulus value $G^*_a$ before healing to eliminate differences between repeated tests. The solid black square represented the variation value of normalized complex modulus before healing. The solid red circle represents the variation value of normalized complex modulus after a 10 min interval. It can be observed that the overall complex asphalt modulus continued to decrease with increasing loading. The decrease tended to be fast at the beginning and then leveled off before being fast again. The increasing degree of asphalt aging led to a rise in the initial complex modulus, but the decrease of complex modulus was hardly affected. The more serious the asphalt aging was, the fewer times the asphalt could be subjected to pre-shear stresses before healing.

By comparing the property of asphalt binders before and after healing, researchers found that the ratio of modulus before and after healing can better assess the self-healing performance of different types of asphalt [34,35]. In this study, the self-healing property of asphalt during aging was assessed using the complex modulus healing ratio with reference to previous studies.

$$HI = \frac{G^*_a}{G^*_b} \times 100\%$$  \hspace{1cm} (7)

where, $HI$ is the self-healing property of asphalt, $G^*_a$ is the initial value of the complex modulus of asphalt before healing, $G^*_b$ is the initial value of the complex modulus of asphalt after healing.
Figure 7. Normalised complex modulus of asphalt versus time under different working conditions: (a) OA; (b) PA0−20; (c) PA5−15; (d) PA10−10; (e) PA15−5; (f) PA20−0.

Figure 8 shows the variation of the self-healing index of the asphalt under different working conditions. Apparently, the self-healing properties of the asphalt were weakened owing to thermal-oxidative aging and will be further exacerbated with the addition of moisture. With increasing time of moisture effect, the asphalt self-healing diminished gradually. For example, the HI of OA asphalt binder was 85%, but after 20 h of aging with anhydrous PAV, the HI dropped to 80.9%, while with 20 h of aging with water PAV, the HI dropped to 75.9%. It indicated that moisture had a significant effect on the self-healing properties of asphalt during aging. Molecular diffusion theory suggested that the self-healing process of asphalt can be viewed as five successive stages of surface rearrangement, surface proximity, wetting, diffusion and randomization [36,37]. In the period of surface proximity, the flow of asphalt colloids can occur after the molecular segment absorbed enough thermal energy to overcome the energy barrier [38,39], so as to realize partial mechanical contact at the cracked surface [40]. The asphalt interfacial wetting and molecular diffusion capabilities were closely related to the mobility of asphalt molecules. In terms of molecular tests in this study, under the coupling of moisture, heat and oxygen, the saturates and aromatics had decreasing content due to volatilization and polymerization, but there was an increase in the content of heavy components (asphaltenes and partial oxides) and a decrease in the content of asphalt colloidal dispersion medium. Thus, the viscous activation energy increased, which required greater heat absorption to overcome the idle state and caused a reduction of mobility. In that sense, it slowed down the surface proximity, wetting and diffusion speed, thereby reducing the self-healing capacity.
3.3. Grey Correlation Analysis of Molecular Components and Rheological Properties

Based on the above analysis, there existed a certain regularity in the chemical components and rheological properties of asphalt during aging. Concerning existing studies, the grey relation theory [41,42] was introduced in this study to analyze the molecular rheological properties. The grey relation theory can be used to analyze data based on a small sample and poor information and to describe the relationship between each factor and the system development in terms of degree. The degree of influence was greater with a higher correlation. The basic procedures of the grey relation analysis were as follows:

(i) Establish reference sequence $X_0^*$ and comparison sequence $X_i^*$

Consider content to be analyzed as a reference sequence:

$$X_0^* = [x_0^*(1), x_0^*(2), \cdots x_0^*(n)]; k = 1, 2, \cdots, n.$$  \hspace{1cm} (8)

Consider content to be compared as a comparison sequence:

$$X_i^* = [x_i^*(1), x_i^*(2), \cdots x_i^*(n)]; k = 1, 2, \cdots, n.$$  \hspace{1cm} (9)

(ii) Nondimensionalize reference sequence and comparison sequence.

The dimensionless reference sequence and comparison sequence were obtained by dividing each value in the sequence by the mean of that sequence.

$$x_i(k) = \frac{x_i^*(i)}{X_i^*}$$  \hspace{1cm} (10)

where $X_i^*$ is the mean of each sequence.

The dimensionless reference sequence is: $X_0 = [x_0(1), x_0(2), \cdots x_0(n)];$

The dimensionless comparison sequence is: $X_i = [x_i(1), x_i(2), \cdots x_i(n)];$

(iii) Calculation difference sequence

$$\Delta_i(k) = |x_0(k) - x_i(k)|$$  \hspace{1cm} (11)

The absolute value of the 2 sequences at moment k is obtained through calculation $\Delta_i = [\Delta_i(1), \Delta_i(2), \cdots \Delta_i(n)].$
(iv) Determine the maximum and minimum value of the two extreme differences

\[ \lambda_{0i}(k) = \frac{\Delta_{\text{min}} + \alpha \Delta_{\text{max}}}{\Delta_i(k) + \alpha \Delta_{\text{max}}} \]  

(12)

(v) Calculate relationship coefficients \( \lambda_{0i}(k) \)

\[ \lambda_{0i}(k) = \frac{\Delta_{\text{min}} + \alpha \Delta_{\text{max}}}{\Delta_i(k) + \alpha \Delta_{\text{max}}} \]  

(13)

where, \( \alpha \) is the discrimination coefficient, which is generally taken as 0.5.

(vi) Calculate the grey relational degree \( \lambda_{0i} \)

\[ \lambda_{0i} = \frac{1}{n} \sum_{k=1}^{n} \lambda_{0i}(k) \]  

(14)

where, \( \lambda_{0i} \) is the correlation degree between the reference sequence and the comparison sequence, and \( n \) is the length of the comparison sequence.

In this study, the correlation degree between molecular components and rheological properties of SBS-modified asphalt after long-term aging was calculated concerning Equations (8)–(14) by taking the viscous activation energy \( E \), fatigue life \( N_f \) and self-healing index \( HI \) of SBS-modified asphalt as reference sequences, and the resins, asphaltenes, aromatics, saturates, \( CIi, LMS \) content, \( MMS \) content and \( SMS \) content of asphalt as comparative sequences. The results were shown in Figure 9.

![Figure 9. Correlation degree between molecular components and rheological properties of SBS-modified asphalt after long-term aging under the influence of moisture.](image)

As can be observed from Figure 9, the correlation between self-healing performance and the dispersion medium (consisting of saturates, aromatics and resins, mostly with \( MMS \) and \( SMS \)) was the highest, averaging above 0.9. Then it was followed by the correlation between fatigue property and the dispersion medium, all greater than 0.8. The correlation between viscous activation energy and the dispersion medium was between 0.65 and 0.75, indicating a close relationship between the dispersion medium, mobility, self-healing property and fatigue property. Compared to the parameters of the other five molecular components, although the correlation among the \( LMS \) and \( CIi \) of asphalt, asphaltenes and...
the rheological properties of asphalt decreased, it was kept between 0.6 and 0.7. The grey relation theory suggested that the correlation was considered prominent if the correlation between two indicators is greater than 0.6 [43]. Based on the test results, the correlation between parameters of eight molecular components and three asphalt rheological indicators was greater than 0.6. It indicated that the molecular components of SBS-modified asphalt still maintained a significant correlation with its rheological properties during the PAV aging process under the influence of moisture.

4. Aging Mechanisms Discussion

At present, very few studies have been reported on the possible physical or chemical reactions between moisture and bitumen. Researchers have conducted some examination of functional groups, molecular weight, microstructure, solubility and other indicators based on available test techniques, which is expected to provide a preliminary understanding of the link between moisture and bitumen oxidation. Here, this paper discusses the long-term aging mechanism of bitumen under the influence of moisture based on the above-mentioned experimental results and also in conjunction with existing research results.

Most studies, with the exception of a few, have shown that the presence of moisture accelerates the aging process of asphalt binders. Asphaltenes, as one of the four components of bitumen, are thought to reduce the asphalt-water interfacial tension, while they contain more polar groups such as -OH, -NH2 and -COOH [9]. These groups induce asphaltenes to move towards the asphalt-water interface, thus enriching the interface to form a strong structural film, and this structural mold will show significant hardening over time. Under the combined action of moisture, thermal oxygen and oxygen, bitumen reacts with both water and oxygen, especially under oxygen-rich conditions, resulting in polar bonded substances such as C-O. These polar bonds are susceptible to further degradation under the influence of water or thermal oxygen, for example, carbonyl substances in bitumen can be further oxidized to carboxylic acids by the reaction formula in Figure 10a [44], and when moisture vapor in the air occupies the space that would otherwise be oxygen, oxygen is in short supply, which may then lead to reduced free radical formation and allow the growth of free radical chains and disproportionation reactions to take place. At the same time, a large number of double bonds in the SBS modifier, which undergoes ionic hydration reactions under moist heat conditions (Figure 10b), results in an increase in polar groups [44,45]. There is a corresponding increase in some functional groups associated with aging, such as aromatics and methylenes [46].

Figure 10. The equation for the oxidation reaction of bitumen in a moisture environment: (a) Oxidation reaction of carbonyl substances; (b) Ionic hydration reactions.
It is commonly believed that, the deeper the bitumen is aged, the higher the content of large molecular weight substances it contains. As can be seen from the results of the tests in this paper, the asphalt $LMS$ and $MMS$ values increase with increasing time of moisture action, indicating an increase in the content of medium and large molecular weight species in the asphalt, which laterally verifies that the presence of moisture exacerbates the aging of the asphalt. Another study also showed that the medium and smaller molecular weight species of the matrix bitumen decreased significantly under moist PAV aging conditions [9].

Some researchers have used Atomic Force Microscopy to examine the microscopic morphology of bitumen after water-soluble immersion at different temperatures and found “nano-bumps” in the “bee” structure on the surface of the bitumen, which they attribute to the complex interaction between moisture, waxes and surfactants in the bitumen, together with the enrichment of polar molecular concentrations on the surface of the bitumen [5], but there is no definite explanation as to how moisture induces chemical reactions within the bitumen and causes changes in the properties of the asphalt mixture [47].

Some useful information can be obtained by testing the properties of the residual solution after reaction with bitumen. The literature [48] uses UV radiation coupled with an aqueous solution to age asphalt binders. The organic carbon analysis test showed that no organic components were found in the solution before aging, but some organic components appeared in the solution after aging, indicating that some organic components in the asphalt can be dissolved or leached into the solution under the effect of coupled aging. In addition, the PH test showed that the PH value of the residual solution became smaller after aging, which indicates that the components should contain acidic components.

The results of this paper indicated that the resin content of bitumen decreases with increasing moisture action time. In addition to the fact that the resins have more polar aromatic compounds, making them more susceptible to oxidation [49], the dissolution of hydrophilic groups in the resins may also be a potential factor in the decrease in resin content. In conclusion, the presence of moisture changes the aging environment of bitumen, making it more complex. More research needs to be invested in how moisture, oxygen and heat alter the chemical and physical reactions of bitumen and affect its chemical properties, microscopic morphology and performance.

5. Conclusions

In this study, the long-term aging characteristics of SBS-modified asphalt under the influence of moisture were analyzed qualitatively and quantitatively from the chemical molecular and theological perspectives. Conclusions were drawn as follows:

(1) During long-term aging, the saturate and aromatic content of asphalt decreased and the content of resins and asphaltenes increased. However, the resin content exhibited an opposite trend with the addition of moisture, which gradually decreased with time. This finding mainly boiled down to the aggravation and complication of the aging of the asphalt by moisture and the dissolution of polar or hydrophilic groups in the resins.

(2) The declining mobility undergone by asphalt during aqueous PAV aging can be explained by variations in the molecular components. The four-component test showed that the increased asphaltenes content of the aqueous PAV-aged asphalt was accompanied by increasing $CIII$ compared to the anhydrous PAV-aged asphalt. This was consistent with the trend in $LMS$ content obtained from the GPC test. The increasing macromolecular substances should account for the observed decrease in mobility in the asphalt.

(3) Moisture weakened the fatigue and self-healing properties of asphalt during aging. The fatigue life $N_f$ and self-healing index $HI$ of PA20-0 decreased by 14.7% and 6.2%, respectively, under the influence of moisture compared to the anhydrous PAV-aged asphalt. This was mainly due to the growth of asphalt microcracks under repeated loading caused by the lower content of asphalt dispersion medium, and the retarded surface proximity, wetting and diffusion during the self-healing process.
The calculated results based on the grey relation theory showed that the asphalt molecular components still maintained a significant correlation with their rheological properties during PAV aging under the influence of moisture, with correlations greater than 0.6. The asphalt dispersion medium was found to have a higher correlation with $N_f$ and $H_I$, reaching more than 0.8.

The results of this paper reaffirm that moisture affects the pressure aging process of asphalt and the test results and analysis have contributed to the understanding of how moisture changes the chemical composition of asphalt and thus its macroscopic properties. In future work, more factors should be considered, such as moisture acidity, water alkalinity, moisture content and oxygen pressure. In the meantime, some new validated test methods are yet to be developed to explore the possible reactions between moisture and substances such as waxes and surfactants in asphalt.

**Author Contributions:** Conceptualization, Resources, Supervision, X.L.; Conceptualization, Resources, Writing—review & editing, K.X.; Methodology, Data curation, Formal analysis, Visualization, S.Z.; Writing—review & editing, Funding acquisition, Writing—original draft, Q.Y.; Writing—review & editing, Software, Y.Q. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was supported by National Vocational Education Team Project Research Project of China (Grant No. YB2020070101).

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** The data for this study are included in the article.

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

**References**


24. Tarefder, R.A.; Arisa, I. Molecular dynamic simulations for determining change in thermodynamic properties of asphaltene and resin because of aging. Energy Fuels 2011, 25, 2211–2222. [CrossRef]


30. Qin, Q.; Schabron, J.F.; Boysen, R.B.; Farrar, M.J. Field aging effect on chemistry and rheology of asphalt binders and rheological predictions for field aging. Fuel 2014, 121, 86–94. [CrossRef]


