buildings

MDPI

Article

The Properties of Sodium-Hypochlorite-Activated Crumb Rubber and the Influence of Aging on the Rheological Properties of Activated Asphalt Rubber

Peng Zhang [1], Dongna Li [2], Bo Li [1,*], Yongning Wang [1,3], Yongzheng Wei [4], Binghui Wang [1] and Binlin Zhang [1]

[1] National and Provincial Joint Engineering Laboratory of Road & Bridge Disaster Prevention and Control, Lanzhou Jiaotong University, Lanzhou 730070, China
[2] School of Mechanical Engineering, Lanzhou Jiaotong University, Lanzhou 730070, China
[3] Gansu Province Transportation Planning, Survey & Designing Institute Co., Ltd., Lanzhou 730030, China
[4] China Communications Construction Group Co., Ltd., Beijing 100088, China
* Correspondence: libo@mail.lzjtu.cn

Abstract: Asphalt rubber shows good road performance. However, the compatibility and aging problems of asphalt rubber limit its application. The improvement of the solubility of crumb rubber in asphalt was investigated in this research, and the mechanism of its aging effect on the rheological properties of activated asphalt rubber was studied. First, the crumb rubber was activated by using a sodium hypochlorite (NaClO) solution, and the pore characteristics and microstructure of the activated crumb rubber were analyzed. Second, the influence of the crumb rubber's activation characteristics on the rheological properties of the asphalt rubber before and after aging was analyzed. Finally, the aging mechanism of the activated asphalt rubber was revealed at a microscopic level. The results showed that with the increase in the activation degree, the pore characteristics of the crumb rubber decreased first and then increased. The surface stacking structure of the crumb rubber increased, and a dense gel film gradually formed. The asphalt rubber prepared by the activated crumb rubber had better rheological properties and had a more significant effect under higher stress conditions. This may have been due to the activation of the crumb-rubber surface, forming oxygen-containing functional groups, which, in turn, increased the combination of the crumb rubber and the asphalt. In addition, the activation degree and aging effect of crumb rubber can reduce the large-particle-size molecule (LMS) content of activated asphalt rubber. There is a significant correlation between LMS content and rheological properties, and LMS content can be used to predict the rheological properties of asphalt rubber.

Keywords: asphalt rubber; activated crumb rubber; short-term aging; rheological properties; micro characterization

check for updates

Citation: Zhang, P.; Li, D.; Li, B.; Wang, Y.; Wei, Y.; Wang, B.; Zhang, B. The Properties of Sodium-Hypochlorite-Activated Crumb Rubber and the Influence of Aging on the Rheological Properties of Activated Asphalt Rubber. *Buildings* **2023**, *13*, 712. https://doi.org/10.3390/buildings13030712

Academic Editors: Romain Balieu, Liang He, Augusto Cannone Falchetto and Jiqing Zhu

Received: 12 January 2023
Revised: 23 February 2023
Accepted: 2 March 2023
Published: 8 March 2023

1. Introduction

Tire production has increased year by year with the development of the vehicle industry, and a large number of abandoned tires have also been produced [1]. In recent years, with the strengthening of people's environmental awareness, the processing of waste tires into crumb rubber for other industries has become a common method to deal with 'black garbage' [2]. The application of waste crumb rubber as a green and environmentally friendly material in road engineering can not only encourage the utilization of solid waste resources and protect the environment, but it can also save resources and reduce costs. At the same time, asphalt rubber can significantly improve pavement-rutting resistance, high-temperature performance, reflective cracking, and fatigue cracking, thereby improving pavement durability. The antioxidants, such as carbon black, contained in tires can improve the anti-aging ability of pavement, which improves the resistance to fatigue of asphalt pavement [3,4]. Asphalt rubber pavements can reduce road maintenance, improve road roughness, and reduce road noise, which are important to high-quality road development.

However, the disadvantages of asphalt rubber, such as high viscosity, poor workability, easy segregation, and poor storage ability at high temperatures, have become a bottleneck in the promotion and application of asphalt rubber [5]. Crumb rubber is one of the main components of asphalt rubber. Crumb rubber cannot fully react with asphalt, since it is a non-polar substance with limited surface activity; hence, it is only used as a filler in asphalt. Therefore, enhancing the compatibility of crumb rubber with asphalt by activating crumb rubber has become a crucial technical challenge to improve the road performance of asphalt rubber [6]. Currently, crumb rubber is often pre-treated by microwave and γ-ray radiation. Prepared asphalt rubber has better high-temperature stability and durability than untreated rubber [7,8]. Zhou and Yang [9,10] analyzed the activation mechanism of microwave-activated crumb rubber. They believed that microwaves destroyed the internal chemical bonds of crumb rubber, making it easier for crumb rubber to form a new chemical crosslinking structure with asphalt. At the same time, chemical activation has good application prospects because of its high reaction efficiency and low energy consumption. Studies have shown that H_2O_2, the silane-coupling agent, and ethylene vinyl acetate can increase the solubility of crumb rubber in asphalt [11–13]. Ren [14,15] analyzed the influence of the expansion–degradation degree of crumb rubber in asphalt on the chemical and rheological properties of rubber asphalt, and considered that the degradation of crumb rubber increased the formation of free hydroxide groups. In an effort to create asphalt rubber with better performance, researchers have activated crumb rubber in a variety of methods. Most researchers, however, concentrate on testing asphalt rubber and pay little attention to how activation degree affects the physicochemical characteristics of crumb rubber. In addition, the correlation between the rheological and micro molecules of asphalt rubber before and after aging and the mechanism of performance change also needs to be further investigated.

As a polymer material, asphalt is prone to various forms of aging under the combined effects of external factors, such as heat, oxygen, light, and water. Asphalt rubber is constantly at high temperatures during production and construction. It is susceptible to short-term aging in thermal-oxygen environments, which affects the road performance of asphalt-rubber pavements. Yin [16] simulated the physical and rheological tests of rubber asphalt before and after thermal aging, and established an anti-aging-mechanism model. Zhang et al. [17,18] studied the aging behavior of rubber asphalt under multiple environmental factors and found that the coupling effect of acid and ultraviolet radiation had the most significant influence on the aging of the rubber asphalt. Liu [19] prepared a composite modified rubber and proposed a secondary reaction method to improve its performance after short-term aging. Chen [20] analyzed the aging characteristics of rubber asphalt and classified the ageing stages of the rubber asphalt. The research on the thermal oxidative aging process and aging mechanism of activated asphalt rubber is mainly conducted in terms of macroscopic properties. There are few studies on the interpretation of the microstructure of aged asphalt rubber. In order to ensure the quality requirements of asphalt-rubber pavements in service, it is necessary to analyze the aging characteristics and aging mechanism of activated asphalt rubber.

In this study, a NaClO solution of four concentrations was used to activate crumb rubber, and the treated crumb rubber was used to prepare the asphalt rubber. First, the pore characteristics and microstructure of the four activated crumb rubbers were studied using the gas-adsorption test and the SEM test. Second, crumb rubber with different activation levels was used to prepare asphalt rubber. The viscosity test and the DSR test were used to compare the rheological characteristics of the asphalt rubber before and after ageing. Finally, the influence of aging on the changes in the characteristic functional groups and molecular weight of the asphalt rubber was analyzed by infrared spectroscopy and GPC test. The correlation between the rheological characteristics and the molecular weight of the asphalt rubber was determined by using a statistical analysis, and a reasonable explanation for the macroscopic rheological behaviors of the asphalt rubber was provided from a micro-analytical perspective. This study analyzes the variation pattern of the aging rheological properties of activated-crumb-rubber-modified rubber asphalt, which provides a research basis for the aging resistance of an activated-crumb-rubber-modified rubber-asphalt mixture in the mixing and transport phases.

2. Materials and Methods

2.1. Materials

The asphalt used to prepare asphalt rubber was produced by SK asphalt plant (Tianjin, China). The primary indicators are shown in Table 1 [21].

Table 1. The performance of virgin asphalt.

Performance	Unit	Test Result	Specification Limits
Penetration (100 g, 5 s, 25 °C)	0.1 mm	86.8	80–100
Softening point	°C	45.5	≥42
Ductility (15 °C, 5 cm/min)	cm	>100	≥100
60 °C dynamic viscosity	Pa·s	145	≥140
RTFOT 163 °C, 85 min			
Mass loss	%	−0.06	≤±0.8
Penetration ratio	%	68	≥54
Ductility (10 °C)	cm	8.8	≥6

The crumb rubber of 425 µm used in the study was provided by Rongtai Rubber Products Co., Ltd. (Lanzhou, China). Table 2 shows the specific technical indicators of crumb rubber, which meet the specification requirements [22].

Table 2. Technical indicators of crumb rubber.

Test Properties	Indicators	Result
Bulk density/(kg/m^3)	260–460	303.2
Moisture content/%	<1	0.0
Metal content/%	<0.03	0.007
Fiber content/%	<1	0.062
Ash content/%	≤8	7.1
Acetone extract/%	≤22	7.0
Carbon-black content/%	≥28	31
Rubber hydrocarbon content/%	≥42	50

2.2. Sample Preparation

The activation process of crumb rubber is shown in Figure 1. The dried crumb rubber is mixed with NaClO solution (available chlorine content ≥6%) at the room temperature in a certain mass ratio. After stirring evenly and conditioning at 20 °C for 24 h, the crumb rubber was filtered out and dried in an oven to a constant weight. The appearance of crumb rubber activated by NaClO solution is shown in Figure 2. Table 3 shows the ratio of NaClO solution to crumb rubber and the sample number.

Figure 2 shows the macroscopic morphology of crumb rubber with different activation degrees. Figure 2a shows the inactivated crumb rubber and Figure 2b shows the activated crumb rubber with amass ratio of NaClO solution to crumb rubber of 1.5:1. It can be observed in Figure 2 that the deactivated crumb rubber took the form of loose granules. After activation by NaClO solution, the crumb rubber became hardened and agglomerated.

The preparation of asphalt rubber is shown in Figure 3. After heating virgin asphalt in the oven to the flow state, a beaker with 500 g asphalt was placed into the constant-temperature oil bath pot to continue heating. When the asphalt reached a temperature of 170 °C, the preheated 100 g of crumb rubber with different activation degrees was slowly added to the oven. The mixture was stirred at 2000 r/min for 180 min [23]. The sample number of asphalt rubber is listed in Table 3. In addition, the rubber asphalt was aged through the rolling thin-film-oven test (RTFOT), according to the standard test method [24].

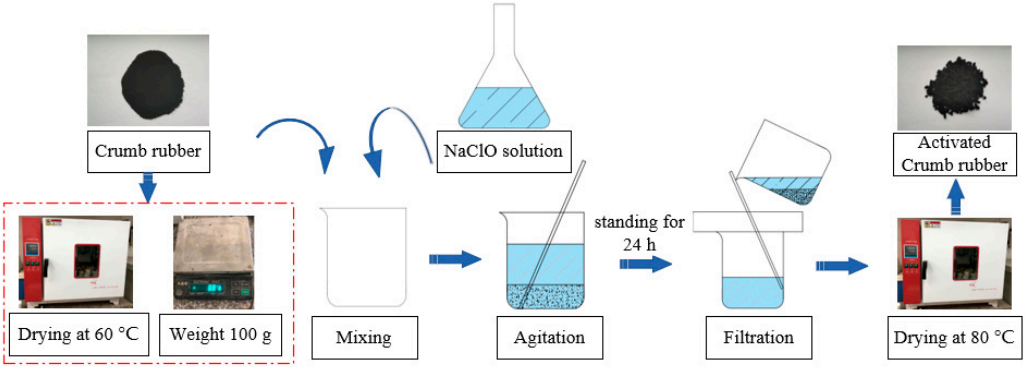


Figure 1. The activation process of crumb rubber.

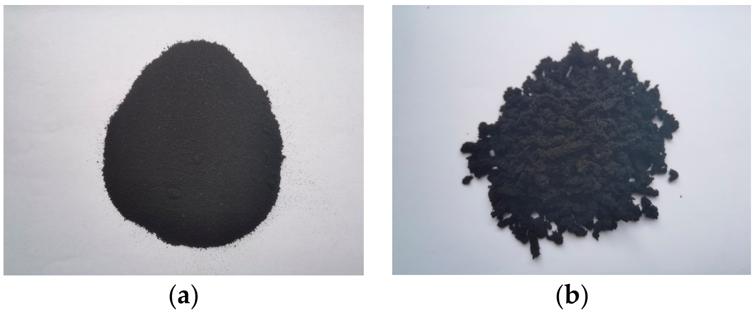


Figure 2. Macroscopic morphology of crumb-rubber activation. (**a**) W0; (**b**) N3.

Table 3. The ratio of NaClO solution to crumb rubber.

Activation Methods	Inactivated	NaClO Solution Activation		
Crumb-rubber sample	W0	N1	N2	N3
Asphalt-rubber sample	W0′	N1′	N2′	N3′
Mass ratio	0:1	0.5:1	1:1	1.5:1

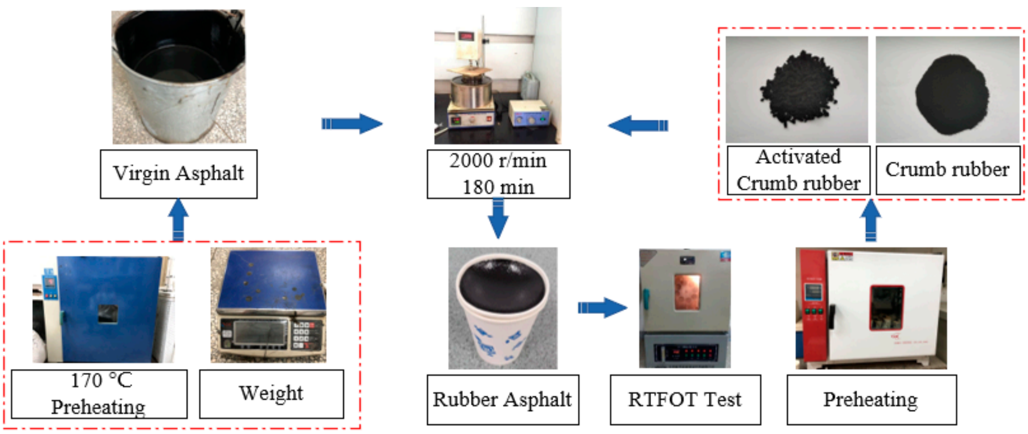


Figure 3. Preparation of asphalt rubber.

2.3. Test Method

The test design and method are shown in Figure 4. A minimum of three replicate experiments were carried out for each group to minimize human error. The average value is calculated as the final result.

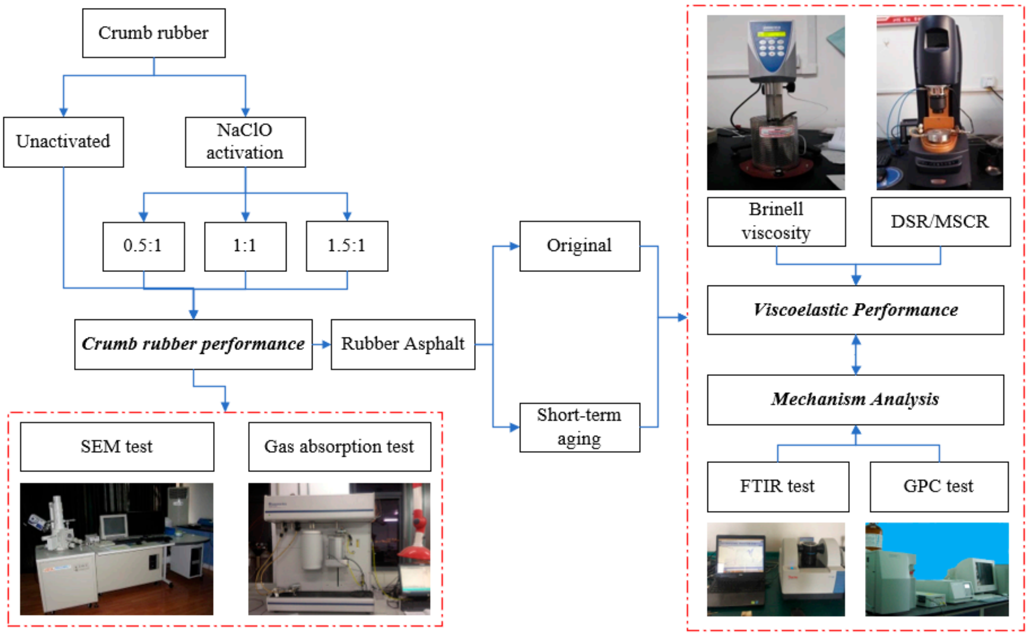


Figure 4. Test design and test method.

The adsorption-isotherm data of crumb rubber (ASTM D5604-96 (2012)) [25] were obtained by nitrogen-adsorption method using the ASAP2020 gas-adsorption instrument. The surface area of crumb rubber was calculated by BET (Brunauer, Emmett and Teller) model [26], and the pore-size distribution and pore volume of crumb rubber were calculated by the Kelvin pore model [27]. The microstructure of asphalt rubber particles was characterized by JSM-5600LV (Japan Electronics Co., Ltd. (JEOL), Tokyo, Japan) scanning electron microscope.

The viscosity of asphalt rubber was tested by Brookfield DV-2T (AMETEK Company Group, Berwyn, MA, USA) rotary viscometer [24]. According to the specification requirements of rubber asphalt [22], the viscosity-test data were adjusted, and the viscosity of rubber asphalt was finally obtained when the torque was 50%.

The AR1500ex DSR (Eurasia Star Technology Co., Ltd. Beijing, China) was used to test the rheological properties of asphalt rubber. The temperature-sweep test was conducted in a temperature range of 58–82 °C with a frequency of 10 rad/s. The frequency-sweep test was applied from 0.1 to 100 rad/s, and the test temperatures were 58 °C, 64 °C, and 70 °C, respectively [28,29].

In the multiple stress creep recovery (MSCR) test, the temperature was 70 °C [30], the loading stresses were 0.1 Pa and 3.2 Pa, and the creep-recovery cycles were calculated for 1 s and 9 s. A total of 10 cycles were calculated. The average strain-recovery rate (R) and average unrecoverable creep compliance (J_{nr}) were used as the primary evaluation indices in the MSCR test, which were calculated as follows:

$$R = \frac{\varepsilon_1 - \varepsilon_{10}}{\varepsilon_1} \times 100\% \tag{1}$$

$$J_{nr} = \frac{\varepsilon_{10}}{\delta} \tag{2}$$

where ε_1 is the instantaneous shear strain, ε_{10} is the unrecoverable shear strain, and δ is the phase angle of the sample.

In the microscopic testing of asphalt rubber, the FTIR test was carried out using the Thermos Nicolle spectrometer [31]. In addition, the molecular weight of asphalt rubber was determined by Waters 1515 gel-permeation chromatograph. Tetrahydrofuran was used as the solvent [32].

3. Results

3.1. Characteristics of Activated Crumb Rubber

After the activation by the chemical reagent, the physicochemical properties of crumb rubber change significantly, which affects the macroscopic performance of asphalt rubber. In this section, the changes in the pore structure and surface microstructure of the crumb rubber after activation by a NaClO solution of multiple concentrations were studied. The influences of chemical activation at different levels on the physicochemical properties of the crumb rubber were compared and interpretated.

3.1.1. Pore Characteristics

The pore-size distribution of the crumb rubber with different activation levels is shown in Figure 5. The activated crumb rubber had a larger pore volume than the W0. The W0 and N2 had a V-shaped pore-size distribution, and the pore volume decreased rapidly after reaching the peak value. The pore volume increased when the pore size was 30 nm, after which it decreased slowly, at around 200 nm. The N1 and N3 had a U-shaped distribution. The pore volume decreased after the peak, and began to rise slowly until the pore size reached 90 nm. In addition, the peak fluctuations were concentrated in the 0–15-nanometer range. The four different types of crumb rubber had peaked at pore sizes of 2–3 nm, with sub-peaks appearing in the range of 3–5 nm. In the 5–15 nanometer range, one peak appeared for W0 and N3 and two peaks appeared for N1 and N2. This suggests that the internal pore sizes of the four crumb rubber species were mainly concentrated in the 0–15 nanometer range, with a maximum ratio of 2–3 nm.

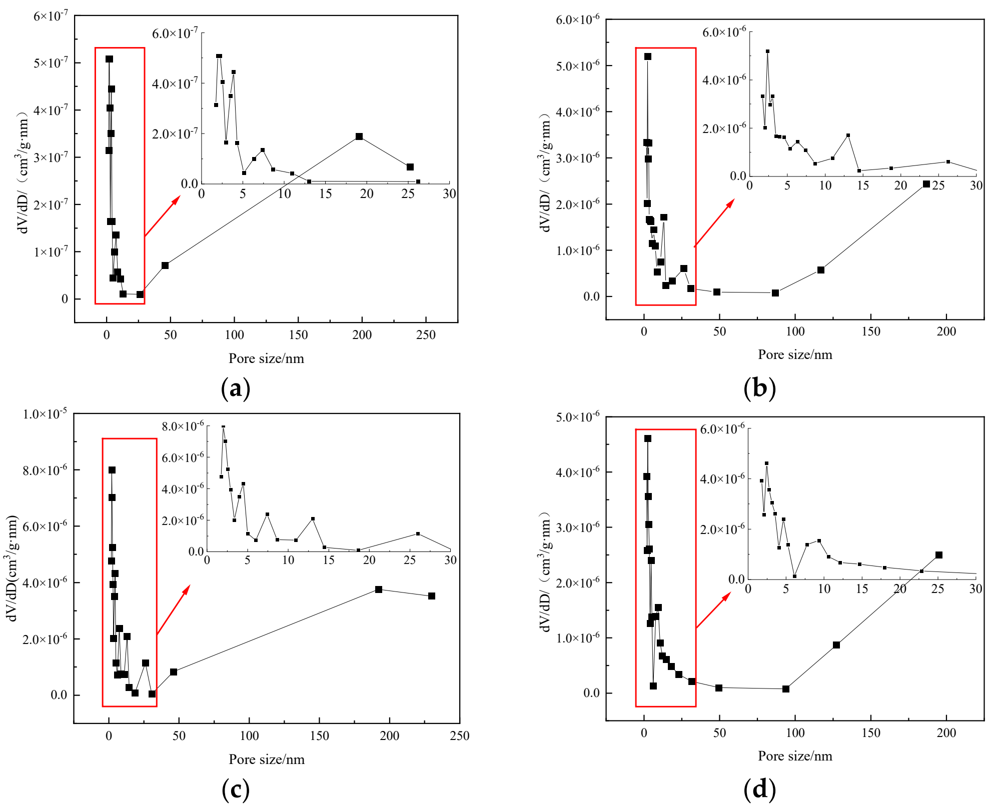


Figure 5. Pore-size distribution. (**a**) W0; (**b**) N1; (**c**) N2; (**d**) N3.

Crumb rubber is usually classified by pore size, as microporous (<2 nm), mesoporous (2–50 nm), and macroporous (>50 nm) [33]. As shown in Figure 6, mesopores made up the majority of the pore area, while macropores comprised the majority of the pore volume in the crumb rubber. It can be seen from the diagram that the N2 had no noticeable effect on the porosity of the crumb rubber compared with the untreated crumb rubber. Regarding the pore-volume characteristics, the N1 and N3 reduced the macropore volume of the crumb rubber and increased the volume ratio of the mesopores and micropores to varying degrees. In terms of the pore-area characteristics, the N1 and N3 reduced the microporous area of the crumb rubber and increased the area ratio of the mesopores and macropores.

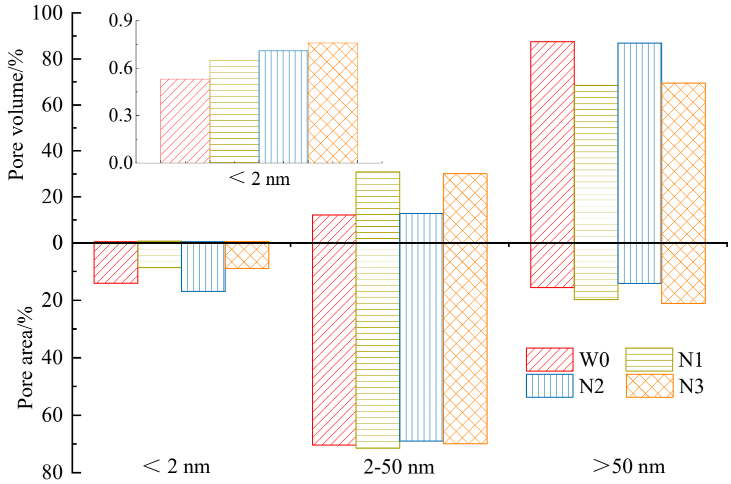


Figure 6. Crumb-rubber void volume and pore-area ratio.

Figure 7 shows the relationship between the cumulative pore volume and cumulative pore area of the crumb rubber and the activation level of the crumb rubber. It can be seen that the two voids' indices had similar trends. With the increase in the activation level, they both exhibited a trend of initially reducing and then increasing. When the crumb rubber had an activation degree of N1, the indices were reduced to the minimum value. These two indicators displayed an upward trend when the degree of activation was larger than N1, rising gradually to N2 and then quickly to N3. The indices rose to above W0 and reached their highest value when the activation degree was N3.

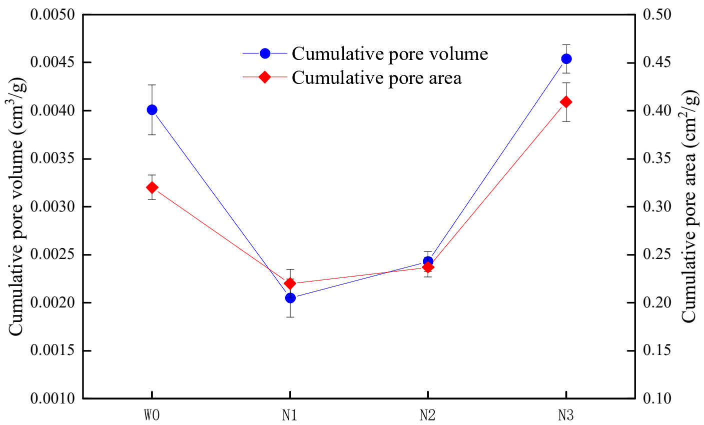


Figure 7. The cumulative void volume and pore area of crumb rubber.

3.1.2. Microstructure

The microstructure of the crumb rubber treated with NaClO solution with various concentrations is shown in Figure 8. The surface of the crumb rubber without NaClO activation was relatively smooth; the particles were plate-like and the gap was large. After the NaClO activation, the surface of the powder became rough, and there were fine particles and fragmented laminated structures. This may have been due to the oxidation corrosion effect of the NaClO solution on the crumb rubber. With the increase in NaClO concentration, the fine particles and fragmentary stacking structure on the crumb-rubber surface gradually increased, covering the whole surface and forming a dense gel membrane. The excessive NaClO solution significantly enhanced the adhesion of the fine particles and laminated structure, and enhanced the surface polarity and surface properties of crumb rubber [34]. The change in microscopic morphology is not only the main factor in the variation of pore parameters, but also the microscopic feature of crumb-rubber hardening and agglomeration.

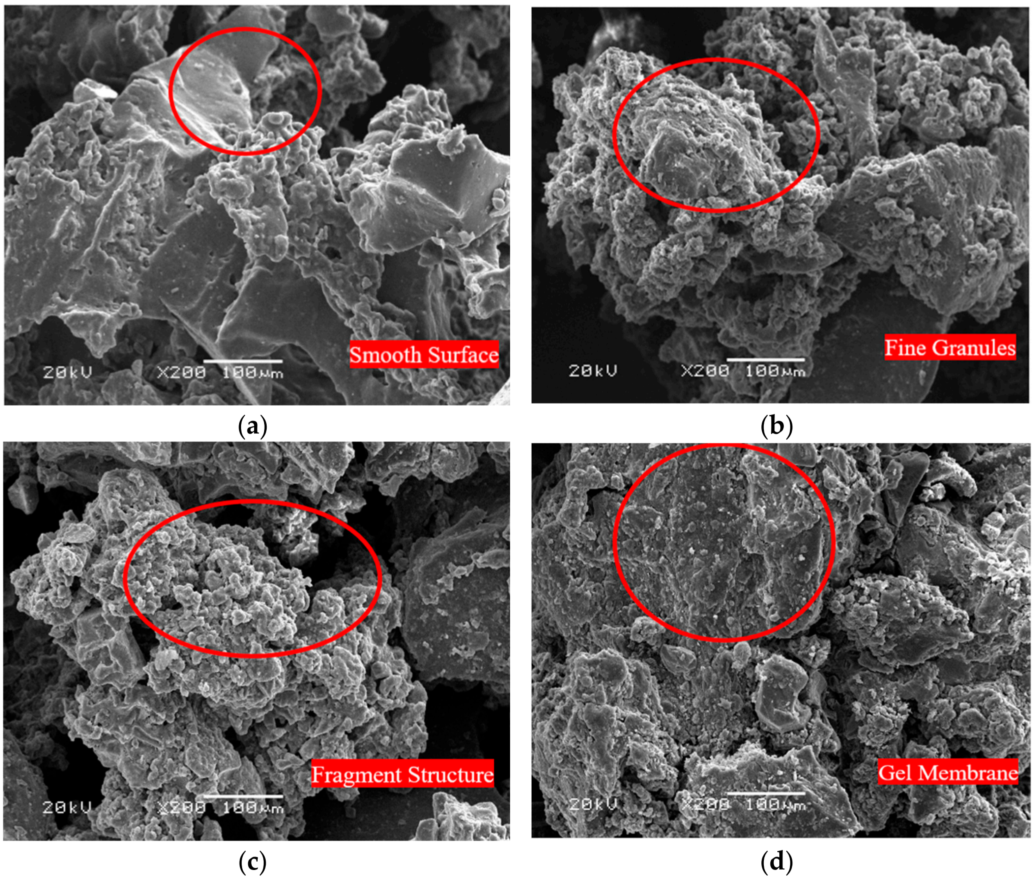


Figure 8. Microstructure of crumb rubber. (**a**) W0; (**b**) N1; (**c**) N2; (**d**) N3.

3.2. Rheological Properties of Crumb Rubber Modified Asphalt

The performance of the asphalt rubber produced by the activated crumb rubber changed dramatically due to the change in its surface morphology. At the same time, thermal oxygen and other factors have an unavoidable ageing effect on asphalt throughout the production process. In this section, the effects of aging on the rheological properties of asphalt rubber with different activation degrees are compared based on an analysis using Brinell viscosity, DSR rheology, and a MCSR test.

3.2.1. Brinell Viscosity Test

The Brinell viscosity of the asphalt rubber decreased with the increase in crumb-rubber activation, as shown in Figure 9. This may have been due to the oxidation of the powder surface by the NaClO solution, resulting in the formation of a gel film, which hardened the asphalt rubber and decreased its viscosity. The viscosity of asphalt rubber decreased to varying degrees after short-term aging, with decreases of 46.0%, 49.3%, 43.9%, and 43.2%, respectively. In the preparation of the asphalt rubber, only a weak swelling effect occurred on the crumb-rubber surface. Under thermal oxygen aging, the crumb rubber continued to decompose, and the components absorbed by the crumb rubber in the swelling stage were released. The decrease in asphalt viscosity caused by the crumb-rubber decomposition and asphalt-component release were more significant than the increase in viscosity caused by the volatilization of the light components due to aging.

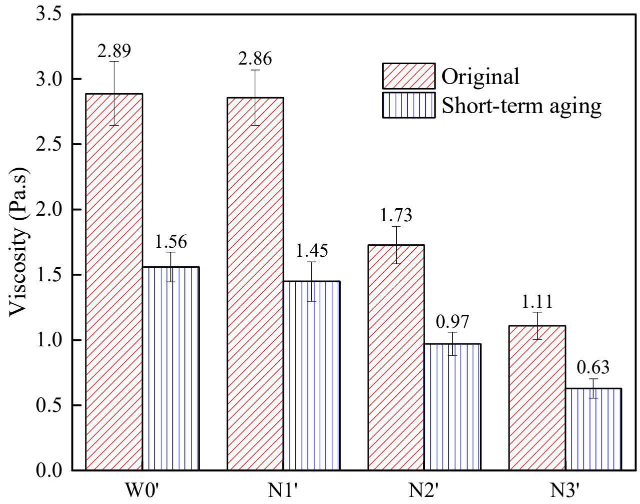


Figure 9. Viscosity-test results.

3.2.2. Temperature-Sweep Test

The phase angle (δ) characterizes the ratio of viscous and elastic components in asphalt. As shown in Figure 10, for the unaged asphalt rubber, the δ of N1′ was positively correlated with temperature, and the δ of N2′ and N3′ was negatively correlated. This shows that the activation degree of the crumb rubber N1 was the demarcation point of the asphalt-rubber phase angle. At the same time, N3′ had the lowest δ, indicating that the treated asphalt rubber exhibited greater elasticity when the crumb-rubber activation degree was high. The activation effect increased the elasticity of the asphalt rubber and reduced its viscosity.

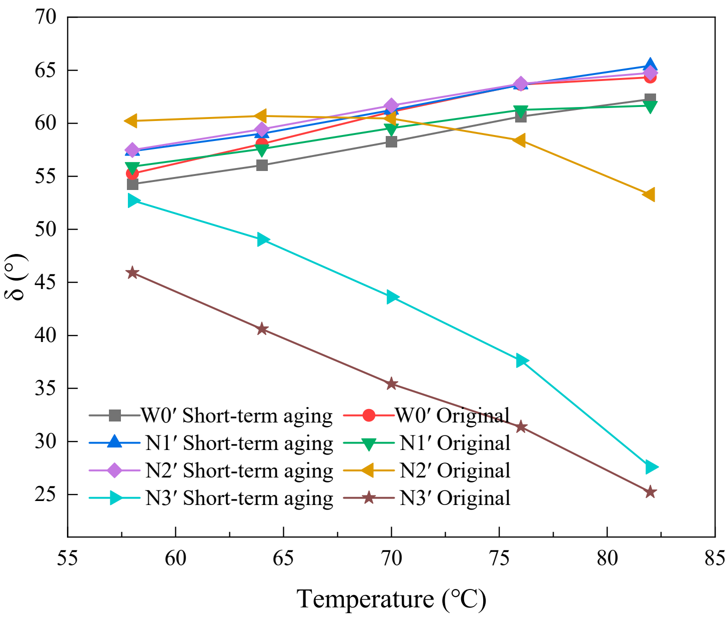


Figure 10. Phase-angle results.

In addition, it was found that the aged asphalt rubber had a similar trend as the unaged asphalt rubber. After aging, the phase angle of the N1′ and N3′ increased, indicating that the aging effect reduced the elasticity of the asphalt rubber and increased its viscosity. The δ of N2′ decreased first and then increased, showing that the higher the temperature, the more significant the aging effect on the viscosity of the asphalt rubber.

The G*/sinδ describes the asphalt's resistance to permanent deformation. The G*/sinδ temperature-sweep curves of asphalt rubber with different activation degrees are shown in Figure 11. With the increase in temperature, the G*/sinδ of the four samples showed a downward trend, indicating that the anti-rutting deformation ability of the asphalt rubber decreased during the heating process. The G*/sinδ values of W0′, N1′, and N2′ were close to one another under different test-temperature conditions. The N3′ had the highest G*/sinδ at each test temperature, which was significantly larger than the other samples, indicating that the activation degree of the crumb rubber had a significant effect on the G*/sinδ of the asphalt rubber. In addition, the G*/sinδ of the activated asphalt rubber decreased after aging, with the most pronounced decrease observed in the N3′ sample. The reason for this may be that the NaClO solution caused the crumb rubber to form a dense gel film, resulting in an insufficient reaction of the asphalt rubber. The hardened and agglomerated crumb rubber of the asphalt rubber decomposed during thermal oxygen aging, reducing the rutting resistance of the activated asphalt rubber.

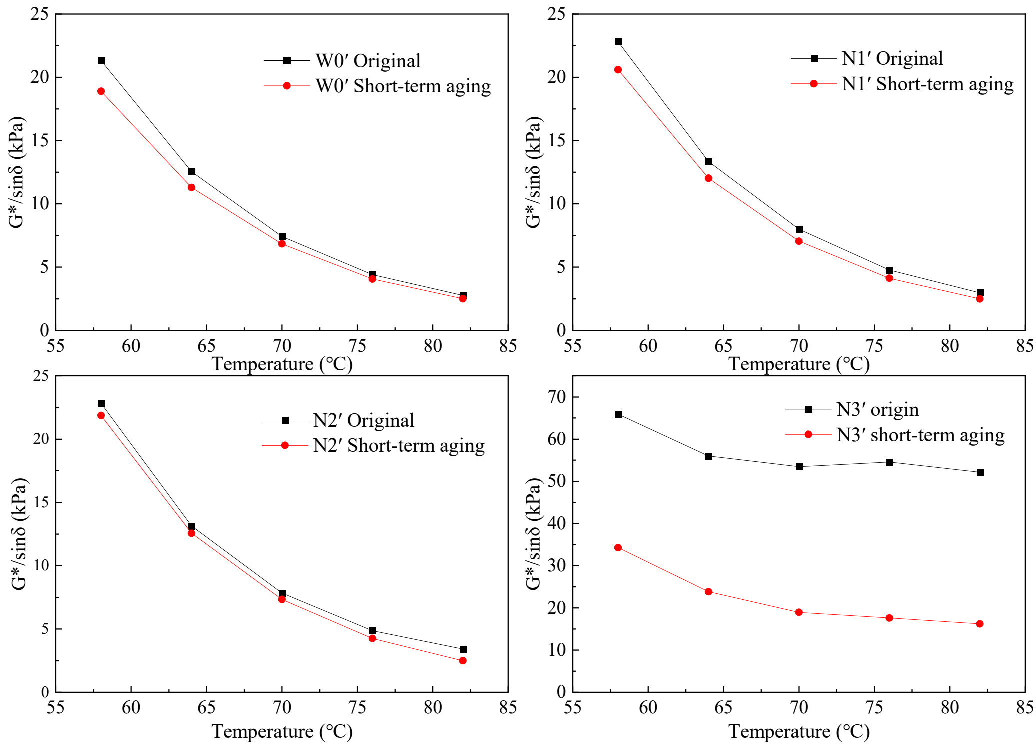


Figure 11. G*/sinδ results.

The complex modulus (G*) characterizes the high temperature-deformation resistance of asphalt. In Figure 12, the complex modulus of the asphalt rubber prepared by four kinds of crumb rubber with different activation degrees had the same changing trend. The higher the test temperature, the smaller the complex modulus. The higher the frequency, the more significant the change in the complex modulus of the asphalt rubber after aging. In addition, the complex modulus decreased after short-term aging. In conclusion, the asphalt rubber samples prepared by the NaClO-solution-activated crumb rubber had higher complex moduli. The higher the degree of activation, the larger the complex modulus under the same conditions.

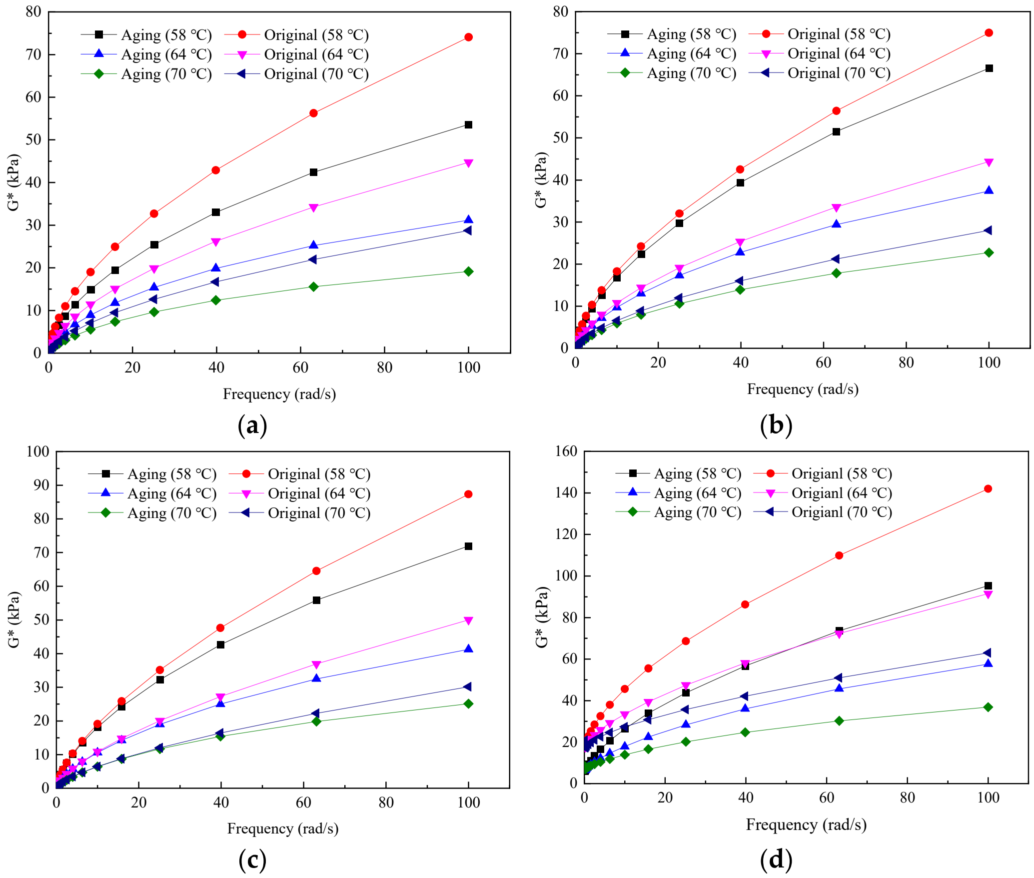


Figure 12. Complex-modulus results. (**a**) W0′; (**b**) N1′; (**c**) N2′; (**d**) N3′.

Further, in order to reveal the variation in the complex modulus of the asphalt rubber under the most unfavorable conditions, the complex modulus with a frequency of 100 rad/s and a temperature of 70 °C was selected. From Figure 13, the G* of the asphalt rubber after aging decreased by 33.4%, 18.9%, 16.7%, and 41.5%, respectively. The complex moduli of the N1′ and N2′ samples were similar. The increase in the initial samples was −2.5% and 4.8% in comparison to W0′, while the increases following short-term ageing were 18.8% and 31.1%, respectively. The N3′ had a significantly higher complex modulus than the W0′. The complex modulus of the N3′ was significantly greater than that of the W0′. The complex moduli before and after aging were 119.0% and 92.4% higher than the W0′, respectively. The N3′ exhibited favorable levels of deformation resistance at high temperature.

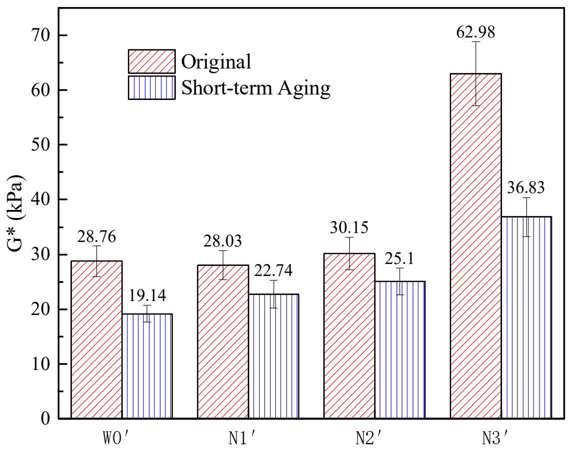


Figure 13. Complex modulus under the most unfavorable conditions.

3.2.3. MSCR Test

Multi-stress creep recovery (MSCR) can reasonably simulate the response relationship between pavement load and deformation. The effect of aging on the performance of asphalt rubber under repeated stress loads is studied in this section [35]. Figure 14 shows that the cumulative strain increased with the increases in the NaClO solution's concentration, increasing by 56%, 60%, and 97%, respectively, over W0′. The reason for this may have been the disintegration of the crumb rubber in the asphalt rubber, which was not fully decomposed and hardened under multi-stress loading, making it less resistant to deformation.

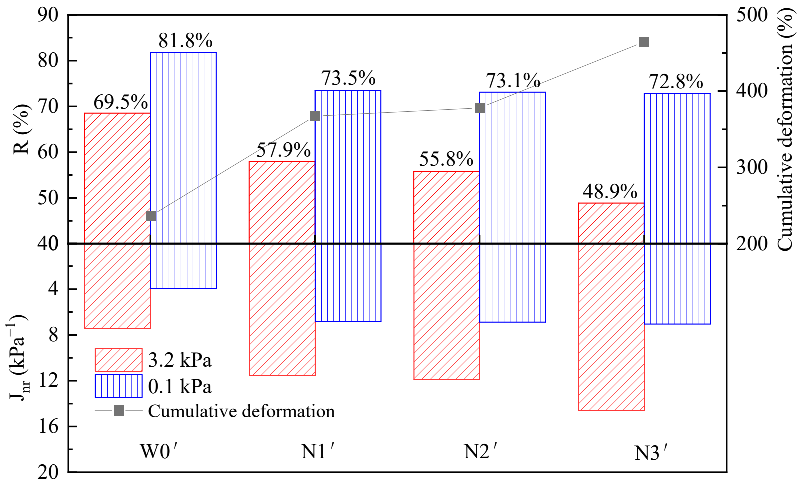


Figure 14. MSCR-test results.

It was also found that the strain-recovery rate of the activated asphalt rubber was consistent with the irreversible creep compliance. When the stress was 0.1 kPa, for instance, the strain-recovery rate of the activated asphalt rubber decreased slightly with the increase in the crumb-rubber activation degree, but it remained at roughly 73%. This shows that under low-stress conditions, the degree of chemical activation had little effect on the strain-recovery rate of the asphalt rubber. The activated asphalt rubber still showed good high-temperature elasticity. The strain-recovery rates of the activated asphalt rubber were 57.9%, 55.8%, and 48.9%, respectively, when the stress was 3.2 kPa. Compared with the inactivated asphalt rubber, the strain-recovery rate decreased by 16.7%, 19.7%, and 29.6%, respectively. It shows that the activation degree of the crumb rubber significantly affected the strain recovery rate of the asphalt rubber under higher-stress conditions.

3.3. Molecular Structure of Activated Asphalt Rubber

The rheological properties of the asphalt rubber prepared by crumb rubber with different activation degrees changed significantly after aging. In this section, the characteristic functional groups and molecular weight of the asphalt rubber before and after aging were analyzed by infrared spectroscopy and a GPC test to provide a mechanism explanation for the macroscopic properties of the activated asphalt rubber from a microscopic point of view. The correlation between high molecular weight and rheological properties was investigated by using a statistical analysis.

3.3.1. FTIR Test

The FTIR test was used to analyze the effect of the NaClO-solution concentration and short-term aging on the characteristic chemical bonds of the asphalt rubber [36,37]. As shown in Figure 15, the absorption peak of the methylene -CH_2- was at wavenumber 1455 cm^{-1}, the C-H vibration effect in the -CH_3- was at 1375 cm^{-1}, and C=C was at 1600 cm^{-1}. In the original asphalt-rubber sample, the absorption peak intensity of the N1′

was slightly lower than that of the W0′, while the peak intensities of the N2′ and N3′ were higher than those of the W0′. However, after aging, the peak strength of the W0′ was the highest, and the higher the NaClO concentration, the lower the peak intensity.

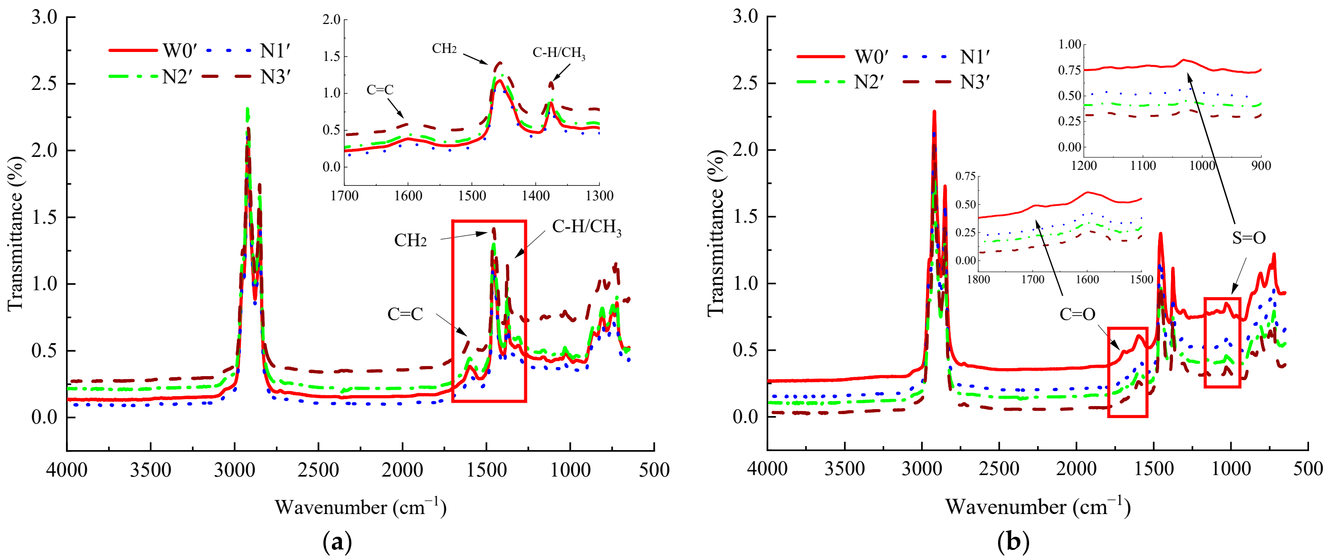


Figure 15. FTIR-test results. (**a**) original; (**b**) short-term aging.

At the same time, C=O (carbonyl) functional groups and S=O (sulfoxide) groups in the infrared spectra of asphalt are often used to characterize the changes in the molecular structure of asphalt after aging. As shown in Table 4, the peak area ratio of the characteristic peaks of the C=O functional group and the S=O functional group in the infrared spectrum to the peak area between 600 cm^{-1} and 2000 cm^{-1} were studied. The carbonyl functional group index (CI) and sulfoxide (SI) functional group indices were calculated to quantify the chemical-structure changes of the rubber asphalt before and after aging.

Table 4. Functional-group index of rubber asphalt before and after aging.

Test Properties		Peak Area C=O	Peak Area S=O	Peak Area 600 cm^{-1}–2000 cm^{-1}	CI	SI
W0′	Original	0	1.728	115.684	0.0000	0.0149
	Short-term aging	0.469	3.226	74.382	0.0063	0.0434
N1′	Original	0	1.394	125.557	0.0000	0.0111
	Short-term aging	0.556	2.293	77.164	0.0072	0.0297
N2′	Original	0	1.511	152.094	0.0000	0.0099
	Short-term aging	0.585	3.361	93.992	0.0062	0.0358
N3′	Original	0	1.135	87.848	0.0000	0.0129
	Short-term aging	0.731	3.66	99.771	0.0073	0.0367

As shown in Table 4, there was no C=O functional group in the original sample, but there were absorption peaks in the S=O functional group. From the original state to the aged state, the C=O functional group started from scratch, and the functional group index of the S=O increased significantly. This might have been because the NaClO solution formed oxygen-containing functional groups on the surface of the crumb rubber. This process causes groups such as methylene and double bonds on crumb-rubber surfaces to be oxidized into groups such as hydroxyl and carbonyl, enhancing the polarity of the surface. At the same time, the crumb rubber reacted with the carboxyl and the sulfoxide in the asphalt, effectively increasing the interfacial bonding between the crumb rubber and the asphalt. The thermal oxygen conditions in the aging process also encouraged this process.

This process is the product of the oxidation of asphalt components, which is consistent with the typical characteristics of asphalt aging.

3.3.2. GPC Test

The effect of aging on the molecular-particle size of the activated asphalt rubber samples was studied using the GPC test [38]. The LMS content in the GPC test results had a good correlation with that of the asphalt, and the change in the LMS was mainly considered [39]. As shown in Figure 16, the LMS of the activated asphalt rubber decreased with the increase in the activation degree. In the untreated asphalt rubber, the LMS content of the W0′ was 21.5%, and the LMS content of the asphalt rubber after activation by the NaClO solution was reduced by 10.2%, 13.5%, and 25.1%, respectively. After the short-term aging, the LMS content of the W0′ increased by 7.4%. However, the LMS content of the asphalt rubber after the NaClO solution's activation decreased by 13.9%, 17.7%, and 22.4%, respectively.

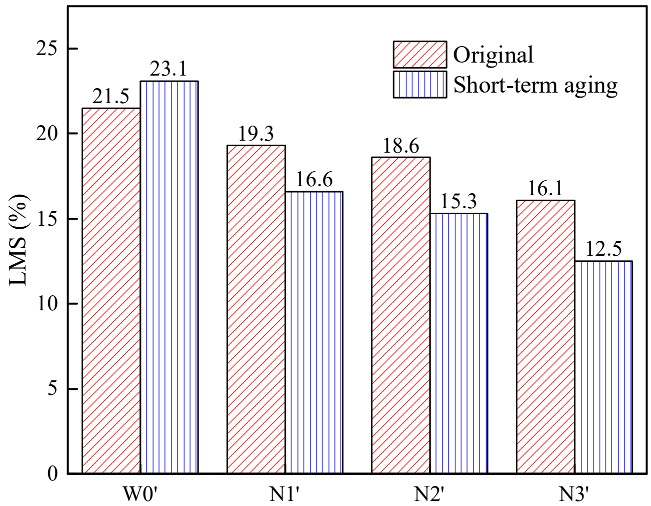
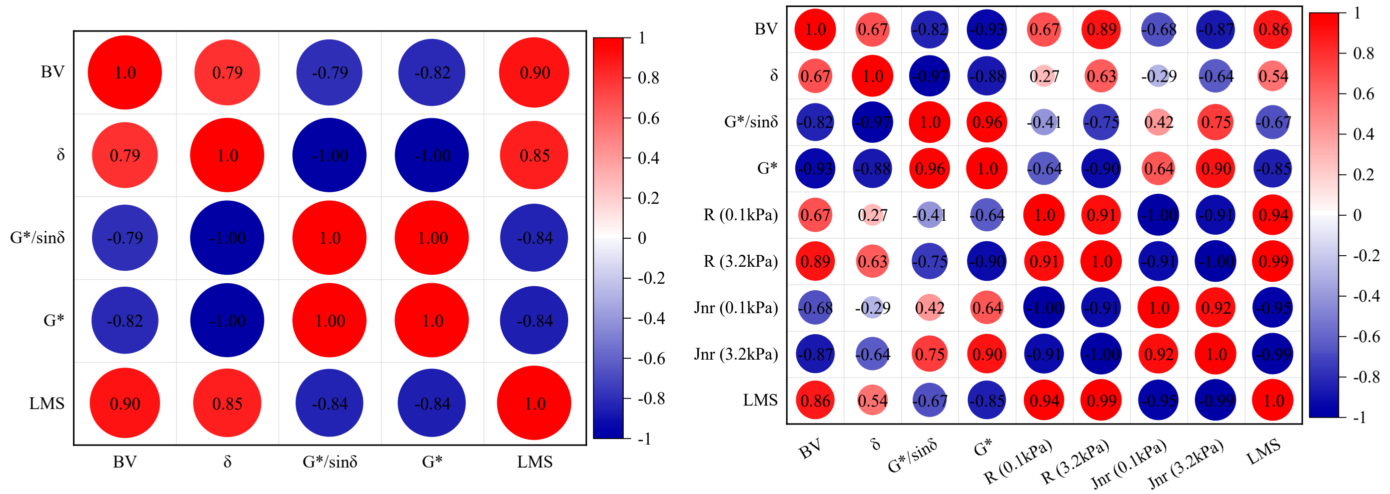


Figure 16. LMS of asphalt rubber.

This is because the NaClO solution acted on the oxidation and corrosion of the crumb rubber, forming a dense gel membrane on the surface of the crumb rubber, which limited the decomposition rate of the crumb rubber in the asphalt. The crumb rubber that entered the asphalt had fewer of the lighter components, such as rubber hydrocarbons, which reduced the content of the LMS. The ageing of the asphalt rubber increased the carbonyl, sulfoxide, and other compounds containing polar functional groups. These compounds polymerize small molecules, increasing the proportion of long-chain molecules, and the LMS content of the W0′. In addition, the NaClO gel film on the surface of the crumb rubber was disrupted by the effects of the thermo-oxidative ageing environment. The agglomerated crumb rubber decomposed, and the rubber hydrocarbon in the crumb rubber began to dissolve in the asphalt, which reduced the LMS content in the activated asphalt rubber.

3.3.3. Correlation Analysis

The correlation matrix was established to study the relationship between the LMS content and the rheological properties of the asphalt rubber, as shown in Figure 17. Since 70 °C was the most unfavorable temperature for G* in the test, δ and G*/sinδ at 70 °C were also selected for the analysis. Figure 17a shows that the correlation coefficient between the LMS and the BV of the original asphalt rubber was 0.90. The lower the LMS content, the smaller the viscosity of the asphalt rubber. The reason for this may be that when the molecular weight is low, there is less internal frictional resistance to the movement of the molecules. In addition, the shorter the molecular chain, the easier the displacement movement; thus, the viscosity decreased with the molecular weight. The correlation coefficient between the δ and the LMS was 0.85, showing a positive correlation. The correlation coefficients of the G*/sinδ and the G* with the LMS were −0.84, exhibiting a negative correlation.



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

Figure 17. Correlation-coefficient analysis. (**a**) original; (**b**) short-term aging.

The correlation-coefficient matrix between the rheological properties of the short-term-aged asphalt rubber and the LMS is shown in Figure 17b. The correlation coefficients of the LMS and the R were 0.94 and 0.99, showing a strong positive correlation. The correlation coefficients between the LMS and the Jnr were −0.95 and −0.99, showing a strong negative correlation. The smaller the LMS content, the lower the strain-recovery rate of asphalt rubber after aging. The reason for this may be that the compounds containing polar functional groups, such as the carbonyl and sulfoxide groups in asphalt rubber, increase after aging. These compounds can strengthen the association between asphalt molecules and make asphalt hard and brittle, resulting in a decline in fatigue resistance. In addition, the correlation coefficients between the LMS and the δ and G*/sinδ were 0.54 and −0.67, respectively, indicating a poor association. A strong correlation was found between the LMS and the V and G*, with correlation coefficients of 0.86 and −0.85, respectively. In general, the LMS of the asphalt rubber was strongly correlated with its rheological properties. In subsequent studies, the LMS content of asphalt rubber can be considered to predict and characterize the rheological properties.

4. Conclusions

This paper focused on the physicochemical properties of crumb rubber with different activation degrees and the differences between the rheological properties of asphalt rubber prepared by activated crumb rubber before and after aging. First, the pore characteristics and microstructure of the activated crumb rubber were analyzed, providing a research basis for the differences between the rheological properties of the activated asphalt rubber. Second, the rheological properties of the activated asphalt rubber before and after aging were measured. The differences between the rheological properties of the asphalt rubber with multiple activation degrees were reasonably explained. Finally, the differences between the rheological properties of the asphalt rubber before and after aging were interpreted from a microscopic perspective. Based on the results of this study, the following conclusions were obtained:

(1) The cumulative pore volume and area of the crumb rubber initially reduced and then increased as the degree of engagement increased. The pore volume and area of the crumb rubber were mainly composed of macropores and mesopores, respectively. The fine particles and stacking structures increased with the NaClO concentration, and,

finally, a dense gel film was formed. This may have been the reason for the changes in the porosity and the agglomeration of the crumb rubber.

(2) Aging causes the viscosity, phase angle, G*/sinδ and complex modulus of asphalt rubber to decrease to varying degrees. The activation can improve the rheological properties of asphalt rubber, and the higher the degree of activation, the more pronounced the effect. The degree of activation has no noticeable effect on the performance of asphalt rubber under low stress. However, it has a significant influence on performance under high stress. In this study, the N3′ rubber-asphalt sample had the best rheological properties.

(3) Activated asphalt rubber is prone to the formation of oxygen-containing functional groups, a process that is facilitated by ageing under thermal-oxygen conditions. The LMS content of asphalt rubber is inversely proportional to the activation degree of crumb rubber. However, the aging effect has the opposite effect on the LMS content of activated and inactivated asphalt rubber. The LMS content has a good correlation with the rheological properties, and LMS content can be used to predict rheological properties.

Author Contributions: Conceptualization, P.Z. and B.L.; methodology, P.Z.; validation, Y.W. (Yongning Wang); formal analysis, Y.W. (Yongzheng Wei); investigation, B.W.; resources, B.Z.; writing—original draft preparation, Y.W. (Yongzheng Wei); writing—review and editing, P.Z.; visualization, B.L.; supervision, Y.W. (Yongning Wang); project administration, B.L.; funding acquisition, B.L.; data curation, D.L.; software, D.L. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Natural Science Foundation of China (51868042), the Distinguished Young Scholars Fund of Gansu Province (1606RJDA318), the Natural Science Foundation of Gansu Province (1506RJZA064), Industry Support and Guidance Project by University and College in Gansu Province (2020C-13), Gansu Provincial Key R&D Program (22YF7GA135), Gansu Science and Technology Major Project (21ZD3GA002, 22ZD6GA010), Special Funds for Guiding Local Scientific and Technological Development by The Central Government (22ZY1QA005) and Gansu Province Excellent Graduate Student 'Innovation Star' Project Fund Project (2022CXZX-598).

Data Availability Statement: Not applicable.

Acknowledgments: The authors appreciate for the supports by the support of the National Natural Science Foundation of China; Gansu Provincial National Natural Science Foundation; and Gansu Provincial Highway Traffic Survey Planning and Design Institute.

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

References

1. Mohajerani, A.; Burnett, L.; Smith, J.V.; Markovski, S.; Rodwell, G.; Rahman, M.T.; Kurmus, H.; Mirzababaei, M.; Arulrajah, A.; Horpibulsuk, S.; et al. Recycling waste rubber tyres in construction materials and associated environmental considerations: A review. *Resour. Conserv. Recycl.* **2020**, *155*, 104679. [CrossRef]
2. Xiao, M.; Yao, J.T.; Chen, L.Z. Progress in combined modification of rubberized asphalt. *IOP Conf. Ser. Earth Environ. Sci.* **2021**, *634*, 012104. [CrossRef]
3. Ma, T.; Chen, C.L.; Zhang, Y.; Zhang, W.G. Development of Using Crumb rubber in Asphalt Modification: A Review. *China J. Highw. Transp.* **2021**, *34*, 1. [CrossRef]
4. Picado-Santos, L.G.; Capitão, S.D.; Neves, J.M. Crumb rubber asphalt mixtures: A literature review. *Constr. Build. Mater.* **2020**, *247*, 118577. [CrossRef]
5. Mohamed, A.S.; Cao, Z.L.; Xu, X.Y.; Xiao, F.P.; Abdel-Wahed, T. Bonding, rheological, and physiochemical characteristics of reclaimed asphalt rejuvenated by crumb rubber modified binder. *J. Clean. Prod.* **2022**, *373*, 133896. [CrossRef]
6. Liang, M.; Ren, S.S.; Sun, C.J.; Zhang, J.Z.; Jiang, H.G.; Yao, Z. Extruded Tire Crumb-Rubber Recycled Polyethylene Melt Blend as Asphalt Composite Additive for Enhancing the Performance of Binder. *J. Mater. Civ. Eng.* **2020**, *32*, 04019373. [CrossRef]
7. Wu, W.J.; Jiang, W.; Xiao, J.J.; Yuan, D.D.; Wang, T.; Xing, C.W. Analysis of thermal susceptibility and rheological properties of asphalt binder modified with microwave activated crumb rubber. *J. Clean. Prod.* **2022**, *377*, 134488. [CrossRef]
8. Ibrahim, I.M.; Fathy, E.S.; El-Shafie, M.; Elnaggar, M.Y. Impact of incorporated gamma irradiated crumb rubber on the short-term aging resistance and rheological properties of asphalt binder. *Constr. Build. Mater.* **2015**, *81*, 42–46. [CrossRef]

9. Zhou, T.; Zhou, J.N.; Li, Q.D.; Li, B. Aging Properties and Mechanism of Microwave-Activated Crumb Rubber Modified Asphalt Binder. *Front. Mater.* **2020**, *7*, 603938. [CrossRef]
10. Yang, X.L.; Shen, A.Q.; Li, B.; Wu, H.S.; Lyu, Z.H.; Wang, H.; Lyu, Z.F. Effect of microwave-activated crumb rubber on reaction mechanism, rheological properties, thermal stability, and released volatiles of asphalt binder. *J. Clean. Prod.* **2020**, *248*, 119230. [CrossRef]
11. Li, B.; Wei, Y.Z.; Wang, Y.; Cui, Y.J. Effect of hydrogen peroxide treated crumb rubber on viscoelasticity of rubber modified asphalt. *Acta Mater. Compos. Sin.* **2019**, *36*, 1008–1016. [CrossRef]
12. Liu, L.; Liu, Z.H.; Yang, C.C. Pretreatment of Crumb rubber with a Silane Coupling Agent to Improve Asphalt Rubber Performance. *Adv. Mater. Sci. Eng.* **2021**, *2021*, 1828145. [CrossRef]
13. Chen, J.H.; Yan, K.Z.; You, L.Y. Rheological and Spectroscopic Properties of Ethylene Vinyl Acetate–Modified Rubberized Asphalt. *J. Mater. Civ. Eng.* **2020**, *32*, 04020142. [CrossRef]
14. Ren, S.S.; Liu, X.Y.; Lin, P.; Wang, H.P.; Fan, W.Y.; Erkens, S. The continuous swelling-degradation behaviors and chemo-rheological properties of waste crumb rubber modified bitumen considering the effect of rubber size. *Constr. Build. Mater.* **2021**, *307*, 124966. [CrossRef]
15. Wang, S.F.; Cheng, D.X.; Xiao, F.P. Recent developments in the application of chemical approaches to rubberized asphalt. *Constr. Build. Mater.* **2017**, *131*, 101–113. [CrossRef]
16. Yin, L.; Yang, X.L.; Shen, A.Q.; Wu, H.S.; Lyu, Z.F.; Li, B. Mechanical properties and reaction mechanism of microwave-activated crumb rubber-modified asphalt before and after thermal aging. *Constr. Build. Mater.* **2021**, *267*, 120773. [CrossRef]
17. Zhang, Y.H.; Wei, H.; Dai, Y.H. Influence of Different Aging Environments on Rheological Behavior and Structural Properties of Rubber Asphalt. *Materials* **2020**, *13*, 3376. [CrossRef]
18. Wang, Q.; Li, S.; Wu, X.Y.; Wang, S.F.; Ouyang, C.F. Weather aging resistance of different rubber modified asphalts. *Constr. Build. Mater.* **2016**, *106*, 443–448. [CrossRef]
19. Liu, X.H.; Bi, Y.F.; An, Y.N.; Zhou, S.Q.; Li, F. Secondary-Reaction Method to Improve Performance of a Compound Modified Rubber Asphalt after Short-Term Aging. *J. Transp. Eng. Part B Pavements* **2021**, *147*, 04021038. [CrossRef]
20. Chen, R.P.; Zhu, H.Z.; Kong, L.Y.; Xu, Y.L.; Ou, L. Stage-aging characteristics and stages division of crumb rubber modified asphalt binder. *Constr. Build. Mater.* **2023**, *367*, 129712. [CrossRef]
21. *JTG F40-2004*; Research Institute of Highway Ministry of Transport. Technical Specifications for Construction of Highway Asphalt Pavements. China Communications Press: Beijing, China, 2004.
22. *JT/T 798-2011*; Research Institute of Highway Ministry of Transport. Asphalt Rubber for Highway Engineering. China Communications Press: Beijing, China, 2011.
23. Yang, X.L.; Li, B.; Liu, X.; Zhang, Z.W. Mechanism of Modification of Rubber Asphalt on Process Parameters. *J. Build. Mater.* **2017**, *20*, 640–645. [CrossRef]
24. *JTG E20-2011*; Research Institute of Highway Ministry of Transport. Standard Test Methods of Bitumen and Bituminous Mixtures for Highway Engineering. China Communications Press: Beijing, China, 2011.
25. *ASTM D5604-96*; American Society for Testing and Materials. Standard Test Methods for Precipitated Silica-Surface Area by Single Point B.E.T. Nitrogen Adsorption. US-ASTM: West Conshohocken, PA, USA, 2012.
26. He, Y.P.; Yang, S.J. Application of BET Specific Surface Area Method in Material Research. *Adv. Fine Petrochem.* **2018**, *19*, 52–56. [CrossRef]
27. Li, L.L.; Huang, X.M.; Zhu, D.Y.; Han, D.; Dong, M.S. Application of generalized Kelvin model in asphalt pavement. *J. Southeast Univ. (Nat. Sci. Ed.)* **2016**, *46*, 413–418. [CrossRef]
28. Li, X.Y.; Ping, L.; Wang, H.N.; Zhang, C.; You, Z.P. Performance test of rubber asphalt based on domestic and abroad test methods. *J. Traffic Transp. Eng.* **2015**, *15*, 10–17. [CrossRef]
29. Li, B.; Wang, J.; Cao, G.; Wang, C.H.; Yang, X.L. Influence Mechanism of Crumb rubber Characteristics on High-temperature Performance for Rubber Modified Asphalt Binder. *J. Basic. Sci. Eng.* **2017**, *25*, 347–355. [CrossRef]
30. Amir, A.; Ziari, H.; Saadatjoo, S.A.; Hashemifar, N.S.; Goli, A. Rutting resistance, fatigue properties and temperature susceptibility of nano clay modified asphalt rubber binder. *Constr. Build. Mater.* **2021**, *267*, 120946. [CrossRef]
31. Xiao, F.P.; Zong, Q.D.; Wang, J.G.; Chen, J.; Liu, J. Storage stability characterization and improvement of SBS and Crumb rubber composite modified asphalt. *Road Mater. Pavement Des.* **2022**, *23*, 509–526. [CrossRef]
32. Li, M.C.; Xing, C.W.; Liu, L.P.; Huang, W.Q.; Meng, Y.F. Gel permeation chromatography-based method for assessing the properties of binders in reclaimed asphalt pavement mixtures. *Constr. Build. Mater.* **2022**, *316*, 126005. [CrossRef]
33. Chalmers, G.R.; Bustin, R.M.; Power, I.M. Characterization of gas shale pore systems by porosimetry, pycnometry, surface area, and field emission scanning electron microscopy/transmission electron microscopy image analyses: Examples from the Barnett, Woodford, Haynesville, Marcellus, and Doig units. *AAPG Bull.* **2012**, *96*, 1099–1119. [CrossRef]
34. Shang, L.N.; Wang, S.F.; Zhang, Y.; Zhang, Y.X. Pyrolyzed wax from recycled cross-linked polyethylene as warm mix asphalt (WMA) additive for SBS modified asphalt. *Constr. Build. Mater.* **2010**, *25*, 886–891. [CrossRef]
35. Tang, N.P.; Huang, W.D. High Temperature Performance Evaluation and Grading of SBS Modified Asphalt Based on Multiple Stress Creep Recovery Test. *J. Build. Mater.* **2016**, *19*, 665–671. [CrossRef]
36. Asib, A.S.M.; Rahman, R.; Romero, P.; Hoepfner, M.P.; Mamun, A. Physicochemical characterization of short and long-term aged asphalt mixtures for low-temperature performance. *Constr. Build. Mater.* **2022**, *319*, 126038. [CrossRef]

37. Yang, Z.; Zhang, X.N.; Yu, J.M.; Xu, W. Study on Multi-scale Characteristics of Matrix Asphalt before and after Aging. *J. Build. Mater.* **2018**, *21*, 420–425. [CrossRef]
38. Kim, H.; Lee, S.J.; Amirkhanian, S.N.; Jeong, K.D. Quantification of Oxidative Aging of Polymer-Modified Asphalt Mixes Made with Warm Mix Technologies. *J. Mater. Civ. Eng.* **2013**, *25*, 1–8. [CrossRef]
39. Xiang, Y.; Fan, H.J.; Liu, Z.H. Structural characteristics of silane-modified ground tyre rubber and high-temperature creep property of asphalt rubber. *Constr. Build. Mater.* **2020**, *236*, 117600. [CrossRef]