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Investigation of the Thermal Degradation of SBS Polymer in Long-Term Aged Asphalt Binder Using Confocal Laser Scanning Microscopy (CLSM)

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Abstract: Styrene–butadiene–styrene (SBS) polymer is extensively employed for asphalt pavement construction, and its degradation significantly damages the durability of asphalt concrete. However, the effect of aging protocols on the degradation of SBS polymer in asphalt binder has not been thoroughly investigated. In this study, confocal laser scanning microscopy (CLSM) was applied to characterize the change in morphology with SBS polymer degradation. Various aging protocols were considered, including accelerated aging processes in laboratory- and field-aged samples from three highway sections with different in-service periods. Scanned images of the polymer phase in the 2D plane at different depths were processed and further reconstructed in three dimensions. Furthermore, the three-dimensional polymer morphology indices derived from the semi-quantitative analysis of the images were correlated with the rheological indices. The results show that the polymer particles change from a relatively large ellipsoidal shape to a relatively small spherical shape as aging proceeds. The increase in aging temperature appears to accelerate the degradation of the polymer at the same rheological level. The effect of the laboratory aging method on the polymer was more pronounced during the early stages of aging compared to that in the field aging process.

Keywords: SBS-modified asphalt binder; polymer degradation; aging; CLSM; rheological indies

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1. Introduction

The performance of asphalt binders is an essential factor in determining the durability of flexible pavement. The application of various modifiers is one of the effective techniques to improve pavement performance [1–3]. Virgin asphalt binder is generally modified by adding polymers or inorganic material. The styrene–butadiene–styrene (SBS) modified asphalt binder has been widely used in pavement construction because of the considerable improvement in temperature sensitivity, durability, adhesion, and anti-aging properties found in previous research and practice [4–6].

Asphalt is inevitably affected by thermal oxygen aging during the in-service phase, which is mainly reflected in the aging of virgin binders and that of polymers for polymer-modified binders [7–9]. The degradation of polymers directly affects the performance of modified asphalt binder, which makes it crucial to clarify the effect of aging conditions on polymers to understand the aging behavior of polymer-modified binders. To detect the degradation characteristics of SBS polymers with aging, previous studies have proposed a feasible method to semi-quantify polymer degradation based on attenuated total reflection (ATR) Fourier-transform infrared (FTIR) spectroscopy [10,11]. However, due to the limitations of this technique, it seems that only functional group intensities in the depth range of 1–2 µm on the scanned asphalt surface can be obtained, and this index is influenced by factors such as the aging level and polymer content [12]. On the other hand, changes in polymer morphology, such as the size and distribution, can be observed by fluorescence microscopy [13]. Some studies employ stereology methods to obtain quantitative indices of two-dimensional images of polymers to characterize the morphological features and distribution density of polymers [14,15].

In recent years, confocal laser scanning microscopy (CLSM), which is mostly applied in the biological, biochemical, and biomedical sciences, has been introduced to explore the microstructural features of asphalt binder [16,17]. CLSM has the advantage of a higher resolution and better image quality than conventional optical microscopes, as it is free from field light sources and the local plane imaging mode. In the CLSM test, the light source is a depth-selective laser beam, based on which images of different depth levels can be obtained by focusing, and if images of different depths are reconstructed, images of local three-dimensional (3D) heterogeneous features can be obtained [18]. In addition to reflection mode or transmission mode, CLSM can also work in fluorescence mode. Some studies have used CLSM's reflection mode and fluorescence mode to characterize the surface micromorphology and the polymer distribution of asphalt materials, respectively [19]. In terms of characterizing the asphalt surface micromorphology, Johan Blom and Pipintakos et al., found that the CLSM technique can obtain a bee-like structure on the asphalt surface similar to the atomic force microscopy (AFM) test by comparing the asphalt surface morphology maps obtained by the AFM and CLSM techniques, indicating that the CLSM technique is also an effective tool for capturing the asphalt surface morphology state [20]. In the case of polymer-modified asphalt, the state of polymer mixing in the asphalt is an important factor in determining the asphalt properties. Fluorescence microscopy is generally applied to qualitatively or quantitatively analyze the homogeneity of polymer blends as an effective method to identify polymers in asphalt [21]. The 2D images obtained by conventional fluorescence microscopy have been widely employed to characterize the morphology of SBS polymers. However, 2D images would induce bias in the real morphology of scanned objects. Recognizing and understanding the volume fraction of polymers in 3D space is essential. Relatively few studies have attempted exploring the 3D morphology of polymers using CLSM [22]. There is still a lack of a comprehensive analysis of the effects of various aging conditions on polymer degradation. It is an intuitive and effective method to obtain microscopic fluorescence images of aged asphalt samples by CLSM to investigate the effect of aging conditions on the morphology of SBS-modified asphalt binder.

The properties of polymers significantly affect the performance of SBS-modified asphalt, and it is necessary to properly characterize the changes in polymers during the aging process. Therefore, in this study, 3D cross-sectional scanned images of aged polymers were obtained from the lab- and field-aged samples employing CLSM. An image processing analysis was also used to obtain the 3D morphological parameters of the polymer and further analyze the relationship between the morphological parameters and rheological properties.

2. Materials

Both field and laboratory aging were considered in this study, resulting in a total of 18 different aged samples. Field-aged 9-, 15-, and 19-year core samples were obtained from three highway sections in Jiangsu, China. The cores were taken from the middle of the wheel track of the low-speed lane for NY and FG sections and from the roadside for YH section. The wearing course with a depth of 4 cm was cut into three slices (13 mm each), noted S1, S2, and S3, and the binder was extracted for testing. The processes of binder extraction and recovery were conducted following AASHTO T 164 and ASTM D5404 with a centrifuge extractor and a rotary evaporator (Buchi R215), respectively. Table 1 shows the summary information for the binder samples extracted from field cores. In addition, a binder with the same performance grade (PG) and SBS content (3% by weight) was applied to prepare lab-aged samples. The binder is widely used in the early stage of highway construction in Jiangsu and was obtained from the plant. The general properties of the SBS-modified binder are listed in Table 2.

Table 1. Summary of field cores from different highway sections.

Code	Depth	Region	Service Year	Gradation Type	Binder Content (%)	Air Void (%)
NY	S1 (0.65 mm) S2 (1.95 mm) S3 (3.25 mm)	Yangzhou	9	SMA-13	5.7 5.8 5.8	3.4 3.6 4.4
YH-2	S1 (0.65 mm) S2 (1.95 mm) S3 (3.25 mm)	Yancheng	15	SMA-13	5.7 5.9 5.9	3.6 3.6 4.2
FG	S1 (0.65 mm) S2 (1.95 mm) S3 (3.25 mm)	Lianyungang	19	AK-13	5.2 5.0 5.2	3.7 3.6 4.2

Note: AK indicates a dense-grade asphalt mixture.

Table 2. General properties of SBS-modified asphalt binder.

Items	SBS-Modified Asphalt Binder	Specification Limits	Test Method
Penetration (25 °C, 0.1 mm)	68	60–80	ASTM D5
Softening point (°C)	67	≥46	ASTM D36
Ductility (5 °C, cm)	38.1	/	ASTM D113
Viscosity (135 °C, Pa·s)	1.59	/	ASTM D4402
Binder grade	PG 70-22	/	/
SBS polymer content	3 wt%	/	/

3. Methodologies

The flowchart is shown in Figure 1. The experiments were carried out at Southeast University.

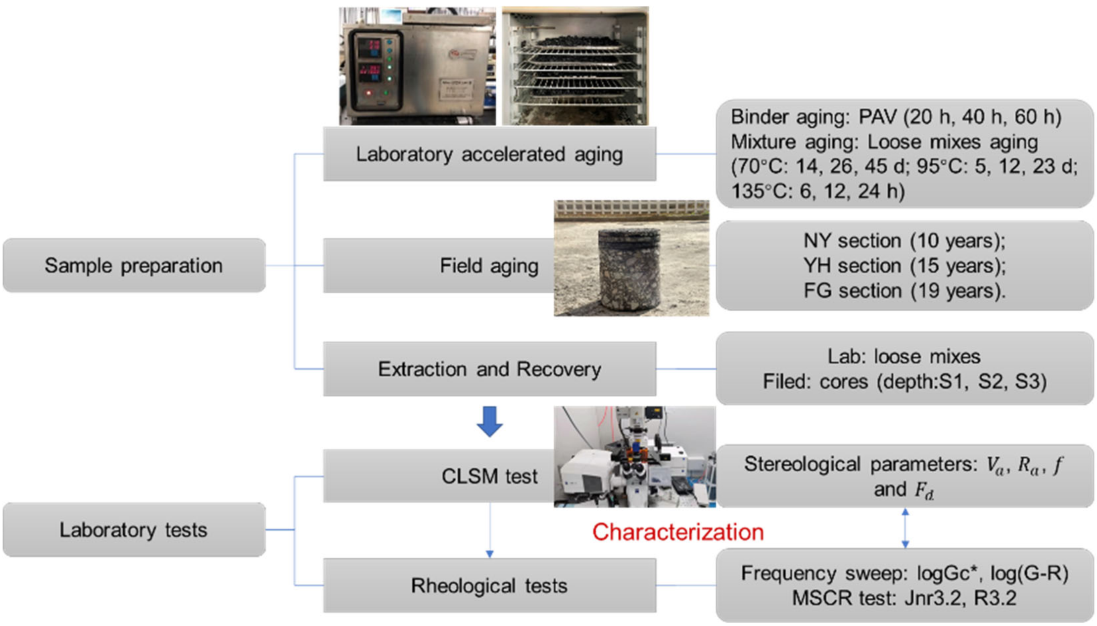


Figure 1. Flowchart of sample preparation and laboratory tests.

3.1. Aging Protocols

A loose asphalt mixture aging protocol was conducted to prepare the short- and long-term aged samples. The short-term aging of asphalt mixtures was performed in accordance with AASHTO R 30. As for the long-term aging protocols of asphalt mixtures, three aging temperatures were considered, including 70 °C, 95 °C, and 135 °C, each containing three different aging durations to simulate various long-term aging levels in the laboratory. The aging processes are summarized in Table 3. Loose asphalt mixtures were evenly and loosely spread in an enamel tray at approximately 21–22 kg/m^2, heated in a controlled forced-draft oven, and re-mixed with a shovel once a day to ensure the uniformity of the loose asphalt mixture's aging. Moreover, the long-term aging in the binder scale was also considered to offer a reference for the value of aging indices. The binder initially achieved a short-term aging level through the rolling thin film oven test (RTFOT) and further achieved a long-term aging level through the standard pressure aging vessel (PAV) aging procedure according to AASHTO R28. Various aging levels were simulated with three different PAV cycles, including the standard aging duration, 40 h, and 60 h.

Table 3. Laboratory aging conditions.

ID	Short-Term Aging		Long-Term Aging	
	Temp (°C)	Duration	Temp (°C)	Duration
PAV	163	85 min	100	20, 40, and 60 h
LM70	135	4 h	70	14, 26, and 45 days
LM95	135	4 h	95	5, 12, and 23 days
LM135	135	4 h	135	6, 12, and 24 h

3.2. Confocal Laser Scanning Microscopy (CLSM) Analysis

3.2.1. Polymer Fluorescence Image Acquisition

The images of the SBS polymer were captured at room temperature with a confocal laser scanning microscope (Olympus, Tokyo, Japan, FV3000). Two-photon fluorescence microscopy is a non-destructive measuring method for 3D imaging analysis. Compared with conventional single-photon imaging, the pulsed light emitted by a femtosecond laser is used to excite the fluorescent sample, avoiding the interference of non-focal-plane fluorescence and improving the brightness and signal-to-noise ratio of the imaging. Adopting a more robust fluorescence method is required for an impervious material such as an asphalt binder. The sample was approximately 1.5 cm in diameter and 20 μm thick.

Due to the impervious nature of asphalt, it is beneficial to prepare the asphalt sample in film form to improve the quality of the scanned image. The specific steps are as follows: First, take 3–5 g of a bitumen sample and heat it to 160 °C. Then, drop the asphalt binder onto the glass slide and cover it with a coverslip. Then, slowly press the sample into a thin layer between the slide and coverslip, as shown in Figure 2. Two replicates were tested for each series.

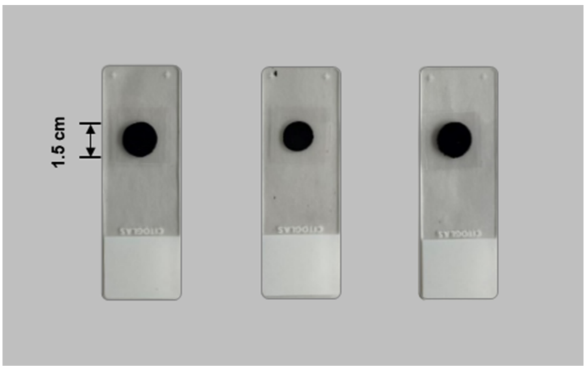


Figure 2. Asphalt sample for the CLSM test.

The excitation spectral line was set to 488 nm, which could make SBS polymer fluoresce after excitation, and was then observed and photographed by microscope imaging. The objective magnification was set to 20×, the observation range was 425 μm × 425 μm, the sampling depth was 10 μm, and the interlayer gap was 1 μm.

3.2.2. CLSM Image Pre-Processing

The impact of aging on the polymer morphology in asphalt can be directly observed by CLSM in fluorescence mode. Figure 3 presents the original CLSM images obtained at different scanning depths. Asphalt binder is a black opaque material, and the maximum investigation depth is generally 5 to 10 μm. In addition, the fluorescence intensity decreases significantly with an increase in the scanning depth and contrasts with the polymer section, which is not strong enough to display relatively small partial polymers. In addition, the stripe noise on an image also affects the quantitative image analysis. To ensure the accuracy of subsequent analysis, image processes are required for original CLSM images.

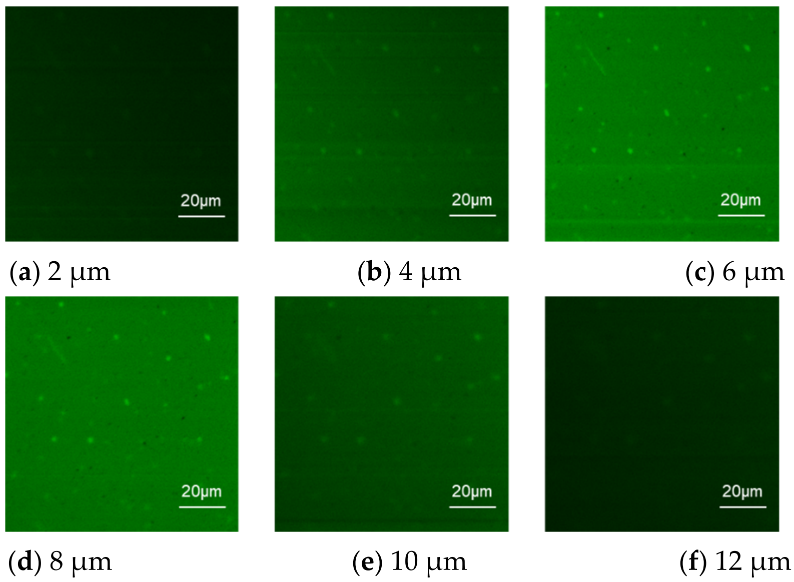


Figure 3. CLSM images at different depths.

In this study, the CLSM images were further processed and quantitatively analyzed by ImageJ software. The image processing tool was employed to transfer the original images into binary images, as shown in Figure 4. In the ImageJ program, a function band-pass filter was utilized to reduce the horizontal stripe noise. Then, the image was processed by the Yen filter function based on ImageJ to enhance the contrast of the SBS polymer section. Finally, the image was further binarized for 3D reconstruction and quantitative analysis.

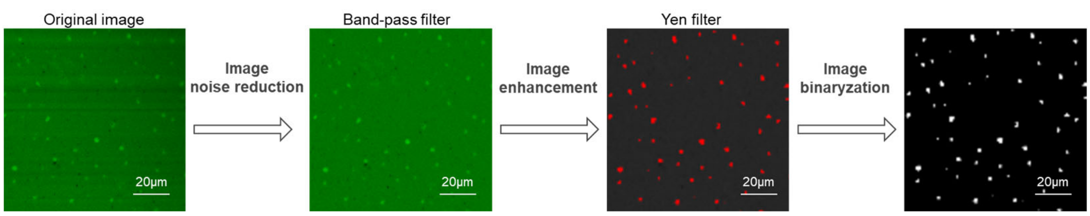


Figure 4. Image process steps for CLSM images.

The image data of the lamellar section sequences with different depths were read sequentially by ImageJ software, and the 3D reconstructed image was drawn using the built-in interactive function, as shown in Figure 5. Numerous studies have characterized the morphology of SBS polymer in asphalt binder through two-dimensional (2D) fluorescence images, providing insight into how the morphology of the polymer changes with the SBS dose and aging duration. However, a 2D projection in a single direction loses some morphological information. A qualitative or semi-quantitative approach to a 3D structure helps to further clarify the effects of aging conditions on the SBS polymer.

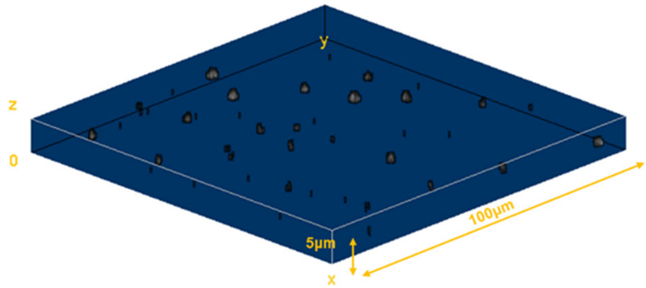


Figure 5. Three-dimensional reconstruction of a CLSM image.

3.2.3. Semi-Quantitative Indicators of Stereology

Stereological analysis is a quantitative morphological research technique based on geometric probability theory and a method to obtain 3D quantitative information about a microstructure based on 2D cross-sectional observations, as shown in Figure 6.

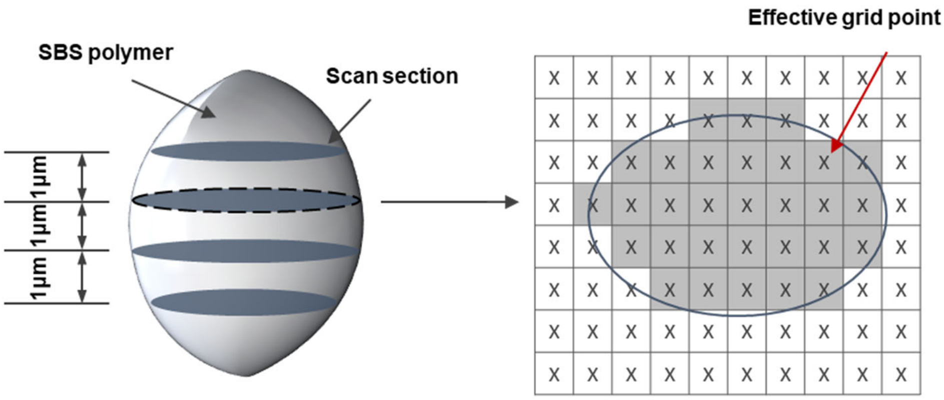


Figure 6. Schematic diagram of effective grid point counting.

In this study, various parameters were employed to describe the 3D structure. The specific surface area (R_a) is the ratio of the surface area (S_a) to the volume (V_a), which can be used to characterize the size of the polymers. The spatial occupation ratio is the ratio of polymer fluorescence volume to total volume, which can be used for the distribution density of the polymer. The shape factor is used to reflect the degree of difference between the cross-sectional shape of the structure and the circle index. The shape factor of a circle is 1, and the more irregular the shape, the greater the value of the parameter. The statistical 2D image shape factor can be used to characterize the irregularity of the 3D shape. In addition, an F_d parameter was proposed to characterize the flattening of the polymer in a 3D view and was obtained by calculating the mean value of Feret's diameter for 2D images with different scan depths. The mentioned parameters are calculated as follows:

$$V_a = d\sum_{i=1}^{n}\left(P_{ni}l^2\right) \tag{1}$$

$$S_a = \frac{4}{\pi}d\sum_{i=1}^{n}C_i = \frac{4}{\pi}d\sum_{i=1}^{n}\left(\frac{\pi}{2}P_{ni}l\right) \tag{2}$$

$$R_a = \frac{S_a}{V_a} = \frac{\frac{4}{\pi}\sum_{i=1}^{n}C_i}{\sum_{i=1}^{n}\left(P_{\mathrm{ni}}l^2\right)} \tag{3}$$

$$f = \frac{1}{N}\sum_{i=1}^{n}\frac{C_i^2}{4\pi P_{ni}l^2} \tag{4}$$

where V_a is the average volume of the polymer; d is the 2D image scanning step; P_{ni} the number of effective grid points of the ith layer of the polymer; l is the pixel point edge length; S_a is the average surface area of the polymer; C_i the equivalent perimeter of the ith layer of the polymer; R_a is the specific surface area of the polymer; f is the shape factor, where the value is between 0 and 1, and a shape factor of 1 corresponds to a perfect circle.

3.2.4. Rheology Testing

In this study, in order to clarify the effect of polymer degradation on the rheological properties of the SBS-modified asphalt binder, four rheological indices, namely the crossover modulus (G_c^*), Glower–Rowe (G–R) parameter, non-recoverable creep compliance (Jnr3.2), and percent recovery (R3.2), were employed to investigate the potential correlations with polymer degradation.

Both the frequency sweep test and multi-stress creep and recovery (MSCR) test were conducted on an Anton Paar MCR 102 DSR. At least two replicates were measured. The frequency sweep test covered a wide range of temperatures from 4 °C to 64 °C in increments of 12 °C and frequencies from 0.1 to 30 Hz. Strain levels ranging from 0.01% to 1% were determined by the amplitude sweep test to ensure the response was in the linear viscoelastic region. The Christensen–Anderson–Marasteanu model was applied to fit the rheological master curves and calculate the crossover modulus and G–R parameters. The reciprocal of the logarithm of the crossover modulus $1/\log(G_c^*)$ was used to characterize the aging level and show the results more clearly. The G–R parameter was calculated at 15 °C and 0.005 rad/s, expressed as Equation (5). Jnr3.2 and R3.2 were calculated from the MSCR test at 64 °C according to ASTM D7405 to evaluate the permanent deformation resistance and the resilient recovery capability of asphalt binders.

$$G - R = \frac{|G^*|(cos\delta)^2}{\sin\delta} \tag{5}$$

where G^* is the modulus and δ is the phase angle.

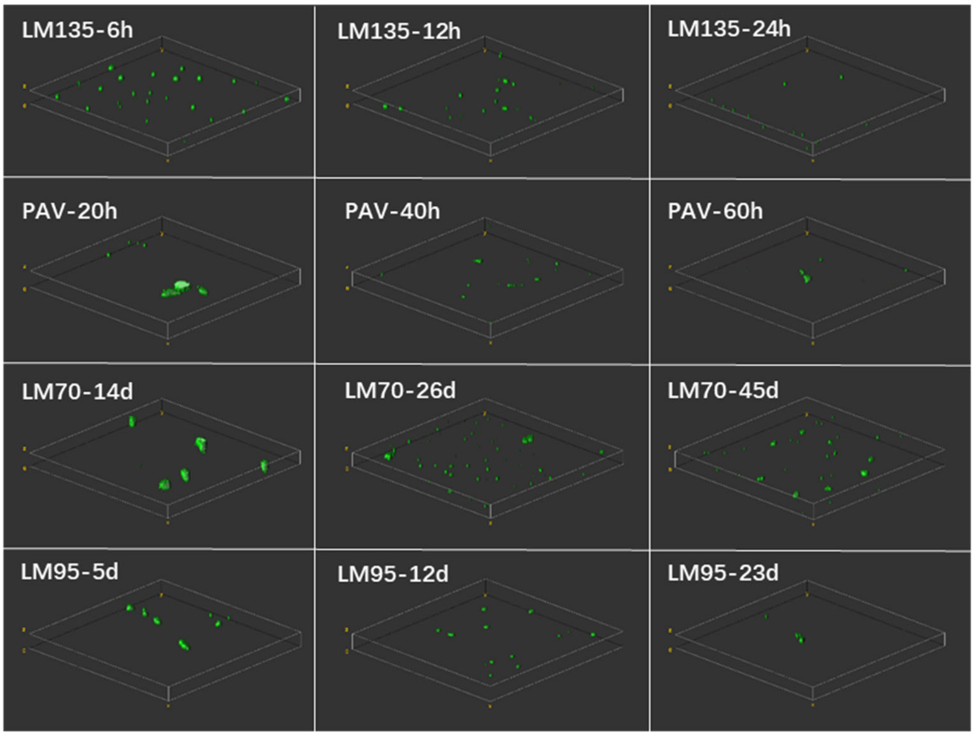
4. Results and Discussion

4.1. Visualization of SBS Polymer with Aging

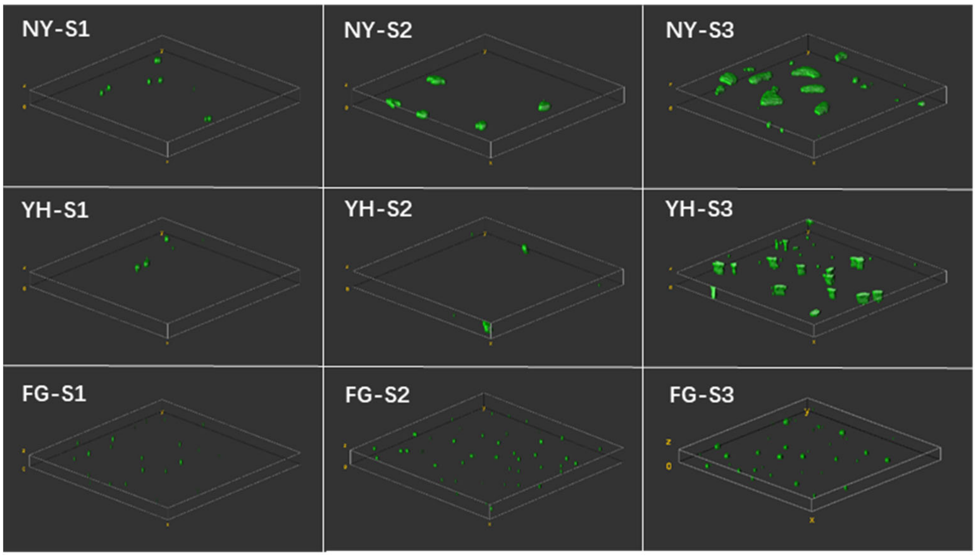
4.1.1. Polymer Morphology Characterization

Figure 7 shows the 3D morphology of SBS polymer for both lab- and field-aged binder samples. It can be observed that SBS polymers in bitumen appear as the particle distribution in three dimensions. In this study, due to the SBS polymer dose ranging from 3% to 4%, polymers in bitumen appear as the particle distribution in three dimensions, which is consistent with the fluorescence images obtained by conventional fluorescence microscopy in previous studies [23,24]. As the SBS polymer dose was consistent for different lab-aged samples, the changes in the morphology of SBS particles was recognized to be mainly affected by the aging procedures.

Figure 7a presents the changes in the polymer morphology of the asphalt binders with various laboratory aging methods. It can be observed that the morphology of the polymer particles changed significantly. Aging resulted in decreased fluorescence intensities for the aged samples with higher aging levels. As the aging progressed, fluorescence particles become smaller and gradually appeared as a dot-like distribution. Figure 7b shows the field aging samples with various in-service years and depths. The fluorescence intensity of the polymer exhibited a gradient change for the samples with different depths, indicating the fluorescence mode based on CLSM can be utilized to detect the aging gradient in field aging samples. In addition, in the 3D view, the shape of the polymer appeared to change from a larger irregular granular shape to a relatively smaller dotted shape as aging proceeded. This may be attributed to the fact that aging destroys the polybutadiene segment of SBS, which is less compatible with the asphalt matrix and thus disintegrates the spatial lattice structure formed in the asphalt matrix.



(**a**)



(**b**)

Figure 7. Three-dimensional morphological maps of SBS polymer (100 × 100 × 5 μm): (**a**) lab-aged samples; (**b**) field-aged samples.

4.1.2. Quantitative Analysis

In this study, the V_a, R_a, f, and F_d stereological parameters were used to quantify the 3D morphology of SBS polymers, as presented in Figure 8. Based on the calculation results, V_a and F_d decreased with aging, whereas f and R_a increased. This indicates that aging leads to a decrease in the volume of the observable polymer, an increase in the fineness, a decrease in the ratio between the long and short axes of the scan plane, and a tendency to develop a spherical shape.

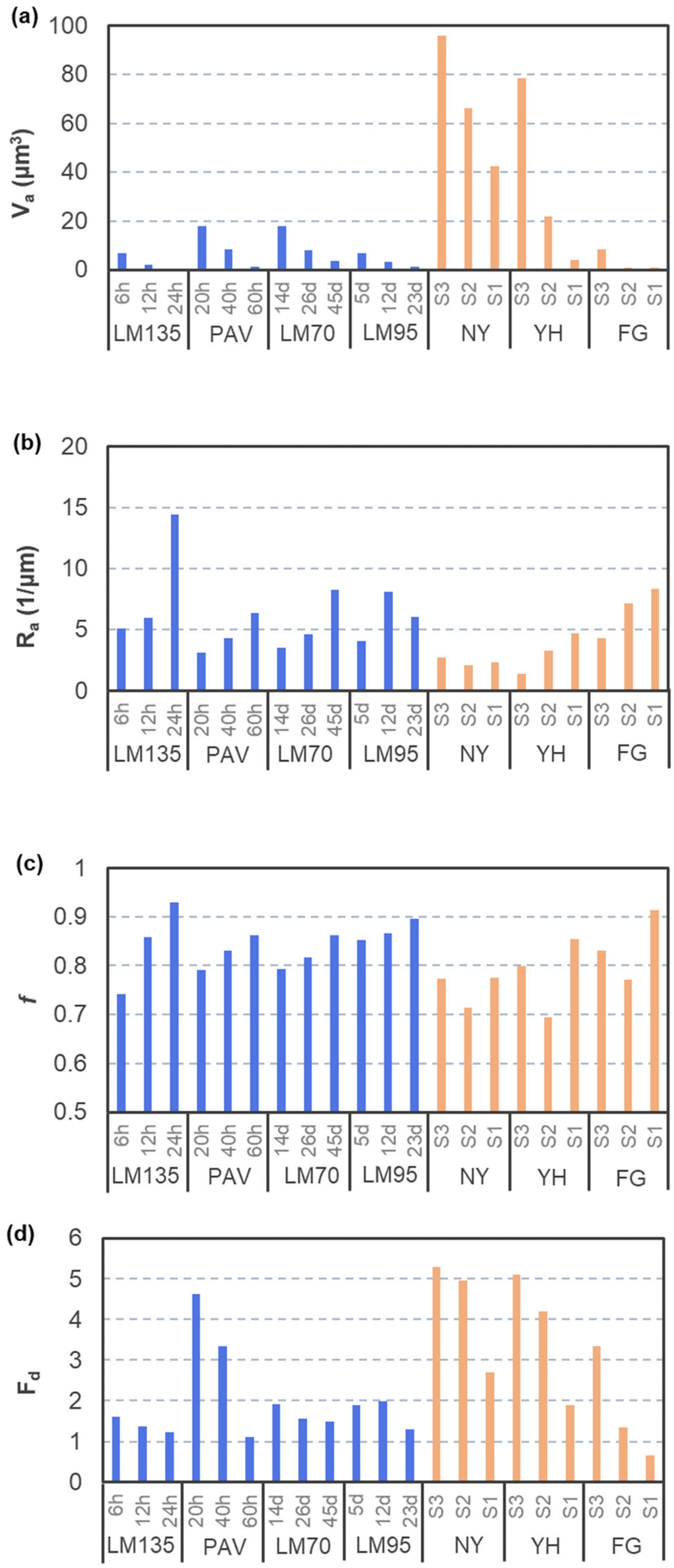


Figure 8. Three-dimensional morphological parameters of SBS polymer: (**a**) V_a; (**b**) R_a; (**c**) f; and (**d**) F_d.

There was an obvious difference in the V_a between the lab- and field-aged samples. It seems that laboratory aging caused a rapid decrease in the fluorescence volume of the polymer obtained by CLSM in the early stage of aging. It could be observed that the degradation rate of the polymer exhibited S1 > S2 > S3. V_a, R_a, and F_d exhibited field aging gradient characteristics, and the trends of these indicators were consistent with the in-service time of the pavement. V_a was strongly affected by pavement depth relative to the other stereological indices. As for the f index, laboratory-aged samples caused a change in the shape of the polymer particles toward circularity. In contrast, field-aged samples did not seem to show consistency with the degree of aging. This may have been due to the greater effect of laboratory aging on the polymer morphology in the early stage of aging, whereas the samples aged in the lab appeared as small particles, which reduced the variability of this indicator for lab-aged samples.

4.2. Correlation Analysis

4.2.1. Effect of Aging Protocols on the Relationship between Stereology and Rheology

The crossover modulus is a potential index that was employed to characterize the aging degree of asphalt binder based on previous studies. In addition, according to the result of CLSM analysis, the most obvious evidence of SBS degradation was the decrease in the fluorescence intensity of the polymer. Therefore, the relationship of the $1/\log(G_c^*)$ and V_a and parameters are further depicted in Figure 9.

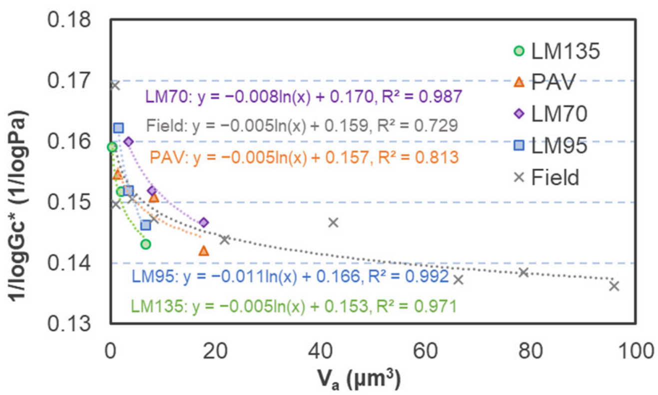


Figure 9. Relationship between the crossover modulus and the fluorescence volume.

As shown in Figure 9, comparing the V_a value of loose asphalt mixtures aging in different temperature conditions with the same aging level, it was found that the degradation of SBS polymer was LM135 > LM95 > LM70. Laboratory aging protocols led to different fitted trendlines at the same linear viscoelastic characterization, indicating different aging conditions may lead to changes in polymer degradation rates. However, it was not found that the polymer degradation rates of field-aged samples were relatively slower than those of lab-aged samples, based on very limited data, due to the much lower aging temperature in the field. Moreover, at the early stage of aging, it seems that laboratory aging has a strong effect on the fluorescence volume of SBS polymers.

4.2.2. Morphological Parameters Correlating with Rheological Indices

The most obvious change for SBS-modified binder with aging is the decrease in the volume of the visible fluorescence phase. In order to clarify the potential effect of polymer degradation on the rheological properties of polymer-modified binder, the relationships between the morphological index, V_a, and all the rheological indices were linked in this study, as shown in Figure 10. Moreover, the results of the rheological indices are summarized in Table 4. There were strong correlations between V_a and $1/\log(G_c^*)$ as well as V_a and R3.2. The R3.2 index provided a much higher correlation with the V_a index, suggesting that the aging-induced decrease in the elastic recovery of SBS-modified asphalt binder was probably closer to the degradation of the polymer.

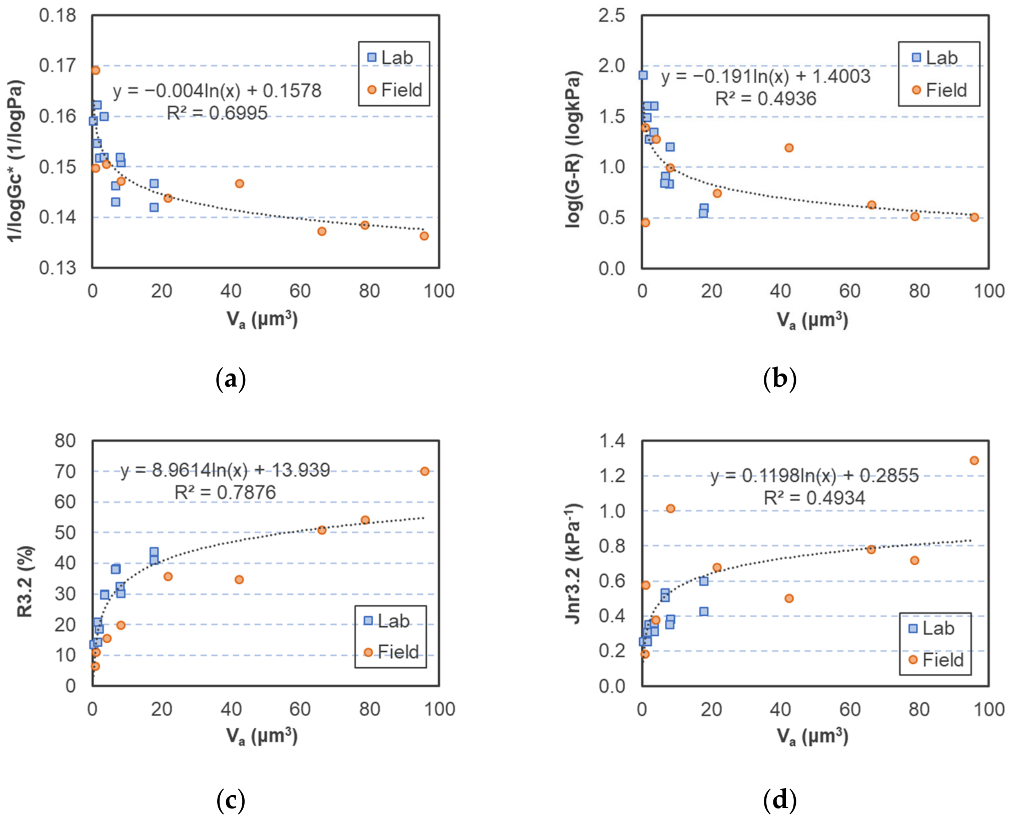


Figure 10. Correlation between V_a and the rheological indices: (**a**) $1/\log(G_c^*)$; (**b**) log(G–R); (**c**) R3.2; and (**d**) Jnr3.2.

Table 4. Summary of rheological test results.

		$1/\log(G_c^*)$	log(G–R)	R3.2	Jnr3.2
Lab aging					
PAV	20 h	0.142	0.594	43.848	0.598
	40 h	0.151	1.200	30.186	0.381
	60 h	0.155	1.490	14.254	0.252
LM70	14 d	0.147	0.541	41.084	0.428
	26 d	0.152	0.831	32.396	0.351
	45 d	0.160	1.602	29.920	0.312
LM95	5 d	0.146	0.843	38.007	0.507
	12 d	0.152	1.342	29.746	0.361
	23 d	0.162	1.604	20.729	0.305
LM135	6 h	0.143	0.912	38.354	0.534
	12 h	0.152	1.274	18.546	0.352
	24 h	0.159	1.908	13.564	0.254
Field aging					
NY	S1	0.136	0.506	70.153	1.290
	S2	0.137	0.627	50.777	0.780
	S3	0.147	1.188	34.745	0.502
YH	S1	0.138	0.512	54.041	0.716
	S2	0.144	0.744	35.758	0.679
	S3	0.151	1.275	15.402	0.380
FG	S1	0.147	0.992	19.783	1.012
	S2	0.150	0.455	10.885	0.576
	S3	0.169	1.391	6.464	0.183

5. Conclusions

This study investigated the effects of lab- and field-aging on the degradation of SBS polymer for SBS-modified asphalt binder, which was detected via CLSM and characterized using the stereological method. Both lab- and field-aged binders were extracted and recovered from asphalt mixtures and examined through CLSM and DSR. Moreover, in order to reveal the effects of SBS polymer degradation on rheological properties, frequency sweep tests and MSCR tests were performed. Finally, the correlations between polymer degradation indices and rheological property indices were analyzed. Based on the results, the following conclusions were derived:

(1) As aging proceeds, the SBS polymer particles showed a decrease in volume and an increase in specific surface area in the three-dimensional view. Moreover, a shortening of Feret's diameter and a tendency to develop round shapes could be obtained in the two-dimensional plane.

(2) Higher aging temperatures led to faster degradation rates of the polymer with a similar stiffness level. Air pressure had a negligible impact on the degradation rate of the SBS polymer.

(3) CLSM could characterize the aging gradient of field-aged samples with different pavement depths. Compared to field-aged samples, laboratory-aged samples had a rapid SBS polymer degradation rate in the early stages of aging.

(4) A certain correlation between the morphology changes in the polymer phase and the rheology changes in the binder phase could be observed for all aged samples, where the degradation of the polymer was strongly correlated with the diminution of the creep recovery rate of the SBS-modified asphalt binder.

6. Future Work

The influence of temperature on polymers will continue to be explored in the future using the CLSM technique, considering the impacts of various polymer contents and polymer types on stereological parameters. In addition, more field-aged samples will be available.

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References

1. Li, Q.; Sun, G.; Lu, Y.; Meng, Y.; Luo, S.; Gao, L. Effects of warm-mix asphalt technologies and modifiers on pavement performance of recycled asphalt binders. *J. Clean. Prod.* **2020**, *282*, 125435. [CrossRef]
2. Sulyman, M.; Sienkiewicz, M.; Haponiuk, J. Asphalt Pavement Material Improvement: A Review. *Int. J. Environ. Sci. Dev.* **2014**, *5*, 444–454. [CrossRef]
3. Yao, L.; Leng, Z.; Lan, J.; Chen, R.; Jiang, J. Environmental and economic assessment of collective recycling waste plastic and reclaimed asphalt pavement into pavement construction: A case study in Hong Kong. *J. Clean. Prod.* **2022**, *336*, 130405. [CrossRef]

4. Yang, X.; Zhang, H.; Chen, Z.; Shi, C. An improved method for separating styrene-butadiene-styrene triblock copolymer (SBS) and bitumen matrix from SBS modified bitumen. *Fuel* **2020**, *286*, 119314. [CrossRef]
5. Yan, C.; Xiao, F.; Huang, W.; Lv, Q. Critical matters in using Attenuated Total Reflectance Fourier Transform Infrared to characterize the polymer degradation in Styrene–Butadiene–Styrene-modified asphalt binders. *Polym. Test.* **2018**, *70*, 289–296. [CrossRef]
6. Ma, T.; Huang, X.; Zhao, Y.; Yuan, H. Aging Behaviour and Mechanism of SBS-Modified Asphalt. *J. Test. Evaluation* **2012**, *40*, 1186–1191. [CrossRef]
7. Mouillet, V.; Lamontagne, J.; Durrieu, F.; Planche, J.-P.; Lapalu, L. Infrared microscopy investigation of oxidation and phase evolution in bitumen modified with polymers. *Fuel* **2008**, *87*, 1270–1280. [CrossRef]
8. Ma, J.; Deng, Y.; Sun, D.; Hesp, S.A. Relationship between thermoreversible and irreversible aging in rejuvenated asphalt binder. *Constr. Build. Mater.* **2022**, *358*, 129463. [CrossRef]
9. Ding, J.; Jiang, J.; Han, Y.; Ni, F.; Ma, X.; Chen, S. Chemical and rheological characterisation of in-situ SBS modified asphalt pavement considering the effect of aging gradient. *Int. J. Pavement Eng.* **2022**. [CrossRef]
10. Yan, C.; Huang, W.; Ma, J.; Xu, J.; Lv, Q.; Lin, P. Characterizing the SBS polymer degradation within high content polymer modified asphalt using ATR-FTIR. *Constr. Build. Mater.* **2019**, *233*, 117708. [CrossRef]
11. Wang, S.; Huang, W. Investigation of aging behavior of terminal blend rubberized asphalt with SBS polymer. *Constr. Build. Mater.* **2020**, *267*, 120870. [CrossRef]
12. Lin, P.; Yan, C.; Huang, W.; Li, Y.; Zhou, L.; Tang, N.; Xiao, F.; Zhang, Y.; Lv, Q. Rheological, chemical and aging characteristics of high content polymer modified asphalt. *Constr. Build. Mater.* **2019**, *207*, 616–629. [CrossRef]
13. Kou, C.; Xiao, P.; Kang, A.; Mikhailenko, P.; Baaj, H.; Wu, Z. Protocol for the morphology analysis of SBS polymer modified bitumen images obtained by using fluorescent microscopy. *Int. J. Pavement Eng.* **2017**, *20*, 585–591. [CrossRef]
14. Soenen, H.; Lu, X.; Redelius, P. The Morphology of Bitumen-SBS Blends by UV Microscopy. An Evaluation of Preparation Methods. *Road Mater. Pavement Des.* **2008**, *9*, 97–110. [CrossRef]
15. Cuciniello, G.; Leandri, P.; Losa, M.; Airey, G. Effects of ageing on the damage tolerance of polymer modified bitumens investigated through the LAS test and fluorescence microscopy. *Int. J. Pavement Eng.* **2020**, *23*, 1083–1094. [CrossRef]
16. Pipintakos, G.; Hasheminejad, N.; Lommaert, C.; Bocharova, A.; Blom, J. Application of Atomic Force (AFM), Environmental Scanning Electron (ESEM) and Confocal Laser Scanning Microscopy (CLSM) in bitumen: A review of the ageing effect. *Micron* **2021**, *147*, 103093. [CrossRef]
17. Li, R.; Leng, Z.; Zhang, Y.; Ma, X. Preparation and characterization of waterborne epoxy modified bitumen emulsion as a potential high-performance cold binder. *J. Clean. Prod.* **2019**, *235*, 1265–1275. [CrossRef]
18. Hao, G.; Wang, Y. 3D Reconstruction of Polymer Phase in Polymer-Modified Asphalt Using Confocal Fluorescence Microscopy. *J. Mater. Civ. Eng.* **2021**, *33*, 04020400. [CrossRef]
19. Handle, F.; Füssl, J.; Neudl, S.; Grossegger, D.; Eberhardsteiner, L.; Hofko, B.; Hospodka, M.; Blab, R.; Grothe, H. Understanding the microstructure of bitumen: A CLSM and fluorescence approach to model bitumen ageing behavior. In Proceedings to the 12th ISAP International Conference on Asphalt Pavements, Raleigh, NC, USA, 1–5 June 2014.
20. Pipintakos, G.; Blom, J.; Soenen, H.; Bergh, W.V.D. Coupling AFM and CLSM to investigate the effect of ageing on the bee structures of bitumen. *Micron* **2021**, *151*, 103149. [CrossRef]
21. Mirwald, J.; Hofko, B.; Grothe, H. Utilising fluorescence spectroscopy and optical microscopy to investigate bitumen long-term ageing. *Road Mater. Pavement Des.* **2020**, *22*, S23–S36. [CrossRef]
22. Kaya, D.; Topal, A.; McNally, T. Correlation of processing parameters and ageing with the phase morphology of styrene-butadiene-styrene block co-polymer modified bitumen. *Mater. Res. Express* **2019**, *6*, 105309. [CrossRef]
23. Lu, X.; Isacsson, U. Modification of road bitumens with thermoplastic polymers. *Polym. Test.* **2000**, *20*, 77–86. [CrossRef]
24. Chen, Z.; Zhang, H.; Duan, H.; Wu, C. Determination of time-temperature superposition relationship of SBS modified asphalt based on special rheological phenomenon caused by SBS-formed structure in asphalt matrix. *Constr. Build. Mater.* **2020**, *260*, 119835. [CrossRef]