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Research Article

Effects of Commercial Antioxidants on Aging Resistances of Asphalt Binders

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Asphalt aging has a direct influence on the durability of asphalt mixture. In order to improve thermal oxidizing aging resistance of asphalt, the commercial antioxidants including Irganox 1010 and Irgafos 168 were selected to modify base asphalt and SBR asphalt. The basic properties of modified asphalt before and after the rolling thin film oven test (RTFOT) are evaluated by penetration, softening point, ductility, and viscosity. The Fourier transform infrared spectroscopy (FTIR) test was applied to determine the antiaging mechanism of modified and unmodified asphalt. According to the test result, Irganox 1010 not only reduces the aging degree of asphalt but also has little adverse effect on other properties. Irgafos 168 with a content of 1% improves the low temperature ductility of asphalt and improves the antiaging performance of asphalt significantly. After RTFOT, the content of oxygen-containing functional groups (carbonyl group and sulfoxide group) declines significantly in antioxidation modified asphalt, and Irganox 1010 and Irgafos 168 inhibit oxidizing reaction in the aging procedure. This study can provide a useful reference for improving the aging property of asphalt in highway construction.

1. Introduction

Asphalt pavement with a good performance has been widely used around the world since the 1850s [1–6]. In the mixing and paving stage of asphalt mixture, the oxidation reaction of asphalt with oxygen occurs at high temperature, which leads to the rapid aging of asphalt. In the service stage, a slow oxidation reaction gradually occurs between asphalt and oxygen in the air [7–9]. Asphalt aging causes the binder to become hard and brittle, with a severe decline in relaxation properties, eventually leads to pavement cracking and other diseases. Therefore, research efforts on asphalt aging research and discussion had never terminated until now [10–14]. Adding additives to asphalt to improve the antiaging performance of asphalt is the most commonly used method [15–18]. Therefore, more and more attention has been paid to the addition of antiaging agents, which can inhibit the thermal and oxygen aging reaction process to improve the antiaging property of asphalt.

The antioxidant was used as antiaging agents frequently. Previous studies have shown that antioxidants can effectively improve the aging resistance of asphalt. Williams et al. [19] have evaluated the antioxidant effects of lignin-containing ethanol coproducts on asphalt binders. They proved that lignin-containing ethanol coproducts can effectively reduce the aging degree of asphalt binders. Reyes et al. [20] have studied the antiaging effect of VE for the base and modified asphalt binders, and the results showed that the viscosity of asphalt decreases and fatigue crack resistance increases. Ouyang et al. [21] have investigated the impacts of antioxidants including zinc dialkyl dithiophosphate (ZDDP) and zinc dibutyl dithiocarbamate (ZDBC) on SBS-modified asphalt, and they suggested that ZDDP and ZDBC can retard the oxidation of asphalt through the inhibition of peroxides and radical scavenging. Li et al. [22] researched the antiaging effect of three antioxidants in asphalt, evaluated antiaging performance using the aging index, and analyzed the antiaging mechanism with FTIR. The result shows that the antioxidants make the aging chain reaction terminated so

that the aging resistance had been effectively improved. The composite antioxidant was more stable for aging resistance improvement of asphalt due to its good synergistic effect. Different kinds of antioxidants in asphalt binders have different effects on resistance oxidation [22, 23].

Among the antioxidants, Irganox 1010 and Irgafos 168 were the common antioxidants. Irganox 1010 was characterized by low volatilization, extraction resistance, nontoxic and high thermal stability, and melting temperature similar to asphalt, and Irgafos 168 has good high temperature resistance, color resistance, strong extraction resistance, and stable hydrolysis. Both of them have significant antiaging effects on polymer materials. Apeagyei et al. [9] used Irganox 1010 and its different combinations with other antioxidants to explore the antiaging effect of antioxidants on asphalt through the dynamic shear rheological (DSR) test and the bending beam rheometer (BBR). Their result shows that the hardness of asphalt after short-term aging did not decrease significantly when the content was less than 1%, but the effect was significant when it is above 5%. The reduction in hardness after aging of asphalt was related to the content of Irganox 1010. Irganox 1010 in combination with carbon black has a good antiaging effect for asphalt binders when its content reaches 3%. Thus, it can be found that Irganox 1010 is beneficial for the improvement of asphalt properties. However, only the rheological properties and antiaging properties of asphalt under the influence of Irganox 1010 were studied, but the impact of different contents on the physical properties of asphalt is required to be researched in the future, and the interaction mechanism between Irganox 1010 and asphalt also should be revealed. Furthermore, Feng et al. [24] studied the effects of Irganox 1010, Irgafos 168 and their different combinations on the physical properties and antiaging properties of asphalt, and the result shows that Irganox 1010 can improve the thermal oxidative aging resistance of asphalt; the oxidative aging resistance of asphalt can also be improved when the content of Irganox 1010 was not more than 0.6 by a total weight of bitumen. Irgafos 168 did not improve the thermal oxidative aging resistance when the content was less than 0.6 by a total weight of bitumen. A notable improvement can be found when the content exceeds 0.6 by a total weight of bitumen. However, the range of antioxidant content was on a small scale and lacked Irganox 1010 and Irgafos 168 in the thermal oxidative aging mechanism of asphalt. Li et al. [25] studied that the reaction mechanism of Irganox 1010 and Irgafos 168 in asphalt, indicating that Irganox 1010 was one of hindered phenols, and it can effectively prevent SBS from oxidation via scavenging free radical; Irgafos 168 can decompose hydroperoxides as phosphite. It can be inferred that the antiaging properties of polymers were improved by adding Irganox 1010 and Irgafos 168; therefore, the antiaging performance of asphalt can also be modified by Irganox1010 and Irgafos168.

Herein, the aging reaction can be reduced by Irganox1010 and Irgafos 168. Though above research studies have studied the effects of Irganox 1010 and Irgafos 168 on asphalt, but the effect of Irganox 1010 and Irgafos 168 on thermal oxidative aging properties of asphalt has not been studied systematically. It is meaningful to investigate the effect of Irganox 1010 and Irgafos 168 on the aging performance of asphalt in order to reduce the aging during the service process of pavement. This will also provide a reference for the application of antiaging asphalt mixture.

The aging of asphalt is closely related to the change in the asphalt structure and the molecular structure, and the chemical composition of asphalt can be studied by Fourier transform infrared spectroscopy. Wu [26] indicated that the antiaging effect of Irganox 1010 on asphalt was improved using FTIR, and Irganox 1010 inhibited gelatinization of asphalt in the thermal oxidation aging process. Lmontagne et al. [27] used the sum of the peak areas at 4000 cm^{-1}-700 cm^{-1} as a benchmark to evaluate the effect of thermal oxidative aging on different asphalt and different functional groups. Studies have shown that the main reason for asphalt aging is that it reacts with oxygen to produce carbonyl polar macromolecules during the aging process. Zhang et al. [28] studied the structure characteristics of asphalt based on FTIR and used five analytical benchmarks in different ranges to study the functional group indexes before and after the aging. The results showed that the peak area at 4000 cm^{-1}~700 cm^{-1} was the most stable.

In this paper, the rolling thin film oven test was used to simulate the short-term aging process in order to study the impact of Irganox 1010 and Irgafos 168 on the thermal oxidative aging property of asphalt. The modified antiaging asphalt was homogenized using a high-speed shearing method. The impacts of both antioxidants on properties were evaluated through penetration, softening point, ductility, and viscosity tests before and after RTFOT. FTIR analysis was conducted to reveal the antiaging reaction mechanism of Irganox 1010 and Irgafos 168.

2. Materials and Experiment

2.1. Raw Materials. Asphalt called AH-70# and SBR-II-A and modified asphalt were selected for experiment, and physical properties of asphalt binders are summarized in Table 1. It should be noted that SBR-modified asphalt was the standard product from an asphalt plant. The antioxidant includes Irganox 1010[pentaerythritol tetrakis 3-(3,5-di-tert-butyl 4-hydroxyphenyl)propionate] and Irgafos168 [tris-(2,4-di-tert-butyl)phosphite]. The common properties of Irganox 1010 and Irgafos 168 are summarized in Table 2.

2.2. Preparation of Modified Asphalt. A high-speed shearing machine was used to prepare modified asphalt in this paper. Base asphalt AH-70# and SBR-modified asphalt were selected for experiment. The contents of Irganox 1010 and Irgafos 168 were 0wt.%,1wt.%,5wt.%, and 10wt.%. In preparing the procedure, asphalt is placed in an oven at 135 °C for 1 hour in order to ensure the fluidity of asphalt and reduce aging of the thermal insulation process, and then, the

Table 1: Physical properties of the asphalt binder.

Physical properties	AH-70#	SBR asphalt	Standard
Penetration (25°C, 0.1 mm)	75	140	ASTM-D5
Ductility (10°C, cm)	38.9	144	ASTM-D113
Ductility (15°C, cm)	>100	>150	ASTM-D113
Softening point (°C)	49.2	49.6	ASTM-D36
Viscosity (135°C, Pa·s)	0.306	0.528	JTG E20-2011

Table 2: The common indexes of antioxidants.

Physical properties	Irganox 1010	Irgafos 168
Color	White	White
Melting point (°C)	110~125	182~186
Content (%)	≥ 98	≥ 99
Density (g•cm^{-3})	1.15	1.03
Ash (%)	≤ 0.1	≤ 0.3
Transmittance (425 nm%)	≥ 95	≥ 93
Transmittance (500 nm%)	≥ 97	≥ 95
Volatile (%)	≤ 0.5	≤ 0.5

Table 3: Preparation conditions of modified asphalt.

No	Antioxidant	Asphalt	Temperature (°C)	Shearing speed (rad/s)
1#	Irganox 1010	AH-70	150	4500
2#	Irgafos 168	AH-70	180	4500
3#	Irganox 1010	SBR-II-A	150	4500
4#	Irgafos 168	SBR-II-A	180	4500

antiaging asphalt in Table 3 is obtained after mixing for 15 minutes. AH-70# asphalt and SBR-modified asphalt should be mixed under the same conditions related to the speed, temperature, and time in order to eliminate the adverse effect caused by operation.

2.3. Experimental Methods. According to the standard JTG E20-2011, oxidative aging of antioxidation aging asphalt binders was performed using the rolling thin film oven test (RTFOT). The penetration test, softening point test, ductility test, and viscosity test before and after RTFOT were performed according to the standard JTG E20-2011. The test temperature of the penetration test was 25°C. The softening point test (ring-and-ball Apparatus) had adopted a standard test. The test temperature of the ductility test was 10°C, and the speed was 5 cm/min because the ductility of SBR modified asphalt at 15°C was overrange, and at 5°C, the 70# binder was easy to fracture. The viscosity was determined by the Brookfield viscometer method, and the test temperatures of the viscosity test were 90°C, 100°C, 110°C, 120°C, and 135°C. Three replicates were prepared for each test.

2.4. Characterization Method. The asphalt aging degree was evaluated by the penetration retention rate (PRR), the ductility retention rate (DRR), the softening point increment (SPI), and the viscosity aging index (VAI).

2.4.1. Penetration Retention Rate (PRR)

$$PRR(\%) = \frac{P}{P_0} \times 100\%, \tag{1}$$

where P_0 indicates the unaged penetration of asphalt, 0.1 mm;P indicates the aged penetration of asphalt, 0.1 mm. The lower the PPR, the more severe the aging.

2.4.2. Ductility Retention Rate (DRR)

$$DRR(\%) = \frac{D}{D_0} \times 100\%, \tag{2}$$

where D_0 indicates the unaged ductility of asphalt, cm; D indicates the aged ductility of asphalt, cm. The lower the DRR, the more severe the aging.

2.4.3. Softening Point Increment (SPI)

$$SPI = SP - SP_0, \tag{3}$$

where SP indicates the aged softening point of asphalt,°C; SP_0 indicates the unaged softening point of asphalt, °C. The greater the SPI, the more severe the aging.

2.4.4. Viscosity Aging Index (VAI)

$$VAI = \frac{V_{aged} - V_{unaged}}{V_{unaged}} \times 100\%, \tag{4}$$

where V_{aged} indicates the aged viscosity of asphalt, Pa·s; V_{unaged} indicates the unaged viscosity of asphalt, Pa·s. The greater the VAI, the more severe the aging.

2.5. FTIR Test. The asphalt sample for FTIR analysis was prepared by the KBr disc method. In the narrow-mouthed bottle, the asphalt sample was dissolved in a toluene solvent to prepare a 5% asphalt/toluene solvent. In order to avoid the water in the air entering into the narrow-mouthed bottle, we put the narrow-mouthed bottle in the desiccator waiting for the test. For the Irganox 1010 and Irgafos 168 sample, the spectra samples were obtained by blending Irganox 1010 and Irgafos 168 with the KBr powder, respectively. FTIR was measured by FTIR-1500 series. The spectra were recorded from 4000 to 400 cm^{-1} averaging 120 scans for each measurement. The testing process is shown in Figure 1. The FTIR data were analyzed and processed by OMNIC.

3. Results and Discussions

3.1. Effects of the Mixing Procedure and Aging on the Properties of Asphalt. Influence of Irganox1010 and Irgafos168 contents on antiaging performances of modified asphalt for virgin bitumen and RTFOT aged one is shown in Table 4. The coefficients of variation of parallel experiments were all within 10%.

As listed in Table 4, it can be seen that both Irganox 1010 and Irgafos 168 have significant effects on asphalt physical properties. For Irganox 1010, with the increase of

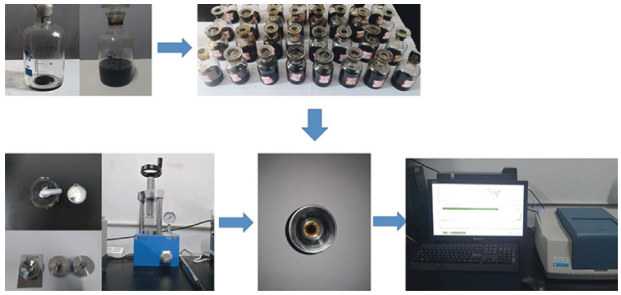

Figure 1: Fourier infrared spectroscopy (FTIR) sample preparation and test.

Table 4: Influence of matrix asphalt on three indexes before and after mixing and aging.

Name	Property	Before aging				After aging			
		0	1	5	10	0	1	5	10
1#	Penetration (0.1 mm)	81	79	76	60	49	49	47	37
	Softening point (°C)	48.9	48.6	48.8	48.4	54.4	53.6	53.9	53.3
	Ductility (10 °C, cm)	39.0	44.8	33.6	—	6.6	7.9	7.2	—
2#	Penetration (0.1 mm)	81	77	80	87	49	49	53	56
	Softening point (°C)	48.9	48.8	48.2	48.0	54.4	54.1	53.0	52.3
	Ductility (10 °C, cm)	39.0	41.6	35.8	50.3	6.6	7.3	7.5	10.0
3#	Penetration (0.1 mm)	145	144	138	117	89	94	88	77
	Softening point (°C)	49.2	48.5	48.8	50.0	49.9	48.9	49.3	50.3
	Ductility (10 °C, cm)	150.0	150.0	142.5	117.1	52.7	53.1	52.6	44.3
4#	Penetration (0.1 mm)	145	145	141	142	89	97	101	98
	Softening point (°C)	49.2	49.0	48.4	48.3	49.9	49.6	48.7	48.5
	Ductility (10 °C, cm)	150.0	150.0	150.0	144.5	52.7	58.5	68.7	70.7

antioxidant contents, the penetration of asphalt gradually decreased and the range of change gradually increased. However, Irganox 1010 has little effect on the softening point of both types of asphalt and will not influence the thermal stability of asphalt. At the same time, it is clearly found that Irganox 1010 has a similar impact on the ductility of both types of asphalt, and adding 1% antioxidant can improve the low temperature performance. Low temperature ductility will be greatly declined with the increase of antioxidants. In particular, the ductility of asphalt 1# dropped significantly when Irganox 1010 content reached 10%. After RTFOT, the ductility of asphalt was optimal when its content was 1%. The addition of Irganox 1010 to asphalt forms an ester-based substance, which causes asphalt to become hard. Thus, the penetration and ductility of the aged asphalt declined when Irganox 1010 is more than 1%.

For Irgafos 168, when the antioxidant content is 1%, the penetration and softening point of asphalt changed slightly. The regularity is also observed in the paper of Feng et al. [24]. With the increase of Irganox 168, the most drastic changes existed in the penetration and ductility, but the softening point changed a little. In particular, the penetration of asphalt 4# decreased but is still greater than original SBR asphalt. The ductility is greater than 150 cm when the content is not more than 5%, but it dropped a little when the content reached 10%. After RTFOT, the penetration and ductility of asphalt had risen notably, and the softening point decreased. It can be seen that large content of Irgafos 168 has a notable improvement on the property after aging.

Influence of Irganox 1010 and Irgafos 168 on the Brookfield viscosity of antiaging modified asphalt is shown in Figure 2.

As shown in Figure 2, it can be seen that Irganox 1010 and Irgafos 168 have similar effects on the viscosity of asphalt. The antioxidants reduced the viscosity, and with the increase of Irganox 1010 and Irgafos 168, the viscosity decreased gradually. In the case of a small content, the effect of antioxidants on base and SBR asphalt is not consistent. Antioxidants have little effect on the viscosity of base asphalt, which made the viscosity of SBR asphalt decrease significantly. The higher the test temperature, the less the effect of antioxidants.

3.2. Evaluation of Antiaging Effects

3.2.1. Mass Loss. During the aging process, the light molecular structure of volatilization reduces the mass of the sample, but the oxidation reaction also occurs during aging, which increases the mass of asphalt. The positive value of mass loss meant that oxygen reacts during the aging process to increase the mass, while a negative value of the mass loss is due to the volatilization of light oils, and the influence of Irganox 1010 and Irgafos 168 on the mass loss is shown in Figure 3.

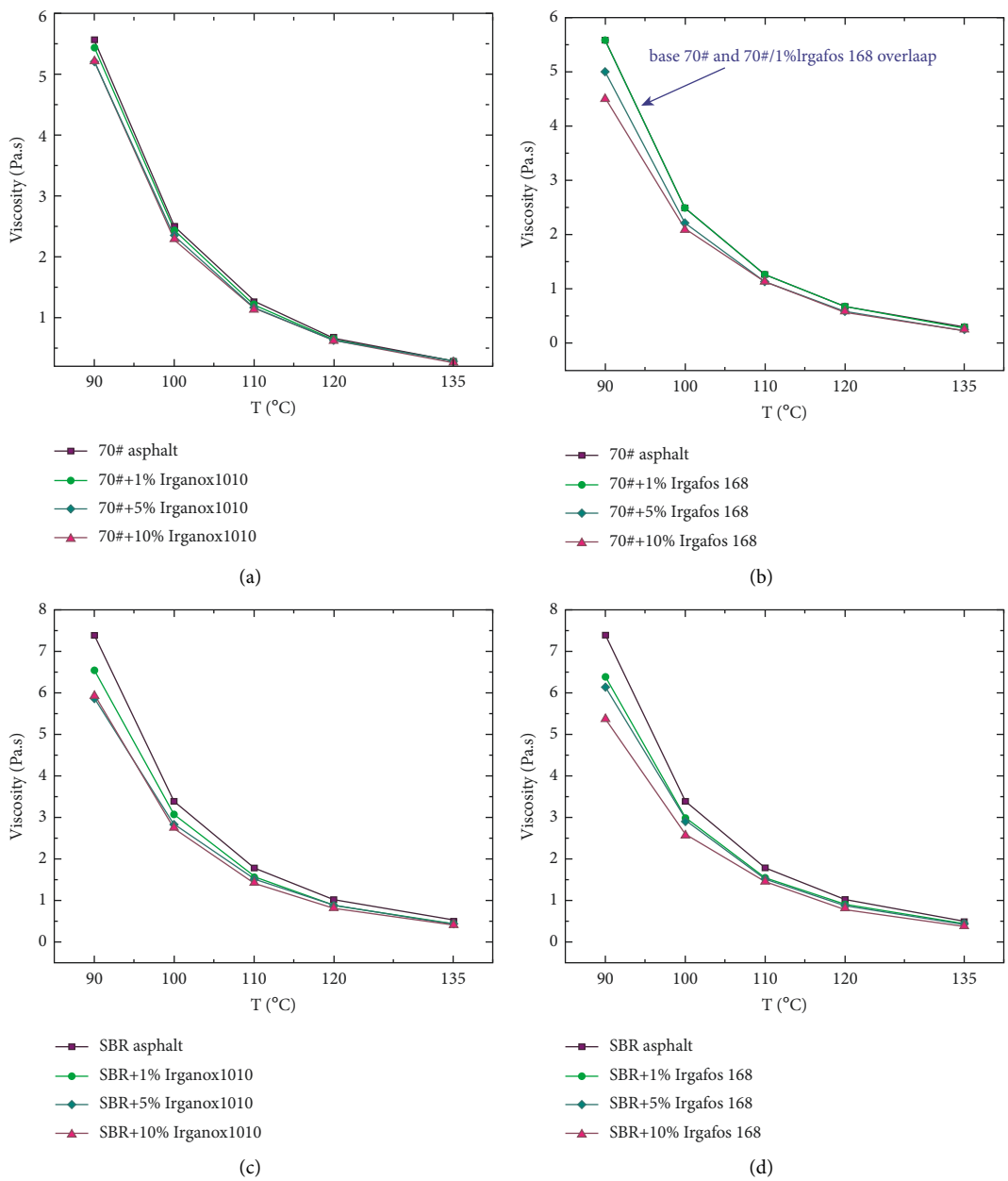

Figure 2: Viscosities of virgin and modified asphalt.

As shown in Figure 3, it could be seen that the mass loss of modified antiaging asphalt decreased after adding Irganox 1010 and Irgafos 168, and with the increase of the content, the mass loss tended to be stable. SBR asphalt generated more mass loss after aging. The antiaging capacity was improved after adding the antioxidants, which weakened the volatilization of light components and also inhibited the aging of SBR asphalt.

3.2.2. Aging Index. The influence of RTFOT aging on the penetration is shown in Figure 4.

The penetration retention rate (PPR) can be used to evaluate the antiaging performance, Yu et al. [18] indicated that the lower the PPR was, the more severe the aging was. As described in Figure 4, it was easy to find that the PPR of base asphalt increased, but its improvement was limited. So, Irganox 1010 has slight influence on the PPR of asphalt 1# when the content of Irganox 1010 was not more than 5%. Although the PPR substantially increased when the content of Irganox 1010 reached 10%, Irganox 1010 would produce adverse effects on the penetration. Therefore, considering the antiaging action and the adverse effect for the penetration, the optimal content of Irganox 1010 is 1% for base asphalt. The PPR of SBR asphalt increased significantly with the increase of Irgafos 168, the PPR was at its peak when the content reached 5%. Therefore, Irgafos 168 effectively reduces the decrease of penetration caused by aging and improves the antiaging performance. From the PPR, the antiaging action of Irgafos 168 is better than that of

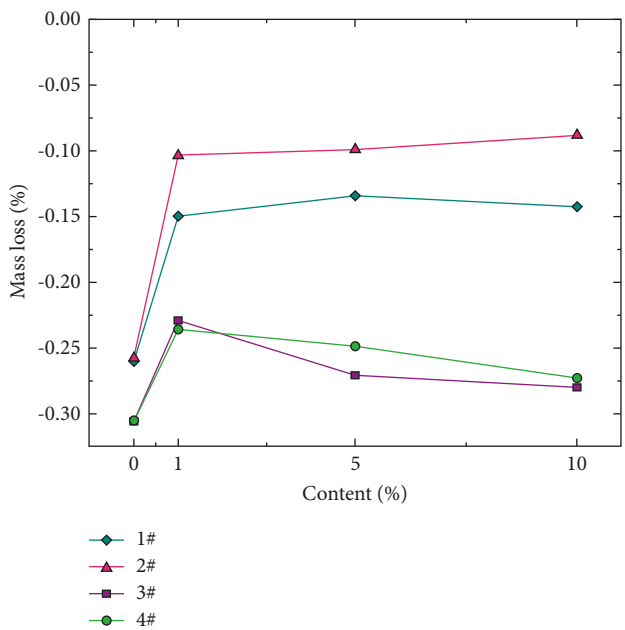

Figure 3: Mass loss of different types of asphalt.

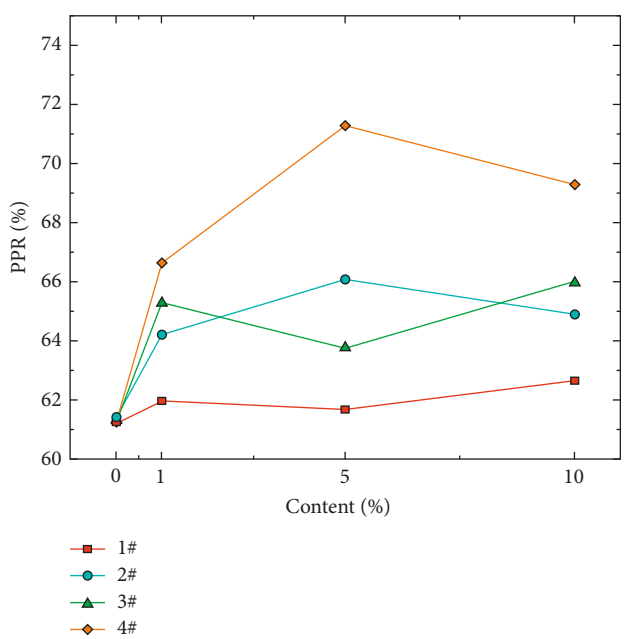

Figure 4: PPR of different types of asphalt.

Irganox1010. The PPR of SBR is higher than that of base asphalt. This is because the antioxidant and SBR have a synergistic effect, and the composite modification has a better antiaging action.

As described in Figure 5, the softening point increment (SPI) can be used to evaluate the antiaging performance, and the larger the SPI, the more severe the aging. The SPI of antioxidant-modified SBR binders is always smaller than that of base asphalt. The SPI dropped with the increase of both antioxidants. The SPIs of modified base and SBR asphalt gradually decreased with the increase of Irgafos 168.

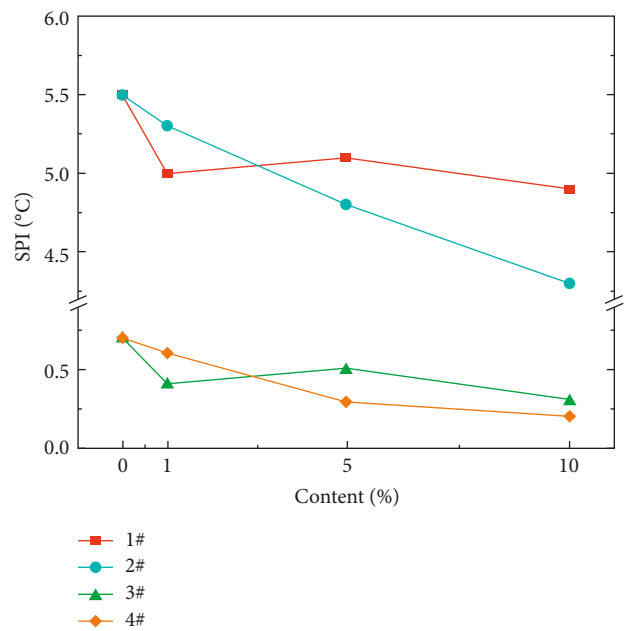

Figure 5: SPI of different binders.

When the content is small, the change in the SPI was relatively small. It can be inferred that the addition of two antioxidants can reduce the oxidative aging degree of modified asphalt. Among them, Irganox 1010 showed a better aging resistance when the content was 1%, and a better antiaging performance was observed when Irgafos 168 was more than 1%.

The ductility retention rate (DRR) can be used to evaluate the antiaging performance, and the lower the DRR was, the more severe the aging was . From Figure 6, it can be seen that DRRs of the modified asphalt with Irganox 1010 and Irgafos 168 are higher than those of the unmodified ones. When the amount of antioxidants is small, the DRR of base asphalt slightly changed. The DRR significantly rose after the amount exceeded 1%. For asphalt 1#, when Irganox1010 reached 10%, the asphalt generated brittle failure before and after aging. Therefore, the DDR of the modified group containing 10% Irganox 1010 was unavailable. The DRR of Irgafos 168 modified SBR asphalt increases with the increase of antioxidants. However, the DDR of asphalt 4# showed a good improvement, while the DDR of asphalt 3# had no significant change.

The viscosity aging index (VAI) can be used to evaluate the antiaging performance, and the higher the VAI was, the more severe the aging was. As shown in Figure 7, the VAI of modified asphalt shows an overall downward trend, especially when the antioxidant content is 10%, the decline is the largest. Among them, Irganox 1010 has a complex effect on the VAI of base asphalt. With the increase of antioxidant content, the VAI of base asphalt first decreased then gradually increased and finally dropped to the lowest value. At the same content, the VAI decline amplitude of modified SBR is obviously larger than that of base asphalt. The antiaging effect of antioxidants on SBR is better.

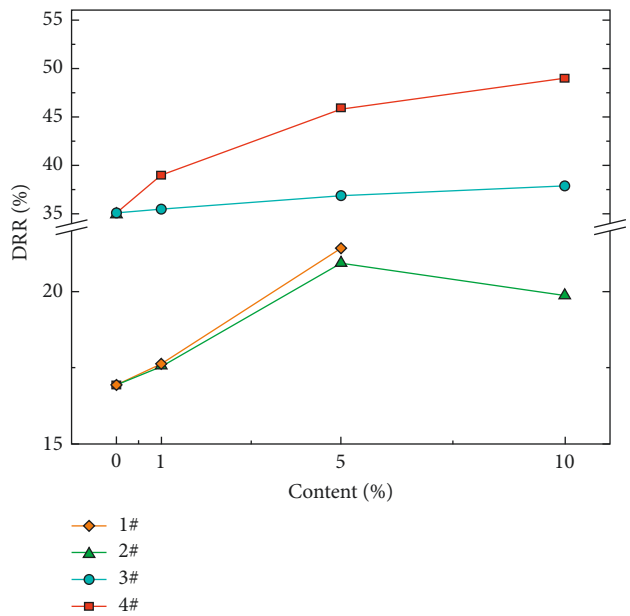

Figure 6: Ductility retention rate of different binders.

3.3. FTIR Analysis of the Antioxidant Mechanism. FTIR tests were performed on the samples of 70# asphalt, SBR asphalt, Irganox 1010, Irgafos 168, and modified asphalt before and after aging. The main absorption peaks in modified asphalt were analyzed , as shown in Table 5. The FTIR analysis of Irganox 1010, Irgafos 168, unmodified asphalt, and modified asphalt is shown in Figures 8–11.

As shown in Figures 8 and 10, for Irganox 1010, it is not difficult to find two peaks in Irganox 1010 spectra observed at 3645 cm^{-1} and 1750 cm^{-1}. From Table 5, it can be found that the corresponding functional group at 3645 cm^{-1} is a phenolic hydroxyl group (O–H) and at 1750 cm^{-1} is an ester group (C=O). Therefore, Irganox 1010 is fused with 70# and SBR asphalt mainly through physical adsorption without chemical reaction.

As shown in Figures 9 and 11, for Irgafos 168, the characteristic peak is located at 856 cm^{-1} and 1083 cm^{-1}. The corresponding functional group at 856 cm^{-1} is a "=CH" nonplanar variable angle vibration on the benzene ring and at 1083 cm^{-1} is a P–H in-plane vibration in phosphorous acid. In particular, the groups of 2# + 10% Irgafos 168 and 4# asphalt+10%Irgafos 168 contain a peak at 970 cm^{-1}. Irgafos 168 and 70# asphalt did not have this peak as shown in Figure 9. So, the difference between the peak at 970 $cm^{-1}$is trans-butyl, and the peak intensity also increased. Therefore, Irgafos 168 is fused with 70# asphalt and SBR asphalt mainly through chemical reaction.

It is found in Figure 12(a) and Figure 13(a) that the sulfoxide group appeared at 1030 cm^{-1}, but no obvious carbonyl group is found at 1700 cm^{-1}, indicating that the content of the carbonyl group is very low before aging, but there is still a small amount of the sulfoxide group, and this finding is consistent with previous research [29, 30]. The peak intensity of the phenolic hydroxyl group at 3645 cm^{-1} and the ester group at 1750 cm^{-1} is increased with the increase of Irganox 1010. The increase of the ester group is the main cause of hardening of asphalt 1# and 3#. Because the ester group can connect different molecules to produce higher relative molecular weight substances, resulting in the increase of asphaltenes, so that the colloidal structure, chemical composition and properties of asphalt would be changed. As the core of the micelles, the increase of asphaltenes leads to the decrease of the solubility of the micelles, the development of the network structure, and the gelation of the asphaltenes. By comparing the FTIR of 1# and 3#, it can be found that Irganox 1010 has a greater impact on 70# asphalt.

As can be seen in Figures 14 and 15, when Irganox 1010 was not added, the absorption peaks of carbonyl groups at 1700 cm^{-1} and sulfoxide groups at 1030 cm^{-1} were significantly enhanced after aging by RTFOT, indicating that the content of oxygen-containing functional groups in asphalt increased during aging. With the addition of Irganox 1010, the absorption peak strength of carbonyl and sulfoxide groups gradually decreased, indicating that the hydroxyl (-OH) functional groups in Irganox 1010 were relatively easy to release hydrogen atoms, which destroys the reaction of free radical automatic oxidation chains, thus inhibiting the generation of oxygen-containing functional groups in asphalt and delaying the aging process. For asphalt 3# after aging, the absorption peak of trans-butadiene at 970 cm^{-1} is also significantly reduced, which was due to the cleavage reaction of the SBR modifier during aging. The synergistic effect of the Irganox 1010 and SBR modifier increases the antiaging capability of asphalt 3#, which is also the reason why 3# has better antiaging capability than 1#.

It is not difficult to see in Figure 14(a) and Figure 15(a), with the increase of Irgafos 168, the absorption peaks of 2# and 4# at 1083 cm^{-1}, 970 cm^{-1}, and 875 cm^{-1} were significantly enhanced, and sulfoxide group absorption peaks appeared at

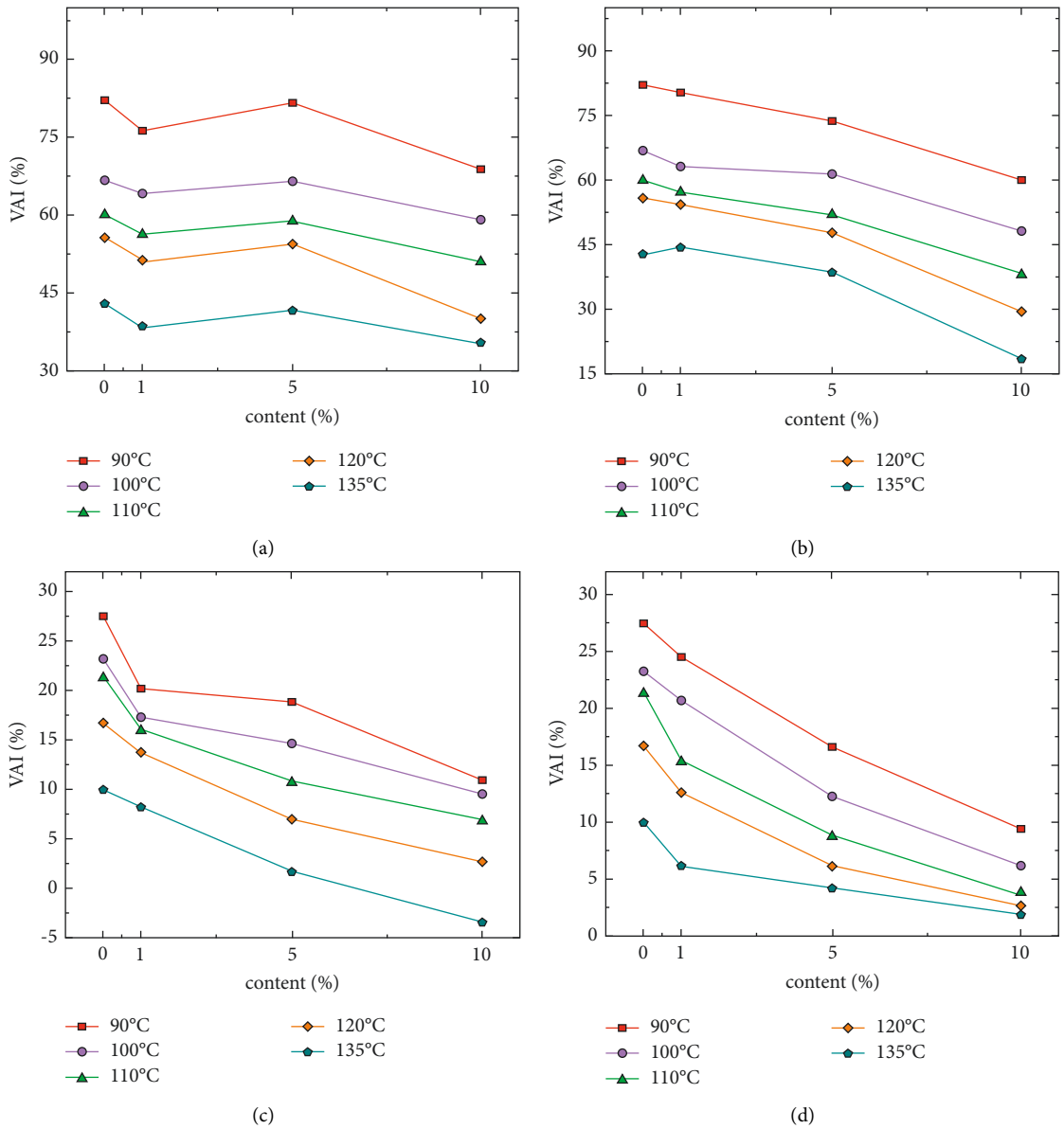

Figure 7: Viscosity aging index of different binders.

1030 cm^{-1}, but no obvious carbonyl absorption peaks were found at 1700 cm^{-1}. The peak at 970 cm^{-1} generated by the chemical reaction in 2# was the alkene functional group, which had the same peak position as the transbutadiene in SBR, and the absorption peak at 970 cm^{-1} in 4# is also significantly enhanced. As shown in Figure 14(b) and Figure 15(b), the content of carbonyl and sulfoxide functional groups in 2# and 4# decreased with the increase of Irgafos 168 after aging by RTFOT. After aging, the absorption peak intensity of 2# and 4# decreased significantly at 970 cm^{-1}, indicating that butadiene can improve the antiaging performance. Therefore, Irgafos 168 can significantly improve the aging resistance of asphalt.

In order to avoid the influence of experimental errors, it is often suggested that we select a part of a peak area and use it as a reference to calculate the functional group index. The change in the relative intensity of functional groups was analyzed by using the functional group index, and the antiaging properties of asphalt were studied by using the change rate of the functional group index before and after aging. In the FTIR analysis of asphalt, the carbonyl index, sulfoxide group index, aromatic index, and aliphatic index are often used as the analysis indexes. Therefore, according to Lmontagne's study [29], the sum of different peak areas within the range of 4 000 cm^{-1}~700 cm^{-1} is adopted as the benchmark. The functional group index is calculated based on equations (5)–(8). The exponential change rates of functional groups before and after aging are calculated based on equation (9).

Table 5: Spectral analysis of main absorption peaks in modified asphalt.

Wavenumber (cm)	Functional groups
3645^{-1}	νO-H
2925^{-1}	vC-H aliphatic
2852^{-1}	vC-H aliphatic
1750^{-1}	$vC = O$
1700^{-1}	$vC = O$ conjugated
1600^{-1}	$vC = C$ aromatic
1460^{-1}	δC-H of -(CH 2)n- (aliphatic index)
1377^{-1}	δC-H of CH3 (aliphatic branched)
1083^{-1}	P–H in-plane vibration in δ phosphite
1031^{-1}	$vS = O$ sulfoxide
965^{-1}	δC-H trans disubstituted –CH=CH- (butadiene block)
856^{-1}	= CH nonplanar variable angle vibration on benzene ring
747^{-1}	δC-H aromatic monosubstituted (styrene block)

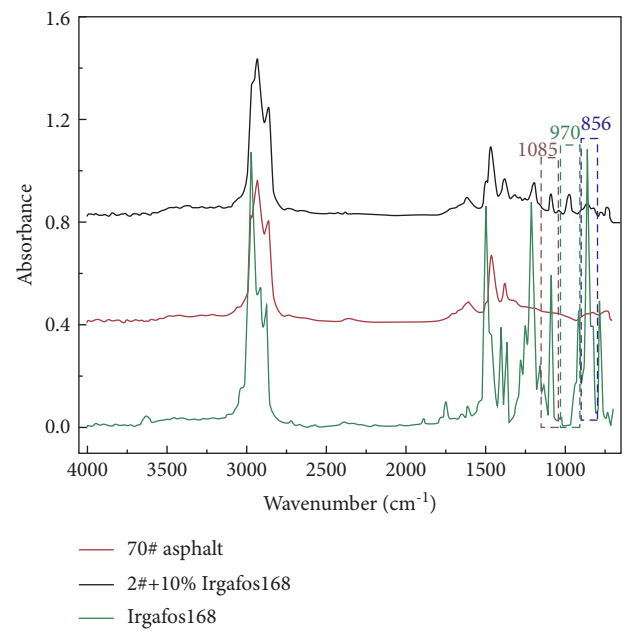

Figure 9: Spectra of Irgafos 168, 70# asphalt, and 2# + 10%Irgafos 168.

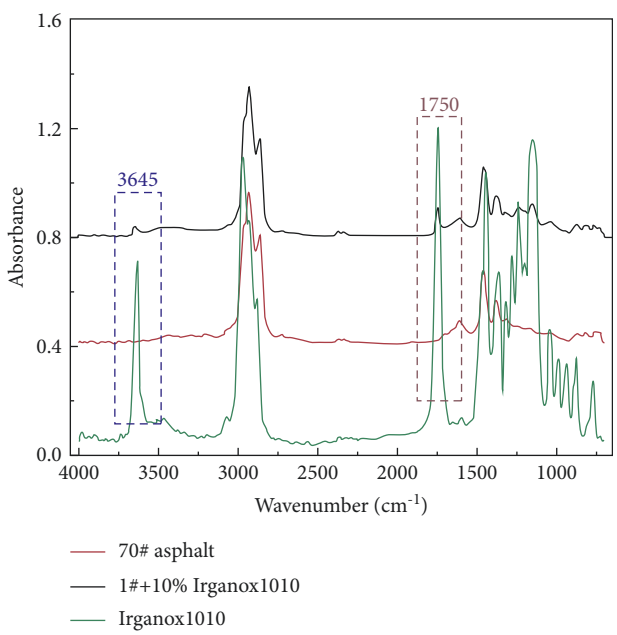

Figure 8: Spectra of Irganox 1010, base asphalt, and 1# + 10% Irganox 1010.

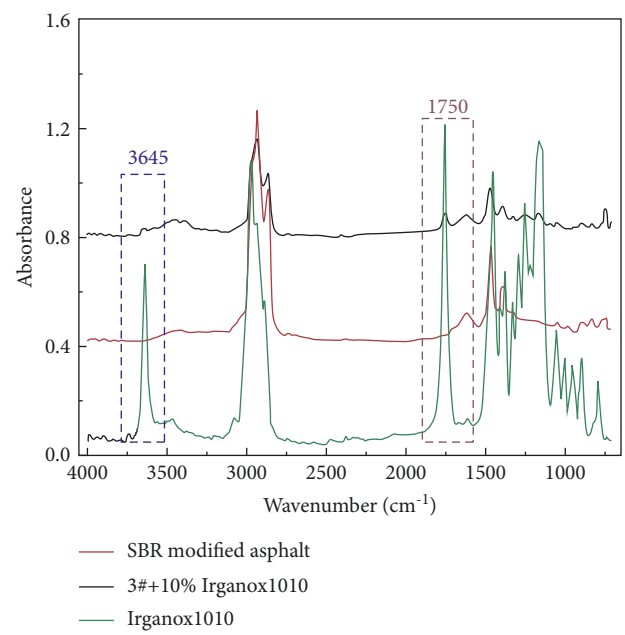

Figure 10: Spectra of Irganox 1010, SBR-modified asphalt, and 3# + 10%Irganox 1010.

$$I_{C=O} = \frac{Area\ of\ the\ carbonyl\ band\ centered\ around\ 1700\ cm^{-1}}{\sum Area\ of\ the\ spectral\ bands\ between\ 4000\ cm^{-1}\ and\ 700\ cm^{-1}}, \tag{5}$$

$$I_{Ar} = \frac{Area\ of\ the\ aromatic\ band\ centere\ daround\ 1600\ cm^{-1}}{\sum Area\ of\ the\ spectral\ bands\ between\ 4000\ cm^{-1}\ and\ 700\ cm^{-1}}, \tag{6}$$

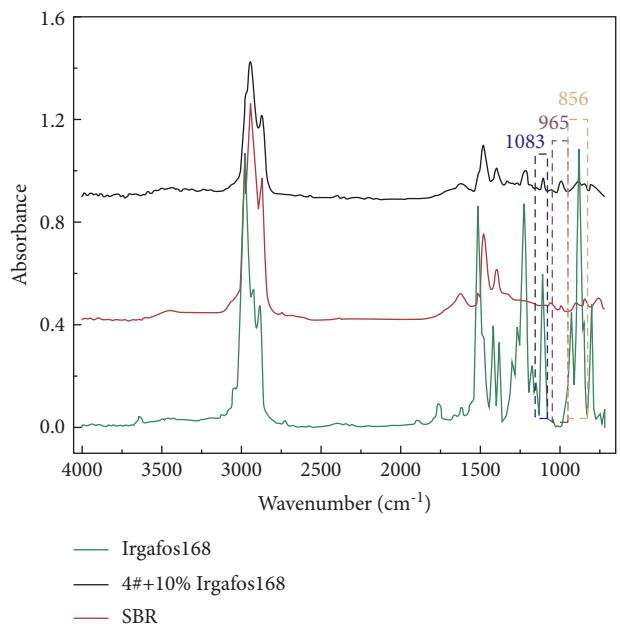

Figure 11: Spectra of Irgafos 168, SBR-modified asphalt, and 4# + 10%Irgafos 168.

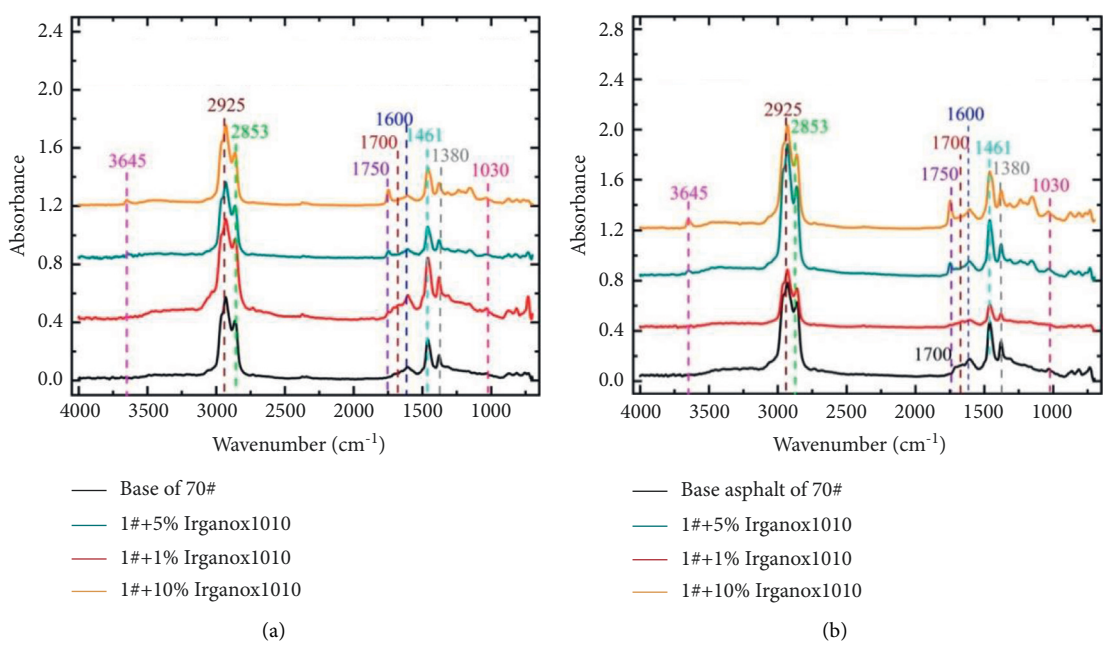

Figure 12: FTIR spectra of asphalt 1# (a) before aging (b) after aging.

$$\begin{cases} I_B = \dfrac{I_{C-H\,of\,CH_3}}{I_{C-H\,of\,CH_3} + I_{C-H\,of-(CH_2)_n}}, \\ I_{C-H\,of\,CH_3} = \dfrac{Area\,of\,the\,aromatic\,band\,centered\,around\,1600\,cm^{-1}}{\sum Area\,of\,the\,spectral\,bands\,between\,4000\,cm^{-1}\,and\,700\,cm^{-1}}, \\ I_{C-H\,of-(CH_2)_n} = \dfrac{Area\,of\,the\,aromatic\,band\,centered\,around\,1600\,cm^{-1}}{\sum Area\,of\,the\,spectral\,bands\,between\,4000\,cm^{-1}\,and\,700\,cm^{-1}}, \end{cases} \tag{7}$$

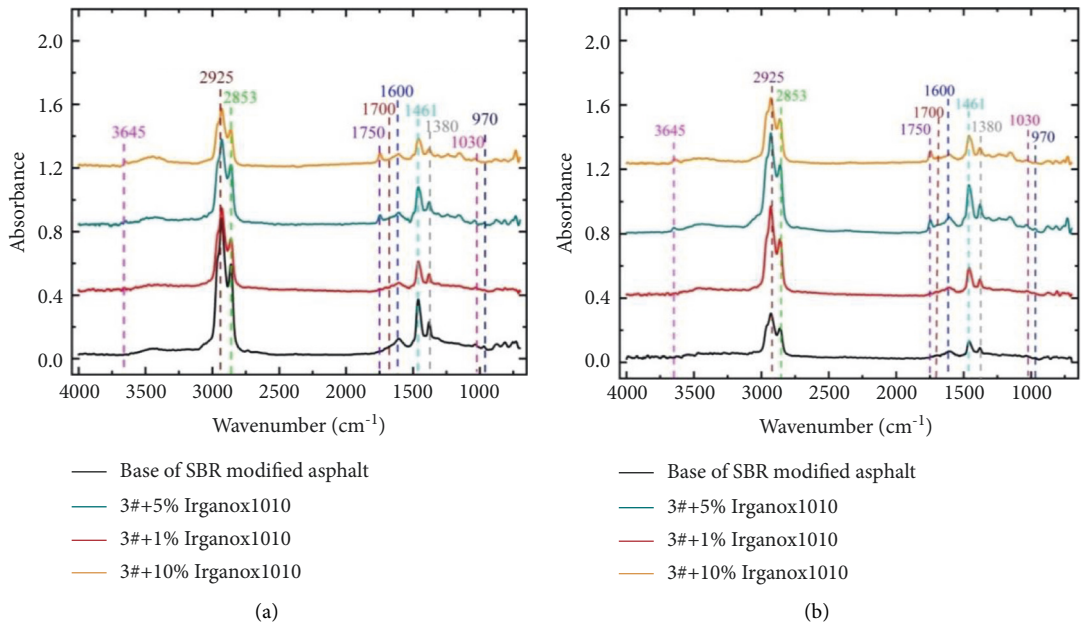

Figure 13: FTIR spectra of asphalt 3# (a) before aging (b) after aging.

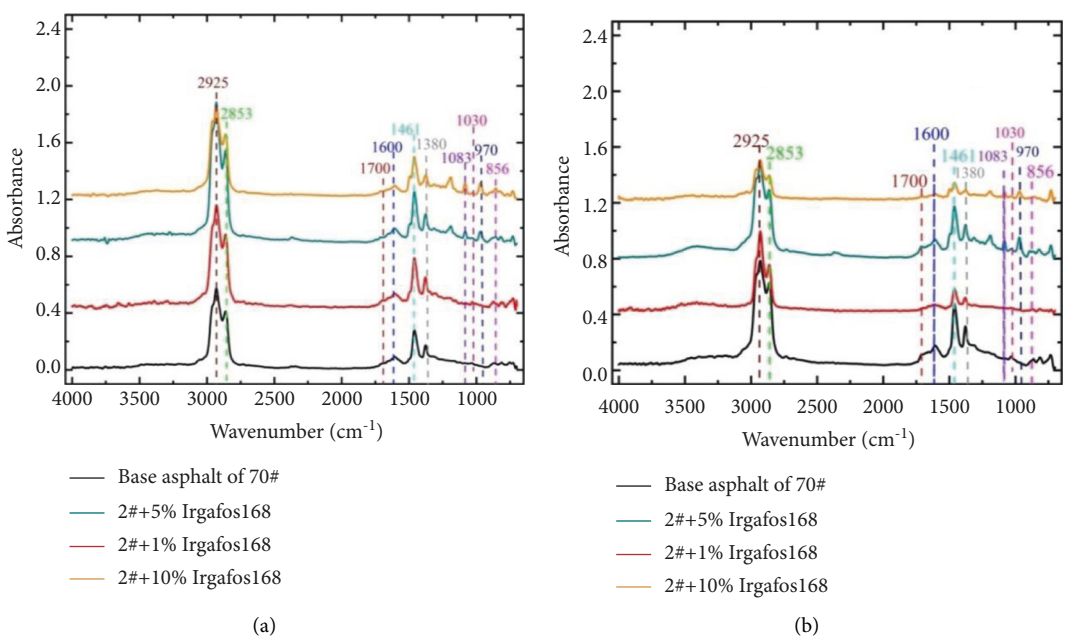

Figure 14: FTIR spectra of asphalt 2# (a) before aging (b) after aging.

$$I_{S=O} = \frac{Area\ of\ the\ sulfoxide\ band\ centered\ around\ 1031\ cm^{-1}}{\sum Area\ of\ the\ spectral\ bands\ between\ 4000\ cm^{-1}\ and\ 700\ cm^{-1}}, \tag{8}$$

$$W = \frac{I_{afteraging} - I_{beforeaging}}{I_{beforeaging}}. \tag{9}$$

Where $I_{C=O}$ is the carbonyl functional group index, I_{Ar} is the aromatic functional group index, I_B is the aliphatic functional group index, sulfoxide functional group index, $A_{1700\text{cm}^{-1}}$ is the peak area of carbonyl at $1700\,\text{cm}^{-1}$, $A_{1030\text{cm}^{-1}}$ is the peak area of the sulfoxide group at $1030\,\text{cm}^{-1}$, $\sum A_{4000\ \text{cm}^{-1}\sim 700\ \text{cm}^{-1}}$ is the peak area in the range

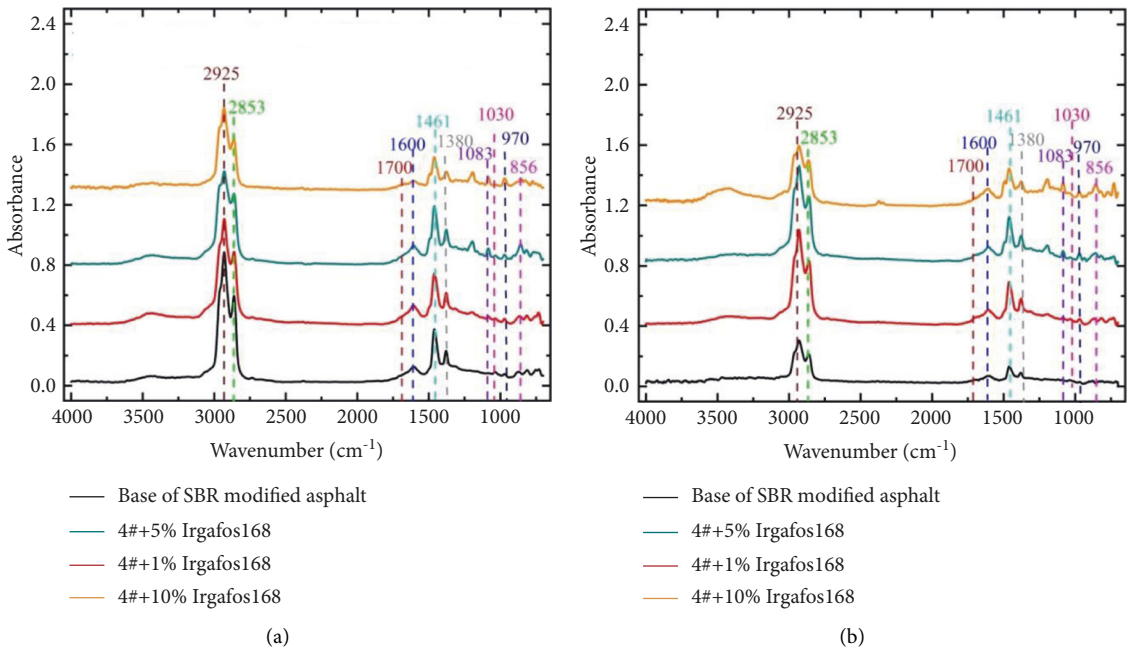

Figure 15: FTIR spectra of asphalt 4# (a) before aging (b) after aging.

of 4000 cm^{-1}~700 cm^{-1}, W is the functional group change rate, $I_{beforeaging}$ is the functional group index before aging, and $I_{afteraging}$ is the functional group index after aging.

Irganox 1010 has different effects on 1# and 3# asphalt. It can be seen from Table 6 that the carbonyl functional group index, sulfoxide functional group index, and aromatic functional group index decrease with the increase of Irganox1010 content, while the aliphatic functional group index remains almost unchanged. As can be seen from the change in the functional group index in Table 7, the carbonyl functional group index and the aromatic functional group index first increase and then decrease, while the contents of the sulfoxide functional group index and the aliphatic functional group index increase, indicating that the Irganox 1010 content has different influences on the functional group index of different asphalt. When studying the chemical structure changes of asphalt in the aging process, the content of carbonyl and sulfoxide functional groups is often used to evaluate the oxidation of asphalt. The functional group index is greater, and the content of carbonyl and sulfoxide functional groups in asphalt is higher [35–39]. The contents of the carbonyl group and the sulfoxide group decrease in 1# and 3# asphalt, and this is because of the oxidation reaction between asphalt and oxygen during the preparation process; thus, the content of the carbonyl and sulfoxide group increased. Therefore, the addition of Irganox 1010 inhibited the oxidation reaction between asphalt and oxygen in the preparation process, and the contents of carbonyl and sulfoxide groups were reduced. The carbonyl functional group index and the sulfoxide functional group index in 3# are lower than that in 1#, indicating that Irganox 1010 has a good synergistic effect on SBR.

After aging by RTFOT, the carbonyl functional group index, sulfoxide functional group index, and aromatic functional group index of 1# and 3# increased. During the short-term aging of asphalt, carbon, sulfur, nitrogen, and other elements in asphalt will be oxidized with the presence of oxygen in the air; thus, the content of a series of oxygen-containing functional group compounds such as carbonyl and sulfoxide increased. The carbonyl and sulfoxide groups of base and SBR asphalt significantly increased after aging, which proves that aging leads to the increase of carbohydrate and sulfur-oxygen groups in asphalt. The functional group index change rate (W) is used to evaluate the aging resistance of asphalt from the perspective of the functional group intensity, as shown in Figure 16(a) and 16(b). After adding Irganox 1010, $W_{C=O}$ and $W_{S=O}$ in asphalt significantly decrease, and with the increase of Irganox 1010, the change in carbonyl and sulfoxide functional groups first decrease, then increase, and lastly decrease, which is consistent with other aging index regularity. After aging, W_{Ar} and W_B of base asphalt and SBR-modified asphalt are both positive, and the aromatic and aliphatic content increased after RTFOT. After adding Irganox 1010, W_{Ar} and W_B tend to decrease gradually. This is because Irganox 1010 improves the antiaging performance, and aging causes polymerization and chain scission of asphalt, thus producing more aromatic groups after aging. Therefore, Irganox 1010 slows down chain scission and polycondensation of asphalt in the aging process, thus reducing the aromatic content in asphalt. W_B close to zero indicates that the chain scission of normal paraffin hydrocarbon in saturated fragrance is effectively inhibited. To sum up, Irganox 1010 produces positive effects during asphalt aging. Irganox 1010 prevents oxidative chain reactions and weakens the aging process of asphalt by capturing the active radicals generated during asphalt aging, and it was found that 3# had better antiaging effects when

Table 6: Effect of Irganox 1010 on the functional group index of 1#.

Content/%	Before aging				After aging			
	$I_{C=O}$	$I_{S=O}$	I_{Ar}	I_B	$I_{C=O}$	$I_{S=O}$	I_{Ar}	I_B
0	0.0055	0.0125	0.0372	0.2106	0.0155	0.0171	0.0561	0.2062
1	0.0048	0.0119	0.0336	0.1909	0.0087	0.0153	0.0368	0.1820
5	0.0030	0.0081	0.0271	0.20634	0.0077	0.0158	0.0272	0.2067
10	0.0015	0.0106	0.0247	0.2229	0.0021	0.0151	0.0268	0.2270

Table 7: Effect of Irganox 1010 on the functional group index of 3#.

Content/%	Before aging				After aging			
	$I_{C=O}$	$I_{S=O}$	I_{Ar}	I_B	$I_{C=O}$	$I_{S=O}$	I_{Ar}	I_B
0	0.0036	0.0043	0.0477	0.1820	0.0065	0.0064	0.1463	0.1790
1	0.0056	0.0036	0.0508	0.1940	0.0054	0.0043	0.078	0.1945
5	0.0027	0.0030	0.0462	0.1942	0.0037	0.0042	0.0840	0.1981
10	0.0032	0.0025	0.0412	0.2030	0.0014	0.0016	0.0811	0.1963

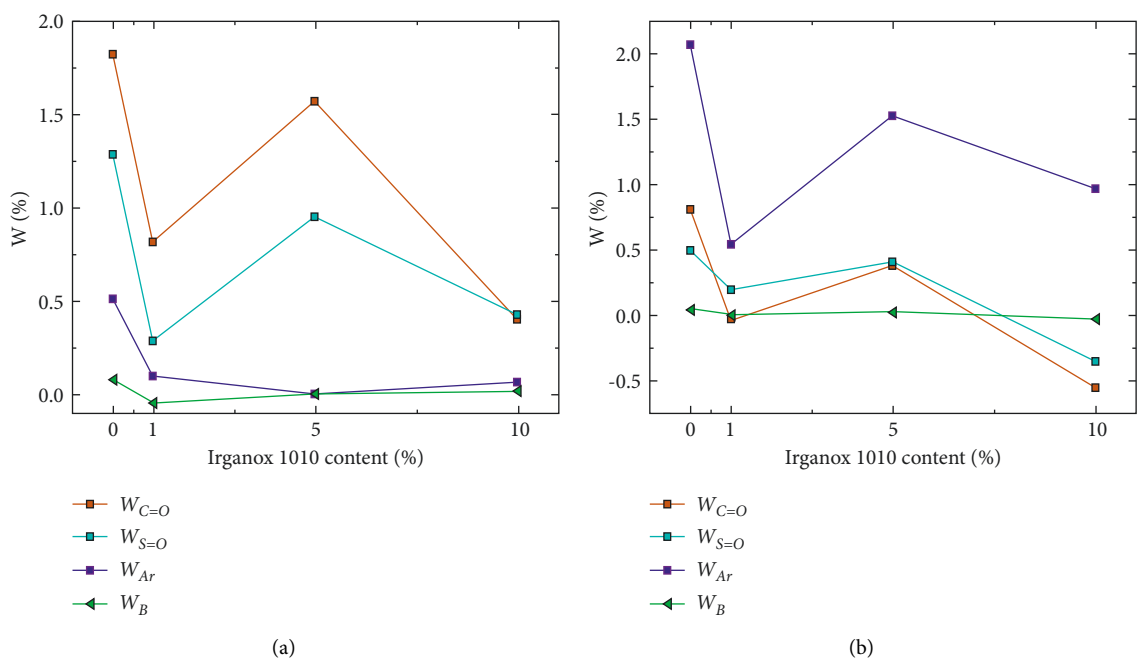

Figure 16: Effect of Irganox 1010 on (W) (a) 1# (b) 3#.

the Irganox1010 content is 1%, which is consistent with the previous conclusion in this paper.

It can be seen from Table 8 that after adding Irgafos 168, the carbonyl functional group index decreased, while the sulfoxide functional group index changed a little. It proved that Irgafos 168 had inhibited the oxidation of asphalt in the preparation and test process but had little influence on the sulfoxide group. It can be found that the carbonyl functional group indexes show a downward trend in different asphalt from Table 9, while the sulfoxide functional group indexes have different changes, indicating that the carbonyl functional group indexes can represent the weak oxidation reaction in asphalt.

As shown in Figure 17, after aging by RTFOT, the carbonyl functional group index, sulfoxide functional group index, and aromatic functional group index all increased, while the aliphatic functional group index decreased. It can be found from Figure 17(a) that adding Irgafos 168 makes $W_{C=O}$ and $W_{S=O}$ in 2# significantly lower, W_{Ar} changes slightly, and W_B first reduced and then gradually flattened. From Figure 17(b), it can be found that adding Irgafos 168 reduces $W_{C=O}$ and $W_{S=O}$ in 4#, while W_{Ar} and W_B first reduced and then gradually flattened. $W_{C=O}$, $W_{S=O}$, and W_{Ar} in 2# and 4# asphalt are due to Irgafos 168 inhibiting the oxidation reaction, and thus the antiaging performance of asphalt is improved. W_B below 0 indicates that W_B not only effectively inhibits the chain scission of normal paraffin hydrocarbon in saturated fractions but also promotes the saturated fraction production. In one word, Irgafos 168 also has a positive effect on the asphalt aging. Irgafos 168 weakens

Table 8: Effect of Irgafos 168 on the functional group index of 2#.

Content/%	Before aging				After aging			
	$I_{C=O}$	$I_{S=O}$	I_{Ar}	I_B	$I_{C=O}$	$I_{S=O}$	I_{Ar}	I_B
0	0.0055	0.0075	0.0372	0.2106	0.0155	0.0171	0.0561	0.2062
1	0.0034	0.0072	0.0516	0.2306	0.0075	0.0068	0.0747	0.1963
5	0.0037	0.0080	0.0577	0.3081	0.0055	0.0106	0.0808	0.1771
10	0.0028	0.0082	0.0731	0.3272	0.0033	0.0085	0.0962	0.1886

Table 9: Effect of Irgafos168 on the functional group index of 4#.

Content/%	Before aging				After aging			
	$I_{C=O}$	$I_{S=O}$	I_{Ar}	I_B	$I_{C=O}$	$I_{S=O}$	I_{Ar}	I_B
0	0.0036	0.0043	0.0477	0.1820	0.0065	0.0064	0.1463	0.1790
1	0.0029	0.0043	0.0879	0.2306	0.0047	0.0070	0.1523	0.1966
5	0.0027	0.0050	0.0984	0.3244	0.0039	0.0074	0.1565	0.2593
10	0.0031	0.0040	0.1042	0.3476	0.0040	0.0046	0.162	0.3228

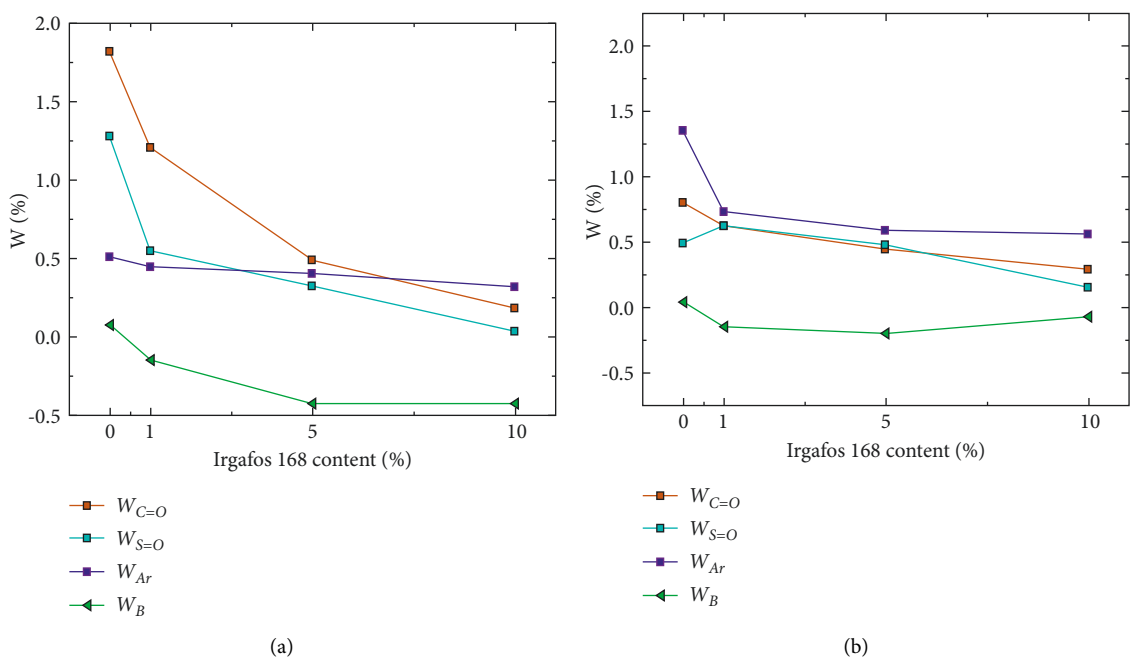

Figure 17: Effect of different Irgafos 168 contents on W of modified antiaging asphalt. (a) 2#. 4#.

the aging degree of asphalt, and Irgafos 168 decomposes hydroperoxides from thermally oxidized aging chain reactions into inactive products. For asphalt 2# and 4#, a higher Irgafos168 content has the better the antiaging effect.

4. Conclusions

From the result discussed above, the conclusions can be drawn as follows:

(1) Commercial antioxidants including Irganox1010 and Irgafos168 improve the aging resistance of base and SBR-modified asphalt. Based on the basic indexes of asphalt binders and their antiaging performance, 1% Irganox 1010 can improve the antiaging performance of asphalt and has little negative influence on the original properties. Asphalt including 1% Irgafos 168 possesses good aging resistance and low temperature ductility. Due to the synergistic effect between SBR and antioxidants such as Irganox 1010 and Irgafos 168, the antiaging effect on SBR is more significant.

(2) FTIR analysis showed that there was physical adsorption between Irganox 1010 and asphalt, while there was a chemical reaction between Irgafos 168 and asphalt. According to the qualitative and quantitative analysis, the main reason for the performance degradation of Irganox 1010 is the ester group. Irganox 1010 and Irgafos 168 effectively

prevented the oxidation reaction during aging and reduced the content of carbonyl and sulfoxide groups after asphalt aging. [31–39].

Data Availability

All the data obtained from several experiments are included in the paper.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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