

Thermooxidative aging mechanism of crumb-rubber-modified asphalt

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ABSTRACT: We investigated the thermooxidative aging mechanism of crumb-rubber-modified asphalts (CRMAs) by tracing the evolution of the chemical structure and physical properties of CRMA during aging. The chemical structural evolution of crumb rubber (CR) in various aged CRMAs was characterized by measurement of the crosslink structure and composition of extracted CR. The residual asphalt of the aged CRMA was investigated by IR spectroscopy. The physical properties of CRMA were characterized by conventional testing before and after aging. We found that the change in the physical properties of CRMA correlated well with both the evolution of the rubber network and the oxidation of asphalt. The thermooxidative aging resistance of CRMA was improved with increasing CR dosage; this further illustrated that aging promoted the dissolution of CR into asphalt. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43323.

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INTRODUCTION

The aging of asphalt severely deteriorates pavement performance, and the service life is shortened.^{1–4} The aging of asphalt involves changes in the asphalt composition; these include the volatilization of light fractions and the transformation of the molecular components of asphalt. Asphalt aging stems from both extrinsic and intrinsic variables. The former includes environmental factors, such as heat, oxygen, rain, and UV radiation.^{5,6} The latter includes asphalt composition, types of aggregates, and asphalt thickness.⁷

It is well known that the principal cause of the aging of asphalt in its service life is its absorption of oxygen from air. The thermooxidative aging of asphalt (primarily short-term aging) is often used to simulate the aging process of road construction; this results in different degrees of change in the physical and chemical performance of asphalt.^{8–10} The oxidation of functional groups in asphalt leads to an increase in polarity, which increases the stiffness of asphalt because of the increasing content of asphaltenes and glial in asphalt.⁹ Therefore, the improvement of the aging resistance of asphalt has been considered as a most attractive area of research in asphalt pavement.

Asphalt modified by crumb rubber (CR) originating from recycled tires shows better aging resistance than base asphalt; this is one of the obvious advantages of using CR as an asphalt modifier.^{10–13} Biliter *et al.*¹⁴ analyzed the oxidative characteris-

tics of crumb-rubber-modified asphalt (CRMA) prepared with different curing conditions. They illustrated that the aging process of CRMA was affected by the curing time, temperature, CR content, and base asphalt composition. Moreover, Ghavibazoo and Abdelrahman¹⁵ found that the degree of interaction between CR and asphalt had a great effect on the aging of CRMA; a higher degree of interaction produced better aging resistance in the extracted asphalt. Xiang *et al.*¹⁶ found that the composition of the modified asphalt changed significantly with the degradation of the modifiers and the evolution of the asphalt components. The Corbett procedure or IR spectra have been used to study compositional changes in CRMA. Although the aforementioned research illustrates that CR improves the aging resistance of base asphalt, its antioxidant mechanism is still unclear.

Historically, the thermooxidative aging resistance of CRMA has been explained by three reasons. The first is that antioxidants of CR released into asphalt improve the aging resistance.¹² The second is that the light fraction of asphalt can be absorbed by CR to protect it from aging.¹⁰ The last one is that some fraction of soluble rubber moves into the asphalt and acts as a plasticizing agent. The first two aspects have been proven to have little effect on the aging resistance of CRMA, whereas the dissolution of CR into asphalt plays an important role in the aging process.^{14,15}

The dissolution or degradation of CR occurs in the preparation of CRMA; this changes the composition of CR and further influences the properties of CRMA. The aforementioned degradation also occurs in the mixing, paving, and compaction of CRMA and is often characterized as thermooxidative aging. Although the interaction between CR and asphalt during thermal aging was investigated by Ghavibazoo and Abdelrahman,^{15,17} the evolution of the crosslinking structure of CR and the chemical changes in asphalt during the aging process are still unclear. Furthermore, the thermooxidative aging mechanism of CRMA needs to be clarified through the establishment of the relationship between the evolution of the chemical structure and the physical properties.

In this study, a rolling thin film oven test (RTFOT) was used to stimulate the thermooxidative aging of CRMA. The standard RTFOT time was used to simulate short-term aging during mixing. The variation of the RTFOT time was also used to simulate the aging index of CRMA. The structural evolution of CR in CRMA was investigated through the characterization of the crosslinking density and composition. The chemical structure of the residual asphalt was studied by IR spectroscopy. Furthermore, the effects of the structural evolution on the physical properties of CRMA with various aging times and CR contents were evaluated.

EXPERIMENTAL

Materials

Asphalt and CR Modifier. Korea-SL was selected as the base asphalt, the penetration was 6.46 mm (25°C), the softening point was 47.6°C, and the ductility was more than 150 cm at 15°C. CR (40 mesh) was supplied by the Jiangsu Yin Gert Asphalt Co., Ltd. The chemical composition of CR consisted of 6.97% soluble materials, 40.25% natural rubber (NR), 14.64% synthetic rubber (SR), 30.44% carbon black (CB), and 7.70% inorganic filler.

Preparation of CRMA. When the asphalt was heated to a fluid state, the stirring equipment was started at 500 rpm to heat evenly to 185°C. Then, the CR was added slowly into the melted asphalt. Subsequently, CRMA was subjected to high-speed shearing at 5000 rpm for 1 h at 190 ± 5°C to acquire a more homogeneous blend.

First, 20 wt % CRMA was prepared. Subsequently, 5, 10, and 15 wt % CRMA were prepared by the dilution of 20 wt % CRMA, respectively. CRMA with a concentration of 15 wt % with different aging times was prepared in the same procedure with 20 wt % CRMA.

Test Methods

Physical Properties. The conventional physical properties of CRMA included the penetration at 25°C, the softening point, and the ductility at 5°C; these were measured in accordance with ASTM D 5, ASTM D 36, and ASTM D 113, respectively.

Thermooxidative Aging. Thermooxidative aging was simulated in the laboratory by RTFOT according to ASTM D 2872. RTFOT was carried measured for 85 min at 163°C under a 15-rpm carriage rotation with an air flow of 4000 mL/min. CRMA

(15% CR) samples were aged for different periods (30, 60, 120, and 240 min) at 163°C to simulate the different degrees of thermooxidative aging.

Extraction of CR from the Aged CRMA. To measure the variation of the crosslinking density, composition, and dissolution of CR in asphalt before and after aging, CR was extracted from CRMA. First, CR was separated from CRMA with a Soxhlet extractor with toluene. An amount of 5 g of CRMA was packed with filter paper and extracted for 24 h until the filtrate became colorless. The retained CR particles were washed with extra toluene until the filtrate was colorless again. Consequently, the washed CR particles were dried in a vacuum oven at 110–120°C for 3 h to assure complete solvent removal. Finally, the extracted CR was used for thermogravimetric analysis (TGA) and other analysis.

Sol Fraction Analysis. To study the effect of the CR particles on the thermooxidative aging of CRMA, the CR fractions of soluble matter (sol content) and insoluble matter (gel content) in the aging process of the modified asphalt were estimated via Soxhlet extraction. The sol content of CR was defined as follows⁹:

$$\text{Sol (\%)} = \frac{m_0 - (m_i - m_1)}{m_0} \quad (1)$$

where m_i is the weight of the filter paper and the residual CR after extraction, m_0 is the weight of CR before extraction, and m_1 is the weight of the filter paper before extraction. The CR extraction tests of each sample were repeated twice to ensure correctness.

TGA. The composition of insoluble CR was characterized by TGA (Q500, TA Instruments). The heating rate was 10°C/min. The sample (10 mg) was heated from room temperature to 550°C with a continuous N₂ flow at 50 mL/min. Subsequently, the purge atmosphere was switched to air, and the sample was heated continuously to 700°C. The sample weight loss and its rate of weight loss were measured as a function of the temperature. The TGA tests were repeated to ensure correctness.

Crosslinking Density of the Extracted CR. An important chemical characteristic of residual CR is the crosslinking density. The crosslinking density was obtained by a swelling test on basis of the theory that vulcanized rubbers swell to equilibrium degrees when immersed in liquids.¹⁸ First, the extracted CR particles were pressed into thin slices three times by a two-roll mill [S(X)K-160A, Shanghai]. The swelling value (Q) was determined with about 0.3 g of the sample in square millimeters. The samples were immersed in toluene at 25°C for 2 days to reach swelling equilibrium. The sample was taken out, and the adhered liquid on the surface was quickly removed by blotting with filter paper. This operation was repeated until the quality difference of the swelling did not change. Q was calculated from the following equation:

$$Q = \frac{\left(\frac{w_1 + w_2}{\rho_1 + \rho_2}\right)}{\frac{w_2}{\rho_2}} \quad (2)$$

where w_1 is the weight fraction of the solvent in the swollen specimen, w_2 is the weight fraction of the residual polymer in

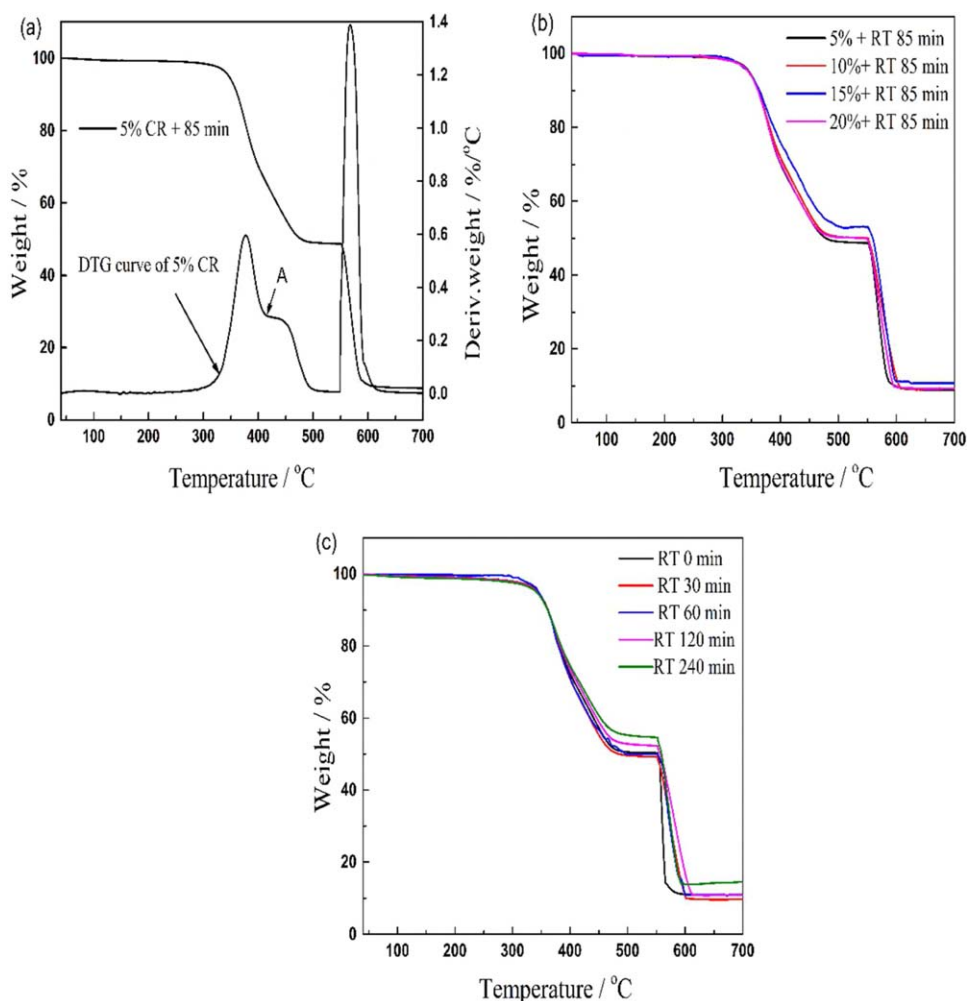


Figure 1. (a) DTG curves of CR in CRMA after aging, (b) thermogravimetry curves as a function of the CR content, and (c) thermogravimetry curves of CR in CRMA as a function of the aging time. RT = RTFOT. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the swollen specimen, ρ_1 is the density of the solvent, and ρ_2 is the density of the CR.

The crosslinking density of the residual CR was calculated with the following equation:

$$M_c = \frac{\rho \nu Q^{\frac{5}{3}}}{0.5 - X} \quad (3)$$

where M_c is the average molecular weight between two crosslinking points, X was selected as 0.40 for CR–toluene system,

X is the parameter of Flory-Huggins, ρ is the density of the CR, ν is the molar volume of toluene ($105.908 \text{ cm}^3/\text{mol}$), and the density of toluene was 0.87 g/cm^3 .

Fourier Transform Infrared (FTIR) Spectroscopy. Changes in the functional groups of CRMA were analyzed with an FTIR spectrometer (IZ10, Nicolet). The residual asphalt after extraction was dissolved into toluene and coated onto the KBr wafer. The solvent was volatilized completely before FTIR analysis. The

Table I. Percentage of Each Component of CR for the Different Aged CRMAs

Sample CR content (%)	Sol fraction (%)	Each component in gel (%)			
		NR	SR	CB	Filler
5	19.13	26.71	14.77	32.12	7.27
10	21.82	24.20	14.82	31.81	7.35
15	23.54	20.45	15.77	32.07	8.17
20	26.44	23.77	13.10	29.74	6.95

Table II. Percentages of Each Component of CR with Different Aging Times

Sample aging time (min)	Sol fraction (%)	Each component in gel (%)			
		NR	SR	CB	Filler
0	32.94	20.43	12.69	26.27	7.65
30	31.94	22.25	12.73	27.17	6.91
60	28.80	22.33	14.17	24.76	9.95
120	30.99	19.99	12.82	28.60	7.06
240	32.35	18.78	11.72	27.63	9.52

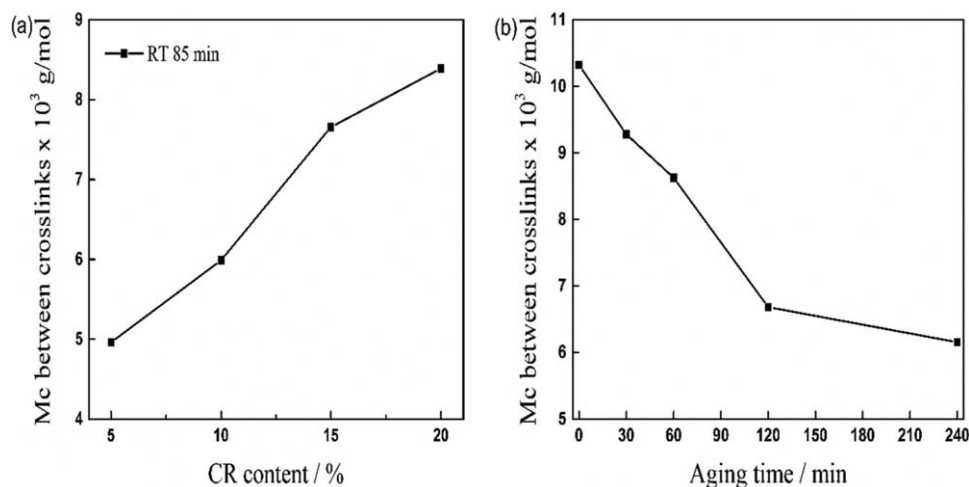


Figure 2. (a) Effect of the CR content on M_c of the aged CR and (b) effect of the aging time on M_c of the aged CR. RT = RTFOT.

Table III. Calculated Results for CI and SI of the Residual Asphalt

Asphalt type	CR content (%)	CI	SI
Residual asphalt	5	0.020	0.004
	10	0.018	0.004
	15	0.019	0.004
	20	0.018	0.005

spectrum ranged from 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1} .

RESULTS AND DISCUSSION

Composition Evolution of CR during the Aging Process of CRMA

The aging of CRMA was more complicated than that of base asphalt because the aging not only included the aging of asphalt and the modifier but also their interactions in the aging process. TGA was used as a tool to analyze the compositional evolution of the extracted CR from aged CRMA. The compositions of the extracted CRs from different aged CRMAs are shown in Figure 1. For brevity, only the derivative thermogravimetry (DTG) curves are presented in Figure 1(a).

Two different polymeric components in tires, namely, NR and SR, can be determined according to the composition analysis of scrap tires.^{19,20} Figure 1(a) shows that point A (derivative of a minimum point, $\sim 410^\circ\text{C}$) corresponded to the NR portion of CR, whereas point A to 550°C belonged to SR. CB was attributed

Table IV. Calculated Results for CI and SI

Asphalt type	Aging time (min)	CI	SI
Residual asphalt	0	0.016	0.004
	30	0.017	0.004
	60	0.022	0.004
	120	0.027	0.003
	240	0.028	0.003

to 550°C to the turning point, whereas the residual corresponded to the inorganic filler of CR. The absolute content of various components of the different CRs are listed in Tables I and II.

As shown in Table I, some rubber was released into asphalt according to the increase in the sol fraction. The higher the CR content was, the greater the sol fraction was. This indicated that the rubber network was destroyed under the action of heat and oxygen during RTFOT. NR contained large amounts of unsaturated double bonds and α -H bonds; these were more prone to degrade in asphalt. The NR dissolution increased about 6% as the CR content increased from 5 to 15%, whereas the contents of SR, CB, and filler showed a slight change. Surprisingly, the change of 20% CR, shown in Table I, was different from the CR content increase from 5 to 15%. As a suspension, asphalt is a continuous phase when the CR content is lower than 15%.

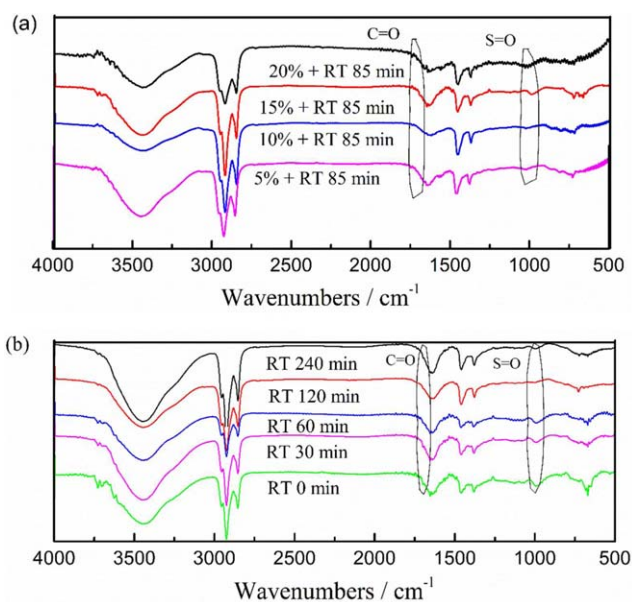


Figure 3. IR spectra of CRMA after thermooxidative aging: (a) RTFOT for 85 min and (b) different aging times. RT = RTFOT. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

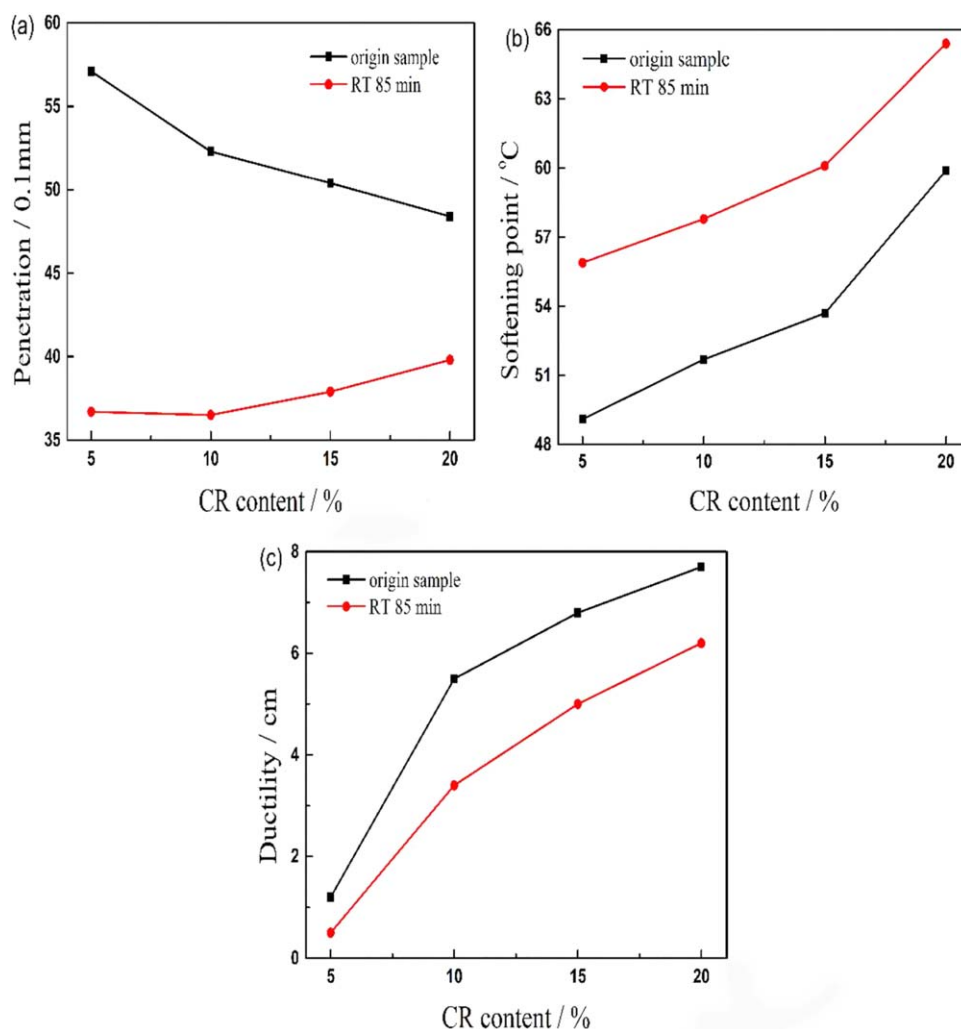


Figure 4. Effect of the CR content on the physical properties of CRMA before and after aging: (a) penetration, (b) softening point, and (c) ductility at 5°C. RT = RTFOT. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Phase inversion occurs at 20% CR, and a continuous phase of rubber forms.¹² The rubber has more chances to be oxidized by air. Therefore, more rubber is susceptible to aging, and this leads to the dissolution of SR and the partial crosslinking of NR.

Table II illustrates that the content of NR in the residual CR increased shortly and then consistently decreased with the increase in aging time. The variation of SR became slight, and this indicated that the degradation of SR was not obvious in asphalt. Moreover, the sol content first decreased with the aging time and then increased. This indicated that the recombination of the network occurred initially and the breakdown of the network became more obvious in the later aging stage. Therefore, the crosslink structure of CR during the aging process was investigated further by the measurement of the crosslinking density of the residual CR.

Changes in the Crosslinking Density of Extracted CR from Aged CRMA

M_c indicates the extent of the crosslinking density of rubber. The higher the M_c is, the lower the crosslinking density is.

M_c of the residual CR is shown in Figure 2. M_c in the original CR was 5349 g/mol. M_c of the aged CR became higher compared with the original CR, as shown in Figure 2(a); this indicated that the crosslinking density of the aged CR decreased with increasing CR content in CRMA. This indicated that the higher content of CR was more susceptible to the breakdown of CR during aging.

As shown in Figure 2(b), M_c in the aged CR decreased with increasing aging time; this indicated that the recombination of the main chain and side chain occurred at longer aging times. A new crosslinking network was formed in the aging process because more oxygen was engaged in the reaction. The variation in the crosslinking density, composition, and chemical properties of rubber occurred during thermal aging.²¹ The degradation of rubber was mainly due to the breakdown or recombination of the crosslinking network.²² The previous results demonstrate that both the crosslinking scission and the new crosslinking network formation of CR occurred during thermooxidative aging; this depended on the aging time and concentration of CR in CRMA.

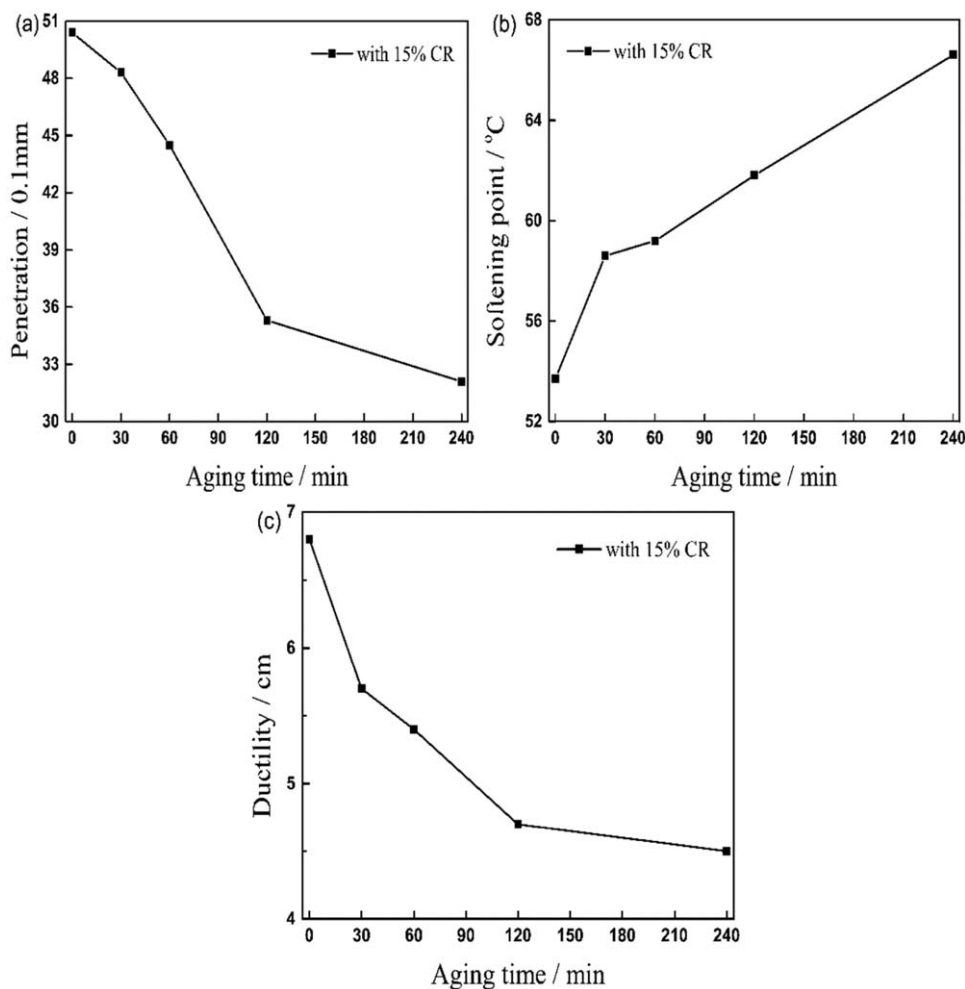


Figure 5. Effect of the aging time on the conventional physical properties of CRMA: (a) penetration, (b) softening point, and (c) ductility at 5°C.

FTIR Analysis of Aged Asphalt in CRMA

FTIR analysis has been used to measure the main functional groups of asphalt during the aging process. The peaks at 1700 and 1030 cm^{-1} were the characteristic peaks of the carbonyl (centered around 1700 cm^{-1}) and the sulfoxide function (centered around 1030 cm^{-1}), respectively. The area of the absorption peaks, including the carbonyl (C=O) and sulfoxide (S=O) contents, were calculated through integrals. Meanwhile, the relative contents of carbonyl and sulfoxide groups were characterized by the introduction of the carbonyl index (CI) and the sulfoxide index (SI), respectively. The aging degree could be determined by either studying the changes in the transmittance of the functional bonds or calculating the structural indices of the following type²³:

$$CI = A_{C=O} / A \quad (4)$$

$$SI = A_{S=O} / A \quad (5)$$

where $A_{C=O}$ is the absorption peak area of the carbonyl group, $A_{S=O}$ is the absorption peak area of the sulfoxide group, and A is the absorption peak area. Both CI and SI were calculated and are listed in Tables III and IV, respectively.

As shown in Figure 3(a) and Table III, we observed that the CI and SI change slightly. This indicates that the content of CR had little effect on inhibiting the carbonyl or sulfoxide generation in asphalt during the aging process. The integral range of C=O was 1690 to 1710 cm^{-1} , the integral range of S=O was 1020 to 1034 cm^{-1} , and the integral range A was 600 to 2000 cm^{-1} .

We observed, as shown in Figure 3(b) and Table IV, that the CI continuously increased with the increase in aging time, whereas SI showed a slight decrease. The increasing intensity of carboxyl illustrated aldehyde, ketone, ester, or carboxylic acid and some other compounds containing oxygen forms during the process of aging. Moreover, the decrease in the sulfoxide group of aged residual asphalt indicated that the thermal decomposition of the sulfoxide group may have existed.

Effect of the CR Content on the Changes in the Physical Properties of CRMA

The physical performance of CRMA with different CR contents before and after aging is illustrated in Figure 4. We observed that the penetration of CRMA decreased with increasing CR

content, whereas the softening points and ductility increased; this indicated that the CR increased both the high- and low-temperature properties of CRMA. The changing trend of the softening point and ductility of aged asphalt was similar to that of the original CRMA. Surprisingly, the penetration of aged CRMA increased with increasing CR content; this showed different trends than that of the original ones. This indicated that the higher rubber content made the aged CRMA more flexible to the resistance of crack caused by aging. The antiaging performance of CRMA was explained by three reasons. First, some fraction of soluble rubber moved into asphalt and acted as a plasticizing agent; this made the penetration of CRMA increase as the CR content increased. Second, the light fraction of asphalt could be absorbed by CR to protect the asphalt from aging. Third, the antioxidants in CR could penetrate into the asphalt. The first point is been proven in Table I. The sol content increased when the content of CR in CRMA increased. Similar results were also reported by Ghavibazoo and Abdelrahman.¹⁵

Effect of the Aging Time on the Performance of CRMA

As shown in Figure 5(a–c), we observed that the penetration and ductility of CRMA decreased with the extension of aging time, whereas the softening point increased. The phenomenon illustrates that the aging degree of CRMA deteriorated with the increase in aging time. This result corresponded to the increase in the CI data proven in the Changes in the Crosslinking Density of Extracted CR from Aged CRMA section.

CONCLUSIONS

The thermooxidative aging mechanism of CRMA was investigated by tracing the evolution of the chemical composition and physical performance of CRMA during thermooxidative aging. We found that the aging of CRMA included the different structural evolutions of asphalt and CR. Conclusions were drawn as follows.

The aging of CR was involved with the breakdown and recombination of the crosslinking network of CR. This led to changes in the crosslinking density and dissolution of CR in CRMA. The crosslinking density of CR decreased with the increase in the CR content in CRMA, whereas it increased with increasing aging time. Moreover, the aging resistance of CRMA was significantly improved by the breakdown of CR, and this increased the penetration of CRMA. The NR dissolution in CR during thermooxidative aging played a major role in increasing the penetration of CRMA, and this made the CRMA more flexible after aging. Meanwhile, the penetration, softening points, and ductility changed accordingly during the aging process of CRMA.

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