



## Weather aging resistance of different rubber modified asphalts



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### HIGHLIGHTS

- Weather aging of rubber modified asphalts was carried out under natural environment.
- Rheological properties of modified asphalts changed with the structural evolution.
- For the given base asphalt, SBSMA showed the worst weather resistance, while TB showed the best.

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### ABSTRACT

The service life of polymer modified asphalt strongly depends on its weather resistance because of its exposure to the natural environment. Three most widely used rubber modified asphalts, namely styrene–butadiene–styrene (SBS) modified asphalt (SBSMA), crumb rubber modified asphalt (CRMA) and terminal blend rubber modified asphalt (TB) are exposed outdoor for weather aging. Effect of aging on the chemical composition of different rubber modified asphalts is analyzed by using infrared spectroscopy. The rheological properties of base asphalt and modified asphalts before and after aging are characterized by using the dynamic shear rheometer (DSR) and dynamic mechanical analysis (DMA). Results show that the chemical structure and rheological properties of modified asphalts change significantly as a result of the weather aging. Different rubber modified asphalts show the different aging behavior. For the given base asphalt, SBSMA is the most susceptible to weather aging, followed by CRMA and TB, respectively.

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## 1. Introduction

Asphalt materials are exposed to the environmental factors such as sunlight, moisture, oxygen and heat that affect the properties of asphalt has been widely investigated [1–3]. The combined interaction of these factors causes asphalt being susceptible to the change of physical, chemical and rheological property, which reduces the durability of asphalt pavements [4,5].

Polymers have been considered as the most cost effective additives to improve the durability of asphalt pavements [6–9]. However, just like base asphalt (BA), polymer modified asphalts (PMAs) also suffer from aging under the action of environmental factors [10–12]. The aging of PMAs not only includes the aging of asphalt and modifiers, but also their interactions in aging process, which contributes to the deterioration of asphalt pavement, and the service life is shorten [12–14]. In terms of the aging of polymers,

the irreversible changes in polymer structure and properties caused by aging have been widely investigated [15–17].

The aging of PMAs, such as styrene–butadiene–styrene modified asphalt (SBSMA) has been taken a great deal of investigation from aspects of chemical structure and physical rheology. Lu and Issacson [18] reports that the polymer couldn't resist the formation of carbonyl group in aging process of SBSMA. The rheological properties evolution of aged modified asphalt depends on a combined effect of asphalt oxidation and polymer degradation. Ruan et al. [19] investigate the dynamic shear properties and extensional properties of PMAs, which shows that oxidative aging reduces the temperature susceptibility of asphalt, damages the polymer network in modified asphalt. Yut and Zofka [10] study the correlation between chemistry and rheology of aged PMAs through DSR and FTIR. They find that the severity of aging procedure affects the viscosity of PMA more than polymer composition and concentration. Complex modulus can be fairly estimated from chemical composition elucidated by ATR-FTIR. Wang et al. [20] evaluate the aging mechanism of SBSMA based on chemical reaction kinetics, which indicates that the activation energy of asphalt will change with the degradation of SBS modifier, and the temperature sensitivity

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of asphalt is improved. Geng et al. [21] report that the aging under thermal moisture conditions changes the properties of asphalt and the color of SBS due to the increasing carbonyl content of asphalt and SBS. The presence of water is shown to accelerate the aging of SBS and its modified asphalt under the action of heat and oxygen.

Generally speaking, SBSMA shows better aging resistance than base asphalt. However, the performance of modified asphalt decreases as the degradation of SBS in aging process. Crumb rubber (CR) has been selected as modifier for the purpose of the improved aging resistance performance and tire recycling [22,23]. Crumb rubber modified asphalts are mainly divided into two types: the traditional crumb rubber modified asphalt (CRMA), and the terminal blend rubber modified asphalt (TB). TB consists of asphalt with CR modifier, which is digested at the refinery or at asphalt terminal and then delivered to the plant [23–25].

Aging of PMAs has been investigated by using the rolling thin film oven test (RTFOT), pressurized aging vessel (PAV), and ultraviolet aging (UV). It is found that two parallel reactions occur during the course of oxidation: oxidation of base asphalts and degradation of polymers, which results in changing the compatibility between asphalt and polymer [26,27]. Due to the complexity of the CRMA, the aging mechanism of CRMA is still unclear. Ghavibazoo and Abdelrahman [28] find that the traditional crumb rubber modifier particles don't prevent base asphalt from thermal aging. Otherwise, the pavement longevity is extended largely by means of the high asphalt aggregate ratio and crack resistance of rubber. Chipps [29] and Ruan [30] analyze the effect of the long-term aging on properties of TB. They find that the aging reduces the hardening and oxidative ration of TB which has better aging resistance than BA.

Currently, the field aging behaviors of PMAs are still mainly studied by simulating the influence of environmental factors in indoor conditions [2,3,26,31,32], such as RTFOT, UV with PAV and so on. However, the aging of PMAs mainly occur outdoor. The thin layer of modified asphalts exposing to the weather conditions need to be investigated.

In this study, SBS, CR and degraded rubber (the crumb rubber digested in the asphalt under high temperature and high shear) were used to prepare three different rubber modified asphalts. Their weather aging properties of different modified asphalts were investigated in terms of the rheological properties and chemical composition. The research results will gain more insight into the aging behaviors of different rubber modified asphalts under real using conditions.

## 2. Experimental

### 2.1. Materials

Base asphalt GS 90# (Saturate, 18.3%; Aromatics, 50.0%; Resin, 32.5%; Asphaltene, 9.2%) was selected as the base asphalt. CR (40 mesh) was produced by the mechanical shredding at ambient temperature, supplied by the Jiangsu Branch Yin Gert Asphalt Co. Ltd. Linear styrene-butadiene-styrene (SBS) with molecular weight is  $1.2 \times 10^5$  g/mol with S/B (30/70), produced by Petrochemical Co., Ltd, China.

### 2.2. Preparation of the modified asphalts

CRMA was prepared in an open iron container by using a high shear mixer (made by Aidong Machine Co. Ltd., China). Base asphalt was first heated to fluid state, the stirring equipment was started with 500 rpm to heat evenly to 175 °C, and 22 wt% CR was added into asphalt matrix with a shearing speed of 5000 rpm for 40 min.

SBSMA was prepared by adding 4 wt% SBS to asphalt with 4000 rpm for 30 min at 175 °C.

TB was prepared with high shearing (3000 rpm) and high temperature (220 °C) for 2 h, subsequently, the blend was stored at 200 °C for 32 h.

The conventional properties of BA, SBSMA, CRMA and TB are given in Table 1.

### 2.3. Aging procedure

The weathering aging procedure of different rubber modified asphalts was adopted according to BS EN ISO 2810-2004 (Paints and varnishes-natural weathering of coatings exposure and assessment). Different modified asphalts were coated on Aluminum plate (200 mm × 200 mm) in thickness of 0.5 mm. Subsequently, the coated samples were placed into an oven (80 °C) to make sure the evenness of PMAs. After that, all samples exposed outdoor (the weather in Shanghai city with humid meso-thermal climates). The weather aging was carried out for 9 months, from August, 2014 to April, 2015. The aging environment conditions were shown in Fig. 1.

### 2.4. Characterization methods

#### 2.4.1. Fourier transform infrared (FTIR)

Changes in functional groups of asphalt and the modified asphalts before and after aging were conducted with Attenuated Total Reflectance Infrared Spectrometer (ATR-FTIR) (iz10, Nicolet, USA). The scan ranges from  $600 \text{ cm}^{-1}$  to  $4000 \text{ cm}^{-1}$  at a resolution of  $4 \text{ cm}^{-1}$ .

Carbonyl group C=O (centered around  $1700 \text{ cm}^{-1}$ ) and sulfoxide group S=O (centered around  $1030 \text{ cm}^{-1}$ ), as well as the butadiene double bonds C=C (centered around  $966 \text{ cm}^{-1}$ ) were monitored to characterize the aging degree of modified asphalts in spectra. Among them, the decrease of C=C content in SBSMA means the degradation of SBS in asphalt during weather aging (especially thermal, oxidation, UV radiation). The carbonyl index (CI), sulfoxide index (SI) and butadiene double bonds index ( $I_{\text{SBS}}$ ) were calculated by integral to evaluate the aging degree by following formulas [33]:

$$\text{CI} = A_{\text{C=O}}/A, \text{ SI} = A_{\text{S=O}}/A, I_{\text{SBS}} = A_{\text{SBS}}/A$$

where the C=O ranges from ( $1690 \text{ cm}^{-1}$  to  $1710 \text{ cm}^{-1}$ ); S=O ( $1020 \text{ cm}^{-1}$  to  $1034 \text{ cm}^{-1}$ ); A ( $700 \text{ cm}^{-1}$  to  $2000 \text{ cm}^{-1}$ );  $I_{\text{SBS}}$  ( $940 \text{ cm}^{-1}$  to  $990 \text{ cm}^{-1}$ ).

This carbonyl indices for BA and modified asphalts in production (carbonyl content of modified asphalt was prepared later subtracting the carbonyl content of base asphalt) and aging process was analyzed.

#### 2.4.2. Dynamic shear rheometer (DSR)

High temperature rheological characterization of BA and modified asphalts was carried out by using a dynamic shear rheometer (rotary rheometer, Gemini 200HR, Bohlin Instruments, UK) configured in parallel plate geometry. Temperature sweep tests were conducted in constant-strain oscillation mode at a fixed frequency of 10 rad/s. The temperature ranged from 46 °C to 86 °C with an increment of 3 °C/min. The parallel plate of 25 mm diameter with a gap width of 1 mm between the two plates was used. The constant strain was 1%. Rheological parameters such as complex modulus ( $G^*$ ) and phase angle ( $\delta$ ) as a function of temperature for all samples were applied to evaluate the rheological properties of asphalts in aging process.

#### 2.4.3. Dynamic mechanical analysis (DMA)

Dynamic mechanical analysis (DMA) was implemented with a dynamic mechanical analyzer (Q800, TA instruments, USA). Samples were cut into size of  $22 \times 5 \times 2 \text{ mm}^3$ . The storage modulus  $G'$  and  $\tan \delta$  was measured at a frequency of 10 Hz with a strain of 0.01% in tensile mode. The temperature ranged from  $-50 \text{ °C}$  to  $5 \text{ °C}$  at a heating rate of 3 °C/min.

## 3. Results and discussion

### 3.1. Rheological properties of different PMAs at high temperature

Different asphalts show different aging behavior because of the different aging sensitivity of molecular structures. The weather aging will cause the composition evolution of different asphalts, which changes the viscoelastic properties of asphalts. The moduli of asphalts are sensitive to temperature. Therefore, complex modulus ( $G^*$ ) and phase angle ( $\delta$ ) of BA and different PMAs before and after aging are applied to evaluate the rheological properties.

**Table 1**

Properties of base asphalt and different modified asphalts.

Properties	BA	SBS MA	CRMA	TB	Standard
Penetration (0.1 mm)	94.0	67.4	54.9	69.4	ASTM D5
Softening point (°C)	49.2	63.4	58.9	53.6	ASTM D36
Ductility (5 °C)/cm	0	21.3	8.5	11.7	ASTM D113

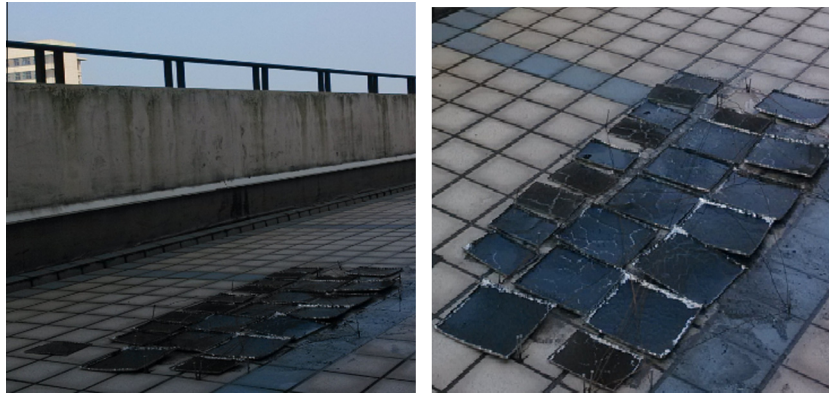


Fig. 1. Aging conditions of the modified asphalts.

As can be seen from Fig. 2a, an obvious increase in complex modulus ( $G^*$ ) of asphalt is obtained by the addition of different polymers. CRMA has the highest complex modulus, which is mainly due to the presence of high percentage of elastic rubber particles in asphalt. Although the same content of tire rubber is added into asphalt, the complex modulus of TB is much lower than that of CRMA. This is caused by the breakage of crosslinking network of rubber under high temperature and high shear during processing. Therefore, the improvement degree of performance of asphalt at high temperature decreases.

As illustrated in Fig. 2b, weather aging increases the complex modulus of all PMAs and BA. The higher the modulus increases, the more sensitive to aging. Weather aging causes an increase of asphaltenes, oxidation of the polymer and volatilization of the light molecular components from asphalt. These factors result in increasing the elasticity and improving the deformation resistance of asphalt at high temperature. In addition, it can be further observed that different asphalts show the different aging resistant performance around 60 °C as shown in Fig. 2b. The detailed values are listed in Table 2.

It is well known that the increasing phase angle indicates the breakage of polymeric network in asphalt [34]. Phase angle significantly increases with temperature, and different asphalts show different temperature susceptibility. As shown in Fig. 3a, aging reduce the whole phase angle curve. The phenomenon means that a more sol-like (viscous and less structured) is transformed to

Table 2

$G^*$  and  $\delta$  of base asphalt and different modified asphalt before and after aging at 60 °C.

Asphalt type	Index	0	9 m	Ratio
BA	$G^*/\text{kPa}$	4.59	15.79	3.44
	$\delta/^\circ$	86.18	81.00	0.94
	$G^*/\sin \delta$	4.60	15.99	3.48
TB	$G^*/\text{kPa}$	7.49	16.99	2.27
	$\delta/^\circ$	66.05	61.70	0.93
	$G^*/\sin \delta$	8.19	19.29	2.36
CRMA	$G^*/\text{kPa}$	14.27	38.82	2.72
	$\delta/^\circ$	66.77	59.05	0.88
	$G^*/\sin \delta$	15.53	45.26	2.91
SBSMA	$G^*/\text{kPa}$	10.26	40.82	3.98
	$\delta/^\circ$	76.52	68.20	0.89
	$G^*/\sin \delta$	10.55	43.96	4.17

more gel-like (elastic and more structured) behavior has occurred [19,34]. Moreover, TB has the lowest temperature susceptibility due to the minimum changes of phase angle. The reduction of phase angle after aging indicates that the rutting resistance of asphalt at high temperature is enhanced because of the increase of elasticity of modified asphalts caused by aging.

$G^*/\sin \delta$  at 10 rad/s has been selected to evaluate the permanent deformation according to the Strategic highway research program (SHRP) specification. The higher  $G^*/\sin \delta$  values show the higher

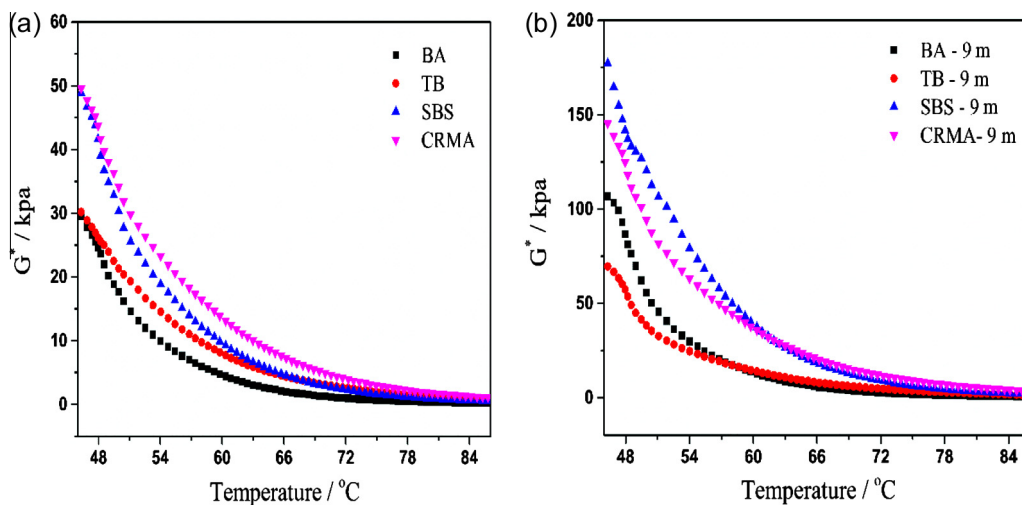


Fig. 2. Complex moduli of the four asphalts: (a) before aging; (b) after aging.

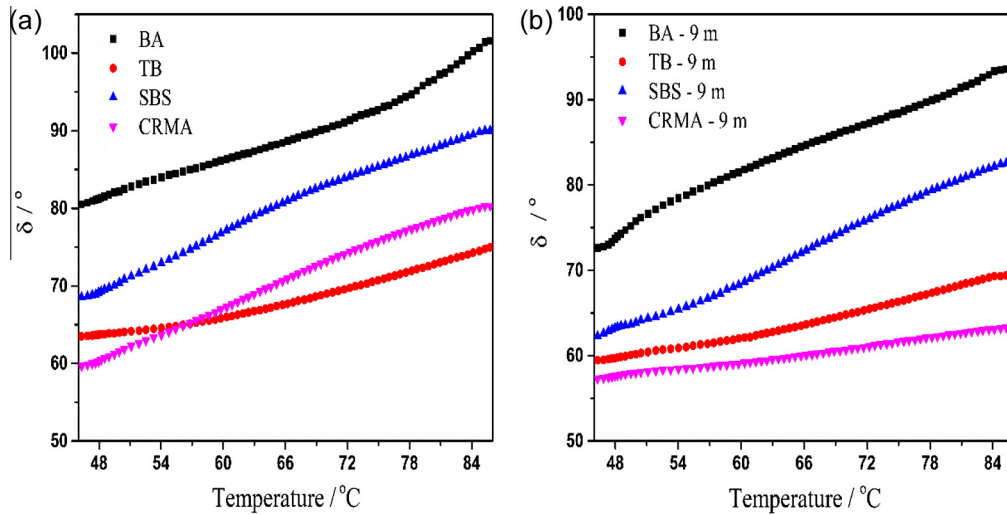


Fig. 3. Phase angle with temperature curves of the four asphalts; (a) before aging; (b) after aging.

rutting resistance. Therefore, the aging resistance of different modified asphalts are evaluated by the change ratio of  $G^*/\sin \delta$  at 60 °C before and after aging.

As shown in Table 2, polymers increase the complex modulus and improve the elasticity (increase  $G^*$ , decrease  $\delta$ ). The changes ratio of complex modulus of SBSMA after aging is highest compared to other modified asphalts. It may be attributed to the presence of C=C in SBS, and the active C–H bonds makes it more susceptible to aging. TB has the best resistance to aging performance because carbon black releases from degraded rubber, which protected if from environmental factors. Moreover, the changing extent of complex modulus and rutting factors ( $G^*/\sin \delta$ ) are lesser in TB compared with CRMA and SBSMA. The phenomenon indicates that the resistance of high temperature is relatively stable, and anti-aging ability is better than others as illustrated in Table 2.

### 3.2. Rheological properties of different PMAs at lower temperature

Low temperature properties of modified asphalts can be evaluated through establishing the relations between the various viscoelastic parameters and temperature showed by dynamic

mechanical thermal analysis (DMA). The smaller the storage modulus is, the better the resistance to crack.

As shown in Fig. 4a, different polymers show different effects on the cracking resistance of asphalts in low temperature range. The storage modulus of TB is highest below –30 °C, while it is lower than BA from –25 °C to 0 °C. The storage modulus of SBSMA is highest above –30 °C. It indicates that the ability to resist the low temperature performance of SBSMA is enhanced as the storage modulus decreases after aging.

As shown in Fig. 4b, the storage modulus of aged BA is the highest among other aged modified asphalts above –30 °C. The rank of storage moduli of modified asphalts before and after aging is in different orders. The values of different asphalts at –20 °C are listed in Table 3. This can be ascribed to the SBS degrade severely to small molecular, resulting in a more flexible in asphalt at low temperature.

The viscoelastic of different asphalts at different temperature were characterized by  $\tan \delta$  as shown in Fig. 5. Low temperature susceptibility of modified asphalts decreased, which may be due to the polymer twined or network breakage occur, the low temperature resistance of modified asphalts are changed with temperature. Among them,  $\tan \delta$  of SBSMA and CRMA before and after aging

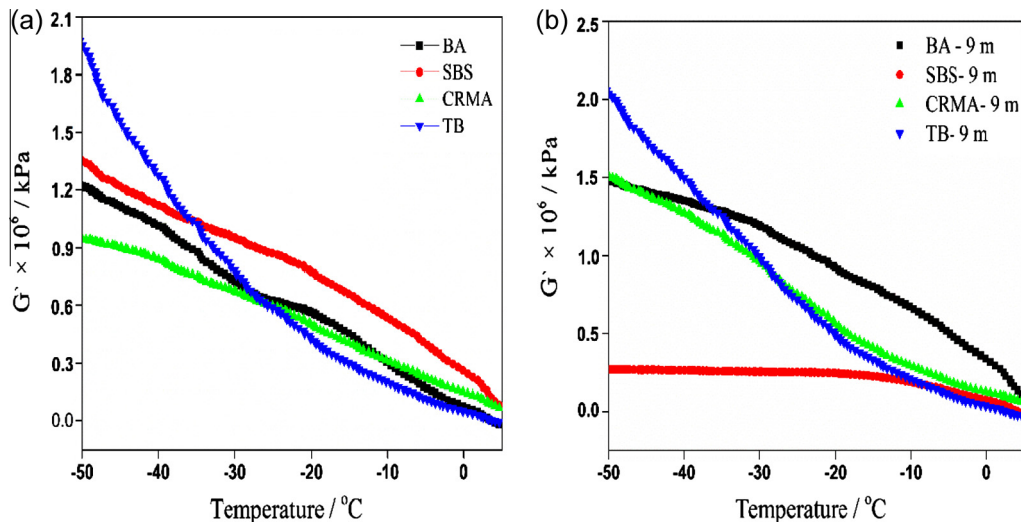


Fig. 4. Storage modulus as function of temperature of BA and modified asphalts. (a) Before aging, (b) after aging.

**Table 3**  
 $G'$  and  $\tan \delta$  of BA and modified asphalts before and after aging at  $-20\text{ }^\circ\text{C}$ .

Asphalt type	Index	0	9 m	Ratio
BA	$G'/\text{Gpa}$	0.54	0.92	1.70
	$\tan \delta$	0.28	0.22	0.25
	$G'^* \tan \delta$	0.15	0.20	1.33
TB	$G'/\text{Gpa}$	0.42	0.48	1.14
	$\tan \delta$	0.42	0.37	0.88
	$G'^* \tan \delta$	0.18	0.18	1
CRMA	$G'/\text{Gpa}$	0.52	0.54	1.04
	$\tan \delta$	0.28	0.26	0.93
	$G'^* \tan \delta$	0.19	0.16	0.84
SBSMA	$G'/\text{Gpa}$	0.83	0.25	0.30
	$\tan \delta$	0.22	0.28	1.27
	$G'^* \tan \delta$	0.19	0.07	0.37

changes with temperature slowly, while TB varies obviously. It indicates that the temperature susceptibility of TB under low temperature is small. The transformation between the viscous and elastic parts is improved effectively.

Aging resistance of modified asphalts is characterized by the modulus evolution (at  $-20\text{ }^\circ\text{C}$ ) as presented in Table 3. Loss modulus ( $G'^* \tan \delta$ ) of the modified asphalts decrease after aging, and the low temperature performance decrease [35].

As shown in Table 3, the loss modulus of the modified asphalts before aging is higher. This indicates more viscous at low temperature. The changing ratio of loss modulus of TB becomes smaller after aging. However, loss modulus of SBSMA after aging shows a significant decrease, which illustrate that the SBSMA is easy to aging. The above result shows the same trend in high temperature.

3.3. Influence of aging on the chemical structure of asphalt and modified asphalts

The chemical changes of BA and modified asphalts before and after aging are shown in Figs. 6 and 7. It can be seen that the obvious oxidation peak at  $1700\text{ cm}^{-1}$  appeared in SBSMA after aging, while the other asphalts are not visible.

The chemical changes in BA and PMAs during the production and aging process can be evaluated through the variation in oxygenic groups [36]. Meanwhile, the carbonyl content of BA is taken as the benchmark to evaluate the additional oxidation during production process.

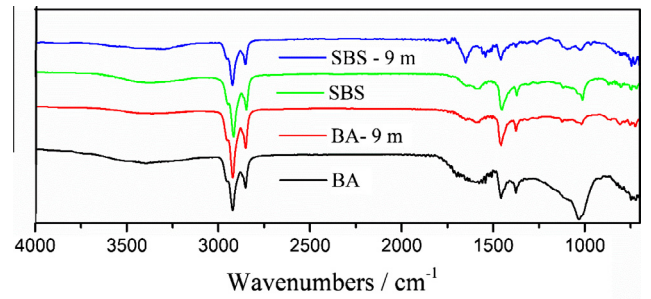


Fig. 6. Spectra of BA and SBSMA before and after aging.

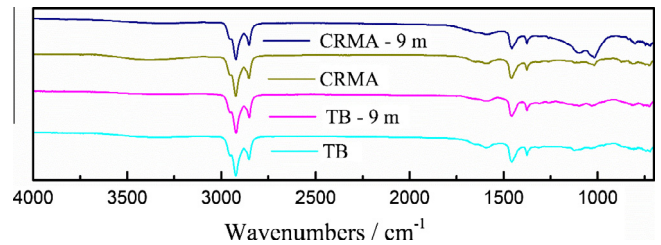


Fig. 7. Spectra of CRMA and TB before and after aging.

As shown in Figs. 7 and 8, it can be observed that SBSMA, CRMA and TB has been subject to oxidation in production. The formation degree of carbonyl compounds in asphalt or rubber is higher in TB due to the preparation at high temperature during production compared with other asphalts. During weather aging process, the increase of carbonyl content is become less in SBSMA, CRMA and TB compared with BA. The CI index of TB increases the least, which is due to the photo-aging of TB can be prevented by a large number of carbon black released from degraded rubber. Meanwhile, the carbonyl content increases is lesser in CRMA and TB compared with SBSMA, which indicates that their aging resistance of are superior to SBSMA. Comparing CRMA with TB, TB displays a relative less susceptible to oxidation. Results are also in agreement with the changes ratio of rheological properties shown in Table 2, the orders of aging resistance is TB, CRMA and SBSMA.

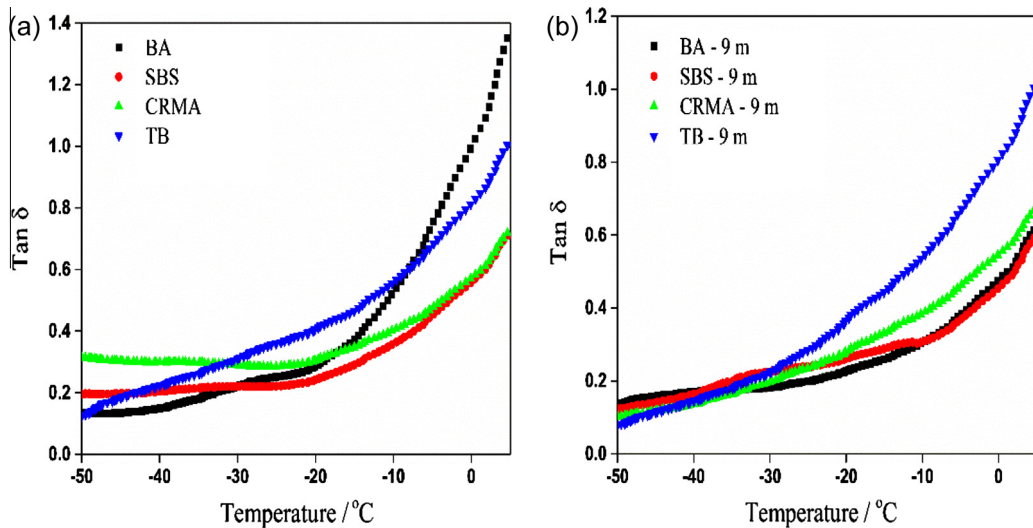


Fig. 5.  $\tan \delta$  as function of temperature of the four asphalts; (a) before aging; (b) after aging.

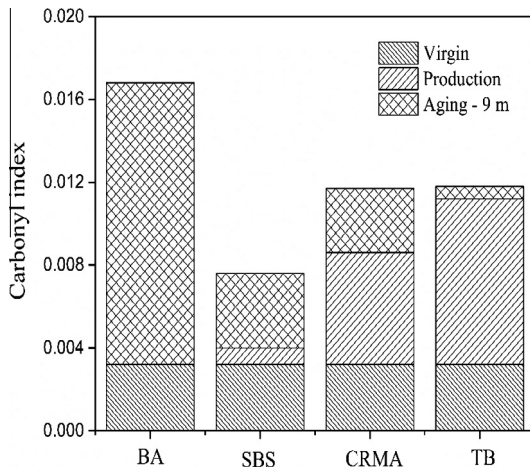


Fig. 8. Carbonyl indices for BA and modified asphalts.

Moreover, SBS modifier evolution in SBSMA before and after aging is evaluated by  $I_{SBS}$ . The index decreases from 0.0249 before aging to 0.0017 after aging, which indicates that a partial butadiene in SBS damaged easily in aging process. The more SBS is degraded, the larger change of physical properties of modified asphalt. This point is corresponding to the changes ratio of rheological properties of aged SBSMA.

#### 4. Conclusions

The physical and chemical changes of different PMAs during the weather aging were studied. The following conclusions can be drawn:

- (1) For the given base asphalt, rheological properties at higher temperature showed that the variation of rutting factors ( $G^*/\sin \delta$ ) was in the order of TB, CRMA, BA and SBSMA.
- (2) Rheological properties at lower temperature indicated that SBSMA was the most sensitive to weather aging, while the low temperature properties of SBSMA was the best.
- (3) For the given base asphalt, the chemical structure evolution of modified asphalts after aging indicated that the weather resistance of SBSMA was the worst, while the TB was the best. The result was in agreement of the evolution of rheological properties. The phenomenon may be due to a larger amount of carbon black was released from degraded rubber, which protected the weather aging of TB. More base asphalts need to be further studied in the future.

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