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Effect of ageing on rheological properties of storage-stable SBS/sulfur-modified asphalts

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ABSTRACT

Oxidative ageing as an inevitable process in practical road paving has a great effect on the properties of polymer-modified asphalts (PMAs). In this article, the effect of short-term and long-term oxidative ageing on the rheological, physical properties and the morphology of the styrene-butadiene-styrene (SBS)- and storage-stable SBS/sulfur-modified asphalts was studied, respectively. The analysis on the rheological and physical properties of the PMAs before and after ageing showed the two major effects of ageing. On one hand, ageing prompted the degradation of polymer and increased the viscous behaviour of the modified binders, on the other, ageing changed the asphalt compositions and improved the elastic behaviour of the modified binders. The final performance of the aged binders depended on the combined effect. After ageing, the storage-stable SBS/sulfur-modified asphalts showed an obvious viscous behaviour compare with the SBS-modified asphalts and this led to an improved low-temperature creep property. The rutting resistance of the SBS-modified asphalts declined by the addition of sulfur due to the structural instability of the SBS/sulfur-modified asphalts. The rheological properties of the modified binders before and after ageing also depended strongly on the structural characteristics of SBS. The observation by using optical microscopy showed the compatibility between asphalt and SBS was improved with further ageing, especially for the storage-stable SBS/sulfur-modified asphalts.

1. Introduction

The use of styrene-butadiene-styrene triblock copolymer (SBS) as an asphalt modifier was developed by the Shell Chemical Company [1]. It has been recognized that the physical and mechanical properties and rheological behaviour of conventional asphalt compositions can be improved by the addition of SBS [2]. SBS exhibits a two-phase morphology consisting of glassy polystyrene (PS) domains connected together by the rubber polybutadiene (PB) segments at the temperatures between glass transition temperatures of the PB and PS, so SBS exhibits crosslinked elastomer network behaviour. Above the glass transition temperature of PS, the PS domains soften and SBS becomes melt processable. This behaviour of a thermoplastic elastomer has allowed SBS to become one of the promising candidates in asphalt modification [3]. However, because of the poor compatibility between SBS and asphalt, the storage stability of SBS-modified asphalt is usually poor at elevated temperatures. Some methods for preparation of practical storage-stable SBS-modified asphalt have been developed [4–6]. One of the most effective and practical ways is to use sulfur. It is commonly believed that sulfur chemically crosslinks polymer molecules and chemically couples polymer and asphalt through sulfide and/or polysulfide bonds. The compatibility between SBS and asphalt can be improved by dynamic vulcanization so the storage stability of SBS-modified asphalt can be improved significantly.

Some publications to date concern the studies on SBS/sulfur-modified asphalts. Wen Guian has studied the rheological properties of SBS/sulfur-modified asphalts systematically and pointed out the effects of some important factors such as sulfur level, SBS structure or content on the rheological behaviour of modified binders and studied the morphology of storage-stable SBS/sulfur-modified asphalts at elevated temperature [1,7,8]. The similar studies were also reported in other publications [9,10]. However, the effect of ageing on the rheological, physical properties and the morphology of storage-stable SBS/sulfur-modified asphalts has not been reported in many publications. Moreover, oxidative ageing as an inevitable process in practical road paving has a great effect on the properties of PMAs. The performance of asphalt pavement actually depends on the properties of aged asphalt binders, especially after short-term ageing. It was reported that the use of sulfur can improve the high-temperature performance of SBS-modified asphalts significantly, however if the improved performance also can be retained after ageing is not still reported in many publications.

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The present work seeks to identify the changes on the rheological and physical properties of the storage-stable SBS/sulfur-modified asphalts through short-term ageing test (thin film oven test, TFOT) and long-term ageing test (pressurized ageing vessel, PAV), to compare the SBS-modified asphalts with the storage-stable SBS/sulfur-modified asphalts by ageing, to investigate the effect of ageing on the morphology of the modified binders by optical microscopy, and finally to point out the problems existing in the practical apply of the storage-stable SBS/sulfur-modified asphalts.

2. Materials and experimental

2.1. Materials

Asphalt, SK-90 paving asphalt, was obtained from the SK Petroleum Asphalt Factory, Southern Korea. The physical properties of the asphalt are as follows: softening point: 46.3 °C (ASTM D36); penetration: 87 dmm (25 °C, ASTM D5); viscosity: 0.32 Pa s (135 °C, ASTM D 4402).

SBS1301 and SBS4303 were produced by the Yueyang Petrochemical Co., Ltd., China. SBS4303 is a star-like polymer, containing 30 wt% styrene, the average molecule weight is 350,000 g/mol. SBS1301 is a linear polymer, containing 30 wt% styrene, the average molecule weight is 110,000 g/mol. Sulfur precipitated is a commercial product (industrial grade) of the Yili Chemical Co., Ltd., China.

2.2. Preparation of samples

The modified asphalts were prepared using a high shear mixer (made by Weiyu Machine Co., Ltd., China). Firstly, asphalt (400 g) was heated until it became a fluid in an iron container, then upon reaching about 180 °C, the SBS or sulfur powder (the amounts were based on 100 parts asphalt) were added to the asphalt, and then the blend was sheared for 40 min, the shearing temperature is 180 °C, the shearing rate is 4000 r/min, subsequently the blend was stirred by a mechanical stirrer at 180 °C for 2 h to make sure the fully swelling of the modifiers in the asphalt. After that, the preparation has been finished.

2.3. Storage stability test

The storage stability of modified asphalts was measured as follows. The sample was poured into an aluminum toothpaste tube (32 mm in diameter and 160 mm in height). The tube was sealed and stored vertically in an oven at 163 °C for 48 h, then taken out, cooled to room temperature, and cut horizontally into three equal sections. The samples taken from the top and bottom sections were used to evaluate the storage stability of the SBS-modified asphalts by measuring their softening points. If the difference of the softening points between the top and the bottom sections was less than 2.5 °C, the sample was considered to have good high-temperature storage stability. If the softening points differed by more than 2.5 °C, the SBS-modified asphalt was considered to be unstable.

2.4. Standard ageing procedure

Oxidative ageing of modified asphalts was performed using the thin film oven test, TFOT (ASTM D1754), and pressurized ageing vessel, PAV (ASTM D6521). TFOT simulates short-term ageing that takes place during the hot mixing of asphalt binder with aggregates and during the pavement construction phase, while PAV simulates long-term ageing that occurs during the in-service life of asphalt pavement.

2.5. Physical properties test

The physical properties of asphalts, including softening point, penetration, viscosity (135 °C), ductility (5 °C), were measured in accordance with ASTM D36, D5, D4402 and Chinese specification GB/T 4508, respectively.

2.6. Thin-layer chromatography with flame ionization detection (TLC-FID)

In the TLC-FID, 2% (w/v) solutions of the unaged and aged base asphalts were prepared in dichloromethane, and 1 μl sample solution spotted on chromarods using a spotter. The separation of bitumen into four generic fractions (saturates, aromatics, resins and asphaltenes) was performed by a three-stage development using n-heptane, toluene and dichloromethane/methanol (95/5 by volume), respectively. The fractions were determined by means of Iatroscan MK-5 analyzer (Iatron Laboratories Inc., Tokyo, Japan).

2.7. Dynamic mechanical analysis

Dynamic mechanical analysis (DMA) was performed using a strain-controlled rheometer (RDA II, Rheometrics). In DMA, frequency sweeps were applied over the range of 0.1–100 rad/s at a fixed strain amplitude at five temperatures: 25, 30, 40, 50, and 60 °C, and temperature sweeps (from 30 to 138 °C) with 2 °C increments were applied at a fixed frequency (10 rad/s) and at variable strains. High-temperature repeated creep tests were performed at 60 °C using a 1 s loading cycle followed by a recovery period of 9 s, and this was repeated 100 times. The repeated creep tests were made at a constant stress level of 30 Pa [11]. Parallel plates, gap 1.0 mm for φ 25 mm, were used. In each test, about 1.0 g of sample was applied to the bottom plate, covering the entire surface, and the plate was then mounted in the rheometer. After heating to the softening point of the binder, the top plate was brought into contact with the sample, and the sample was trimmed. The final gap was adjusted to 1 mm. A sinusoidal strain was then applied by an actuator. The actual strain and torque were measured and input to a computer for calculating various viscoelastic parameters such as complex modulus (G^*) and phase angle (δ) and so on.

2.8. Low-temperature creep test

Low-temperature creep tests were carried out at the low temperature (−18 °C) using a bending beam rheometer (BBR, Cannon Instrument Company, USA). In tests, the sample was heated to fluid condition, poured into the mold and then allowed to cool at room temperature for about 90 min. The sample was cooled to approximately −5 °C for 1 min and demolded. After demolding, the sample beam (125 mm long, 12.5 mm wide and 6.25 mm thick) was submerged in a constant temperature bath and kept at the test temperature (−18 °C) for 60 min. A constant load of 100 g was then applied to the rectangular beam of the sample which was supported at both ends by stainless steel half-rounds (102 mm apart), and the deflection of center point was measured continuously. Creep stiffness (S) and creep rate (m) of the sample were determined at several loading times ranging from 8 to 240 s.

2.9. Morphology observation

The sample morphology was observed using an optical microscope made by Nikkon Co., Japan. Squashed slides of modified binders were prepared using very small amounts of the heated sample and viewed under the microscope at a magnification of 400.

Table 1
Effect of sulfur on storage stabilities of SBS-modified asphalts (SBS content: 3.5 wt%).

Sulfur content (wt.%)	ΔS/°C	
	SBS1301	SBS4303
0	14	35.8
0.03	7.9	12.9
0.065	2.8	7
0.1	0.2	0.1

3. Results and discussion

3.1. Storage stability

Due to the difference in the solubility parameter and density between SBS and asphalt, phase separation would take place in SBS-modified asphalts during storage at elevated temperatures. Droplets of the SBS melt dispersed in asphalt are usually accumulated and float on the top of the asphalt at a high temperature and static state. The high-temperature storage stabilities of the modified asphalts with two SBS structures and varying sulfur levels were tested and the results are shown in Table 1. Obviously, for the SBS-modified asphalts in the absence of sulfur, the differences in the softening points are large. As shown in Table 1, the differences in softening points are 14 °C for the SBS1301-modified asphalt and 35.8 °C for the SBS4303-modified asphalt. Due to the higher molecule weight of SBS4303, the phase separation of the SBS4303-modified asphalt is more severe. Storage-stable SBS-modified asphalts can be prepared by reaction with sulfur at high temperature under high shear mixing. The sulfur level is based on the base asphalt. It can be seen that the storage stabilities of the SBS-modified asphalts are improved with the addition of sulfur. With increasing the sulfur level, the differences in softening points decline and when the sulfur level increases to 0.1 wt%, the differences are not more than 2.5 °C for the modified asphalts with different SBS structures. The storage-stable SBS/sulfur-modified asphalts can be made with the addition of 0.1 wt% sulfur.

3.2. Physical properties

For the base asphalt, to clarify the relationship between the chemical compositions and the physical properties, the chemical compositions of the base asphalt before and after ageing were studied using TLC-FID, the four generic fractions, namely saturates, aromatics, resins and asphaltenes, were determined and the physical properties of the aged binders were measured, as shown in Table 2. Upon ageing, the contents of the hard asphalt compositions such as asphaltenes and resins increase, while the content of aromatics decreases and the content of saturates remains constant. The variation becomes more apparent with further ageing. The expected increase in softening point and viscosity and the decrease in penetration are observed after ageing, and this trend becomes very apparent with increasing the hard asphalt compositions. This reinforces the assumption that the variation in the physical properties of the base asphalt after ageing depends on the changes in the hard asphalt compositions.

Table 2
The chemical compositions and physical properties of the base asphalt before and after ageing.

	Unaged	After TFOT	After PAV
Saturates (%)	16.3	15.66	15.76
Aromatics (%)	49.19	46.06	38.36
Resins (%)	24.55	26.69	28.1
Asphaltenes (%)	9.96	11.99	17.78
Softening point (°C)	46.3	50.2	54.7
Penetration (25 °C, 0.1 mm)	87	54	46
Viscosity (135 °C, Pa s)	0.32	0.62	0.93
Ductility (5 °C, 0.1 cm)	4.5	–	–

–, unavailable.

The physical properties of the SBS-modified asphalts and storage-stable SBS/sulfur-modified asphalts before and after ageing were measured and shown in Tables 3 and 4, respectively. In Table 3, it can be seen that the softening point and viscosity of the SBS1301-modified asphalt increase and the penetration declines correspondingly with the addition of sulfur, indicating that the high-temperature performance is improved by dynamic vulcanization. This can be attributed to the formation of a chemically crosslinked SBS network structure in the modified binder [1,8], by which the elasticity of the binder is improved. However the crosslinked polymer network structure in asphalt matrix restricts the movements of the polymer molecules to some extent and results in the loss of the low-temperature ductility as compared to the SBS1301-modified asphalt. Usually the influence of oxidative ageing on the high-temperature performance of PMAs can be divided into the two major sides, on one hand, the increase of the hard asphalt compositions such as asphaltenes and resins by ageing improves the high-temperature performance of binders and declines the temperature susceptibility, on the other, the decom-

Table 3
Effects of ageing on the physical properties of the SBS1301-modified asphalt and the storage-stable SBS1301/sulfur-modified asphalt.

	Unaged		After TFOT		After PAV	
	0[a]	0.1[a]	0[a]	0.1[a]	0[a]	0.1[a]
Softening point (°C)	53.2	58.8	53	57.4	60.1	59.5
Penetration (25 °C, 0.1 mm)	49.1	46.1	49.6	47.3	42.7	44.2
Viscosity (135 °C, Pa s)	1.29	1.4	1.23	1.38	2.01	1.93
Ductility (5 °C, 0.1 cm)	39.1	29.4	20.1	18.2	2.9	1.1

[a] Sulfur content (wt.%).

Table 4
Effects of ageing on the physical properties of the SBS4303-modified asphalt and the storage-stable SBS4303/sulfur-modified asphalt.

	Unaged		After TFOT		After PAV	
	0[a]	0.1[a]	0[a]	0.1[a]	0[a]	0.1[a]
Softening point (°C)	53.7	65.9	53.1	64.3	58	64
Penetration (25 °C, 0.1 mm)	49	40.9	48.9	40	46.6	40.3
Viscosity (135 °C, Pa s)	1.34	2.19	1.13	2.03	1.83	2.49
Ductility (5 °C, 0.1 cm)	23.4	31	21.9	13.3	3.4	0.8

[a] Sulfur content (wt.%).

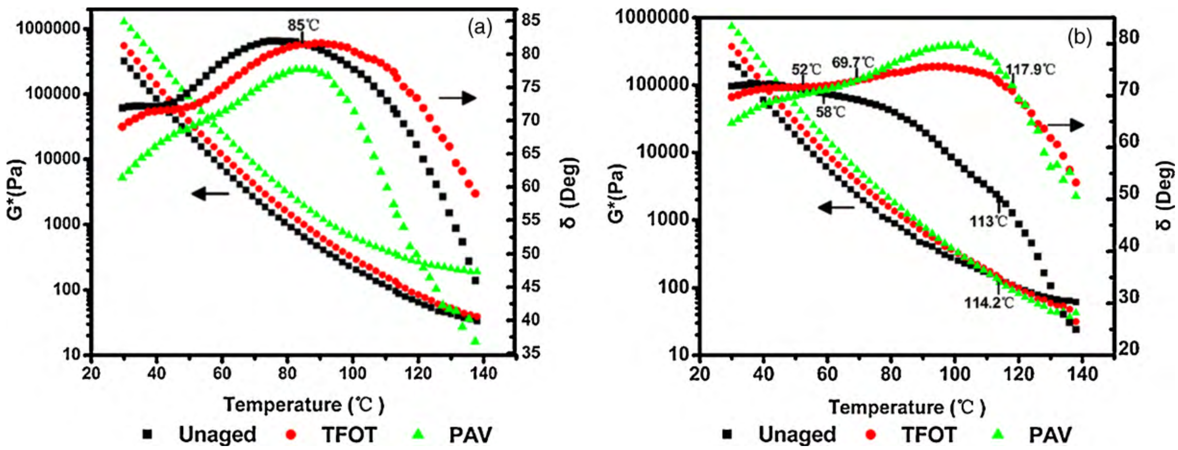

Fig. 1. Effect of ageing on the rheological behaviour of SBS1301- and storage-stable SBS1301/sulfur-modified asphalts (temperature sweep, 10 rad/s, 30–138 °C). (a) SBS1301-modified asphalt. (b) Storage-stable SBS1301/sulfur-modified asphalt.

position of polymer dispersed in asphalt after ageing will led to an opposite result. For the SBS1301 binders (with and without sulfur), the slight changes on the softening point, viscosity and penetration values after TFOT ageing do not show the predominant role of either side. However, after PAV ageing, the changed asphalt compositions are mainly responsible for the obviously improved high-temperature performance of the two binders, as shown by the increase in the softening point and viscosity values. By evaluating the magnitude of the increase in softening point or viscosity of each binder after PAV ageing, we can see the degradation of polymer has a more significant effect on the high-temperature physical properties of the storage-stable SBS1301/sulfur-modified asphalt.

For the SBS4303-modified asphalt, the improvement on the high-temperature performance is very evident through vulcanization. It can be seen in Table 4 that the softening point and viscosity increase evidently with the addition of sulfur and the penetration declines correspondingly. The increase in the low-temperature ductility by vulcanization shows the improvement on the low-temperature cracking resistance of the binder, this can be attributed to the structural characteristics of SBS4303. SBS4303 is more elastic due to the larger molecule weight. Moreover, the more butadiene structures in SBS4303 block copolymer molecules make it more reactive with sulfur, therefore the elasticity of the polymer dispersed in asphalt is improved by the modest vulcanization, as shown in the increased low-temperature ductility. Similar to the effect of TFOT ageing on the high-temperature performance of the SBS1301 binders, the same conclusion can be drawn for the SBS4303 binders, as shown by the slight changes in the softening point, viscosity and penetration values after TFOT ageing in Table 4. After PAV ageing, there is an increase on the softening point and viscosity of the SBS4303-modified asphalt, indicating the improvement on the high-temperature performance. Nevertheless, the increase on the viscosity is not obvious for the SBS4303/sulfur-modified asphalt and the softening point declines slightly even after the ageing. For all binders shown in Tables 3 and 4, the reduced low-temperature ductility with further ageing shows the increased brittleness, and the binder with sulfur has a lower ductility compare with the corresponding binder without sulfur after ageing.

3.3. Dynamic rheological properties

3.3.1. Temperature sweep

The influence of ageing on the rheological behaviour of the SBS1301-modified asphalt is shown in Fig. 1(a). Similar to the influence of ageing on the physical properties of PMAs, the change of the rheological behaviour after ageing can be attributed to the major two factors. Firstly, the changed chemical compositions of asphalt. Owing to the effect of ageing, a modification of both the quantity and quality of asphaltenes and resins is likely to occur. The increase in asphaltenes and resins contents is a consequence of the effect that ageing has on the elastic properties of asphalt. Secondly, the degradation of polymer in asphalt after ageing. The degradation (rearrangement) of polymer into lower molecular weight fragments after ageing leading to the increase of the viscous behaviour of PMAs [12]. In Fig. 1(a), it can be seen that a constant increase in complex modulus, G^*, over the temperature domain after TFOT and PAV ageing, respectively. The evident increase in G^* after PAV ageing is understandably greater than after TFOT ageing due to the prolonged ageing process in the PAV. There is also a regular decrease of the phase angle, δ, over the temperature domain after PAV ageing. Measurements of δ are generally considered to be more sensitive to the chemical structure and therefore the modification of bitumen than complex modulus [13]. The behaviour of the decrease in phase angle after TFOT ageing is observed from 30 to 85 °C, however, within the temperature range of 85–138 °C, the behaviour of the phase angle differs form that before 85 °C in that the magnitude of the decrease in phase angle after TFOT ageing is severely reduced and there is even an evident increase in phase angle with increasing the temperature compare with the unaged binder due to the fusion of polymer after ageing.

The influence of ageing on the rheological behaviour of the storage-stable SBS1301/sulfur-modified asphalt is shown in Fig. 1(b). In Fig. 1(b), it can be seen the rheological behaviour of the SBS1301/sulfur-modified asphalt differs considerably from that of the SBS1301-modified asphalt. Compared to the rheological behaviour of the SBS1301-modified asphalt, the G^* of the SBS1301/sulfur-modified asphalt increases slightly in high-temperature range and the varying trend of δ is slowed down to a great extent. Owing to the sensibility of phase angle, the change on the chemical structure of a PMA often can be observed by the plot of phase angle versus temperature or frequency. In Fig. 1(b), the flat phase angle curve illustrates the appearance of the plateau region between 58 and 113 °C, which shows the formation of a continuous elastic network in asphalt matrix by vulcanization. The change in phase angle after TFOT or PAV ageing is very different form that of the aged SBS1301 binder. It can be seen that there is an obvious increase in phase angle after TFOT ageing in the most temperature range (after 52 °C) and the shift of the curve towards higher phase angle after PAV ageing is observed from 69.7 to 117.9 °C. The viscous behaviour of the SBS1301/sulfur-modified asphalt becomes

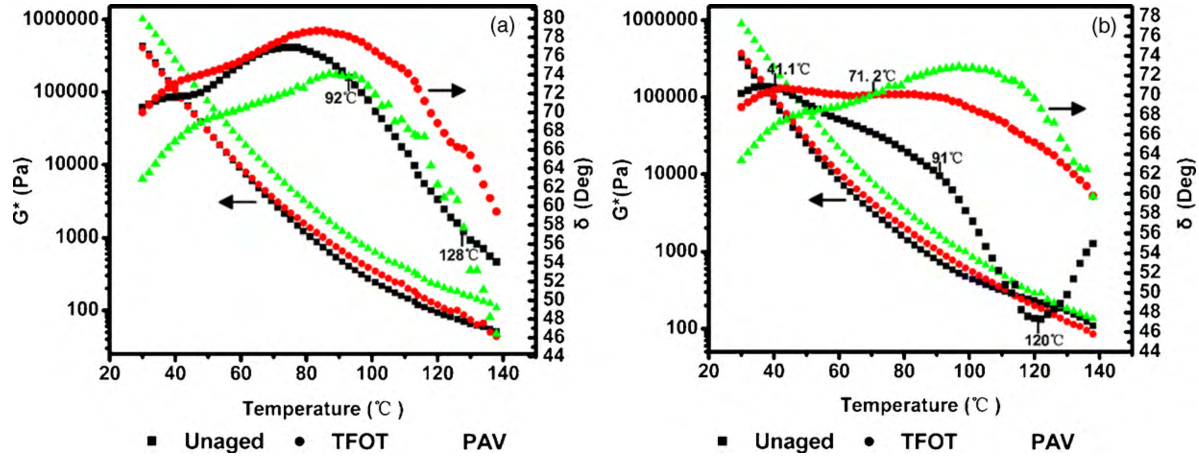

Fig. 2. Effect of ageing on the rheological behaviour of SBS4303- and storage-stable SBS4303/sulfur-modified asphalts (temperature sweep, 10 rad/s, 30–138 °C). (a) SBS4303-modified asphalt. (b) Storage-stable SBS4303/sulfur-modified asphalt.

very obvious compare with the SBS1301-modified binder through TFOT and PAV ageing. This tends to confirm the hypothesis that there is a severe rearrangement of the vulcanized SBS copolymer into lower molecular weight fragments after ageing leading to a "softening" of the PMA and this phenomenon is more noticeable with further ageing. This conclusion also can be confirmed by the varying trend of G^*. As shown in Fig. 1(b), the complex modulus of the SBS1301/sulfur-modified asphalt increases with further ageing over a wide range of test temperatures (before 114.2 °C), however the difference of the complex modulus among three binders decreases rapidly with increasing the temperature and when the temperature is over 114.2 °C, the complex modulus of the unaged is the most highest, the TFOT aged binder is the second, the PAV aged one is the most poorest, obviously the degradation of polymer plays a predominant role in the influence of ageing on the rheological behaviour of the storage-stable SBS1301/sulfur-modified asphalt.

The complex modulus and phase angle versus temperature plots for the SBS4303-modified asphalt before and after ageing are shown in Fig. 2(a). In Fig. 2(a), it can be seen that there is a similar shift in G^* after ageing, as shown for the SBS1301-modified asphalt, the complex modulus increases with the further ageing in the whole temperature range, however the change of the phase angle curve after ageing is very different. The higher phase angle curve can be observed in the whole temperature range after TFOT ageing, which implies the SBS4303-modified asphalt is easier to be oxidized. Compared to the structural characteristics of SBS1301, there are more butadiene structures in the molecule of SBS4303 copolymer. Because the unsaturated carbon–carbon double bonds of butadiene are easy to be oxidized, so the SBS4303-modified asphalt is more susceptible to ageing. After PAV ageing, the high and incontinuous phase angles also can be seen from 92 to 128 °C due to the further degradation of the polymer. The influence of sulfur on the rheological properties of the SBS4303-modified asphalt is shown in Fig. 2(b). As indicated in the phase angle versus temperature plot before ageing, the pronounced plateau region from 41.1 to 91 °C and the phase angle minimum around 120 °C indicate the presence of polymer elastic networks or entanglements in the modified binder [2] as the consequence of dynamic vulcanization. Owing to the more reactive behaviour of SBS4303, a noticeable network is formed in the modified asphalt as shown in the varying trend of the phase angle curve. However a very different phase angle variation can be observed after TFOT ageing. As shown in Fig. 2(b), the phase angle increases evidently in the whole temperature range nearly and the phase angle minimum disappears completely, indicating that polymer network is nearly destroyed [14]. This conclusion can be confirmed further after PAV ageing, the higher phase angles after 71.2 °C show the aged binder becomes a viscous fluid at the elevated temperature.

3.3.2. Frequency sweep

In order to understand the dependence of the rheological behaviour of the PMAs on frequency at high temperature, we conducted the frequency sweep test (0.1–100 rad/s) on each binder. The test temperature, 60 °C, is chosen since it is usually the high

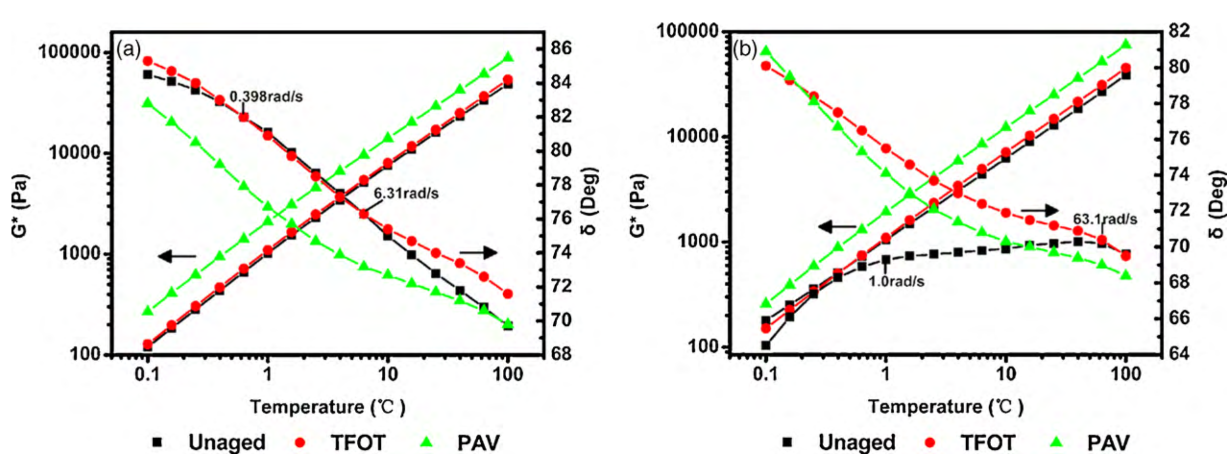

Fig. 3. Effect of ageing on the rheological behaviour of SBS1301- and storage-stable SBS1301/sulfur-modified asphalts (frequency sweep, 0.1–100 rad/s, 60 °C). (a) SBS1301-modified asphalt. (b) Storage-stable SBS1301/sulfur-modified asphalt.

temperature which asphalt pavement endures in summer. For the SBS1301-modified asphalt, the rheological behaviour under different loading frequencies is shown in Fig. 3(a). The short-term ageing increases the viscous behaviour of the modified binder, as shown by the elevated phase angle curve in the frequency ranges (before 0.398 rad/s and after 6.31 rad/s) the shift of the complex modulus curve is slight. With further ageing, the complex modulus curve is elevated over the whole frequency range and the phase angle curve is lowered correspondingly. For the storage-stable SBS1301/sulfur-modified asphalt, as shown in Fig. 3(b), the varying trend of the complex modulus curve after ageing is similar to that of the unvulcanized SBS1301 binder. However the change in the phase angle curve is noticeable. The pronounced plateau zone between 1.0 and 63.1 rad/s shows the formation of a polymer network structure in asphalt by vulcanization. However the plateau zone disappears completely after TFOT ageing and the obviously elevated phase angle curve shows the network is destroyed. After PAV ageing, the phase angle curve become a little flat due to the influence of the changed asphalt compositions.

The influence of TFOT ageing on the rheological behaviour of the SBS4303-modified asphalt is shown in Fig. 4(a). Similar to the influence of the short-term ageing on the rheological behaviour of the SBS1301-modified asphalt, the viscous behaviour of the SBS4303-modified asphalt becomes more obvious after TFOT ageing. As shown in Fig. 4(a), the elevated phase angle curve can be seen in the wider frequency ranges (before 1.58 rad/s and after 6.31 rad/s), the difference between the two complex modulus curves is difficult to distinguish. Those can be related to the susceptibility of the SBS4303-modified asphalt to ageing as mentioned before. After PAV ageing, the varying trend of complex modulus and phase angle shows the predominant role of the changed asphalt compositions. For the storage-stable SBS4303/sulfur-modified asphalt, as shown in Fig. 4(b), the pronounced plateau zone of the phase angle curve after 1 rad/s shows the entanglements of the polymer network in the modified binder. After TFOT ageing, the crosslinked polymer network is destroyed, as shown by the elevated phase angle curve and this variation is slowed down to a great extent after PAV ageing.

To understand the temperature dependence of the viscoelastic behaviour in the normally operating temperature range of asphalt pavement, we conducted the frequency sweep test on each binder at five different temperatures: 25, 30, 40, 50, and 60 °C, and calculated the shift factors by the master curves of complex modulus respectively according to the time-temperature superposition principle (TTSP), the reference temperature is 25 °C. As has been previously reported by other researchers, the temperature dependence of the shift factor for bitumen may fit the Arrhenius equation [15,16]. Within the temperature range studied in this work, the temperature dependence of the shift factor for all the samples studied is described by an Arrhenius equation fairly well:

Table 5
Effect of ageing on asphalt activation energy E_a.

Asphalts	E_a (kJ/mol)		
	Unaged	TFOT aged	PAV aged
SBS 1301	166.81	171.79	180.78
SBS 1301/sulfur	164.01	166.69	171.62
SBS 4303	174.37	172.08	181.53
SBS 4303/sulfur	167.89	170.88	173.97

$$\alpha(T)_0 = \exp\left[\frac{E_a}{R(1/T - 1/T_0)}\right] \quad (1)$$

where $\alpha(T)_0$ is the shift factor relative to the reference temperature; E_a, the activation energy; $R = 8.314$ J/mol K; T, the temperature (K); and T_0 is the reference temperature. The r^2 values ranged from 0.9977 to 0.9995. While the limited number of materials studied precludes making general conclusions, the differences that occur upon ageing these samples appear to be significant. The values of E_a for each sample are shown in Table 5. As can be observed, the binder always holds a higher activation energy after ageing or with further ageing, one reason is that ageing results in more interactions between asphalt components, especially after PAV ageing. For the SBS4303-modified asphalt, the slight decline in E_a after TFOT ageing is still attributed to the susceptibility to ageing. Compare with the SBS-modified asphalts, the corresponding SBS/sulfur-modified asphalts hold a lower activation energy before and after ageing, which shows the structural instability of the vulcanized binders. Therefore the SBS/sulfur-modified asphalts are easier to be degraded under the influence of heat or dynamic shear. The activation energy of the binder with SBS4303 is higher than that of the corresponding binder with SBS1301 due to the effects of polymer molecule weight and crosslinking density.

3.3.3. Repeated creep

Recently, the validity of the Superpave binder specification parameter $G^*/\sin\delta$ was questioned, Hu et al. [17] proposed the use of dynamic creep measurement for the study of high-temperature rutting resistance of binder. This issue was also examined in the National Cooperative Highway Research Program (NCHRP) Report 459 [11]. Repeated creep testing was suggested as a better method for estimating the binder resistance to permanent strain accumulation. The viscous component of the creep stiffness was found to be a good indicator of the permanent strain accumulation and was proposed as a better specification parameter.

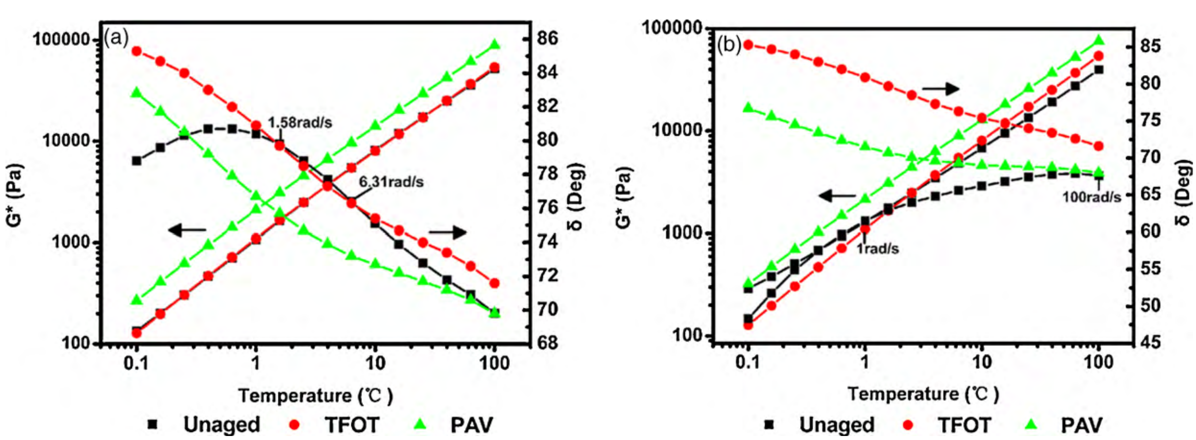

Fig. 4. Effect of ageing on the rheological behaviour of SBS4303- and storage-stable SBS4303/sulfur-modified asphalts (frequency sweep, 0.1–100 rad/s, 60 °C). (a) SBS4303-modified asphalt. (b) Storage-stable SBS4303/sulfur-modified asphalt.

Table 6
Effect of sulfur on G_v of binders before and after ageing.

Asphalts	G_v/Pa (60 °C)		
	Unaged	TFOT aged	PAV aged
SBS 1301	1098.21	1269.63	2212.61
SBS 1301/sulfur	990.1	1146.67	2027.07
SBS 4303	1386.82	1271.21	2306.65
SBS 4303/sulfur	1090.99	1175.86	2202.01

The repeated creep recovery test was conducted on all binders. The repeated creep recovery test simulates field conditions better as it applies a stress for a short duration of time and then leaves the material to recover for a longer duration of time, and repeats this many times. This in a way simulates vehicles passing on a pavement [18]. The test consisted of 100 cycles of loading with a stress of 30 Pa for 1 s, and recovery for 9 s. These testing parameters are based on the suggestions from the NCHRP study [11].

Based on the recommendations, the time and strain data from the 50th and 51st cycles of the repeated creep recovery test were fitted to the four-element Burgers model as shown in Eq. (2)

$$\gamma(t) = \frac{\tau_0}{G_0} + \frac{\tau_0}{G_1}\left(1 - \exp\left(\frac{-tG_1}{\eta_1}\right)\right) + \frac{\tau_0 t}{\eta_0} \quad (2)$$

where $\gamma(t)$ is shear strain; τ_0, constant shear strain; G_0, spring constant of Maxwell model; G_1, spring constant of Kelvin model; η_1, dashpot constant of Kelvin model; t, loading time; η_0, dashpot constant of Maxwell model.

The following equation represents the creep compliance, $J(t)$, in terms of its elastic component (J_e), its delayed-elastic component (J_{de}), and its viscous component (J_v):

$$\begin{aligned} J(t) &= \frac{1}{G_0} + \frac{1}{G_1}\left(1 - \exp\left(\frac{-tG_1}{\eta_1}\right)\right) + \frac{t}{\eta_0} \\ &= J_e + J_{de}(t) + J_v(t) \end{aligned} \quad (3)$$

The viscous component is inversely proportional to the viscosity, η_0, and directly proportional to stress and time of loading. Base on this separation of the creep response, the compliance could be used as an indicator of the contribution of binders to rutting resistance. Instead of using the compliance ($J_v(t)$), which has a unit of 1/Pa, and to be compatible with the concept of stiffness introduced during SHRP, the inverse of the compliance, G_v, could be used. G_v is defined as the viscous component of the creep stiffness [11], as shown in Eq. (4).

$$G_v(t) = \frac{1}{J_v(t)} = \frac{\eta_0}{t} \quad (4)$$

The viscous component of the creep stiffness, $G_v(t)$, was found to be a good indicator of the permanent strain accumulation and is proposed as a better specification parameter. The rutting resistance of binder is evaluated by $G_v(t)$. A higher viscous stiffness is an indicator for higher resistance to permanent deformation of the binder.

The values of G_v for each binder are shown in Table 6. Before ageing, the G_v of the SBS/sulfur-modified asphalts is lower than that of the SBS-modified asphalts accordingly, which means the rutting resistance of the SBS-modified asphalts declines with the addition of sulfur. This can be related to the susceptibility of the vulcanized PMAs to dynamic shear, the crosslinking polymer network structure in asphalt matrix is destroyed under the influence of repeated shear force. After ageing, the most aged binders hold a higher G_v and the values of G_v increase with further ageing, which shows the improved rutting resistance of the most aged binders as the result of the changed asphalt compositions. The particularity of the SBS4303-modified asphalt in G_v after TFOT ageing can be accounted for the structural characteristics of SBS4303, as confirmed by the corresponding shift in E_a and rheological curve. After ageing, the vulcanized binders also hold a lower G_v compare with the unvulcanized binders accordingly, which shows the lower rutting resistance of the SBS/sulfur-modified asphalts after ageing. The poor resistance of the SBS/sulfur-modified asphalts to permanent deformation before and after ageing is mainly due to the structural instability. Owing to the influences of polymer molecule weight and crosslinking density, the SBS4303 binders always hold a higher G_v as compared with the corresponding SBS1301 binders.

The structural instability of the storage-stable SBS/sulfur-modified asphalts is mainly related to the relative weak polysulfide bonds $-(S)_x-$ (x: 4–6) formed among SBS polymer molecules. There is a reactive π bond in the carbon–carbon double bonds C=C of the butadiene structure. In the dynamic vulcanization of SBS without accelerants, the reactive π bond is broken and converted into the carbon–sulfur bond C–S connected together by the polysulfide bond $-(S)_x-$ (x: 4–6) among polymer molecules [19], so a crosslinked polymer network is formed in asphalt matrix. However, the bond length of the polysulfide bond is longer and the bond energy is lower. Under the influence of heat or dynamic shear, these weak polysulfide bonds exposed outside of the main molecule chains of SBS block copolymers are broken, so the crosslinked polymer network is destroyed and the rutting resistance declines.

In the opinion of conventional experiments, the high-temperature rutting resistance of asphalt binder can be evaluated by the values of softening point or viscosity, because there is a good correlation between them. The binder with higher softening point or viscosity often owns a better rutting resistance. However, the drawn conclusions about rutting resistance by DMA do not conforms to the results of the conventional experiments, as shown by the changes of the softening point and viscosity values before and after TFOT ageing in Tables 3 and 4. This is because the conventional experiments cannot identify the differences in rheological behaviour, it seems to be a problem when dealing with the more rheologically complicated PMAs.

3.4. Low-temperature creep

To investigate the influence of ageing on the low-temperature creep behaviour of the modified binders before and after vulcanization, we conducted the creep test on samples at different loading time by using a bending beam rheometer (BBR). The test temperature, −18 °C is chosen, it is usually the low temperature which asphalt pavement endures in winter. The results are presented from Fig. 5(a)–(f). Obviously, the base asphalt always owns the highest creep stiffness (S) and lowest creep rate (m-value) before and after ageing, the addition of SBS can improve the low-temperature cracking resistance of the base asphalt evidently as shown by the declined creep stiffness and increased creep rate (m-value) under different conditions. For the SBS1301-modified asphalt, as shown in Fig. 5(a), the change of the creep stiffness is very slight and the creep rate declines with increasing the loading time after adding sulfur, which implies the low-temperature cracking resistance of the SBS1301-modified asphalt declines through vulcanization. The opposite result can be found for the SBS4303-modified asphalt. As can be seen in Fig. 5(d), the creep stiffness declines and the creep rate increases evidently by the addition of sulfur, indicating that the low-temperature cracking resistance is improved. These results seem to confirm the drawn conclusions on the low-temperature ductilities. On one hand, for the SBS1301-modified asphalt, the loss of the low-temperature ductility by dynamic vulcanization shows the declined low-temperature cracking resistance due to the formation of the carbon–sulfur bond and the polysulfide bond among polymer molecules, on the other, owing to the structural characteristics of SBS4303, the modest vulcanization can increase the elasticity of the polymer further as the cause of the improved ductility, therefore the low-temperature

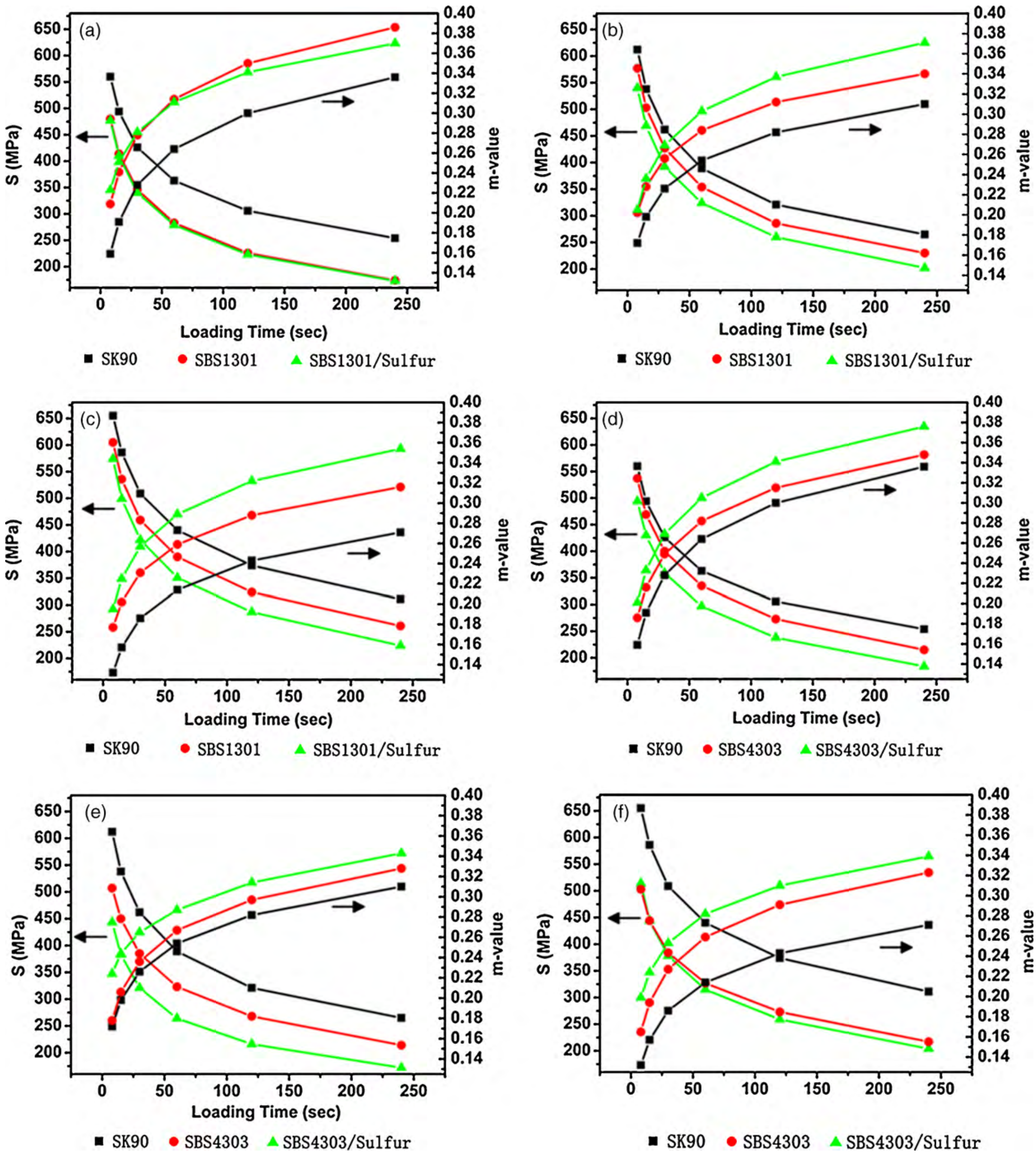

Fig. 5. Curves of creep stiffness (*S*) and creep rate (*m*-value) versus loading time for SBS- and storage-stable SBS/sulfur-modified asphalts before and after ageing at −18 °C. (a) SK90 and SBS1301-, storage-stable SBS1301/sulfur-modified asphalts. (b) SK90 and SBS1301-, storage-stable SBS1301/sulfur-modified asphalts after TFOT ageing. (c) SK90 and SBS1301-, storage-stable SBS1301/sulfur-modified asphalts after PAV ageing. (d) SK90 and SBS4303-, storage-stable SBS4303/sulfur-modified asphalts. (e) SK90 and SBS4303-, storage-stable SBS4303/sulfur-modified asphalts after TFOT ageing. (f) SK90 and SBS4303-, storage-stable SBS4303/sulfur-modified asphalts after PAV ageing.

cracking resistance is improved. However, after ageing, the drawn conclusion about the low-temperature cracking resistance of the binders by using BBR is different. For the SBS1301 binders, the use of sulfur improved the low-temperature cracking resistance of the aged binders evidently, as shown by the declined creep stiffness and the increased creep value in Fig. 5(b) and (c) after short-term or long-term ageing, respectively. For the SBS4303 binders, the same phenomenon also can be seen after ageing, as shown in Fig. 5(e) and (f). These can be attributed to the increased viscous behaviour of the vulcanized binders after ageing, the severe fusion and rearrangement of the vulcanized polymer softened the modified binder to a great extent. However, the changes on the low-temperature ductilities shown in Tables 3 and 4 do not conform to the conclusion above. Because the conventional ductility test also cannot provide the complete information description about the low-temperature creep behaviour of the modified binders and led to a misleading result. This may be another limiting factor when dealing with the more rheologically complicated PMAs.

3.5. Morphology analysis

The compatibility between polymer and asphalt is critical to the properties of PMAs [20]. The morphology of the PMAs before and after ageing was investigated using optical microscopy by char-

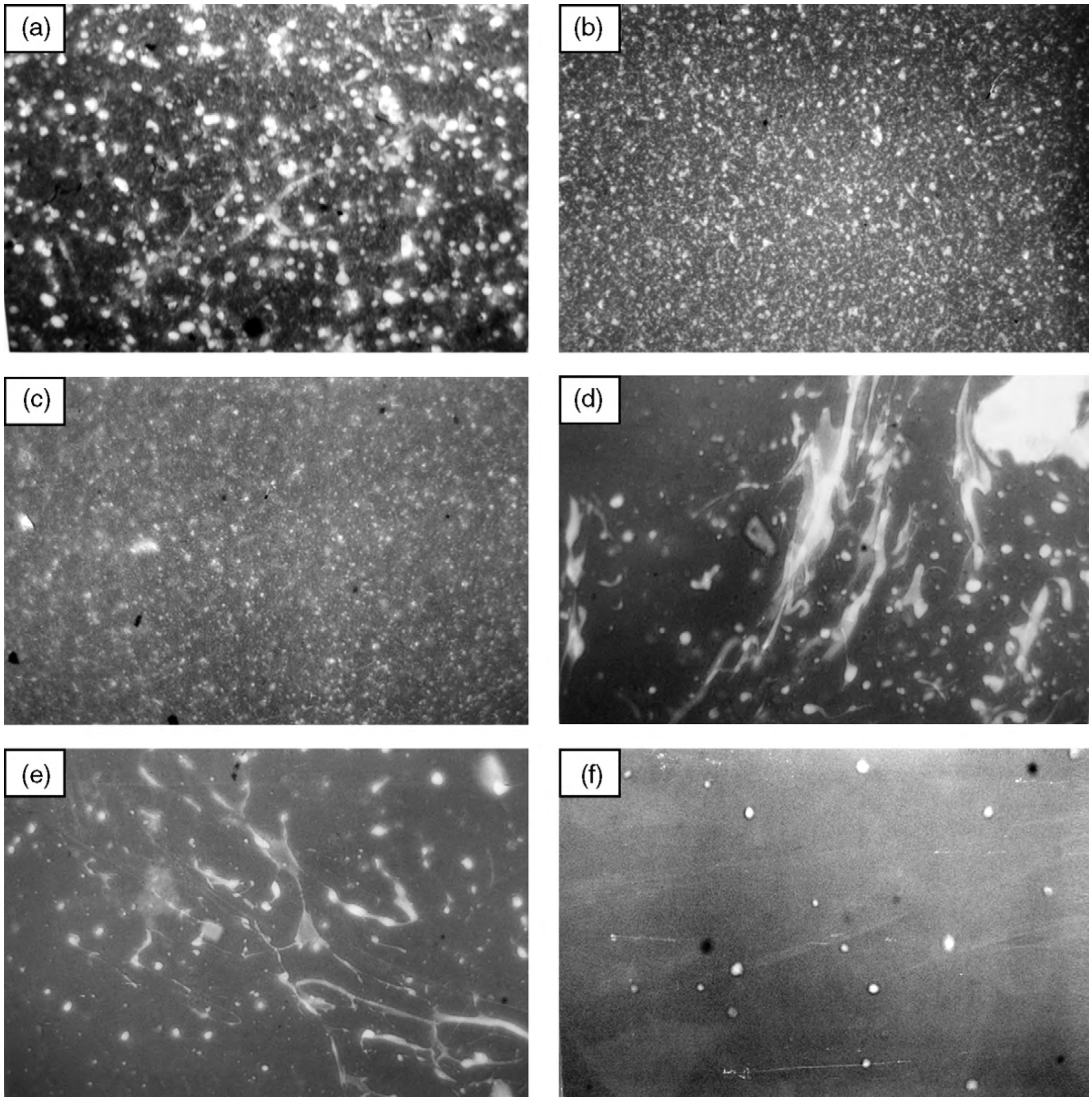

Fig. 6. Morphology development of SBS1301- and storage-stable SBS1301/sulfur-modified asphalts before and after ageing (optical microscopy) at a magnification of 400. (a) SBS1301-modified asphalt. (b) SBS1301-modified asphalt after TFOT ageing. (c) SBS1301-modified asphalt after PAV ageing. (d) Storage-stable SBS1301/sulfur-modified asphalt. (e) Storage-stable SBS1301/sulfur-modified asphalt after TFOT ageing. (f) Storage-stable SBS1301/sulfur-modified asphalt after PAV ageing.

acterizing the distribution and the fineness of polymer in asphalt matrix. For the SBS1301-modified asphalt, a continuous bitumen phase with lots of dispersed coarse SBS particles can be seen in Fig. 6(a). The influence of ageing on the morphology is shown in Fig. 6(b) and (c). Compared to Fig. 6(a), the number of polymer particles dispersed in asphalt increases and their sizes decrease after TFOT ageing, as shown in Fig. 6(b). From Fig. 6(c), it can be seen that the particle sizes decline further and the outlines become very dim after PAV ageing, which implies the degradation of SBS (chain scission) and the compatibility between polymer and asphalt is improved. For the storage-stable SBS1301/sulfur-modified asphalt, as shown in Fig. 6(d), an obvious morphological change can be observed by the addition of sulfur. Compared to the coarse polymer particles shown in Fig. 6(a), the filamentous polymer network structure with some dispersed SBS particles can be seen in Fig. 6(d). The morphological change from the granular rubber particles to the filamentous polymer network shows the compatibility between SBS and asphalt is improved by dynamic vulcanization [21,22]. The influence of oxidative ageing on the morphology is shown in Fig. 6(e) and (f). Compared to the SBS1301-modified asphalt, the SBS1301/sulfur-modified asphalt is more susceptible to ageing. As shown in Fig. 6(e), the network is destroyed evidently and the sizes of the filamentous polymers decline due to the fusion of the vulcanized SBS after TFOT ageing. As a consequence of the prolonged ageing time in PAV, the same conclusion can be confirmed further after the ageing. In Fig. 6(f), there are only few unvulcanized polymer particles dispersed in asphalt matrix and the filamentous network disappears completely.

For the SBS4303 binders, the morphological changes before and after ageing are similar to those of the SBS1301 binders. Owing to the more higher molecule weight of SBS4303, the more larger rubber particles can be seen in Fig. 7(a) as compared to the SBS1301-modified asphalt. Similar to the influence of ageing on the morphology of the SBS1301-modified asphalt, for the SBS4303-modified asphalt, the number of polymer particles increases and their sizes decline evidently after TFOT ageing and the sizes of polymer particles decline further after PAV ageing, as shown in Fig. 7(b) and (c), respectively, indicating the degradation of SBS4303. The

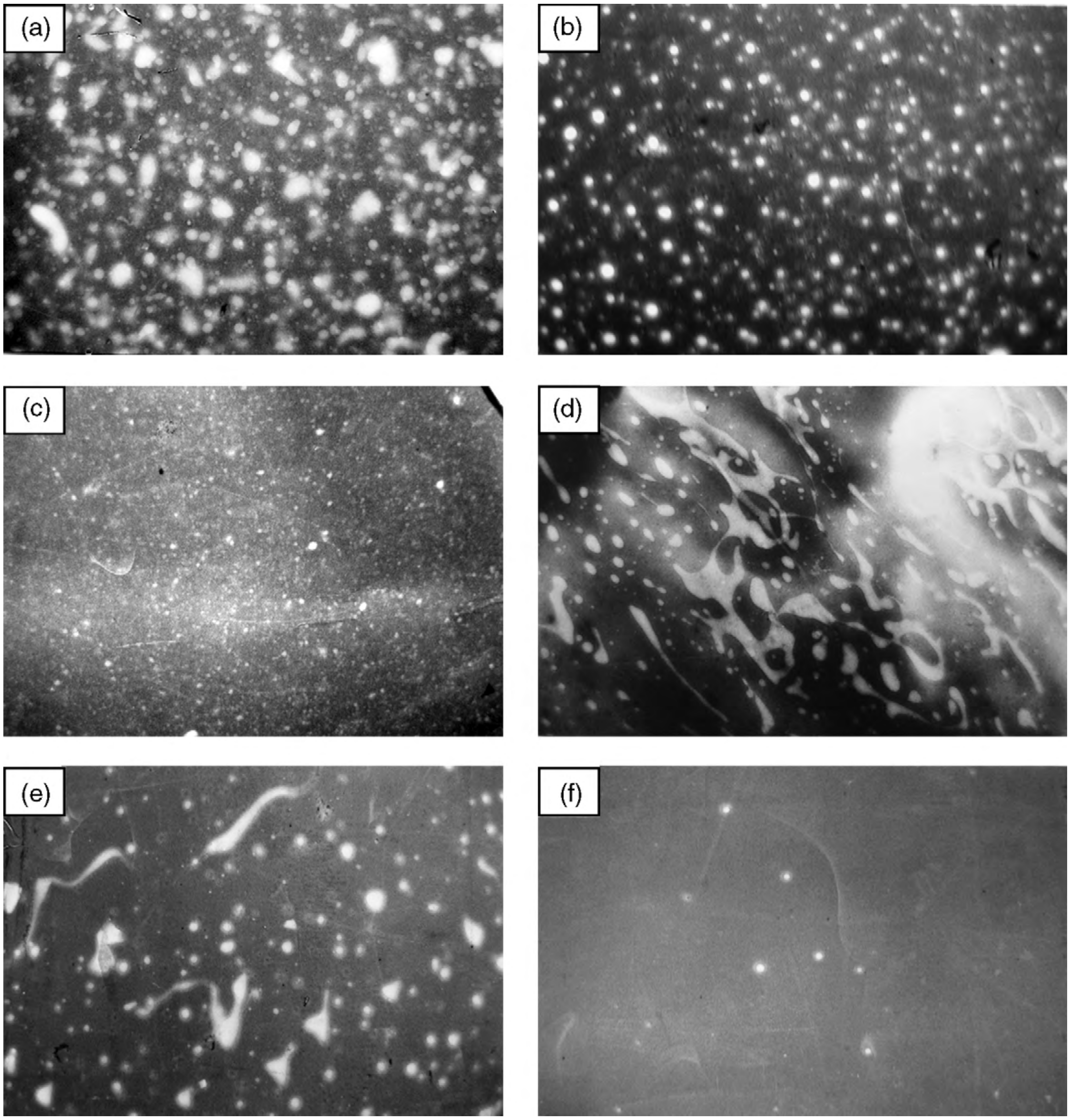

Fig. 7. Morphology development of SBS4303- and storage-stable SBS4303/sulfur-modified asphalts before and after ageing (optical microscopy) at a magnification of 400. (a) SBS4303-modified asphalt. (b) SBS4303-modified asphalt after TFOT ageing. (c) SBS4303-modified asphalt after PAV ageing. (d) Storage-stable SBS4303/sulfur-modified asphalt. (e) Storage-stable SBS4303/sulfur-modified asphalt after TFOT ageing. (f) Storage-stable SBS4303/sulfur-modified asphalt after PAV ageing.

compatibility between SBS and asphalt can be improved significantly by the addition of sulfur, as shown in Fig. 7(d), a continuous alveolate network consisting of the filamentous SBS is formed in asphalt by dynamic vulcanization. The influence of ageing on the morphology of the storage-stable SBS4303/sulfur-modified asphalt shows a similar tendency to the storage-stable SBS1301/sulfur-modified asphalt. As shown in Fig. 7(e), the network disappears nearly due to the obvious fusion of the vulcanized SBS after TFOT ageing and long-term ageing can deepen the influence further, as illustrated in Fig. 7(f), there are few polymer particles dispersed in asphalt matrix after PAV ageing. The phase change from the heterogeneous structure at the origin to the homogeneous one after ageing shows the major effect of TFOT and PAV ageing is to homogenise the copolymer distribution through the bituminous matrix [23]. Compared to the SBS-modified asphalts, the SBS/sulfur-modified asphalts are easier to be decomposed by ageing as the cause of the much better homogeneous system formed.

4. Conclusion

The dynamic rheological analysis confirmed the results of the conventional tests (softening point and viscosity) only to a little extent and illustrated the two major influences of oxidative ageing (short-term and long-term) on the rheological behaviour of the modified asphalts. On one hand, ageing prompted the degradation of the polymer dispersed in asphalt matrix and led to the increase in the viscous behaviour of the modified binders, especially for the storage-stable SBS/sulfur-modified asphalts, on the other, the changed asphalt compositions greatly contributed to the increase in the elastic behaviour of the modified binders after ageing. Due to the structural instability of the storage-stable SBS/sulfur-modified asphalts, the binders are more susceptible to oxidative ageing and dynamic shear, the crosslinked polymer network in asphalt degraded obviously under the influences of heat and dynamic shear. Besides the rheological behaviour of the modified binders before and after ageing depended strongly on the structural characteristics of SBS. Owing to the increase in the viscous behaviour of the aged binders, the low-temperature cracking resistance of the storage-stable SBS/sulfur-modified asphalts was improved compare with the SBS-modified asphalts after ageing, as demonstrated by the BBR tests.

The conventional softening point, viscosity and low-temperature ductility tests were unable to identify the differences of the rheological behaviour and led to some misleading results. This may be a limiting factor when dealing with the more rheologically complicated PMAs.

The major effect of ageing on the morphology of the modified binders is to homogenise the dispersion of SBS in asphalt matrix. The compatibility between polymer and asphalt can be improved evidently with further ageing due to the severe degradation of SBS (chain scission). For the storage-stable SBS/sulfur-modified asphalts, the phase change from heterogeneous structure to homogeneous one after ageing is more obvious due to the low thermal stability.

In considering the susceptibility of the storage-stable SBS/sulfur-modified asphalts to ageing and dynamic shear, sulfur as an additional modifier for the SBS-modified asphalts will lead to some problems in practice, therefore it is unreasonable for us to use sulfur as an sole additional modifier in improving the properties of the SBS-modified asphalts.

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