

## The research for high-elastic modified asphalt

Feng Zhang, Changbin Hu

Department of Civil Engineering, Fuzhou University, Fuzhou 350108, People's Republic of China

Correspondence to: F. Zhang (E-mail: wucifanying@163.com)

**ABSTRACT:** High-elastic modified (HEM) asphalt was prepared by the addition of styrene-butadiene-styrene (SBS), plasticizer, and crosslinker to base asphalt. The effect and proportion of each modifier in asphalt were studied using physical and rheological tests. It was found that SBS determined the high-temperature performance of HEM asphalt mainly. Plasticizer (dioctyl phthalate) is very helpful in improving the low-temperature flexibility and elastic recovery. Crosslinker (sulfur) is necessary in maintaining high-temperature stability. In this study, Fourier transform infrared, hydrogen nuclear magnetic resonance analysis, and microscopy observation were used to investigate the structural characteristics of modified asphalts further before and after ageing. The research showed the structural characteristics of modified asphalt were influenced evidently by ageing. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 2015, 132, 42132.

**KEYWORDS:** crosslinker; high-elastic modified asphalt; plasticizer; SBS

Received 2 November 2014; accepted 20 February 2015

**DOI:** 10.1002/app.42132

### INTRODUCTION

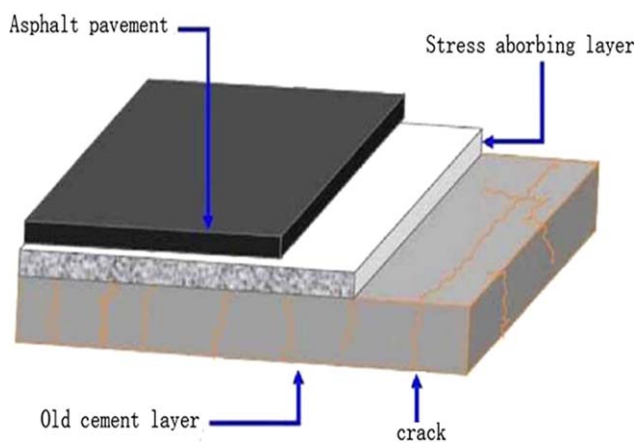
HEM asphalt is a kind of special SBS compound modified asphalt which has excellent elastic recovery rate and better high- and low-temperature properties compared to ordinary SBS modified (SM) asphalt. The asphalt is usually used in the reconstruction of old cement road face nowadays. In the reconstruction of old cement road, the asphalt pavement overlayed on old road is easy to crack, which will decrease the load bearing of old road greatly and lead to a short service period. This is because there is too much stress concentration on the bottom of asphalt pavement, caused by the crack of old cement pavement.<sup>1</sup> Therefore, it is very necessary to overlay a new pavement called stress absorbing pavement between old cement road and asphalt pavement, as shown in Figure 1. Stress absorbing layer can disperse the concentrated stress at the bottom of asphalt pavement effectively and prevent the asphalt pavement from cracking in a long period of time. Stress absorbing layer can be made of different materials such as plastic geogrid, geotextile, and asphalt mixture in many engineering projects;<sup>2,3</sup> however, it has been found that asphalt mixture is more excellent in deformation recovery and crack resistance of fatigue durability than others.<sup>4</sup> This kind of asphalt mixture is made of very fine aggregate and HEM asphalt.

Stress absorbing technology has been widely applied in the United States since 1994. Nowadays, the strata stress absorbing system suggested by Koch company is a patented technology and recognized as the most proven in this area.<sup>5</sup> However, the HEM asphalt and packaged technique supplied by Koch com-

pany is very expensive and can not be afforded by many countries and areas, which restricts the application to a great extent.<sup>5</sup> In China, the reconstruction of old cement road is a very important project and need to be finished in the development of transportation industry. There are lots of old cement roads that need to be overlayed by asphalt pavement to meet the increasing traffic volume. However, the lack of HEM asphalt in many construction units made the project to be finished more difficultly.<sup>6</sup> Although some domestic asphalt factories also can produce the product, the prescription is secret and the price is also expensive. Therefore, it is very necessary for many construction units or researchers to know the key technique about HEM asphalt, so as to produce it in practice.

In this study, we pointed out the characteristics of HEM asphalt in proportion and performances and showed an efficient way in preparing HEM asphalt by the addition of SBS, plasticizer, and crosslinker and studied the effect of each modifier. The provided proportion and preparation way for HEM asphalt are simple. Dioctyl phthalate as a good plasticizer is used firstly in asphalt modification, which is not reported in other publications. The performances of HEM asphalt are wonderful and can compete with the similar products. To understand the modification mechanism further, more effective analysis ways including HNMR were used to investigate the structural characteristics of modified asphalts:

1. Rheological testing was used to investigate the effect of modifier and ageing on the rheological behavior and structural characteristics of asphalt by comparing master curves.



**Figure 1.** The position of stress absorbing layer. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

- Morphology observation was used to study the morphological characteristics of binder and the compatibility between polymer and asphalt under different ageing or modification conditions.
- Fourier transform infrared (FTIR) and HNMR tests were used to investigate the effect of modifier and ageing on the distribution of the major functional groups of modified asphalt.

The obtained results using different ways are complementary, which describes the structural characteristics of each binder from different aspects.

## MATERIALS AND MEASUREMENTS

### Materials

Fuzhou-70 paving asphalt was obtained from the Fuzhou Petroleum Asphalt Factory, China. The physical properties were as follows: penetration, 61 dmm (0.1 mm, 25°C, ASTM D 5); softening point, 49.8°C (ASTM D 36); viscosity, 0.77 Pa s (135°C, ASTM D 4402). SBS1301 was produced by the Yueyang Petrochemical, China. SBS1301 is linear polymer, containing 30 wt % styrene, the average molecule weight is 110,000 g/mol. Plasticizer (dioctyl phthalate) was produced by Puyang Petrochemical, China. Crosslinker (sulfur) was produced by Wenhe Chemical, China. Both plasticizer and crosslinker are chemically pure reagents.

### Preparation of Samples

The modified asphalts were prepared using a high shear mixer (made by Qishuang Machine, China). First, asphalt (300 g) was heated until it became fluid in an iron container, then upon reaching about 180°C, the SBS and plasticizer (based on 100 parts asphalt) were added. The shearing time was 20 min and then crosslinker (based on 100 parts asphalt) was added, heated until reaching about 180°C, and sheared 1 h at the shearing speed of 5000 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.

### The Ageing of Modified Asphalt

The ageing of asphalt was performed using the thin film oven test (TFOT, ASTM D 2872) which simulates the changes in the

properties of asphalt during the hot mixing and the lay down process.

### Physical Properties Test

The physical properties of asphalts, including softening point, penetration, toughness and tenacity, ductility, elastic recovery were tested in accordance with ASTM D36, D5, D5801-95, D113, D 6084-97, respectively.

### 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 a polymer modified asphalt (PMA) 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 PMA was considered unstable.

### Rheological Characterization

A strain-controlled dynamic shear rheometer (DSR, Annton Paar, MCR 102, Germany) with parallel plate geometry (25 mm or 8 mm in diameter) was used to determine the rheological behavior of asphalts.

High temperature sweeps (from 30 to 140°C, 25 mm parallel plate, 1 mm gap) with 2°C increments were applied at a fixed frequency of 10 rad/s and variable strain. Frequency sweeps were applied over the range of 0.1–100 rad/s at a fixed strain amplitude at 20, 30, 40, 50, 60°C, respectively.

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 50 times. The repeated creep tests were made at a constant stress level of 30 Pa.<sup>7</sup> Parallel plates, gap 1.0 mm for  $\phi$  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 actual strain was measured to calculate various viscoelastic parameters such as complex modulus ( $G^*$ ) and phase angle ( $\delta$ ). All tests were performed within the linear viscoelastic range of the sample.

### Morphology Observation

The sample morphology was observed using an optical microscope made by Nikon, 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.

### Fourier Transform Infrared Spectroscopy

A FTIR spectrometer, infinity 60 AR (Mattson, resolution 0.125 cm<sup>-1</sup>), was used to determine the functional characteristics of modified binders before and after ageing in wavenumbers

**Table I.** Physical Properties Suggested by Koch Company

Softening point (°C)	>65
Penetration (25°C/0.1 mm)	>60
Viscosity (135°C, Pa s)	<4
Ductility (5°C, cm)	>30
Softening point difference (°C)	<6
After TFOT ageing	
Elastic recovery (25°C/%, 1 h)	>70
Ductility (5°C, cm)	>20

ranging from 4000 cm<sup>-1</sup> to 400 cm<sup>-1</sup>. Binders were dissolved in chloroform with 10 wt % concentration, then dropped onto KBr table and dried for the FTIR analysis.

### HNMR Spectrophotometry

A Bruker NMR Spectrometer (Avance 500 MHz) was used. Asphalt was dissolved by deuteriochloroform (CDCl<sub>3</sub>) with 20 wt % concentration. Tetramethylsilane (TMS) was used as internal standard.

## RESULTS AND DISCUSSION

### The Preparation of HEM Asphalt

The physical properties of HEM asphalt are vital in determining the proportion of each modifier in asphalt. Before the preparation of HEM asphalt, we need to know the physical properties of a similar product and corresponding standard. The standard of physical properties suggested by Koch company is listed in Table I,<sup>6</sup> and the detailed physical properties of base asphalt and

**Table II.** Physical Properties of Base Asphalt and HEM Asphalt

	AH-70	HEM
Softening point (°C)	49.8	88.5
Penetration (25°C/0.1 mm)	60	72.9
Viscosity (135°C, Pa s)	0.77	3.69
Ductility (5°C, cm)	0	56.4
Flexibility (5°C, cm/N)	0	0.87
Toughness (25°C/N m)	5.1	24.3
Tenacity (25°C/N m)	0	18.3
Elastic recovery (25°C/%, 3 min)	10	90
(25°C/%, 1 h)	18.5	100
Softening point difference (°C)	-	0.2
After TFOT ageing		
Softening point (°C)	54.3	80.2
Penetration (25°C/0.1 mm)	34	59
Ductility (5°C, cm)	0	47.2
Flexibility (5°C, cm/N)	0	0.71
Toughness (25°C/N m)	8.9	24.3
Tenacity (25°C/N m)	0	18.7
Elastic recovery (25°C/%, 5 min)	7	80
(25°C/%, 1 h)	28	100

AH-70: Base asphalt.

HEM: The HEM asphalt supplied by Luxiang company.

a HEM asphalt product are listed in Table II. The HEM asphalt product was supplied by Luxiang company which is a famous asphalt enterprise in China.

The standard of HEM asphalt suggested by Koch company only shows some basic requirements for physical properties. It can be seen in Table I that the requirements focus on high- and low-temperature properties and elastic recovery, which shows HEM asphalt should be more predominant in these physical properties. Actually, most HEM asphalts made in China can meet the standard.

The physical properties of base asphalt and HEM asphalt are listed in Table II. Compared with base asphalt, HEM asphalt owns wonderful high- and low-temperature properties before and after ageing, as shown by the values of softening point, ductility, and flexibility. Besides, HEM asphalt has a better holding stress and deformation resistance, as shown by the toughness and tenacity. Usually toughness and tenacity are the major properties to be considered in the application of HEM asphalt. Toughness indicates the holding stress to road stone matrix and the tenacity shows the deformation resistance, and the tenacity is a major element of the toughness.<sup>8</sup> High elastic recovery is also a major characteristic of HEM asphalt, it can be seen that the elastic recovery rate at 3 min before ageing or 5 min after ageing is very high and the elastic recovery at 1 h reach at 100%, which means HEM asphalt has good deformation recovery after traffic loading released. The result of storage stability test shows that HEM asphalt has good storage stability. The improved physical properties of HEM asphalt compared to base asphalt indicates the improvement for base asphalt should depends on the addition of SBS mainly, SBS is still the major modifier by our evaluation.

In this study, we selected the modifiers including SBS, plasticizer, and crosslinker to prepare HEM asphalt. To investigate the effect of each modifier, we prepared SM asphalt, SBS/crosslinker modified (SCM) asphalt, SBS/plasticizer modified (SPM) asphalt, and SBS/plasticizer/crosslinker modified (SPCM) asphalt, the proportion for each binder and the corresponding physical properties are listed in Table III. It can be seen that the physical properties of SM asphalt were improved greatly compared to base asphalt. Because of the structural characteristics of hard polystyrene segments and soft butadiene domains of SBS, SM asphalt has better high- and low-temperature properties, as shown by the increased softening point and low-temperature ductility and flexibility before and after ageing. Because a continuous polymer network was formed in asphalt, so SM asphalt became elastic and the deformation resistance was also improved greatly, as shown by the value of elastic recovery, toughness, and tenacity. However, SM asphalt was very unstable, the softening point difference of storage stability test is 49.2°C. Because of the difference of molecule weight between asphalt and SBS, SBS was easily separated from asphalt and float on the top of the asphalt when stored at high temperature. Therefore, it is necessary to modify further by the addition of crosslinker, and the physical properties of SCM asphalt are shown in Table III. The softening point difference of SCM

**Table III.** Effect of Crosslinker and Plasticizer on Physical Properties of SM Asphalt

	SM	SCM	SPM	SPCM
Softening point (°C)	91.1	93.3	81.7	84.3
Penetration (25°C/0.1 mm)	39.1	52.7	75.5	93.5
Viscosity (135°C, Pa s)	7.2	7.7	3.4	2.4
Ductility (5°C, cm)	40.4	27	91.6	70.2
Flexibility (5°C, cm/N)	0.45	0.34	1.9	2.19
Toughness (25°C/N m)	23.3	20.7	13.9	16.1
Tenacity (25°C/N m)	15.7	13.1	10.9	13.6
Elastic recovery (25°C/%, 3 min)	88	80	100	97
(25°C/%, 1 h)	100	100	100	100
Softening point difference (°C)	49.2	1.1	48.7	0.3
After TFOT ageing				
Softening point (°C)	60.8	85.9	51.9	77.5
Penetration (25°C/0.1 mm)	37.4	39.9	64.1	69
Ductility (5°C, cm)	17.5	23.7	61.7	40.7
Flexibility (5°C, cm/N)	0.13	0.25	1.2	1.09
Toughness (25°C/N m)	18.9	21.1	18.7	18.5
Tenacity (25°C/N m)	10.5	12.4	15	14.4
Elastic recovery (25°C/%, 5 min)	68.5	77.5	53.5	81
(25°C/%, 1 h)	89.5	94.5	77	100

SM: SBS1301-modified asphalt (6 wt % SBS1301).

SCM: SBS1301/crosslinker-modified asphalt (6 wt % SBS1301, 0.2 wt % crosslinker).

SPM: SBS1301/plasticizer-modified asphalt (6 wt % SBS1301, 4 wt % plasticizer).

SPCM: SBS1301/plasticizer/crosslinker-modified asphalt (6 wt % SBS1301, 4 wt % plasticizer, 0.2 wt % crosslinker).

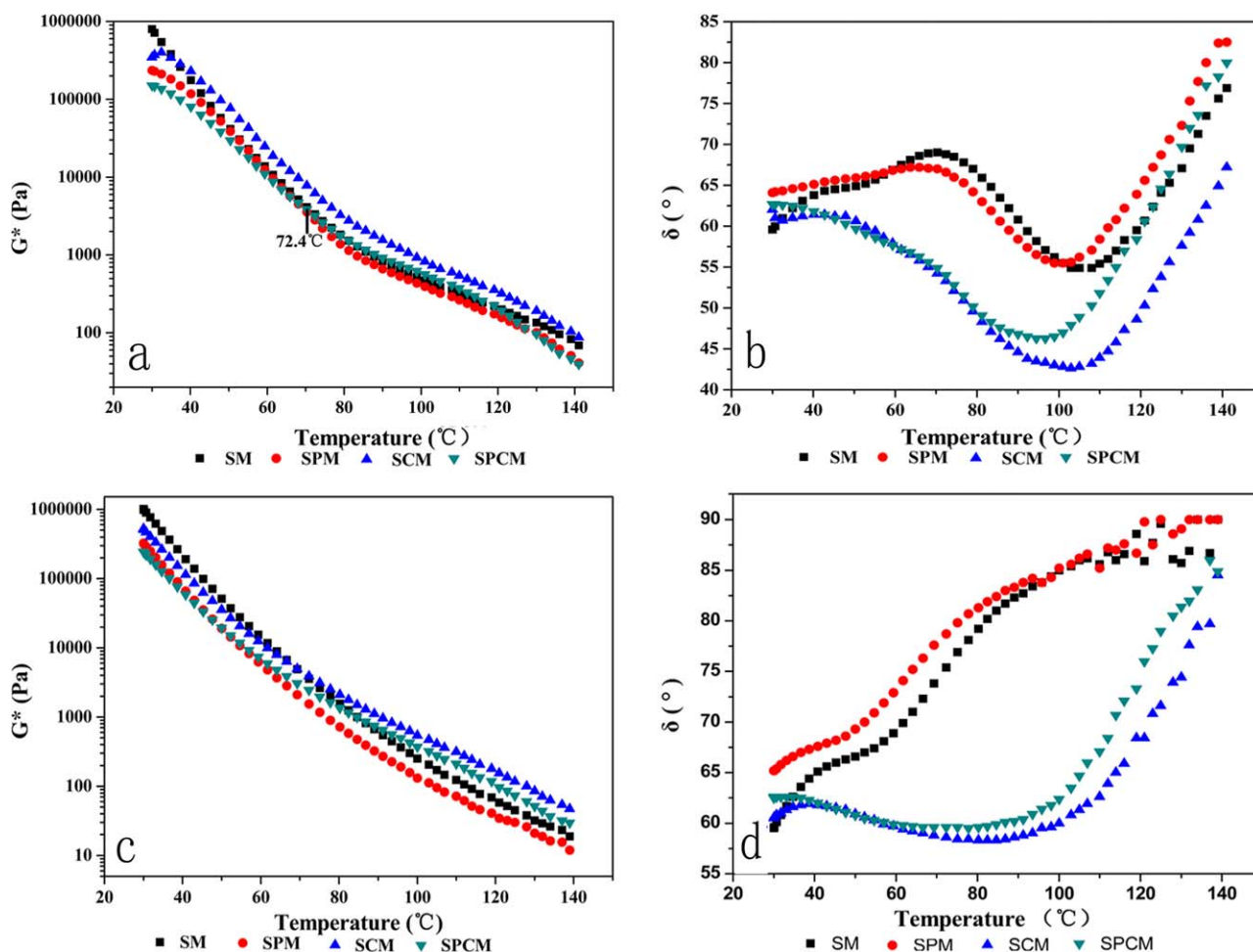
asphalt is only 1.1°C after storage stability test, showing a good compatibility polymer and asphalt, this can be attributed to the reaction taken place between SBS and crosslinker. Meanwhile, the particle size of SBS decreased by crosslinking reaction and SCM asphalt became soft, so the penetration increased, and the elastic recovery in 3 min, toughness and tenacity decreased compared to SM asphalt. Besides the softening point and viscosity of SCM asphalt increased a little, due to the formation of a crosslinked polymer network in asphalt. However, the ductility and flexibility decreased, because there were more restrictions among polymer molecules by the formation of new chemical bond. After ageing, compared with SM binder, the higher softening point of SCM binder shows the crosslinked polymer did not degrade completely after ageing, moreover the increased hard asphalt compositions after ageing made the asphalt become tough, leading to the increased toughness and tenacity, elastic recovery.

The physical properties of SPM asphalt are listed in Table III. It can be seen that the addition of plasticizer improved the ductility, flexibility, elastic recovery rate greatly compared to SM and SCM asphalt. Because SBS was swelled fully by the addition of plasticizer, so SBS particles became more elastic. At the same time, the addition of plasticizer decreased the density of asphalt and made asphalt more soft, so the high-temperature property, deformation resistance decreased, as shown by the decreased softening point, toughness, and tenacity. After ageing, the softening point and elastic recovery are lower than that of SM,

SCM binders. Although the hard asphalt compositions such as asphaltene or resin increased after ageing, the loss of polymer still played a predominant role on the changed physical properties, moreover the loss of polymer after ageing made the asphalt softer, as shown by the poor softening point and elastic recovery. However, the tenacity of the binder is higher than that of the others, this is because the SBS swelled fully became more elastic and the asphalt thread can be stretched longer in the toughness testing, which leads to the increased tenacity. However, the storage stability of SPM asphalt is still poor, the softening point difference between the top and bottom sections is 48.7°C. It can be seen that both storage stability and elastic recovery rate of SPM and SCM asphalt still can not compete with that of HEM asphalt.

The physical properties of SPCM asphalt are shown in Table III. Compared with SPM and SCM asphalts, SPCM asphalt owns better storage stability and elasticity recovery. The major physical properties including softening point, ductility and flexibility, toughness and tenacity before and after ageing are reasonable. Considering the improvement for the physical properties of HEM asphalt roundly, the reasonable penetration of HEM asphalt should be the range: 80–90 dmm, as studied by other researchers.<sup>6</sup> The softening point difference of all samples after storage stability test is not higher 2.5°C, showing a good stability. Although there was an inevitable loss of physical properties for SPCM asphalt after ageing, the aged binders still owned good high- and low-temperature properties and elasticity. For





**Figure 2.** (a) The isochronal plots of  $G^*$  versus temperature for SBS compound modified asphalts (10 rad/s, 30–140°C). (b) The isochronal plots of  $\delta$  versus temperature for SBS compound modified asphalts (10 rad/s, 30–140°C). (c) The isochronal plots of  $G^*$  versus temperature for SBS compound modified asphalts after TFOT ageing (10 rad/s, 30–140°C). (d) The isochronal plots of  $\delta$  versus temperature for SBS compound modified asphalts after TFOT ageing (10 rad/s, 30–140°C). SM: SBS1301-modified asphalt (6 wt % SBS1301). SCM: SBS1301/crosslinker-modified asphalt (6 wt % SBS1301, 0.2 wt % crosslinker). SPM: SBS1301/plasticizer-modified asphalt (6 wt % SBS1301, 4 wt % plasticizer). SPCM: SBS1301/plasticizer/crosslinker-modified asphalt (6 wt % SBS1301, 4 wt % plasticizer, 0.2 wt % crosslinker). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

SPCM asphalt, the reasonable penetration and the better ductility, flexibility, and tenacity after ageing show this proportion (SBS 6 wt %; plasticizer 4 wt %; crosslinker 0.2 wt %) is optimal and reasonable for the preparation of HEM asphalt.

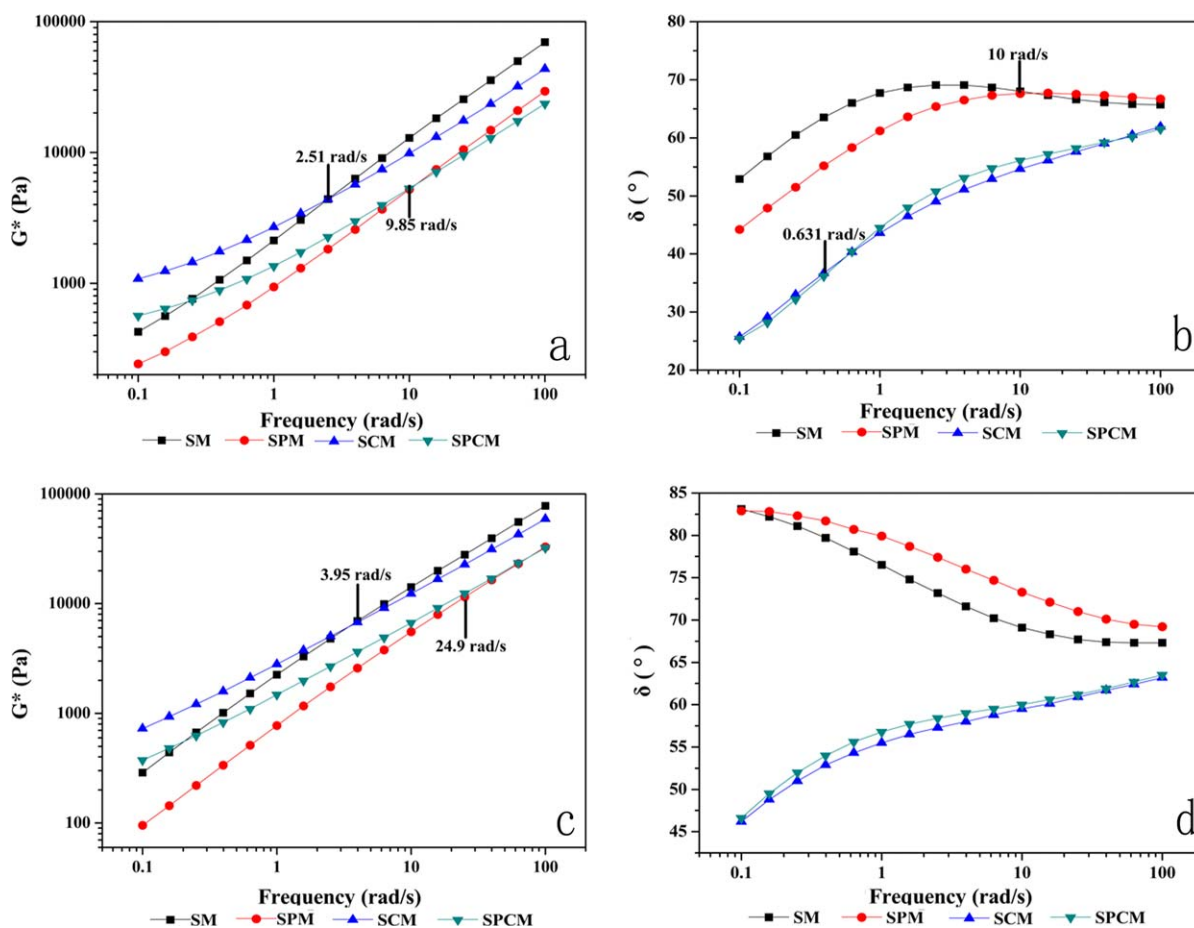
It is necessary to highlight the advantages of HEM asphalt further compared to other research. In other research for SBS-modified asphalt, the emphasis is the improvement for stability; however, the research for other major physical properties such as elastic recovery and toughness and tenacity were not made at all, especially for the use of plasticizer,<sup>7,9–12</sup> so it would be impossible for the reported binders to be used in stress absorbing layer.

Besides HEM asphalt owns wonderful physical properties before and after ageing compared to other modified binders made in my previous research.<sup>7,13–15</sup> There still is a lack for some major physical properties including toughness and tenacity, elastic recovery in previous work, these properties play a vital role in the apply of stress absorbing layer,<sup>7,13–15</sup> moreover the use for

plasticizer was also not made previously. The toughness and tenacity of HEM asphalt are more than 10 N m before and after ageing, far beyond that of the styrene–butadiene rubber (SBR) binder reported previously.<sup>14</sup> Higher softening point (80°C before ageing and 70°C after ageing) of HEM asphalt compared to the reported SBS binders<sup>7,15</sup> shows the better high-temperature performance and ageing resistance. Besides the wonderful elastic recovery rate (97% before ageing and 80% after ageing) of HEM asphalt shows the excellent deformation recovery, which can not be afforded by all binders in previous work.<sup>7,13–15</sup>

### Rheological Properties

**Temperature Sweep.** To investigate the effect of additional modifier on the rheological properties of SM asphalt, SBS compound modified asphalts with additional modifiers for the optimal proportion were tested using different rheological testing modes. The tested samples are SM, SCM, SPM, and SPCM asphalts. The rheological behaviors of the PMAs in the high-



**Figure 3.** (a) The isochronal plots of  $G^*$  versus frequency for SBS compound modified asphalts before ageing (0.1–100 rad/s, 60°C). (b) The isochronal plots of  $\delta$  versus frequency for SBS compound modified asphalts before ageing (0.1–100 rad/s, 60°C). (c) The isochronal plots of  $G^*$  versus frequency for SBS compound modified asphalts after TFOT ageing (0.1–100 rad/s, 60°C). (d) The isochronal plots of  $\delta$  versus frequency for SBS compound modified asphalts after TFOT ageing (0.1–100 rad/s, 60°C). SM: SBS1301-modified asphalt (6 wt % SBS1301). SCM: SBS1301/crosslinker-modified asphalt (6 wt % SBS1301, 0.2 wt % crosslinker). SPM: SBS1301/plasticizer-modified asphalt (6 wt % SBS1301, 4 wt % plasticizer). SPCM: SBS1301/plasticizer/crosslinker-modified asphalt (6 wt % SBS1301, 4 wt % plasticizer, 0.2 wt % crosslinker). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

temperature range are shown in Figure 2(a,b). In Figure 2(a), it can be seen that with increasing the temperature, the  $G^*$  of SPM asphalt becomes more lower after 72.4°C. Because of the

further swelling of plasticizer, the SBS particles became softer and can be sheared easily in preparation, therefore the particle size of SBS is smaller than that of SM asphalt, which results in

**Table IV.**  $E_a$  of SBS Compound Asphalts Before and After Ageing

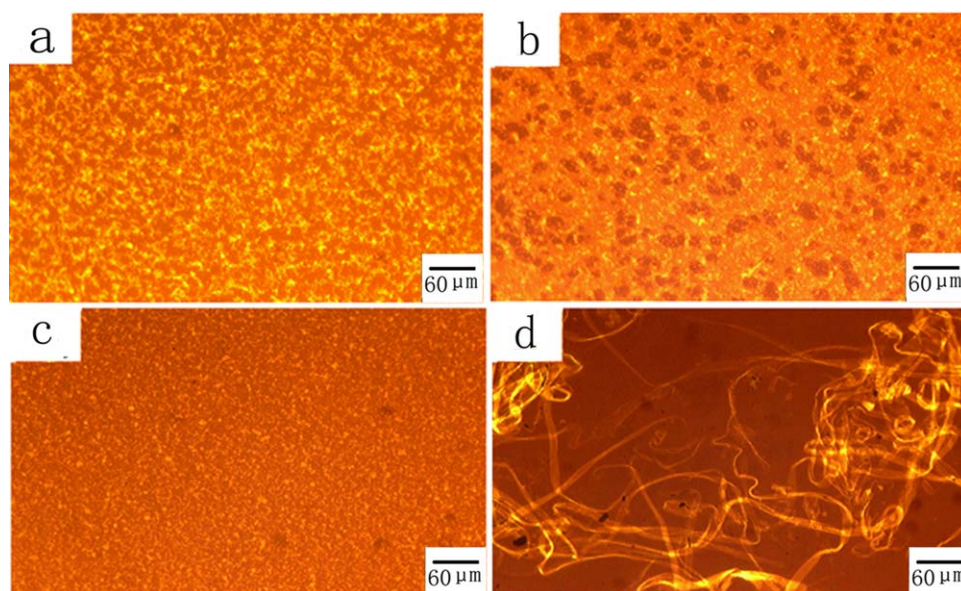
	$E_a$ (KJ/mol)	
	Unaged	Aged
SM	177.6	178.1
SPM	156.5	162.2
SCM	170.9	172.8
SPCM	154.8	161.1

SM: SBS1301-modified asphalt (6 wt % SBS1301).  
 SCM: SBS1301/crosslinker-modified asphalt (6 wt % SBS1301, 0.2 wt % crosslinker).  
 SPM: SBS1301/plasticizer-modified asphalt (6 wt % SBS1301, 4 wt % plasticizer).  
 SPCM: SBS1301/plasticizer/crosslinker-modified asphalt (6 wt % SBS1301, 4 wt % plasticizer, 0.2 wt % crosslinker).

**Table V.**  $G_v$  of SBS Compound Modified Asphalt Before and After Ageing

	$G_v(t)$ (Pa)	
	Unaged	Aged
SM	6593.4	8928.9
SPM	2103.8	3610
SCM	5084.7	6157.1
SPCM	2253.9	3604

SM: SBS1301-modified asphalt (6 wt % SBS1301).  
 SCM: SBS1301/crosslinker-modified asphalt (6 wt % SBS1301, 0.2 wt % crosslinker).  
 SPM: SBS1301/plasticizer-modified asphalt (6 wt % SBS1301, 4 wt % plasticizer).  
 SPCM: SBS1301/plasticizer/crosslinker-modified asphalt (6 wt % SBS1301, 4 wt % plasticizer, 0.2 wt % crosslinker).



**Figure 4.** The morphology of SBS compound asphalts (optical microscopy) at a magnification of 400. (a) SM asphalt. (b) SCM asphalt. (c) SPM asphalt. (d) SPCM asphalt. SM: SBS1301-modified asphalt (6 wt % SBS1301). SCM: SBS1301/crosslinker-modified asphalt (6 wt % SBS1301, 0.2 wt % crosslinker). SPM: SBS1301/plasticizer-modified asphalt (6 wt % SBS1301, 4 wt % plasticizer). SPCM: SBS1301/plasticizer/crosslinker-modified asphalt (6 wt % SBS1301, 4 wt % plasticizer, 0.2 wt % crosslinker). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

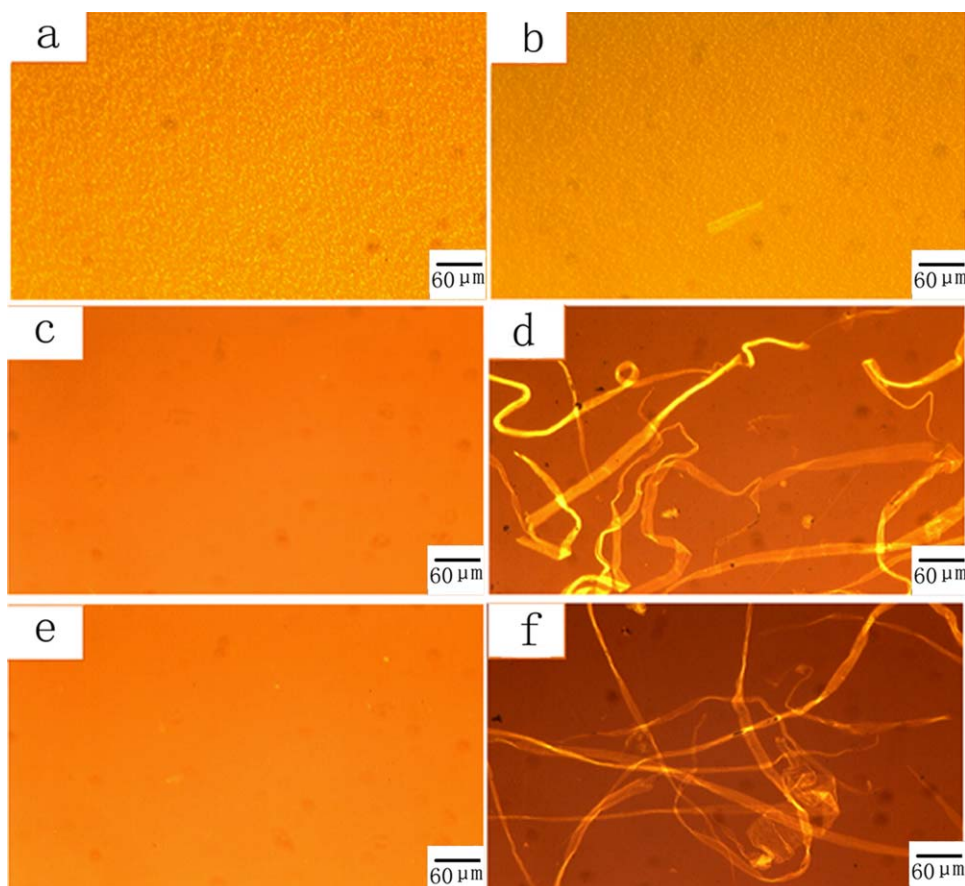
the lower  $G^*$  at high temperature partly. By vulcanization reaction, the SBS molecules were crosslinked together by polysulfide bonds, so the SBS particles changed form irregular shape to filamentous one and these filamentous polymers were entangled further, leading to the formation of a dense polymer network in asphalt. Therefore, the elastic behavior of the vulcanized binder was improved to some extent, which is demonstrated by the higher  $G^*$  of SPCM asphalt after 72.4°C compared to SPM asphalt. For SCM asphalt, a more elastic polymer network can be formed without the swelling of plasticizer, leading to a higher  $G^*$  than that of others. In Figure 2(b), the phase angle curves show a minimum value around 100°C with increasing the temperature, which indicates there is a continuous polymer network in asphalt. The value differs for samples, depending on the polymer characteristics and asphalt compositions. The lower value in phase curve indicates more interactions among polymer molecules.<sup>16</sup> Because of the further swelling of plasticizer, the SBS particles dispersed in asphalt became loose and the interactions among polymer molecules declined, as demonstrated by the minimum value of phase angle compared to SM asphalt. However, as for the crosslinked PMAs, more interactions exist among polymer molecules, because most molecules are connected together by polysulfide bonds, therefore there will be more an evident minimum value on the phase curves. The deeper turning on the phase curves of SCM and SPCM asphalts with increasing the temperature indicates the structural characteristics. As the result of swelling, SPCM asphalt holds a smaller turning and higher value comparatively.

The rheological behaviors after TFOT ageing are shown in Figure 2(c,d). In Figure 2(c), with increasing the temperature, the SCM holds highest  $G^*$  and the SPCM is second, which means the crosslinked polymer network still exists in the asphalts partly. Because of the dilution of plasticizer, the aged SPM

binder still owns lowest  $G^*$ . The phase angle curves for all binders are shown in Figure 2(d). It can be seen the characteristic protruded section and minimum value of curves before ageing disappear completely, showing that the crosslinked polymer network was destroyed seriously. However, the phase curves of SCM and SPCM binders still are much lower than those of the others, which means that the crosslinked polymer network did not degrade completely after ageing. The elevated phase angle curves of SPM and SM binders show the degradation of polymer after ageing and there is a more viscous behavior for SPM binder.

**Frequency Sweep.** To understand the dependence of the rheological behavior 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 as it is usually the high temperature which asphalt pavement endures in summer. In Figure 3(a), it can be seen that the crosslinked PMAs are more susceptible to dynamic shearing. Before 2.51 rad/s, both SCM and SPCM asphalts own higher  $G^*$  compared to SM and SPM asphalts, respectively. There is a transition frequency at 2.51 rad/s for SCM and SM asphalts. Before 2.51 rad/s, SCM asphalt owns higher  $G^*$  due to the elastic polymer network formed by crosslinking reaction; however, the  $G^*$  of SCM asphalt decreases quickly with increasing frequency, when the frequency is over 2.51 rad/s, the  $G^*$  of SM asphalt is higher than that of SCM asphalt, which means the crosslinked polymer network is very susceptible to dynamic shearing, the improved  $G^*$  diminishes quickly with increasing the frequency. The same conclusion also can be drawn for the SPM and SPCM asphalts. The improved  $G^*$  of SPCM asphalt compared to SPM asphalt decreases quickly with increasing the frequency, when the frequency is over 9.85 rad/s, the  $G^*$  of SPCM is lower than that of SPM asphalt. In Figure 3(b), SCM and SPCM asphalts own





**Figure 5.** The morphology of SBS compound asphalts after TFOT ageing (optical microscopy) at a magnification of 400. (a) SM asphalt. (b) SPM asphalt. (c, d) SCM asphalt. (e, f) SPCM asphalt. SM: SBS1301-modified asphalt (6 wt % SBS1301). SCM: SBS1301/crosslinker-modified asphalt (6 wt % SBS1301, 0.2 wt % crosslinker). SPM: SBS1301/plasticizer-modified asphalt (6 wt % SBS1301, 4 wt % plasticizer). SPCM: SBS1301/plasticizer/crosslinker-modified asphalt (6 wt % SBS1301, 4 wt % plasticizer, 0.2 wt % crosslinker). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

lower phase curves over the whole frequency due to the formation of an elastic polymer network and SPCM asphalt shows a more viscous behavior after 0.631 rad/s. For SM and SPM asphalts, there is a more elastic behavior for SPM asphalt before 10 rad/s, as shown by lower phase angle, this is because that the swelled SBS becomes more elastic. However, with increasing the frequency, SPM binder is not resistant to dynamic shearing and shows a little viscous behavior.

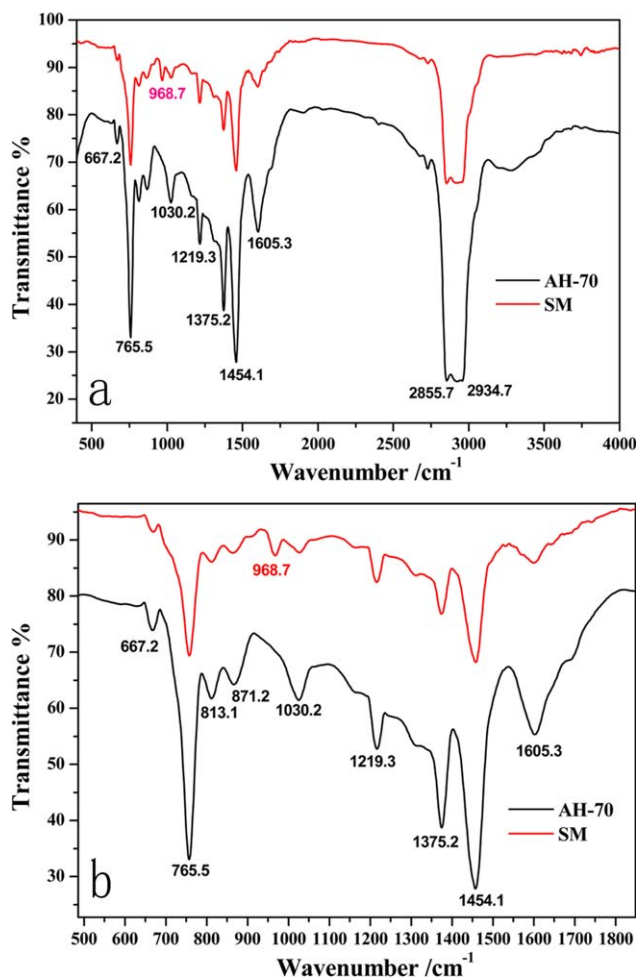
After ageing, as shown in Figure 3(c), the elastic behavior of the aged SCM and SPCM binders increases to some extent, as indicated by higher transition frequency at 3.95 and 24.9 rad/s than before ageing. The declined susceptibility to dynamic shearing can be attributed to the two factors. On one hand, the hard asphalt compositions such as asphaltene or resin increased, on the other hand, the crosslinked polymer network was destroyed seriously after ageing and no more susceptibility appeared. In Figure 3(d), the elastic behavior indicated by the lower phase curves of SCM and SPCM binders shows the crosslinked polymer network did not degrade completely after ageing. The elevated phase angle curves of SPM and SPCM binders compared to SM and SCM binders, respectively, show a more viscous behavior, which can be attributed to the swelling of plasticizer.

To understand the temperature dependence of viscoelastic behavior in the normally operating temperature range of asphalt pavement, we conducted the frequency sweep test on each binder at five different temperatures: 20, 30, 40, 50, 60°C, the reference temperature was 40°C. We calculated the shift factors by the master curves of complex modulus, respectively, according to the time–temperature superposition principle (TTSP). As has been previously reported by other researchers, the temperature dependence of the shift factor for bitumen may fit the Arrhenius equation.<sup>17,18</sup> 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:

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

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. Although the limited number of materials studied precludes making general conclusions, the differences that occur upon ageing these samples appear to be significant. The  $E_a$  value for each sample is shown in Table IV,

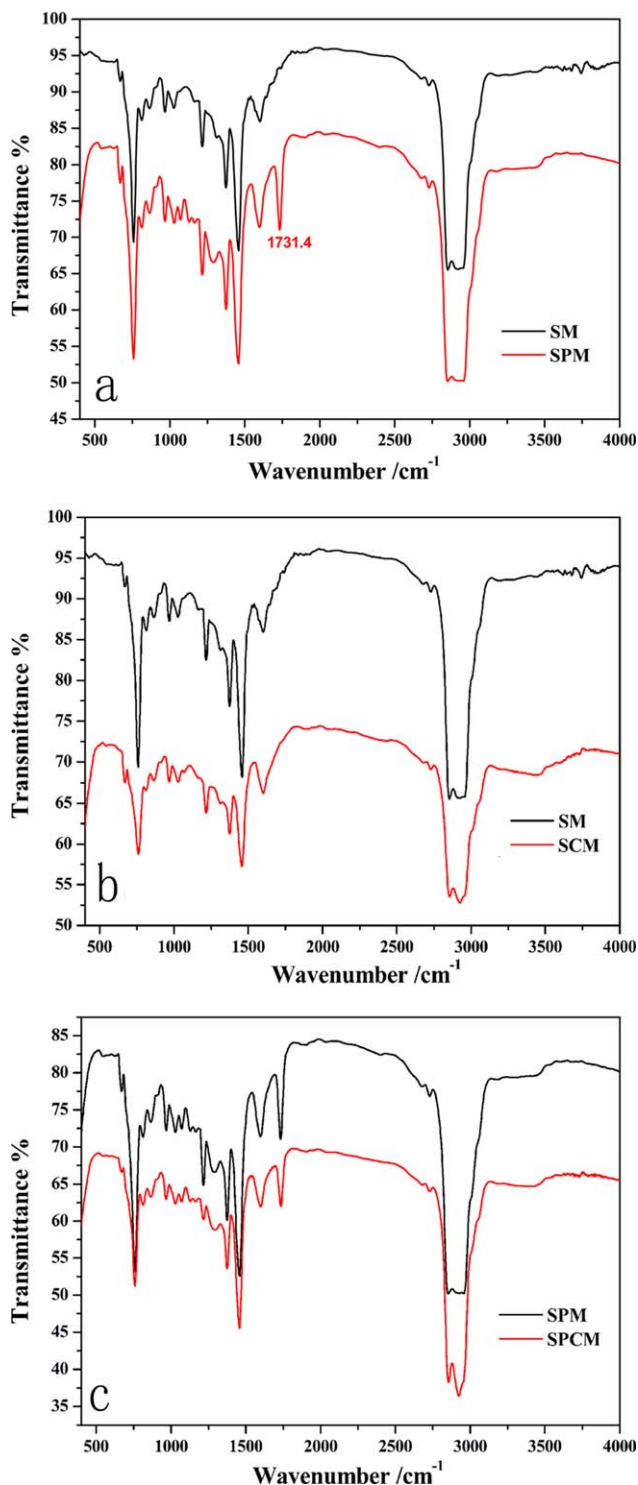




**Figure 6.** (a) FTIR spectra of base and SM asphalts ( $400\text{--}4000\text{ cm}^{-1}$ ). (b) FTIR spectra of base and SM asphalts ( $500\text{--}1800\text{ cm}^{-1}$ ). SM: SBS1301-modified asphalt (6 wt % SBS1301). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

which indicates the acting force between asphalt or polymer molecules. Whether the interactions between asphalt or polymer molecules are strong or feeble can be described by the value of  $E_a$  to a great extent.

In Table IV, it can be seen that the addition of plasticizer declines the  $E_a$  of binder obviously, SPM asphalt holds a lower  $E_a$  than that of SM asphalt. It is reasonable for the interactions among asphalt or polymer molecules to decrease by the dilution of plasticizer. Crosslinker also had a same effect, the  $E_a$  values of SPCM and SCM asphalts are lower than that of SPM and SM, respectively. The interactions between polymer and asphalt molecules declined by the addition of crosslinker, because the morphology and distribution of polymer particles in asphalt changed greatly by chemical crosslinking. As the result of crosslinking reaction, most polymer molecules were connected together by polysulfide bond, the coarser SBS particles in asphalt became smooth, the friction between SBS and asphalt decreased to a great extent, so no more interactions appeared between polymer and asphalt, leading to a decrease in  $E_a$ . After ageing, the  $E_a$  values of all binders increase correspondingly, the



**Figure 7.** (a) FTIR spectra of SM and SPM asphalts ( $400\text{--}4000\text{ cm}^{-1}$ ). (b) FTIR spectra of SM and SCM asphalts ( $400\text{--}4000\text{ cm}^{-1}$ ). (c) FTIR spectra of SPM and SPCM asphalts ( $400\text{--}4000\text{ cm}^{-1}$ ). SM: SBS1301-modified asphalt (6 wt % SBS1301). SCM: SBS1301/crosslinker-modified asphalt (6 wt % SBS1301, 0.2 wt % crosslinker). SPM: SBS1301/plasticizer-modified asphalt (6 wt % SBS1301, 4 wt % plasticizer). SPCM: SBS1301/plasticizer/crosslinker-modified asphalt (6 wt % SBS1301, 4 wt % plasticizer, 0.2 wt % crosslinker). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

**Table VI.** Changes of  $I_{CH=CH}$  Before and After Ageing

	Before ageing	After ageing
SM	0.09	0.067
SCM	0.065	0.051
SPM	0.1	0.081
SPCM	0.092	0.075

SM: SBS1301-modified asphalt (6 wt % SBS1301).

SCM: SBS1301/crosslinker-modified asphalt (6 wt % SBS1301, 0.2 wt % crosslinker).

SPM: SBS1301/plasticizer-modified asphalt (6 wt % SBS1301, 4 wt % plasticizer).

SPCM: SBS1301/plasticizer/crosslinker-modified asphalt (6 wt % SBS1301, 4 wt % plasticizer, 0.2 wt % crosslinker).

interactions among asphalt molecules become obvious due to the increased hard asphalt compositions. Plasticizer and crosslinker still have similar effect on the  $E_m$ , as mentioned before ageing, so the  $E_a$  sequence among binders does not change.

**Repeated Creep.** Recently, the validity of the Superpave binder specification parameter  $G^*/\sin \delta$  was questioned, Hu *et al.*<sup>19</sup> 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.<sup>19,20</sup> 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.

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.<sup>21</sup> The test consisted of 100 cycles of loading with a stress of 30 Pa for 1 s, and recovery for 9 s. These testing

**Table VII.** The Assignment of Protons in <sup>1</sup>H-NMR Spectra

Parameter	Chemical shift	Type of protons
H <sub>ar</sub>	6.0–9.0	Aromatic hydrogen
H <sub>alk1</sub>	4.8–5.8	Alkene hydrogen
H <sub>α</sub>	2.0–4.0	Aliphatic hydrogen on C <sub>α</sub> to aromatic rings
H <sub>alk2</sub>	1.9–2.1	CH <sub>2</sub> on alkylene
H <sub>β</sub>	1.0–2.0	Aliphatic hydrogen on C <sub>β</sub> and the CH <sub>2</sub> , CH, beyond the C <sub>β</sub> to aromatic rings
H <sub>γ</sub>	0.5–1.0	Aliphatic hydrogen on C <sub>γ</sub> and the CH <sub>3</sub> beyond the C <sub>γ</sub> to aromatic rings

parameters are based on the suggestions from the NCHRP study.<sup>20,21</sup>

Based on the recommendations, the time and strain data from the 50th and 51th cycles of the repeated creep recovery test were fitted to the four-element Burgers model as shown in the 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;  $\tau_0$ , constant shear strain;  $G_0$ , spring constant of Maxwell model;  $G_1$ , spring constant of Kelvin model;  $\eta_1$ , dashpot constant of Kelvin model;  $t$ , loading time;  $\eta_0$ , 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 ( $J_v$ ):

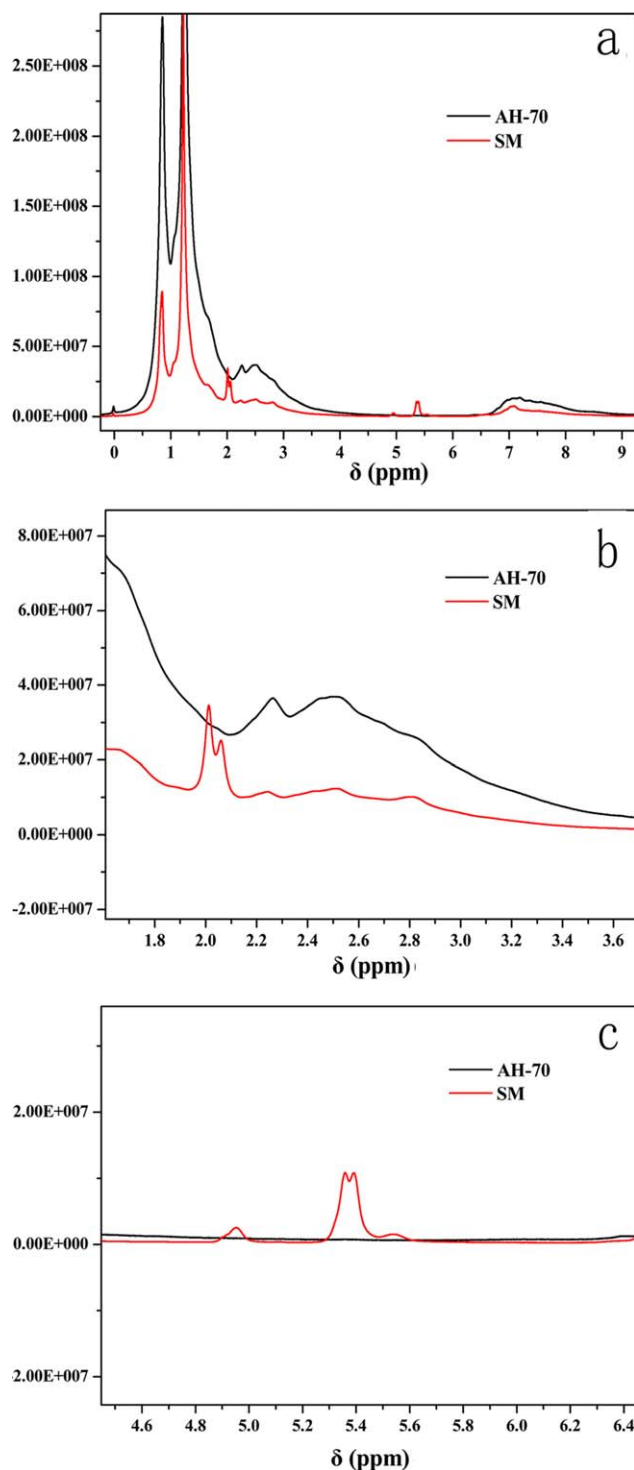
$$J(t) = \frac{1}{G_0} + \frac{1}{G_1} \left( 1 - \exp\left(\frac{-tG_1}{\eta_1}\right) \right) + \frac{t}{\eta_0} = J_e + J_{de}(t) + J_v(t). \quad (3)$$

The viscous component is inversely proportional to the viscosity,  $\eta_0$ , and directly proportional to stress and time of loading. Based 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,<sup>7,20</sup> as shown in the 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.

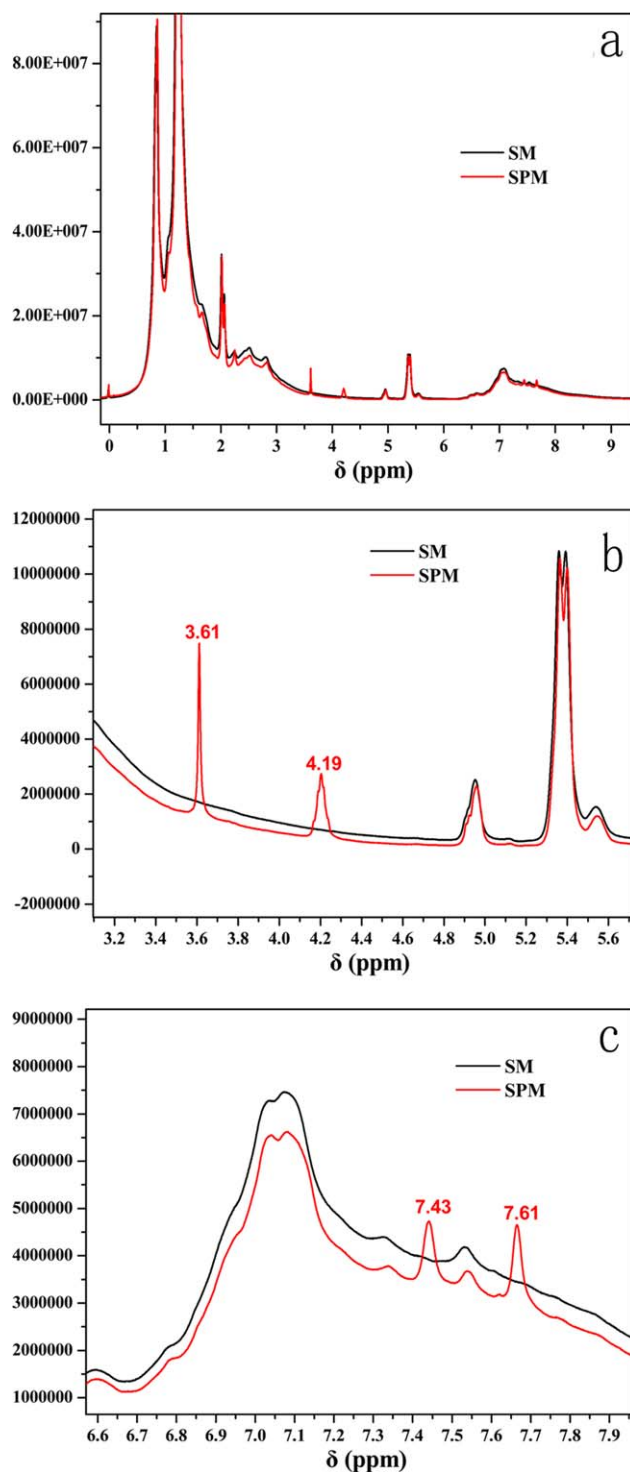
The  $G_v$  value for each binder is shown in Table V. Before ageing, SM asphalt seems to be more tough than others and owns the highest  $G_v$ , which means SM asphalt is much more resisting deformation at high temperature. By vulcanization, the rutting resistance of SM asphalt declined, as shown by the  $G_v$  of SCM asphalt. The crosslinked polymer network is susceptible to dynamic shearing and was destroyed under the repeated dynamic shearing. As the result of dilution of plasticizer, the  $G_v$  of SPM and SPCM asphalts declined evidently compared to SM asphalt, the  $G_v$  of SPCM asphalt is a little higher than that of SPM due to the existence of elastic polymer network in asphalt. After ageing, the hard asphalt compositions such as asphaltene and resin increased, leading to the improved rutting resistance, as shown by the higher  $G_v$  than before ageing. The sequence of  $G_v$  value among the aged binders still depends on the effects of plasticizer and crosslinker, SM binder owns the highest  $G_v$  and SCM is the second. The  $G_v$  of SPM and SPCM is lower and the difference in  $G_v$  between the two binders is negligible.



**Figure 8.** (a) H-NMR spectra of base and SM asphalts (−0.5 to 9.5 ppm). (b) H-NMR spectra of base and SM asphalts (1.6–3.7 ppm). (c) H-NMR spectra of base and SM asphalts (4.5–6.5 ppm). SM: SBS1301-modified asphalt (6 wt % SBS1301). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

### Morphology

The morphology of the PMAs before and after ageing was investigated using optical microscopy by characterizing the distribution and the fineness of polymer in asphalt matrix. In the



**Figure 9.** (a) H-NMR spectra of SM and SPM asphalts (−0.5 to 9.5 ppm). (b) H-NMR spectra of SM and SPM asphalts (3.1–5.7 ppm). (c) H-NMR spectra of SM and SPM asphalts (6.65–7.95 ppm). SM: SBS1301-modified asphalt (6 wt % SBS1301). SCM: SBS1301/crosslinker-modified asphalt (6 wt % SBS1301, 0.2 wt % crosslinker). SPM: SBS1301/plasticizer-modified asphalt (6 wt % SBS1301, 4 wt % plasticizer). SPCM: SBS1301/plasticizer/crosslinker-modified asphalt (6 wt % SBS1301, 4 wt % plasticizer, 0.2 wt % crosslinker). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

sample preparation process, the SBS particles were sheared fully in asphalt by a high-speed shear machine at 4500 r/min (1 h) and the shear force was powerful, and then was stirred by a mechanical mixer with higher speed (2 h), the whole preparation was proceeded at high temperature (180°C). With such a preparation process, larger polymer particles were sheared into smaller ones and dispersed in asphalt and the phase distribution was uniform.

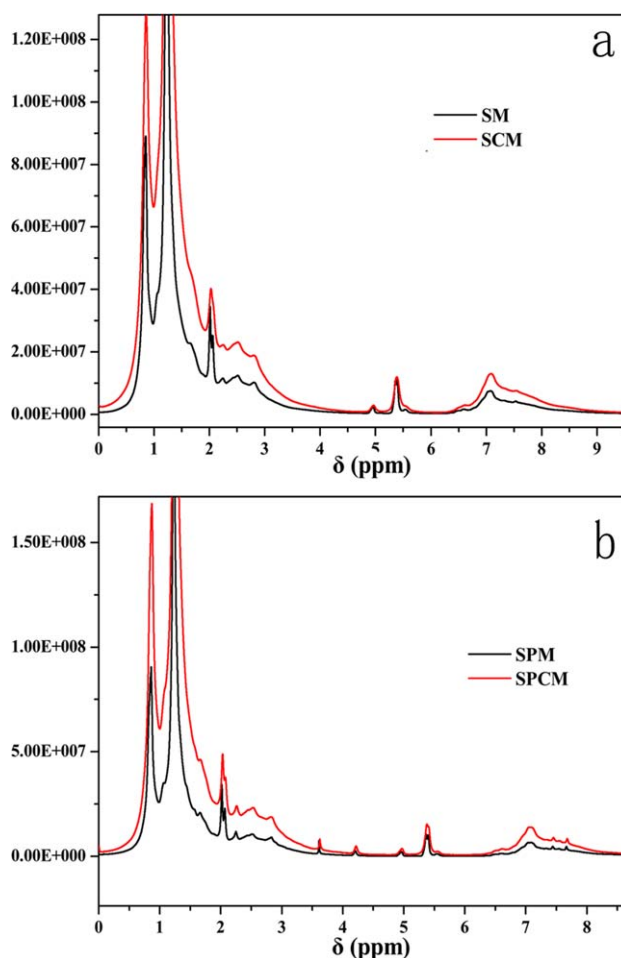
In engineering practice, the SBS content in asphalt is usually 4 wt % or 5 wt %, when the SBS content increases to 6 wt %, the distribution of polymer in asphalt matrix becomes very dense and the polymer phase in asphalt becomes continuous.<sup>11,22</sup> For SM asphalt, as shown in Figure 4(a), a dense and continuous polymer network consisting of coarser SBS particles is dispersed around asphalt matrix. The clear outline of polymer particles shows the poor compatibility between SBS and asphalt. The morphology of SCM asphalt is shown in Figure 4(b), obviously the addition of crosslinker changed the morphology of polymer particles to a great extent, the SBS particles are crosslinked together closely and formed to a continuous polymer network around the whole asphalt matrix. The polymer network is so dense that the gap among polymer particles seems to be very small. The morphology of SPM asphalt is shown in Figure 4(c). It can be seen that the swelled polymer particles were sheared into smaller ones in asphalt. The particle size decreases and the outline becomes dim, a continuous polymer network consisting of tiny SBS particles is distributed around asphalt matrix. The morphology of SPCM asphalt is shown in Figure 4(d). Obviously, there is a great change in morphology compared to SPM asphalt. The SBS particles changed to the filamentous polymer network and the loose polymer network is distributed in asphalt matrix somewhere. Compared with SCM asphalt, the crosslinking density of polymer particles declined to a great extent and the morphology of polymer is also quite different, the filamentous polymer shows the SBS particles were swelled fully.

After TFOT ageing, the morphology of SM binder is shown in Figure 5(a). As the result of polymer degradation, the particle size of SBS decreases obviously and the tiny SBS particles are distributed uniformly.<sup>7,23</sup> For SPM binder, the result of polymer degradation is more apparent, as shown in Figure 5(b), there are very tiny SBS particles dispersed in asphalt and most particles decomposed and were dissolved in asphalt. For SCM binder, it can be seen in Figure 5(c) that most areas in asphalt are blank, and only a few polymer filaments are dispersed in asphalt, as shown in Figure 5(d), which means most polymers decomposed and were dissolved in asphalt after ageing and the polymer network was destroyed seriously. The morphology of SPCM asphalt after ageing is shown in Figure 5(e,f), it can be seen that the morphology is similar to that of the aged SCM asphalt, which demonstrates the effect of ageing again. The blank areas shown in Figure 5(e) show that lots of crosslinked polymer were dissolved in asphalt after ageing. In Figure 5(f), the filamentous polymer dispersed in asphalt indicates that the crosslinked polymer network was very susceptible to ageing and destroyed seriously after ageing.

### FTIR Analysis

The FTIR spectrum of base asphalt was given in Figure 6(a). The strong peaks within 2850–2960  $\text{cm}^{-1}$  region are typical C—H stretching vibrations in aliphatic chains. The peak at 1605.3  $\text{cm}^{-1}$  is attributed to C=C stretching vibrations in aromatics. The C—H asymmetric deforming in  $\text{CH}_2$  and  $\text{CH}_3$ , and the C—H symmetric deforming in  $\text{CH}_3$  vibrations are observed at 1454.1  $\text{cm}^{-1}$  and 1375.2  $\text{cm}^{-1}$ , respectively. The peak at 1219.3  $\text{cm}^{-1}$  corresponds to the frame vibration of  $(\text{CH}_3)_3\text{C—R}$ . The peak at 1030.2  $\text{cm}^{-1}$  is ascribed to S=O stretching vibrations. The small peaks within 667.2–871.2  $\text{cm}^{-1}$  region are typical C—H vibrations of benzene ring.<sup>24</sup>

The FTIR spectra of SM asphalt are also illustrated in Figure 6(a). Compared with base asphalt, the addition of SBS brought one new peak at 968.7  $\text{cm}^{-1}$  corresponding to the bending vibration of C—H in butadiene double bonds SBS molecule chain. The FTIR spectras of SM and SPM asphalts are listed in



**Figure 10.** (a) H-NMR spectra of SM and SCM asphalts (0–9.5 ppm). (b) H-NMR spectra of SPM and SPCM asphalts (0–8.5 ppm). SM: SBS1301-modified asphalt (6 wt % SBS1301). SCM: SBS1301/crosslinker-modified asphalt (6 wt % SBS1301, 0.2 wt % crosslinker). SPM: SBS1301/plasticizer-modified asphalt (6 wt % SBS1301, 4 wt % plasticizer). SPCM: SBS1301/plasticizer/crosslinker-modified asphalt (6 wt % SBS1301, 4 wt % plasticizer, 0.2 wt % crosslinker). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



Figure 7(a). Compared with SM asphalt, a new peak appears at  $1731.4\text{ cm}^{-1}$  corresponding to the stretching vibration of  $\text{C}=\text{O}$ , which can be attributed to a structural characteristic of plasticizer molecule.<sup>24</sup> Therefore, there is no obvious chemical reaction taken place between plasticizer and asphalt molecules. The FTIR spectras of SCM and SPCM asphalts are shown in Figure 7(b,c) and no new peak appears compared to SM and SPM asphalts correspondingly.

In this study, because the spectra of each binder before and after ageing are very similar and no new peak appears after age-

ing, so the aged spectra also can be illustrated by that before ageing. For SBS binders, the butadiene bond content (centered around  $968.7\text{ cm}^{-1}$ ) is helpful in investigating the structural characteristics of asphalts before and after ageing. By calculating the structural parameter  $I_{\text{CH}=\text{CH}}$  of the eq. (5), we can assess the deterioration of SBS copolymer as a result of further modification or ageing.<sup>25,26</sup>

Area of the ethylene band centered around  $968.7\text{ cm}^{-1}$

$$I_{\text{CH}=\text{CH}} = \frac{\text{Area of the ethylene band centered around } 968.7\text{ cm}^{-1}}{\sum \text{Area of the spectral bands between } 2000\text{ cm}^{-1} \text{ and } 600\text{ cm}^{-1}} \quad (5)$$

The calculated result for each binder before and after is listed in Table VI. Before ageing, it can be seen that the  $I_{\text{CH}=\text{CH}}$  of SCM asphalt is lower than that of SM asphalt, which indicates the crosslinker interacted with the conjugated carbon bond of SBS molecule chain, so the corresponding bending vibration of  $\text{C}-\text{H}$  declined. The  $I_{\text{CH}=\text{CH}}$  of SPM asphalt is higher than that of SM asphalt, this is related to the  $\text{C}-\text{H}$  deformation vibration of aromatic nucleus of plasticizer molecule,<sup>24</sup> which shows a low absorption peak at  $968.7\text{ cm}^{-1}$ , therefore the overlap of the two kinds of  $\text{C}-\text{H}$  vibration increases the peak area. The influence of crosslinker on this peak is shown by the lower  $I_{\text{CH}=\text{CH}}$  of SPCM asphalt again. After ageing, the  $I_{\text{CH}=\text{CH}}$  of each binder is lower than that before ageing. As the result of the SBS degradation, the butadiene content declined. The influence of crosslinker and plasticizer on  $I_{\text{CH}=\text{CH}}$  is still similar to that before aging, therefore the  $I_{\text{CH}=\text{CH}}$  sequence among different binders is similar to that before ageing.

**Table VIII.** Distribution of Hydrogen Before and After Ageing

Sample	$H_{\text{ar}}$	$H_{\text{alk1}}$	$H_{\text{alk2}}$	$H_{\text{alk}}$	$H_{\alpha}$	$H_{\beta}$	$H_{\gamma}$
AH-70	7	0.3	2.6	2.9	15.6	52.6	21.6
SM	8	1.8	4.4	6.2	16.3	54.9	16.6
SCM	7.8	1.6	4	5.6	16.4	54.4	16.5
SPM	7.6	1.8	4.3	6.1	15.4	55.4	17.3
SPCM	7.6	1.5	3.9	5.4	15.8	55.5	17
After TFOT ageing							
AH-70	6.7	0.3	2.6	2.9	15.2	52.6	21.1
SM	7.9	1.8	4.3	6.1	16.4	55	16.3
SCM	7.7	1.6	3.9	5.5	16.1	55.3	16.1
SPM	7.5	1.6	4.0	5.8	16	54.6	16.5
SPCM	7.4	1.4	3.8	5.2	15.4	55.5	16.3

SM: SBS1301-modified asphalt (6 wt % SBS1301).

SCM: SBS1301/crosslinker-modified asphalt (6 wt % SBS1301, 0.2 wt % crosslinker).

SPM: SBS1301/plasticizer-modified asphalt (6 wt % SBS1301, 4 wt % plasticizer).

SPCM: SBS1301/plasticizer/crosslinker-modified asphalt (6 wt % SBS1301, 4 wt % plasticizer, 0.2 wt % crosslinker).

### HNMR Analysis

The distribution of aromatic protons,  $H_{\text{ar}}$  ( $\delta = 6-9$ ), and aliphatic protons,  $H_{\text{sat}}$  is shown in Table VII. The HNMR data of base asphalt and SBS modified binders are presented in Table VII. The aliphatic region is subdivided into three parts:  $H_{\alpha}$  ( $\delta = 2.0-4.0$ ),  $H_{\beta}$  ( $\delta = 1.0-2.0$ ), and  $H_{\gamma}$  ( $\delta = 0.5-1.0$ ).<sup>27</sup> The corresponding peaks are also shown in Figure 8(a). In the shift ranges: 4.8–5.8 and 1.9–2.1, SM asphalt shows a pair of new double peaks compared to base asphalt, respectively, as shown in Figure 8(b,c), which can be attributed to the shift of alkene hydrogen and ethyl hydrogen on ethylene. These peaks also can be found in the HNMR of other modified asphalts. The HNMR of SM and SPM asphalts is shown in Figure 9(a). In Figure 9(b), the new peaks at 3.61 ppm and 4.19 ppm compared to SM asphalt can be attributed to the chemical shift of methyne to ester base and the shift of methane to benzoic acid ester base, respectively.<sup>28</sup> Compared with SM asphalt, two new slight peaks also can be found at 7.43 and 7.61 ppm in the HNMR of SPM asphalt, as shown in Figure 9(c), which is attributed to the chemical shift of aromatic hydrogen under the influence of ester group on benzene ring.<sup>28</sup> Because the new chemical shifts appearing in Figure 9(b,c) also can be found in the structural characteristics of plasticizer molecule, so there was no reaction taken place between plasticizer and asphalt.

The HNMR diagrams of SCM and SPCM asphalts are shown in Figure 10(a,b) and no new peak appears compared to SM and SPM. Because the HNMR diagram of each binder after ageing is very similar to that before ageing, so the HNMR diagram of aged binder can be illustrated by that before ageing.

The percent hydrogen distribution of all binders before and after ageing is given in Table VIII. It can be seen that  $H_{\text{ar}}$ ,  $H_{\alpha}$ ,  $H_{\beta}$  of modified asphalts increase compared to base asphalt. This is because there are more styrene entanglements with  $C_{\alpha}$  and  $C_{\beta}$  in the molecule chain of SBS. However, the lack of  $C_{\gamma}$  in the styrene and butadiene entanglements of SBS molecule chain also decreases the original  $H_{\gamma}$  content in asphalt. The increased  $H_{\text{alk}}$  content can be attributed to the butadiene entanglements in SBS molecule chain. Because of the dilution of plasticizer, the  $H_{\text{alk}}$ ,  $H_{\alpha}$  content of SPM and SPCM asphalts is lower than that

of SM and SCM asphalts correspondingly. The use of crosslinker decreased the  $H_{alt}$  content, as shown by that of SCM and SPCM asphalts compared to SM and SPM asphalts, respectively, before and after ageing. After ageing, the lower  $H_{ar}$  content of all binders than before ageing indicates the aromatic condensation and the lower  $H_{\gamma}$  content is an apparent evidence of the increased alicyclic system and the presence of short aliphatic straight chains. Besides the decreased  $H_{alk}$  content of all SBS binders shows the susceptibility of butadiene to ageing.

## CONCLUSION

HEM asphalt can be prepared by mixing SBS, plasticizer, crosslinker in base asphalt under high temperature, and shearing. SBS was the major modifier and determined the physical properties of HEM asphalt. Plasticizer and crosslinker were additional modifiers. Plasticizer was helpful in improving the elasticity and low-temperature properties further. Crosslinker was necessary to maintain a good stability.

The effect of ageing and additional modifiers on the structure and rheological properties of SM asphalt was studied by adopting different rheological tests. Plasticizer declined the high-temperature properties of SM asphalt and the interactions between polymer and asphalt molecules. Crosslinker led to the formation of polymer network in asphalt and increased the susceptibility of SM asphalt to dynamic shear. Ageing destroyed the polymer network in asphalt partly and increased the interactions among asphalt molecules.

Morphology observation confirmed the effect of modifier and ageing further. The crosslinked polymer network was formed in asphalt due to vulcanization. Plasticizer prompted the further swelling of SBS in asphalt and declined the density of polymer network in asphalt. Ageing had a destructive effect on the polymer dispersed in asphalt.

FTIR and HNMR analysis showed the structural characteristics of modified asphalts before and after ageing by displaying different characteristic peaks. The results confirmed the consumption for the butadiene domain of polymer molecule in vulcanization and the destruction for the molecule structure of polymer and asphalt in ageing further, which supported the results of other testing and observation in details.

## REFERENCES

1. Monismith, C. L.; Coetzee, N. F. *Proc. AAPT* **1980**, *49*, 268.
2. Morian, N. E. Effect of Geotextile Fabrics on Reflective Cracking of Hot Mix Asphalt Overlays on Washoe Country, Nevada [PhD Dissertation]; University of Nevada: Reno.
3. Rigo, J. M.; Degeimbre, R.; Francken, L. Reflective Cracking in Pavements State of the Art and Design Recommendation, 1th ed.; CRC Press: Belgium, **1993**.
4. Dempsey, B. J. *Transport. Res. Rec.* **2002**, *1809*, 175.
5. Liao, W. D.; Chen, Q. F.; Li, Z. Z. Material Properties and Structural Behaviours of Modified HMA Reflective Cracking Relief Interlayers, 1th ed.; Science Press: Beijing, **2010**.
6. Zhou, Y. Research on Properties and Key Evaluation Index of Stress Absorbing Layer Asphalt, Xian China [PhD Dissertation]; Changan University (in Chinese).
7. Zhang, F.; Ying, Y. J.; Wu, S. P. *J. Hazard. Mater.* **2010**, *182*, 507.
8. Shen, J. A. Modified Asphalt and SMA Pavement, 1st ed.; People Communication Press: Beijing, **1999**.
9. Wen, G. A.; Zhang, Y.; Zhang, Y. X.; Sun, K.; Fan, Y. Z. *Polym. Test.* **2002**, *21*, 295.
10. Wen, G. A.; Zhang, Y.; Zhang, Y. X.; Sun, K.; Chen, Z. Y. *J. Appl. Polym. Sci.* **2001**, *82*, 989.
11. Wen, G. A.; Zhang, Y.; Zhang, Y. X. *Polym. Eng. Sci.* **2002**, *42*, 1070.
12. Sun, D. Q.; Ye, F.; Shi, F. Z.; Lu, W. M. *Petrol. Sci. Technol.* **2006**, *24*, 1067.
13. Zhang, F.; Yu, Y. J.; Wu, S. P. *J. Polym. Eng. Sci.* **2012**, *52*, 71.
14. Zhang, F.; Yu, Y. J. *Constr. Build. Mater.* **2010**, *24*, 410.
15. Zhang, F.; Hu, C. B. *Constr. Build. Mater.* **2013**, *43*, 461.
16. Lu, X.; Isacson, U. *Constr. Build. Mater.* **1997**, *11*, 23.
17. Partal, P.; Martinez, B.; Gallegos, C. *Fuel* **1999**, *78*, 1.
18. Ruan, Y. H.; Davison, R. R.; Glover, C. J. *Fuel* **2003**, *82*, 1763.
19. Bahia, H. U.; Hanson, D. I.; Zeng, M.; Zhai, H.; Khatri, M. A.; Anderson, R. M. *Nat. Coop. Highway Res. Prog. Rep.* **2001**, *459*, 46.
20. Hu, R. Y.; Bahia, H. U.; Zhai, Z.; Zheng, M. Measuring Resistance of Asphalt Binders to Permanent Deformation Using the DSR Device. In: TRB 80th Annual Meeting, Washington, 2001.
21. Binard, C.; Anderson, D.; Lapalu, L.; Planche, J. P. Zero Shear Viscosity of Modified and Unmodified Binders. In: Proceeding of the 3rd Eurasphalt & Eurobitume Congress, Vienna, 2004.
22. Liu, X. H. *Polym. Test.* **2001**, *20*, 77.
23. Cortizo, M. S.; Larsen, D. O.; Bianchetto, H.; Alessandrini, J. L. *Polym. Degrad. Stabil.* **2004**, *86*, 275.
24. Bellamy, L. J. Infrared Spectrum of Complex Molecules, 1st ed.; Science Press: Beijing, **1975**.
25. Lamontagne, J.; Dumas, P.; Mouillet, V.; Kister, J. *Fuel* **2001**, *80*, 483.
26. Ouyang, C. F.; Wang, S. F.; Zhang, Y.; Zhang, Y. X. *Polym. Degrad. Stabil.* **2006**, *91*, 795.
27. Ahmad, I.; Shakirullah, M.; Rehman, H. U.; Ishaq, M.; Khan, M. A.; Shah, A. A. *Energy* **2009**, *34*, 127.
28. Zhao, J. Z. H Nuclear Magnetic Resonance, 1st ed. Peking University Press: Beijing, **1983**.