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Characterizing SBS modified asphalt with sulfur using multiple stress creep recovery test

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HIGHLIGHTS

- Sulfur can decrease J_{nr} and improve percent recovery of SBS modified asphalt.
- The effect of increasing SBS content is prominent for binders at lower SBS content.
- Percent recovery correlates linearly to J_{nr} of SBS modified asphalt.
- The nonlinear parameter G_2 can identify the existence of cross-linking agent.
- It is promising for PS% to evaluate binder's resistance to permanent deformation.

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ABSTRACT

The effect of cross-linking agent and SBS content on SBS modified asphalt were investigated using multiple stress creep recovery (MSCR) test. Nonlinear viscoelastic characterization of MSCR curve was also performed to derive nonlinear viscoelastic parameters. Cross-linking agent can prominently improve high temperature properties of SBS modified asphalt, especially at lower polymer content. The effect of increasing SBS content is more prominent for binders at lower SBS content. MSCR test failed to distinguish 5.0% and 5.5% SBS modified asphalt in this limited study. All binders modified from 3.0% to 5.5% SBS with sulfur have sufficient delayed elastic response according to AASHTO TP 70. When cross-linking agent was not used, only high dosage SBS modified binders are considered to be modified with an acceptable elastomeric polymer in this study. In addition, there is strong linear relationship between percent recovery and J_{nr} and such relationship is not dependent on stress level, but is concerned with test temperature. The nonlinear parameter G_2 derived from MSCR curve can be used to identify the existence of cross-linking agent and characterize the elastic response of SBS modified binder. The parameter PS% shows potentiality in evaluating modified binder's ability to resist permanent deformation. However, PS% used in this study should be further investigated to confirm the applicability for highly modified asphalt.

1. Introduction

There has been a long history of asphalt modification to achieve better performance in road engineering. As an outstanding representative, styrene–butadiene–styrene (SBS) modified asphalt is widely used across the world due to its excellent performance. Of all the performance characterization of asphalt binders, rutting resistance has been considered as one of the most important properties due to global warming and increasing heavy traffic. In recent years, applicability of Superpave specification parameter, $G^*/\sin\delta$, in evaluating modified asphalt raised concerns [1,2]. Alternative parameters have been developed in order to characterize modified binders appropriately [3–7]. Bahia et al. [4] proposed repeated creep and recovery test and a new parameter called viscous component of the creep stiffness G_v was used to characterize high temperature properties. Shenoy [6] derived the unrecoverable strain from dynamic oscillatory test using a frequency sweep and the non-recoverable compliance $(1–1/(\tan\delta\cdot\sin\delta))/G^*$ was used to evaluate rutting resistance. More recently, D'Angelo [7] proposed multiple stress creep recovery (MSCR) test and the non-recoverable creep compliance J_{nr} and the percent recovery were used to evaluate binder's high temperature properties. The MSCR test has been used to characterize the extent of dispersion of styrene–butadiene–styrene (SBS) in polymer-modified asphalts (PMA) and MSCR can be considered as an alternative to Elastic

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Recovery test, typically run by many highway agencies [8,9]. The validation of the MSCR compliance value J_{nr} to rutting demonstrated that the MSCR test provides a better correlation to mixture rutting than the existing Superpave binder criteria [10]. AASHTO has published standard specification for performance-graded asphalt binder using MSCR test [11].

2. Objectives and scope of work

The variation of SBS content will have a significant effect on rheology properties and morphology of SBS modified binders. With the increase of SBS content, the complex modulus increases as a function of the amount of SBS and continuous polymer structure begins to from at 5% SBS concentration [12]. However, research on how SBS content influence creep and recovery properties is limited. By comparing J_{nr} and percent recovery results at varying SBS content, this study investigated the effect of SBS content on SBS modified asphalt using MSCR test. In addition, as cross-linking agent is widely used in asphalt industry to achieve storage-stable binders, the effect of cross-linking agent on creep and recovery properties was also investigated. Based on the research above, all J_{nr} and percent recovery data points were plotted in a scatter graph to compare with a curve of J_{nr} 3.2 versus percent recovery given by AASHTO TP 70 [13] to determine whether those binders have sufficient delayed elastic response. In the end, nonlinear viscoelastic characterization of MSCR curve will be performed to derive nonlinear viscoelastic parameters and their correlations to SBS and sulfur will be discussed.

3. Materials and experimental

3.1. Materials

In this study, one base binder, one SBS modifier and elemental sulfur were selected to prepare modified binders in laboratory. Base binder was ESSO asphalt (PG64-16). SBS T161B was produced by DuShanZi Petroleum and Chemical Corporation, China. SBS T161B is a kind of radial polymer with average molecule weight of 230,000 g/mol, containing 30 wt% of styrene. The amount of SBS modifier ranged from 3.0% to 5.5% by weight of base binder. Elemental sulfur and organic sulfide are commonly used as cross-linking agent to produce storage stable polymer modified asphalt. The cross-linking mechanism is rather similar to that of vulcanization in rubber industry [14]. Under high temperature, e.g. 180 °C in this study, partial carbon–carbon double bonds of PB chains in SBS molecules were opened to form free radicals. Sulfur were then added to crosslink those free radicals and network structure would be formed when polymer concentration is high enough. Besides, sulfur can chemically couple the polymer and asphalt through sulfide and/or polysulfide bonds since there are active components in asphalt molecules which can react with sulfur [15]. In this study, elemental sulfur was used as a cross-linking agent with 0.15 wt% of base binder. The details of modified asphalt composition are presented in Table 1. Batch 1 was used to investigate the effect of SBS content on modified binders. Batch 2 was taken as control group to investigate the effect of cross-linking agent on modified binders.

3.2. Sample preparation

The following procedure was taken to prepare the first batch of SBS modified asphalt according to the method disclosed in the patent [14]. Firstly, SBS was added to base binder and sheared for 30 min at 180 °C with high shear mixer and the shear speed is 4000 r/min. Secondly, the blend was stirred for 60 min using mechanical stirrer at 180 °C. Thirdly, cross-linking agent was added to the blend and stirred for another 90 min at 180 °C. The resulted binders satisfied the requirements of storage stability test.

For the second batch of SBS modified asphalt, the third step was removed and the stirring time in the second step was extended to 2 h.

All samples were taken for the following RTFO aging procedure before the ending of binder blending to make sure there is no phase separation. This is especially important for modified binders without sulfur since SBS could not stably disperse in asphalt without the help of cross-linking.

3.3. MSCR test

All binders used in MSCR test went through short term aging using RTFO test according to ASTM D2872 [16].

The TA dynamic shear rheometer (DSR) AR 1500ex was used to perform MSCR test. The MSCR test was operated in rotational mode at 64 °C and 70 °C using 1 s creep load followed by 9 s recovery for each cycle according to ASTM D7405 [17]. Ten creep and recovery cycles were run at 0.1 kPa creep stress followed by ten at 3.2 kPa creep stress. Fig. 1 presents the typical creep and recovery cycle. For each cycle, two parameters, the percent recovery (R) and non-recoverable creep compliance (J_{nr}) are calculated using the following equations:

$$R = \frac{\varepsilon_p - \varepsilon_u}{\varepsilon_p} \times 100\% \tag{1}$$

$$J_{nr} = \frac{\varepsilon_u}{\sigma} \tag{2}$$

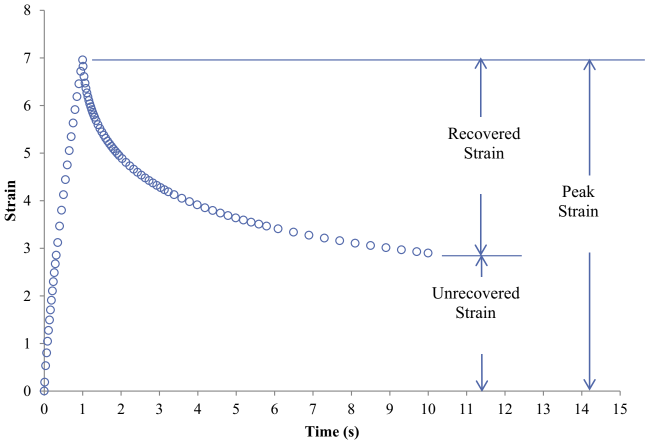

Fig. 1. Typical creep and recovery cycle in MSCR test.

Table 1
Modified asphalt composition.

Batch 1	SBS modified asphalt (with 0.15 wt% sulfur)					
Polymer amount (radial SBS)%	3.0	3.5	4.0	4.5	5.0	5.5
Batch 2	SBS modified asphalt (without sulfur)					
Polymer amount (radial SBS)%		3.5		4.5		5.5

where ε_p represents the peak strain, ε_u represents the unrecovered strain, σ is the stress level.

Then, the average percent recovery of 10 cycles at 0.1 kPa and 3.2 kPa are calculated and expressed as $R100$, $R3200$ respectively. The average non-recoverable creep compliance at 0.1 kPa and 3.2 kPa are expressed as J_{nr} 0.1 and J_{nr} 3.2. Besides, stress sensitivity parameters, R_{diff} and $J_{nr\text{-}diff}$ are calculated using the following equations:

$$R_{diff} = (R100 - R3200)/(R100) \cdot 100 \tag{3}$$

$$J_{nr\text{-}diff} = (J_{nr}3.2 - J_{nr}0.1)/(J_{nr}0.1) \cdot 100 \tag{4}$$

3.4. Nonlinear viscoelastic characterization of MSCR curve

The modeling of MSCR curve follows the procedure developed by Mehta, and only the 6th creep and recovery cycle at 0.1 kPa, 3.2 kPa for each binder was selected for analysis since Mehta suggested that the derived parameters are similar for each cycle [18].

The analysis procedure is briefly described as follows:

(1) Fit the recovery strain data (1–10 s) at 0.1 kPa using Eq. (5). The calculated linear parameters B, C, D, E was used in next step:

$$\begin{aligned}\varepsilon(t) = {} & 0.1\left[A + B\left(1 - e^{\frac{-t}{C}}\right) + D\left(1 - e^{\frac{-t}{E}}\right)\right] \\ & - 0.1\left[A + B\left(1 - e^{\frac{-(t-1)}{C}}\right) + D\left(1 - e^{\frac{-(t-1)}{E}}\right)\right]\end{aligned} \tag{5}$$

(2) Determine the nonlinear viscoelastic parameters.

The parameter G_1 is derived through fitting the first part of recovery strain data (1–2 s) at 3.2 kPa using Eq. (6):

$$\begin{aligned}\varepsilon(t)_{NLVE-G_1} = {} & G_1\left\{3.2\left[B\left(1 - e^{\frac{-t}{C}}\right) + D\left(1 - e^{\frac{-t}{E}}\right)\right] - 3.2\left[B\left(1 - e^{\frac{-(t-1)}{C}}\right)\right.\right. \\ & \left.\left. + D\left(1 - e^{\frac{-(t-1)}{E}}\right)\right]\right\}\end{aligned} \tag{6}$$

Parameters G_2, G_3 are derived through fitting the second part of recovery strain data (2–10 s) at 3.2 kPa using Eq. (7):

$$\begin{aligned}\varepsilon(t)_{NLVE-G_2-G_3} = {} & G_2\left\{3.2[J_{LVE(t=2)} - J_{LVE(t=1)}]\right\} + G_3\left\{3.2\left[B\left(1 - e^{\frac{-t}{C}}\right)\right.\right. \\ & \left.\left. + D\left(1 - e^{\frac{-t}{E}}\right)\right] - 3.2\left[B\left(1 - e^{\frac{-(t-1)}{C}}\right) + D\left(1 - e^{\frac{-(t-1)}{E}}\right)\right]\right\}\end{aligned} \tag{7}$$

where

$$J_{LVE(t=1)} = B\left(1 - e^{\frac{-1}{C}}\right) + D\left(1 - e^{\frac{-1}{E}}\right) \tag{8}$$

$$J_{LVE(t=2)} = B\left(1 - e^{\frac{-2}{C}}\right) + D\left(1 - e^{\frac{-2}{E}}\right) \tag{9}$$

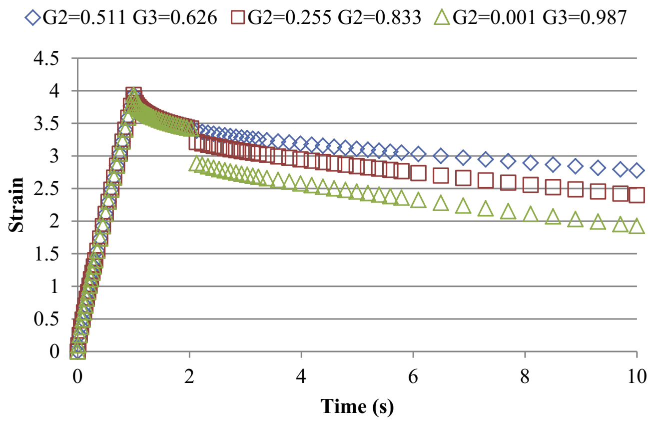

Fig. 2. Effect of G_2 and G_3 on recovery behavior.

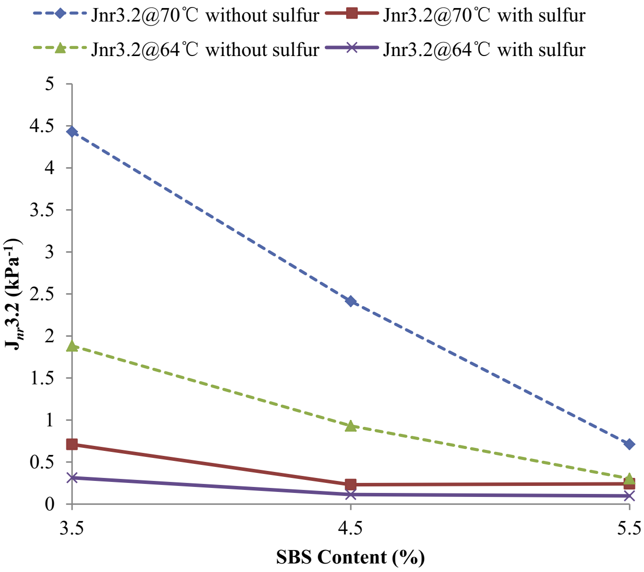

Fig. 3. Non-recoverable creep compliance results at 3.2 kPa.

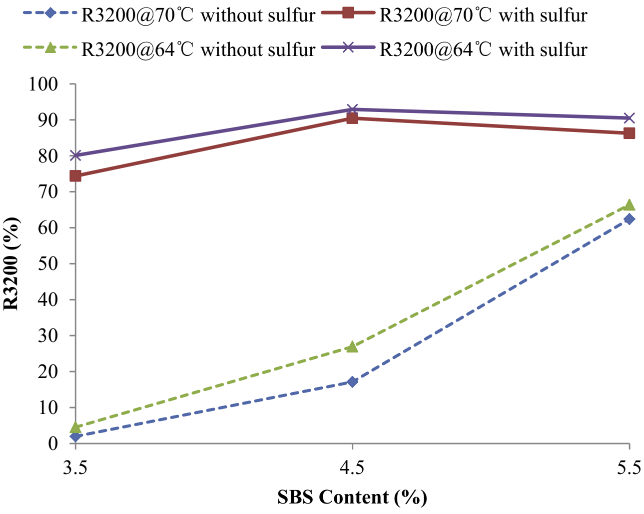

Fig. 4. Percent recovery at 3.2 kPa.

The effect of G_2 and G_3 on binder's recovery behavior from 2 s to 10 s is presented in Fig. 2. The smaller G_2 and larger G_3 favor the recovery and result in smaller strain.

(3) Calculate permanent strain (PS) using Eq. (10):

$$\begin{aligned}\text{Permanent strain, } \%(\text{PS}\%) = {} & 100\{\text{Measured strain} \\ & -\text{Calculated strain}\}@10\text{ s}\end{aligned} \tag{10}$$

4. Results and discussion

4.1. Effect of cross-linking agent

Cross-linking agent has been proved to improve storage stability of SBS modified asphalt, morphology of which was changed through observation of fluorescent microscopy [19].

In this study, SBS modified asphalt with and without cross-linking agent under 3.5%, 4.5%, 5.5% polymer content were investigated using MSCR test. Fig. 3 presents the J_{nr} results from

Table 2
Effect of cross-linking agent on stress sensitivity, 70 °C.

SBS content (%)		3.5	4.5	5.5
R_{diff} 70 °C	With sulfur	6	1	9
	Without sulfur	75	63	29
$J_{nr\text{-}diff}$ 70 °C	With sulfur	23	1	174
	Without sulfur	15	83	263

MSCR test. It is obvious that the J_{nr} value has significantly decreased due to the use of cross-linking agent, which implies that cross-linking agent can prominently improve high temperature properties of SBS modified asphalt. For example, J_{nr} 3.2 of 4.5% SBS modified asphalt reduced from 2.41 to 0.23 at 70 °C due to the use of cross-linking agent. Besides, J_{nr} 3.2 of control group show significant change with the increase of SBS content, while J_{nr} 3.2 of SBS modified binders containing cross-linking agent show small variations, which demonstrates that the use of cross-linking agent can reduce SBS amount while achieving similar high temperature properties in comparison with modified binders without cross-linking agent. With the increase of SBS content, the J_{nr} gap between modified binders with and without sulfur is reducing, which indicates that cross-linking agent is more effective for SBS modified asphalt at lower polymer content.

In addition, for the control group, the slope of J_{nr}-SBS content curve at 70 °C is greater than that of 64 °C, which indicates that the role of polymer is more pronounced at high temperature.

The MSCR percent recovery results are presented in Fig. 4. Obviously, the use of cross-linking agent has improved percent recovery of SBS modified asphalt significantly. This is also confirmed by D'Angelo that blends made without elemental sulfur cross-linker have poor recovery properties [8]. Besides, it can be seen from Fig. 4 that the percent recovery gap between binders with and without sulfur is reducing with the increase of SBS content, which indicates that the cross-linking agent is much more effective at lower SBS content.

When the cross-linking agent was not used, the increase of SBS content will benefit a lot to percent recovery results. However, if the cross-linking agent is used, the effect of variation of SBS content on percent recovery is not prominent. It should be noted that percent recovery of 5.5% SBS modified binder made with cross-linking agent is slightly less than that of 4.5% SBS modified binder, which is out of expectation. In addition, percent recovery results have shown little difference at 64 °C and 70 °C, especially for the blends using cross-linking agent.

Table 2 presents the stress sensitivity parameter $J_{nr\text{-}diff}$ and R_{diff}. It can be clearly seen that use of sulfur can significantly decrease the stress sensitivity. However, there is no clear relationship between stress sensitivity and SBS content. In addition, it can be found that $J_{nr\text{-}diff}$ and R_{diff} have shown contrary trend with the increase of SBS content for the control group without cross-linking agent.

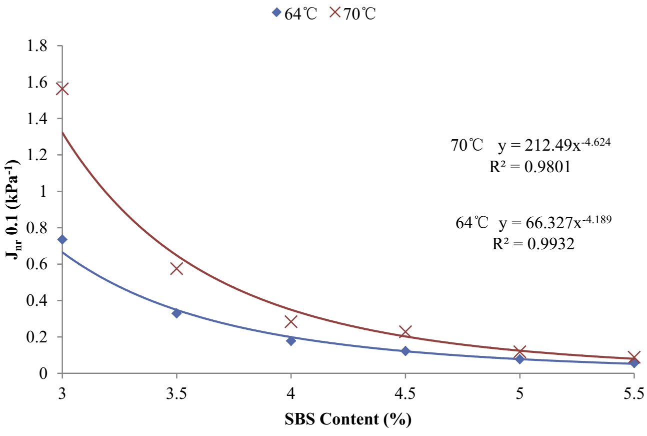

Fig. 5. Non-recoverable creep compliance results at 0.1 kPa.

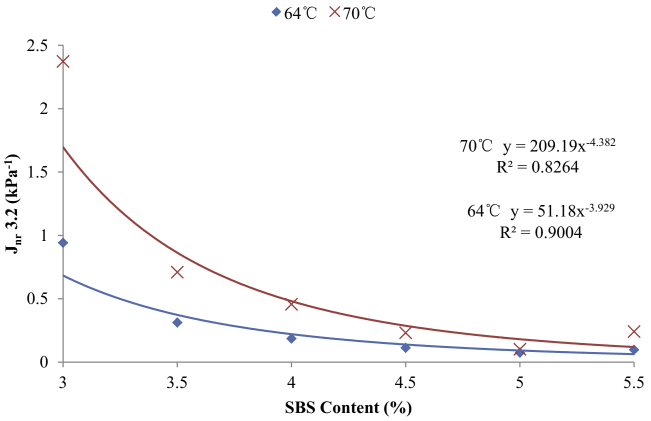

Fig. 6. Non-recoverable creep compliance results at 3.2 kPa.

Table 3
Linear SBS modified asphalt MSCR test results.

Test temperature	64 °C			70 °C		
Linear SBS content (%)	4.5	5	5.5	4.5	5	5.5
R100 (%)	73.0	88.4	86.7	74.5	89.9	89.1
R3200 (%)	74.6	88.8	87.1	74.2	89.1	87.9
J_{nr} 0.1 (kPa^{-1})	0.296	0.108	0.115	0.518	0.167	0.167
J_{nr} 3.2 (kPa^{-1})	0.287	0.110	0.118	0.539	0.182	0.190

In summary, cross-linking agent can prominently improve high temperature properties of SBS modified asphalt, especially at lower polymer content. Compared with modified binders without cross-linking agent, the use of cross-linking agent can reduce SBS amount while achieving similar high temperature properties. In addition, the use of cross-linking agent can significantly decrease the stress sensitivity.

4.2. Effect of SBS content

The change of SBS content influences properties of SBS modified asphalt due to variation of polymer dispersion and swelling. In this

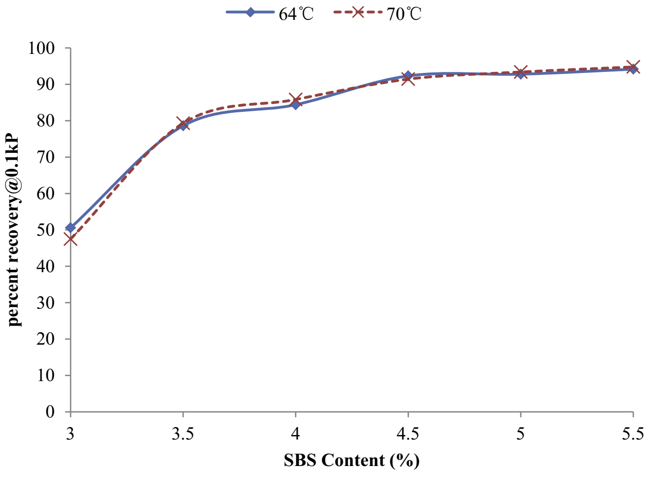

Fig. 7. Percent recovery at 0.1 kPa.

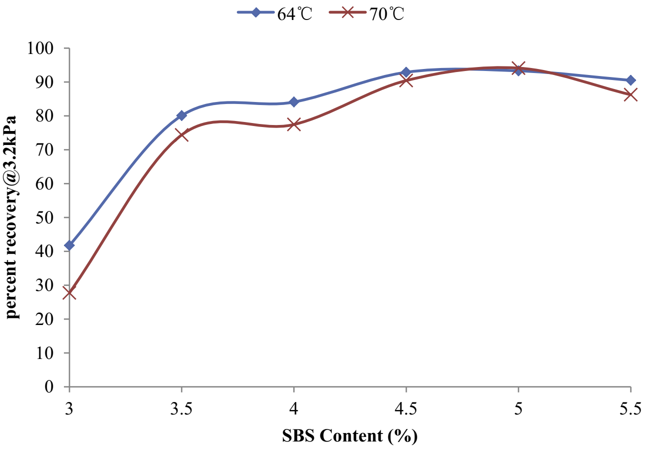

Fig. 8. Percent recovery at 3.2 kPa.

study, SBS content ranged from 3.0% to 5.5% with an interval of 0.5%. MSCR test was used to investigate the difference among modified binders at varying SBS content.

It can be seen from Figs. 5 and 6 that there is a power relationship between J_{nr} and SBS content. The fitting equation and R^2 are presented in the figures. J_{nr} show downward trend with the increase of SBS content, which manifests the improvement of high temperature properties. However, the slope of the fitting curve is decreasing with the increase of SBS content, which means J_{nr} is becoming less sensitive to the variation of SBS content at high value. In other word, the effect of increasing SBS content is more prominent for binders at lower SBS content.

Besides, with the increase of SBS content, the J_{nr} gap between 64 °C and 70 °C is reducing, which indicates that the J_{nr} parameter is becoming less sensitive to temperature at high SBS content.

It should be noted that the J_{nr} value of 5.5% SBS modified binder is greater than that of 5.0% SBS modified binder at 3.2 kPa stress level, which is out of expectation. However, when the stress level is 0.1 kPa, the test results conform to expectation. As a result, it is necessary to clarify whether MSCR is effective when polymer is at high content. Additional MSCR test were performed on linear SBS modified asphalt at 4.5%, 5.0%, 5.5% polymer content and test results are presented in Table 3. It can be found that the J_{nr} value of 5.5% linear SBS modified asphalt is slightly greater than that of 5.0% linear SBS modified asphalt. In this limited study, MSCR failed to distinguish 5.0% and 5.5% SBS modified asphalt. Therefore, MSCR test should be used with caution when characterizing modified asphalt with high polymer content.

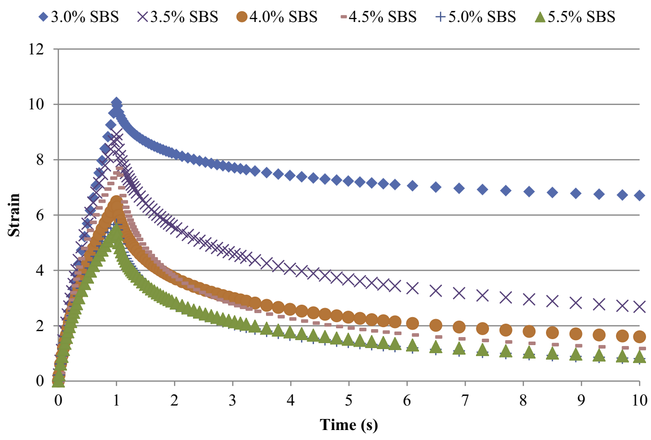

Fig. 9. The first creep and recovery cycle, 3.2 kPa, 70 °C for radial SBS modified binder.

Table 4
Effect of SBS content on stress sensitivity.

SBS content (%)		3	3.5	4	4.5	5	5.5
R_{diff} (%)	64 °C	17	−2	0	−1	−1	4
	70 °C	42	6	10	1	−1	9
$J_{nr\text{-}diff}$ (%)	64 °C	28	−5	4	−8	−3	73
	70 °C	52	23	61	1	−14	174

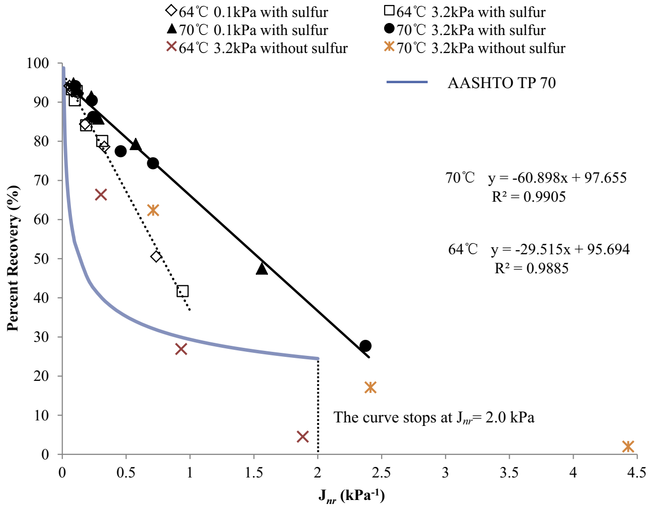

Fig. 10. Plot of percent recovery against J_{nr}.

Fig. 7 reveals that there is no significant difference between *R*100 tested at 64 °C and 70 °C. From Fig. 8, *R*3200 tested at 64 °C is a bit higher than that of 70 °C at lower SBS content, while the percent recovery gap between 64 °C and 70 °C is reducing with the increase of SBS content. On the whole, increased use of SBS will benefit percent recovery, which can be clearly observed in Fig. 9. However, the percent recovery growth is becoming slow with the increase of SBS content, which indicates that the effect of increasing polymer amount is much more prominent at lower SBS content. Similar to J_{nr}, percent recovery of 5.5% SBS modified asphalt is less than that of 5.0% SBS modified asphalt at 3.2 kPa stress level.

From Table 4, it can be found that J_{nr} and percent recovery show much more stress sensitive at 70 °C. There is no clear relationship between SBS content and stress sensitivity. In this study, when the SBS content is around 4.5% and 5.0%, stress sensitivity of both J_{nr} and percent recovery is not prominent.

In summary, with the increase of SBS content, high temperature properties were improved. The effect of increasing SBS content is more prominent for binders at lower SBS content. MSCR test failed to distinguish 5.0% and 5.5% SBS modified asphalt in this study, therefore, MSCR test should be used with caution when characterizing modified asphalt with high polymer content. At high SBS content, both J_{nr} and percent recovery show no significant difference between 64 °C and 70 °C, which demonstrates that MSCR parameters are becoming less sensitive to temperature variation. In addition, there is no clear relationship between SBS content and stress sensitivity. But the stress sensitivity of MSCR parameter will become prominent at elevated test temperature.

4.3. Relationship between J_{nr} and percent recovery

In AASHTO TP 70, there is a curve of J_{nr} 3.2 versus percent recovery as shown in Fig. 10 to determine whether an elastomeric-modified asphalt binder have sufficient delayed elastic response. Plot data from 3.2 kPa stress and compare to the curve given by AASHTO TP 70. If the data point is above this curve, this binder is considered to be modified with an acceptable elastomeric polymer [13]. In this study, percent recovery and J_{nr} of binders modified from 3.0% to 5.5% SBS with sulfur and binders without sulfur are presented in Fig. 10. It is obvious that, data points from SBS modified binders with sulfur at 3.2 kPa stress are above the curve. However, when sulfur was not used, only the 5.5% SBS modified binders are above the curve. In addition, for binders with sulfur, data points from 70 °C seem to distribute around the same line regardless of the stress level and data points from 64 °C seem to distribute around the other line. To confirm this, hypothesis test was performed to identify whether the relationship between percent recovery and J_{nr} is dependent on stress level. For each test temperature, linear regression was applied to data retrieved at 0.1 kPa and 3.2 kPa, respectively and the resulted two lines were compared whether they are different by using hypothesis test [20,21]. The specified procedure is shown as follows:

(1) Hypothesis: H_0: the two lines are same. H_a: the two lines are different.
(2) Fit each data set to obtain sum of squares for error $SSE(F) = SSE_1 + SSE_2$, where SSE_1 represents sum of squares for error from regression line 1 and SSE_2 represents sum of squares for error from regression line 2; the total degrees of freedom $df(F) = df_1 + df_2$.
(3) Fit the combined data set under the H_0 hypothesis to obtain sum of squares for error $SSE(R)$ and degrees of freedom $df(R)$.
(4) Calculate the F^* statistic using the following equation:

$$F^* = \frac{SSE(R) - SSE(F)}{df(R) - df(F)} \div \frac{SSE(F)}{df(F)} \qquad (11)$$

(5) Obtain the p-value using FDIST function in MS EXCEL:

$$p\text{-value} = \text{FDIST}(F^*, df_a, df_b) \qquad (12)$$

where df_a equals $df(R) - df(F)$ and df_b equals $df(F)$.

(6) Reject H_0 if p-value $\leqslant \alpha$ to conclude that the two lines are different; otherwise accept H_0 hypothesis, where α is the value of Type I error and the traditional value is 0.05.

Table 5
Hypothesis test results.

Test temperature (°C)	SSE1	SSE2	SSE(*F*)	SSE(*R*)	F^*	*p*-Value
64	12.356	12.682	25.037	31.661	1.058	0.391
70	8.050	31.392	39.441	54.253	1.502	0.279

The hypothesis test results are presented in Table 5. For both 64 °C and 70 °C, as p-value is greater than 0.05, the regression lines at 0.1 kPa and 3.2 kPa are statistically the same. Therefore, the relationship between percent recovery and J_{nr} is not dependent on stress level, but such relationship is concerned with test temperature. The combined regression line is presented in Fig. 10 for each test temperature.

4.4. Nonlinear viscoelastic characterization

In order to investigate the effect of cross-linking agent on nonlinear viscoelastic parameters G_1, G_2, G_3 and PS%, MSCR curve at 3.2 kPa for modified asphalt at three SBS contents with and without sulfur were characterized and the results are presented in Table 6. For modified asphalt without sulfur, G_2 decreases and G_3

Table 7
Effect of SBS content on nonlinear viscoelastic parameters and PS%.

Test temperature (°C)	SBS content (%)	G_1	G_2	G_3	PS%
64	3	1.128	0.335	0.817	7.727
	3.5	0.999	−0.023	0.987	3.703
	4	1.005	0.033	0.933	0.979
	4.5	0.968	0.000	0.912	−2.035
	5	1.029	−0.011	1.006	−2.043
	5.5	1.098	0.107	1.035	−5.174
70	3	1.162	0.729	0.477	11.651
	3.5	1.004	0.142	0.848	9.538
	4	1.024	0.231	0.794	1.695
	4.5	0.886	0.048	0.800	1.456
	5	0.938	0.002	0.862	−0.413
	5.5	1.108	0.244	0.984	−10.463

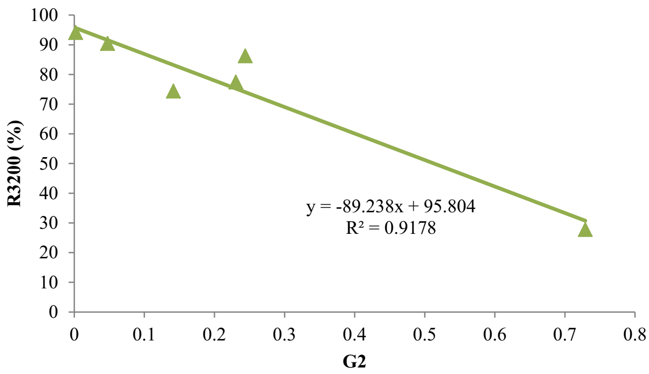

Fig. 11. Plot of $R3200$ against G_2, 70 °C.

Table 6
Effect of cross-linking agent on nonlinear parameters and PS%.

Test temperature (°C)	Sulfur content (%)	SBS content (%)	G_1	G_2	G_3	PS%
64	0	3.5	1.074	0.815	0.241	0.640
		4.5	1.115	0.558	0.589	2.657
		5.5	1.166	0.345	0.906	−2.406
	0.15	3.5	0.999	−0.023	0.987	3.703
		4.5	0.968	0.000	0.912	−2.035
		5.5	1.098	0.107	1.035	−5.174
70	0	3.5	1.099	0.967	0.112	1.250
		4.5	1.280	0.985	0.354	4.110
		5.5	1.341	0.634	0.890	−6.740
	0.15	3.5	1.004	0.142	0.848	9.538
		4.5	0.886	0.048	0.800	1.456
		5.5	1.108	0.244	0.984	−10.463

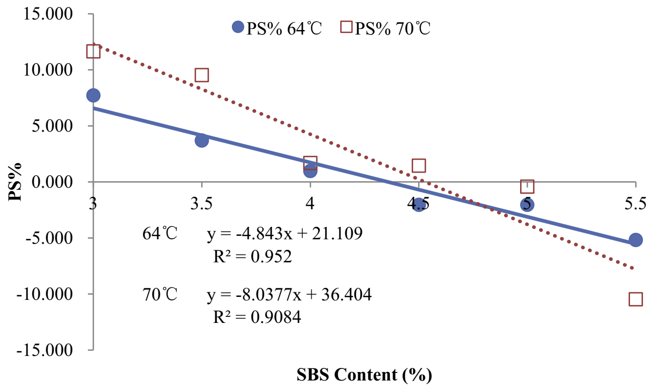

Fig. 12. Plot of PS% against SBS content.

increases with the increase of SBS content, which is beneficial to the recovery after stress is removed and indicates that parameter G_2 and G_3 can be used to characterize the recovery behavior for binders without cross-linking agent in this study. However, for binders with sulfur, there is no clear relationship between SBS content and G_2, G_3. Meanwhile G_2 of cross-linked binders are smaller than that of binders without sulfur, and G_3 of cross-linked binders are larger, which demonstrates that the use of sulfur can significantly improve the recovery behavior. As to PS%, for binders without sulfur, PS of 4.5% SBS is larger than that of 3.5% SBS at both 64 °C and 70 °C. When the percentage of SBS increases to 5.5%, the PS value turns negative, which means the calculated strain is larger than measured strain at 10 s. As to the effect of sulfur on PS, the cross-linking effect did decrease the PS value when the percentage of SBS is at 4.5% and 5.5%, while increasing the PS value for 3.5% SBS. The PS analysis results are not consistent with the above J_{nr} analysis. In this limited study, it is deduced that PS may not be appropriate for identifying the existence of cross-linking agent.

MSCR curve of modified binders with sulfur at varying SBS amounts were characterized for both 64 °C and 70 °C test temperature. For MSCR curve under 64 °C, G_2 is almost zero when the percentage of SBS ranges from 3.5% to 5.0%, which could be caused by fitting errors. Thus, it is considered that there is no significant difference between G_2 derived at 64 °C for binders with 3.5–5.0% SBS in this study. However, 3% SBS, 5.5% SBS have shown difference in G_2 compared to that of 3.5–5.0% SBS. Due to the lack of polymer amount, binder with 3% SBS may not form cross-linking structure thus exhibiting smaller percent recovery (R3200) and larger G_2 than the others. As to 5.5% SBS modified asphalt, 0.15% sulfur may not be sufficient to support the cross-linking reaction, which may cause the decrease of R3200 (Fig. 8) and increase of G_2 (Table 7).

For MSCR under 70 °C, there is difference for G_2 between binders at varying SBS contents, but the changing trend is not clear. However, the correlation analysis between G_2, G_3 and R3200 was carried out. It was found that there is strong linear relationship between G_2 and R3200 at 70 °C (Fig. 11), while the relationship between G_2 and R3200 at 64, the relationship between G_3 and R3200 at 64 °C and 70 °C are not that clear. Based on this and the above sulfur effect analysis, it can be concluded that the nonlinear parameter G_2 can be used to identify the existence of cross-linking agent and characterize the elastic response of SBS modified binder.

Fig. 12 presents the relationship between PS% and SBS content. When SBS content is above 4.5%, the derived PS value turned to be negative, which indicates that PS% may not be appropriate for highly modified binder. However, the regression analysis between PS% and SBS content at 64 °C and 70 °C were carried out and the regression functions and R^2 are presented in Fig. 12. It is obvious that PS% decreases linearly with the increase of SBS content. The parameter PS% shows potentiality in evaluating modified binder's ability to resist permanent deformation. However, the methodology should be further investigated to confirm the applicability for highly modified asphalt.

5. Conclusions and further works

This study investigates the effect of cross-linking agent and SBS content on SBS modified asphalt using MSCR test. The following conclusions can be drawn from the test results and data analysis:

(1) Cross-linking agent can prominently improve high temperature properties of SBS modified asphalt, especially at lower polymer content. The use of cross-linking agent can reduce SBS amount without degrading high temperature performance. In addition, cross-linking agent can significantly decrease the stress sensitivity of SBS modified binders.
(2) With the increase of SBS content, high temperature properties were improved. The effect of increasing SBS content is more prominent for binders at lower SBS content. MSCR test failed to distinguish 5.0% and 5.5% SBS modified asphalt in this limited study. At high SBS content, MSCR parameters become less sensitive to temperature variation. In addition, there is no clear relationship between SBS content and stress sensitivity. But the stress sensitivity of MSCR parameter will become prominent at elevated test temperature.
(3) All binders modified from 3.0% to 5.5% SBS with sulfur have sufficient delayed elastic response according to AASHTO TP 70. When sulfur was not used, only high dosage SBS modified binders are considered to be modified with an acceptable elastomeric polymer in this study.
(4) There is strong linear relationship between percent recovery and J_{nr} and such relationship is not dependent on stress level, but is concerned with test temperature.
(5) The nonlinear parameter G_2 derived from MSCR curve can be used to identify the existence of cross-linking agent and characterize the elastic response of SBS modified binder. The parameter PS% shows potentiality in evaluating modified binder's ability to resist permanent deformation.

Further works are as follows:

(1) Applicability of MSCR test for highly modified asphalt should be confirmed with extending base binders.
(2) PS% used in this study should be further investigated to confirm the applicability for highly modified asphalt.
(3) Effect of sulfur content shall be investigated to identify the optimal dosage.

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