

Experimental characterization of viscoelastic behaviors, microstructure and thermal stability of CR/SBS modified asphalt with TOR

Ren, Shisong; Liu, Xueyan; Li, Mingliang; Fan, Weiyu; Xu, Jian; Erkens, Sandra

DOI

[10.1016/j.conbuildmat.2020.120524](https://doi.org/10.1016/j.conbuildmat.2020.120524)

Publication date

2020

Document Version

Final published version

Published in

Construction and Building Materials

Citation (APA)

Ren, S., Liu, X., Li, M., Fan, W., Xu, J., & Erkens, S. (2020). Experimental characterization of viscoelastic behaviors, microstructure and thermal stability of CR/SBS modified asphalt with TOR. *Construction and Building Materials*, 261, 1-17. Article 120524. <https://doi.org/10.1016/j.conbuildmat.2020.120524>

Important note

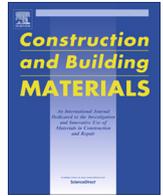
To cite this publication, please use the final published version (if applicable).
Please check the document version above.

Copyright

Other than for strictly personal use, it is not permitted to download, forward or distribute the text or part of it, without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license such as Creative Commons.

Takedown policy

Please contact us and provide details if you believe this document breaches copyrights.
We will remove access to the work immediately and investigate your claim.



Experimental characterization of viscoelastic behaviors, microstructure and thermal stability of CR/SBS modified asphalt with TOR



Shisong Ren^{a,*}, Xueyan Liu^a, Mingliang Li^b, Weiyu Fan^c, Jian Xu^b, Sandra Erkens^a

^a Section of Pavement Engineering, Faculty of Civil Engineering & Geosciences, Delft University of Technology, Stevinweg 1, 2628 CN Delft, The Netherlands

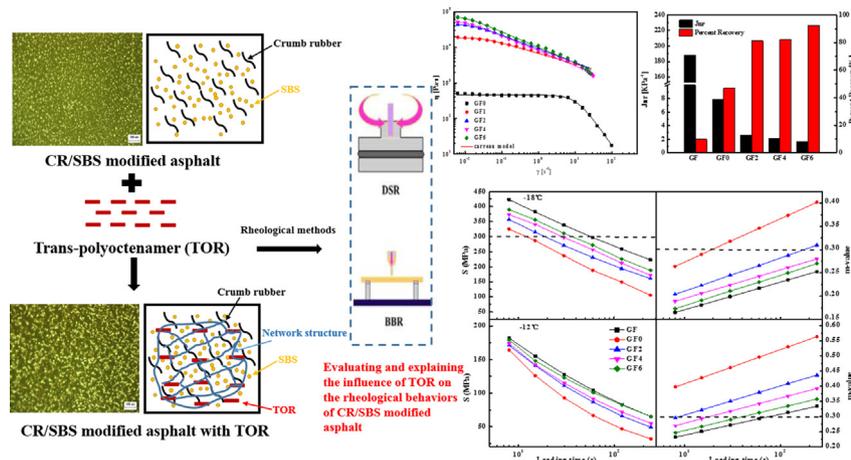
^b Road Research Center, Research Institute of Highway Ministry of Transport, Xitucheng Road No. 8, Beijing, PR China

^c State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Qingdao, Shandong Province, PR China

HIGHLIGHTS

- TOR improves the rutting resistance and temperature sensitivity of CR/SBS modified asphalts.
- The flow behavior of CR/SBS modified asphalt turns into non-Newtonian fluid with TOR dosage increasing.
- High asphaltene content is beneficial for improving the rheological properties effect of TOR.
- TOR has a crosslinking effect on improving viscoelastic behaviors and thermal stability of CR/SBS modified asphalt.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 23 August 2019

Received in revised form 6 August 2020

Accepted 9 August 2020

Keywords:

Trans-polyoctenamer (TOR)

CR/SBS modified asphalt

Viscoelastic behaviors

FM

FT-IR

TG analysis

ABSTRACT

It is well known that crumb rubber (CR) and styrene-butadienestyrene (SBS) composite modified asphalt has better rheological and engineering performance. However, it always presents very poor compatibility and storage stability. Meanwhile, Trans-polyoctenamer (TOR) can effectively improve the compatibility and thermal stability of rubber asphalt. Thus, this study aims to investigate the effectiveness of TOR on rheological properties, microstructure and thermal stability of CR/SBS modified asphalt. The results show that TOR has a significant influence on strengthening anti-rutting and temperature sensitivity of CR/SBS modified asphalt. However, TOR has a slightly negative influence on the anti-cracking ability for CR/SBS modified asphalt, which still maintains the critical low temperature requirement. Furthermore, TOR could be able to promote the conformation of cross-linked structure between polymer and asphalt, resulting in a significant enhancement in rheological properties and thermal stability of CR/SBS modified asphalt. Lastly, the effects of TOR on viscoelastic performance for modified asphalt markedly depend on the component of neat asphalt, and high asphaltene content is beneficial for improving the rheological behavior effects of TOR.

© 2020 The Author(s). Published by Elsevier Ltd. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

* Corresponding author.

E-mail addresses: Shisong.Ren@tudelft.nl (S. Ren), x.liu@tudelft.nl (X. Liu), ml.li@rioh.cn (M. Li), j.xu@rioh.cn (J. Xu), S.M.J.G.Erkens@tudelft.nl (S. Erkens).

1. Introduction

Asphalt concrete, due to the viscoelastic nature in which it distributes load and sustains significant plastic deformation, has been widely used for pavement and waterproofing roof construction [1,2]. Unfortunately, the asphalt concrete pavement is easy to suffer some distresses during its service life, such as rutting and thermal cracking [3]. Therefore, polymer modified asphalt is extensively used to enhance pavement performance and extend duration pavement service life, for instance crumb rubber powder (CR), styrene-butadienestyrene copolymer (SBS) as well as some other polymers [1,4–6].

SBS and CR are the most common polymers utilized for asphalt modification in order to enhance various properties of asphalt. After being dispersed in asphalt uniformly, SBS copolymer would improve the elastic behaviors of asphalt because of its physical cross-linked action on forming three-dimensional networks [4,7–9]. Nevertheless, some weaken exist for SBS modified asphalt, for example, high production cost and dissatisfactory workability [10]. Recently, crumb rubber modified asphalt (CRMA) is extensively studied and applied in asphalt pavement for decades [11–14]. The addition of crumb rubber into asphalt is an efficient method for environmental protection and low cost of asphalt road. Meanwhile, previous studies have shown that CR can enhance the mechanical and rheological properties of asphalt by reducing fatigue and low-temperature cracking distinctly [11,15–18]. Nevertheless, the high viscosity and limited high-temperature performance of CRMA result in higher energy consumption and restrict its wide use [10,19,20].

Based on an economic, environmental and high-performance point of view, researchers incorporated SBS copolymer in CRMA and investigated the mechanical properties, rheological behaviors, compatibility, storage stability and modification mechanism for CR/SBS modified asphalt. It was well recognized that CR/SBS modified asphalts showed significant improvement of viscoelastic behaviors, rutting resistance performance as well as temperature sensitivity [10,19,21]. However, CR/SBS modified asphalt also had some drawbacks, especially in term of its storage stability and construction workability. Liang et al. [10] hold the view that CR/SBS modified asphalts appeared clear and inevitable phase separation after being stored for a specified time. Therefore, CR/SBS modified asphalts must be produced and operated rapidly because of poor storage stability. Similarly, the poor storage stability characteristic of CRMA was also reported [19,22,23]. The compositional hetero-

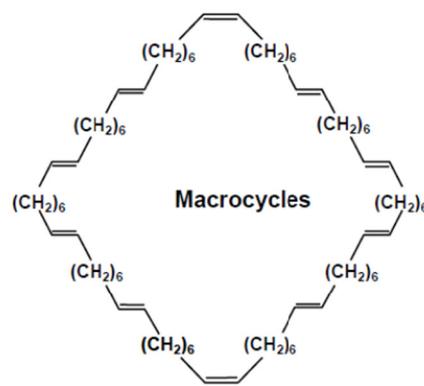
geneous dispersion and discrepancy of density are the main reasons for the separation of crumb rubber particle in asphalt binders. At present, a number of ways are designed to improve storage stability property for crumb rubber modified asphalt. One way is to increase degradation and desulfurization level of crumb rubber, another way is to add chemical compounds promoting interactions between crumb rubber and asphalt [23,24–28]. TOR is commonly used to be a reactant and compatibilizer of crumb rubber modified asphalt, the physical form and molecular structure of which are shown in Fig. 1. TOR is a solid and opaque polymer, which can chemically crosslink the sulfur on the surface of crumb rubber to the sulfur in asphalt and form three dimensional networks [25,29–31]. Obviously, the crosslinking effect of TOR is beneficial for improving the viscoelastic and pavement performance of CR modified asphalt.

Many previous papers studied the influence of TOR on the properties and modification mechanism of CRMA. Xie et al. [32] reported that TOR can enhance rutting resistance ability and decrease phase separation of asphalt rubber binders. Other researchers have come to similar conclusions [33–36]. TOR interacts with crumb rubber, improving more swelling of rubber particles. Liu et al. [37] investigated the rheological modification mechanism of CRMA with TOR additive and the results demonstrated that TOR not only improved mechanical performance but also increased workability and compatibility of CRMA. Meanwhile, this study [37] verified that there was a complex chemical reaction between TOR and CRMA, contributed to improvement in viscoelastic properties as well as storage stability of CRMA.

Even though it is evident that TOR can improve rheological properties, storage stability together with the workability of crumb rubber asphalt, the impacts of TOR on viscoelastic behaviors and morphology for CR/SBS modified asphalts have not been reported yet. It is well recognized that composite modified asphalt is a key method to solve the performance imbalance of single polymer modified asphalt [1,2]. Moreover, CR/SBS modified asphalt has been proved to be most commonly used in asphalt road construction and has excellent pavement performance [10,19]. Therefore, it is necessary to assess the effects of TOR on properties and modification mechanism for CR/SBS modified asphalt, which will benefit to the engineering practice of using TOR technology in CR/SBS modification technology and promote its wider application. The purpose of this study focuses on evaluating the influence of TOR on the rheological behaviors and morphology for CR/SBS modified asphalt. To reach the objective, the effects of TOR on the viscoelas-



(a)



(b)

Fig. 1. The physical form and molecular structure of TOR particles.

tic properties, temperature sensitivity, flow behavior, low-temperature performance, creep recovery characteristic, microstructure as well as thermal storage stability for CR/SBS modified asphalts are evaluated by using DSR, BBR, FM, FTIR and TGA tests.

2. Experiment and methods

2.1. Raw materials

Neat asphalt materials (coded as GF and K) with the penetration grade of 60/80, which was obtained from PetroChina Co., Ltd. were used for modification. The conventional properties and chemical components of two base bitumen are displayed in Table 1. As can be seen, although the penetration grade of two asphalts is the same, their chemical composition is different significantly, especially for asphaltenes content and colloidal stability index. Compared to asphalt GF, asphalt K possesses the lower asphaltene dosage and better colloidal stability.

40-mesh crumb rubber powder was prepared from waste truck tires and purchased from Shandong, China. Before preparation of modified asphalt, crumb rubber powders were placed in a drying oven to ensure moisture content being less than 0.1%. Styrene butadiene styrene copolymer modifier (SBS) was supplied from Xinjiang, China. Trans-polyoctenamer (TOR) spherical additive was provided by EVONIK Company and its properties are shown in Table 2.

2.2. Preparation of asphalt samples

Based on our previous researches [4,11,29] and cost-effectiveness of modified asphalt, the dosage of crumb rubber and SBS copolymer in this study is determined as 10 wt% and 3 wt%, respectively. The base asphalt was firstly heated to 180 °C, and then 10 wt% of crumb rubber was incorporated into base asphalt. The CR modified asphalt was stirred under the speed of 1000 rpm for 2 h at 200 °C. Secondly, the 3.0 wt% of SBS was mixed in CR modified asphalt for 30 min at 185 °C, 4000 rpm to prepare CR/SBS modified asphalt. Thirdly, a certain amount of

TOR was added to above CR/SBS modified asphalt to reach a dosage of 0 wt%, 2.0 wt%, 4.0 wt% and 6.0 wt% (by weight of CR/SBS modified asphalt), respectively. Finally, CR/SBS modified asphalts with various TOR dosages were obtained after being mixed for 2 h at 180 °C, 1000 rpm. For comparing various asphalts easily, CR/SBS modified asphalt GF with various TOR dosages are recorded as GF0, GF2, GF4 and GF6 respectively and modified asphalt K are coded as K0, K2, K4 and K6.

2.3. Characterization methods

In this study, rheological tests, involving temperature and frequency sweep test, MSCR together with steady-state flow experiments, were conducted using a dynamic shear rheometer (DSR) with a plate geometry (25 mm diameters, 1 mm gap) to evaluate the influence of TOR on the viscoelastic properties' evaluation for CR/SBS modified asphalt. Furthermore, in order to obtain reliable results, tests in all modes were measured on two replicates of asphalt samples.

On the one hand, asphalt samples underwent temperature sweep tests at 10 rad/s and increasing temperature from 0 °C to 40 °C for fatigue property as well as from 48 °C to 84 °C for rutting property. Meanwhile, 60 °C frequency sweep tests for modified asphalts were conducted using DSR with the frequency increasing from 10^{-1} rad/s to 10^2 rad/s. The association between rheological parameters with testing temperature and frequency can be evaluated [42]. Besides, the viscoelastic properties, failure temperature and temperature sensibility for CR/SBS modified asphalts with various TOR dosages can also be calculated and evaluated.

To further determine the influence of TOR additive on the creep recovery capability for CR/SBS modified asphalts, MSCR test was executed on RTFO aged asphalts with two stress levels of 0.1 kPa and 3.2 kPa at 60 °C, respectively [43]. In addition, 60 °C steady-state flow tests were carried out using DSR to measure the viscous flow behavior of asphalt binders. The shear rate region of flow test was from 10^{-3} s $^{-1}$ to 10^2 s $^{-1}$. Meanwhile, Bending Beam Rheometer (BBR) measurement was performed to determine low-temperature rheological properties for all RTFO-PAV aged asphalt samples at -12 and -18 °C according to AASHTO M320 [44]. And then two parameters the creep stiffness (S) and rate of relaxation (m-value) were obtained.

Microstructure changes for CR/SBS modified asphalts with various TOR contents were directly observed through Olympus BX53 Fluorescence Microscope (FM). Detailed preparation and testing process of samples for observation were described in our previous works [10,11,30]. The thin glass slides with asphalt samples were observed under the microscope with a magnification of 100x at room temperature.

In order to investigate the effect of TOR on the storage stability of CR/SBS modified asphalt, each modified asphalt was subjected the thermal storage test at 163 °C for 48 h. The detailed testing method can be seen in our previous papers [46–47]. After thermal storage, the softening point difference between first and third parts of the tube was tested to evaluate the storage stability of modified asphalts.

Fourier Transform Infrared Spectrometer (FTIR) (Cary 630 FTIR Microscope) was used to explore the variation in the functional groups of base and modified asphalt with the wavenumber changing from 400 cm $^{-1}$ to 4000 cm $^{-1}$. Meanwhile, Thermogravimetric Analysis (TGA) method was applied to assess the thermal stability of the base and modified asphalt from room temperature to 800 °C at a heating speed of 10 °C/min under nitrogen N $_2$ air flow of 20 ml/min [46].

Table 1
The conventional properties and chemical compositions of neat asphalts.

Items	Results		Specifications
	GF	K	
Penetration (25 °C, 0.1 mm)	71	68	ASTM D5[38]
Softening point (R&B, °C)	49.2	48.6	ASTM D36[39]
Ductility (15 °C, cm)	>100	>100	ASTM D113[40]
Saturates (wt%)	23.4	27.1	ASTM D4124[41]
Aromatics (wt%)	41.2	32.9	
Resins (wt%)	26.8	39.1	
Asphaltenes (wt%)	8.6	0.9	
Colloidal stability index*	2.13	2.57	

* Colloidal stability index = (Aromatic + Resin)/(Saturate + Asphaltene).

Table 2
The properties of Trans-polyoctenamer (TOR).

Items	Results
Crystallinity@23 °C (%)	30
Melting point (°C)	54.2
Thermal decomposition (°C)	275
Mooney viscosity@100 °C (M)	5.5
Cis/trans ratio	20:80
Molecular weight (Da)	75,000

3. Results and discussion

3.1. Effect of TOR on conventional properties

The effects of TOR on the conventional properties of CR/SBS modified asphalt are shown in Fig. 2, including penetration, softening point as well as 5°C ductility. For both asphalt GF and K, the penetration of base asphalt decreases, while both softening point and ductility values increase when CR and SBS are added. That is to say, CR and SBS can effectively improve the high and low temperature properties of asphalt simultaneously. Meanwhile, with the addition of TOR, the softening point of CR/SBS modified asphalt increases markedly and the improvement is evident when the TOR concentration is more than 2.0 wt%. The results indicate that TOR can significantly improve the high temperature performance of CR/SBS modified asphalt, which is related to the formation of network structure [11,29]. And this result also can be evidenced by the decline of penetration. However, the addition of TOR would decrease the ductility of CR/SBS modified asphalt, which means that TOR has an adverse effect on the low-temperature performance of CR/SBS modified asphalt. Therefore, to balance the high and low temperature properties of modified asphalt, the TOR dosage should be selected reasonably.

3.2. Effect of TOR on temperature sensitivity

The temperature sensibility properties for asphalt binder could reflect the long-term performance of asphalt pavement. In the study, the complex modulus index G^* obtained from temperature sweep tests using DSR was preferred to investigate the impact of TOR on the temperature sensitivity of CR/SBS modified asphalt.

Fig. 3 presents the relationship between $\lg G^*$ and temperature of neat asphalt and CR/SBS modified asphalts. As mentioned before, the complex modulus index G^* of all asphalt binders were tested from 48 °C to 84 °C using DSR. At least two replicates were measured for all asphalt blends at a fixed temperature. It can be seen that $\lg G^*$ of asphalt samples drop dramatically with the increment of test temperature, showing a reduction of total resistance to deformation for asphalt binders. This may be attributed to the transition of the macro-molecular chain and viscous-elastic properties in asphalt, which could be explained using the free volume theory [44]. Thus, the temperature sensitivity is important to determine the geographical coverage for using asphalt. In this section, equations of the relation between $\lg G^*$ and $\lg T$ for all asphalt samples were reached through a mathematical linear curve fitting. Besides, the parameters values for all regression lines, including absolute slope, intercept and R^2 , are presented in Table 3. Obviously, the asphalt binders with lower absolute slope value would be more insensitivity and stable to temperature. A good linear relationship can be observed between $\lg G^*$ and $\lg T$ according to the coefficients of determinations (R^2) of these linear equations are all over 0.99. As expected, the absolute slope values of liner equations for all modified asphalts are larger in comparison with neat asphalt signally, which means CR and SBS are both beneficial to enhance temperature sensitivity.

In terms of impacts of TOR on the temperature sensitivity for CR/SBS modified asphalts, absolute slope value of CR/SBS modified asphalt declines gradually with an increment of TOR content, indicating TOR can weaken temperature sensitivity of CR/SBS modified asphalt effectively. Additionally, the improvement level of TOR on temperature insensitivity for CR/SBS modified asphalts is also dependent on the asphalt component. The difference in absolute slope values among CR/SBS modified asphalt GF is more obvious in comparison with asphalt K because of variant chemical composition and oil source for neat asphalt, showing the beneficial effect

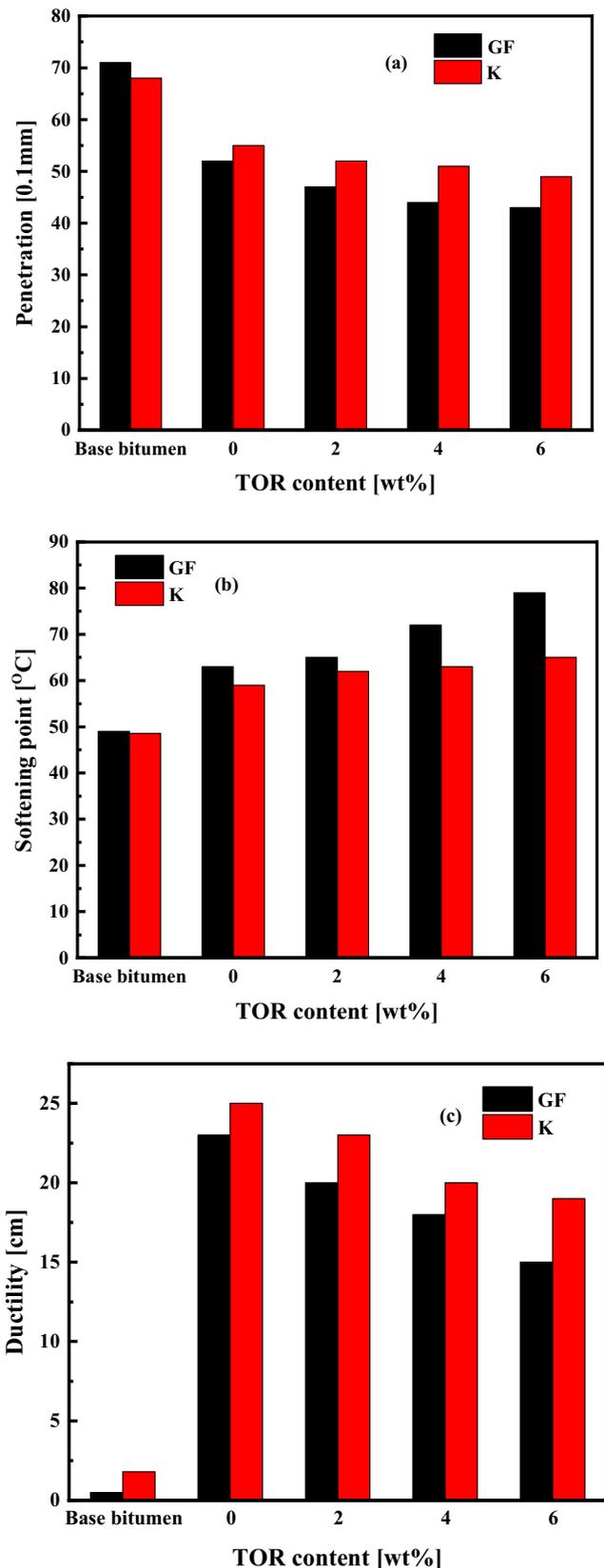


Fig. 2. Influence of TOR on the conventional properties of CR/SBS modified asphalt.

of TOR on weakening temperature sensitivity of CR/SBS modified asphalts are more remarkable for asphalt GF. Furthermore, effects of TOR on improving temperature sensitivity performance among

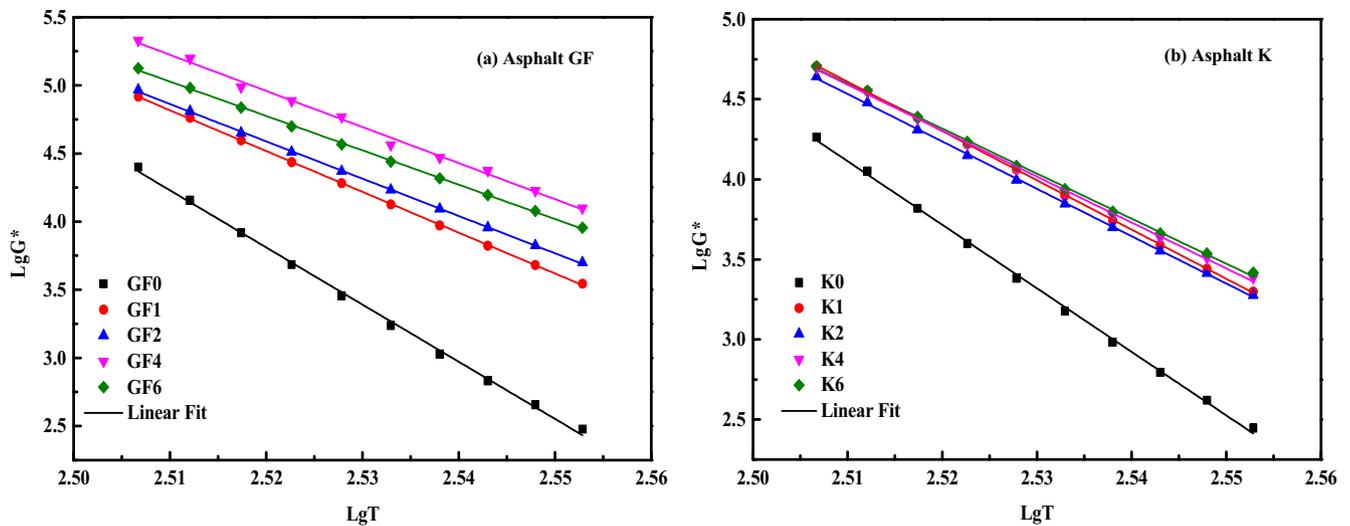


Fig. 3. Relationship between IgG^* and temperature of unmodified asphalt and CR/SBS modified asphalt with various TOR contents.

Table 3

Parameter values for the regression lines in Fig. 3.

	TOR contents (wt%)				
	Neat asphalt	0	2	4	6
Asphalt GF					
Absolute slope	41.946	29.944	27.387	26.495	25.216
Intercept	109.513	79.976	73.604	71.727	68.319
R^2	0.998	0.999	0.999	0.995	0.999
Asphalt K					
Absolute slope	39.679	30.755	29.585	28.689	28.131
Intercept	103.708	81.803	78.790	76.600	72.207
R^2	0.999	0.999	0.999	0.999	0.999

modified asphalt GF is more obvious and distinguishable than asphalt K, which also could be reflected by analyzing other rheological properties of CR/SBS modified asphalts with various TOR contents.

3.3. Effect of TOR on viscoelastic properties

In regard to CR/SBS modified asphalts with various TOR dosages, characterization in linear viscoelasticity is an efficient method to assess the influence of TOR on the viscoelastic behaviors and mechanical performance. For the sake of achieving this goal, temperature and frequency sweep tests are employed in linear viscoelastic range, respectively. Fig. 4 shows the influence of TOR on elastic modulus G' and viscous modulus G'' against temperature for CR/SBS modified asphalts under different temperatures from 48 °C to 84 °C.

As can be seen in Fig. 4, storage modulus G' always exhibits lower value than loss modulus G'' in the temperature regions, regardless of base asphalt and CR/SBS modified asphalts. It indicates that the main rheological property of the asphalt sample is universally dominated by viscous behavior [47]. With increasing of testing temperature, G' and G'' of asphalts both show declining trend smoothly, which is attributed to the changes of asphalts in internal structure. It should be noticed that, for all modified asphalt samples, the value of G' drops significantly than G'' as the increase of testing temperature, especially at high temperature, which is consistent with typical rheological behaviors of asphalt [47]. Meanwhile, compared with neat asphalt, CR/SBS modified asphalt presents higher G' and G'' obviously, which is contributed to both elastic and viscous characteristics of asphalt simultaneously. The

effects of CR and SBS on the viscoelastic behaviors and mechanical properties of asphalt have been studied already by many researchers through previous papers [10,19]. However, there are few articles have been published to study the effects of TOR on the viscoelastic behaviors for CR/SBS modified asphalts. It is clear that the TOR can dramatically increase storage and loss modulus of CR/SBS modified asphalt, which indicates that the TOR not only can increase viscosity, but also enhance the elasticity for CR/SBS modified asphalt. Obviously, TOR addition is beneficial to strengthen high-temperature rheological behaviors. Despite the improvement on modification mechanism of TOR in CR/SBS modified asphalt is still under discussion, obtained results have mainly resulted from the formation of a three-dimensional network between modifiers [34–36]. Liu et al. [37] evidenced that there were spatial cross-linked structures between neat asphalt and crumb rubber after adding TOR. TOR can vulcanize and chemically crosslink the sulfur on the surface of the CR to the sulfur in the asphalt, which changes the composite material structures tremendously and contributes to the rheological behaviors of CR/SBS modified asphalts efficaciously.

Moreover, it can be found that CR/SBS modified asphalt presents a remarkable difference in terms of an increasing trend in G' and G'' as the increase of TOR concentration. It is clear that the increasing trend is more evident for asphalt GF with higher asphaltene content, while less outstanding for asphalt K containing lower asphaltene content. This comparison shows that a stronger reaction exists between TOR and modified asphalt GF for the same TOR dosage, which further verifies the functional mechanism of TOR. In a word, the effects of TOR on the viscoelastic properties for CR/SBS modified asphalt also greatly depends on the type and the composition of base asphalt. Compared to asphalt K, asphalt

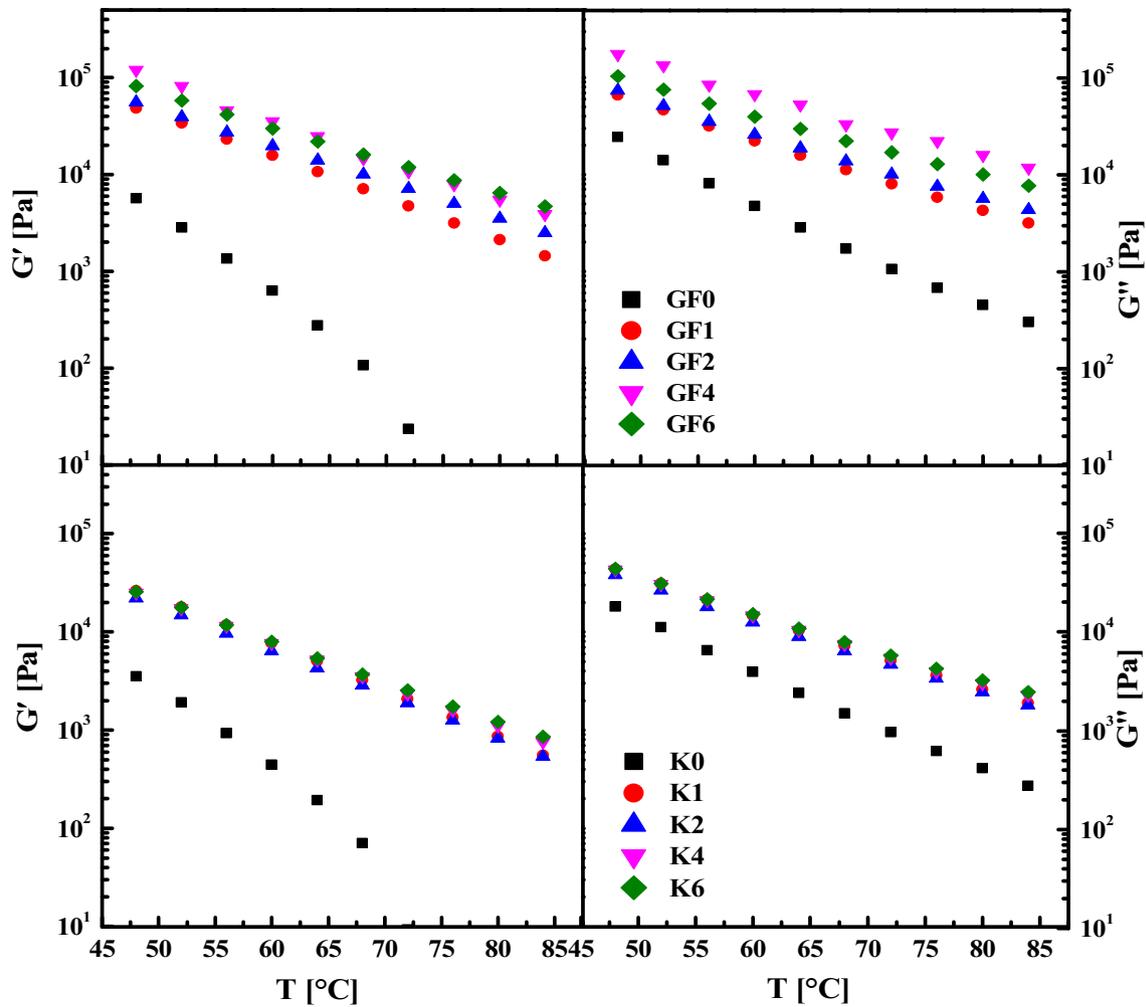


Fig. 4. Influence of TOR on G' and G'' versus temperature for CR/SBS modified asphalt.

GF has higher asphaltene dosage and lower colloidal stability index, which prompts it possesses greater elastic properties under the action of TOR. Therefore, chemical composition of base asphalt is crucial for CR/SBS modified asphalt with TOR to obtain a satisfactory modification.

In order to study the influence of TOR on the rutting and fatigue resistance properties for CR/SBS modified asphalt, rutting factor $G^*/\sin\delta$ and fatigue parameter $G^*\sin\delta$ of all asphalt samples were calculated. The effects of TOR and temperature on the $G^*/\sin\delta$ as well as $G^*\sin\delta$ values for base and CR/SBS modified asphalts are reported in Fig. 5. It seems that rutting and fatigue parameters of asphalt sample both gradually drop with the increment of temperature. Meanwhile, there is a good linear relation between $G^*/\sin\delta$ and $G^*\sin\delta$ values with testing temperature according to the high coefficients of determinations (R^2). Via this linear relation, it is useful to figure out the performance grade of asphalt binders at the high and intermediate temperatures.

Furthermore, it can be found that the $G^*/\sin\delta$ of asphalt increases dramatically after adding CR and SBS. Besides, the addition of TOR results in markedly improving $G^*/\sin\delta$ values due to its cross-linked effect. In addition, $G^*/\sin\delta$ values for CR/SBS modified asphalts gradually are enhanced with the increase of TOR concentration, which is thought to be related to the intensity of three-dimensional network structure [32,37]. As the same with the above analysis, the influence degree of TOR to asphalt GF is more significant than asphalt K, which is caused by the difference of asphalt composition, including asphaltene dosage and colloidal

stability. Meanwhile, with the increase of temperature, the $G^*\sin\delta$ of asphalt samples linearly decrease, which shows that high temperature would be beneficial to fatigue resistance of asphalt.

3.4. Effect of TOR on steady-state flow behavior

The aforementioned analysis reflects the beneficial impacts of TOR on the high-temperature viscoelastic properties for CR/SBS modified asphalt within linear viscoelastic ranges for minor deformation. For the sake of determining the correlation between CR/SBS modified asphalt with different TOR contents and its pavement performance clearly, steady-state shear tests were conducted within larger shear deformation rate ranges (10^{-3} – 10^2s^{-1}) at 60 °C, in which the polymer chains would dramatically have conformational changes. Evaluations of steady-state viscosities of base asphalt and CR/SBS modified asphalt with various TOR contents versus shear rates are displayed in Fig. 6. At low shear rate regions, viscosity values for blank and CR/SBS modified asphalts with various TOR dosages all remain constant with increasing of shear rate, which is correlated to the typical Newtonian behavior. Generally, the most adopted theoretical model for asphalt is a colloidal structure [4]. It is widely believed that asphaltenes from the micelles, which are dispersed in an oily medium and peptized by resins [1]. Therefore, Newtonian behavior can be observed in a wide region of shear rates for studied blank asphalt. At the same time, the viscosity values for neat and CR/SBS modified asphalts show a prominent dependence on shear rate, especially when shear rates

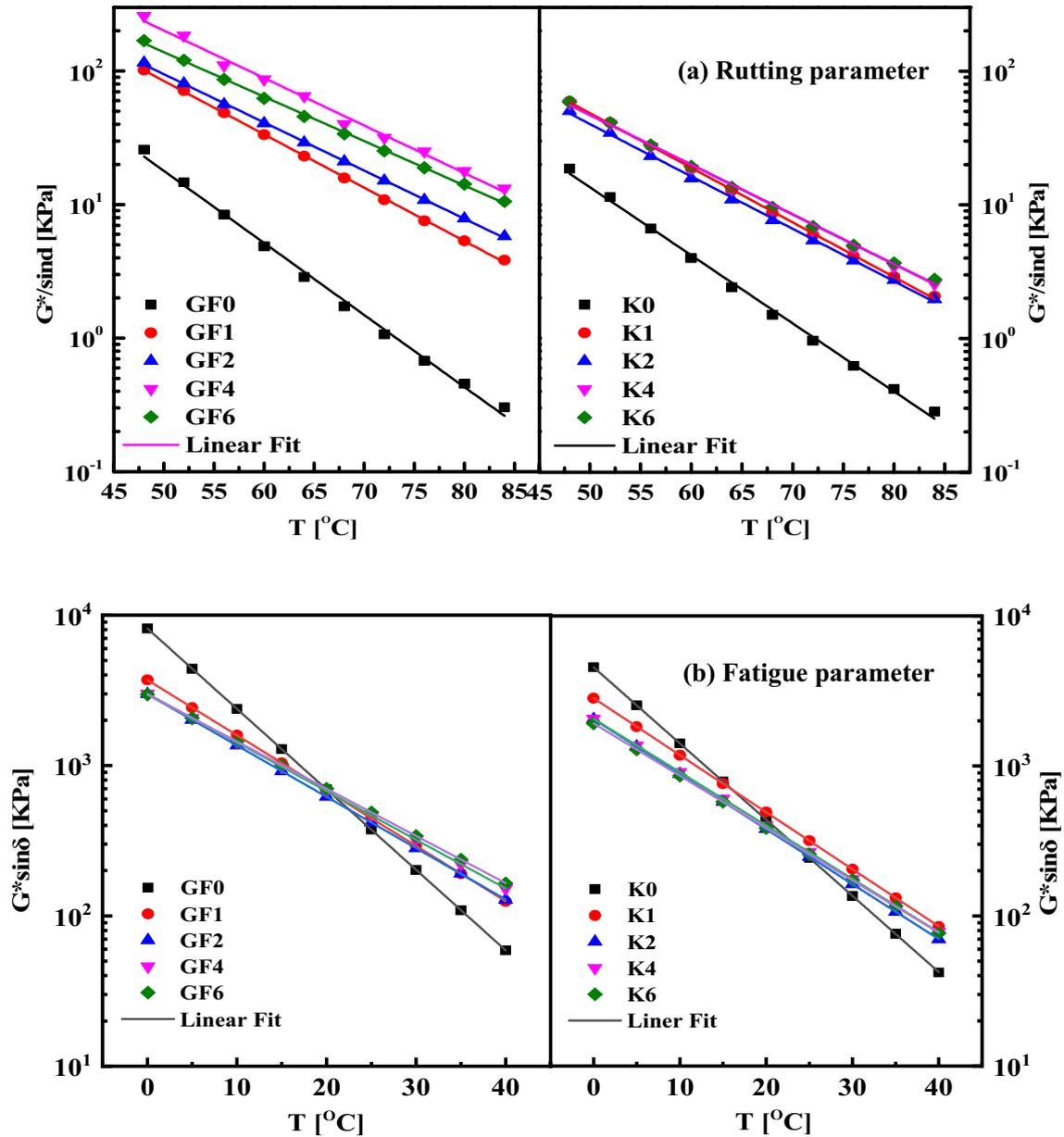


Fig. 5. Influence of TOR on the rutting (a) and fatigue (b) parameters for CR/SBS modified asphalts.

exceed $10^{-2}s^{-1}$ for modified asphalts. At high shear rates range, the viscosity of asphalt samples has a remarkable decrease, indicating an apparent shear-thinning behavior. This may be related to the asphaltic micelles structure of asphalt binders [1,29].

In general, flow curves of blank and modified asphalts show Newtonian behaviors within low shear rate ranges, besides shear-thinning phenomenon is remarkable at high shear rate ranges, which further verifies the viscoelastic behaviors of asphalt binders. It is clear that CR/SBS modified asphalt exhibit a prominent shear-thinning behavior than blank asphalt, especially with high TOR dosage, indicating the more complicated entanglement between asphalt and modifiers.

The distinctions of the flow behavior among blank asphalt and CR/SBS modified asphalt with different TOR dosages can be characterized quantitatively using Carreau model [10,11]:

$$\frac{\eta_0}{\eta} = \left[1 + \left(\frac{\dot{\gamma}}{\dot{\gamma}_c} \right)^{21} \right]^s \quad (1)$$

where s means the slope within shear-thinning behavior range, $\dot{\gamma}_c$ is related to the essential shear rate connected with the inflection point of the shear-thinning range meanwhile η_0 corresponds to the critical viscosity with zero shear rate. These Carreau model parameters of all studied samples are presented in Table 4. In terms of the viscosities of all asphalt samples, CR/SBS modified asphalt has a larger zero shear viscosity than neat asphalt significantly, which is a benefit to rutting resistance properties for asphalt binders. Meanwhile, zero shear viscosity of CR/SBS modified asphalt increases with the increment of TOR dosage, indicating that the introduction of TOR enhances viscous property and flow resistance ability for CR/SBS modified asphalt. This may be because of the formation of the cross-linked network structure between crumb rubber and TOR [32,37].

Effect of TOR dosage on the 60 °C zero shear viscosity (ZSV) η_0 parameter of CR/SBS modified asphalt is showed in Fig. 7. It is clear that η_0 yields an exponential increase with increasing TOR content at 60 °C. The equations of relation curves between η_0 and TOR contents for asphalt GF and asphalt K are as follows:

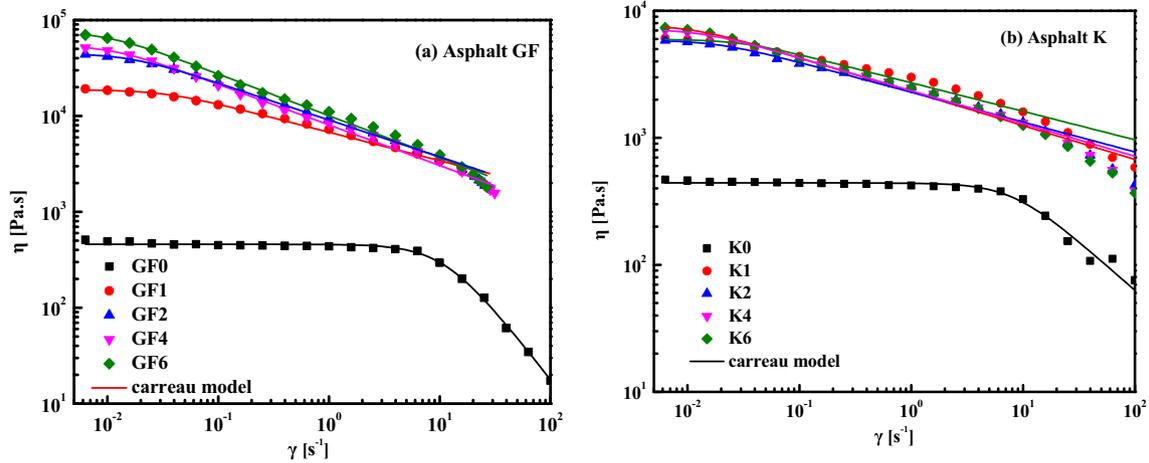


Fig. 6. Flow curves of unmodified asphalt and CR/SBS modified asphalt with different TOR contents at 60 °C.

Table 4

The results calculated from Carreau model at 60 °C of asphalt binders.

	TOR contents (wt%)				
	Neat asphalt	0	2	4	6
<i>Asphalt GF</i>					
$\eta_0 \times 10^{-3}$ (Pa.s)	0.459	18.701	44.813	54.954	76.115
$\dot{\gamma}_c$ (s^{-1})	11.143	0.033	0.016	0.011	0.010
s	0.739	0.149	0.193	0.212	0.218
R^2	0.984	0.994	0.999	0.999	0.999
<i>Asphalt K</i>					
$\eta_0 \times 10^{-3}$ (Pa.s)	0.441	5.962	5.855	7.165	7.722
$\dot{\gamma}_c$ (s^{-1})	8.237	0.030	0.018	0.013	0.011
s	0.389	0.112	0.118	0.129	0.133
R^2	0.985	0.986	0.991	0.996	0.996

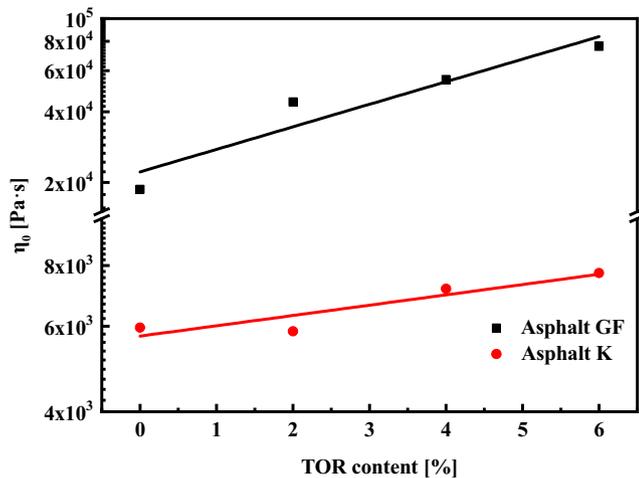


Fig. 7. Effect of TOR content on the zero-shear viscosity of CR/SBS modified asphalt at 60 °C.

$$\eta_{0,GF} = 22187.58e^{0.09618TOR} \quad (2)$$

$$\eta_{0,K} = 5724.79e^{0.02124TOR} \quad (3)$$

In detail, TOR raises the ZSV values for CR/SBS modified asphalts significantly, and the increasing degree of viscosity for CR/SBS modified asphalt GF is more significant than asphalt K enormously, although these two asphalts have similar performance grade. Com-

pared to asphalt K, asphalt GF possesses higher asphaltene dosage and smaller colloidal stability index. That means variation of viscosity and TOR dosage of CR/SBS modified asphalt is also associated with the chemical composition of blank bitumen. In terms of effects of TOR on the s and $\dot{\gamma}_c$ value of CR/SBS modified asphalt, it is clear that with the increase of TOR content, s value increases and $\dot{\gamma}_c$ value decreases slightly, which are far less than blank asphalt. Thus, CR/SBS modified asphalt is closer to non-Newtonian behavior than blank asphalt, and the former is less sensitive to shear rates than the latter. Meanwhile, the addition of TOR increases the shear-thinning behavior region and shear sensitivity of CR/SBS modified asphalt slightly, indicating the improvement effect of TOR on viscous characteristics for CR/SBS modified asphalt.

3.5. Effect of TOR on creep and recovery behavior

Except for $G^*/\sin\delta$ indicator, the impact of TOR on the rutting resistance for CR/SBS modified asphalt was also measured with MSCR tests on the basis of AASHTO TP 70 [43]. Many previous studies have verified that $G^*/\sin\delta$ parameter only could divide asphalt into viscous and elastic sections, rather than considering the delayed elastic recovery characteristics. Hence, the traditional Superpave grading protocol is not an ideal standard to assess the permanent deformation performance for asphalt binders [46]. In consideration of this, MSCR test is applied to further evaluate high-temperature permanent deformation of CR/SBS modified asphalt with various TOR dosages. In this section, the blank asphalt and CR/SBS modified asphalt samples were all subjected to multiple shear loading and unloading cycle of 1 s and 9 s separately. Ten

cycles of loading were carried out at both stress levels of 0.1 kPa and 3.2 kPa [43].

Fig. 8 displays the representative date of the one-second creep and nine-second recovery cycle to show the strain responses of blank asphalt and CR/SBS modified asphalt with various TOR contents. It is as expected that an increase in loading time results in a remarkable increment of actual strain. Meanwhile, in the recovery phase, the strain value recovers dramatically at the beginning but it drops slowly with time to reach a certain strain value. Above results are reflections of viscoelastic properties for asphalt binders. As long as removing the creep load, the elastic strain section recovers immediately, while the viscous strain phase recovers slowly.

The average non-recoverable creep compliance (Jnr) and average percent recovery (R%) were calculated to assess the effect of TOR on the rutting resistance for CR/SBS modified asphalts quantitatively and accurately. It is well known that asphalt with higher R% and lower Jnr values would have more elastic component and be adept at high-temperature regions. The details of MSCR test results with two stress level for all studied samples are presented in Fig. 9. It is as expected that CR/SBS modified asphalt with lower Jnr and higher R% value outperform the blank asphalt at both stress levels, indicating the existence of elastic response in the modified asphalt makes them less sensitive to rutting and permanent deformation. This may be attributed to interlocked crumb rubber and SBS network in asphalt, which is a benefit to hinder the accumulation of permanent strain [19].

In terms of the influence of TOR on creep and recovery behaviors of CR/SBS modified asphalt, it is observed that all CR/SBS modified asphalts with TOR have lower Jnr and higher R% values regardless of stress levels. For example, the Jnr values of GF2, GF4 and GF6 modified asphalts are 59.0%, 67.4% and 75.38% lower than the control binder, respectively, while the Jnr values of K2, K4 and K6 modified asphalts are 28.8%, 44.6% and 47.2% lower than K0 modified asphalt at shear stress level of 3.2 kPa. In regard to R%, CR/SBS modified asphalts with various TOR contents exhibit superior percent recovery, which shows the beneficial effect of TOR on improving the recovery performance of CR/SBS modified asphalt. At 3.2 kPa creep stress, the R% values for GF2, GF4 and GF6 modified asphalts are 22.2%, 24.0% and 28.1% higher than GF0 modified asphalt at 3.2 kPa stress, while K2, K4 and K6 modified asphalts are 7.7%, 19.5% and 20.4%, which are higher than K0 modified asphalt. Overall, with the increase of TOR contents, the Jnr value presents a decreasing tendency as well as %R reveals an increasing trend significantly. This results evidence that TOR addition can dramatically improve the elasticity and high-temperature performance for CR/SBS modified asphalts, which is likely to be reason for cross-linking effect of TOR on strengthening the interlocked crumb rubber

and SBS network in asphalt and reducing rutting risk for CR/SBS modified asphalt [10,19,21].

Apart from the addition of TOR, the above analysis reveals that the MSCR test results are also dependent on the stress level and blank asphalt composition. With the increment of loading stress from 0.1 kPa to 3.2 kPa, R% value drops and Jnr raises distinctly, and the variation tendency is smaller for modified asphalts. The comparison among modified asphalt with various TOR dosage shows that addition of TOR can lower the stress sensitivity of CR/SBS modified asphalt, while TOR content has a slightly negative effect on the stress sensitivity of asphalt. Moreover, it is clear that GF modified asphalt always shows lower Jnr and higher R than asphalt K for the same TOR content and stress level. On the basis of the decreasing degree of Jnr at both stress levels, it can be concluded that the active roles of TOR on high-temperature anti-deformation properties and viscoelastic behaviors seem to be more remarkable for GF asphalt binders.

3.6. Effect of TOR on low-temperature performance

The dependence of rheological behaviors of CR/SBS modified asphalt on TOR has been evaluated using DSR. To assess the impact of TOR on the creep behavior and anti-cracking properties of CR/SBS modified asphalt at low-temperature regions, bending beam rheometer (BBR) tests with diverse loading time were conducted at -12 and -18 °C in terms of AASHTO M320[42]. Two parameters, including creep stiffness (S) and rate of relaxation (m-value), were obtained to assess the low-temperature performance of base and CR/SBS modified asphalt. Fig. 10 presents the evolution of S and m-value versus loading time for RTFO-PAV aged CR/SBS modified asphalt GF and K with various TOR content at -12 and -18 °C. As expected, the creep stiffness values of all asphalt samples decline and m-value enhance dramatically with the decrease of test temperature. The creep stiffness S values drop with the elongation of loading time, nevertheless m-value counter to raising. As is well known, the lower S value together with higher m-value mean greater low-temperature cracking resistance performance for road pavements. Compared with neat asphalt, the addition of CR and SBS have great effects on the decrease of stiffness value and increase of m-value apparently, which indicates the dispersion of CR and SBS brings about more flexible construction structure. CR and SBS composite modification would urge the further decrease in creep stiffness value and increment of m-value, which represents the improvement of the low-temperature anti-cracking properties, thus satisfy the criteria requirements ($S < 300$ MPa, $m > 0.3$) at -18 °C, while the blank asphalt only conforms to the criteria at -12 °C.

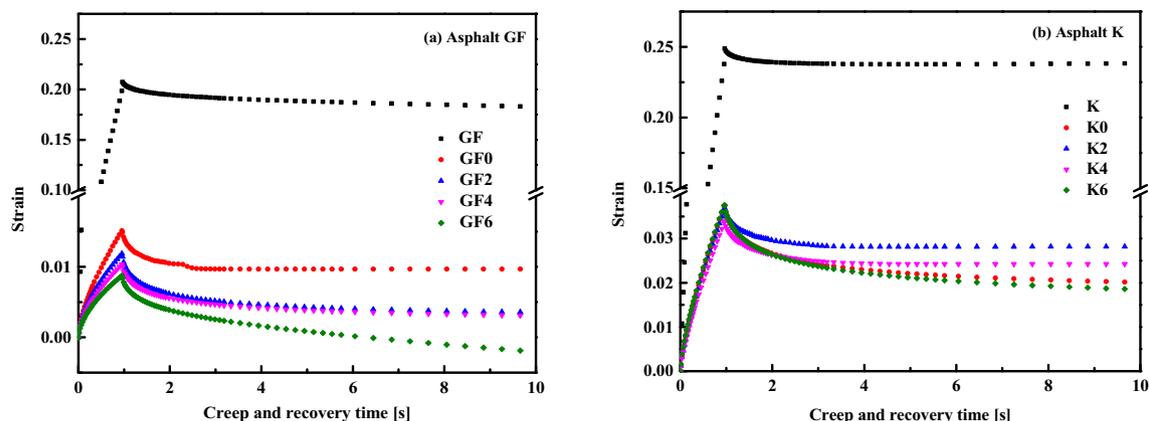


Fig. 8. Typical creep and recovery representation for CR/SBS modified asphalts with various TOR contents at 0.1 kPa.

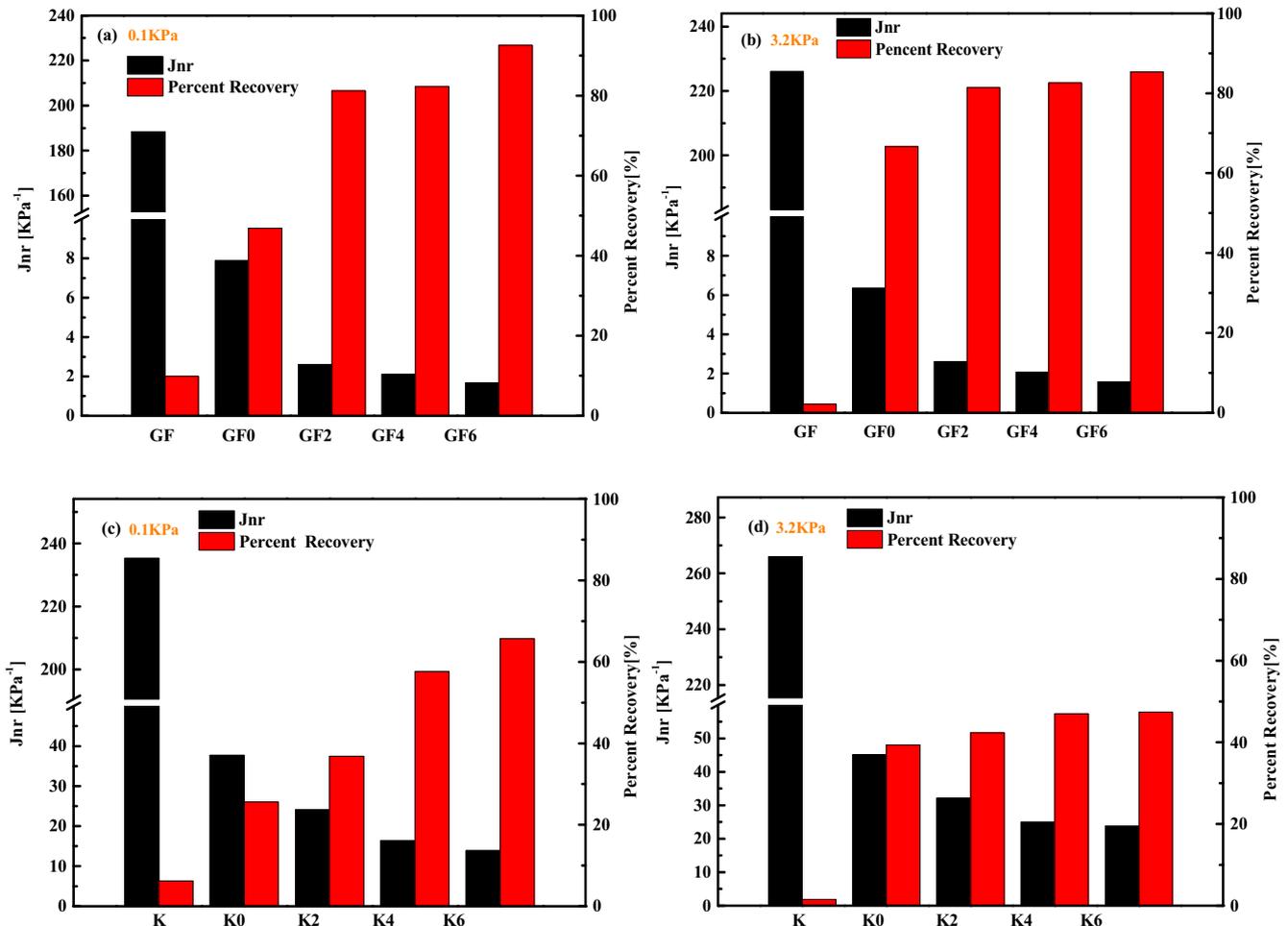


Fig. 9. Average Jnr and average percent recovery for unmodified and CR/SBS modified asphalt GF (a, b) and K (c, d) at 60 °C.

In terms of the impact of TOR on the low-temperature performance of CR/SBS modified asphalt, TOR addition has a slightly negative function on the anti-cracking properties of modified asphalts. As can be seen that the S value of CR/SBS modified asphalts increase, while the m-value undergo a decreasing process with the increasing of TOR dosage. However, in spite of the adverse impact of TOR on anti-cracking properties for CR/SBS modified asphalt, the S and m values for modified asphalts with various TOR dosages are lower and higher than that of neat asphalt, respectively. The results mean that TOR addition would maintain the critical low temperature for CR/SBS modified asphalt, except for the m-value for asphalt GF at -18 °C. As a result, optimal TOR dosage can be obtained to ensure the best modification impact on rheological properties and not breakdown the low-temperature cracking behavior sharply for CR/SBS modified asphalt.

In addition, the influence degree of TOR on low-temperature anti-cracking properties for CR/SBS modified asphalt also depends on the properties and components of base asphalt. Comparing asphalt GF and K, the latter one has lower S-value and larger m-value than that of the former one, which is attributed to the less asphaltene content and better colloidal stability for asphalt K. The asphalt K with lower asphaltene dosage and better colloidal stability presents superior flexibility and low-temperature cracking resistance performance. Meanwhile, the stiffness raises, while m-value declines effectively for asphalt K as the testing temperature drops gradually from -12 °C to -18 °C and verifies its poor temperature sensitivity resistance performance again. Furthermore, the difference in stiffness and m-value among CR/SBS mod-

ified asphalt with various TOR contents becomes larger. Above all, CR/SBS modified asphalt K all can fulfill the minimum requirement criteria ($S < 300$ MPa, $m > 0.3$) at -18 °C, while modified asphalt GF only can meet the criteria at -12 °C, except for the modified asphalt without TOR. Thus, TOR content and asphalt components both should be optimized and considered when in view of the low-temperature behaviors for CR/SBS modified asphalts with various TOR dosages.

3.7. Effect of TOR on the performance grade (PG)

Table 5 demonstrates the influence of TOR on the performance grade of CR/SBS modified asphalt. In terms of high temperature performance grade, the failure temperatures (when $G^*/\sin\delta$ is equal to 1.0 KPa) for CR/SBS modified asphalt GF and K are 34.1% and 26.36% higher than that of the neat asphalt, respectively. Furthermore, in term of the impact of TOR on rutting resistance performance for CR/SBS modified asphalt, failure temperatures for CR/SBS modified asphalt GF with 2%, 4% and 6% TOR are 6.7%, 16.9% and 17.5% higher than that of GF0, respectively. As to asphalt K, the failure temperatures of K2, K4 and K6 are 0.8%, 4.1% and 6.2% higher than that of K0. It is demonstrated that TOR addition further enhances the high-temperature anti-rutting ability for CR/SBS modified asphalts dramatically. Meanwhile, the active effect of TOR on high-temperature performance seems to be more remarkable for asphalt GF, which has smaller asphaltene content and better colloidal stability.

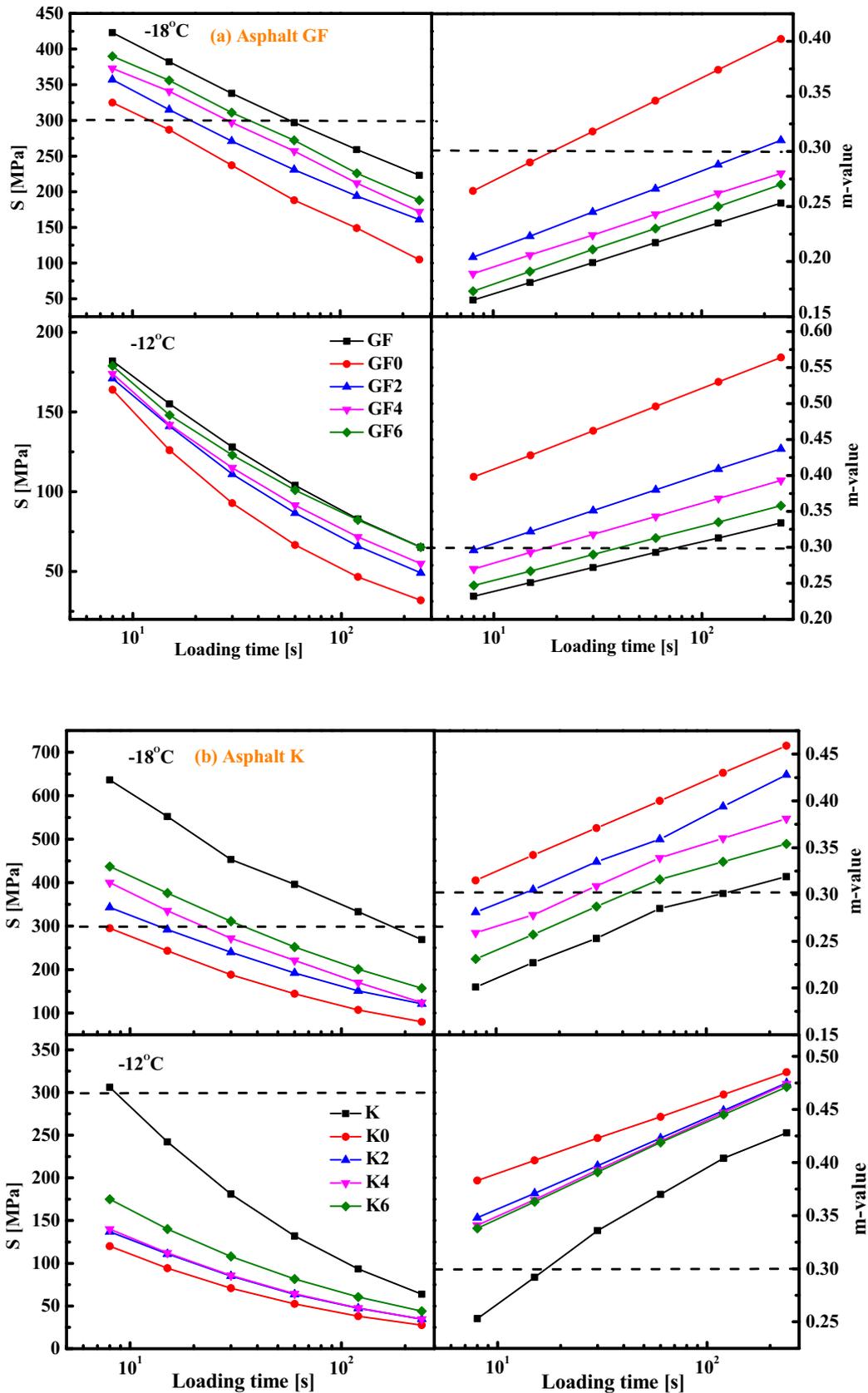


Fig. 10. Evolution of S and m-value versus loading time for CR/SBS modified asphalt GF (a) and K (b).

The fatigue temperatures calculated from $G^* \sin \delta = 5000$ KPa for all asphalt samples are also shown in Table 5 [29,47]. It can be found that the addition of CR and SBS can decline the fatigue tem-

perature and strengthen the fatigue resistance ability of base bitumen. Compared to asphalt GF, the asphalt K has lower fatigue temperature and better anti-fatigue property, which is related to

Table 5
The continuous performance grade (PG) of asphalt binders.

Asphalt type	TOR contents (wt%)	Neat asphalt	0	2	4	6
GF	High temperature PG (°C)	73.22	98.20	104.79	114.81	115.40
	Intermediate temperature PG (°C)	3.98	-3.52	-6.55	-6.85	-7.20
	Low temperature PG (°C)	-23.01	-32.50	-29.98	-27.23	-25.03
K	High temperature PG (°C)	72.22	91.26	91.94	94.96	96.95
	Intermediate temperature PG (°C)	-0.81	-6.49	-10.47	-10.81	-11.92
	Low temperature PG (°C)	-25.92	-38.07	-31.36	-29.02	-28.88

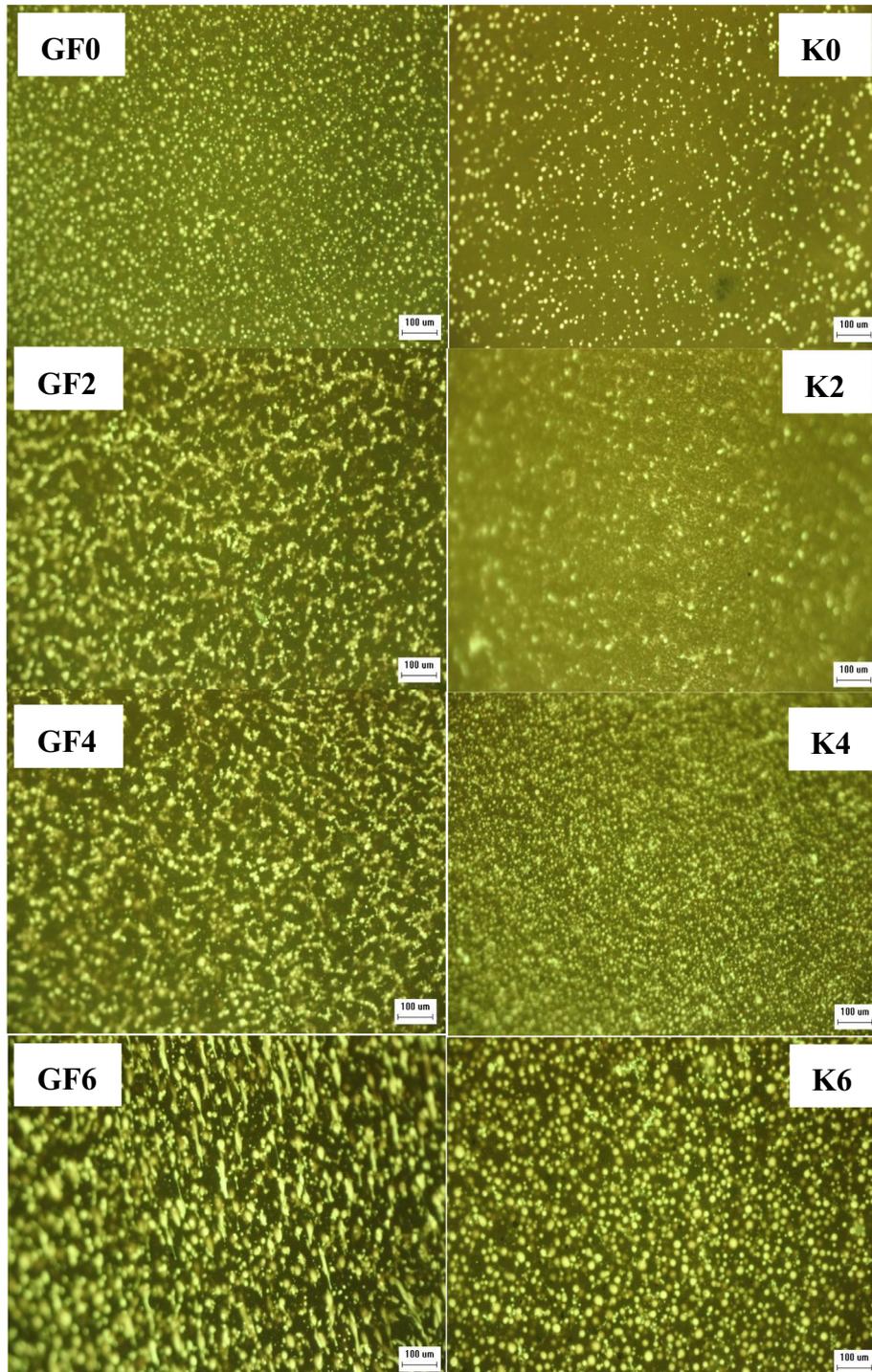


Fig. 11. Fluorescence microscopy of CR/SBS modified asphalt GF and K with TOR contents in 0 wt% (GF0, K0), 2.0 wt% (GF2, K2), 4.0 wt% (GF4, K4), 6.0 wt% (GF6, K6).

its lower asphaltene dosage and better colloidal stability. On the other hand, the increase of TOR content remarkably declines the fatigue temperature of CR/SBS modified asphalt. For example, when the CR/SBS modified asphalt GF and K was added by 2 wt% TOR, the fatigue temperature decreases by 86.08% and 62.87%, respectively. Therefore, the addition of TOR can further strengthen the fatigue resistance performance of CR/SBS modified asphalt.

As expected, the addition of CR and SBS can improve the high and low temperature performance of asphalt dramatically, including rutting and cracking resistance. With the increase of TOR content, the high critical temperature of CR/SBS modified asphalt is enhanced, indicating that the addition of TOR can remarkably improve the high temperature properties of CR/SBS modified asphalt. The detailed effects of TOR on the high temperature properties can be found in the above analysis. However, it is also found that the addition of TOR would increase the low critical temperature, which has an adverse influence on the low-temperature grade of CR/SBS modified asphalt. Meanwhile, all modified asphalts have the smaller low critical temperature than base asphalt. In detail, all modified asphalt GF can meet the low temperature grade of $-22\text{ }^{\circ}\text{C}$, while all modified asphalt K can have the low temperature grade of $-28\text{ }^{\circ}\text{C}$. Thus, to balance both high and low temperature performance of CR/SBS modified asphalt, TOR concentration should be controlled.

3.8. Effect of TOR on morphology and storage stability

In order to better evaluate the microstructural changes caused by TOR addition and further explain the effect mechanism of TOR on the viscoelastic behaviors, morphology for CR/SBS modified asphalt GF and K with various TOR contents were observed by using fluorescence microscopy (FM), which are shown in Fig. 11. As can be seen, the light area represents the decentralized composite polymer-rich phase of swollen SBS and CR granules absorbing light fractions of asphalt, meanwhile, the dark section donates asphalt-rich phase. Obviously, the polymer particles in modified asphalt without TOR are dispersed in the asphalt phase with the shape of spherical particle sparsely and alone. The morphology result is equal to incompatibility for CR/SBS modified asphalt without TOR, which may result in phase separation. Fig. 11 shows fluorescence images for CR/SBS modified asphalts with various TOR dosages. It can be found that the addition of TOR leads to the significant difference in dispersion state of CR and SBS domains in asphalt, which prone to be more intensive when TOR dosage raises from 0 wt% to 6 wt%. Besides, it can be seen that TOR can promote the formation of cross-linked network structure obviously, which could improve the rheological behaviors and compatibility of CR/SBS modified asphalt, especially for asphalt GF. The CR/SBS modified asphalt with higher content TOR has larger crosslinking density with more complicated network structure. This explains that asphalt binders with higher content TOR have greater zero shear-rate viscosity and elastic response performance. However, when the TOR content reaches to 6 wt%, the dimension of polymer particles in asphalt increases unexpectedly, indicating TOR concentration should be limited to ensure the compatibility of CR/SBS modified asphalt. Therefore, comprehensive considering the rheological behaviors and compatibility of CR/SBS modified asphalts, the optimal addition proportion of TOR is about 4 wt%.

Furthermore, if the effects of base asphalt with the different composition are considered, the influence of TOR on the morphology of CR/SBS modified asphalts shows discriminating due to the difference of asphalt composition. As can be found in Fig. 11, the influence degree of TOR on the formation for cross-linked network of CR/SBS modified asphalt GF is more evident than asphalt K, which is related to the asphaltene dosage and colloidal stability of asphalt. In addition, the effect of TOR on the dispersion of poly-

mer particles of asphalt K is more prominent than asphalt GF. The lower asphaltene concentration and better colloidal stability of asphalt K are both beneficial to the dispersion of polymers in asphalt. The morphology results are consistent with the analysis of viscoelastic behavior and BBR test results, which is that high-temperature rheological behaviors for asphalt GF is greater than asphalt K, at the same time the low-temperature properties for asphalt K is better. TOR plays an important role of cross-linking point and brings about enrichment of polymer. Once TOR is mixed into CR/SBS modified asphalt binders, the cross-linked network structure is constituted soon, which improves the viscoelastic behaviors and compatibility for CR/SBS modified asphalts simultaneously. Furthermore, the statistical results of particle size for TOR/CR/SBS modified asphalts are obtained by using the Image-Pro Plus tool, which can be found in Table 6. With the increase of TOR dosage, the diameter and area size of particles in FM morphology rises gradually, which is related to the cross-linking effect of TOR. It is clear that the addition of TOR can increase the cross-linking degree of crumb rubber particle and form the network structure [11,29]. According to the particle size, it can be found that the polymers in asphalt K has a better dispersity than asphalt GF, which is associated to the lower asphaltene content and higher colloidal stability of asphalt K.

It is well known that storage stability is very important to polymer modified asphalt. Thus, the impact of TOR on the storage stability of CR/SBS modified asphalt is evaluated by thermal storage method. The difference of softening point of modified asphalt with various TOR dosage is shown in Fig. 12. Based on the standard [45],

Table 6

The Image-Pro plus statistical results of TOR/CR/SBS modified asphalts.

Asphalt samples	Diameter mean (μm)	Area mean (μm^2)	Area (polygon, μm^2)
GF0	6.27	36.60	24.03
GF2	10.05	98.73	77.19
GF4	10.78	118.71	95.31
GF6	12.53	169.80	142.18
K0	6.14	36.21	23.97
K2	6.84	46.38	32.89
K4	7.55	57.85	43.12
K6	8.40	73.40	56.57

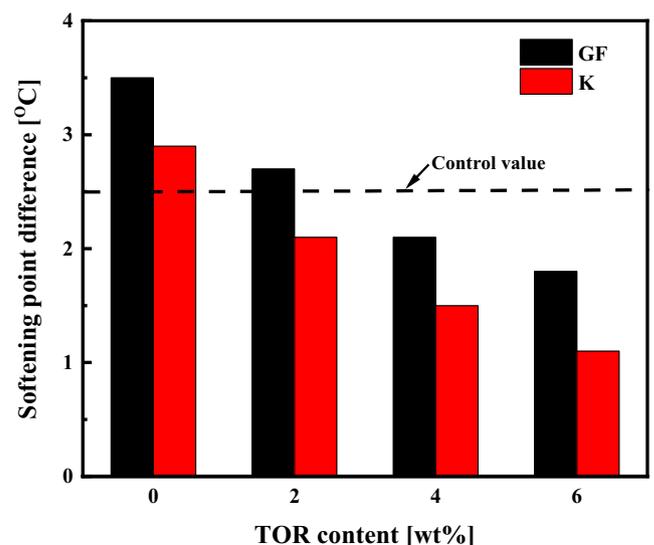


Fig. 12. Influence of TOR on the softening point difference of CR/SBS modified asphalt.

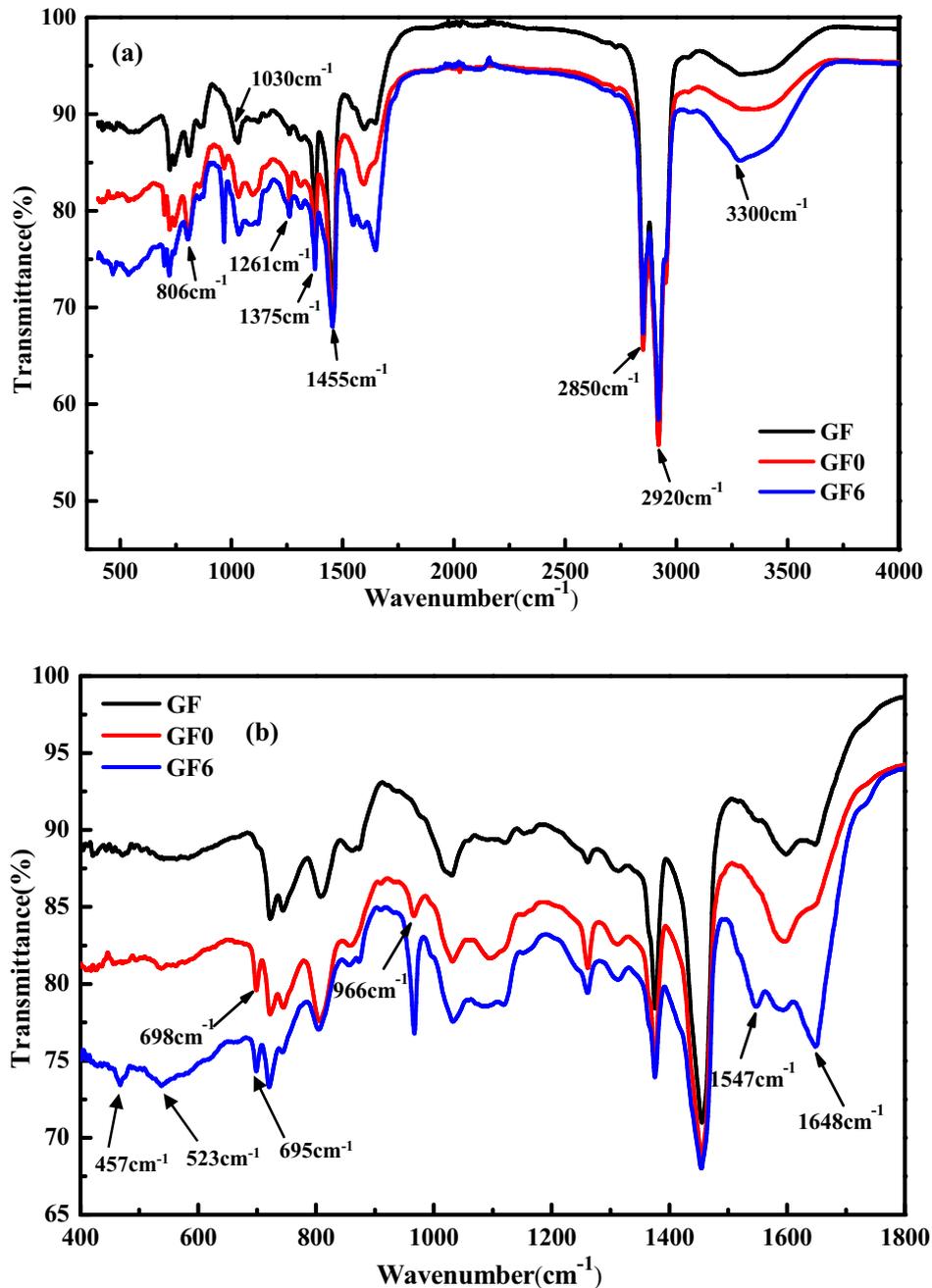


Fig. 13. FTIR spectra of asphalt binders.

the polymer modified asphalt with lower softening point difference than 2.5 °C would have satisfying thermal storage stability. However, it is clear that the softening point difference values of CR/SBS modified asphalts are both larger than 2.5 °C, showing CR/SBS modified asphalt has worse thermal storage stability. Fortunately, the addition of TOR can remarkably reduce the softening point difference value and enhance the thermal storage stability of CR/SBS modified asphalt, which is related to the increasing cross-linking degree and interaction force between the polymers in asphalt. Meanwhile, the increase of viscosity also hinders the motion of polymer particles [11,29]. Furthermore, the CR/SBS modified asphalt K has smaller softening point difference than asphalt GF, which means the asphalt composition with lower asphaltene content and higher colloidal stability index would be beneficial to the storage stability of CR/SBS modified asphalt. In order to meet

the requirement of thermal storage stability for polymer modified asphalt [45], the TOR dosage for CR/SBS modified asphalt GF should be larger than 2 wt%, which is enough to the CR/SBS modified asphalt K.

3.9. FTIR analysis

FTIR spectra were generated for the virgin asphalt (GF) as well as CR/SBS modified asphalt with (GF0) and without TOR (GF6), respectively. It is well known that FTIR spectra can reflect the changes of functional groups and distinguish whether there is chemical reaction in asphalt and modifiers. Meanwhile, FTIR spectra can also shed some light on the rheological results [29]. Fig. 13 shows the FTIR spectra of asphalt binders to investigate the influence of TOR on the microstructural properties of CR/SBS modified

asphalt. To observe the changes in functional groups, the FTIR spectra with wavenumber from 400 cm^{-1} to 1800 cm^{-1} is displayed in Fig. 13(b). Some typical absorption peaks occur at similar wavenumbers for base asphalt, CR/SBS modified asphalt and CR/SBS modified asphalt with TOR [29]. These similar absorption positions mainly focus on 3300 cm^{-1} , 2920 cm^{-1} , 2850 cm^{-1} , 1455 cm^{-1} , 1375 cm^{-1} , 1260 cm^{-1} , 1030 cm^{-1} and 804 cm^{-1} . In detail, the absorption peak at 3300 cm^{-1} , 2920 cm^{-1} , 2850 cm^{-1} and 1455 cm^{-1} is attributed to the -O-H stretch in hydroxyl, C-H antisymmetric stretch in Methyl -CH_3 of aliphatic, C-H symmetric stretch in Methylene $\text{-CH}_2\text{-}$ of aliphatic and C-H antisymmetric bend in alkenes, respectively. Moreover, the absorption peak at 1375 cm^{-1} , 1260 cm^{-1} , 1030 cm^{-1} and 804 cm^{-1} represents the C-H symmetric bend of methyl CH_3 in aliphatic, bending vibration of O-H, stretching vibrations of S=O, bending vibration of C-H in benzene, respectively [29].

From Fig. 13, it can be seen that compared with base asphalt, the significant difference in FTIR for CR/SBS modified asphalt occurs at the peak of 698 cm^{-1} and 966 cm^{-1} , which are identified as the C-H bending vibration of benzene and =C-H bending vibration. Obviously, the two characteristic peaks of 698 cm^{-1} and 966 cm^{-1} are attributed to the polystyrene domain and polybutadiene domain in SBS copolymer. Meanwhile, it can be deduced that both CR and SBS only affect the physical properties of asphalt because of physical modification [29]. In addition, the addition of TOR enhances the absorption peaks of 1547 cm^{-1} and 1648 cm^{-1} , indicating there is a conjugate effect between the carbonyl group and the benzene ring. Moreover, adding TOR can remarkably enhance the peak intensity of 966 cm^{-1} , which is owing to the existence of the unsaturated bond in the TOR molecule. Importantly, it can be found that CR/SBS modified asphalt has two specific absorption peaks at the position of 457 cm^{-1} and 523 cm^{-1} , which is related to the stretching vibration of S-S_m and C-S_m in the polysulfide. Meanwhile, it can be seen that the intensity of peak at 695 cm^{-1} for CR/SBS modified asphalt with TOR decreases, which is associated with the stretching vibration of a single sulfur key. The FTIR results indicate that TOR can urge the formation of polysulfur bonds and crosslinking network, which can significantly improve the rheological properties and thermal stability of CR/SBS modified asphalt. These above results are consistent to previous research, showing that TOR can chemically crosslink the sulfur elements in asphalt and crumb rubber [29,30]. Besides, the chemical reaction of TOR can give good explanations on the improvement of viscoelastic properties of CR/SBS modified asphalt, including modulus, temperature sensitivity, flow resistance, and stress recovery ability.

3.10. TG analysis

In order to evaluate the influence of TOR on the thermal stability of CR/SBS modified asphalt, thermogravimetric analysis (TGA) was performed. Fig. 14 presents the TGA curves of base asphalt, CR/SBS modified asphalt without and with TOR, respectively. The left coordinate axis is the mass change of asphalt samples, while the right part represents the heat flow change with the increase of temperature. It is well known that asphalt and polymer both have three different typical rheological behaviors, including glassy state, high-elastic state as well as viscous condition. As the temperature increase, the viscoelastic properties of asphalt sample change from glassy state to high-elastic state, and further to viscous condition. When the system temperature continues to increase, the asphalt sample starts to break down to complete. Certainly, when the state of asphalt from glassy to high-elastic, the corresponding temperature is glass transition temperature. It can be found polymer and TOR have no distinct effect on the glass transition temper-

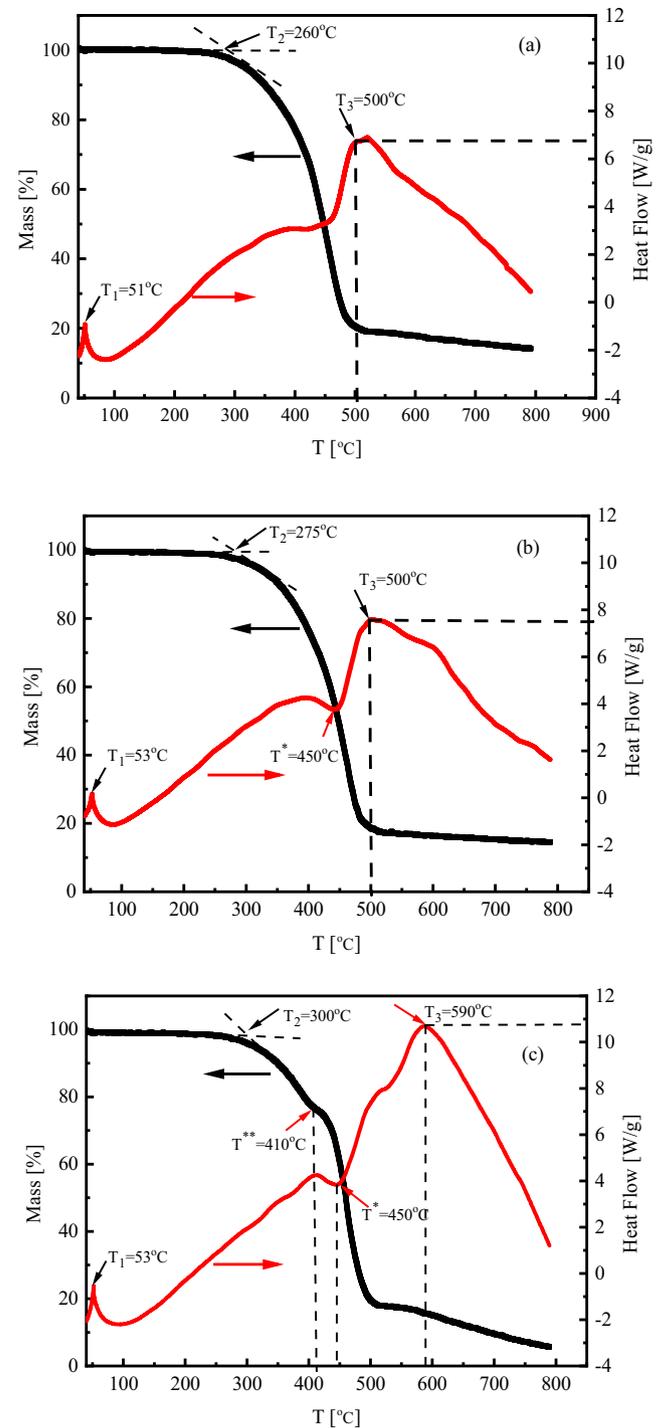


Fig. 14. TGA curves of asphalt binders (a) Base asphalt; (b) CR/SBS modified asphalt; (c) CR/SBS modified asphalt with TOR.

ature of the asphalt. From Fig. 14 (a), the decomposition temperature of base asphalt is about $260\text{ }^{\circ}\text{C}$, which can be improved by adding polymer and TOR. It can be seen that the decomposition temperature of CR/SBS modified asphalt is $15\text{ }^{\circ}\text{C}$ higher than that of base asphalt, which can be further increased by $25\text{ }^{\circ}\text{C}$ after adding TOR. It is indicated that CR and SBS can remarkably improve the thermal stability of asphalt, which can be further strengthened by adding TOR. This phenomenon is attributed to the existence of the compact network structure between asphalt, polymer and TOR.

In addition, when the temperature increases to 500 °C, the decomposition rate of base asphalt slows down rapidly. From Fig. 14 (a), the mass residue and heat flow of base asphalt are about 20 wt% and 7w/g, respectively. As the temperature increasing from 500 °C to 800 °C, the mass residue decreases to 10 wt% and the heat flow declines by 0w/g. Compared to base asphalt, the addition of SBS and CR can make the heat flow increase by 0.5w/g and has no effect on the decomposition temperature, seen from Fig. 14 (b), which verifies that there is not network structure in CR/SBS modified asphalt. Interestingly, CR/SBS modified asphalt with TOR has a specific decomposition inflection point at 410 °C, seen from Fig. 14 (c), which is attributed to the existence of network structure between asphalt, CR and TOR. Meanwhile, when the temperature is 500 °C, the mass residue of CR/SBS modified asphalt with TOR is about 17 wt%, which is larger than that of CR/SBS modified asphalt and indicates that TOR can remarkably enhance the thermal stability of modified asphalt. Meanwhile, the addition of TOR increases the temperature of complete decomposition from 500 °C to 590 °C and boosts the heat flow from 7.5w/g to 11w/g, which means that the decomposition process of CR/SBS modified asphalt with TOR need absorb more energy. In a word, TOR can have a great effect on improving the thermal stability of CR/SBS modified asphalt and the TG analysis result further confirm the formation of three-dimensional crosslinking network structure between asphalt, polymer, and TOR.

4. Conclusions

In this paper, the impacts of Trans-polyoctenamer (TOR) on the viscoelastic behaviors, microstructure and thermal stability of CR/SBS modified asphalt were evaluated by using DSR, BBR, FM, FTIR as well as TGA tests. The main research conclusions are drawn and listed below:

- (1) TOR increases softening point, G' , G'' and $G^*/\sin\delta$ values of CR/SBS modified asphalt, indicating TOR can strengthen both stiffness and rutting resistance ability of modified asphalt at high temperature dramatically. Meanwhile, temperature sensitivity of modified asphalt can also be further improved dramatically by adding TOR.
- (2) Steady-state flow tests show that the 60 °C zero shear viscosity in low shear rates zone increases with the increment of TOR dosage, which indicates that TOR can improve the viscous property of CR/SBS modified asphalt. Moreover, MSCR tests can quantify the effect of TOR on the elastic recovery behavior of CR/SBS modified asphalt. TOR can decrease J_{nr} and intensify $\%R$ values, showing potentiality in enhancing the stress recovery and permanent deformation resistance performance of modified asphalt.
- (3) In terms of the effect of TOR on low-temperature behavior for CR/SBS modified asphalts, TOR has a slightly negative impact on the anti-cracking ability of modified asphalt, which still maintains critical low-temperature performance requirement.
- (4) The effects of TOR on rheological properties of CR/SBS modified asphalt markedly depends on the component of neat asphalt. In this study, the positive effects of TOR on high-temperature properties and elastic response are more significant for modified asphalt GF with higher asphaltene content, while modified asphalt K with lower asphaltene content and better colloidal stability has better low-temperature cracking resistance performance.
- (5) The addition of TOR can significantly improve the rheological properties and thermal storage stability of CR/SBS modified asphalt, which is related to the formation of polysulfur bonds and crosslinking network structure.

CRedit authorship contribution statement

Shisong Ren: Methodology, Investigation, Formal analysis, Writing - original draft, Writing - review & editing. **Xueyan Liu:** Supervision, Methodology. **Mingliang Li:** Resources, Supervision. **Weiyu Fan:** Supervision, Writing - review & editing. **Jian Xu:** Resources, Supervision. **Sandra Erkens:** Supervision, Visualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The first author gratefully acknowledges the financial support from the China University of Petroleum Postgraduate Innovation Project (No. YCX2018043) and China Scholarship Council (No. 201906450025).

References

- [1] G. Polacco, J. Stastna, D. Biondi, L. Zanzotto, Relation between polymer architecture and nonlinear viscoelastic behavior of modified asphalts, *Curr. Opin. Colloid. In.* 11 (2006) 230–245.
- [2] Y. Yildirim, Polymer modified asphalt binders, *Constr. Build. Mater.* 21 (2007) 66–72.
- [3] L. Zhang, T. Li, F. Gao, Y. Tan, Rheological and physical properties of asphalt mixed with warm compaction modifier, *Constr. Build. Mater.* 123 (2016) 309–316.
- [4] M. Liang, X. Xin, W. Fan, H. Wang, S. Ren, J. Shi, Effects of polymerized sulfur on rheological properties, morphology and stability of SBS modified asphalt, *Constr. Build. Mater.* 150 (2017) 860–871.
- [5] C. Roman, A. Cuadri, I. Liashenko, M. García-Morales, P. Partal, Linear and non-linear viscoelastic behavior of SBS and LDPE modified bituminous mastics, *Constr. Build. Mater.* 123 (2016) 464–472.
- [6] L. Yut, A. Zofka, Correlation between rheology and chemical composition of aged polymer-modified asphalts, *Constr. Build. Mater.* 62 (2014) 109–117.
- [7] R. Zhang, H. Wang, J. Gao, Z. You, X. Yang, High temperature performance of SBS modified bio-asphalt, *Constr. Build. Mater.* 144 (2017) 99–105.
- [8] W. Huang, N. Tang, Characterizing SBS modified asphalt with sulfur using multiple stress creep recovery test, *Constr. Build. Mater.* 93 (2015) 514–521.
- [9] L. Liu, F. Xiao, H. Zhang, S. Amirkhanian, Rheological characteristics of alternative modified binders, *Constr. Build. Mater.* 144 (2017) 442–450.
- [10] M. Liang, X. Xin, W. Fan, H. Luo, X. Wang, B. Xing, Investigation of rheological properties and storage stability of CR/SBS modified asphalt, *Constr. Build. Mater.* 74 (2015) 235–240.
- [11] M. Liang, X. Xin, W. Fan, H. Sun, Y. Yao, B. Xing, Viscous properties, storage stability and their relationships with microstructure of tire scrap rubber modified asphalt, *Constr. Build. Mater.* 74 (2015) 124–131.
- [12] F. Zhang, C. Hu, The research for structural characteristics and modification mechanism of crumb rubber compound modified asphalts, *Constr. Build. Mater.* 76 (2015) 330–342.
- [13] F.J. Navarro, P. Partal, F. Martínez-Boza, C. Gallegos, Influence of crumb rubber concentration on the rheological behavior of a crumb rubber modified bitumen, *Energ. Fuel.* 19 (2005) 1984–1990.
- [14] K. Formela, M. Klein, X. Colom, M.R. Saeb, Investigating the combined impact of plasticizer and shear force on the efficiency of low temperature reclaiming of ground tire rubber (GTR), *Polym. Degrad. Stabil.* 125 (2016) 1–11.
- [15] T. Wang, F. Xiao, X. Zhu, B. Huang, J. Wang, S. Amirkhanian, Energy consumption and environmental impact of rubberized asphalt pavement, *J. Clean. Prod.* 180 (2018) 139–158.
- [16] O. Xu, F. Xiao, S. Han, S.N. Amirkhanian, Z. Wang, High temperature rheological properties of crumb rubber modified asphalt binders with various modifiers, *Constr. Build. Mater.* 112 (2016) 49–58.
- [17] M. Myhre, S. Saiwari, W. Dierkes, J. Noordermeer, Rubber recycling: chemistry, processing and applications, *Rubber. Chem. Technol.* 85 (2012) 408–449.
- [18] F. Moreno, M. Sol, J. Martín, M. Pérez, M.C. Rubio, The effect of crumb rubber modifier on the resistance of asphalt mixes to plastic deformation, *Mater. Des.* 47 (2013) 274–280.
- [19] F. Dong, X. Yu, S. Liu, J. Wei, Rheological behaviors and microstructure of SBS/CR composite modified hard asphalt, *Constr. Build. Mater.* 115 (2016) 285–293.

- [20] F.J. Navarro, P. Partal, F.J. Martínez-Boza, C. Gallegos, Thermo-rheological behavior and storage stability of ground tire rubber-modified bitumens, *Fuel* 83 (2004) 2041–2049.
- [21] R. Rasool, S. Wang, Y. Zhang, G. Zhang, Improving the aging resistance of SBS modified asphalt with the addition of highly reclaimed rubber, *Constr. Build. Mater.* 145 (2017) 126–134.
- [22] S. Wang, D. Cheng, F. Xiao, Recent developments in the application of chemical approaches to rubberized asphalt, *Constr. Build. Mater.* 131 (2017) 101–113.
- [23] M. Sienkiewicz, K.B. Labuda, A. Wojtkiewicz, H. Janik, Development of methods improving storage stability of bitumen modified with ground tire rubber: a review, *Fuel. Process. Technol.* 159 (2017) 272–279.
- [24] R.K. Padhan, A.A. Gupta, C.S. Mohanta, R.P. Badoni, A.K. Bhatnagar, Performance improvement of a crumb rubber modified bitumen using polyoctenamer and cross linking agent, *Road. Mater. Pavement.* 18 (2017) 1–8.
- [25] G. Yadollahi, H.S. Mollahosseini, Improving the performance of crumb rubber bitumen by means of poly phosphoric acid (PPA) and Vestenamer additives, *Constr. Build. Mater.* 25 (2011) 3108–3116.
- [26] H. Yu, Z. Leng, Z. Gao, Thermal analysis on the component interaction of asphalt binders modified with crumb rubber and warm mix additive, *Constr. Build. Mater.* 125 (2016) 168–174.
- [27] X. Deng, Z. Li, Y. Huang, Y. Luan, Improving mechanism and effect analysis of sulfured and grafted *Eucommia Ulmoides* Gum modified rubber asphalt, *Constr. Build. Mater.* 715–722 (2017).
- [28] V. González, F.J. Martínez-Boza, F.J. Navarro, C. Gallegos, A. Pérez-Lepe, A. Páez, Thermomechanical properties of bitumen modified with crumb tire rubber and polymeric additives, *Fuel. Process. Technol.* 91 (2010) 1033–1039.
- [29] M. Liang, S. Ren, W. Fan, H. Wang, W. Cui, P. Zhao, Characterization of fume composition and rheological properties of asphalt with crumb rubber activated by microwave and TOR, *Constr. Build. Mater.* 154 (2017) 310–322.
- [30] M. Liang, X. Xin, W. Fan, S. Ren, J. Shi, H. Luo, Thermo-stability and aging performance of modified asphalt with crumb rubber activated by microwave and TOR, *Mater. Des.* 127 (2017) 84–96.
- [31] P.J. Carreau, Rheological equations from molecular network theories, *Trans. Soc. Rheol.* 16 (1972) 99–127.
- [32] Z. Xie, J. Shen, Effect of cross-linking agent on the properties of asphalt rubber, *Constr. Build. Mater.* 67 (2014) 234–238.
- [33] K.N. Puga, R.C. Williams, Low temperature performance of laboratory produced asphalt rubber (AR) mixes containing polyoctenamer, *Constr. Build. Mater.* 112 (2016) 1046–1053.
- [34] K.E. Min, H.M. Jeong, Characterization of air-blown asphalt/trans-polyoctenamer rubber blends, *J. Ind. Eng. Chem.* 19 (2013) 645–649.
- [35] Ng Puge, Ka Lai Nieve, Rheology and performance evaluation of Polyoctenamer as Asphalt Rubber modifier in Hot Mix Asphalt. Graduate Theses and Dissertations, Paper 13279, 2013.
- [36] H. Wang, X. Liu, P. Apostolidis, S. Erkens, T. Scarpas, Numerical investigation of rubber swelling in bitumen, *Constr. Build. Mater.* 214 (2019) 506–515.
- [37] H. Liu, Z. Chen, W. Wang, H. Wang, P. Hao, Investigation of the rheological modification mechanism of crumb rubber modified asphalt (CRMA) containing TOR additive, *Constr. Build. Mater.* 67 (2014) 225–233.
- [38] ASTM D5-06, Standard test method for penetration of bituminous materials.
- [39] ASTM D36-06, Standard test method for softening point of bitumen (ring and ball apparatus).
- [40] ASTM D113-99, Standard test method for ductility of bituminous materials.
- [41] ASTM D4124-01, Standard test methods for separation of asphalt into four fractions.
- [42] AASHTO M 320, Standard specification for performance-graded asphalt binder.
- [43] AASHTO TP70, Standard method of test for multiple stress creep recovery (MSCR) test of asphalt binder using a Dynamic Shear Rheometer (DSR), American Association of State Highway and Transportation Officials, Washington (DC), 2009.
- [44] X. Yu, S. Liu, F. Dong, Comparative assessment of rheological property characteristics for unfoamed and foamed asphalt binder, *Constr. Build. Mater.* 122 (2016) 354–361.
- [45] JTJ T0661-2000, Standard Test Method for Segregation of Polymer Modified Asphalt.
- [46] P. Liang, M. Liang, W. Fan, Y. Zhang, C. Qian, S. Ren, Improving thermo-rheological behavior and compatibility of SBR modified asphalt by addition of polyphosphoric acid (PPA), *Constr. Build. Mater.* 139 (2017) 183–192.
- [47] S. Ren, M. Liang, W. Fan, Y. Zhang, C. Qian, Y. He, J. Shi, Investigating the effects of SBR on the properties of gilsonite modified asphalt, *Constr. Build. Mater.* 190 (2018) 1103–1116.