Effects of SBS Configuration on Performance of High Modulus Bitumen Based on Dynamic Mechanical Analysis

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Abstract

High modulus bitumens modified by polystyrene-*block*-polybutadiene-*block*-polystyrene (SBS) with different molecular structure were investigated on dynamic shear rheometer and fluorescence microscopy to evaluate viscoelastic properties and morphology of binders. The results shows that storage modulus (G') is obviously less than loss modulus (G''), which means viscous behaviour of bitumen is dominant, and anti-rutting factor ($G^*/\sin\delta$) is markedly enhanced by star SBS than by linear SBS. The morphology indicated that star SBS improved the softening point more obviously, tending to form a cross-linked network in bitumen. As for linear SBS, it is dispersed in bitumen in the form of globules and enhances the ductility of binder.

Keywords

Dynamic mechanical analysis, anti-rutting, microstructure, high modulus bitumen

1. Introduction

In recent years, pavement distress, such as rutting, fatigue and cracks, have become a problem with the increase in traffic volume, number of heavy vehicles and the influence of climate change.[1,2] In semirigid and flexible pavement, bitumen mixtures support most vehicle loads, and bitumen has a great effect on the function of the bitumen mixture.[3] The results of the study show that the main cause of serious rutting in China is that the penetration of selected bitumen is high and the modulus is low.[4,5]

High modulus bitumen has excellent ability to resist deformation, because it produces small strain when subjected to stress. Therefore, the development and application of high modulus bitumen is important for improving pavement's ability to resist rutting and prolonging life span of pavement.[6] The earliest attempt in HMBC (high modulus bitumen concrete) had been carried out in France. The French standard NFP98-140 gives the definition of HMBC, whose complex modulus is higher than 14 000 MPa at 15 °C and 10 Hz.[7] However, there are no specific standards related to high modulus bitumen in China. In engineering applications, we usually regard bitumen whose complex modulus is greater than 10 000 MPa at 60 °C and 10 Hz as high modulus bitumen.

Nowadays, the solvent de-asphalting process has become a widely applied heavy oil process. When asphaltene, resin, and metal are removed from residue to produce light oils, it can also produce de-oiled bitumen with high asphaltene, low wax, and high softening point. In recent years, the issue of the utilization of de-oiled bitumen has become an important subject in the solvent de-asphalting process. De-oiled bitumen, as main material, was mixed with soft bitumen components and SBS with different structure to produce high modulus bitumen, which achieved a win-win situation for making effective use of de-oiled bitumen and producing pavement bitumen with high added-value. In this paper, high modulus bitumen modified by SBS with different molecular structure were carried out on dynamic shear rheometer by means of temperature sweep and fluorescence microscopy to evaluate anti-rutting performance, viscoelastic properties and morphology of binders.

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2. Experimental

2.1 Materials

Oil slurry and aromatic oil were obtained from Jingmen Petrochemical Company, while the base bitumen was prepared by blending de-oiled bitumen with oil slurry and aromatic oil. The base bitumen was then modified by SBS. The basic properties of the three materials are presented in Table 1. The author selected star Daogai 2# SBS and linear YH-791H, both of SBS with 30/70 in block ratio styrene/polybutadiene, from Yueyang Baling Petrochemical Company.

Table 1 – Properties and compositions of raw materials
Tablica 1 – Svojstva i sastav sirovih materijala

Properties Svojstva	Softening point Mekšište / °C	Penetration Prodiranje / 0,1 mm	w(S) / %	w(A) / %	w(R) / %	w(As) / %
DOA	88.9	2	7.1	24.9	46.1	17.8
oil slurry uljni mulj	36.2	–	14.4	62.0	14.0	4.9
aromatic oils aromatska ulja	–	–	12.2	47.4	30.2	8.32

2.2 Preparation of high modulus bitumen

Base bitumen was prepared by de-oiled bitumen, oil slurry and aromatic oil at the ratio of 53 : 37 : 10. SBS with different structure was added into the base bitumen with FLUKE FM300-digital high-shear, and then samples were sheared for 10 min at 170 °C and 3000–4000 rpm. Finally, the samples were stirred for 2 h in order to prepare HMA. The dosage (in mass) of SBS was 3 % and 5 %, and that of stabilizer was 0.3 %.

2.3 Performance evaluation

Conventional properties, such as ductility, penetration, softening point, were analysed according to T0606-2000, T0604-2000 and T0605-2000 in JTJ052-2000 "Experimental regulation of highway project bitumen and bitumen mixture". Dynamic viscosity was measured by RVDV-II+P Brookfield viscosity instrument produced by Brookfield engineering laboratory. Morphology was detected by BX51 microscope produced by Olympus, and magnification was 100. Oscillation tests were carried out on rheometer AR2000EX produced by US TA Company in LVR (linear viscoelasticity region). 25 mm parallel-plate in diameter and 1 mm gap was selected. LVR was previously tested for all samples based on stress sweep.

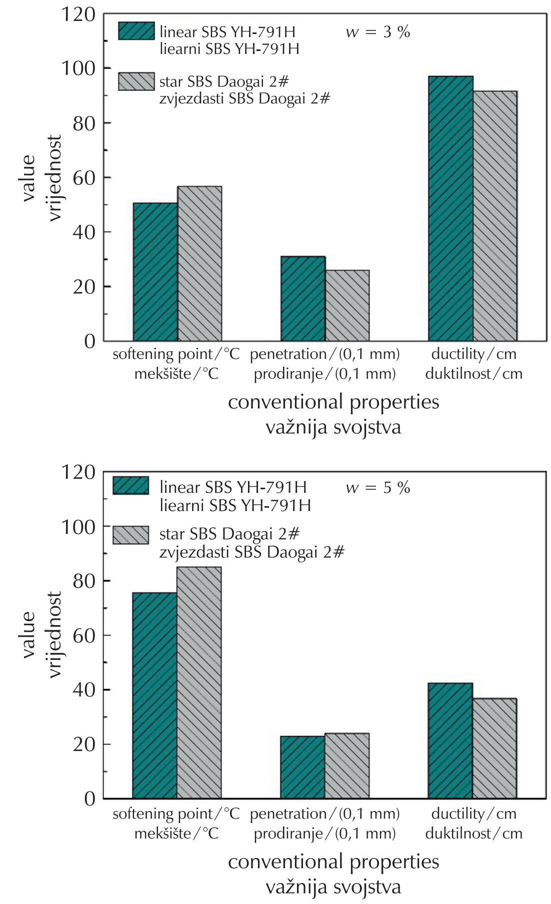

Fig. 1 – Effects of different SBS on the conventional properties of HMA

Slika 1 – Učinci različitih SBS-a na važnija svojstva HMA

3. Results and discussion

3.1 Conventional performance

Conventional properties, including low temperature ductility, penetration, softening point, are utilized to measure low temperature performance, consistency and high temperature performance of bitumen. Conventional performance of high modulus bitumen produced by SBS with different structure are shown in Fig. 1. The structure of SBS has great effect on conventional performance of bitumen, especially for softening point and ductility. Star Daogai2# has a greater softening point and linear YH-791H has greater ductility. However, the structure of SBS has little effect on penetration. This is due to the fact that three-dimensional network structure formed by polybutadiene has more crosslinking domains.[8] Thus, high modulus bitumen possesses better high-temperature properties. However, high modulus bitumen modified by linear YH-791H has better low-temperature properties, and its ductility is higher at low temperatures.

The relation between temperature and viscosity of bitumen is used to evaluate bitumen's susceptiveness to temperature. Characterization of viscosity-temperature properties of high modulus bitumen with different structure SBS is displayed in Fig. 2. The Saal formula was used,

$$\log\left(\log\frac{\eta\cdot 10^3}{\mathrm{Pa\,s}}\right) = m - n\log\frac{t+273.15\ °\mathrm{C}}{°\mathrm{C}} \quad (1)$$

to describe the relation between temperature and viscosity of high modulus bitumen, where η denotes viscosity of bitumen, and m and n are coefficients. The results in Fig. 2 show that the relation between viscosity and temperature is a good linear relation in a relatively wide temperature range, and the curve fitted fairly well. Correlation coefficients obtained by Saal formula are displayed in Table 2.

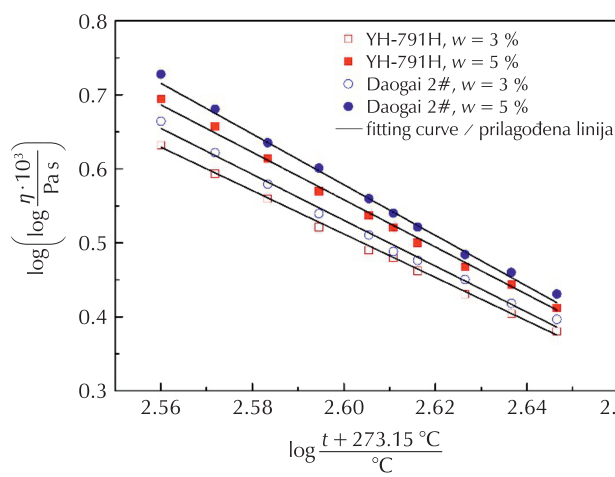

Fig. 2 – Viscosity-temperature dependence of bitumen modified by different SBS

Slika 2 – Ovisnost viskoznosti o temperaturi bitumena modificiranog različitim SBS-ovima

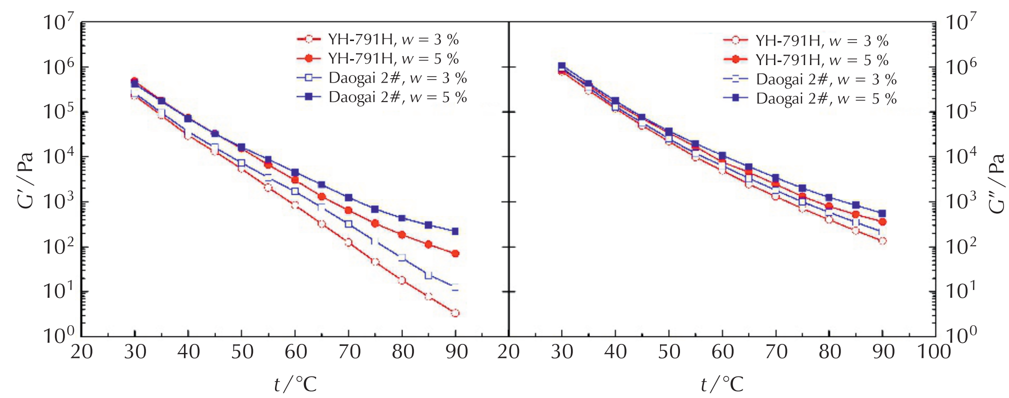

Fig. 3 – Evolution of G' and G'' for high modulus bitumens with different structure of SBS
Slika 3 – Promjena G' i G'' bitumena visokih modula s SBS-om različitih struktura

Regression coefficient n represents the slope of fitting curve in Saal formula in viscosity–temperature curve, which reflects the change of viscosity with temperature of bitumen. The changes in viscosity with temperature of bitumen is more obvious when n is greater. The data in Table 2 show that n of high modulus bitumen produced by star Daogai SBS is larger than linear YH-791H. This indicates that the changes in viscosity with temperature of high modulus bitumen produced by star SBS is more obvious. The n of $w = 5$ % SBS is larger than $w = 3$ % SBS with the same type of SBS. This indicates that a larger dosage of SBS produces a more obvious change in viscosity with temperature. Thus, it is less susceptible to temperature.

Table 2 – Coefficients of viscosity–temperature curve for various SBS modified bitumen
Tablica 2 – Rezultat regresijske analize ovisnosti visokoznost-temperatura bitumena modificiranih različitim SBS-ovima

SBS structure Struktura SBS-a	w(SBS) / %	m	n	R^2
linear linearni	3	8.146	3.172	0.991
	5	8.893	3.206	0.986
star zvjezdasti	3	8.605	3.279	0.993
	5	9.491	3.428	0.987

3.2 Dynamic mechanical properties

The permanent deformation which developed under heavy loads at a high environmental temperature are mainly distress in pavement.[9,10] In order to describe the permanent deformation, dynamic mechanical parameters were obtained on DSR (dynamic shear rheometer) by temperature sweep tests. Elasticity and viscosity of bitumen was evaluated by the relation between G^*, G', G'' and δ, while anti-rutting factor $G^*/\sin\delta$ represents anti-rutting performance.

Variation in G' and G'' with temperature of high modulus bitumen prepared by different SBS are displayed in Fig. 3. The results in Fig. 3 show that G' and G'' will be lower in high-temperature regions. Storage modulus G' together with loss modulus G'' decreased by three to four magnitudes when temperature increased from 30 °C to 90 °C. This indicates that temperature has great effect on modulus of bitumen. Storage modulus G' is usually less than loss modulus G''. Thus, high modulus bitumen mainly presents viscous properties. G' decreased more obviously than G'' when the temperature increased. This shows that temperature influences the storage modulus G' more easily. When the dosage of SBS was the same, it was observed that G' as well as G'' for star SBS is higher than that of linear SBS. This is because the star SBS easily formed a crosslinking system within the bitumen, which accounted for the increased viscosity of the bitumen. Anti-rutting performance improved because the crosslinking system was able to maintain the original structure and morphology with imposed external force. G' together with G'' is higher when the dosage of SBS is greater at the same temperatures. This indicates that the anti-distortion capacity of bitumen will be stronger.

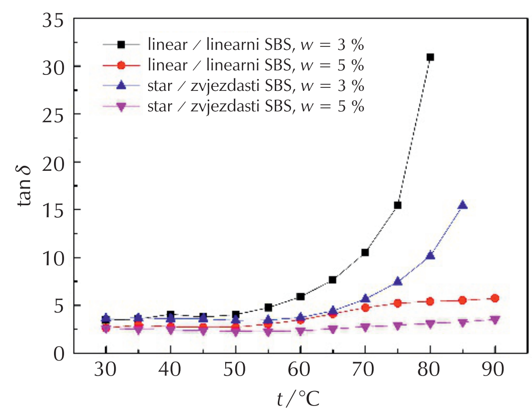

Fig. 4 – Evolution of phase angle for high modulus bitumens
Slika 4 – Promjena faznog kuta bitumena visokih modula

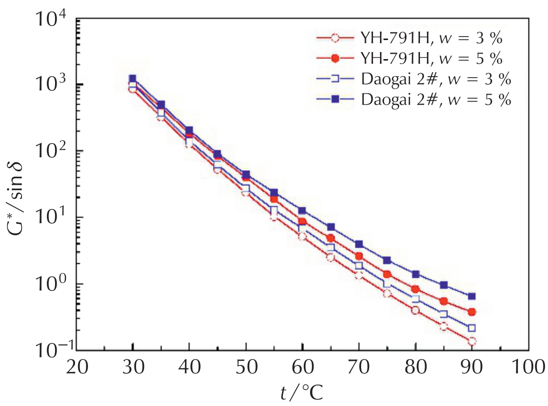

Fig. 5 – Effect of SBS structure on $G^*/\sin\delta$
Slika 5 – Utjecaj strukture SBS-a na $G^*/\sin\delta$

Evolutions of phase angle for high modulus bitumens are shown in Fig. 4. As can be seen, the phase angle increased drastically with temperature for both SBS with the dosage of 3 %. However, the phase angle almost kept constant in a wide temperature range, indicating less temperature susceptibility. The change in $G^*/\sin\delta$ with temperature of high modulus bitumen prepared by different SBS is presented in Fig. 5. The results in Fig. 5 show that $G^*/\sin\delta$ decreased when temperature increased. $G^*/\sin\delta$ of bitumen prepared by star SBS is higher than linear SBS. This shows that the structure of star SBS had a great effect on the modulus of bitumen. Owing to special structure of star SBS, the three-dimensional network structure formed by polybutadiene in star SBS had more crosslinking points, and star SBS easily formed a network structure in the bitumen medium. Therefore, the modulus and high temperature properties of bitumen will be improved obviously. Density and stability of network structure formed by bitumen in linear SBS are far worse than that in star SBS.

3.3 Relation between micro-morphology and dynamic mechanical properties

Fluorescence optical microscopy structures of high modulus bitumen with different SBS are presented in Fig. 6. The result in Fig. 6 shows that linear YH-791H was dispersed in the form of globules in colloid system of bitumen. But star Daogai2# formed a crosslinking structure within the bitumen with the help of a stabilizer, and the crosslinking structure improved the high-temperature properties and anti-rutting performance of the bitumen. This phenomenon reflected in fluorescence optical microscopy structures is in line with the result in Fig. 1. Comparing Fig. 6

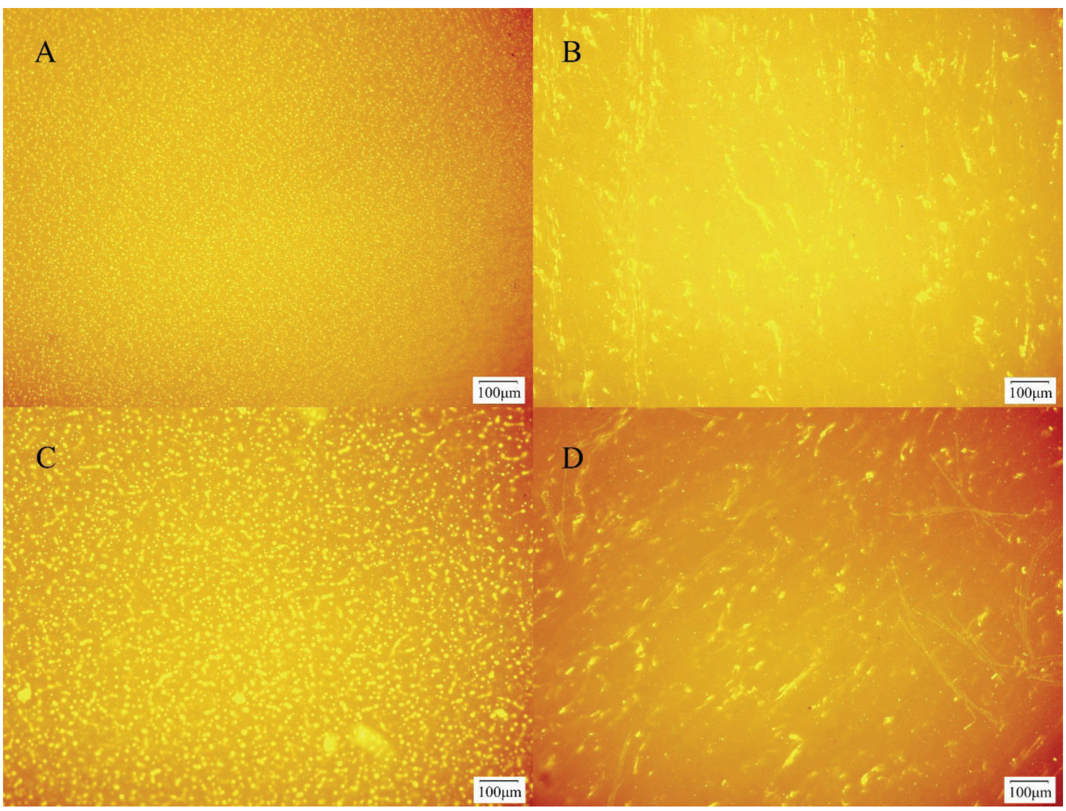

Fig. 6 – Effect of SBS structure on the micromorphology of high modulus bitumen (× 100)
A – *w*(YH-791H) = 3 %, B – *w*(Daogai2#) = 3 %, C – *w*(YH-791H) = 5 %, D – *w*(Daogai2#) = 5 %
Slika 6 – Utjecaj strukture SBS-a na morfologiju bitumena visokih modula (× 100)
A – *w*(YH-791H) = 3 %, B – *w*(Daogai2#) = 3 %, C – *w*(YH-791H) = 5 %, D – *w*(Daogai2#) = 5 %

(B) and Fig. 6 (D), it was found that bitumen was a continuous phase, and SBS generates a slight improvement in the softening point when the dosage of SBS was small. SBS particle distance decreased and polymers tended to form a network structure when the mixing amount of SBS increased. The network confined the ability of flowing and deformation of bitumen, which consequently improved softening point, viscosity and anti-rutting performance.[11]

4. Conclusion

Temperature sweep of high modulus bitumen with different SBS was carried out on dynamic shear rheometer. The conventional tests indicate that high-temperature performance for star SBS is better than the linear one, while the ductility of star SBS is lower than that of linear SBS. Moreover, the linear SBS has lower viscosity compared to star SBS at the same temperature, which indicates that former has better mixing ability. The dynamic test results show that G' together with G'' decreases when temperature increases, and that storage modulus G' is less than loss modulus G''. G', G'' and $G^*/\sin\delta$ for star SBS is higher than that of linear SBS in the same concentration. The morphology indicates that star SBS improve the softening point more obviously compared to linear SBS because of the dense cross-linked network formed by SBS molecule in bitumen phase. Linear SBS dispersed in bitumen presents spherical particles, which enhances the ductility of binder.

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List of abbreviations and symbols
Popis kratica i simbola

A	– aromatics – aromati
As	– asphaltene – asfalteni
DOA	– de-oiled bitumen – bitumen preostao nakon deasfaltizacije
DSR	– dynamic shear rheometer – dinamički smični reometar
HMA	– high modulus bitumen – bitumen visokih modula
HMBC	– high modulus bitumen concrete – bitumenski beton visokih modula
LVR	– linear viscoelasticity region – područje linearne viskoelastičnosti
R	– resin – smole
S	– saturate – zasićeni ugljikovodici
SBS	– polystyrene-*block*-polybutadiene-*block*-polystyrene – polistiren-*block*-polibutadien-*block*-polistiren
G^*	– complex modulus, MPa – kompleksni modul, MPa
$G^*/\sin\delta$	– anti-rutting factor, Pa – parametar kolotraga, Pa
G'	– storage modulus, Pa – modul pohrane, Pa
G''	– loss modulus, Pa – modul gubitaka, Pa
m, n	– coefficients in linear regression analysis – koeficijenti u linearnoj regresijskoj analizi
R^2	– coefficient of determination – determinacijski koeficijent
t	– temperature, °C – temperatura, °C
w	– mass fraction, % – maseni udjel, %
δ	– phase angle, ° – fazni kut, °
η	– viscosity, Pa s – viskoznost, Pa s

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SAŽETAK

Dinamička mehanička analiza, sprječavanje kolotraženja, mikrostruktura, bitumen visokih modula

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Dinamičkim smičnim reometrom i fluorescencijskim mikroskopom istražena su viskoelastična svojstva i morfologija bitumena modificiranih polistiren-*block*-polibutadien-*block*-polistirenom (SBS) različitih molekulskih struktura. Rezultati pokazuju da je modul pohrane (G') uočljivo manji od modula gubitaka (G'') što znači da dominira viskoznost bitumena, a parametar kolotraga ($G^*/\sin\delta$) znatno više raste uz zvjezdasti nego linearni SBS. Morfologija ukazuje na to da zvjezdasti SBS, koji može premrežiti bitumen, primjetno više poboljšava mekšište. Linearni SBS povećava duktilnost, a raspršen je u bitumenu u obliku globula.

Ključne riječi
Dinamička mehanička analiza, sprječavanje kolotraženja, mikrostruktura, bitumen visokih modula

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