Evaluation of the Properties of Bitumen Modified by SBS Copolymers with Different Styrene–Butadiene Structure

Qinqin Zhang,[1] Tiezhu Wang,[2] Weiyu Fan,[3] Yang Ying,[4] Yumin Wu[1]

[1]College of Chemical Engineering, Qingdao University of Science and Technology, 266042 Qingdao, People's Republic of China
[2]Petrochina Karamay Petrochemical Company, 834000 Karamay, People's Republic of China
[3]College of Chemical Engineering, China University of Petroleum, 266555 Qingdao, People's Republic of China
[4]Petrochina Fuel Oil Company Limited, 100102 Beijing, People's Republic of China
Correspondence to: W. Fan (E-mail: fanwyu@upc.edu.cn)

ABSTRACT: Four styrene–butadiene–styrene(SBS) modified bitumens had been prepared by a base bitumen, a crosslinking agent and four SBS copolymers which differ in styrene blocks content and molecular configuration (radial or linear) under the same experimental conditions. Conventional properties, morphology, thermal behavior and microstructure were investigated by means of conventional tests, fluorescence microscopy, differential scanning calorimetry (DSC), and Fourier transform infrared (FT-IR) spectroscopy. In terms of linear SBS polymers, the SBS molecule with the styrene content of 30% has a perfect dispersion and complete stretching in bitumen matrix, and in this case, the conventional properties and thermal stability of bitumen are enhanced substantially. However, the star SBS polymer due to long branched chains forming the preferable steric hindrance to enhance the intensity of base bitumen, plays a more important role in improving the conventional properties of base bitumen than linear SBS polymers. Furthermore, the FT-IR spectra indicate that, the main bands assignations of four modified bitumens are identical and the significant variation is the peak intensity. And a noncomplete crosslinking reaction happens between the bitumen and each SBS polymer, which can efficiently prevent excessive crosslinking from affecting the intrinsic bitumen characteristics. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40398.

INTRODUCTION

Bitumen binders are widely used in pavements building and their viscoelastic properties are dependent on their chemical composition.[1–3] A series of polymers are usually used to modify bitumen binders to enhance their application performance, such as thermal susceptibility, aging at medium and intermediate temperatures and resistance to rutting and fatigue.[4,5] And the most successful polymer for bitumen binder modification to date is the styrene-butadiene-styrene (SBS) tirblock copolymers.[3–7] For example, a typical bitumen paving formulation may work well in places at temperatures between 10 and 50°C; however, a SBS modified bitumen may work well from −20 to 76°C.[8]

These copolymers are thermoplastic elastomers and exhibit a two-phase morphology, a plastic phase of the polystyrene end-blocks with a glass transition temperature (T_g) around 100°C, and an elastomeric phase attributed to the polybutadiene central blocks with the T_g around −80°C. As the pavement temperature is normally between these two T_g values, polystyrene blocks undergo intermolecular interactions dispersing in the elasto-

meric polybutadiene matrix and creating immovable points in bitumen to give viscoelastic properties.

When SBS polymer is mixed with bitumen binder, the polybutadiene phase absorbs the bitumen maltene fraction and swells up to nine times its initial volume. At a suitable SBS concentration, normally between 3 and 5%, a polymer network is homogenously formed throughout the bitumen matrix and this changes substantially the bitumen properties.[9–11]

Microstructure parameters such as styrene-butadiene diblock content and molecular configuration (radial or linear) from SBS polymers have a strong effect on bitumen.[8] Thus, the aim of this work is to observe conventional properties, morphology, thermal behavior, and microstructure of bitumens modified by four SBS copolymers with different styrene content and molecular configuration from SBS.

EXPERIMENTAL

Materials
Caltex AH-70 bitumen was provided by Shandong Highway Construction Material, Jinan, China. To characterize properties

Table I. Properties of Base Bitumen

Test	Specifications	Results
Penetration (25°C, 0.1 mm)	ASTM D5	67
Penetration index (PI)[a]	–	−1.62
Softening point (°C)	ASTM D36	45.9
Ductility (5 cm min^{-1}, 5°C, cm)	ASTM D113	2
Ductility (5 cm min^{-1}, 15°C, cm)	ASTM D113	>150
Four fractions		
Saturates (S, %)	ASTM D 4124	14.4
Aromatics (A, %)	ASTM D 4124	45.0
Resins (R, %)	ASTM D 4124	30.1
Asphaltenes (At, %)	ASTM D 4124	10.5

[a] $PI = \frac{1952 - 500 \times \log(Pen_{25}) - 20 \times T_{SP}}{50 \times \log(Pen_{25}) - T_{SP} - 120}$, where, Pen_{25} is the penetration at 25°C and T_{SP} is the softening point temperature of specimens.

of the base bitumen, conventional tests such as penetration, softening point and ductility, etc., were conducted. The relevant test results and specifications are presented in Table I. SBS copolymers were produced by LCY Chemical, Taiwan and Yueyang Baling Petrochemical, China. Table II presents the main properties from these polymers and Figure 1 describes the chemical structure of linear and star SBS polymers. The crosslinking agent was provided by Panjin PetroChina LiaoHe Asphalt, China.

Methods
Modified bitumen was prepared using a high-speed shearer (Fluko FM 300) at 3000 rpm for 1 h with 3% by weight (the same content for each of the polymers) of SBS polymer and 0.3% by weight of crosslinking agent in compound matrix, in which process the blend was kept at 175°C ± 5°C.

Morphological characteristics was observed on a FM-400C microscope (produced by Shanghai Pudan optical instrument, China) with blue fluorescence (generated from a high pressure Xenon lamp) at magnification of 100 × 4, as samples were prepared by heating and homogenizing at 163°C in an oven for 10

min to form a thin film between the glass slide and the cover slip. Images were taken and digitized by a camera and then stored into the computer as an image file.

The DSC analysis was performed on a NETZSCH DSC 204 F1 calorimeter using 5–10 mg samples sealed in crucibles, under a nitrogen flow of 20 mL min^{-1} at a heating rate of 10°C min^{-1}. The tested temperature range is between −40 and 150°C.

The FT-IR spectroscopy was performed on a Nicolet IS 10 to probe the existing functional groups on modified bitumens. Samples were analyzed using a thin disk of the sample mixed with KBr in the range of 4000 and 400 cm^{-1}.

RESULTS AND DISCUSSION

Conventional Properties
The modified bitumens composed of polymers YH-796, LCY 3501, YH-792, and Daogai 2# are denoted as M_A, M_B, M_C, and M_D, which properties are presented in Table III.

Overall, compared to base bitumen, the penetration values of SBS modified bitumens decreases slightly, while the softening point values increase greatly, which arises from the addition of SBS copolymers. For ductility at 5°C, it has no significant change when the discrepancy is ignored. Furthermore, the PI values have considerable changes indicating a decline in temperature susceptibility.

Compared to base bitumen, the properties of modified bitumens are improved substantially and display different increment. However, for M_A, M_B, M_C with the same molecular configuration and different styrene content from SBS, the properties of modified bitumens do not increase with increasing styrene content from SBS. The M_B shows the best properties, especially softening point, PI and elastic recovery, in terms of the styrene content of 30% from SBS, followed by M_C and M_A. This is mainly because the properties of modified bitumen are bound up with the compatibility between bitumen and SBS copolymer. When the styrene content is 30% from SBS, the SBS copolymer is swollen in the bitumen forming the best compact three-dimensional network structure, but it has no apparent

Table II. Properties of SBS Polymers

Typical properties	YH-796	LCY 3501	YH-792	DAOGAI 2#
Molecular structure	Linear	Linear	Linear	Star
S/B ratio[a]	20/80	30/70	40/60	30/70
Volatility (≤%)	0.50	0.17	0.50	0.70
Total ash (≤%)	0.20	0.11	0.20	0.20
Stress at 300% (≥MPa)	1.80	–	3.40	2.2
Tensile strenth (≥MPa)	10.00	–	22.00	8.0
Elongation (≥%)	900	–	750	550
Permanent deformation (≤%)	20	–	50	40
Hardness shore (A)	58	75	85	70
Melt flow rate (g/10 min)	0.10–5.00	0.10–5.00	0.10–5.00	0.00–1.00
Molecular weight	160,000	120,000	90,000	160,000

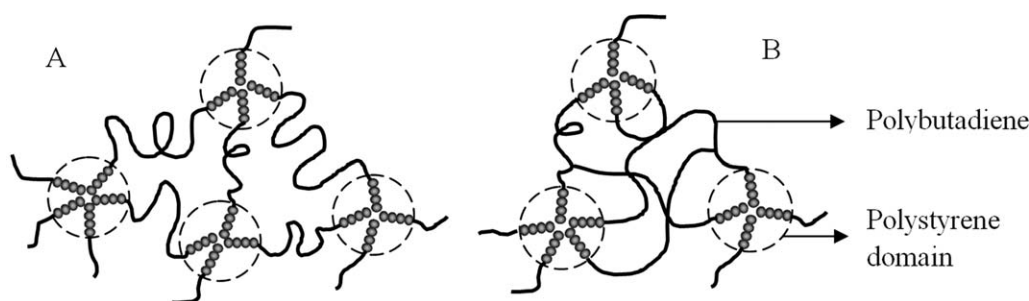[a] It represents the blocks content ratio between polystyrene and polybutadiene.

Figure 1. Schematic representation of molecular structure from linear and star SBS: (A) linear and (B) star.

influence on penetration, ductility at 5°C and storage stability of modified bitumens.

On the other hand, for M_B and M_D with different molecular configuration and identical styrene content from SBS, the properties of star SBS modified bitumen are much more enhanced than that of linear SBS modified bitumen. Thus, the M_D displays much preferable high temperature performance, temperature sensitivity and elasticity to other modified bitumens due to higher values in softening point, PI and elastic recovery percentage. The reason is that the star SBS has long branched chains which form the favorable steric hindrance so that it plays an important role in enhancing the intensity of base bitumen. Therefore, the bitumen modified by star SBS has an advantage for advanced practical application, e.g., in a high-temperature region of south China or for a first-class highway design, over others modified by linear SBS polymers. The bitumen modified by the linear SBS with 30% of styrene content can meet the need of general application. What's more, according to specification of highway industry of China (Technical Specification for Construction of Highway Asphalt Pavements, JTG F 40-2004), properties of modified bitumens can fully meet the requirements of I-C and I-D series, especially M_B and M_D, far exceeded those requirements.

Morphology

The morphology of modified bitumens has been investigated using a fluorescence microscopy at room temperature to determine the characteristic of the dispersion fineness of the discrete phase.

Morphological images for base and modified binders are presented in Figure 2. In the images, the swollen polymer phase appears light while the bitumen rich phase appears dark.[12]

In general, both linear and star SBS particles are spread homogenously throughout the bitumen matrix. This is attributed to saturates and naphthene aromatics in the base bitumen that are compatible components to swell copolymer. However, delicate difference is presented with bitumen modified by various SBS polymers. In terms of linear SBS polymers, as the styrene content from SBS increases, the molecular size of SBS globules becomes more pronounced, in that the elastic polybutadiene segment is liable to absorb the bitumen maltene fraction and swells to form homogenous dispersion.[13] For M_A, the distribution of the polymer phase throughout the bitumen matrix is extremely fine, which is not preferable for enhancing the properties of bitumen at all. The reason is that the swollen SBS molecules segregate from the bitumen maltene fraction so that SBS particles becomes much finer and shows inerratic appearance. Consequently, it forms a slack three-dimensional network and makes unobvious increase in bitumen stretching ability. Moreover, perfect dispersion and complete stretching can be monitored for SBS LCY 3501 molecule in base bitumen and this is consistent with previous results for conventional properties. For M_C, the SBS particles can be clearly observed in the form of minor round or elliptical grain so that the three-dimensional network is defectively compact. Hence, the conventional results for properties of M_A and M_C inferior to M_B are further verified by above-mentioned morphological analysis.

Furthermore, as depicted in Figure 2, there is more uniformity in the micrographs of the bitumen modified by linear SBS relative to that of star SBS in which the polymer particle size is lager. Therefore, it is likely to deduce that for the same styrene content from SBS, the linear SBS show better distribution throughout the bitumen matrix than the star SBS due to the

Table III. Properties of SBS Modified Bitumens

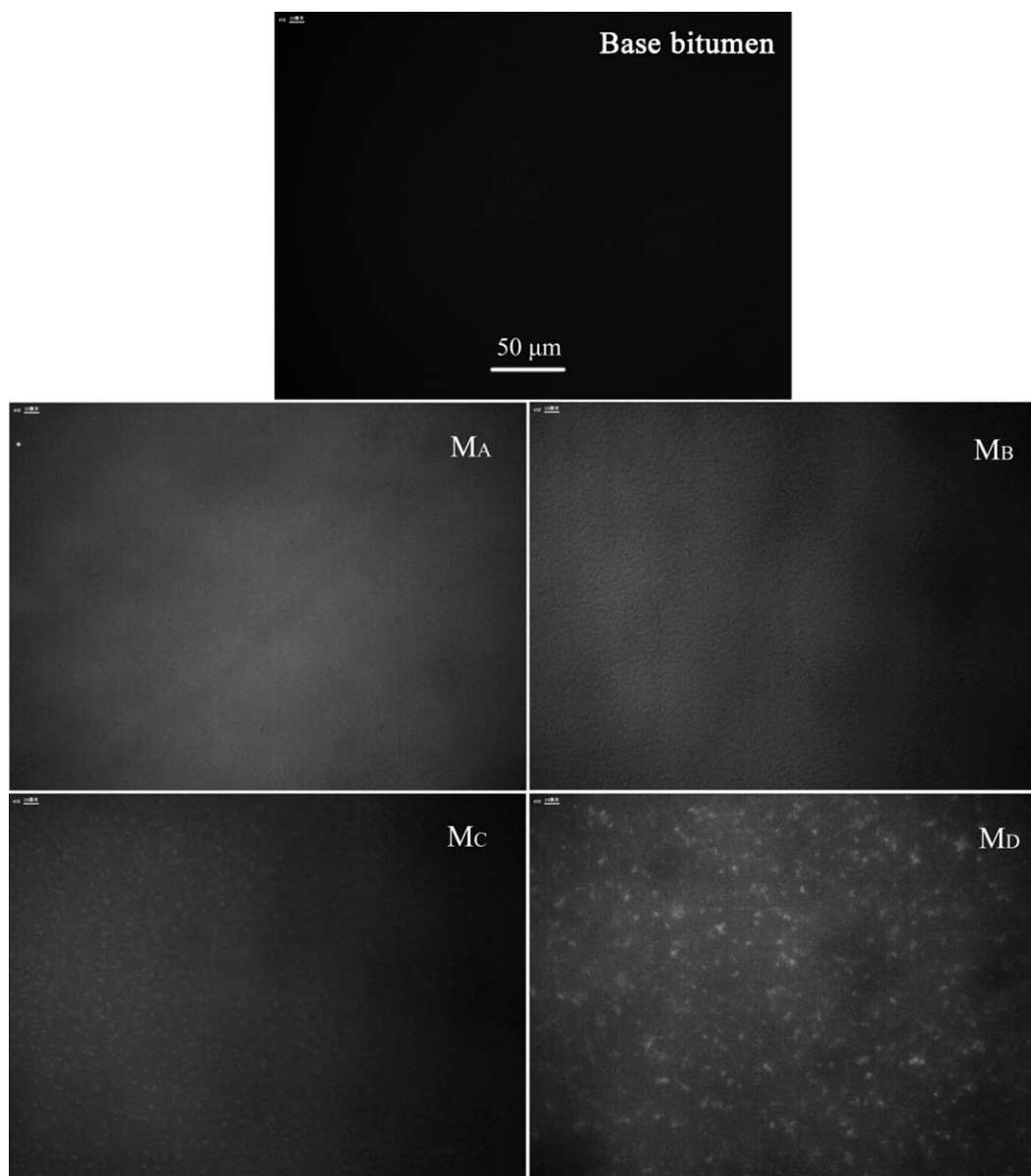| Items	Results				Specification	
	M_A	M_B	M_C	M_D	I-C	I-D
Penetration (25°C), 0.1 mm	59	63	61	58	60–80	30–60
Softening point (°C)	57.4	79.9	63.8	91.0	55	60
Ductility (5°C) (cm)	32	32	36	34	30	20
PI	0.92	4.96	2.29	6.10	−0.40	0.00
Elastic recovery test (%)	87	96	94	100	65	75
Separation test (°C)	0.4	0.5	0.3	0.5	≤2.5	≤2.5

Figure 2. Fluorescence micrographs of base bitumen and modified bitumens, magnification 40 × 10.

linear macromolecules swollen well in the maltene without inducing instability in the micellar structure of the bitumen.

Thermal Behavior

DSC curves for bitumen are critically dependent on thermal and shear history.[14] For this reason, the thermal characterization has been carried out on samples that were previously subjected to heating above their melting temperature and further cooling to −40°C. Therefore, all the samples had the same thermal history. As can be seen in Figure 3, DSC curves for bitumen modified by various SBS polymers reveals similar thermal events. The heat flow curves of these binders display glass transitions at low and high temperatures, indicating the structure responsible for the transitions. The T_g rises as the molecular structure becomes more rigid in terms of the increase in molecular weight, the presence of rings or polar groups.[15] The T_g at

around −20°C is likely related to the low-molecular weight structures, i.e., nonpolar structures in saturates and aromatics of bitumen, while the higher T_g at about 60–80°C may be
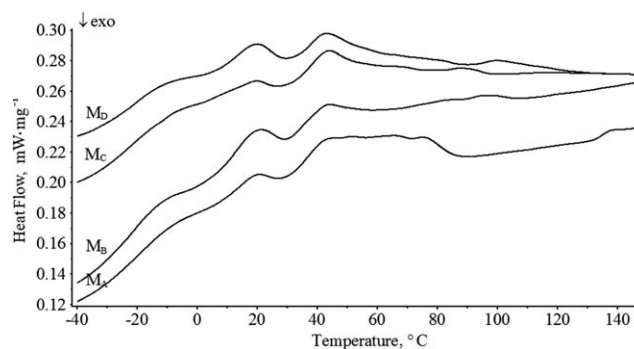

Figure 3. DSC curves of modified bitumens in a nitrogen atmosphere.

Table IV. Absorbed Heat of Modified Bitumen at Different Temperatures

Item	Temperature range (°C)	Absorbed heat (J g^{-1})	Temperature range (°C)	Absorbed heat (J g^{-1})	Total absorbed heat (J g^{-1})
M_A	2.8–26.9	0.570	26.9–87.8	5.136	5.706
M_B	3.3–28.8	1.185	28.8–58.7	1.142	2.327
M_C	0.4–26.7	0.539	26.7–73.8	2.248	2.787
M_D	1.4–29.6	1.039	29.6–71.8	1.672	2.711
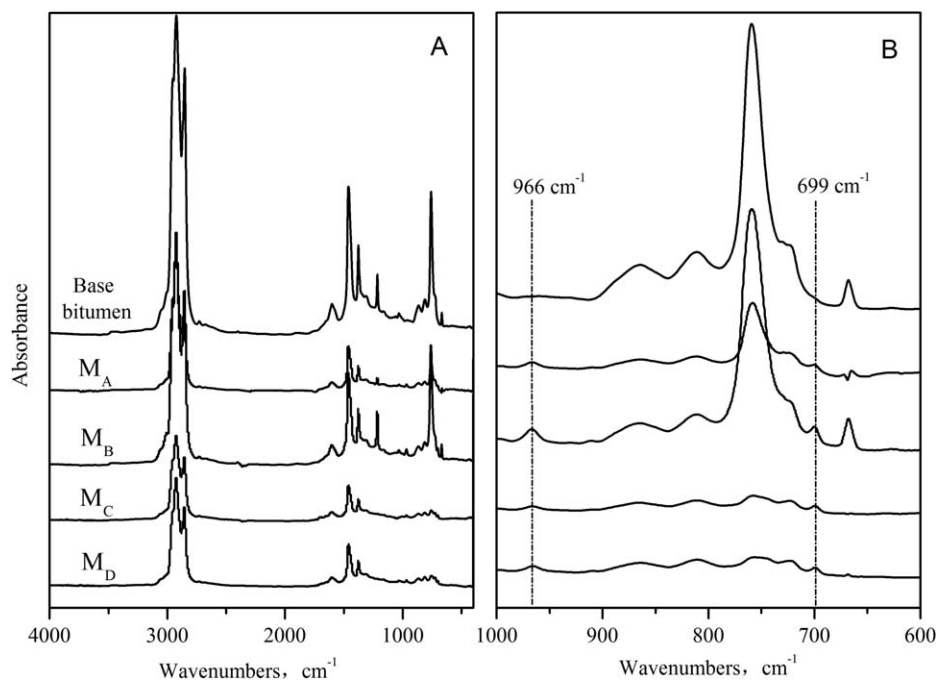
Figure 4. FT-IR Spectra of modified bitumens, (A) original spectra and (B) Partial enlarged spectra.

associated with the high-molecular weight structures, such as highly branched or cyclic structures in resins and asphaltenes,[15,16] as well as polystyrene segments of SBS.

As shown in Figure 3, two noticeable endothermic peaks are clearly visible for all the binders. The first thermal event is an endothermic peak that the top is around 20°C and the peak appearance for four modified bitumens is extremely similar. This is most likely arises from the melting of partly crystalline saturates and the ordering of simple aromatic structures.[16] On the other hand, difference appears over the second endothermic peak, and it displays a broad endothermic peak for M_A while others are identical. In this case, the absorbed heat at ambient and high temperatures is calculated from the peak area and presented in Table IV. The thermal stability of modified bitumen is dependent on the total absorbed heat over the heat flow curves.[17] As listed in Table IV, the total absorbed heat of M_B reaches a minimum, following by M_D, M_C, and M_A. It reveals the thermal stability of M_B is most preferable; consistent with morphological analysis for compact three-dimensional network to resist agglomeration and separation of SBS molecules from bitumen matrix. In terms of M_D, although the SBS particle size is the biggest among four modified bitumens, it displays relatively better thermal stability but

still has tiny inferior to M_B in light of same styrene content from SBS. This is consistent with previous conclusion that linear SBS provides more blends stability than branched SBS and that SBS branching does not affect blend stability significantly.[18–20]

Table V. Assignations of the Main Bands of the FT-IR Spectra

Wavenumber (cm^{-1})	Assignations of the main absorption bands
2924, 2853	v C—H of —CH$_2$—
1601	v C=C aromatic
1463	δ C—H of —(CH$_2$)n—
1377	δ C—H of —CH$_3$
1215	δ C—H tertiary butyl
1032	δ S=O sulfoxide
966	δ C—H trans disubstituted —CH=CH— of butadiene block
759	δ C—H aromatic monosubstituted
699	δ C—H aromatic monosubstituted of styrenen block

Table VI. IR Peak Intensity Ratio and Crosslinking Rate of Modified Bitumens

Items	Peak area at 966 cm^{-1}	Peak area at 699 cm^{-1}	Real IR peak intensity ratio	Theoretical IR peak intensity ratio	Crosslinking rate (%)
M_A	20.69	6.51	3.18	4.00	21.5
M_B	46.86	22.97	2.04	2.33	12.4
M_C	13.94	10.66	1.31	1.50	13.3
M_D	20.72	10.90	1.90	2.33	26.6

Microstructure

Because FT-IR spectroscopy is a simple analytical technique that has been widely applied to study chemical and structural changes in different samples and reveal the aging of modified bitumen,[21] we used this method to assess the microstructure of modified bitumens. The FT-IR spectra of the base and modified bitumens are shown in Figure 4.

The identical assignations for most bands can been seen in Figure 4(A) and critical difference in characteristic bands can be observed in Figure 4(B) as the partial enlarged spectra in the range of 1000 and 600 cm^{-1}. The band at 966 cm^{-1} is assigned to C—H trans disubstituted —CH=CH— of butadiene block and 699 cm^{-1} is assigned to C—H aromatic monosubstituted of styrene blocks as the dotted line marked in Figure 4(B), which are the characteristic peaks for modified bitumens, whereas those do not appear on FT-IR spectrum of the base bitumen.[22] In terms of other bands, the identical assignations are listed in Table V and the significant difference is the peak height that is closely related to the measuring sample mass. However, the variation has no effect on content for a particular group since it is normally a relative content for that group to methylene peak area or peak height.

The intensity ratio of characteristic bands at 966 and 699 cm^{-1} (denoted as IR peak intensity ratio) can be utilized to calculate the crosslinking rate of modified bitumens. According to Beer's law, the IR peak intensity ratio (Table VI) is equal to the area ratio between those two bands [eq. (1)], which is actually the content ratio between polybutadiene central-blocks and polystyrene end-blocks from modified bitumens.[17] It depicts the real crosslinking condition for SBS and bitumen molecules, in which there is a reaction taking place between SBS molecule and bitumen molecule. If there is simply a physical blend between SBS and bitumen molecules, the theoretical IR peak intensity ratio is the content ratio between polybutadiene blocks and polystyrene blocks from SBS as listed in Table VI. And the real ratio is less than the theoretical ratio, which indicates that the reaction between polybutadiene blocks and bitumen is a domain. Therefore, the crosslinking rate can be calculated. Taking M_A as an example, it is assumed that no reaction between polystyrene blocks and the bitumen. Then m(S1) equals to m(S2) in eqs. (2) and (3), and the crosslinking rate (Table VI) is calculated as eq. (4). As a result, a noncomplete crosslinking reaction happens at a cross-linking rate of 21.5% and it can efficiently prevent excessive crosslinking from affecting the intrinsic bitumen characteristics.

$$\text{IR pear intensity ratio} = \frac{\text{Pear intensity at 966 cm}^{-1}}{\text{Pear intensity at 699 cm}^{-1}} \quad (1)$$
$$= \frac{\text{Pear area at 966 cm}^{-1}}{\text{Pear area at 699 cm}^{-1}}$$

$$\frac{\text{Theoretical polybutadiene content}}{\text{Theoretical polystyrene content}} = \frac{m(B_1)}{m(S_1)} = 4.00 \quad (2)$$

$$\frac{\text{Real polybutadiene content}}{\text{Real polystyrene content}} = \frac{m(B_2)}{m(S_2)} = 3.18 \quad (3)$$

$$\text{Cross-linking Rate} = \frac{\text{Grated SBS content}}{\text{Original SBS content}} \times 100\%$$
$$= 1 - \frac{m(B_2)}{m(B_1)} = 21.5\% \quad (4)$$

CONCLUSIONS

In this work a base bitumen had been modified by four SBS copolymers which differ in styrene blocks content and molecular configuration (radial or linear) under same experimental conditions. Conventional properties have been studied showing improved performance in comparison to base bitumen and the bitumen modified by the linear SBS polymer with a styrene content of 30% displays the best conventional properties, while it is inferior to that of the bitumen modified by the star SBS polymer. Meanwhile, the properties of them can fully meet and far exceed the requirements of the highway industry specification of China. And a pronounced homogenous and ideal dispersion is observed by the fluorescence microscopy for the bitumen modified by the linear SBS polymer with the styrene content of 30%, and it is the same case for great thermal stability obtained from DSC analysis. In terms of FT-IR spectroscopy, it is found that the assignations of main bands of four modified bitumens are identical and the significant variation is the peak intensity. And a noncomplete crosslinking reaction happens between the bitumen and each SBS polymer, which can efficiently prevent excessive crosslinking from affecting the intrinsic bitumen characteristics.

REFERENCES

1. Pérez-Lepe, A.; Martinez-Boza, F. J.; Gallegos, O.; Muñoz, M. E.; Santamaría, A. *Fuel* **2003**, *82*, 1339.

2. García-Morales, M.; Partal, P.; Navarro, F. J.; Martíez-Boza, F.; Gallegos, C.; González, N.; González, O.; Muñoz, M. E. *Fuel* **2004**, *83*, 31.

3. Wen, G.; Zhang, Y.; Zhang, Y.; Sun, K.; Fan, Y. *Polym. Test.* **2002**, *21*, 295.

4. Gordon, D. A. *Fuel* **2003**, *82*, 1709.

5. Lu, X.; Isacsson, U. *Polym. Test.* **2001**, *20*, 77.

6. Silva, L. S.; Forte, M. M. C.; Vignol, L. A.; Cardozo, N. S. M. *J. Mater. Sci.* **2004**, *39*, 539.

7. Fawcett, A. H.; McNally, T. *Polym. Eng. Sci.* **2001**, *41*, 1251.

8. Hernández, G.; Medina, E. M.; Sánchez, R.; Mendoza, A. M. *Energy Fuels* **2006**, *20*, 2623.

9. Yetkin, Y. *Constr. Build. Mater.* **2007**, *21*, 66.

10. Brulé, B.; Brion, Y.; Tanguy, A. *J. Assoc. Asph. Pav. Tech.* **1988**, *57*, 41.

11. Gordon, D. A. *Fuel* **2003**, *82*, 1709.

12. Sengoz, B.; Isikyakar, G. *J. Hazard. Mater.* **2008**, *150*, 424.

13. Fernandes, M. R. S.; Forte, M. M. C.; Leite, L. F. M. *Mater. Res.* **2008**, *11*, 381.

14. Masson, J. F.; Polomark, G. M. *Thermochim. Acta* **2001**, *374*, 105.

15. Masson, J. F.; Polomark, G. M.; Collins, P. *Energy Fuels* **2002**, *16*, 470.

16. Navarro, F. J.; Partal, P.; Martínez-Boza, F.; Gallegos, C. *Energy Fuels* **2005**, *19*, 1984.

17. Zhang, Q.; Fan, W.; Wang, T.; Nan, G.; Sunarso, J. *Constr. Build. Mater.* **2012**, *29*, 97.

18. Lu, X.; Isacsson, U. *Mater. Struct.* **1997**, *30*, 618.

19. Lu, X.; Isacsson, U.; Ekblad, J. *J. Mater. Civ. Eng.* **1999**, *11*, 51.

20. Masson, J.-F.; Collins, P.; Robertson, G.; Woods, J. R.; Margeson, J. C. *Energy Fuels* **2003**, *17*, 714.

21. Cortizo, M. S.; Larsen, D. O.; Bianchetto, H.; Alessandrini, J. L. *Polym. Degrad. Stab.* **2004**, *86*, 275.

22. Larsen, D. O.; Alessandrini, J. L.; Bosch, A.; Cortizo, M. S. *Constr. Build. Mater.* **2009**, *23*, 2769.