Storage stability and its relationship with microstructure of SBS modified de-oiled asphalt

Ming Liang, Shisong Ren, Weiyu Fan *, Xue Xin
State Key Laboratory of Heavy Oil Processing, China University of Petroleum (East China), Shandong Qingdao 266580

Corresponding author

ABSTRACT: SBS modified hard asphalt was prepared by de-oiled asphalt and radial SBS at 170℃ by high speed mixer. The samples were evaluated by conventional properties and fluorescence microscopy. Conventional properties showed that SBS drastically improve the high temperature stability and low temperature crack resistance of hard asphalt. Stabilizer improve the high temperature storage stability of asphalt obviously. Fluorescence microscopy showed that mean particle size of SBS in asphalt phase become larger as the increase of penetration, which indicate disperse of polymer in asphalt become difficult for harder asphalt. As a result, the macroscopic properties of modified asphalt were related to microstructure. In order to achieve desired macroscopic properties, SBS should be dispersed in asphalt uniformly and continuously.
KEYWORD: de-oiled asphalt, hard asphalt, modification, microstructure

1 INTRODUCTION

In recent years, with the heavier trend of crude oil and the improvement of heavy oil processing depth, solvent de-asphalt processing is developed . Thus, the improved yield makes price of hard asphalt lower than common heavy asphalt (Li HP, 2009). De-oiled asphalt has better high temperature stability, poor low temperature performance and storage stability. It can't meet with requirement of pavement asphalt. Therefore, it is important to seek efficient utilization of hard asphalt for promoting the development of solvent de-asphalt processing (Jin H, 2002). Asphalt, which is modified by styrene butadiene styrene block copolymers (SBS), has excellent performance in both high and low temperature stability, anti-fatigue cracking. Now it is widely used in highway construction and maintenance engineering. Asphalt which is modified by polymers shows great weather ability, high temperature characteristics and flexibility (Wu S, 2009). However, the dispersion of polymers in asphalt has a great influence on the macroscopic properties. It is an effective way that using fluorescence microscope to analyze the relationships of microstructure with high temperature performance and storage stability (Ouyang C, 2006).

Hard asphalt with 30 and 50 in penetration is prepared by de-oiled asphalt in this paper. SBS and stabilizer are added in asphalt. Microstructure of modified asphalt is researched by fluorescence microscope. Conventional properties of asphalt before and after TFOT were also determined. Lastly, modification mechanism of asphalt and the relationships of macroscopic properties with morphology were explained by microcosmic scale.

2 MATERIALS AND METHODS

2.1 *Materials and preparation*

The research used de-oiled asphalt and aromatic oils as raw materials. Hard asphalts were prepared in high speed mixer with 500rpm, 2.5h. Basic properties of de-oiled asphalt and aromatic oils are showed in Table.1. Hard asphalt was modified by radial SBS with 30/70 block ratio and Using NH4L with 65% sulfur as stabilizer.

Table 1 Properties of de-oiled asphalt and aromatic oils

Material	20℃Debsity (g/cm3)	Softening point(℃)	Penetration(0.1 mm)	SARAs(%)			
				Saturates	Aromatics	Resins	Asphaltenes
De-oiled asphalt	1.0460	88.9	2.0	7.1	24.9	46.1	17.8
Aromatic oils	1.1103	36.2	--	14.4	62.0	14.0	4.9

2.2 *Test methods*

Softening point and viscosity in 60℃ were used to characterize high temperature stability. While ductility in 10℃, 15℃ were tested to characterize low temperature crack resistance. Moreover, the changes in some properties, such as mass, penetration and viscosity, of asphalt after TFOT test were applied to characterize anti-aging performance. 10 mg asphalt was put on glass slide. Then, cover glass was put on samples and glass was put in oven for 10 minutes, 135℃. Microstructure of sample was observed by BX51 fluorescence (Liang M, 2015).

3 RESULTS AND DISCUSSIONS

3.1 *Storage stability and conventional property of modified asphalt without and with stabilizer*

Storage stability of polymer modified asphalt depend on compatibility between SBS and asphalt (Liang M,2015). The compatibility of SBS and hard asphalt is evaluated by the difference of softening point before and after high temperature storage test. The results in Table 3 show that modified asphalt without stability appear serious phase separation. Difference of softening point increases with increase of amount of SBS. When the amount of SBS is same, phase separation of 50 asphalt is more obvious than that of 30 asphalt. A number of researches show that there is no chemical reaction between SBS and asphalt, SBS disperses physically in asphalt uniformly. Because SBS are very different with asphalt in terms of molecular weight, chemical structure and so on. So the suspension belongs to thermodynamic incompatible system. Thus, phase separation become obvious with the increase of SBS.

However, crosslinking bond was generated between SBS and asphalt. Storage stability and conventional property of modified asphalt with stabilizer are shown in Table 3. It can be seen that softening point increases with increase of stabilizer, so does ductility. It is important to note that phase separation is decrease with the increase of stabilizer, which means more chemical bond are formed. As a result, the ageing performances are also improved because of crosslinking.

Table 2 Phase separation of 30 and 50 modified hard asphalt without stabilizers

Amount of SBS/%	2	3	4	5	6
30 hard asphalt/℃	5.9	10.3	16.2	24.2	30.8
50 hard asphalt/℃	7.8	15.2	21.5	29.6	36.8

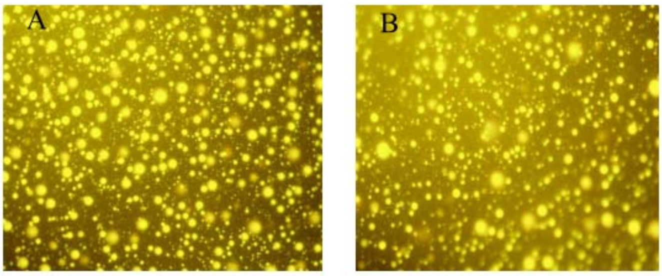
Table 3 Storage stability and conventional property of modified asphalt with stabilizer

Items	Dosage of stabilizer%			
	0	0.1	0.2	0.3
25℃penetration/0.1mm	24	23	23	23
Softening point/℃	58.7	62.6	68.8	74.7
10℃ductility/cm	11.5	13.5	14.6	16.5
Ratio of TFOT residual penetration%	79.2	78.3	78.3	87.0
Phase separation /℃	12.3	3.2	1.9	0.9

3.2 *Microstructure and its relationship with storage stability and conventional property*

Asphalt is a colloid system. Asphaltenes which covered by resins are dispersed in oil medium composed by aromatics and saturates. Microscopic images of 30 and 50 modified asphalt with 5.0% SBS and without stabilizer are showed in Fig.1.The results show that modified asphalt is inhomogeneous dispersed system. The yellow part is polymer phase and the black part is asphalt phase. SBS are block copolymers with styrene and butadiene. Molecular chains include hard segments and soft segments. When SBS are dispersed in molten asphalt, light component of asphalt can infiltrate into molecular chains. This effect makes polymer molecular chain smoother and greater in volume. This is so called swelling effect (Polacco G, 2006). When SBS particles disperse in asphalt, swelling happens and polymers absorb light oils in asphalt. The colloidal equilibrium shift and two phase has competition effect.

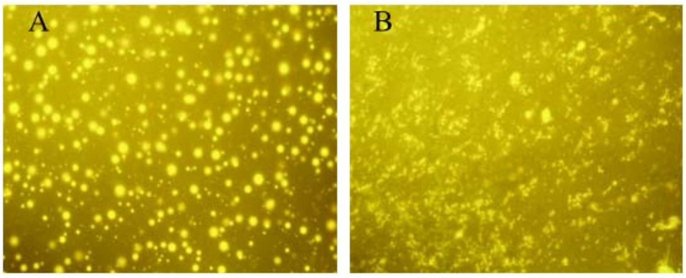
In addition, Fig.1 show that SBS particles, which are dispersed in 50 hard asphalt, is smaller and the interface of asphalt phase is obscure. Comparing 50 asphalt with 30 asphalt, there is more light components in 50 asphalt. Polymer absorb more light component. Thus, superficial molecular chains of SBS particles are smoother and swelling effect is better.



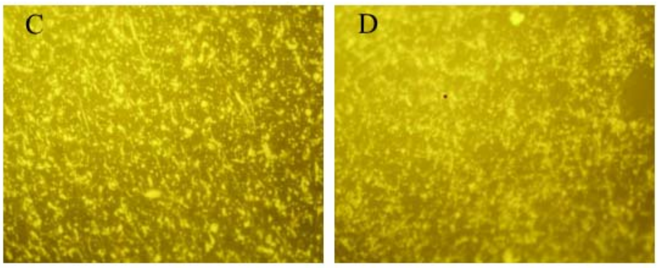
A: 30 hard asphalt B: 50 hard asphalt

Fig.1 30 # and 50 # SBS modified bitumen microscopic structure with 5% SBS

In order to improve storage stability of modified asphalt, the effect of stabilizer was investigated.



A: 30#hard asphalt B: 30#hard asphalt+0.1%stabilizer;



C: 30#hard asphalt+0.2%stabilizer; D: 30#hard asphalt+ 0.3%stabilizer

Fig.2 influence of stabilizer on microscopic structure with 3% SBS

Influence of stabilizer on microscopic structure are shown in Fig.2. It can be seen that there are various microstructure with the increase of stabilizer. SBS particles is spherical in asphalt without stabilizer. SBS is flocculent in asphalt and the volume of polymer phase becomes larger after adding stabilizer. As stabilizer increase, SBS particles change more intersected flocculent and polymer phase becomes continuous phase. This is because there is sulfur in NH4L. It can make sulfur bond formed among SBS molecular chains to crosslink and form reticular formation to encapsulate asphalt phase. So polymer phase are more difficult to separate from asphalt phase. This improves storage stability of modified asphalt.If the amount of stabilizer is too much, the crosslinking will be excessive. This will have negative effect on mechanical properties of modified asphalt, such as low temperature ductility. The recommended amount is 0.1~0.3%.

Dosage of SBS is a critical factor which influences performance and microstructure of modified asphalt. Micro-morphology of modified asphalt changes obviously with the dosage of SBS. When the amount of SBS is little, the single continuous structure has less effect on softening point. Asphalt binder forms reticular formation with increasing amount of SBS and the crosslinking of stabilizer. This structure has restriction effect on flowing, gliding deformation of asphalt molecular. It improves softening point, viscosity and anti-aging performance.

4 CONCLUSIONS

SBS and stabilizer can effectively improve storage stability and conventional properties of modified asphalt. Amount of modifier is the critical factor which influences performance and microstructure of modified asphalt. Spherical particles of modifier in asphalt system increase as increase of modifier. This improves softening point and viscosity. Adding stabilizer can improve high temperature storage stability and microstructure of modified asphalt. SBS particles is spherical in asphalt without stabilizer. Modifier molecular crosslinks and aggregates with stability and forms reticular formation. What's more, there is no interface between modifier molecular and asphalt. And dispersion is uniform. This improves storage stability of asphalt. Macroscopic performance is associated with microstructure. When modifier and asphalt in microstructure are dispersed uniformly and continuously, modified asphalt has better macroscopic performance.

REFERENCES

Jin H, Gao G, Zhang Y, et al. Improved properties of polystyrene-modified asphalt through dynamic vulcanization(J). Polymer testing. Vol. 21 (2002) No. 6, p. 633-640.

Liang M, Liang P, Fan W, Qian C, Xin X, Shi J, Nan G. Thermo-rheological behavior and compatibility of modified asphalt with various styrene–butadiene structures in SBS copolymers. Mater Des Vol. 88 (2015) No. 1, p. 177–185.

Liang M, Xin X, Fan WY, Luo H, Wang XB, Xing BD. Investigation of the rheological properties and storage stability of CR/SBS modified asphalt. Constr Build Mater Vol. 74 (2015) No. 1, p. 235–240.

Lesueur D. The colloidal structure of bitumen: Consequences on the rheology and on the mechanisms of bitumen

modification. Advances in colloid and Interface Science. Vol. 145 (2009) No. 1, p. 42-82.
Li HP, Shen J. Production of paving asphalt by blending RFCC slurry in deoiled asphalt. Pet Sci Technol Vol. 27 (2009) No. 1, p. 46–55.
Ouyang C, Wang S, Zhang Y, et al. Improving the aging resistance of styrene–butadiene–styrene tri-block copolymer modified asphalt by addition of antioxidants. Polymer degradation and stability. Vol. 91 (2006) No. 4, p. 795-804.
Polacco G, Stastna J, Biondi D, et al. Relation between polymer architecture and nonlinear viscoelastic behavior of modified asphalts. Current opinion in colloid & interface science. Vol. 11 (2006) No. 4, p. 230-245.
Sun D, Ye F, Shi F, et al. Storage stability of SBS-modified road asphalt: Preparation, morphology, and rheological properties. Petroleum science and technology. Vol. 24 (2006) No. 9, p. 1067-1077.
Sengoz B, Isikyakar G. Evaluation of the properties and microstructure of SBS and EVA polymer modified bitumen. Construction and Building Materials. Vol. 22 (2008) No. 9, p. 1897-1905.
Wu S, Pang L, Mo L, et al. Influence of aging on the evolution of structure, morphology and rheology of base and SBS modified bitumen. Construction and Building Materials. Vol. 23 (2009) No. 2, p. 1005-1010.