Construction and Building Materials 107 (2016) 38–43

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

Evaluation of storage stability of styrene–butadiene–styrene block copolymer-modified asphalt via electrochemical analysis

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HIGHLIGHTS

- Electrochemical analysis determines SBS content variation after hot tube storage.
- The method provides an accurate segregation assessment for SBS modified asphalt.
- The method reveals the thermo-oxidative degradation of SBS in modified asphalt.

ARTICLE INFO

Article history:
Received 17 August 2015
Received in revised form 2 December 2015
Accepted 22 December 2015
Available online 5 January 2016

Keywords:
Modified asphalt
SBS content
Electrochemical analysis
Storage stability

ABSTRACT

The stability of styrene–butadiene–styrene (SBS) block copolymer-modified asphalt during hot storage and transportation is an important issue. Considering the shortcomings of the present storage stability test implementing softening point, an electrochemical technique was developed to evaluate the segregation behavior of SBS-modified asphalt. Quantitative analysis of SBS content in asphalt based on potentiometric titration was employed to determine the difference in SBS content between the top and the bottom samples taken from a hot tube storage test. An accurate variation of SBS content was traced with a fractional error of less than 0.5%, and the possible thermo-oxidative degradation of SBS during hot storage was also discussed. Results showed that electrochemical analysis can be a viable technique to evaluate the storage stability of SBS-modified asphalt directly as opposed to an indirect measurement with softening point.

1. Introduction

Asphalt has been widely used in road construction for decades. However, with the rapid increase of traffic volume, the emergence of many severe pavement distresses (e.g., deformation, rutting and cracking) has necessitated modification of asphalt to enhance performance. Polymer modification is one of the most promising approaches to improve asphalt performance for flexible pavements [1,2]. Polymer-modified asphalt (PMA) is a binder prepared by incorporation of polymer into asphalt through mechanical mixing or chemical reaction. Several studies have shown that the physical properties of bitumen can be improved significantly by polymer modification, including durability, aging properties, permanent deformation, and thermal susceptibility [3–7]. Various polymers are compatible with asphalt for polymer modification. The polymers for bitumen modification are classified into two categories, namely, plasterers and thermoplastic elastomers [1]. Among these polymers, thermoplastic styrene–butadiene–styrene (SBS) block copolymer has attracted considerable attention because of its good dispersibility in asphalt, as well as excellent mechanical properties [1,8,9]. The biphasic morphology of SBS copolymers composed of rigid polystyrene (PS) domains and flexible polybutadiene (PB) is beneficial for the formation of interlocked continuous phases (bitumen-rich phase and SBS-rich phase) in SBS-modified asphalt, which leads to the good performance of SBS-modified asphalt [1].

However, the storage stability of SBS-modified asphalt remains a concern during hot storage and transportation, especially at high temperatures and prolonged absence of stirring. Given the difference of properties between asphalt and SBS, such as molecular structure, density, viscosity, and polarity [10], they are thermodynamically incompatible with each other in most SBS-modified asphalts, which may lead to the coalescence of polymer particles and give rise to phase separation [11,12]. Therefore, developing an accurate evaluation technique for monitoring the storage stability of SBS-modified asphalt is necessary.

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http://dx.doi.org/10.1016/j.conbuildmat.2015.12.174
0950-0618/

The most traditional method to evaluate the storage stability of asphalt is the softening point test [7]. However, previous studies have demonstrated the defects of using this parameter in the case of modified binders. Lu et al. [12] reported that the softening points for the top and bottom samples will be affected when implementing the hot storage test because of the increase in elasticity of the top samples and the hardness of the bottom samples. In this way, the softening points display a variation tendency that is significantly different from the occurrence of segregation. Isacsson and Lu [4] also claimed that softening point is generally more valid for conventional asphalts than PMA because of the different viscoelasticities between the matrix asphalt and the modified binder. Some methods have been developed to evaluate storage stability, including fluorescence microscopy, dynamic mechanical analysis (DMA), dynamic shear rheometer (DSR) test, and Fourier transform infrared (FTIR) spectroscopy [4,10–14]. Fluorescence microscopy [4,11,13] can reveal the morphology of the physical dispersion state of PMA by providing visual images. However, the changes in chemical structure and performance of asphalt during storage cannot be shown by fluorescence microscopy. DMA [12] and DSR [14] have been chosen to evaluate the storage stability of PMA through rheological property (complex shear modulus and phase angle) measurements, which are also indirect indicators similar to softening point. FTIR [10,12] is the only measurement that can provide a quantitative assessment of stability by characterizing the SBS polymers in asphalt. Unfortunately, the correlated coefficient (only 0.91) between IR absorption and separation index is poor, indicating that further study is necessary to improve the precision of the FTIR method.

The segregation of SBS-modified asphalt during hot storage refers to, in essence, the variation of SBS content. If the SBS content can be detected accurately and in a timely manner, segregation can be traced in real time. SBS is a kind of hydrocarbon polymer containing unsaturated double bonds that are proportional to the SBS concentration in SBS-modified asphalt. Thus, the SBS content can be determined by measuring the number of unsaturated double bonds in SBS-modified asphalt. For example, the above-mentioned FTIR method focuses on the specific infrared (IR) characteristic of double bonds in SBS molecules; however, its precision is still out of the scope of trace quantification [10,12]. Fortunately, halogen addition of an unsaturated hydrocarbon is a stoichiometric reaction [15]. If enough halogen is applied to react with SBS in SBS-modified asphalt, the remaining halogen can be determined by corresponding redox titration, so the SBS content can be traced in real time.

In this paper, a rapid and quantitative method for detection of SBS content based on electrochemical analysis was developed to accurately determine the storage stability of SBS-modified asphalt. To the best of our knowledge, this study is the first to report on the detection of hot storage stability of SBS-modified asphalt through direct potentiometric titration of the SBS content of the top and the bottom samples obtained from a hot tube storage test.

2. Experimental

2.1. Materials

Two matrix asphalts were used in this research. The SK70 and Shell 70 matrix asphalts were purchased from Korea SK Group and Shell Group of Companies, respectively. The physical and chemical parameters of the matrix asphalt are shown in Table 1. Two types of SBS (YH-791 and 4303-2) from Yueyang Petro-chemical Co., Ltd., China were selected for this investigation. The basic properties of the two SBS copolymers are listed in Table 2. Aromatic hydrocarbon oil and elemental sulfur were supplied by Jiangsu Baoli Asphalt Co., Ltd., China. The chloroform, Wijs reagent (0.1 mol/L iodine monochloride acetic acid solution), sodium thiosulfate, and potassium iodide purchased from Aladdin Industrial Corporation, China were all of analytical grade.

Table 1
Physical properties and chemical components of the matrix asphalts.

Items	Matrix asphalt		Test specification
	SK 70	Shell 70	
Softening point (°C)	46.6	47.5	ASTM D36
Ductility (15 °C) (cm)	>150	>100	ASTM D113
Penetration (25 °C) (0.1 mm)	71	72	ASTM D5
Saturates (%)	21	22	ASTM D4124
Aromatics (%)	48	47	
Resins (%)	23	19	
Asphaltenes (%)	8	12	

Table 2
Characteristics of the SBS polymers.

Items	SBS Polymer	
	YH-791	4303-2
Structure	Linear	Radial
Block ratio (styrene/butadiene)	30/70	40/60
Average molecular weight (dalton)	290,000	300,000
Permanent deformation (⩽%)	45	40
Elongation ratio (⩾%)	700	550

2.2. Preparation of SBS-modified asphalt samples

The standard calibration curve method was used to determine the SBS content in an unknown sample. To establish the calibration curve, SBS-modified asphalt standard samples were prepared according to the following procedure. The matrix asphalt was heated to 18 °C, and the temperature was kept constant. A certain amount of aromatic oil was added to the matrix asphalt at 500 rpm shearing speed, and then a given weight of SBS was mixed into asphalt under 3000 rpm for 30 min using a high speed shearing machine (BME100LT). After shearing, mixing was continued using an agitator (BME100LT-N) at 180 °C and speed of 500 rpm for 4 h. Simultaneously, the stabilizer was slowly added. After completion, the homogeneous SBS-modified asphalt samples were cooled to room temperature for further testing. Two series of standard samples were prepared with two types of SBS. The SBS contents used were 0%, 2.5%, 3.5%, 4.5%, and 5.5% by weight of the corresponding blends. The experimental prescriptions of the standard samples are described in Table 3. Meanwhile, three modified asphalt samples containing 4.5% SBS by mass denoted by Samples A, B, and C with the same experimental prescriptions of the corresponding standard samples, were provided by a modified asphalt production plant in ChangSha, China and used in the following hot storage test. The structure of the SBS added to Samples A, B, and C were linear, linear, and radial types, respectively, similar to those used for standard samples.

2.3. Hot tube storage test

In this study, Samples A, B, and C were applied for hot tube storage test according to conventional procedure [11]. The SBS-modified asphalt sample was melted in an oven at 163 °C, and then poured into an aluminum foil tube with a diameter of 25 mm and a height of 140 mm. The tube containing the sample was sealed and stored vertically in an oven at 163 °C for 6, 24, 48, 72, and 120 h. The tubes were removed from the oven and cooled in a freezer at −2 °C for 4 h to solidify the

Table 3
Experimental prescriptions of SBS-modified asphalt standard samples.

Calibration curve		Matrix asphalt	SBS modifier	Compatibilizer	Stabilizer
1	Type	SK70 matrix asphalt	Linear YH-791	Aromatic hydrocarbon oil	Sulfur
	Content	/	0, 2.5%, 3.5%, 4.5%, 5.5%	1.5%	0.3%
2	Type	Shell70 matrix asphalt	Radial 4303-2	Aromatic hydrocarbon oil	Sulfur
	Content	/	0, 2.5%, 3.5%, 4.5%, 5.5%	1.5%	0.3%