Polymer Degradation and Stability 98 (2013) 2627–2634

Contents lists available at ScienceDirect

Polymer Degradation and Stability

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

# Investigation on properties of polymer modified asphalt containing various antiaging agents

Peiliang Cong*, Xiao Wang, Peijun Xu, Jianfei Liu, Rui He, Shuanfa Chen

*Engineering Research Center of Transportation Materials of Ministry of Education & School of Materials Science and Engineering, Chang'an University, Xian 710064, China*

ARTICLE INFO

*Article history:*
Received 23 July 2013
Received in revised form
24 September 2013
Accepted 25 September 2013
Available online 4 October 2013

*Keywords:*
SBS modified asphalt
Antiaging
Viscosity
Rheology
Susceptibility

ABSTRACT

The Styrene–butadiene–styrene copolymer (SBS) triblock copolymer modified asphalt binder (SBSMA), applied in an overlay, and is easy to age in the field. Thus, the thermal aging and ultraviolet (UV) radiations aging of SBSMA must be considered for the research on the performance of asphalt pavement. Antioxidants and UV absorbers were employed to improve the antiaging resistance of SBSMA in this study. The results indicated that the SBSMA with antioxidants has good heat aging resistance, and SBSMA with UV absorbers blends have good photostability. The compound antiaging agents containing antioxidants and UV absorbers are a best choice to prepare SBSMA with better physical and antiaging resistance. The experimental results also indicated that the effects of antiaging agents on the physical properties of SBSMA are little at low contents. Especially conventional physical properties of SBSMA with 1 wt% of ZDDP and 0.5 wt% of UV531 are close to that of SBSMA.

## 1. Introduction

Asphalt binder is used as adhesive materials in many fields, especially in roadway and roofing construction. However, there are many types of distress like low temperature cracking, fatigue cracking, and permanent deformation at the high temperature, that can reduce the quality and performance of road pavement during “in life” service [2,11]. The polymer modified asphalt binder can extend the service life and improve the performance of asphalt pavement. Among the polymer modifiers of asphalt, Styrene–butadiene–styrene copolymer (SBS) triblock copolymer presented the best results in improving asphalt properties [1,12]. But the SBS modified asphalt binder applied in overlays that is easy to age in the field, especially under heat, sunlight, oxygen or combination of these factors. The aging of the asphalt binder can be broken into two types, thermal aging and ultraviolet radiation aging. Thermal aging and/or ultraviolet (UV) radiation aging causes the asphalt binder to get stiffer and more brittle, and causes serious degradation in the performance of asphalt binder, and attenuates the durability of the pavement [4,6,8,10,15].

The thermo-oxidative degradation of the polymer modified asphalt binders during blend preparation and under aging treatment has been investigated [3,13]. But the effects of solar radiation, particularly of the ultraviolet (UV) irradiation, on SBS modified asphalt binder aging have given little consideration in early researches. Because of the difference in atmospheric composition and length of solar radiation between high altitude and low altitude, there is a different climate and environment due to sunshine duration and UV radiation content. In addition, some researcher showed that solar radiation only affects the upper layers of the pavement due to the high absorption coefficient of the asphalt binder [7,14]. Pressure aging vessel (PAV) is selected to simulate the long-term aging. But it is not considerate the effect of solar radiation on the aging resistance. Thus, asphalt binder aging due to the ultraviolet radiation should consider when the performance of asphalt pavement is researched, especially in the geographical regions where high solar radiation intensity, high relative humidity of air occurs [5,9]. Recently much work reported that the influence of ultraviolet radiation on the aging of asphalt. The results indicated that ultraviolet radiation promotes asphalt aging and it needs more studies, especially SBS modified asphalt binders that are applied in the upper layers of pavement (Ref. [16]).

In addition, many researchers focused only on the aging process of the asphalt binder, the methods for improving aging resistance were actually neglected. Some studies have been carried out on antiaging materials aiming to improve the antiaging performances of the asphalt binders. However, the data dealing with the aspect of asphalt binder antiaging are rather scarce making this research field still interesting to be studied.

---

* Corresponding author. Tel./fax: +86 29 82337349.
*E-mail address:* congpl@chd.edu.cn (P. Cong).

0141-3910/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.polymdegradstab.2013.09.024

This paper aims to characterize the properties of the SBS modified asphalt binder containing various antiaging agents, and determine if SBS modified asphalt binder aging could be controlled by use of the antiaging agents utilizing conventional and empirical test methods. The effects of antioxidants, UV absorbers and compound antiaging agents on the properties of SBSMA were investigated. In order to assess the influence of antiaging agents on aging resistance of SBS modified asphalt binder, the aging properties of SBS modified asphalt binders with different type antiaging agents were compared.

## 2. Material and methods

### 2.1. Raw materials

The 60/80 penetration grade asphalt, with softening point of 46.8 °C (ASTM D36), penetration of 69 dmm (deci-millimeter, 25 °C, ASTM D5), ductility of 179 cm (25 °C, ASTM D113) and viscosity of 0.35 Pa s at 135 °C and 275 Pa s at 60 (ASTM D4402), was used to prepare modified asphalt binder. Chemical compositions of asphalt binders are listed in Table 1.

The Styrene–Butadiene–Styrene (SBS) triblock copolymer used, grade 1301, was manufactured by the Yueyang Petrochemical Co., Ltd., in China. The grade 1301 SBS polymer was a linear-like material, containing 30% of styrene by weight with an-average molecular weight of 120,000 g/mol. The 4.5 wt% SBS modified asphalt binder had the following properties: a penetration of 58 mm at 25 °C, a ductility of 45 cm at 5 °C, and a softening point of 81.8 °C.

Two antioxidants and two UV absorbers used in this study were zinc dialkyl dithio phosphate (ZDDP), carbon black, octabenzone (UV531) and bumetrizole (UV326). ZDDP, with density of 1.05–1.15 g/cm$^3$, a melting point of $-10$ °C, was procured from Lanzhou Petroleum Processing and Chemical Complex of China. Its molecular structure and the schemes of degradation are shown in Fig. 1. The two UV absorbers (UV531 with density of 1.158 g/cm$^3$, melting temperature ranges from 47 to 49 °C, maximum ignition loss of 0.1% and UV326 with melting temperature ranges from 138 to 141 °C, and maximum volatiles of 0.3%) were procured from Shanghai Renpu Chemical Co., Ltd, China. The molecular structure and the hydrogen transfer mechanism of UV531 and UV326 is shown in Figs. 2 and 3. Carbon black (CB, N990), with maximum particle size of 500 nm, maximum ignition loss of 0.5%, absorption oil value of $15 \times 10^{-5}$ m$^3$/kg, pour density of 595 kg/m$^3$, was obtained from Shanxi Sanqiang Carbon Black Co., Ltd, China.

### 2.2. Preparation of modified asphalts binders

All the modified asphalt binders were prepared using a high shear mixer (made by Fluke Machine Co., Ltd., Germany). Asphalt binder was heated to 175 °C ± 5 °C in an oil-bath heating container until it flowed freely. The 4.5 wt% SBS was mixed into the asphalt under 5000 rpm rotation speeds for about 60 min to ensure that the mixture became essentially homogeneous. And the antiaging agents (antioxidants and/or UV absorbers) were added slowly at a low mixing speed. The mixture was sheared under 2500 rpm rotation speed for 30 min to ensure the blend became essentially homogenous. The neat SBS modified asphalt binder was also treated using the same process for the purpose of preferable in comparison with the antiaging agent modified asphalt binders.

**Table 1**
Chemical composition of base binder.

| Composition | Measured values (wt %) |
|---|---|
| Saturates | 23.24 |
| Aromatics | 32.17 |
| Resins | 33.86 |
| Asphaltenes | 10.73 |

### 2.3. Conventional physical properties tests

Conventional physical properties of asphalt binders, including softening point, penetration and ductility, were tested in accordance with ASTM D36, ASTM D5 and ASTM D113-86, respectively.

### 2.4. Storage stability

Hot storage test is used to evaluate the high temperature storage stability of modified asphalt binders. Storage stability of modified asphalt binders was tested as the following procedure: the sample was poured into an aluminum tube (25 mm in diameter and 140 mm in height). The tube was sealed and stored vertically in an oven at 163 ± 5 °C for 48 h. Then the aluminum tube containing the modified asphalt binder was took out of the oven and cooled in a refrigerator at $-7$ °C for 4 h ± 5 min. Finally, the tubes were cut into three equal sections. The sections at the top and bottom were placed in separate dishes in an oven at 163 °C until the asphalt binder had well fluid to pour into softening point rings. If the difference of the softening point ($\Delta S$) between the top and bottom sections of the tube was less than 2.2 °C, the sample could be regarded as storage stable blend.

### 2.5. Aging procedure

Oxidative aging of modified asphalt binder was performed using the thin film oven test (TFOT) according to ASTM D1754. In this test, the 50 g asphalt samples are aged during 5 h at 163 °C in air. The TFOT has been validated for some time for unmodified asphalts for which it is considered to be more severe than the actual field condition. But it has been used with considerable success to compare different modified during laboratory studies.

UV aging tests were performed in a UV weathering oven. As soon as the time of TFOT of asphalt binder was over, each asphalt sample was immediately poured into the marked pans and approximately 3 mm thickness film was obtained. Then the sample was placed together in the UV weathering oven to undergo UV aging. The UV lamp was 500 W with main wavelength of 340 nm and the average intensity of UV irradiation on the asphalt binder surface was about 0.45 W/m$^2$. Asphalt binders undergo UV irradiation 7 days under 60 °C in the UV weathering oven.

### 2.6. Rotational viscosity

Brookfield viscometer (Model DV-II+, Brookfield Engineering Inc., USA) was employed to measure the rotational viscosity of asphalt binders according to ASTM D4402.

### 2.7. Dynamic shear rheological characteristics

Dynamic shear properties were measured with a dynamic shear rheometer (DSR, MCR101, Anton Paar Co. Ltd of Austria) in a parallel plate configuration with a gap width of 1 mm. Rheological tests were performed under controlled strain condition. Principal rheological parameters obtained from the DSR were complex modulus ($G^*$), storage modulus ($G'$), loss modulus ($G''$) and the phase angle ($\delta$). $G^*$ is defined as the ratio of maximum shear stress to the maximum strain and provides a measure of the total resistance to deformation. The $\delta$ is the phase shift between the applied stress and strain responses during a test and is a measure of the viscoelastic balance of the material behavior. Temperature sweeps (from 0 to 35 °C) with 2 °C increments were applied at a fixed frequency of