SBS/Carbon Black Compounds Give Asphalts With Improved High-Temperature Storage Stability

Shifeng Wang*, Yong Zhang and Yinxi Zhang
Research Institute of Polymer Materials, Shanghai Jiao Tong University, Shanghai, 200240, China

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SUMMARY

Styrene-butadiene-styrene tri-block copolymer (SBS) modified asphalts are usually unstable during high-temperature storage, which presents an obstacle to their application. In this paper, SBS modified asphalts with improved high-temperature storage stability were prepared by incorporating carbon black (CB) into the SBS compounds. The effect of CB on the high-temperature storage properties, dynamic rheology, mechanical properties (softening point, viscosity etc.) and the morphologies of the modified asphalts were studied. It was found that the ratio of SBS to CB in the compound had a great effect on the high-temperature storage behavior. The modified asphalts were stable when the ratio of SBS/CB was around 2. CB had almost no effect on the dynamic rheology or the mechanical properties of the modified asphalts. The improvement in high-temperature storage behavior could be caused by decreasing the density difference and improving the compatibility between SBS and asphalt.

1. INTRODUCTION

SBS endows good properties on asphalt when it is used as a modifier for it [1, 2]. Because SBS is not totally compatible with asphalt [3,4], if a mixture of SBS and asphalt is kept at elevated temperatures, as is often required in practice, the SBS will separate out, and the advantages of SBS modification will be totally lost. Thus, phase separation has been a major obstacle to the use of SBS modified asphalts in paving.

In order to improve the high-temperature storage-stability of SBS modified asphalt, many methods are adopted, such as reactive blending and so on [6-9], but these reaction processes cannot be controlled easily, and they may cause gelation.

CB can improve the high temperature resistance, ageing resistance and wear resistance of an asphalt road [10-12]. In contrast to the inorganic fillers currently used in asphalt, CB is hydrophobic, and has good interactions with both SBS and asphalt. Adding CB to the SBS modified asphalts should bring some attractive properties to them. However, there have been few reports about the modification of asphalt by using SBS/CB compound till now [13].

In this paper, SBS/CB compound modified asphalts were studied. For comparison purposes, asphalts modified by directly adding SBS and CB were also prepared. The effects of CB on the high-temperature storage stability, mechanical properties and rheological properties were analyzed.

2. MATERIALS AND EXPERIMENTAL

2.1 Materials

Asphalt, AH-90 paving asphalt was obtained from the Zhongyou Xingneng Asphalt Factory of Jiangyin, Jiangsu Province, China. The physical properties of the asphalt were as follows: Penetration, 90 dmm (deci-millimetre, 25°C, ASTM D5); Softening point, 47.5 °C (ASTM D36); Viscosity, 0.35Pa.s (135°C, ASTM D4402).

SBS, Grade 1301, produced by the Yueyang Petrochemical Co. Ltd., China. It was a linear-like SBS, containing 30 wt% styrene, and the weight average molecular weight was 120,000.

* author to whom correspondence should be addressed
E-mail: shfwang@sjtu.edu.cn
CB, HAF (N330), provided by Nanjing Chemical Co., Ltd., China.

2.2 Preparation of SBS/CB compounds

SBS, CB and a certain amount of asphalt (used as a processing aid, SBS/asphalt=2/1) were mixed to form the SBS/CB compounds in a two-roll mill at 145 °C. After about 5 minutes, an SBS/CB compound was formed. Compounds with different SBS to CB ratios were prepared in the same way.

2.3 Preparation of modified asphalts

All the modified asphalts were prepared using a high shear mixer (made by Weiyu Machine Co. Ltd., China) at 170 °C with a shearing speed of 3500rpm, and the shearing time was all 45 min. First, 500g asphalt was heated to become a fluid in an iron container, then upon reaching about 170 °C, a certain amount of SBS/CB compound, or CB, or SBS and CB was added to the asphalts. 4% SBS content was adopted unless otherwise stated.

2.4 High-temperature storage stability test

After mixing, some of the prepared modified asphalt was transferred into an aluminum toothpaste tube (32 mm in diameter and 160 mm in height). The tube was sealed and stored vertically in an oven at 163 °C for 48h, then taken out, cooled to room temperature, and cut horizontally into three equal sections. The samples taken from the top and bottom sections were used to evaluate the storage stability of the SBS modified asphalts by measuring their softening points and viscosities at 135 °C. If the difference between the softening points of the top and the bottom sections was less than 2.5 °C while the viscosities for the top and the bottom sections were about the same, the sample was considered to have good high-temperature storage stability. If the softening points differed by more than 2.5 °C or the ratio of the two viscosities was above 1.1 or below 0.97, the SBS modified asphalt was classified as less stable on storage.

2.5 Rheological characterization

A strain-controlled rheometry, ARES with parallel plate geometry (25 mm in diameter), was used to determine the rheological properties of the modified asphalt. A temperature sweep was applied over the range 25~75 °C at a fixed frequency of 10 rad/s and variable strain. About 1.0 g of sample was placed on the low plate. After the sample was heated to become a melt, the upper parallel plate was lowered to contact the sample and trimmed. The final gap was adjusted to 1.25 mm. All the samples were held at a defined, constant temperature for 10 min, and then the temperature was varied in 2 °C increments. Various viscoelastic parameters, such as G* and tan delta were automatically collected by the RSI Orchestrator® software.

2.6 Gel content analysis

About 1g sample of SBS/CB (2/1) compound was wrapped in filter paper, and the outside was covered with copper mesh in case of leakage. Three identical wrapped samples were immersed in toluene solvent for 7 days. After that, we took them out and dried them in the vacuum oven at 80 °C to constant weight.

\[
\text{Gel}\% = 100 \left( \frac{G_1 - G_2}{G_0 - G_2 - G_3} \right)
\]

where \(G_1\) was the weight after extraction; \(G_2\) was the weight of CB in the blend; \(G_3\) was the weight of asphalt in the blend, and \(G_0\) was the sample weight before extraction.

2.7 Morphological analysis

A small drop of the modified asphalt was placed onto a heated microscope glass slide. On squeezing the two glass slides together, a thin film was formed, which could be viewed by transmitting light. The morphology of the modified asphalts was observed under an optical microscope (made by Leica Co., Germany). The magnification was 400 times.

3. RESULTS AND DISCUSSION

3.1 CB modified asphalts

In order to learn more about the SBS/CB compound modified asphalt, the CB modified asphalt was first studied. The effect of CB on the properties of asphalt is given in Table 1. This shows that a small amount of CB has no effect on the softening point and high-temperature storage stability of asphalts. The observation can be explained by assuming that the interactions between the molecules do not change much when the CB content is less than 2%. Observation of CB modified asphalt shows that it became dark without any obvious particles after CB was added, as shown in Figure 1.
Table 1. Effect of CB content on the properties of original asphalt

<table>
<thead>
<tr>
<th>CB content (%)</th>
<th>Softening point, °C</th>
<th>Viscosity (135°C), Pa.s</th>
<th>Top softening point, °C</th>
<th>Bottom softening point, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>47.5</td>
<td>0.35</td>
<td>47.5</td>
<td>47.5</td>
</tr>
<tr>
<td>1</td>
<td>47.5</td>
<td>0.36</td>
<td>47.5</td>
<td>48.0</td>
</tr>
<tr>
<td>2</td>
<td>48.0</td>
<td>0.38</td>
<td>48.0</td>
<td>48.0</td>
</tr>
</tbody>
</table>

Figure 1. Micrographs of original asphalt and 2% CB modified asphalt. (a) original asphalt, (b) 2% CB modified asphalt (×400)

3.2 SBS/CB compound modified asphalts

3.2.1 Morphology

These samples show a macroscopic phase separation with relatively large size of SBS in our preparation method and condition.

Figure 2a shows the morphology of 4% SBS modified asphalt. Figure 2b shows the morphology of the modified asphalt into which 4% SBS and 2% CB (denoted as 4% SBS+2% CB) had been directly added. From those two figures, it can be judged that the CB mainly stayed in the asphalt when it was directly mixed into asphalt. The morphology of SBS/CB (2/1) compound modified asphalt (denoted as 4% SBS/2% CB) is shown in Figure 2c. The micrograph shows that some CB remained in the SBS particles, and some was dispersed in the asphalt. The gel content of SBS/CB (2/1) compound was 11.2%, which indicates that gel forms during the mixing of SBS and CB. So, the SBS particles in the SBS/CB modified asphalt must have contained some CB.

3.2.2 High-temperature storage properties

Because the solubility parameters and densities of SBS and asphalt are different, phase separation takes place in SBS modified asphalts during storage at high temperature, which leads to a great deterioration in practical performance. Proper measures should be taken to prevent the separation of SBS from asphalt.

The high-temperature storage stabilities of SBS/CB compound modified asphalts are presented in Table 2. Obviously, for asphalts modified by SBS in the absence of CB, the difference in softening points and viscosities was large, which means that the phase separation of the mixture is serious. The difference in the softening points or viscosities between the top and the bottom became smaller when the CB was added. With increasing CB content, the differences decreased progressively. It indicates that storage stability increased significantly with increasing CB content. When the SBS content was 4% and CB was 2% or 2.5%, the modified asphalts were all stable.

Micrographs of the top and bottom sections of SBS modified asphalt after high temperature storage are...
shown in Figures 3a and 3b. In the top section SBS aggregates, while in the bottom section only a few small SBS particles disperse, which further demonstrates that SBS modified asphalts are unstable during high-temperature storage. The micrographs for SBS/CB (2/1) compound modified asphalt after

Table 2. High-temperature storage stabilities analysis of SBS/CB compounds modified asphalts

<table>
<thead>
<tr>
<th>Material</th>
<th>Formulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Asphalt, % (w/w)</td>
<td>96 95 94 93.5</td>
</tr>
<tr>
<td>SBS, % (w/w)</td>
<td>4 4 4 4</td>
</tr>
<tr>
<td>CB, % (w/w)</td>
<td>0 1 2 2.5</td>
</tr>
</tbody>
</table>

Storage stability analysis

| Top viscosity (135°C), Pa.s | >10 | 1.20 | 1.02 | 1.10 |
| Bottom viscosity (135°C), Pa.s | 0.54 | 0.91 | 1.01 | 1.12 |
| Top / Bottom ratio          | >18.5 | 1.32 | 1.01 | 0.98 |
| Top softening point, °C     | >80 | 63 | 63 | 63 |
| Bottom softening point, °C  | 51 | 58 | 62 | 63 |
| (Top-Bottom), °C            | >29 | 5 | 1 | 0 |
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Figures 3c and 3d. They show that the top section and bottom sections were almost the same, which further demonstrates the stability of SBS/CB (2/1) compound modified asphalt.

Table 3 shows the effect of CB on the high-temperature storage stability of asphalt modified by directly adding SBS and CB to asphalt. The storage stability changes a little with increasing CB content. Even when the CB content was 3%, the modified asphalt was still unstable at high temperature. This indicates that compounding SBS and CB is necessary to improve high-temperature storage stability.

3.2.3 Rheological properties

For rutting resistance at high temperatures, increasing complex modulus and decreasing tan delta values are favourable because they reflect a more elastic behaviour. Figures 4a and 4b show the dynamic properties of SBS-modified asphalt as a function of the amount of CB. The complex modulus (G*) of all the modified asphalts was almost the same over the whole temperature range, as shown in Figure 4a. This figure indicates that the CB content and the processing technique had no effect on the G*. However, the tan delta decreased a little with the addition of CB at high temperature, which is because CB can increase the elastic modulus of the modified asphalts.

3.2.4 Softening point and viscosity

During the preparation of the asphalts modified with SBS and CB, the CB contents and blending methods will lead to different distributions of SBS and CB in the asphalts. They will lead to changes in the properties of modified asphalt. So, the effect of CB content on the properties of modified asphalts blended in two different ways was studied.

The softening point is usually used to characterize the high temperature properties of asphalt. The higher the softening point, the better the behaviour at high temperature. Figure 5 shows the effect of CB content on the softening points of two kinds of modified
Table 3. High-temperature storage stabilities analysis of asphalts modified by directly adding SBS and CB

<table>
<thead>
<tr>
<th>Material</th>
<th>Formulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Asphalt, % (w/w)</td>
<td>96  95  94  93</td>
</tr>
<tr>
<td>SBS, % (w/w)</td>
<td>4   4   4   4</td>
</tr>
<tr>
<td>CB, % (w/w)</td>
<td>0   1   2   3</td>
</tr>
</tbody>
</table>

Storage stability analysis

| Top viscosity (135°C), Pa.s | 10 | 2.51 | 1.90 | 1.87 |
| Bottom viscosity (135°C), Pa.s | 0.54 | 0.79 | 0.82 | 0.83 |
| Top / Bottom ratio | >18.5 | 3.18 | 2.32 | 2.25 |
| Top softening point, °C | >80 | >80 | >80 | >80 |
| Bottom softening point, °C | 51 | 55 | 56 | 56 |
| (Top-Bottom), °C | >29 | >25 | >24 | >24 |

Figure 4. Effect of CB content on the rheological properties of asphalt and modified asphalts (a) $G^*$ vs T curves. (b) Tan delta vs T curves
When CB and SBS are added directly into the asphalt, the softening points are independent of the amount of CB, and even if the amount of CB is raised to 2.5%, the softening points do not change much. However, the softening points of SBS/CB compound-modified asphalts increase a little with increasing CB content.

Figure 5 gives the effect of CB content on the softening point of modified asphalt. The change in the viscosities closely resembles the change in softening points in Figure 5.

3.2.5 Low temperature ductility
The low temperature ductility was tested in order to characterize the low temperature performance of modified asphalt. With an increase in the ductility, the low temperature properties become better and the pavement does not easily crack at low temperature.
Figure 7 shows the effect of CB content on the low temperature ductility of two kinds of modified asphalt. With increasing CB content, the ductilities of modified asphalt with SBS and CB directly added showed no change, while those of the SBS/CB compound modified asphalt decreased slightly.

3.3. Storage stable mechanism analysis

Asphalt is traditionally regarded as a dynamic colloidal system consisting of a suspension of high molecular weight asphaltene micelles dispersed in a lower molecular weight oily medium (maltenes). The introduction of any polymer will disturb the dynamic equilibrium and reduce the homogeneity of the asphalt system, so the polymer modified asphalts may have a tendency to separate into polymer-rich and asphalt-rich phases. This is especially serious under quiescent conditions at high temperatures [7].

SBS modified asphalt can be regarded as a suspension system. To a suspension system, the particles in the liquid bear the buoyancy force and gravitational force, and the falling velocity \( v \) of the particles in the system is given by Stoke’s law [8],

\[
\nu = 2(\rho_0 - \rho_s)gr^2/9 \eta
\]

where \( \rho_0 \) is the density of asphalt, \( \rho_s \) is the density of SBS, \( g \) is the gravitational force constant, \( r \) is the radius of the SBS particle, and \( \eta \) is the viscosity of the modified asphalt.

Reducing the falling velocity of the particles is the key to preventing the separation of SBS and asphalt. Then, in order to reduce the phase separation of a suspension system, one method is to reduce the diameter of the particles, and another is to reduce the density difference.

Because CB has many active sites on its surface, chemical or physical interactions with rubber can form during processing [14]. SBS is a kind of thermoplastic rubber, and when the SBS is compounded with CB, some CB can attach to the SBS because of strong interactions between them. The interactions between SBS and CB have been demonstrated by gel content measurements as stated above.

The density of the SBS was 0.94 g/cm\(^3\) and of the asphalt used here was 1.02 g/cm\(^3\) at room temperature. The density difference became larger at high temperatures because the SBS swelled with the light fraction of the asphalt. The density of CB is around 1.83 g/cm\(^3\) at room temperature. When the CB becomes attached to SBS, the density difference is minimized and the separation force becomes zero at a certain CB content, so the high-temperature storage stability is improved.

When CB is added to asphalt, the CB preferentially absorbs the high molecular weight compounds of the asphalt such as asphaltenes and asphaltene-derivatives [15, 16]. It will be covered by a thin film of asphaltenes. So the surface of the SBS/CB particles
in the asphalt will also absorb some asphaltenes, the compatibility between the SBS and asphalt is improved, and the high-temperature storage stability becomes better.

CONCLUSIONS

The high-temperature storage stability of SBS modified asphalts was achieved by dispersing SBS/CB compound into asphalt. The ratio of SBS to CB in the compound had a great effect on the high-temperature storage behaviour, the modified asphalts were stable when the ratio of SBS/CB was around 2. CB had almost no effect on the mechanical and rheological properties of the 4% SBS modified asphalts when the amount was less than 3%. The interaction between SBS and CB was the main factor that influenced the stabilization of SBS in the asphalt, decreasing the density difference and improving the compatibility between SBS and asphalt.

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