Research Article

Rheological Properties and Antiaging Performance of Graphene Oxide-Modified Bio-Asphalt

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To enhance the performance of bio-asphalt, an attempt was made to modify bio-asphalt using graphene oxide (GO). Two bio-asphalts were prepared and modified with different GO dosage levels of 0 to 0.08% to obtain GO-modified bio-asphalts (GOMBA). The two GOMBA were tested in the conventional properties (penetration, softening point, and ductility), high- and low-temperature rheological properties, and aging properties. The results showed that the penetration decreases and the ductility increases slightly with the increase in the dosage of GO, while the softening point increases stably to the maximum by 17.84%, and 15.99% for the two GOMBA, respectively. GO is beneficial to improve the high temperature performance and the recovery after the deformation of the GOMBA; on the contrary, it does not significantly affect the low temperature cracking resistance of those. The maximum residual penetration ratio is 10.58% and 8.84%, respectively, and the maximum residual ductility is 10.79% and 27.51%, respectively, for the two GOMBA after short-term aging. GO modification plays a role in the change of carbonyl index (CI) and sulfoxide index (SI) of the GOMBA before and after aging based on the FT-IR spectra, indicating that the GO can effectively improve the antiaging performance of bio-asphalt.

1. Introduction

Asphalt mixtures for road pavement are mainly produced by petroleum asphalt derived from fossil fuels, currently. As oil reserves dwindle and the price of oil rises, the cost of petroleum asphalt mixtures enhances, accordingly. Bio-oil has obvious advantages over fossil fuels, as it comes from waste biomass and can be blended into traditional petroleum asphalt to produce a bio-asphalt mixture. The bio-asphalt mixture has good social and economic benefits in terms of improving the service level and service life of the asphalt concrete pavements while protecting the environment [1–4].

A number of studies have tested the performance of bio-asphalt from different sources. Fini developed a bio-asphalt by using pig manure and studied the rheological properties of the bio-asphalt blended with base asphalt (usually called blended asphalt) [5]. It was found that the complex modulus of the blended asphalts decreased as the content of the bio-asphalt and the slope of the low temperature creep decreased. Wen et al. prepared bio-asphalts by blending bio-oil derived from waste edible fats at 10%, 30%, and 60% with PG58-28, PG82-16, and PG76-22 petroleum asphalts, respectively, and then determined the performance grade of the bio-asphalts [6]. Yang et al. used the bio-oil from wood pyrolysis to prepare bio-asphalts at a temperature of 120°C.
and a shear rate of 5000 r/min and then tested the high-
temperature viscosity and rheological properties of the bio-
asphalts [7]. However, the performance of the bio-asphalt is
not satisfactory and does not meet the requirements for the
asphalt pavements, mainly in terms of its susceptibility to
aging at high temperatures, poor low temperature cracking
resistance, and poor resistance to water damage [8–10].

To improve and enhance all aspects of the performance of
the bio-asphalt, one or more modifiers are adopted
[11–13]. More and more nanomaterials are being used in the
field of pavement materials currently, such as nano-clay,
nano-SiO$_2$, nano-TiO$_2$, and nano-ZnO to enhance the
performance of the asphalt and the mixture [14–16].
Compared to other nanomaterials, graphene oxide (GO)
used as a modifier for asphalt binders has attracted more
and more attention recently. Abdelrahman et al. [17] and Li et al.
[18] found that the addition of small amounts of GO could
increase the viscosity and the stiffness modulus of the as-
asphalts and improve the high-temperature rutting resistance
and the low-temperature cracking resistance of the asphalts.
Zhu et al. studied the effects of GO dosage on the aging of
asphalt and found that GO could hinder the passage of
oxygen molecules and slow down the aging rate of the as-
phalt [19]. GO can significantly improve the performance of
the asphalt, but there are few studies on the GO-modified
bio-asphalt (GOMBA) at present.

2. Objectives and Scopes

To improve the performance of the bio-asphalt, an attempt
was made to modify the bio-asphalts using GO. Two bio-
asphalts were prepared and modified with different GO
dosage levels of 0 to 0.08% to obtain the GOMBA. The
conventional properties such as penetration, softening point,
ductility, high- and low-temperature rheological properties,
and aging properties of the two bio-asphalt types were in-
vestigated. The flowchart of this study is shown in Figure 1.

3. Materials and Methods

3.1. Raw Materials

3.1.1. Base Asphalt. The base asphalt used in the study is
ESSO 70# A-Class asphalt. The performance indexes are
shown in Table 1. All indexes met the requirements of the
specification in China.

3.1.2. Bio-Oil. Two bio-oils, noted as bio-oil I and bio-oil II,
used in the study were produced by a company in Shandong
and were mainly produced from waste biomass such as straw
and wood chips through a fast pyrolysis method. The main
performance indexes of the two bio-oils are shown in
Table 2.

3.1.3. GO. The GO used in the study was produced by a new
material company in Guangzhou. The GO sample is shown
in Figure 2, and the main performance indexes are shown in
Table 3.

3.2. Test Asphalts Preparation

3.2.1. Bio-Asphalts Preparation. The base asphalt was heated
and melted in an oven at 160°C. To melt the bio-oil in the
base asphalt evenly, a set mass of bio-oil was added to the
molten base asphalt in stages and sheared at 4500 r/min for
30 minutes by using a high-speed shear. The bio-asphalt was
then stirred manually for 10 minutes to disperse the air
bubbles in the asphalt after shearing. The test bio-asphalt
sample was then obtained after standing. In this study, the
amount of bio-oil blended was set at 15% of the mass of the
base asphalt. The two bio-oils, bio-oil I and bio-oil II, were
used to produce bio-asphalts as bio-asphalt A and bio-as-
phalt B, respectively.

3.2.2. Preparation of GO-Modified Bio-Asphalts. GOMBA
was also prepared by using the shear mixing method
described above. The GO dosages used in this study were
0, 0.02%, 0.05%, and 0.08% by weight of the bio-asphalt. A
diagram of the bio-asphalt preparation process is shown
in Figure 3. For ease of presentation and to avoid am-
biguity, the test asphalts were numbered as shown in
Table 4. Fractions of the two bio-asphalts are shown in
Table 5.

3.3. Test Methods

3.3.1. Basic Performance Index Test. The test methods
T0604-2011, T0605-2011, and T0606-2011 in the Test Pro-
cedure for Asphalt and Asphalt Mixtures for Highway
Engineering (JTG E20-2011) (subsequently referred to as the
test procedure) were adopted to evaluate the effects of GO on
the conventional performance indexes of penetration,
ductility, and softening point of the bio-asphalts. The test
temperature of the penetration and ductility was 25°C and
10°C, respectively.

3.3.2. Dynamic Shear Rheology Test (DSR). A high tem-
perature rheological test was conducted on a DSR (Dynamic
shear rheology SYD-0628, Anton Paar Trading Co., Shang-
hai, China) by using different test asphalts. The di-
ameter of the parallel plates was 25 mm and the space be-
tween the parallel plates was 1 mm. The sweep frequency was
set at 10 rad/s. The sweep temperature ranged from 46 to
76°C, with an interval of 6°C. The complex modulus (G*)
and phase angle (δ) were recorded to calculate the rutting
factor G* / sinδ and to evaluate the high temperature rhe-
ological performance.

3.3.3. Bending Beam Rheometer Test (BBR). After aging in a
pressure aging vessel (PAV, pressure aging vessel-I,
Hangzhou Hanghua Metal Container Co., Hangzhou,
China), the different test asphalt samples were subjected to
beam bending tests using a bending beam rheometer.
BBR and TE-BBR (ThermoFisher Scientific (China) Co.,
Shanghai, China) were used to evaluate the low temperature
cracking resistance. The test temperatures were set −12°C.
and −18°C. The stiffness modulus ($S$) and the creep rate ($m$) at 60 s were recorded to evaluate the low temperature cracking resistance of the asphalt binders.

### 3.3.4. Asphalts Aging Test

To study the effects of GO dosage on the aging resistance of bio-asphalts, the different test asphalt aging samples were prepared using the rolling thin film oven test (RTFOT) according to the test method T0610-2011. The aging temperature of the asphalt samples was controlled at $(163 \pm 1){}^\circ C$ and the aging duration was 75 minutes in the RTFOT aging test. A control group was also evaluated by using the same method. The change in mass, the change in penetration, and the residual ductility at 10°C were analyzed.

### 3.3.5. Fourier Transform Infrared Spectroscopy Test (FT-IR)

During the aging process, the asphalt molecules were oxidized and the content of oxygen-containing functional groups, such as the carbonyl and sulfoxide groups, increased accordingly, so that the changes in the peaks of the carbonyl and sulfoxide functional groups can be used to characterize the changes in the chemical structure of the asphalt during aging. The infrared spectrum test was often used to evaluate the characteristics of the functional groups before and after aging of the asphalt. In this study, a FT-IR spectrometer (Fourier transform infrared spectroscopy-650S, Shanghai Haogang Optoelectronic Equipment Co., Shanghai, China) was adopted to analyze the chemical structure of the GOMBA before and after aging. The asphalt samples of A0, B0, A4, and B4 before and after aging were selected for the infrared spectroscopy test to compare and analyze the effects of GO on the functional groups of the two bio-asphalts before and after aging.

### 4. Results and Discussion

#### 4.1. Effects on Conventional Property Indexes

The three conventional property indexes of penetration, softening point, and ductility of the GOMBA with different GO dosages were evaluated first to clarify the effects of GO on the properties of bio-asphalts.
Figure 4 shows the results of the penetration tests of the modified bio-asphalts with different GO dosage levels. From Figure 1, it can be seen that the penetration of the bio-asphalt A1 and B1 increases after the addition of bio-oil I and II compared to the base asphalt A0. It was found that the bio-oil has more light components (saturated and aromatic fractions), which play a role in softening the base asphalt. The penetration of A4 and B4 decreases by 3.89% and 4.26% compared to A1 and B1, respectively. The analysis suggested that the GOMBA samples were probably hardened by the volatilization of the light components during the preparation process and the adsorption of the light components by the GO powder with large specific surface area. The reduction of the light components resulted in a certain degree of decrease in the GO-modified asphalt penetration.

The results of the softening point tests on the modified asphalt with different GO dosage levels are shown in Figure 5. From Figure 5, with the increase of GO dosage, the softening points of both bio-asphalt samples show an increasing trend. The softening points of the samples A2, A3, and A4, and B2, B3, and B4 increase by 11.45%, 16.52%, 17.84%, and 9.23%, 14.19%, 15.99%, respectively, compared with A1 and B1 with the increase of 0.08% from 0.02% GO. It shows that the softening points of the bio-asphalts increase substantially after GO addition, but the increase tends to slow down with increasing amount of GO. The analysis suggests that GO has good thermal conductivity to dissipate the heat inside the asphalt, resulting in the increasing of the softening point. When the dosage of GO reaches to a certain amount, the increase in thermal conductivity is not obvious, so the increasing trend of the softening point tends to slow down.

Figure 6 shows the results of the GOMBA ductility tests with different GO dosage levels. The test results show that the ductility of the GOMBA increases slightly with the increase in the amount of GO, but the increase is not significant. The ductility of GOMBA with bio-oil II is higher than that of GOMBA with bio-oil I. The main reason is that the components of bio-asphalt A and B are different, while GO does not play a significant role in increasing the ductility.

4.2. Effects on High Temperature Rheological Properties. Complex modulus (G*), phase angle (δ), and rutting factor (G*/sin δ) were used to evaluate the high temperature rheological properties. The complex modulus G* reflects the ability of asphalt to resist the deformation in shear, with larger values indicating greater resistance to the shear behavior [20, 21]. The phase angle δ indicates the ratio of viscosity to the elasticity of asphalt, with higher values indicating greater viscosity and poorer recovery from deformation [22, 23]. The rutting factor (G*/sin δ) indicates the ability of asphalt to resist permanent deformation, with higher values indicating greater resistance to permanent deformation. The results of the complex modulus (G*), phase angle δ, and rutting factor (G*/sin δ) measured at 46–76°C for the two GO-modified bio-asphalt A and B are shown in Figures 7, 8, and 9, respectively.

The complex modulus test results on the GOMBA are shown in Figure 7. For both bio-asphalts, the complex modulus decreases with increasing temperature at different GO dosage levels. The higher the dosage, the greater the complex modulus of the GOMBA. It shows that the addition of GO plays a role in the increase of the complex modulus of the bio-asphalts, and the higher the dosage, the greater the complex modulus of the GOMBA within the tested dosage range. Overall, the complex modulus of the GO-modified bio-asphalt A is higher than that of the GO-modified bio-asphalt B. It indicates that the fractions of the different bio-oils have a significant impact in the complex modulus of the prepared GOMBA.

As shown in Figure 8, the phase angle δ in both types of GOMBA increases in temperature at different GO dosages and decreases with increasing dosage at the same temperature conditions. It indicates that the addition of GO to bio-asphalts can serve to reduce the viscous component of the viscoelastic ratio and facilitate the recovery of the asphalts after deformation.

Figure 9 shows the results of the rutting factor calculations for the different dosages of GOMBA. As shown in
penetration ratio of both GOMBA steadily increase by 3.88%, 8.47%, 10.58%, and 1.47%, 6.63%, 8.84%, respectively, with the increase of GO dosage.

The residual ductility at 10°C of bio-asphalt A and B decrease by 53.2%, and 63.3% compared to the base asphalt, respectively, which indicates that the GO has a significant improvement on the bio-asphalts. The residual ductility at 10°C increases by 3.32%, 6.22%, 10.79%, and 14.29%, 17.99%, 27.51%, respectively, with increasing GO dosage.

On the one hand, according to the results of the mass loss rate, the residual penetration ratio, and the residual ductility at 10°C, it shows that the aging resistance of the two bio-asphalts decreases largely relative to the base asphalt. On the other hand, GO modification steadily increases the aging resistance of the bio-asphalts with the increasing of GO dosage in the test dosage range.

### 4.5. Effects on Functional Groups.

To analyze in depth, the differences in the influence of GO on the aging resistance of different bio-asphalts, four asphalts before and after RTFOT aging were evaluated and analyzed using FT-IR. The results of the FT-IR spectra for the four bio-asphalts are shown in Figure 11.

As can be seen from Figure 12, the peaks of all four asphalt species remain unchanged, at both 2932 cm$^{-1}$ and 1460 cm$^{-1}$. The wave peak at 2932 cm$^{-1}$ represents the stretching vibration of the C-H bond and the wave peak at 1460 cm$^{-1}$ represents the bending vibration of C-H bond. The main groups of these four bio-asphalts have not changed and are still dominated by the C-H bond.

FT-IR can effectively distinguish the changes in the composition of the asphalts based on the changes in the wave peaks, therefore also suitable for observing the changes in the individual components during aging [24, 25].

To analyze the magnitude of the aging resistance of the four asphalts in more depth, a comparative analysis of the FT-IR of the four bio-asphalts before and after aging was conducted. It can be seen from Figure 11 that the carbonyl group (C = O) represented at 1700 cm$^{-1}$ and the sulfoxide group (S = O) peak at 1030 cm$^{-1}$ change for the four asphalts after different degrees of aging. These two sets of chemical bonds are produced by the absorption of oxygen by the unsaturated carbon chains and the sulphur elements in the asphalt during aging, respectively, indicating the dominance of oxygen-absorbed aging in the asphalt aging process.

The carbonyl index (CI) and the sulfoxide index (SI) are defined by using the area of the peak at the stretching

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Table 4: Code abbreviation of the test asphalts.

<table>
<thead>
<tr>
<th>Test asphalt material composition</th>
<th>No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base asphalt</td>
<td>A0</td>
</tr>
<tr>
<td>Bio-asphalt A</td>
<td>A1</td>
</tr>
<tr>
<td>Bio-asphalt B</td>
<td>B1</td>
</tr>
<tr>
<td>0.02%GO + bio-asphalt A</td>
<td>A2</td>
</tr>
<tr>
<td>0.05%GO + bio-asphalt A</td>
<td>A3</td>
</tr>
<tr>
<td>0.08%GO + bio-asphalt A</td>
<td>A4</td>
</tr>
<tr>
<td>0.02%GO + bio-asphalt B</td>
<td>B2</td>
</tr>
<tr>
<td>0.05%GO + bio-asphalt B</td>
<td>B3</td>
</tr>
<tr>
<td>0.08%GO + bio-asphalt B</td>
<td>B4</td>
</tr>
</tbody>
</table>

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4.3. Effects on Low Temperature Cracking Resistance. The stiffness modulus and the creep rate obtained from the BBR test are shown in Figure 10 and Figure 11. The lower the modulus of stiffness or the higher the creep rate for a given low temperature condition, the better the low temperature cracking resistance of the asphalt binder. From Figure 10, the increased stiffness modulus and the reduced creep rate of both bio-asphalt A and bio-asphalt B compared to the base asphalt A0 indicate that both the bio-asphalts show a decrease in low temperature cracking resistance relative after PAV aging to the base asphalt. The S and m values of the asphalt binders A2, A3, and A4 or B2, B3, and B4 vary within a small range (2% variation) at all temperatures; that is, the addition of GO does not significantly affect the low temperature cracking resistance of the asphalt binders.

4.4. Effects on Aging Resistance. The results of the RTFOT aging tests on the different asphalt samples are shown in Table 6. The results of the mass loss rate show that there is a certain increase in the mass loss rate for all samples of bio-asphalt A and B relative to the base asphalt, with a decreasing trend in mass loss rate after GO modification.

In terms of the residual penetration ratio, both bio-asphalt A and B show a relatively large decrease compared to base asphalt after short-term aging by RTFOT. The residual
vibration of C-H bond (2923 cm\(^{-1}\)) as a reference. The ratio of the absorption peak area of the carbonyl group (1700 cm\(^{-1}\)) and the sulfoxide group (1030 cm\(^{-1}\)) to the wave area at the C-H bond stretching vibration (2923 cm\(^{-1}\)) is used to characterize the CI and SI, respectively [26, 27]. The CI and SI are calculated as follows [28, 29]:

\[
CI = \frac{A_{\text{C=O}}}{A_{\text{C-H}}},
\]

\[
SI = \frac{A_{\text{S=O}}}{A_{\text{C-H}}},
\]
where $A_{c=\omega}$ is the carbonyl absorption peak area, $A_{s=\omega}$ is the sulfoxide absorption peak area, and $A_{c-H}$ is the C-H bond stretching vibration absorption peak area.

As can be seen from Figure 13, the CI and SI of the four bio-asphalts of A0, A4, B0, and B4 increase accordingly before and after aging. The change in CI before and after aging for samples is 63.29%, 61.73%, 59.52%, and 57.47%, respectively. Similarly, the change in SI before and after aging is 51.59%, 28.57%, 47.80%, and 35.37%, respectively.

The results indicate that GO modification plays a role in the changes of CI and SI of the bio-asphalts before and after aging, in other words, the addition of GO to bio-asphalt could effectively improve the aging resistance of bio-asphalts.
Figure 9: Rutting factors of GOMBA at different dosage levels. (a) Effects of different GO dosages on the rutting factor of bio-asphalt A and (b) effects of different GO dosages on the rutting factor of bio-asphalt B.

Figure 10: Modulus of stiffness of the GOMBA at different dosage levels. (a) Effects of different GO dosages on the stiffness modulus of bio-asphalt A and (b) effects of different GO dosages on the stiffness modulus of bio-asphalt B.
Figure 11: Creep rate of GOMBA at different dosage levels. (a) Effects of different GO dosages on the creep rate of bio-asphalt A and (b) effects of different GO dosages on the creep rate of bio-asphalt B.

Table 6: Aging test results.

<table>
<thead>
<tr>
<th>Type of asphalt</th>
<th>Quality loss rate (%)</th>
<th>Residual penetration ratio (%)</th>
<th>Residual ductility at 10°C(cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A0</td>
<td>-0.05</td>
<td>74.1</td>
<td>51.5</td>
</tr>
<tr>
<td>A1</td>
<td>-0.68</td>
<td>56.7</td>
<td>24.1</td>
</tr>
<tr>
<td>A2</td>
<td>-0.54</td>
<td>58.9</td>
<td>24.9</td>
</tr>
<tr>
<td>A3</td>
<td>-0.44</td>
<td>61.5</td>
<td>25.6</td>
</tr>
<tr>
<td>A4</td>
<td>-0.34</td>
<td>62.7</td>
<td>26.7</td>
</tr>
<tr>
<td>B1</td>
<td>-0.75</td>
<td>54.3</td>
<td>18.9</td>
</tr>
<tr>
<td>B2</td>
<td>-0.52</td>
<td>55.1</td>
<td>21.6</td>
</tr>
<tr>
<td>B3</td>
<td>-0.41</td>
<td>55.9</td>
<td>22.3</td>
</tr>
<tr>
<td>B4</td>
<td>-0.39</td>
<td>56.1</td>
<td>24.1</td>
</tr>
</tbody>
</table>

Figure 12: Continued.
To improve the performance of bio-asphalt, an attempt was made to modify the bio-asphalts using GO, and the conventional properties such as penetration, softening point, and ductility, high and low temperature rheological properties, and aging properties of two bio-asphalts with different GO dosage levels were studied. The following conclusions can be drawn:

(1) With the GO dosage increasing from 0 to 0.08% for both the bio-asphalt A and B, the penetration at 25°C decreases slightly and the ductility at 10°C increases slightly with the increase in the amount of GO, while the softening point increases stably to the maximum by 17.84%, and 15.99%, respectively.

(2) The modification of GO is beneficial to improve the high temperature performance of the bio-asphalts and to the recovery of asphalt after deformation. After PAV aging, GO could not significantly affect the low temperature cracking resistance of the bio-asphalts.

Figure 12: The results of the FT-IR spectra of the four bio-asphalts before and after aging. (a) A0, (b) A4, (c) B0, and (d) B4.

Figure 13: CI and SI before and after aging of the different bio-asphalts. (a) CI and (b) SI.

5. Conclusions

To improve the performance of bio-asphalt, an attempt was made to modify the bio-asphalts using GO, and the conventional properties such as penetration, softening point, and ductility, high and low temperature rheological properties, and aging properties of two bio-asphalts with different GO dosage levels were studied. The following conclusions can be drawn:

(1) With the GO dosage increasing from 0 to 0.08% for both the bio-asphalt A and B, the penetration at 25°C decreases slightly and the ductility at 10°C increases slightly with the increase in the amount of GO, while the softening point increases stably to the maximum by 17.84%, and 15.99%, respectively.

(2) The modification of GO is beneficial to improve the high temperature performance of the bio-asphalts and to the recovery of asphalt after deformation. After PAV aging, GO could not significantly affect the low temperature cracking resistance of the bio-asphalts.
(3) After short-term aging of RTFOT, the increase in GO dosage results in a decreasing trend in the mass loss rate and a steady increase in residual penetration ratio and residual ductility at 10°C. The maximum residual penetration ratio is 10.58% and 8.84%, respectively. The maximum residual ductility at 10°C is 10.79%, and 27.51%, respectively, for the two GOMBA.

(4) GO modification plays a role in the change of CI and SI of bio-asphalts before and after aging. GO can effectively improve the antiaging performance of the bio-asphalt.

Data Availability

No data were used to support this study.

Disclosure

The results and opinions presented are those of the authors and do not necessarily reflect those of the sponsoring agencies.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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