Research on Rheology and Micro-properties of Modified Room Temperature Biological Asphalt

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Abstract. In order to explore the rheological property and principles of modified room temperature biological asphalt made with petroleum asphalt, vegetable asphalt, and unsaturated fatty acids as raw materials, waste rubber powder as modifier, and calcium hydroxide powder as curing agent, this paper compared and tested the rheological properties and the original petroleum asphalt by using DSR and BBR, and the micro-properties of the asphalt were studied by using SEM. The PG classification of modified room temperature biological asphalt has been upgraded from PG58-28 of the original petroleum asphalt to PG82-28. Compared with the original petroleum asphalt, the high temperature rheological property of the modified room temperature biological asphalt has been greatly improved. Its low temperature rheological property is equivalent to the original one, but the possibility of cracking is lower. SEM test showed that the components of the modified room temperature biological asphalt are well combined. The calcium hydroxide curing agent reacts with fatty acid and the rubber particles cross link with each other to form a mesh package in the asphalt, which provides strength for the modified temperature biologic asphalt at room temperature.

Keywords: Road Engineering, Biology Asphalt at Room Temperature, Rheological Property, Micro-Properties.

1. Introduction
As the world’s largest energy producer and energy consumer, China is vigorously developing clean energy and green low-carbon industries. In the white paper China’s Energy Development in the New Era released in 2020, it is planned that China will reach the peak of carbon dioxide emissions by 2030 and achieve the goal of carbon neutrality by 2060.

In 2020, China’s apparent demand for asphalt was 83.485 million tons, of which about 82% was used for large-scale highway construction and maintenance engineering [1-3]. At present, asphalt pavement mainly uses hot mix asphalt mixture for paving, which in the paving process will produce a lot of CO2, NO, SO2, benzopyrene, asphalt smoke and other toxic and harmful gases. It will not only will cause environmental pollution, but also harm the health of operators. With the advent of the development phase of the new era, China has also put forward new requirements for the construction of asphalt pavements. It results in that traditional hot-mix asphalt mixtures is no longer in line with the current era of green, low-carbon, and environmentally friendly concepts. Vegetable asphalt has the...
characteristics of large yield, easy access, and light pollution. It can be mixed with petroleum asphalt to make room temperature biological asphalt, which can effectively meet China's new era concept of green, low carbon and environmental protection [4~9].

The research of biological asphalt began in the 21st century. Emmanuel C et al. [10] analyzed the complex modulus curves of vegetable asphalt and petroleum asphalt matrixd on mathematical methods, and verified the possibility of vegetable asphalt as a substitute for petroleum asphalt. Williams R.C et al. [11] used waste wood plant asphalt as raw materials and mixed petroleum asphalt to make biological asphalt, which has improved high-temperature performance compared with ordinary petroleum asphalt. Wen H et al. [12] made biological asphalt with different amounts of oil and vegetable asphalt, and found that its viscosity was greatly reduced compared with the original petroleum asphalt. However, the low temperature performance was improved to a certain extent, and the maximum amount of vegetable asphalt should not exceed 30 %. Bao Jianye et al. [13] used 5% as the division value, and added vegetable asphalt at a content of 0% to 30% to the rubber-modified petroleum asphalt to make a hot-mix modified bio-asphalt. With the increase of the content, the viscosity of the rubber modified asphalt will gradually decrease, the high temperature performance will be weakened, and the low temperature performance will be improved. The best content is 15%. He Min et al. [14] obtained the conclusion that the polymer modifier has good compatibility with biological asphalt by adding different types of modifiers to the biological asphalt.

In view of the existing research, this paper used vegetable asphalt derived from castor oil feet and unsaturated fatty acids as raw materials, waste rubber powder as modifier, calcium hydroxide powder as curing agent, mixed with petroleum asphalt to make modified room temperature biological asphalt. They also conducted rheological and micro-property tests.

2. Experiment

The petroleum asphalt used in this experiment is Donghai brand A grade 70# asphalt. The vegetable asphalt is obtained from castor oil refining waste black feet after high temperature and high pressure distillation and purification. The appearance is brown-black liquid viscous material. The content of higher fatty acids is 78.9%. The unsaturated fatty acid liquefaction agent is derived from castor oil, and the content of unsaturated fatty acid is 95%. The waste rubber powder is made by pulverizing and grinding radial tires under normal temperature conditions. The particle size is 40 meshes, and the curing agent is calcium hydroxide powder of 800 meshes.

First, put the matrix asphalt and vegetable asphalt in a certain ratio in an incubator at a temperature of 140°C for 1 hour to fully dissolve the matrix asphalt and vegetable asphalt. Then, mix the matrix asphalt with vegetable asphalt, and use a shearing instrument at 200r/min. Shear at low speed for 15 minutes to make the matrix asphalt and vegetable asphalt evenly mixed. Then add a certain proportion of waste rubber powder to the uniformly mixed solution, and place it in an incubator at 160°C for 15 minutes to fully swell the waste rubber powder. After that, use a shear meter to high-speed shearing for 1 hour at 4500r/min at 160°C. After shearing, it was placed in an incubator at 160°C and developed for 15 minutes to fully disperse the waste rubber powder in the asphalt. Finally, after the mixture was cooled to below 100°C, add a certain proportion of unsaturated fatty acids, use a shear meter to stir at a low speed of 200r/min for 15 minutes. After cooling, the modified biological liquid asphalt at room temperature finished product was obtained. The modified room temperature biological asphalt was obtained by adding curing agent. In this paper, the rheological properties and micro-principles of the above samples were studied using a dynamic shear rheometer, a low-temperature curved beam rheometer and a scanning electron microscope.

3. Conclusion and Analysis

3.1 Dynamic Shear Rheological Properties

In this paper, Dynamic shear rheometer (DSR) was used to evaluate the high-temperature rheological property of asphalt. The dynamic shear rheological test is proposed by the US SHRP program. The
dynamic shear rheometer was used to test the complex shear modulus $G^*$ and phase angle $\delta$. The rutting factor $G^*/\sin (\delta)$ obtained by dividing $G^*$ and $\sin (\delta)$ was used to evaluate the high temperature performance of asphalt. The dynamic shear rheometer was used to test unaged 70# matrix asphalt, modified normal temperature biologic asphalt and two kinds of asphalt aged by rotary film oven (RTFOT) at a shear rate of 10rad/s and a temperature range of 58°C~88°C respectively. The test results are shown in Table 1.

Table 1. Dynamic shear rheological test results

| Temperature(℃) | 58 | 64 | 70 | 76 | 82 | 88 |
|----------------|----|----|----|----|----|----|
| 70# asphalt    | G*(kPa) | Before aging | 2.16 | 0.98 | 0.54 | 0.31 | 0.18 | 0.12 |
|                | after RTFOT | 5.65 | 2.63 | 1.43 | 0.68 | 0.54 | 0.31 |
|                | $\delta$(°) | Before aging | 82.9 | 84.6 | 86.1 | 87.4 | 88.1 | 89.2 |
|                | after RTFOT | 79.1 | 82.4 | 83.6 | 84.1 | 85.3 | 86.8 |
|                | $G^*/\sin\delta$(kPa) | Before aging | 1.51 | 0.66 | 0.36 | 0.21 | 0.18 | 0.12 |
|                | after RTFOT | 4.09 | 1.83 | 0.98 | 0.46 | 0.36 | 0.35 |
| Modified room temperature biological asphalt | G*(kPa) | Before aging | 43.38 | 22.98 | 10.08 | 4.78 | 2.77 | 1.45 |
|                | after RTFOT | 47.49 | 29.26 | 18.37 | 7.82 | 3.48 | 2.04 |
|                | $\delta$(°) | Before aging | 59.6 | 62.2 | 66.2 | 70.5 | 72.1 | 72.7 |
|                | after RTFOT | 56.8 | 58.4 | 61.7 | 64.1 | 68.6 | 69.5 |
|                | $G^*/\sin\delta$(kPa) | Before aging | 41.71 | 21.17 | 8.73 | 3.89 | 2.20 | 1.52 |
|                | after RTFOT | 47.90 | 28.71 | 17.06 | 6.99 | 2.91 | 2.18 |

It can be seen from the test results that the complex shear modulus of 70# matrix asphalt has been significantly improved after aging. This is because the oil in the asphalt underwent a series of irreversible reactions under the action of hot oxygen in the rotating film oven, and gradually transformed into asphaltenes, thereby increasing the complex shear modulus of the asphalt. The complex shear modulus of the modified room temperature biological asphalt after aging in the rotating film oven has also been greatly improved. On the one hand is due to the biological matrix asphalt in asphalt modification temperature component changed. On the other hand, under the action of high temperature, the fluidity of components in the modified normal temperature biologic bitumen increased, and the specific surface area of the fatty acid in the asphalt and the unreacted curing agent increased, so that the curing agent could continue to react with the fatty acid, thus greatly improving the complex shear modulus of the modified normal temperature biologic bitumen. Comparing the two asphalts, it is found that the complex shear modulus of the modified room temperature biological asphalt is much greater than that of the matrix asphalt. This is because the curing agent reacted with fatty acids to form fatty acid calcium, which was more stable under high temperature conditions. At the same time, it was added with waste rubber powder to form a better high temperature performance.
The phase angles of 70# matrix asphalt and modified room temperature biological asphalt have been reduced after aging in the rotating film oven, and the reasons are the same as above. And due to the addition of waste rubber powder, there were more elastic components in the modified room temperature biological asphalt, making the phase angle of the modified room temperature biological asphalt generally smaller than the phase angle of 70# asphalt, and it has better resistance ability to deformation under high temperature conditions.

Rutting factor \((G^*/\sin\delta)\) can characterize the ability of asphalt mixture to resist permanent deformation under high temperature conditions. The larger the rutting factor, the better the anti-rutting ability of the asphalt mixture. The SHRP plan uses 58°C to 94°C as the temperature range, and PG grades the asphalt every 6°C. It stipulates that the rutting factor of the asphalt without aging in the rotating film oven at a certain temperature should be no less than 1.0kPa, and the asphalt after aging in the rotating film oven should be no less than 2.2kPa. The asphalt should be classified by PG at a temperature exceeding the required maximum. According to the test results, the PG classification of 70# matrix asphalt obtained according to this classification standard is PG58, and the PG classification of modified normal temperature biological asphalt is PG82.

3.2 The Rheological Property of Low Temperature Bending Beam

In this paper, a low-temperature bending beam rheometer (BBR) is used to evaluate the low-temperature performance of asphalt. The low-temperature bending beam rheological test is also proposed by the US SHRP program. The creep rate \(m\) and the creep stiffness \(S\) obtained through the bending beam rheological test are Indexes to evaluate the low temperature performance of asphalt, the test results are shown in Figure 1.

According to the requirements of the specification, the creep stiffness \(S\) of the BBR test specimens should be less than 300Mpa and the creep rate \(m\) should be greater than 0.3 after a load of 60s to be qualified. Among them, the stiffness modulus \(S\) characterizes the resistance to constant load of the asphalt, and the creep rate \(m\) characterizes the stress relaxation performance of the asphalt. The smaller the \(S\) and the larger the \(m\), the better the low-temperature crack resistance of the asphalt. It can be seen from the test results that the creep rate and creep stiffness modulus of 70# matrix asphalt were unqualified under the condition of -24°C. When the modified room temperature biological asphalt mixture was under the condition of -24°C, the modulus of creep stiffness was qualified but the creep rate was not qualified. Existing studies have shown that oil-based bio-asphalt generally has good low-temperature performance. However, since the solidified product in this study is fatty acid calcium, which is a hard salt, it degrades the low-temperature performance of asphalt to a certain extent. Compared with ordinary 70# petroleum asphalt, the low temperature performance of modified room temperature biological asphalt has not been significantly improved. However, the modified room
temperature biological asphalt has a smaller creep stiffness and a larger creep rate under low temperature conditions. Its cracking possibility under low temperature conditions is less.

3.3 Scanning Electron Microscope Analysis

Scanning electron microscope (SEM) is to pass an electron beam through the sample and amplify the electrical signal generated by the interaction of the two to generate the surface topography image. In this study, scanning electron microscopy was used to analyze the surface morphology of the asphalt section, so as to determine the product produced after the solidification of the modified room temperature biological asphalt, and to determine the strength formation mechanism of the asphalt. In this paper, the ZEISS EVO MA10 scanning electron microscope was used to observe the cured modified room temperature biological asphalt at 500 times and 2000 times, respectively, and the results are shown in Figure 2.

![Scanning Image of Scanning Electron Microscope](image)

Figure 2. Scanning Image of Scanning Electron Microscope

It can be seen from Figure 2 (a) that the asphalt surface is smooth and flat, indicating that the vegetable asphalt and unsaturated fatty acids are evenly dispersed and stable in the asphalt. The filaments in the figure are crosslinked by the fatty acid calcium generated by the reaction of fatty acid and calcium hydroxide. The column or network structure of calcium fatty acid crosslinked with each other is embedded in the asphalt, forming a bridge or network connection in the asphalt, these structures play a role of encapsulation and reinforcement in the asphalt, providing strength for the modification of normal temperature biological asphalt.

As can be seen from Figure 2 (b), because the sample made by the test was pulled by external force, the deformation caused by resistance to external force could be seen from the joint of asphalt and fatty acid calcium. The particles of waste rubber powder expand in bitumen fatty acid, forming granular structure on the surface of bitumen fatty acid, and resist external force jointly through the interaction of waste rubber powder itself, providing toughness for the modification of normal temperature biological asphalt.

4. Conclusion

This paper mainly uses DSR, BBR and SEM to study the rheological and micro-properties of the modified room temperature biological asphalt. The main conclusions are as follows:

(1) After the rheological performance test of the modified room temperature biological asphalt, its PG classification was improved to PG82-28 compared with the PG58-28 of 70# matrix asphalt;

(2) Hard fatty acid salt has significantly improved the high temperature performance of asphalt, and also caused an adverse effect on the low temperature performance of asphalt. However, because the
oil-based bio-asphalt itself has good low temperature performance and added waste rubber powder, its low temperature performance has been balanced to a certain extent;

(3) The microstructure of the modified room temperature biological asphalt shows that the fatty acid calcium forms a bridge-like reinforcement structure between the asphalt molecules to improve the high temperature performance of the asphalt, while the waste rubber powder particles wrap the asphalt and fatty acid calcium to improve the toughness of the asphalt.

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