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Performance evaluation and modification mechanism analysis of asphalt binders modified by graphene oxide

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HIGHLIGHTS

- GO enhanced the rutting resistance of non-modified and SBS modified binders.
- GO has no significant effect on the low-temperature property of binders but increases their crosslinking degree.
- The optimal GO contents of non-modified binder and SBS modified binder are different.
- The modification mechanisms of GO to non-modified and SBS modified binders are different.

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ABSTRACT

This work presents a laboratory study conducted to evaluate the potential impacts of different graphene oxide (GO) dosages on properties of non-modified binder and SBS modified binder. The effects of GO on viscosity, rheological properties, creep and recovery behavior, cracking resistance, and thermal properties of unaged/RTFO aged binders were characterized respectively. It was demonstrated that the addition of trace amounts of GO (no more than 0.2 wt%) enhanced the paving temperature (120–135 °C) viscosity, high-temperature elasticity and rutting resistance of non-modified/SBS modified binders. The performance improvements were attributed to an increase in the crosslinking degree of the binders induced by the GO. The amount of GO needed to improve the high-temperature performance of the non-modified binder is smaller than that needed for the SBS modified binder. The modification mechanism of GO to non-modified binder includes both chemical reactions and physical blending, whereas it only entails physical blending in the case of SBS modified binder.

1. Introduction

Nano-modification of asphalt binder has exhibited outstanding potential in meeting the needs of pavement industry, but emerging carbon-based nanomaterials have yet to be studied in depth for their possible impacts on asphalt binder, mortar, or concrete. In China and other countries, the increasing number of heavy traffic and the complex climate types make the road users demand increasingly more of road performance [1,2]. Modified asphalt binders are increasingly used in high-grade highways, and the study of new asphalt modifiers has attracted great attention [2–5]. In the past decade, using nanomaterials (e.g., nanoclays, nano-zinc oxide, nano-titanium dioxide and nanosilica) to modify asphalt binder is of great interest because it greatly enhanced the mechanical performance and durability of asphalt binder [6–10]. However, asphalt compositions are so complicated and composed of many organic molecules, which can react with various types of modifiers. Therefore, it is desirable to study the modification effect and mechanism of different types of nanomaterials on asphalt.

Compared with other nanomaterials, graphene oxide (GO) features unique quasi two-dimensional layered structure with layer spacing of 0.7–1.2 nm. With the increase in the interlayer spacing, the Van der Waals force between layers is reduced, and GO can be readily dispersed in the aqueous solution or organic solvent to form a homogeneous monolayer GO suspension after proper ultrasonic shock treatment [11,12]. In addition, the surface of GO contains a large number of polar oxygen-containing groups such as carboxylic group, hydroxyl group, epoxy group and ester group [13]. Theses functional groups make GO reactive and compatible with many polymer matrices. Thus, GO has been used to modify epoxy resin, methylmethacrylate, and butadiene-styrene-vinyl pyridine rubber to improve their thermal performances, mechanical properties or tensile strengths [14–16]. However, few studies

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have investigated the GO modified asphalt [17,18], and they only focused on the macroscopic performance of GO modified asphalt binder. There is a lack of study on the modification mechanisms of GO on asphalt binder, which is critical for the design and selection of GO with appropriate functional groups to modify asphalt.

In this study, different dosages of GO were blended with a non-modified asphalt binder and a SBS modified asphalt binder, respectively. The mechanical performance, modification mechanism, and thermal property of GO modified asphalt binders were investigated to shed light on the effects of GO on the asphalt binder performance. The results can lay the foundation for further research and application of GO in asphalt binders.

2. Materials and experiments

2.1. Materials

The control asphalt binders with performance grade (PG) 64-22 and PG 58-34 were used. The PG 64-22 asphalt binder is non-modified and referenced as A0, its physical and chemical properties are shown in Table 1 and Fig. 1(a). The PG 58-34 asphalt binder is modified by poly(styrene-butadiene-styrene) or SBS and referenced as B0, its physical and chemical properties are shown in Table 1 and Fig. 1(b). As shown in Table 1, the physical properties of control asphalt binder A0 and B0 are in accordance with the requirements of PG64-22 and PG58-34, respectively. Compared with asphalt A0, the Fourier transform infrared (FTIR) spectrum of asphalt B0 exhibits two new peaks at 699 cm^{-1} and 966 cm^{-1}, which represent the functional groups of styrene and butadiene, respectively [19].

The GO was produced from 325 mesh flake graphite following the Hummers method in laboratory [12,20], featuring an extremely high specific surface area (~2600 $m^2 g^{-1}$). The GO used in this work features a zeta potential of −30 mV in the neutral aqueous solution, due to the presence of negatively charged groups on this nano-sized material [21]. The FTIR spectrum of the GO sample (shown in Fig. 1(c)) matched well with the work conducted by Sudesh et al. [22]. The strong peak at 3436.92 cm^{-1} is attributed to the O—H stretching vibration in hydroxyl. The peak at 2928.06 cm^{-1} corresponds to the typical C—H stretching vibration in carboxyl. The small peaks between 1100 cm^{-1} and 1400 cm^{-1} indicate the typical C—O vibrations of epoxide. The C=O bond in ketonic species vibration is observed at 1624.35 cm^{-1}, and the peak at 2352.83 cm^{-1} is ascribed to the CO_2 (O=C=O) vibration [23].

2.2. Sample preparation

The GO modified asphalt binders were prepared by a high speed shear mixer to achieve homogenous dispersion of the GO in asphalt binders. Based on the viscosity characteristics of the two kinds of control asphalt binders, GO modified asphalt binders were prepared at the control asphalt's mixing temperature (i.e., viscosity range 0.15–0.19 Pa·s). The preparation process of GO modified asphalt is illustrated by a flowchart as shown in Fig. 2. The produced GO modified asphalt binders were used in the following tests. To simplify the analysis, the GO modified PG 64-22 asphalt binder with different GO dosages are referenced to as A0, A0.02, A0.05, A0.1, A0.2 and A1, respectively and the PG 58-34 SBS modified asphalt binder B were named in the same way.

In order to compare the properties of studied binders under different aging conditions, the rolling thin film oven (RTFO) test and pressure aging vessel (PAV) test were conducted, to simulate the effect of construction aging and in-service aging, respectively.

2.3. Experimental

2.3.1. Rotational viscosity (RV) test

Viscosity is an important index to evaluate the workability and high-temperature performance of asphalt binder [24], because the flow state of asphalt at 100–200 °C has practical significance related to the quality control of production, storage, transportation, and construction of asphalt binders. The viscosity of each binder was measured at 120 °C, 135 °C, 150 °C, and 165 °C, following the AASHTO T316-13 method [25].

2.3.2. Rheological performance test

The dynamic shear rheometer (DSR) test was conducted to evaluate the rheological performance of the unaged and RTFO aged control asphalt binders and the GO modified asphalt binders. The SHRP grade determination tests were conducted following the AASHTO T315-12 method [26]. The 25-mm in diameter plates and 1-mm gap were used for both unaged and RTFO aged asphalt binders. The test starts from the high PG temperature grade and increases every six degree celsius until the values of the $G^*/sin\delta$ for the unaged and RTFO aged binders are lower than 1.0 kPa and 2.2 kPa, respectively. The rutting parameter ($G^*/sin\delta$) and failure temperature (T) are reported to quantify the rheological properties of the GO modified asphalt binders. Subsequently, the optimal dosages of GO were determined based on the rheological properties of GO-modified asphalt binders.

2.3.3. Multiple stress creep recovery (MSCR) test

The MSCR test, considered as a PG Plus test, has been recently adopted by more agencies to evaluate the rutting resistance of polymer modified asphalt binders [27,28]. It is known to provide insights beyond what the RV or DSR test provides. As such, the rutting resistance of the GO modified asphalt binders were evaluated by the MSCR test following the AASHTO T350-14 method [29]. The MSCR test was conducted on the RTFO aged binders at the stress levels of 0.1 kPa and 3.2 kPa, respectively [3]. The test temperature for binder group A and B was 64 °C, and 58 °C, respectively. The MSCR test was conducted at a constant stress creep of 1.0 s duration followed by a zero stress recovery of 9.0 s duration, run 20 cycles at the 0.1 kPa stress level followed by 10 cycles at the 3.2 kPa stress level, for a total of 30 cycles. The average percent recovery (R) and non-recoverable creep compliance (Jnr) values were used to evaluate the rutting resistance of the studied GO modified asphalt binders.

2.3.4. Bending beam rheometer (BBR) test

The BBR test was conducted to characterize the risk of low-temperature cracking of GO modified asphalt binders following the AASHTO T313-12 method [30]. The BBR test was conducted on the PAV aged samples. The test temperatures of binder group A were −12 °C and −18 °C, and the test temperatures of binder group B were −24 °C and −30 °C, respectively. And then the creep stiffness (S) and rate of relaxation (m-value) of samples were determined.

Based on the rheological performance, MSCR and BBR results, the optimum dosage of GO for the two control asphalt binders were determined. The FTIR and differential scanning calorimetry (DSC) tests were conducted only for the GO modified asphalt binders at the optimum dosage to investigate the GO modification mechanisms and their thermal properties, respectively.

2.3.5. FTIR spectroscopy

The FTIR test was conducted to analyze the changes in functional groups between the control asphalt binders and the GO modified asphalt binders to identify the modification mechanisms. The test wavelengths ranged from 400 cm^{-1} to 4000 cm^{-1} with a resolution of 8 cm^{-1}. The binder samples were dissolved with the dichloromethane and stirred with potassium bromide powder until the solvent evaporated completely, then the samples were tested by a FTIR instrument.

2.3.6. DSC test

In order to evaluate the thermal properties of the GO modified asphalt binders, the STAR^e System Instrument (Mettler Toledo Company, United States) was used to conduct the DSC on all binders. Approximately 5–10 mg binder sample was used in the test. The range of the testing temperature was from −60 to 50 °C, and the heating rate was 5 °C/min under a nitrogen atmosphere. Five specimens of each asphalt binder were measured to ensure reliability of the DSC results. Two parameters, glass transition temperature T_g and endothermic energy value Δcp, were used to quantify the thermal properties of the GO modified asphalt binders. An example of DSC result of the asphalt binder A0 is shown in Fig. 3.

Table 2 summarizes the tests conducted on the various asphalt binder samples in this study.

3. Results and discussion

3.1. Viscosity-temperature performance

Fig. 4 presents the changes of viscosity of GO modified asphalt binders at different dosages and temperatures, based on the RV

Table 1
Physical properties of two control asphalt binders.

Asphalt type	$G^*/sin\delta$ (unaged, kPa)	$G^*/sin\delta$ (RTFO unaged, kPa)	Creep stiffness S (MPa)	Rate of relaxation m
A0 (PG 64-22)	1.23 (64 °C)	2.63 (64 °C)	185.2 (−12 °C)	0.309 (−12 °C)
B0 (PG 58-34)	1.27 (58 °C)	2.63 (58 °C)	238.4 (−24 °C)	0.303 (−24 °C)