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**Research paper** 

# Evaluation of different functionalized multi-walled carbon nanotubes (MWCNTs) modified asphalts

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Abstract: To improve the aging resistance and prolong the service life of asphalt pavement, this study utilized modified multi-walled carbon nanotubes (MWCNTs) functionalized with carboxyl (MWCNTs-COOH), hydroxyl (MWCNTs-OH), and amino (MWCNTs-NH<sub>2</sub>) groups. These nanotubes were incorporated into SBS-modified asphalt at a concentration of 1%. The study sought to examine the impact of MWCNTs and their functional groups on asphalt's rheological and anti-aging characteristics, alongside exploring their modification mechanisms. The findings indicated that rheological tests showed that MWCNTs/SBS composite-modified asphalt, particularly MWCNTs-OH/SBS, exhibited remarkable resistance to hightemperature deformation, a crucial characteristic for asphalt performance in hot climates. Nevertheless, it is important to note that the addition of MWCNTs led to an increase in asphalt's creep strength and creep rate, which could potentially reduce its resistance to low-temperature cracking. However, the covalent functionalization of MWCNTs mitigated these adverse effects on low-temperature performance. Moreover, the inclusion of MWCNTs in asphalt served as a barrier, impeding the penetration of oxygen molecules and ultraviolet radiation into the asphalt matrix. This proved to be an effective means of inhibiting the aging process, a critical factor in extending the service life of asphalt pavement. Among the different formulations of MWCNTs modified asphalt, the MWCNTs-OH/SBS composite-modified asphalt exhibited notably effective anti-aging properties. Both rheological and anti-aging evaluations demonstrated that hydroxyl functional groups played a pivotal role in enhancing performance, chiefly by fostering interactions with asphalt molecules.

**Keywords:** modified asphalt, multi-walled carbon nanotubes, high and low temperature characteristics, fatigue properties, anti-aging performance

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## **1. Introduction**

Asphalt pavements are subject to repetitive loading and environmental stresses. The growth in road traffic volume, driven by socioeconomic expansion, places substantial demands on the performance of asphalt surfaces [1]. To address the escalating demands imposed by varying traffic loads, primary strategies include augmenting asphalt performance through the introduction of modifiers, natural asphalt, and mineral fillers [2, 3]. Polymer-modified asphalt surpasses conventional matrix asphalt in terms of performance across a wide temperature range and fatigue resistance [4]. However, achieving improved performance is not solely contingent on augmenting the quantity of polymer modifiers, as challenges like compatibility issues and storage stability often arise [5, 6]. The adoption of composite modified asphalt has effectively overcome these limitations, prompting researchers to explore composite-modified materials progressively [7].

In recent years, advances in science and technology have increased our understanding of composite-modified materials. Inorganic nanomaterial modifiers, distinct from traditional additives, have the capacity to alter asphalt's microstructure and enhance its nanoscale performance [8,9]. Carbon nanotubes (CNTs), remarkable inorganic nanostructures, exhibit a high modulus, exceptional strength, flexibility, and excellent electrical and thermal conductivity. When integrated with polymers, CNTs significantly enhance the interfacial strength and toughness of composites [10]. CNTs, whether single-walled (SWCNTs) or multi-walled (MWCNTs), have unique characteristics that contribute to their effectiveness. MWCNTs, in particular, with their multilayer structure, offer superior electron acceptor properties, reduced charge recombination, and enhanced resistance to aggregation, making them especially effective in enhancing molecule solubility [11, 12]. MWCNTs have found applications in various fields, including asphalt binders, owing to these attributes. Previous research has established that MWCNTs significantly extend the fatigue life and durability of asphalt. This enhancement is attributed to the potent intermolecular forces resulting from the intricate interaction between MWCNTs and asphalt, leading to improved thermal stability and SBS dispersion [13, 14]. Nevertheless, multi-walled carbon nanotubes (MWCNTs) tend to form intricate aggregates and exhibit limited interfacial interaction with the polymer matrix, leading to their pronounced agglomeration within SBS modified asphalt [15]. To address this challenge, researchers devised a method for introducing polar functional groups onto MWCNTs, which were subsequently covalently bonded to the matrix polymer molecules or intermediate layer molecules, creating a MWCNTs-polymer composite system. This process enhances its chemical compatibility with other polymers [16, 17].

In conclusion, the integration of MWCNTs into asphalt demonstrates a substantial impact on enhancing high-temperature stability and aging resistance. However, further research exploring the influence of various functionalized MWCNTs on asphalt performance, especially in terms of aging resistance, is warranted. This study, which combined four distinct types of MWCNTs with Styrene-Butadiene-Styrene (SBS) and employed various aging techniques, serves as a guide for the judicious selection of MWCNTs modifiers and offers a theoretical foundation for their broader utilization in asphalt pavement.

## 2. Materials and experimental methods

## 2.1. Materials

High-viscosity SBS modified asphalt made by a Hunan business was the asphalt utilized in the test. The ultra-pure multi-walled carbon nanotube powder made by a new material technology company (Co., Ltd.) in Jiangsu Province was used to select MWCNTs. Tables 1 and 2 display the primary technical indications of SBS modified asphalt and MWCNTs, respectively.

Performance	Measured	RTFOT	PAV	UV	Test methods
Softening point/°	58.7	61.8	70.5	66.4	T0606-2011
Penetration (25°)/mm	53.2	45.5	38.3	42.8	T0605-2011
Ductility (25°)/cm	31.5	22.7	14.6	19.4	T0604-2011
Viscosity (135° Brookfiled)/Pa.s	1.74	2.23	3.04	2.68	T0625-2011

Table 1. Main technical indexes of SBS modified asphalt

Table 2. Main technical indexes of MWCNTs

Technology Index	Purity	Outside diameter, (nm)	Specific surface area, (m <sup>2</sup> /g)	Resistivity, (uΩ · m)	Tube Length, (um)	Tap Density
MWCNTs	>99%	7–11	220-300	<1000	5–15	0.1 g/cm <sup>3</sup>

### 2.2. Preparation of functionalized MWCNTs

The highly pure powder of multi-walled carbon nanotubes (MWCNTs) was procured from a specialized materials technology company located in Jiangsu Province. The study employed three distinct types of functionalized MWCNTs, including carboxyl-functionalized MWCNTs (MWCNTs-COOH), hydroxyl-functionalized MWCNTs (MWCNTs-OH), and aminofunctionalized MWCNTs (MWCNTs-NH2). An oxidation treatment process was employed to graft carboxyl groups onto the surface of MWCNTs and eliminate impurities. In summary, one gram of pristine MWCNTs was immersed in a 400-gram solution of HNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> (in a 1:3 volume ratio) and subjected to one hour of sonication. The resulting suspension was then refluxed in a water bath at 80°C for 12 hours, followed by dilution with deionized (DI) water and filtration through a 0.4 µm membrane. The purified MWCNTs-COOH were rinsed with DI water at least three times to achieve a neutral pH and subsequently dried in a vacuum oven at 40°C overnight. For the hydroxylation of MWCNTs (MWCNTs-OH), two grams of pristine MWCNTs were dispersed in a 100 mL aqueous solution of potassium hydroxide (2.0 mol/L). Following one hour of ultrasonic treatment, the suspension was transferred to the polytetrafluoroethylene liner of a stainless-steel reaction autoclave and heated at 180°C for two hours. The purification of MWCNTs-OH followed the procedure mentioned earlier. To synthesize amino-functionalized MWCNTs (MWCNTs-NH<sub>2</sub>), carboxyl groups from MWCNTs-COOH

were converted into acyl chloride groups through a reaction with thionyl chloride (SOCl<sub>2</sub>), followed by a subsequent reaction with diamine. The preparation of MWCNTs-NH<sub>2</sub> entailed refluxing one gram of MWCNTs-COOH with SOCl<sub>2</sub> at 60°C for 12 hours [18].

#### 2.3. Preparation of MWCNTs / SBS composite modified asphalt

In this study, all asphalt samples were prepared using a high-speed shear mixer, the Shanghai Frank Company FM300, through a melt-mixing process. Previous research has indicated that more than 1% (mass fraction) of MWCNTs will form agglomeration in asphalt and can significantly improve the performance of asphalt [11,19]. Therefore, this study adopts a unified content of 1%, modified asphalt preparation engineering from previous research [20]. During the experiment, the asphalt was heated until it reached a molten state, following the pre-drying of MWCNTs powder in a vacuum oven. A 1% mass fraction of MWCNTs was subjected to low-speed shearing (4000 rad/min) for 30 minutes while being gently mixed at a temperature of 175°C. After achieving uniform dispersion within the asphalt, high-speed shearing (6000 rad/min) was employed for an additional 30 minutes to establish a stable structure. Similar procedures were followed for the preparation of other SBS composite modified asphalt, MWCNTs/SBS composite modified asphalt, MWCNTs-OH/SBS composite modified asphalt, and MWCNTs-COOH/SBS composite modified asphalt.

### 2.4. Asphalt aging indoor simulation method

In this study, three distinct aging modes were employed to investigate and assess the anti-aging properties of modified asphalt. To replicate short-term aging processes in asphalt samples, the RTFOT test (T 0610-2011) was conducted. Additionally, the PAV test (T 0630-2011) was used to simulate the thermo-oxidative aging conditions experienced by asphalt after prolonged use. To recreate the photo-oxidative aging environment encountered by asphalt samples over an extended duration, a UV aging chamber was equipped with six UVA340 ultraviolet lamp tubes, each measuring 600 mm in length, serving as the light source. Finally, the asphalt samples were subjected to an ultraviolet aging temperature of  $60^{\circ}$ C for a duration of 10 days, considering that typical pavement temperatures in the summer reach  $60^{\circ}$ C.

## 3. Test results and discussion

### 3.1. Thermal storage stability

This research aimed to evaluate the storage stability of MWCNTs/SBS composite-modified asphalt using the segregation test method specified in T0661 of the JTG E20-2011 standard. The procedure involved hermetically sealing the modified asphalt samples in aluminum tubes and subjecting them to a 48-hour heating cycle at 163°C in an oven. Each sample was evenly divided into

three sections, with softening points measured for both the upper and lower sections. Storage stability was quantified using the softening point difference index, which represents the difference between the softening points of the lower and upper sections. Enhanced storage stability in MWCNTs/SBS composite-modified asphalt is indicated by a smaller difference in softening points.

The softening point difference of different modified asphalts is shown in Fig. 1. The results indicate that the inclusion of all four types of MWCNTs enhances the storage stability of SBS-modified asphalt. Notably, OMA exhibits the most significant improvement, with a reduction of nearly 1°C. The mechanism behind MWCNTs enhancing the stability of SBS-modified asphalt lies in their ability to create a stable cross-linked network structure when combined with SBS-modified asphalt. This network substantially boosts the interaction between SBS and asphalt, thereby mitigating the propensity for phase separation.



Fig. 1. Thermal storage stability of different modified asphalt

### 3.2. Analysis of modification mechanism

The Nicolet IS50 Fourier transform infrared spectrometer (FTIR) was used in this investigation to investigate the mechanisms involved in asphalt modification using both pristine MWCNTs and their functionalized samples. The scanning range was 400 to 4000 cm<sup>-1</sup>.

Figure 2 demonstrates a consistent pattern across all modified asphalt samples, with peak absorbance occurring at the same wavenumber for SBS, MA, NMA, OMA, and CMA. Identification of the corresponding functional groups for these absorbance peaks is facilitated by comparing them to the infrared spectra of known compounds. These functional groups primarily encompass four categories: C-H aliphatic at 2921 cm<sup>-1</sup>, C-H aliphatic of CH<sub>2</sub> at 1369 cm<sup>-1</sup>, C-H aliphatic of CH<sub>2</sub> at 1456 cm<sup>-1</sup>, and C=C aromatic at 1600 cm<sup>-1</sup>. The constancy of the asphalt absorbance peak suggests the absence of new functional group formation. Consequently, no chemical reaction takes place between the MWCNTs samples and the SBS modified asphalt; their interaction is purely through physical mixing. The observed change is a shift in absorption

peak intensity, with no emergence of new absorption peaks. This stability in the asphalt can be attributed to the inorganic nature of both MWCNTs and each functionalized sample. Upon incorporation into the asphalt, they effectively absorb all incident light, faint peak in the spectrum [21]. The primary enhancement in the mechanical properties of asphalt through MWCNTs/SBS composite modified asphalt results from their physical combination [22].



Fig. 2. FTIR spectra of different asphalt samples

### 3.3. Analysis of asphalt performance before and after modification.

#### 3.3.1. Temperature scanning test

According to the test method of T0628-2011 in JTGE20-2011, the temperature sweep method was used and the temperature test range was 30–70°C. The temperature sweeping results are displayed in Fig. 3.

Figure 3 visually demonstrates the influence of temperature on the rutting factor  $G^*/\sin \delta$  for each asphalt sample. As temperature increases, the  $G^*/\sin \delta$  value exhibits a consistent decrease, indicating that elevated temperatures lead to a decline in asphalt's resistance to rutting. Notably, MWCNTs/SBS composite modified asphalt with various functional groups exhibits a superior rutting factor compared to SBS modified asphalt at equivalent temperatures. Specifically, the  $G^*/\sin \delta$  values follow this order: OMA > CMA > MA > NMA > SBS.

The introduction of MWCNTs fosters crosslinking with SBS, resulting in a more compact network structure. This interaction enhances the binding energy between molecules in asphalt and the SBS polymer, bolstering the stability of SBS modified asphalt and its resistance to high-temperature shear eformation. Furthermore, the presence of interlayer pores in MWCNTs allows for the embedding of asphalt molecules, expanding the interlayer and increasing



Fig. 3. Rutting factor-temperature diagram of different asphalt samples

the likelihood of asphalt molecule embedding. This results in a mosaic-like structure that impedes the mobility of asphalt molecules and fortifies the modified asphalt's resistance to deformation [14]. MWCNTs-OH exhibit the most robust interaction with the asphalt binder. This heightened interaction is attributed to the stronger polarity of the hydroxyl functional group, leading to a larger dipole moment between the polar functional group and the polar asphalt molecule, surpassing that of carboxyl and amino groups [23]. Enhanced molecular polarity not only improves the crosslinking effect between SBS and asphalt but also reduces the polarity disparity between them. An increase in carboxyl content enhances the crosslinking network structure in asphalt by forming additional chemical linkages involving nitrogen, sulfur, and other heteroatoms [24]. As a result, MWCNTs-OH prove effective in enhancing the high-temperature performance of SBS modified asphalt.

#### 3.3.2. Bending beam rheometer test (BBR)

To evaluate the low-temperature performance of MWCNTs/SBS composite modified asphalt samples with diverse functional groups, we conducted the BBR test. The test was conducted at a temperature of  $60^{\circ}$ C for 200 total seconds. This test assesses asphalt's ability to relax under load and resist deformation at low temperatures, quantified through *S* and *m*. The experimental findings are presented graphically in Fig. 4 and Fig. 5.

Figure 4 and Figure 5 demonstrate that at test temperatures of 12°C and 18°C, S and m values of each asphalt sample conform to the established standards. However, the inclusion of unfunctionalized MWCNTs leads to an increase in S of SBS modified asphalt, rendering it more brittle and rigid. This has a marginal adverse impact on the low-temperature performance of SBS modified asphalt, with the effect remaining relatively modest. The adoption of functionalized MWCNTs presents an opportunity to enhance the low-temperature performance of SBS modified asphalt. Notably, at a test temperature of 12°C, NMA, OMA, and CMA exhibit S

values increased by 30.7%, 23.8%, and 27.9%, respectively, relative to SBS modified asphalt, with concurrent increases in m values of 16%, 6.1%, and 7%, respectively. Furthermore, when compared to SBS modified asphalt, at a test temperature of  $-18^{\circ}$ C, NMA, OMA, and CMA demonstrate S values increased by 37.5%, 28.6%, and 34.2%, respectively, along with m values increased by 19.6%, 10%, and 13.4%, respectively.

Functionalization results in an augmented presence of surface-active sites and wall flaws in MWCNTs. This, in turn, enhances the compatibility between SBS and MWCNTs, as well as the dispersion of MWCNTs within the asphalt matrix. Among these functional groups, the amino group exhibits the highest reactivity due to its enhanced reactivity [25]. Consequently, MWCNTs-NH<sub>2</sub> prove particularly advantageous in improving the low-temperature fracture resistance of SBS modified asphalt.



#### **3.3.3.** Multi-stress creep recovery test (MSCR)

To more accurately evaluate the high-temperature rutting resistance of composite modified asphalt, we conducted the MSCR test on samples of SBS modified asphalt and four distinct groups of MWCNTs/SBS composite modified asphalt. This assessment utilized the average creep recovery rate (R) and the average irrecoverable creep compliance ( $J_{nr}$ ) to gauge the viscoelastic properties and resistance to permanent deformation (rutting) of the asphalt binder at a test temperature of 60°C. Fig. 6 visually presents the experimental outcomes.



Fig. 6. Average R value and  $J_{nr}$  value of different asphalt samples. (a) 100 Pa, (b) 3200 Pa

As depicted in Fig. 6, the addition of various types of MWCNTs to SBS asphalt binder under stress levels of 100 Pa and 3200 Pa results in an increase in the R value and a decrease in the Jnr value. However, the test results for each modified asphalt under a stress of 100 Pa exhibit greater variability. This underscores how the incorporation of MWCNTs consistently infiltrates the structure of SBS modified asphalt, enhancing the elasticity of the MWCNTs/SBS composite modified asphalt, and reducing the irreversible deformation of asphalt under load. Among these modifications, MWCNTs-OH exerts the most substantial enhancement on SBS modified asphalt. Its mechanism of improvement can be elucidated as follows: SBS modified asphalt contains a higher proportion of lighter components. The adsorption layer of the micelles undergoes thinning when subjected to temperature or mechanical stress, causing the light components to relax the colloidal structure. Incorporating and dispersing MWCNTs enables the establishment of a cross-linked solid network and efficacious prevention of colloidal structure breakdown, consequently augmenting the flexibility of the asphalt binder [26]. The hydroxyl group exhibits the highest molecular polarity, yielding the most effective cross-linking enhancement within the asphalt network.

#### 3.4. Linear amplitude scanning test (LAS)

To gauge the fatigue resistance of MWCNTs/SBS composite modified asphalt samples incorporating various functional groups, we employed the LAS test within a DSR test. As specified by AASHTOTP-101-14, the test was conducted at a temperature of 25°C,



employing an 8mm shock plate fixture with a 2mm spacing [27]. The resulting data, including the stress-strain curve, fatigue damage curve, and fatigue life diagram, are depicted in Figs. 7–9.

Fig. 8. Damage characteristic curves

Figure 8 depicts the stress-strain curves of SBS modified asphalt and four sets of MWCNTs in the LAS test. Across all five asphalt sets, a consistent stress-strain behavior emerges during linear amplitude scanning, marked by the presence of a distinct shear stress peak. Notably, MA, NMA, OMA, and CMA modified asphalt display substantial increases of 35.1%, 17.7%, 61.9%, and 39.3%, respectively, in peak stress compared to SBS modified asphalt.

The VECD model allows us to assess two critical factors influencing asphalt fatigue resistance: cumulative fatigue damage strength (D) and material integrity (C). Figure 8 presents the doping curve for MWCNTs in relation to asphalt damage characteristics, showcasing four distinct doping scenarios. When comparing the damage characteristic curves of the five asphalt

groups, it becomes evident that the damage characteristic curve of SBS modified asphalt experiences rapid decay. Conversely, the characteristic damage curve of each MWCNTs/SBS modified asphalt exhibits a more gradual attenuation after the introduction of various MWCNTs types. Notably, the maximal D follows the order OMA > CMA > MA > NMA > SBS. The incorporation of MWCNTs significantly enhances the fatigue damage resistance of SBS modified asphalt, with MWCNTs-OH/SBS composite demonstrating the most exceptional fatigue performance.

Figure 9 illustrates how the inclusion of various MWCNTs can extend the fatigue life of SBS treated asphalt. Among these, MWCNTs-OH exerts the most substantial influence on the anti-fatigue performance of SBS modified asphalt, resulting in a 114% longer fatigue life compared to pure SBS modified asphalt. This enhancement can be attributed to the unique interlayer pores of MWCNTs, which enable the entrapment of SBS modified asphalt molecules and the formation of a distinctive mosaic structure. This, in turn, fortifies the network structure created by MWCNTs and SBS modified asphalt, intensifying the crosslinking effect and ultimately improving the asphalt binder's fatigue life. Notably, the hydroxyl functional group, known for its strong polarity, plays a pivotal role in reducing the polarity disparity between SBS and asphalt, consequently bolstering the fatigue resistance of the asphalt.



#### 3.5. Analysis of anti-aging performance of asphalt

In our investigation, we utilized the Rutting Factor Aging Index (RAI) as a metric to scrutinize and evaluate the anti-aging properties of MWCNTs/SBS composite modified asphalt. This analysis relied on data obtained from the DSR temperature scanning experiment, with the formula clearly illustrating the calculation process. It's noteworthy that a lower RAI value signifies improved anti-aging performance and reduced susceptibility to aging effects.

(3.1) 
$$RAI = \frac{(G^*/\sin\delta)_a - (G^*/\sin\delta)_f}{(G^*/\sin\delta)_f}$$

In this formula, a represents after aging, f represents before aging.

Figure 10 and Figure 11 present the RAI values for both SBS modified asphalt and various types of MWCNTs/SBS composite modified asphalt following RTFOT aging and PAV aging. The figures indicate that both MWCNTs and other functionalized MWCNTs contribute to enhancing the aging resistance of asphalt. Figure 10 and Figure 11 depict a substantial reduction in RAI values with the incorporation of MWCNTs, indicating a significant improvement in asphalt's anti-aging performance and a decrease in oxidation and pavement hardness during usage. This enhancement can be primarily attributed to the multi-layer structure of MWCNTs, which retards the volatilization and flow of lightweight asphalt constituents due to geometric constraints. Additionally, it impedes the diffusion of heat and oxygen molecules through the asphalt at elevated temperatures, thereby bolstering the material's resistance to aging. Furthermore, the introduction of functional groups through covalent functionalization enhances MWCNTs dispersion within the asphalt, while the increase in oxygen-containing functional groups decelerates asphalt aging, consequently augmenting the asphalt's antiaging properties [28]. Consequently, MWCNTs-OH exerts a more pronounced influence on enhancing the high-temperature resistance of SBS modified asphalt during RTFOT and PAV.

As depicted in Fig. 12, we subjected various asphalt samples to UV light exposure to emulate the RAI values of asphalt after undergoing ultraviolet aging. The introduction of MWCNTs-NH<sub>2</sub> yielded the most substantial reduction in RAI values, indicating a remarkable enhancement in asphalt's resistance to UV aging. This improved resistance can be attributed, to some extent, to MWCNTs' notable UV absorption capacity and their effective UV dispersion, which is influenced by their size [29]. Following covalent functionalization, MWCNTs exhibit reduced aggregation tendencies and enhanced dispersion within the asphalt matrix, leading to discernible alterations in both interlayer structure and surface area. The natural integration of MWCNTs with asphalt leads to the formation of supplementary intercalation and mosaic



Fig. 10. Short-term aging rutting factor index of different asphalt samples



Fig. 11. Long-term aging rutting factor index of different asphalt samples

structures, effectively impeding the penetration of ultraviolet light. This process bolsters the anti-ultraviolet aging properties of modified asphalt by imparting a distinct reflective function and mitigating the volatilization of light constituents within the asphalt matrix.



Fig. 12. UV aging rutting factor index of different asphalt samples

## 4. Conclusions

This research utilized diverse functionalized multi-walled carbon nanotubes (MWCNTs) to improve SBS modified asphalt. The findings are as follows:

- The incorporation of four MWCNT modifiers augmented the spatial network effect established by the SBS polymer within the asphalt matrix, enhancing the high-temperature performance of MWCNTs/SBS composite modified asphalt. Among these, the addition of MWCNTs-OH notably heightened the temperature sensitivity of SBS modified asphalt. Notably, functionalized MWCNTs improved the low-temperature crack resistance of SBS asphalt when surface-applied.
- The incorporation of the four MWCNTs modifiers led to an enhanced fatigue life of SBS modified asphalt, intensifying the crosslinking interaction between SBS and asphalt. MWCNTs-OH exhibited the most pronounced effect on improving the fatigue life of SBS modified asphalt.
- 3. MWCNTs addition inhibited the diffusion of heat and oxygen molecules within SBS modified asphalt, as well as the scattering of ultraviolet light. Consequently, the composite modified asphalt exhibited a lower rheological property aging index following short-term thermal oxygen aging, long-term thermal oxygen aging, and extended ultraviolet aging, thereby retarding asphalt aging. Notably, MWCNTs-OH/SBS composite modified asphalt outperformed other variants in terms of mechanical properties.

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