

Development and Mechanism Analysis of High Temperature Resistant Nanocomposite Modified Asphalt

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Abstract. With the intensification of global warming, continuous extreme high temperature weather occurs frequently, and asphalt materials are prone to softening under continuous high temperature conditions, which can easily cause traffic accidents. Therefore, it is necessary to develop a high-temperature resistant modified asphalt. This study focuses on the research and development of high-temperature resistant nanocomposite modified asphalt under sustained extreme high temperature weather conditions, selects nanocomposite modification schemes, conducts aging, dynamic shear creep, bending small beam, and segregation tests on nanocomposite modified asphalt, comprehensively analyzes the aging resistance, segregation resistance, and high and low temperature performance of nanocomposite modified asphalt, and analyzes the mechanism of nanocomposite modified asphalt from the perspective of molecular dynamics. The research results indicate that the nano/polymer composite modification scheme for sustained extreme high temperature areas is: 3% ZnO+0.5% TiO₂+3.5% SBS; The aging resistance and high temperature resistance of nanocomposite modified asphalt are obviously better than that of base asphalt; At a temperature of 413K (160°C), a more stable structure can be formed between asphalt and SBS. At a temperature of around 140°C, each interaction can reach its maximum value, and the modification effect is good.

Keywords: High temperature resistance; Nanomaterials; Modified asphalt; Molecular dynamics.

1. Introduction

High temperatures can cause diseases such as rutting and hugging on asphalt pavement, and extreme and sustained high temperatures can exacerbate and develop rapidly[1,2]. Improving the performance of asphalt materials through modifiers can effectively overcome the shortcomings of ordinary asphalt, improve its high-temperature resistance under extreme conditions, and solve various diseases of asphalt pavement[3-5].

Nanotechnology has developed rapidly since the 1990s, with more and more research on material modification using nanoparticles[6]. In recent years, nanotechnology has gradually been introduced into the road engineering industry and has been preliminarily applied, especially in the field of nano modified asphalt materials, which has become a major hotspot in the research of asphalt pavement[7]. The fundamental reason why nano modified asphalt is different from other modified asphalt is that nano modified asphalt changes the performance of asphalt from a microstructure perspective[8,9]. Nano materials are mixed into asphalt materials by certain means to improve various properties of asphalt with magical nano effects, such as high temperature stability[10], low temperature crack resistance, fatigue resistance[11], friction performance (slip resistance), aging resistance, water stability[12], etc. Nano material modified road petroleum asphalt is mainly divided into two categories: one is single nano material modified asphalt[13], and the other is nano particle polymer composite material modified asphalt[14]. Many

high-performance polymer based nanocomposites have been developed, laying a solid foundation for their widespread application in the field of road asphalt modification[15,16].

Looking at the research on nanomaterials and technologies both domestically and internationally, it can be found that all current improvement plans are aimed at comprehensive modification effects and are not suitable for sustained extreme high temperature areas with higher requirements for high-temperature performance. At the same time, there is little research on the mechanism of nano modified asphalt based on molecular simulation. Therefore, this article will focus on the special needs of asphalt performance in areas with sustained extreme high temperatures, develop nanocomposite modified asphalt, and conduct relevant research on the modification mechanism of nanocomposite modified asphalt, in order to provide direct guidance in the research and development of nanocomposite modified asphalt to combat extreme high temperatures and determine the type and dosage of nanomaterials in specific asphalt modification.

2. Materials and Methods

2.1 Selection of the base asphalt

The main issue addressed in this study is the high-temperature stability of asphalt mixtures. During the process of modifying asphalt, A-grade 70 # asphalt is used as the base asphalt. Considering the basic performance requirements of asphalt mixtures in extreme high temperature areas during road paving and maintenance, nano ZnO and nano TiO₂ were selected as nano modifiers for base asphalt.

2.2 Selection of polymer improvers

SBS (block copolymer composed of styrene and butadiene) is currently the most commonly used asphalt polymer modifier in China due to its high temperature plasticity and strong elasticity at room temperature. Therefore, in the research of asphalt composite modification, SBS is used as a polymer modifier for modified asphalt.

2.3 Experimental design

The orthogonal test table was used to test the properties of nano-materials and polymers with different dosage. During the experimental process, the levels of each factor in the orthogonal test table were selected as shown in Table 1.

Table 1. Orthogonal test factors and levels

Factor	Level 1	Level 2	Level 3
ZnO/%	2	3	4
TiO ₂ /%	0.2	0.5	0.8
SBS/%	2.5	3	3.5

In the stage of optimizing the modified asphalt scheme, this study comprehensively tested the relevant performance indicators such as penetration, softening point, and ductility of the modified asphalt. The test results are shown in Figure 1. The final optimized experimental scheme was: 3% ZnO+0.5% TiO₂+3.5% SBS.

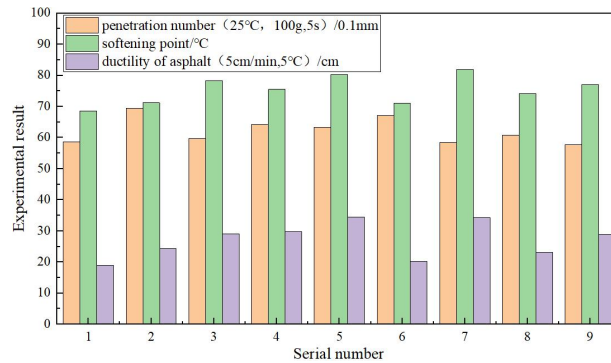


Fig. 1 Histogram of performance test results for composite modified asphalt

2.4 Modeling of asphalt molecules and modifiers

To supplement macro experiments, molecular dynamics was used to explain the modification mechanism of nano asphalt at the micro level. In this paper, the software Material Studio is used to establish the structure of ZnO cell, SBS copolymer and asphalt macromolecule, taking nano-ZnO/nano-TiO₂/SBS composite modified asphalt as an example. The solubility parameters and intermolecular interaction energy of this system were analyzed under the canonical ensemble, and the compatibility between polymer particles and asphalt is studied from the molecular level; And analyze the improvement of mechanical properties of asphalt after adding nanoparticles and polymers.

3. Results and Discussion

3.1 Performance analysis of nanocomposite modified asphalt

3.1.1 Analysis on anti-aging performance of nanocomposite modified asphalt

To fully study the aging performance of nanocomposite modified asphalt, a thin film oven aging test method was used to age the nanocomposite modified asphalt. The relevant experimental data of the aged nanocomposite modified asphalt are shown in Table 2.

Table 2. Short term aging test result data

Asphalt Type	Before aging			After aging		
	quality/g	penetration /0.1mm	ductility/cm	penetration/ 0.1mm	Residual penetration ratio/%	ductility/cm
Base asphalt	50.49	74.6	68.2	54.7	71.9	9.55
Composite modified asphalt	50.69	63.4	32.8	53.4	84.9	16.58
SBS modified asphalt	50.92	61.0	102	52.3	85.5	24.30

From Table 2, it can be seen that the mass loss corresponding to the nanocomposite modified asphalt after thin film heating and aging is very small, only 0.08%. This value is found to be reduced by 84.3% when corresponding to the aging index of the base asphalt; By comparing the changes in residual penetration before and after aging, it was found that the experimental results of nanocomposite modified asphalt were much higher than those of the base asphalt, and comparable to SBS modified asphalt. In conclusion, nanocomposite modified asphalt has good anti-aging performance.

3.1.2 Analysis of complex shear modulus and rutting factor of nanocomposite modified asphalt

In order to comprehensively analyze the dynamic mechanical related experimental performance of nanocomposite modified asphalt, this article conducted DSR tests on it, and the test results of various experimental indicators obtained are shown in Figure 2.

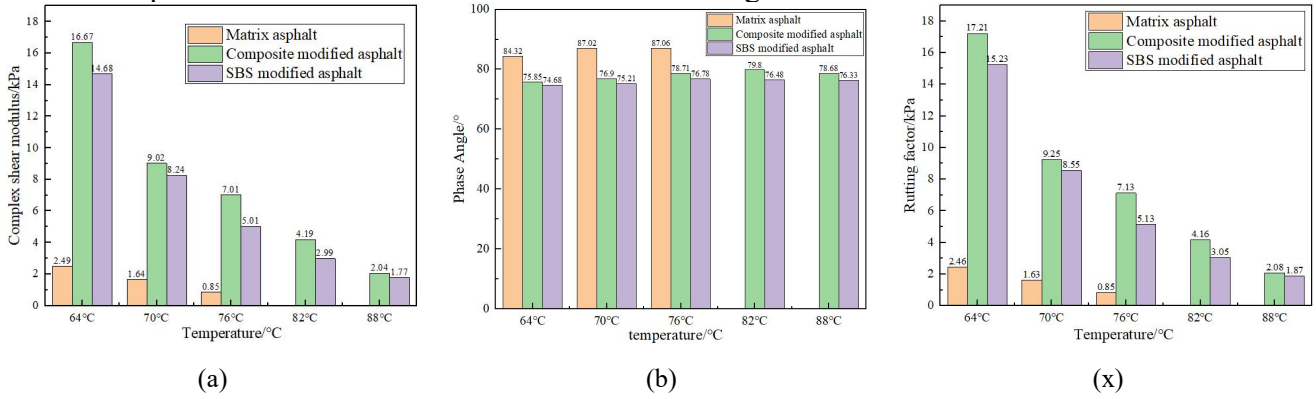
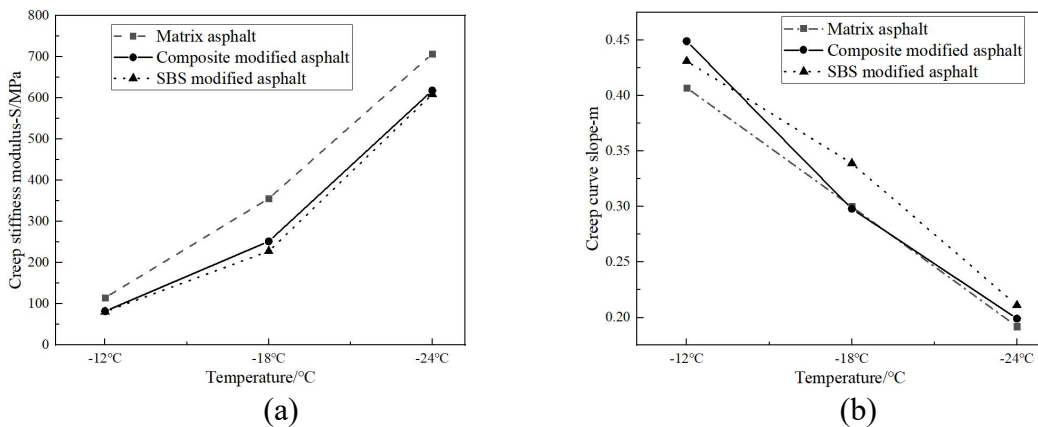


Fig. 2 Histogram of (a) phase angle, (b) complex shear modulus and (c) rutting factor of different bitumen

It can be seen from Figure 2 that the complex shear modulus G^* of three kinds of asphalt shows a downward trend with the increase of test temperature, but the G^* of nanocomposite modified asphalt is much higher than that of the base asphalt at each temperature, 10%-20% higher than that of SBS modified asphalt. At the same temperature, the rutting factor of nanocomposite modified asphalt is 10%-20% higher than that of SBS modified asphalt. This indicates that nanocomposite modifiers have a very significant improvement effect on the high-temperature stability of asphalt.

3.1.3 Analysis of creep stiffness modulus of nanocomposite modified asphalt

In order to study the low-temperature cracking resistance and other performance of nanocomposite modified asphalt, this article used BBR test to conduct relevant tests, considering



three standards: -12°C, -18°C, and -24°C. The test results are shown in Figure 3.

Fig. 3 (a) S value and (b) m value of different asphalt

According to the experimental results, the S value of nanocomposite modified asphalt is basically equivalent to that of SBS modified asphalt at the same temperature. As the experimental temperature gradually decreases, the linear slope m corresponding to nanocomposite modified asphalt decreases more than that of the base asphalt. Therefore, comprehensive analysis shows that nanocomposite modified asphalt exhibits excellent low-temperature performance.

3.2 Mechanism analysis of modified asphalt

The solubility parameters of the above three systems at different simulated temperatures are shown in Figure 4. As shown in Figure 4, as the temperature increases, the difference in solubility parameters between SBS and asphalt decreases, and at a temperature of 413K, the solubility parameters of the two are the most similar, indicating that the structure formed by SBS and asphalt is the most stable at this simulated temperature.

The non bonding energy, van der Waals potential energy, and electrostatic potential energy of the above systems at different temperatures can be obtained through software. Subsequently, the relationship between the interaction energy of each system and temperature change can be calculated as shown in Figure 5. Therefore, it can be seen that the system formed by SBS and asphalt is the most stable at 413K, which is consistent with the law obtained from solubility parameters. This indicates that the optimal temperature for SBS preparation is 413K.

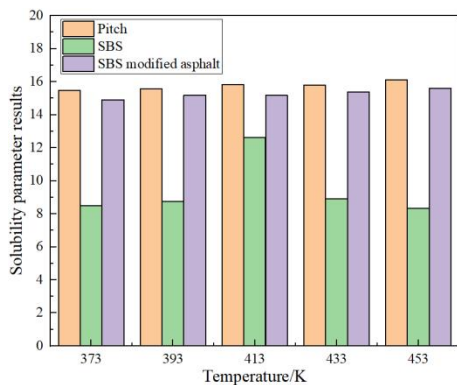


Fig. 4 Solubility parameter results

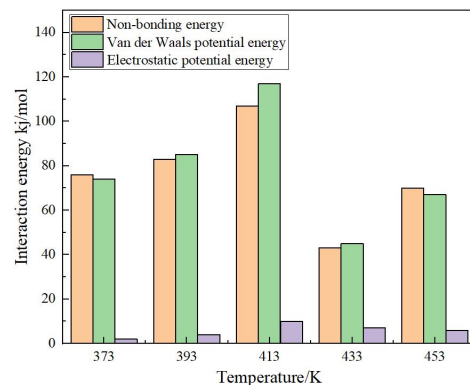


Fig. 5 The relationship between interaction energy and temperature changes

Figure 6 shows the energy histogram of the system at different temperatures. It can be seen from Figure 6 that the multi-layer nano modified asphalt system, SBS blend system, and nano material surface system all show a trend of energy first decreasing and then increasing with increasing temperature. The energy of the system is related to the stability of the system itself. Through calculation, it can be concluded that at a certain temperature, the blending reaction of each system has the most stable structure. Calculate the interfacial interaction energy between nanomaterials and SBS asphalt system based on the data in the table (as shown in Figure 7).

From Figure 7, it can be seen that as the simulated temperature increases, the interaction energy between the nano material surface and asphalt first increases and then decreases, and the surface interaction energy reaches its maximum at a temperature of 433K (160 °C). From the simulation results of nanomaterials and asphalt surfaces, it can be concluded that 160 °C should be the optimal temperature for mixing the two during actual engineering operations.

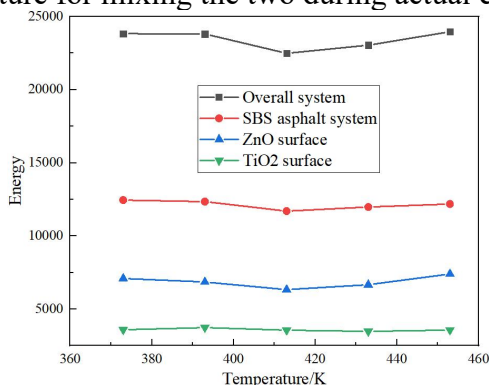


Fig. 6 Energy of each system at different temperatures

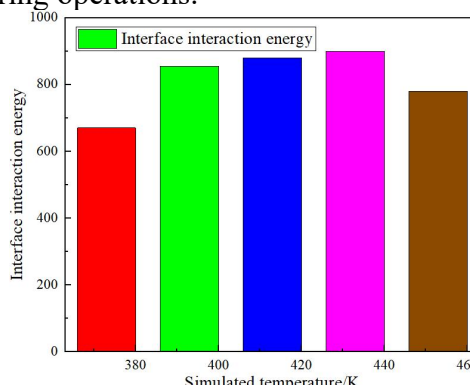


Fig. 7 Interface interaction energy between asphalt and nanomaterials

4. Conclusion

This article uses orthogonal experiments to preliminarily select the modification scheme of nanocomposites, tests the corresponding modification performance indicators, and compares and analyzes each indicator; At the same time, a nano modified asphalt model was established based on molecular dynamics to analyze its high-temperature resistance modification mechanism. The main conclusions are as follows:

(1) Through thin film oven aging test, DSR test, and BBR test, a nano/polymer composite modification scheme suitable for sustained extreme high temperature areas was ultimately selected, which is 3% ZnO+0.5% TiO₂+3.5% SBS.

(2) The test results after asphalt aging indicate that under the same conditions, the anti-aging performance of nanocomposite modified asphalt is better than that of the base asphalt. The results of SHRP tests such as DSR and BBR indicate that the recommended nanocomposite modified asphalt is significantly superior to the base asphalt in terms of high and low temperature performance.

(3) The addition of nano ZnO materials changed the interaction of various components in asphalt, improved the compatibility between asphalt and modifiers to a certain extent, and improved the storage stability of modified asphalt.

(4) A more stable structure can be formed between asphalt and SBS at a temperature of 413K; When the temperature is around 140 °C, the maximum interaction energy can be reached, indicating that the modification effect of SBS is good at this temperature; The interaction between the surface of the nano modifier and the asphalt system can reach its maximum at a temperature of 160 °C

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