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STUDY OF THE PROPERTIES AND INTERFACIAL ENERGY OF GRAPHENE-MODIFIED ASPHALT BASED ON MOLECULAR DYNAMICS

ŠTUDIJ LASTNOSTI IN ENERGIJE NA MEJAH Z GRAFENOM MODIFICIRANEGA ASFALTA S POMOČJO MOLEKULARNE DINAMIKE

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In this paper, a molecular dynamics simulation was used to examine the physical, mechanical, and interfacial adhesion characteristics of graphene-modified asphalt. The results show that the physical properties, mechanical properties and interfacial adhesion work of modified graphene are higher than those of the base asphalt model, indicating that the addition of graphene can improve the mechanical properties and interfacial interaction of asphalt. Asphalt and aggregate mainly interact through physical adsorption, and the Van der Waals force plays an important role in the adhesion behavior of the asphalt-calcite interface. There is an optimal value for the content of graphene, such that the content of graphene added to the asphalt should not be too high. Considering the graphene price factor and modification effect, the graphene content studied is optimal at 1.79 *w*/%.

Keywords: asphalt, molecular dynamics, graphene, adhesion interface

Povzetek: v tem članku avtor opisuje simulacije na osnovi molekularne dinamike za določitev fizikalnih in mehanskih lastnosti ter medmejne adhezije z grafenom modificiranega asfalta. Rezultati simulacij so pokazali, da ima z grafenom modificirani asfalt boljše fizikalne in mehanske lastnosti ter večje adhezijsko delo kot osnovni asfalt. Dodatek grafena asfaltu torej lahko izboljša mehanske lastnosti in medmejno interakcijo med sestavinami asfalta. Asfaltno vezivo (običajno bitumen) in dodani agregati (pesek oziroma apnenec) medsebojno v glavnem reagirajo preko fizikalne adsorpcije in Van der Waalsove sile igrajo pomembno vlogo pri adheziji na mejah med asfaltom in kalcitom. Avtor ugotavlja, da obstaja optimalna vsebnost grafena in da dodatek le-tega ne sme biti previsok. Upoštevajoč ceno grafena in učinek modifikacije z grafenom, avtor na osnovi izveden študije ugotavlja, da je 1,79 masnih % optimalni dodatek grafena.

Ključne besede: asfalt, molekularna dinamika, grafen, adhezija na mejah med sestavinami asfalta

1 INTRODUCTION

Asphalt is a complex mixture of organic molecules with various molecular weights, polarities, and functional groups.[1] An asphalt pavement is vulnerable to fatigue cracking, rutting, and other pavement diseases due to its material and structure, which reduces the use capacity of the asphalt mixture.[2] Among them, the structural stability of an asphalt mixture is largely determined by the adhesion of the asphalt and aggregate in the mixture. It has an important influence on the service performance of the asphalt pavement.[3] Thus, to improve the mechanical properties of the asphalt mixture, it is essential to study and improve the adhesion strength of the asphalt-aggregate interface.

Since the preparation and separation of monolayer graphene were first reported in 2004,[4] it has been widely used in various fields. It is considered to be a revolutionary nanomaterial,[5] because the addition of nanomaterials can improve the compatibility of asphalt materials.[6] In recent years graphene has been used in modified asphalt by many researchers. Fernández et al.[7] studied the mechanical properties and thermal sensitivity of graphene-modified asphalt. Test results showed that 0.05 % graphene-modified asphalt had better heat transfer, a complex modulus and resistance to plastic deformation at high temperatures. Although there has been a significant improvement in this ability, it does not have an effect on the self-healing ability. Yang et al.[8] found that the addition of graphene and carbon nanotubes increased the stiffness, high-temperature performance, and durability of asphalt through DSR and microstructure analysis. Nazki et al.[9] thought that the anti-rutting properties of graphene-modified asphalt improved with the rheological test, and the optimum content of graphene was between 1 % and 1.5 %. Yang et al.[10] considered that graphene could improve the elasticity, viscosity, and rutting resistance of asphalt. Hafeez et al.[11] found GNPs to be effective in increasing the pavement modulus, reducing the phase angle, increasing the pavement rutting resistance, significantly reducing the pavement water sensitivity and improving the pavement durability.

At present, in the field of road asphalt materials, molecular dynamics simulation is an effective and intuitive

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method to characterize the molecular model and nanostructure of the asphalt binder and quantify its physical and mechanical properties,[12–15] which provides an effective and considerable test and evaluation method for understanding and revealing the molecular basis of the asphalt material's performance evolution and attenuation mechanism. This shows that a molecular dynamics simulation could be used to investigate the interaction between asphalt and aggregate at the nanoscale, providing vital insights into the relationship between the chemical composition of asphalt concrete and its macroscopic behavior. Shishehbor et al.[16] studied the adhesion properties of asphalt, graphene, and mineral aggregate at different temperatures with a molecular dynamics simulation. The results showed that the graphene improved the viscosity, but there was no advantage in the interaction between binder and aggregate. Yao et al.[17] used molecular dynamics to simulate graphene nanosheet-modified asphalt, in which the asphalt model used a three-component model. The results showed that the modified asphalt's density, viscosity, and thermal conductivity were higher than the asphalt model. The trend of laboratory data is consistent with the change in the these characteristics at different temperatures. Qu et al.[18] studied the self-healing properties of asphalt binders by molecular dynamics and found that graphene positively affected the self-healing process of asphalt binders. Zhou et al.[19] used a molecular simulation to investigate the influence of graphene and carbon nanotubes on the thermomechanical characteristics of asphalt binders. They discovered that adding graphene or carbon nanotubes to asphalt considerably enhanced its thermodynamic characteristics. Hu et al.[20] also studied the mechanism of SBS-modified asphalt alteration by including different percentages of graphene oxide (GO) in the molecular model.

In this paper the physical properties, mechanical properties, and interfacial adhesion properties of graphene-modified asphalt were studied with a molecular dynamics simulation. Firstly, the AAA-1 asphalt and graphene model were constructed, the content of graphene sheets in the blended asphalt model was controlled by adjusting the number of sheets, and the physical and mechanical properties of the modified asphalt were calculated. Finally, the asphalt-calcite interface model was constructed to calculate the interaction energy of the interface under different contents. The mechanical properties and interface effects of graphene-modified asphalt molecular dynamics simulation were studied.

2 ESTABLISHING THE MODEL

2.1 Asphalt model

This paper used the molecular dynamics simulation software Materials Studio2019 to establish the molecular models of base asphalt and graphene-modified asphalt. The COMPASS II force field was used to describe the interaction potential of the molecular system, and the improvement effect of different graphene contents on the adhesion of asphalt and limestone was studied. The four-component, 12-molecule asphalt model proposed by Li and Greenfield[21] in 2014 on behalf of the American Strategic Highway Research Program AAA-1 asphalt was selected as the base asphalt, and the molecular structure is shown in **Figure 1**. Gray is the carbon atom; white is the hydrogen atom; blue is the nitrogen atom; yellow is the sulfur atom; and red is the oxygen atom. The basic information about its various compounds is shown in **Table 1**. In the simulation, the graphene and asphalt were physically blended because the graphene molecules did not break their chemical bonds to form a new structure. Firstly, the 12-component monomer structure model of asphalt was established by the Monte Carlo method using the amorphous unit module in MS, and each molecule's energy minimization and geometric optimization were carried out. After the molecular system reached stability, the initial asphalt model was constructed by mixing it into a box. The initial density was set to 0.8 g/cm^3. After geometric optimization and annealing, the 200 ps NVT simulation was carried out. To enable the system to stabilise initially, a Nose-Hoover thermostat was used to control the constant temperature. The NPT simulation of 300 ps was carried out, and the

Table 1: Details of the AAA-1 bitumen model system.

Components	Molecular Label	Molecular Formula	Number of Atoms	Molar mass	Number in Model system	Mass Ratio (%)
Asphaltene	Pyrrole	$C_{66}H_{81}N$	148	888.4	2	5.45
	Phenol	$C_{42}H_{54}O$	97	574.9	3	5.29
	Thiophene	$C_{51}H_{62}S$	114	707.1	3	6.51
Resin	Quinolinohopane	$C_{40}H_{59}N$	100	553.9	4	6.80
	Benzobisbenzothiophene	$C_{18}H_{10}S_2$	30	290.4	15	13.36
	Thioisorenieratane	$C_{40}H_{60}S$	101	573.0	4	7.03
	Pyridinohopane	$C_{36}H_{57}N$	94	503.9	4	6.18
	Trimethylbenzene-oxane	$C_{29}H_{50}O$	80	414.7	5	6.36
Saturate	Squalane	$C_{30}H_{62}$	92	422.8	4	5.19
	Hopane	$C_{35}H_{62}$	97	482.9	4	5.93
Aromatic	PHPN	$C_{35}H_{44}$	79	464.7	11	15.68
	DOCHN	$C_{30}H_{46}$	76	406.7	13	16.22

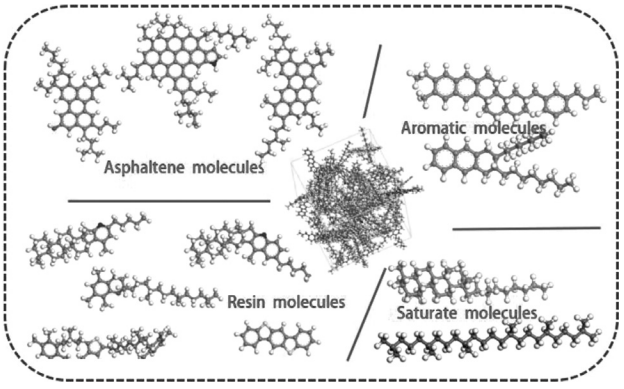

Figure 1: Asphalt 4-component 12-molecule system

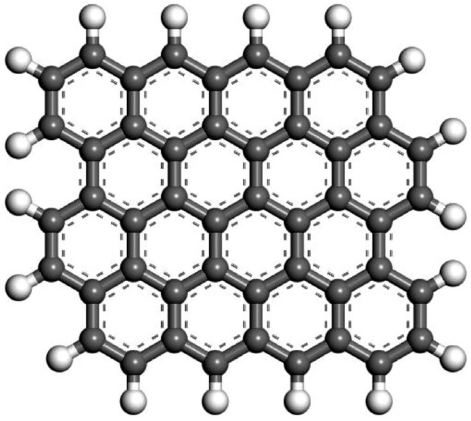

Figure 2: Typical molecular structure of graphene

density of the system was stabilized by using Andersen's constant pressure controller to control a constant pressure. Finally, the 100 ps NVT simulation was carried out to stabilize the system further, and finally, the base asphalt and graphene-modified asphalt model were obtained.

According to the literature, graphene is modeled by Qu et al.[18], as shown in **Figure 2**. The content of graphene in modified asphalt was calculated according to the graphene content in modified asphalt, as shown in **Table 2**.

Table 2: Content of graphene in the model.

Number of graphene sheets/sheet	0	1	2	3	4	5
Graphene content (*w*/%)	0	1.79	3.52	5.19	6.8	8.36

2.2 Aggregate molecular model

Limestone is widely used as aggregate for road pavement materials in China. Limestone is ground into powder for an XRD test to test its mineral composition. The results are shown in **Figure 3a**.

According to the results of the X-ray diffraction analysis, the content of calcite in this batch of limestone is 92.2 *w*/%, and the content of dolomite is 7.8 *w*/%. Therefore, this paper will establish a calcite crystal model to simulate the aggregate model. For calcite surfaces, past researchers have found that the crystal {1 0 4} cleavage surface is the most stable cleavage plane because it has the largest interlayer spacing and the lowest surface energy.[21] Therefore, the {1 0 4} cleavage surface is used to construct a supercell for building the calcite molecular model, and the aggregate model is shown in **Figure 3b**.

2.3 Asphalt-calcite interface model

The asphalt-calcite interface model is constructed by combining the asphalt and aggregate mineral models with the interface construction tool. To eliminate the influence of the three-dimensional periodic boundary conditions, a 5-nm vacuum layer is placed at the top of each asphalt-calcite interface model. When the model size is

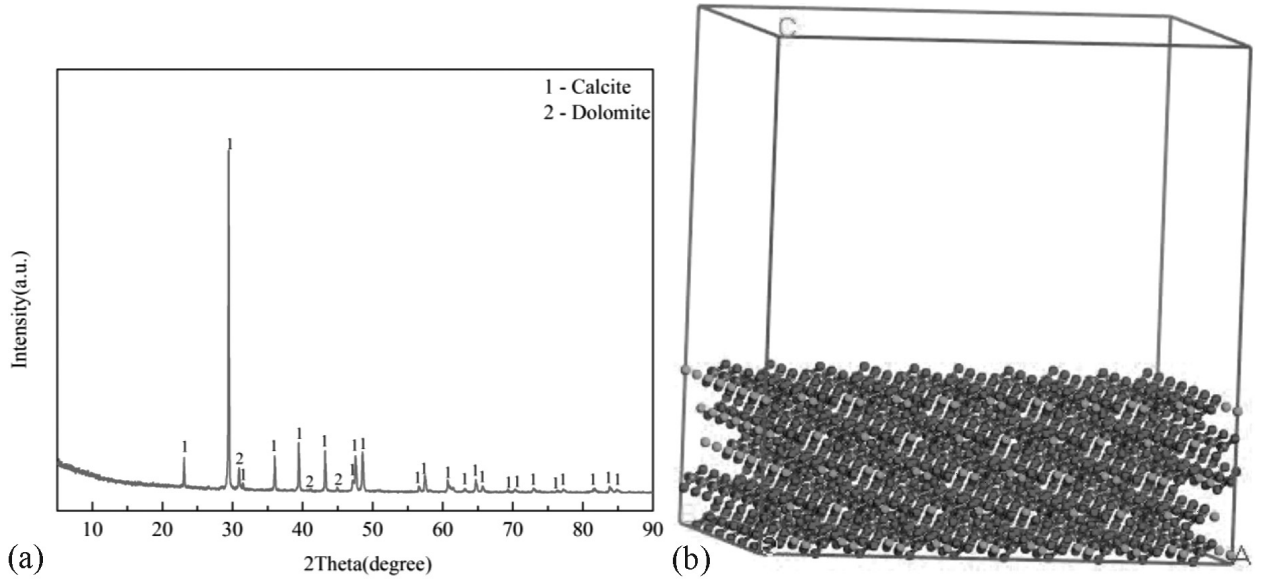

Figure 3: Aggregate composition and model: a) aggregate composition, b) aggregate molecular model

greater than 3.5 nm × 3.5 nm, the system energy converges and meets the accuracy requirements. In the final modeling, the size is roughly 4 nm × 4 nm. The constructed asphalt-calcite interface system was first subjected to 5000 iterations of energy and geometry optimization, followed by a 300 ps dynamic equilibrium operation with an NVT ensemble at 298.15 K. The last 20 frames of the trajectory are exported for subsequent energy calculations.

2.4 Verification of the equilibrium of the model

Density is an important physical and mechanical property of asphalt, which is normally used to verify the reliability of the molecular model in a MD simulation. To determine whether the system reaches equilibrium in the last 1 ns dynamics, the density-time curve of all asphalt models is calculated. It can be seen from **Table 3** that the density of the model is stable in the last 1 ns.

Table 3: Density Fluctuation Data

Graphene content (%)	Average density (g/cm^3)	Final density (g/cm^3)	Standard deviation
0	0.979	1.003	0.034
1.79	0.996	1.009	0.027
3.52	0.998	1.011	0.031
5.19	1.005	1.022	0.032
6.80	1.012	1.042	0.026
8.36	1.034	1.055	0.030

That is, it fluctuates within a specific range. The standard deviation of the density fluctuation is 0.026–0.034 g/cm^3, which is very small and far less than the average density, indicating that the simulated density fluctuation range is weak and tends to be stable. Therefore, it is determined that all the models reach the equilibrium state in the last 1ns, and the following analysis can be carried out. The density calculated by the AAA-1 asphalts model system at 298.15K is 1.003g/cm^3, which is close to the experimental density of 1.023g cm^3. This result verifies the correctness of the simulation process. Furthermore, the density increases with the increase of graphene content, which is consistent with the actual conditions.

3 PERFORMANCE SIMULATION

3.1 Simulation of Physical Properties of Modified Asphalt

The cohesive energy density (CED) is the energy required to overcome intermolecular forces per unit volume of aggregates, which is an index to evaluate the strength of intermolecular interactions. **Figure 4a** shows the cohesive energy-density simulation results of the base asphalt and the graphene-modified asphalt models at different temperatures. The results show that the cohesive energy density of the modified asphalt model is higher than that of the base asphalt model. This result is reasonable because the introduction of graphene increases the intermolecular non-bond interaction, especially the van der Waals force. Solubility is frequently utilized to assess the validity of the asphalt molecular model, as it serves as a metric for the intermolecular forces among the asphalt molecules and one of the characteristics of the asphalt itself. The simulation results of the solubility parameters of the original asphalt and the graphene-modified asphalt model at different temperatures are shown in **Figure 4b**. The solubility parameter of the base asphalt simulated in this paper is 18.548 (J/cm^3) ^ 0.5, and the solubility parameter range after modification is 18.708–19.368, which is within the solubility parameter range of asphalt 13.3–22.5.[22] This indicates that the MD simulation parameter setting and optimization process used in this paper are reliable for analyzing and evaluating the physical properties of the

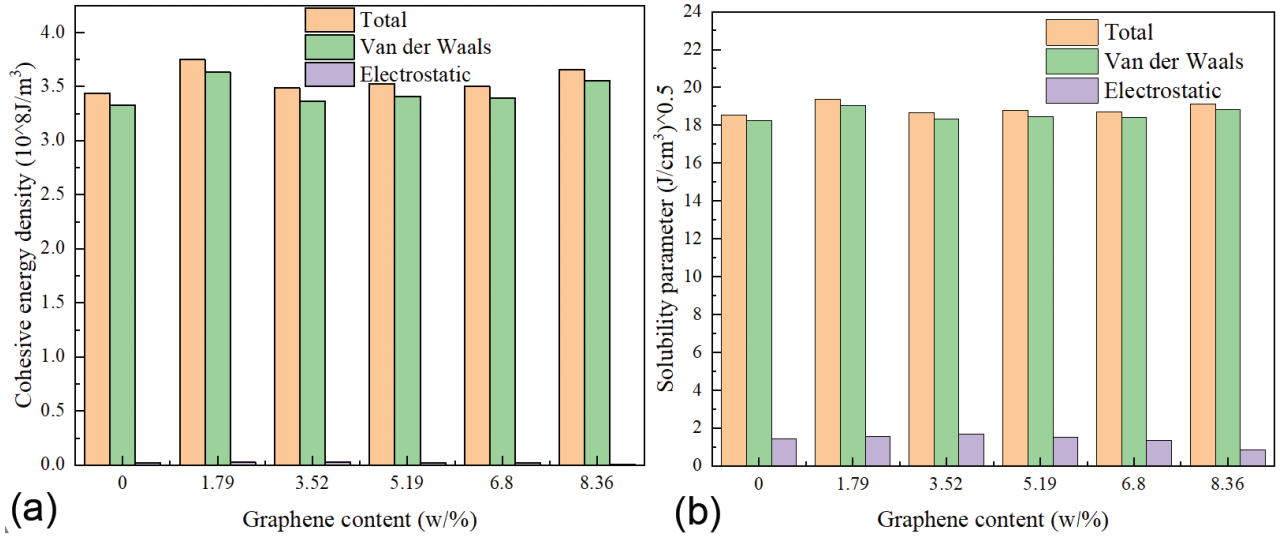

Figure 4: Change of physical properties of modified asphalt with graphene content: a) cohesive energy density, b) solubility parameters

asphalt model, the base asphalt model, and the graphene-modified asphalt model constructed in this paper are also reasonable. No matter the cohesive energy density or solubility parameter, the modified asphalt is larger than the base asphalt model. The physical properties under the van der Waals force also show the same results. It can also be seen from **Figure 4** that the cohesive energy density and solubility parameter are mainly affected by the van der Waals force, and the electrostatic force is relatively weak. With the increase of graphene content, the cohesive energy density and solubility are as in the figure.

3.2 Simulation of Mechanical Properties of Modified Asphalt

After the structural optimization and dynamic relaxation, the mechanical properties of the modified asphalt were studied with a molecular dynamics simulation of different moduli of graphene-modified asphalt, including bulk modulus, shear modulus, and Young's modulus. The constant- strain method is used to solve the mechanical parameters, and the bulk modulus B and shear modulus S of the graphene-modified asphalt are calculated. Then Young's modulus is calculated by the isotropic material's standard Equation (3), and multiple tests take the average value. The results are shown in **Figure 5**. The Voigt method is used to approximate the maximum values of the bulk modulus and shear modulus, and the minimum values are approximately calculated by the Reuss method. Hill[23] found that the actual bulk and shear modulus are usually between the estimated values of Voigt and Reuss, so the VRH (Voigt-Reuss-Hill) approximation method was proposed to correct them, as shown in Equations (1) and (2).

$$B = B_{\mathrm{VRH}} = \frac{B_{\mathrm{V}} + B_{\mathrm{R}}}{2} \tag{1}$$

$$S = S_{\mathrm{VRH}} = \frac{S_{\mathrm{V}} + S_{\mathrm{R}}}{2} \tag{2}$$

$$E = \frac{9S}{3 + S/B} \tag{3}$$

It can be seen from **Figure 5** that for the bulk modulus, the modulus of graphene-modified asphalt with 1.79 *w*/% content is the largest and then this gradually decreases but gradually increases with the increase of the content. The bulk modulus at 8.36 *w*/% is 2.369 GPa. The shear modulus generally increases first and then decreases with the increase of the content, and the maximum modulus of graphene at 5.19 *w*/% is 0.975 GPa. Young's modulus shows a wave trend with the increase of graphene content, and the maximum modulus of graphene at 5.19 *w*/% is 2.554 GPa. In general, when the graphene content is in the range of 8.36 %, the bulk modulus, shear modulus, and Young's modulus of modified asphalt are greater than those of the base asphalt. It shows that the increase of graphene can improve the mechanical properties of the asphalt. However, when the content is too high above 5.19 %, it can be seen that the shear modulus and Young's modulus decrease, so the content of graphene in asphalt should not be too high.

3.3 Interface Adhesion of Modified Asphalt

Adhesion energy is defined as the energy required to desorb the asphalt-mineral interface model into two independent asphalt and mineral models. Many researchers have proved this calculation method to be effective for evaluating the interface model's bonding strength [24]. Asphalt-aggregate interface's interaction energy and adhesion work are calculated as Equations (4) and (5). In this paper, the interface interaction is evaluated by the adhesion work calculated by the interaction energy. Interfacial interaction increases with adhesion work.

$$E_{\mathrm{interactions}} = E_{\mathrm{asphalt}} + E_{\mathrm{aggregate}} - E_{\mathrm{total}} \tag{4}$$

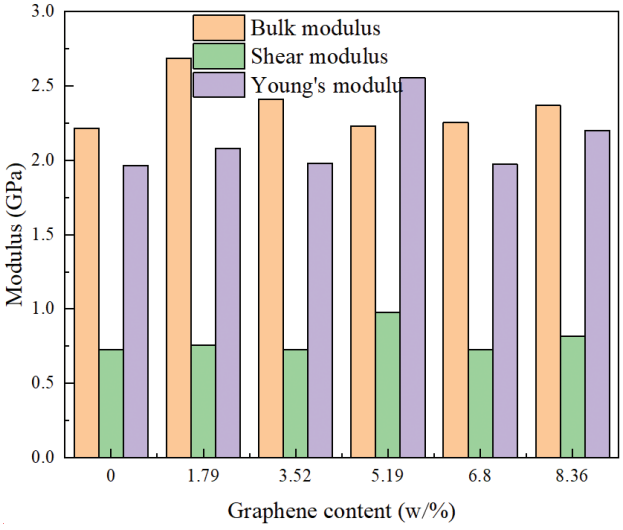

Figure 5: Change of modified asphalt modulus with graphene content

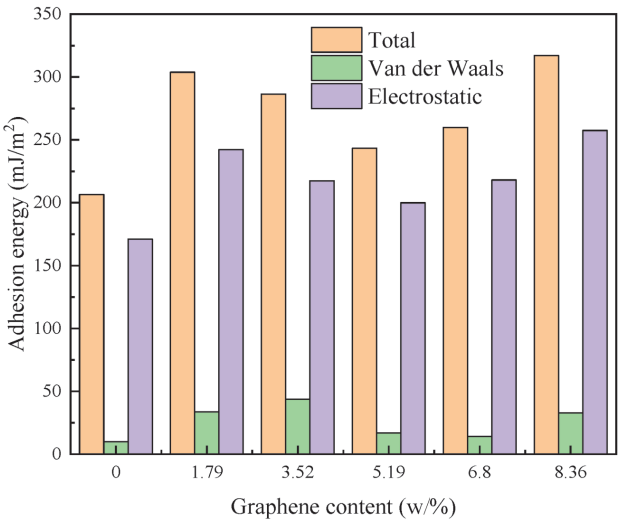

Figure 6: Adhesion work of modified asphalt-calcite interface

$$W_{\text{ass-agg}} = \frac{E_{\text{asphalt}} + E_{\text{aggregate}} - E_{\text{total}}}{A} \quad (5)$$

In the formula, $W_{\text{as-agg}}$ is the adhesion energy between asphalt and aggregate interface (mJ/m^2); $E_{\text{interaction}}$ is the interaction energy of interface (mJ); E_{total} is the total potential energy of the interface model after NVT equilibrium (mJ); E_{asphalt} and $E_{\text{aggregate}}$ are the potential energy (mJ) of the single asphalt model and the aggregate surface model, respectively; A is the contact area between the asphalt and the aggregate interface (m^2).

The bond strength of the interface between the graphene-modified asphalt and the aggregate is shown in **Figure 6**. In the calcite-asphalt interface model, the interaction between the asphalt and the aggregate is mainly physical adsorption behaviour, as the total adhesion work is mainly composed of the non-bonding energy. The Van der Waals interaction energy and electrostatic interaction energy are significant contributors to the adhesion energy. It can also be seen from the diagram that the van der Waals force plays a significant role in the adhesion behavior of the base asphalt-calcite interface. The main reason for this phenomenon is that the parallel arrangement structure of the base asphalt can provide a more considerable intermolecular interaction, which helps to improve the van der Waals interaction. Therefore, the interface between asphalt and aggregate has a higher van der Waals energy. In general, the adhesion work increases first and then decreases, and then increases with the increase of dosage and is higher than that of unmodified base asphalt. Although the graphene content reached the maximum value of 317.03 mJ/m^2 at 8.36 *w*/%, it was not much different from the 303.75 mJ/m^2 at 1.79 *w*/% and did not bring a great improvement. With comprehensive graphene price factors and modified interface effect, a graphene content of 1.79 *w*/% is the optimal value.

4 CONCLUSIONS

In this paper we conducted a molecular dynamics simulation to investigate the interfacial mechanical properties of graphene-modified asphalt. Initially, the density of AAA-1 asphalt was determined at room temperature and pressure (p = 1 atm, T = 298.15 K), resulting in a value of 0.979 g/cm^3. Moreover, the solubility parameter fell within the range of the asphalt test and closely resembled the experimental value, confirming the accuracy of our asphalt model. Subsequently, we conducted experiments to explore the mechanical properties and interface interactions of the graphene-modified asphalt through a molecular dynamics simulation, leading to the following conclusions.

(1) Upon analysing the cohesive energy density and solubility parameter of the modified asphalt in comparison to the base asphalt model, higher values for both parameters were observed in the modified asphalt. The physical properties of both the base and modified asphalt were primarily influenced by the van der Waals force, with the electrostatic force playing a relatively minor role. Interestingly, as the graphene content increased, the cohesive energy density and solubility exhibited a pattern of initial increase, followed by a decrease, and finally a subsequent increase again, reaching a peak at 1.79 *w*/%. Moreover, the bulk modulus, shear modulus, and Young's modulus of the modified asphalt were significantly higher than those of the base asphalt, indicating that the addition of graphene enhanced the mechanical properties of the asphalt. However, it is worth noting that when the graphene content exceeded 5.19 *w*/%, both the shear modulus and Young's modulus showed a decline.

(2) Graphene-modified asphalt significantly enhances the adhesion performance with weakly alkaline aggregate calcite compared to the base asphalt. The main interaction between the asphalt and aggregate is the physical adsorption behavior. Both the van der Waals and electrostatic interaction energies make a substantial contribution to the adhesion energy. The adhesion behavior of the asphalt-calcite interface is mainly governed by the Van der Waals force.

(3) From a comprehensive perspective, including physical properties, mechanical properties, and adhesion with the aggregate interface, it was found that the performance of the modified asphalt does not improve indefinitely with an increasing graphene content. Instead, there exists an optimal value for the graphene content, and the addition of graphene to the asphalt content should not exceed this value. Considering both the graphene price and its modification effect, the optimal graphene content studied in this paper is 1.79 *w*/%.

5 REFERENCES

[1] I. A. Wiehe, K. S. Liang, Asphaltenes, resins, and other petroleum macromolecules. Fluid Phase Equilibria, 117 (**1996**) 1–2, 201–210

[2] W. Wang, L. Wang, H. Xiong, R. Luo, A review and perspective for research on moisture damage in asphalt pavement induced by dynamic pore water pressure, Construction and Building Materials, 204 (**2019**), 631–642, doi:10.1016/j.conbuildmat.2019.01.167

[3] F. Guo, J. Pei, J. Zhang, B. Xue, G. Sun, R. Li, Study on the adhesion property between asphalt binder and aggregate: A state-of-the-art review, Construction and Building Materials, 256 (**2020**), doi:10.1016/j.conbuildmat.2020.119474

[4] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, M. I. Katsnelson, I. V. Grigorieva, S. V. Dubonos, A. A. Firsov, Two-dimensional gas of massless Dirac fermions in graphene, Nature, 438 (**2005**) 7065, 197–200, doi:10.1038/nature04233

[5] S. Wu, O. Tahri, State-of-art carbon and graphene family nanomaterials for asphalt modification, Road Materials and Pavement Design, 22 (**2019**) 4, 735–756, doi:10.1080/14680629.2019.1642946

[6] R. Li, F. Xiao, S. Amirkhanian, Z. You, J. Huang, Developments of nano materials and technologies on asphalt materials – A review, Construction and Building Materials, 143 (**2017**), 633–648, doi:10.1016/j.conbuildmat.2017.03.158

[7] S. Fernández, A. Mercado, E. Cuara, C. Yeverino-Miranda, U. Sierra, Asphalt as raw material of graphene-like resources, Fuel, 241 (**2019**), 297–303, doi:10.1016/j.fuel.2018.12.026

[8] Q. Yang, Q. Liu, J. Zhong, B. Hong, D. Wang, M. Oeser, Rheological and micro-structural characterization of bitumen modified with

carbon nanomaterials, Construction and Building Materials, 201 (**2019**), 580–589, doi:10.1016/j.conbuildmat.2018.12.173

[9] M. Ahmad Nazki, T. Chopra, A. K. Chandrappa, Rheological properties and thermal conductivity of bitumen binders modified with graphene, Construction and Building Materials, 238 (**2020**), doi:10.1016/j.conbuildmat.2019.117693

[10] L. Yang, D. Zhou, Y. Kang, Rheological Properties of Graphene-modified Asphalt Binders, Nanomaterials (Basel), 10 (**2020**) 11, doi:10.3390/nano10112197

[11] M. Hafeez, N. Ahmad, M. Kamal, J. Rafi, M. Haq, Jamal, S. Zaidi, M. Nasir, Experimental Investigation into the Structural and Functional Performance of Graphene Nano-Platelet (GNP)-Doped Asphalt, Applied Sciences, 9 (**2019**) 4, doi:10.3390/app9040686

[12] A. Bhasin, R. Bommavaram, M. L. Greenfield, D. N. Little, Use of Molecular Dynamics to Investigate Self-Healing Mechanisms in Asphalt Binders, Journal of Materials in Civil Engineering, 23 (**2011**) 4, 485–492, doi:10.1061/(asce)mt.1943-5533.0000200

[13] L. Zhang, M. L. Greenfield, Relaxation time, diffusion, and viscosity analysis of model asphalt systems using molecular simulation, J Chem Phys., 127 (**2007**) 19, 194502, doi:10.1063/1.2799189

[14] L. He, G. Li, S. Lv, J. Gao, K. J. Kowalski, J. Valentin, A. Alexiadis,. Self-healing behavior of asphalt system based on molecular dynamics simulation, Construction and Building Materials, 254 (**2020**), doi:10.1016/j.conbuildmat.2020.119225

[15] W. Sun, H. Wang, Self-healing of asphalt binder with cohesive failure: Insights from molecular dynamics simulation, Construction and Building Materials, 262 (**2020**), doi:10.1016/j.conbuildmat.2020.120538

[16] M. Shishehbor, M. R. Pouranian, M. G. Ramezani, Molecular investigations on the interactions of graphene, crude oil fractions and mineral aggregates at low, medium and high temperatures, Petroleum Science and Technology, 37 (**2019**) 7, 804–811, doi:10.1080/10916466.2019.1566254

[17] H. Yao, Q. Dai, Z. You, A. Bick, M. Wang, S. Guo, Property Analysis of Exfoliated Graphite Nanoplatelets Modified Asphalt Model Using Molecular Dynamics (MD) Method, Applied Sciences, 7 (**2017**) 1, doi:10.3390/app7010043

[18] X. Qu, D. Wang, Y. Hou, Q. Liu, M. Oeser, L. Wang, Investigation on Self-Healing Behavior of Asphalt Binder Using a Six-Fraction Molecular Model, Journal of Materials in Civil Engineering, 31 (**2019**) 5, doi:10.1061/(asce)mt.1943-5533.0002676

[19] X. Zhou, X. Zhang, S. Xu, S. Wu, Q. Liu, Z. Fan, Evaluation of thermo-mechanical properties of graphene/carbon-nanotubes modified asphalt with molecular simulation, Molecular Simulation, 43 (**2017**) 4, 312–319, doi:10.1080/08927022.2016.1274985

[20] K. Hu, C. Yu, Q. Yang, Y. Chen, G. Chen, R. Ma, Multi–scale enhancement mechanisms of graphene oxide on styrene–butadiene–styrene modified asphalt: An exploration from molecular dynamics simulations, Materials & Design, 208 (**2021**), doi:10.1016/j.matdes.2021.109901

[21] S. L. Stipp, M. F. Hochella, Structure and bonding environments at the calcite surface as observed with X-ray photoelectron spectroscopy (XPS) and low energy electron diffraction (LEED), Geochimica et Cosmochimica Acta, 55 (**1991**) 6, 1723–1736, doi:10.1016/0016-7037(91)90142-R

[22] X. X. Zhou, G. F. Zhang, R. M. Liu, L. Zheng, Molecular Simulations of Anti-Aging Mechanisms on Nano-LDHs Modified Asphalt, Key Engineering Materials, 599 (**2014**), 198–202, doi:10.4028/www.scientific.net/KEM.599.198

[23] R. Hill, The elastic behaviour of a crystalline aggregate, Proceedings of the Physical Society, Section A. 65 (**1952**) 5, 349

[24] G. Xu, H. Wang, Study of cohesion and adhesion properties of asphalt concrete with molecular dynamics simulation, Computational Materials Science, 112 (**2016**), 161–169, doi:10.1016/j.commatsci.2015.10.024