Improvement Mechanism of Adhesion Performance of Anti-stripping Agents and Coupling Agents on Asphalt-Aggregate Interface Based on Molecular Dynamics

SONG Jing, *XIE Jianguang**, *DAI Zexinyu*

College of Civil Aviation, Nanjing University of Aeronautics and Astronautics, Nanjing 211106, P. R. China

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Abstract: This study examined the mechanisms for improving the adhesion performance of the asphalt-aggregate interface with two anti-stripping agents and two coupling agents. The investigation of contact behavior between various asphalt-aggregate surfaces was conducted using molecular dynamics (MD) simulations. The interaction energy and the relative concentration distribution were employed as the parameters to analyze the enhancement mechanisms of anti-stripping agents and coupling agents on the asphalt-aggregate interface. Results indicated that the adhesion at the asphalt-aggregate interface could be strengthened by both anti-stripping agents and coupling agents. Anti-stripping agents primarily improve adhesion through the reinforcement of electrostatic attraction, while coupling agents primarily upgrade adhesion by strengthening the van der Waals. Hence, the molecular dynamics modeling and calculation techniques presented in this study can be utilized to elucidate the development mechanism of the asphalt-aggregate interface through the use of anti-stripping agents and coupling agents.

Key words: asphalt-aggregate interface; adhesion performance; anti-stripping agents; coupling agents; molecular dynamics

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0 Introduction

Asphalt mixtures, being composite materials, are extensively employed in road infrastructure owing to their exceptional road performance. At present, the aggregates employed in asphalt pavements predominantly consist of neutral or alkaline materials, with acidic aggregates being less frequently utilized[1]. One primary factor contributing to the aforementioned issue is the inadequate adhesion qualities of asphalt and acidic aggregates. This deficiency leads to the displacement of the asphalt film by a water film when exposed to moisture. Consequently, this phenomenon results in the deterioration of the pavement, such as the formation of potholes and pavement loosening, ultimately compromising the overall performance of the asphalt pavement[2-3]. Thus, it is imperative to conduct research on the water damage resistance of the asphalt-aggregate interface to efficiently harness acidic aggregate resources and address issues like deteriorated and pockmarked asphalt pavement.

Molecular dynamics (MD) is a computational simulation method used to study the motion and interactions of microscopic particles, such as atoms, molecules, or ions in time. Researchers have conducted numerous studies on molecular dynamics simulations of asphalt-aggregate interfacial interactions at the molecular level, including the study of adhesion properties at the asphalt-aggregate interface. For example, Lu et al.[4-5] established a molecular model of the asphalt-silica interface and simulated the interface with uniaxial tensile and shear tests to investigate the stress-strain state of the interface

*Corresponding author, E-mail address: xiejg@nuaa.edu.cn.

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and the bond damage mechanism. Yao and Xu et al.[6-7] established asphalt-aggregate and water-aggregate interfacial systems to study the adhesion mechanism between asphalt and aggregates and the water damage mechanism.

Currently, there exists a substantial body of research findings concerning the water damage resistance of asphalt mixtures, both domestically and internationally. The primary approaches employed in these studies involve the incorporation of anti-stripping agents into asphalt[8-9] and the utilization of coupling agents to improve the adhesion of asphalt and aggregates[10-11]. The primary focus of these studies was to assess the extent of enhancement in the water damage resistance of asphalt mixtures through the application of anti-scalping agents and coupling agents. However, the employed methodology predominantly relied on macro tests, which limited the ability to elucidate the underlying mechanism of water damage resistance at the micro level.

The MD approach uses computational techniques to solve the equations of motion governing a molecular system. This method offers advantages over macroscopic testing by enabling the investigation of intermolecular interactions at the nanoscale. At present, the scholarly community has developed simulation techniques for studying asphalt-aggregate interfacial systems, with a primary emphasis on investigating the impacts of different asphalt and mineral compositions[12-13]. Hence, the application of MD enables the investigation of the underlying mechanisms involved in the functioning of anti-stripping agents and coupling agents.

Therefore, employing the MD approach, this study proposed a model of the asphalt-aggregate interface to investigate the impact of anti-stripping agents and coupling agents on the adhesive characteristics of said interface. The objective was to elucidate the underlying mechanisms through which these agents exert their effects.

1 MD Models

1.1 Construction of asphalt models

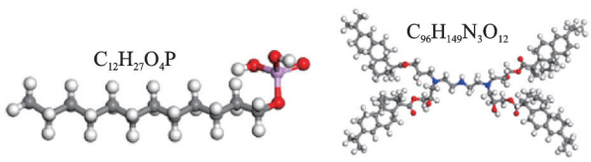
Bitumen is a heterogeneous substance characterized by its dark brown color and consisting of a diverse range of hydrocarbons with varying molecular weights and associated non-metallic compounds. Typically, bitumen comprises an extensive array of thousands of distinct molecular species[14]. Researchers have discovered that employing several molecules to depict the composition of asphalt can enhance the fidelity of asphalt structure simulations, resulting in more accurate representations of real-world asphalt structures. The AAA-1 asphalt molecular model, which was proposed by Li et al.[15] in 2014 as part of the U. S. Strategic Highway Research Program, is currently regarded as one of the most sophisticated and widely embraced model asphalts in the realm of asphalt molecular simulation. Hence, the 12-component asphalt model will be used in this study as a typical model of asphalt for conducting molecular dynamics computations and investigations. Table 1 displayed the precise parameters of the 12-component asphalt model.

Table 1 Precise parameters of 12-component in asphalt model

Composition	Molecule	Formula	Number	Mass fraction /%
Saturates	Hopane	$C_{30}H_{62}$	4	12.8
	Squalane	$C_{35}H_{62}$	5	
Aromatics	DOCHN	$C_{30}H_{46}$	17	44.2
	PHPN	$C_{35}H_{44}$	16	
Resins	Benzobisbenzothiophene	$C_{18}H_{10}S_2$	4	29.2
	Trimethylbenzeneoxane	$C_{29}H_{50}O$	4	
	Pyridinohopane	$C_{36}H_{57}N$	2	
	Quinolinohopane	$C_{40}H_{59}N$	4	
	Thioisorenieratane	$C_{40}H_{60}S$	6	
Asphaltenes	phenol	$C_{42}H_{54}O$	2	13.8
	thiophene	$C_{51}H_{62}S$	1	
	pyrrole	$C_{66}H_{81}N$	3	

In addition to incorporating the matrix asphalt model, the study introduced non-amine anti-stripping agents (NASA) and amine anti-stripping agents (ASA) into the asphalt mixture to investigate their impact on the adhesion properties at the asphalt-aggregate interface. Consequently, modified asphalt models were derived for each respective

agent. Fig.1 shows the chemical structures of the non-amine anti-stripping agent ($C_{12}H_{27}O_4P$) and the amine anti-stripping agent ($C_{96}H_{149}N_3O_{12}$).



(a) Non-amine anti-stripping agents ($C_{12}H_{27}O_4P$) (b) Amine anti-stripping agent ($C_{96}H_{149}N_3O_{12}$)

Fig.1 Chemical structure of anti-stripping agent

This study utilized factors such as density and glass transition temperature to validate the fidelity of the asphalt model by a comparative analysis with real-world asphalt samples. Density is a physical property that quantifies the mass of a substance per unit volume. The dissimilarity in density between the asphalt model and its real density can serve as an indicator of the model's degree of validity. Fig.2 illustrates the variation in density of the matrix asphalt model throughout the kinetic computation at a temperature and pressure held constant under a constant pressure and constant temperature (NPT) system, specifically at a time of 200 ps.

The density curves of the asphalt model, as depicted in Fig.2, exhibite consistent fluctuations before reaching a state of stability. Upon conducting calculations, it is determined that the ultimate density of the matrix asphalt model is 0.970 1 g/cm^3. Furthermore, the ultimate densities of the modified asphalt models, which incorporate a non-amine anti-stripping agent and an amine anti-stripping agent, are found to be 0.972 7 g/cm^{3}and 0.974 6 g/cm^3, respectively. It is worth noting that the actual density of asphalt at a temperature of 298 K is 1.000 g/cm^3. Hence, the discrepancy between the observed density of asphalt and the simulated densities of the three asphalt models is found to be within a 5% margin. This suggests that the three asphalt models can be preliminarily determined to be sufficiently accurate and applicable.

The glass transition temperature (T_g) is a significant characteristic that influences the properties of asphalt, specifically referring to the temperature at which asphalt transitions from the viscous flow condition to the glassy state. The distinct characteristics exhibited by bitumen in its viscous flow and glassy stages give rise to significant alterations in its properties, including density, in close proximity to T_g. Thus, by utilizing molecular dynamics software, it is possible to simulate the variation in density parameters of asphalt at various temperatures. This simulation enables the determination of the glass transition temperature of the asphalt model, facilitating a comparison with the real asphalt system and validating the appropriateness of the model.

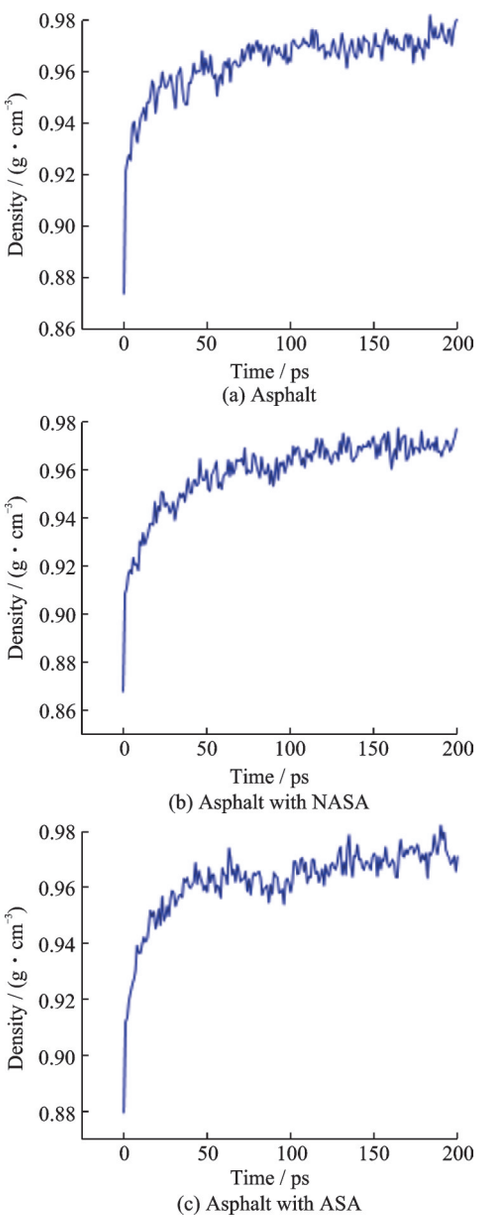


Fig.2 Density variation curves of asphalt model

The procedural sequence employed in the molecular dynamics program for simulating molecular systems is outlined as follows. (1) Conduct kinetic

simulations of the NPT system for three asphalt models at various temperatures ranging from 50 K to 450 K, with a 25 K interval, in order to derive the density parameters. (2) Determine the specific volume values for the respective temperatures and create a graph illustrating the relationship between specific volume and temperature. (3) Determine the glass transition temperature of the asphalt model by performing a linear fit of the particular volume values to the asphalt model across the whole temperature range.

Fig.3 displays the simulation outcomes of the three asphalt models. The matrix asphalt exhibites a glass transition temperature of 258 K. The glass transition temperatures of the modified asphalt model, when integrating non-amine anti-stripping agents and amine anti-stripping agents, are determined to be 260 K and 257 K. The test findings obtained indicate that the glass transition temperature range of asphalt lies between 256 K and 262 K[16].

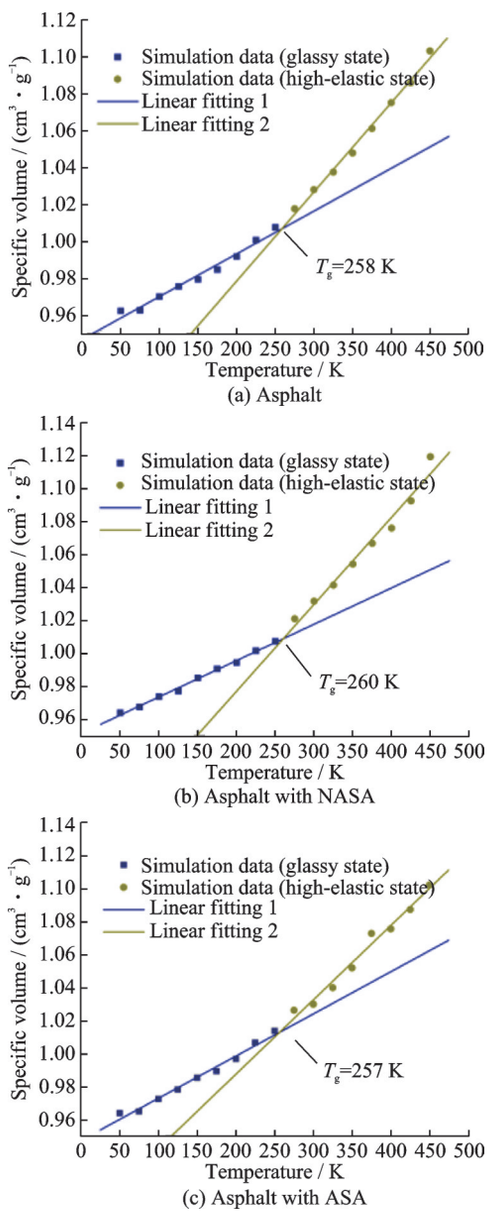


Fig.3 Relationship between specific volume and temperature of asphalt model

Aforementioned results confirmed the precision and rationality of the matrix asphalt model, the non-amine anti-stripping agent modified asphalt model, and the amine anti-stripping agent modified asphalt model developed in this study. These models were suitable for conducting molecular dynamics simulations.

1.2 Construction of aggregate models

Silica was selected for this study as a representative of acidic aggregates. The data on silica crystals were retrieved through the American Mineralogist Crystal Structure Database (AMCSD). The crystal structure was built in Materials Studio (MS) according to the retrieved crystal structure information, and the crystal cell model was shown in Fig.4.

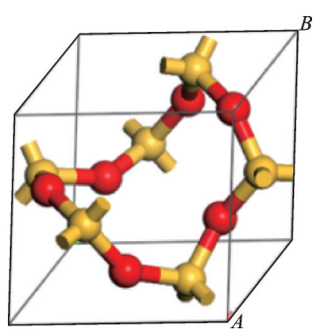


Fig.4 Silicon dioxide crystal cell

Following the construction of the crystal, it needs to be faceted. For silica, this study chose the {0 0 1} surface that occurs more often in nature. According to Ref.[17], a fully hydroxylated silica surface is highly hydrophilic and best represents the actual aggregate. Therefore, this study hydroxylated the silica surface. Subsequently, a supercell operation was performed to expand it into a mineral surface close to 40 Å × 40 Å, and finally, a vacuum layer was created for the aggregate model. The geometry optimization function in the Forcite module was used to optimize the structure. At this point,

the aggregate model is established. The final aggregate model was shown in Fig.5.

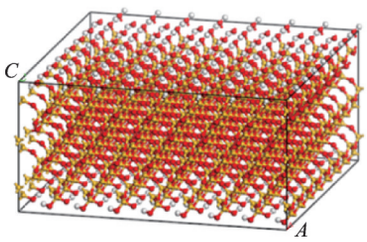


Fig.5 Aggregate layer model

To investigate the impact of a coupling agent on the interface between asphalt and aggregate, coupling agent molecules were grafted on the aggregate model surface in MS. For silane coupling agent (SCA), it was shown that the grafting density of SCA molecules on the aggregate surface is an important influence on the adhesion at the asphalt-aggregate interface. Therefore, the grafting density of this study was chosen to be 1.5/nm^2[18], and 24 SCA molecules were grafted on the aggregate surface. For titanate coupling agent (TCA), according to Ref.[19], TCA can bind to the filler surface through alkoxy fracture. Therefore, the product after grafting will have breakage on the aggregate surface. Moreover, two TCA molecules were grafted on the aggregate surface to ensure the comparability of the final two coupling agent simulation results. The aggregate surface after grafting the coupling agent molecules was shown in Fig.6.

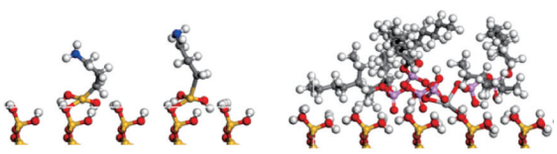


Fig.6 Schematic diagram of coupling agent molecular grafting

The build layer function in MS was employed to represent the interface between asphalt and aggregate subsequent to the modeling of both materials. The model representing the interface between asphalt and aggregate consists of four distinct layers, as depicted in Fig.7. The layered structure also consisted of four distinct layers. The initial layer was referred to as the aggregate layer. Following this, there was a vacuum layer with a thickness of 5 Å, which serves the purpose of emulating the contact behavior between asphalt and aggregate. The subsequent layer was the asphalt layer. Lastly, there was another vacuum layer with a thickness of 60 Å, which was implemented to prevent any potential interference between models along the z-axis direction. In the above procedure, contact models were made for three types of asphalt (matrix asphalt, non-amine anti-stripping modified asphalt, and amine anti-stripping modified asphalt) with silica, as well as for matrix asphalt with silica modified by two coupling agents (SCA and TCA). This resulted in a total of five asphalt aggregate models.

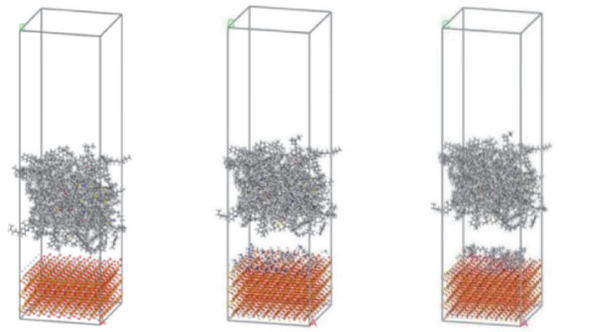


Fig.7 Asphalt-aggregate interface model

1.3 Molecular dynamics calculations

The energy optimization of the asphalt-aggregate interface model was conducted utilizing the Geometry Optimization tool inside the Forcite module of the MS program. The optimization process utilized the Smart method, with a maximum iteration step size of 5 000 steps, in order to minimize the energy of the model. The electrostatic forces were determined utilizing the Edwardian calculation approach, while the van der Waals were computed employing an atom-based calculation method, with a truncation radius of 15.5 Å.

Subsequently, the model underwent kinetic calculations within the framework of a constant temperature and constant volume (NVT) system. The force field utilized in this study was COMPASS Ⅱ. The temperature of the system was maintained at

438 K. The NOSE algorithm was employed for temperature management. The time step used in the simulations is set to 1 ps. The beginning velocities of the particles were assigned randomly. A series of kinetic calculations, spanning a duration of 500 ps (equivalent to 50 000 steps), were conducted. During this process, a frame was generated every 1 000 steps. The Edwardian calculation approach was employed to determine the electrostatic force, while the atom-based calculation method was utilized for the van der Waals.

2 Analysis and Discussion of Results

Based on five asphalt-aggregate interface models, molecular dynamics simulations were carried out to investigate the mechanism of action of anti-stripping agents and coupling agents, and the simulation results were analyzed.

2.1 Analysis of interaction energy

The aggregate system comprising asphalt possesses a total potential energy that can be categorized into two components: Valence energy and non-bonding energy. Among these forces, the non-bonding energy encompasses the van der Waalss and the electrostatic attraction. The evaluation of the adhesion between asphalt and aggregate can be conducted by assessing the interaction energy. The equation used to determine the interaction energy for the asphalt-aggregate contact model is as follows

$$E_{\text{as-ag}} = E_{\text{total}} - \left(E_{\text{as}} + E_{\text{ag}}\right) \tag{1}$$

where $E_{\text{as-ag}}$ represents the interaction energy between asphalt and aggregates, E_{total} the total energy of the asphalt-aggregate interface system, E_{as} the energy of the asphalt layer, and E_{ag} the energy of the asphalt layer.

The final estimate for the interaction energy in the asphalt-aggregate interface model was determined by averaging the values obtained from the last five frames of kinetic calculations, which were conducted over a duration of 500 ps. Fig.8 displays the interaction energy pertaining to the five interface models between asphalt and aggregate. It shows a graphical representation where the horizontal axis represents five distinct categories of asphalt-aggregate interaction models. Within the set of models, the designation a1-s refers to the matrix asphalt-silica interface model. Similarly, a2-s represents the NASA modified asphalt-silica interface model, while a3-s corresponds to the ASA modified asphalt-silica interface model. Furthermore, a1-s(sca) signifies the matrix asphalt-SCA modified silica interface model, and a1-s(tca) designates the matrix asphalt-TCA modified silica interface model. The vertical axis represents the energy level. The provided figure illustrates the interaction energy through a line graph, while the two components of the interaction energy are represented by a bar graph. Specifically, the van der Waals and the electrostatic attraction are denoted by the green and orange hues, respectively.

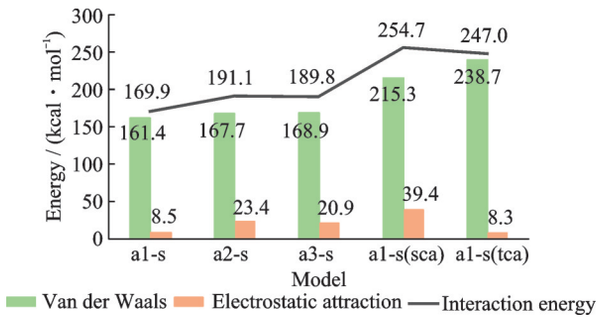


Fig.8 Interaction energy from MD simulations

The contact energy between asphalt and aggregate was raised by both the non-amine anti-stripping agent modified asphalt and the amine anti-stripping agent modified asphalt, as depicted in Fig. 8. The enhancement percentages of the two variables were 12.5% and 11.7%, respectively. The incorporation of an anti-stripping agent into the system primarily led to an augmentation of electrostatic attraction, hence enhancing the interaction energy. Both the SCA-modified aggregate and TCA-modified aggregate approaches demonstrated improved adhesion between asphalt and aggregate. The enhancement ratios of the interaction energy were found to be 49.9% and 45.4% for the SCA and TCA approaches, respectively. In the case of the SCA-modified interface, there was a notable augmentation in the van der Waals, accompanied by a conspicuous enhancement in electrostatic attraction. Conversely, for the

TCA-modified interface, the primary factor contributing to the rise in interaction energy was the amplification of the van der Waals.

2.2 Analysis of relative concentration distribution

This study explored the process by which anti-stripping compounds enhance the interaction energy at the interface between asphalt and aggregate, focusing on the distribution of relative concentration. Fig.9 illustrates the comparative concentration distribution of anti-stripping agent molecules prior to and subsequent to a kinetic simulation.

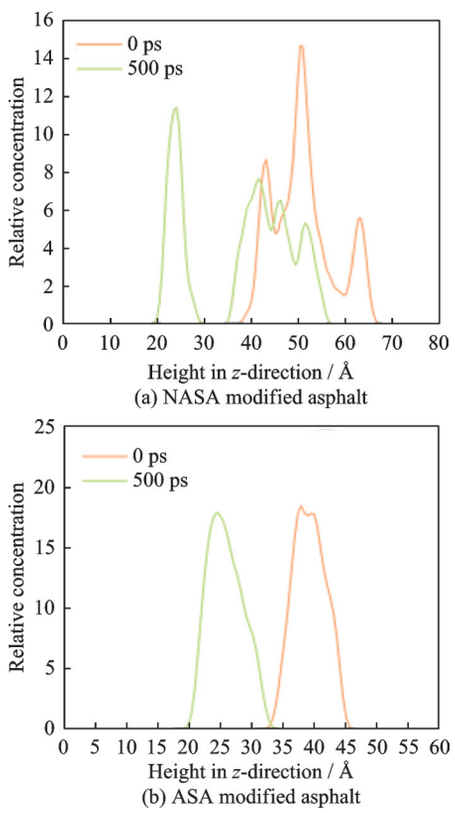


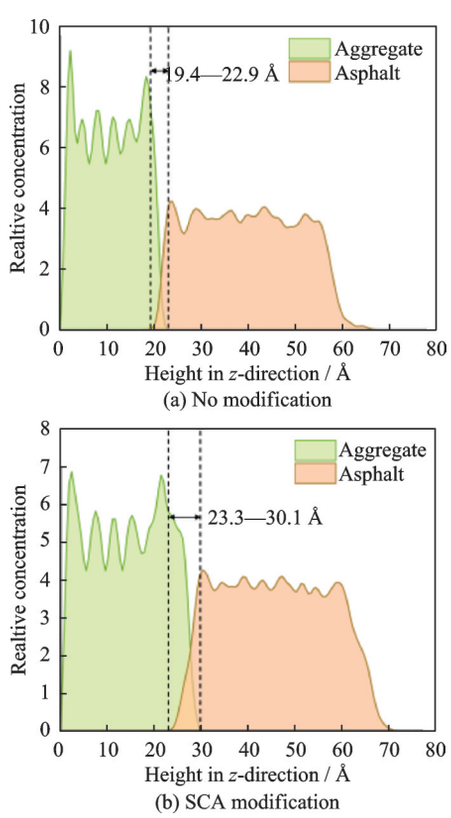
Fig.9 Molecular relative concentration distribution of anti stripping agents

The movement of NASA molecules towards the aggregate surface and their interaction with it during the kinetic simulation are evident in Fig. 9 (a). The interaction energy between the NASA and the aggregate was computed individually in MS. The electrostatic attraction between them was determined to be 17.0 kcal/mol, constituting approximately 72.6% of the overall electrostatic attraction.

Fig.9(b) displays the comparative distribution of ASA molecules in terms of concentration prior to and subsequent to kinetic simulation. In a similar manner, the molecules of the ASA exhibited a progressive migration towards the surface of the aggregate and engaged in interactions with it throughout the kinetic simulation. The calculation of the interaction energy between the amine anti-stripping agent and the aggregate was conducted in MS. The electrostatic attraction between them was determined to be 12.2 kcal/mol, which constituted approximately 58.4% of the overall electrostatic attraction.

As depicted in Fig.9, the kinetic simulation procedure revealed a gradual approach of anti-stripping agent molecules towards the aggregate. This approach led to an augmentation in the electrostatic attraction between the asphalt and aggregate, thereby enhancing the interaction energy between the two entities. This enhancement was achieved through the interaction of polar groups present in the anti-stripping agent with the surface of the aggregate.

The determination of the size of the transition zone between asphalt and aggregate is reliant on the relative concentration of both materials along the z-direction within the contact region, as visually depicted in Fig.10. There is observable variation in the



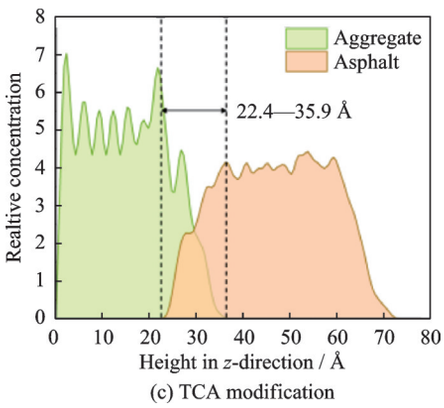


Fig.10 Relative concentration of transition layer for different asphalt-aggregate interfaces

thickness of the interfacial transition zone among different asphalt particles. In the unaltered interface, the interfacial transition zone spanned a distance of 19.1 Å to 22.9 Å. The measurement of the transition zone's thickness yields a value of 3.8 Å, primarily attributed to the interplay between the hydroxyl groups present on the aggregate surface and the asphalt material. In the case of the SCA-modified interface, the transition zone exhibits a thickness of 6.8 Å. This increase in thickness can be attributed to the presence of SCA molecules on the aggregate surface, which penetrated into the asphalt and established interactions with the asphalt molecules. Consequently, the interaction energy was enhanced, leading to the expansion of the transition zone. On the other hand, the TCA-modified interface displayed a larger transition zone thickness of 13.5 Å compared to the SCA-modified interface. This disparity can be primarily attributed to the larger physical dimensions and longer branched chain length of the TCA molecules. The primary factor contributing to this phenomenon was the comparatively larger size of TCA molecules, coupled with the longer length of their branched chains. The increased thickness of the transition zone leads to enhanced van der Waals at the interface between asphalt and aggregate treated with TCA.

This study presented a model for the asphalt-aggregate interface, which can be utilized in molecular dynamics simulations to investigate the impact of various anti-stripping agents and coupling agents on the adhesion properties of the asphalt-aggregate interface. Through the employment of molecular dynamics simulations, the study examined interaction energies, relative concentration distributions, and other relevant parameters to elucidate the underlying mechanism by which the anti-stripping agents and coupling agents enhanced the adhesion properties of the asphalt-aggregate interface.

3 Conclusions

This study utilized the molecular dynamics simulation technique to develop molecular models for the asphalt-aggregate interface. The objective was to investigate the impact of various anti-stripping agents and coupling agents on the adhesive properties of the asphalt-aggregate interface. By analyzing parameters including interaction energy and relative concentration distribution, the improvement mechanism of these agents on the interface was elucidated. Results can be summarized as follows:

(1) The molecular dynamics simulation approach to establish five distinct models representing the asphalt-aggregate interface was proposed. These models encompassed the matrix asphalt-silica interface, NASA modified asphalt-silica interface, ASA modified asphalt-silica interface, matrix asphalt-SCA modified silica interface, and the matrix asphalt-TCA modified silica interface. The rationality of these models was assessed by examining the density and glass transition temperature.

(2) The enhancement mechanism of anti-stripping agents on the adhesion performance of the asphalt-aggregate interface can be explained as follows: The presence of polar groups within the anti-stripping agent molecule facilitated interaction with the surface of silica aggregates. This interaction led to an improvement in the electrostatic attraction between the asphalt and aggregates, ultimately resulting in enhanced adhesion between the two. Additionally, it had been observed that the non-amine anti-stripping agent exhibited a superior modification effect on the asphalt-aggregate interface compared to the amine anti-stripping agent.

(3) The advancement mechanism of a coupling agent on the adhesion performance of the asphalt-aggregate interface can be described as follows: By

grafting coupling agent molecules onto the surface of the aggregate, the thickness of the transition zone at the asphalt-aggregate interface was increased. This resulted in an improvement in the van der Waals between the asphalt and aggregate, ultimately enhancing the adhesion between them. Furthermore, it had been observed that the silane coupling agent possessed a more effective modification effect compared to the titanate coupling agent.

(4) Results derived from the molecular simulation indicated that the approach of grafting a coupling agent onto the surface of the aggregate suggested greater efficacy compared to the way of altering asphalt with an anti-stripping agent. Therefore, the molecular model and calculation approach for the asphalt-aggregate interface proposed in this study can effectively investigate the impact of various anti-stripping agents or coupling agents on the adhesive characteristics of said interface.

References

[1] YIN Y, CHEN H, KUANG D, et al. Effect of chemical composition of aggregate on interfacial adhesion property between aggregate and asphalt[J]. Construction and Building Materials, 2017, 146: 231-237.

[2] MILLER J S, BELLINGER W Y. Distress identification manual for the long-term pavement performance program: FHWA-HRT-13-092[R]. United States: Federal Highway Administration, Office of Infrastructure Research and Development, 2003.

[3] KAKAR M R, HAMZAH M O, VALENTIN J. A review on moisture damages of hot and warm mix asphalt and related investigations[J]. Journal of Cleaner Production, 2015, 99: 39-58.

[4] LU Y, WANG L. Nano-mechanics modelling of deformation and failure behaviours at asphalt-aggregate interfaces[J]. International Journal of Pavement Engineering, 2011, 12(4): 311-323.

[5] LU Y, WANG L. Nanoscale modelling of mechanical properties of asphalt-aggregate interface under tensile loading[J]. International Journal of Pavement Engineering, 2010, 11(5): 393-401.

[6] YAO H, DAI Q, YOU Z. Investigation of the asphalt-aggregate interaction using molecular dynamics[J]. Petroleum Science and Technology, 2017, 35(6): 586-593.

[7] XU G, WANG H. Study of cohesion and adhesion properties of asphalt concrete with molecular dynamics simulation[J]. Computational Materials Science, 2016, 112: 161-169.

[8] NAZIRIZAD M, KAVUSSI A, ABDI A. Evaluation of the effects of anti-stripping agents on the performance of asphalt mixtures[J]. Construction and Building Materials, 2015, 84: 348-353.

[9] PARK D W, SEO W J, KIM J, et al. Evaluation of moisture susceptibility of asphalt mixture using liquid anti-stripping agents[J]. Construction and Building Materials, 2017, 144: 399-405.

[10] CUI B, WANG H. Molecular interaction of asphalt-aggregate interface modified by silane coupling agents at dry and wet conditions[J]. Applied Surface Science, 2022, 572: 151365.

[11] LI J, ZHANG A Q. Surface modification research for asphalt mixture filler[J]. Applied Mechanics and Materials, 2012, 174: 821-825.

[12] CHEN W, CHEN S, ZHENG C. Analysis of micromechanical properties of algae bio-based bio-asphalt-mineral interface based on molecular simulation technology[J]. Construction and Building Materials, 2021, 306: 124888.

[13] BAO C, ZHENG C, XU Y, et al. Role of rejuvenator properties in determining the activation effects on aged asphalt based on molecular simulations[J]. Journal of Cleaner Production, 2023, 405: 136970.

[14] PAULI A T, MIKNIS F, BEEMER A, et al. Assessment of physical property prediction basedon asphalt average molecular structures[J]. Preprints-American Chemical Society Division of Petroleum Chemistry, 2005, 50(2): 255-259.

[15] LI D D, GREENFIELD M L. Chemical compositions of improved model asphalt systems for molecular simulations[J]. Fuel, 2014, 115: 347-356.

[16] WANG D, FALCHETTO A C, RICCARDI C, et al. Investigation on the low temperature properties of asphalt binder: Glass transition temperature and modulus shift factor[J]. Construction and Building Materials, 2020, 245: 118351.

[17] LUO L, CHU L, FWA T F. Molecular dynamics analysis of moisture effect on asphalt-aggregate adhesion considering anisotropic mineral surfaces[J]. Applied Surface Science, 2020, 527: 146830.

[18] ZHAO Y, QI X, MA J, et al. Interface of polyimide-silica grafted with different silane coupling agents: Molecular dynamic simulation[J]. Journal of Applied Polymer Science, 2018, 135(4): 45725.

[19] LI H L, DONG B, HAN Y A, et al. The coupling mechanism and research progress on titanate coupling agents[J]. Surface technology, 2012, 41: 99-102.

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Authors Mr. **SONG Jing** received his B.S. degree from Nanjing University of Aeronautics and Astronautics (NUAA) in 2021 and is currently pursuing his M.S. degree at the School of Civil Aviation, NUAA. His current research focuses on asphalt and materials.

Prof. **XIE Jianguang** is currently a full professor at the School of Civil Aviation, NUAA, and his main research interests are in asphalt roadways, including drainage asphalt pavement, recycled asphalt pavements, and new materials for asphalt roadways.

Author contributions Mr. **SONG Jing** designed the study, developed the model and wrote the manuscript. Prof. **XIE Jianguang** participated in the discussion and revision of this study. Miss **DAI Zexinyu** participated in the experimental analysis. All authors commented on the manuscript draft and approved the submission.

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基于分子动力学的抗剥落剂及偶联剂对沥青-集料界面黏附性能改善机理

宋璟, 解建光, 戴泽昕煜

(南京航空航天大学民航学院, 南京 211106,中国)

摘要:研究了两种抗剥落剂和两种偶联剂对沥青-集料界面黏附性能改善机理。基于分子动力学(Molecular dynamics,MD),分别研究了不同沥青-集料界面的接触行为;采用相互作用能、相对浓度分布等参数,揭示抗剥落剂及偶联剂对沥青-集料界面改善机理。结果表明:抗剥落剂和偶联剂均能提高沥青-集料界面的黏附力,其中抗剥落剂主要通过提升静电吸引力来增加黏附力,偶联剂主要通过提升范德华力来增加黏附力。因此,本文提出的分子动力学建模及计算方法可用于揭示抗剥落剂及偶联剂对沥青-集料界面改善机理。

关键词:沥青-集料界面;黏附性能;抗剥落剂;偶联剂;分子动力学