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Chemo-physical characterization and molecular dynamics simulation of long-term aging behaviors of bitumen

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ABSTRACT

To further explore the long-term aging behaviors of bitumen from the multiscale perspectives, the experimental characterization and molecular dynamics (MD) simulation methods were performed. Series of chemical properties for the virgin and various aged bitumen were evaluated using the TCL-FID, ATR-FTIR, Elemental analysis and GPC tests. The molecular models of virgin and aged bitumen were established firstly, and the influence of long-term aging on the thermodynamics properties was predicted from the MD simulation results. The experimental results revealed that with the aging degree deepened, the resin and asphaltene fractions both increased dramatically, which resulted in the increment of average molecular weight and the more uneven molecular weight distribution in aged bitumen. Moreover, the aging of bitumen led to the increase of the oxidized functional groups (C═O and S═O) index, oxygen content, aromaticity and polarity, while the carbon, hydrogen element contents and the H/C ratio reduced. The density values from MD simulation agreed well with the experimental results, which significantly validated the reliability of molecular models for the virgin and different aged bitumen binders. The MD simulation results demonstrated that the long-term aging remarkably improved the cohesive energy density, solubility parameter and activation energy, however it deteriorated the surface free energy, work of cohesion and self-diffusion coefficient of the bitumen molecular system. This study develops the molecular models of virgin and aged bitumen with different long-term aging degrees, and provides a fundamental understanding regarding the influence of long-term aging influence on the chemo-physical and thermodynamic properties of bitumen.

1. Introduction

It is estimated that the current world use of bitumen is approximately 102 million tons per year due to its superior engineering performance and comfortability. The asphalt mixture is composed of the aggregate, sand, filler, bitumen binder and air voids. The asphalt pavement is exposed to the complex environment with the various atmosphere temperature and loading conditions, which accelerates the diseases occurrence of asphalt roads, such as the rutting deformation, thermal and fatigue cracking [1–3]. Lots of modifiers have been proposed to improve the rutting, adhesion, and cracking resistance of bitumen binder, such as the styrene-butadienestyrene copolymer, nano-caly, carbon black, nano-silica and other nanomaterials [4–9]. Apart from the external factors, the aging phenomenon of bitumen is the internal cause of performance deterioration [10]. These diseases greatly shorten the service life of asphalt pavement, and increase the cost of reconstruction and maintenance. Moreover, a large amount of reclaimed asphalt pavement (RAP) waste material are produced [11,12]. It was reported that the aging degree of bitumen significantly affected the selection of rejuvenators type and dosage, which was directly associated with the performance restoration of RAP material [13]. Therefore, before rejuvenation, the fully understanding on the aging mechanism of bitumen is of the significance, especially for its long-term aging behaviors.

A lot of work has been conducted to investigate the aging behaviors of bitumen with the mechanical measurements, microscale morphological analysis, chemical and physical properties characterizations [14,15]. From the perspective of material composition, the bitumen is separated into four-groups fractions according to the difference of molecular weight as well as polarity, which are the Saturate S, Aromatic A,

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Resin R and Asphaltene A_s (called the SARA fractions). It was reported that these four fractions contributed to the colloidal structure of bitumen, where the asphaltene molecules as the colloidal core part is distributed in the maltene phase. It was also proved that the ratio of SARA fractions showed a significant influence on the rheological and mechanical properties of bitumen [16]. During the aging process of bitumen, the saturate and aromatic fractions decrease gradually, while the resin and asphaltene heavy components increase. At the same time, the asphaltene clusters in aged bitumen start to agglomerate due to the lower dispersion ability of the maltene phase, which is related to the higher stiffness and viscosity of the binder. In addition, the oxidation reaction of different molecules is the main aging mechanism of bitumen, and it would significantly accelerate the formation of polar functional groups, such as the carbonyl C═O and sulfoxide S═O chemical groups [17,18]. To sum up, the aging of bitumen would result in the ratio changes of SARA compositions and microstructures of various molecules. Hence, the aging behavior of bitumen remarkably influences the service life of asphalt pavements, and the comprehensive understanding of bitumen aging mechanism would be beneficial to optimize the appropriate rejuvenator for the recycling technology of reclaimed asphalt pavement [11–13]. However, the long-term aging mechanism of bitumen at the nanoscale is still not clear, and series of extensive experimental tests are required to assess the aging influence on the chemical, thermodynamics and mechanical properties of bitumen binder during its service life.

Currently, the multiscale methods for exploring the effects of modification, aging or rejuvenation on the properties of bitumen [19] or bitumen-aggregate interfacial systems [20,21] from the microscale to macroscale perspectives have attracted researchers' attentions dramatically. As shown in Fig. 1, asphalt binder and mixture are both composed of different types of molecules, and their macroscale performance is essentially determined by the microstructure, thermodynamics properties and nanoscale molecular interactions [22]. Molecular dynamics (MD) simulation is an effective method to predict the physical and mechanical properties of complex molecular systems, design proper advanced materials, as well as verify and explain the experimental results from the viewpoints of molecular interaction and microstructure. Previous studies demonstrated that MD simulation was a useful supplementary technology to further insight into the modification and rejuvenation mechanisms of bitumen binder [23–25]. Zhang et al. employed the MD simulation to verify the positive role of an anti-stripping agent on improving the cohesive, adhesive and moisture damage resistance of bitumen, and found that the improvement mechanism was due to the formation of hydrogen bonding between bitumen and anti-stripping agent molecules [26]. Su et al. investigated the effects of Nano-ZnO/SBS modifiers on the physical properties and molecular structure of bitumen through the MD simulation method, and clarified that the adequate high-temperature properties and durability of the modified binder was associated with the facilitation function of these two materials on accumulating the molecular interaction and structural tightness in bitumen system [27]. Besides, Cui et al. implemented the MD simulation to evaluate the rejuvenator effects on aged bitumen at the microscale level, and concluded that the addition of rejuvenator would not only be beneficial to improve the cracking and moisture resistance, but also mitigate the self-aggregation of asphaltene molecules and restore the colloidal structure of aged binder [28].

At the same time, MD simulation technology has been widely utilized to explore the aging mechanism as well as its influence on the molecular structures and thermodynamics properties of bitumen. Li and Greenfield proposed the 12-components molecular models to represent the SARA fractions of bitumen, and the corresponding molecular model of virgin bitumen was used to predict its thermodynamics properties, which is the most-common molecular model selected for bitumen [29,30]. Regarding the aging reaction mechanism, Hu et al. conducted the MD simulation method with a ReaxFF force-field to explore the potential oxidation reactions during the aging of bitumen [31]. And the results revealed that the aging oxidation accelerated the formation of polar functional groups, such as the ketones and sulfoxide groups, which led to the deterioration of rheological properties and compatibility of bitumen. These simulation results were also found in the simulation study by Yang et al, which further reported that the sulfoxide was formed earlier than the ketone, and the high temperature and oxygen dosage would accelerate the formation of polar groups [32]. Liu et al. ran the MD simulation and validated the existence of aging gradient along with the layer depth due to the concentration gradient of oxygen in the bitumen [33]. Based on the chemical characteristics of the aging products and basic 12-components molecular model of virgin bitumen, the molecular models of short-term and long-term aged bitumen were established in a way of introducing oxygen atoms to form the polar carbonyl and sulfoxide groups as well as adjusting the SARA fractions distribution. The aging influence on the thermodynamics properties and molecular structure of bitumen could be predicted by the MD simulation. It is summarized that the aging would significantly increase the binder density, viscosity, modulus and agglomeration potential of bitumen, which is associated with the forceful molecular interactions between the additional polar molecules [34–36].

However, the research gaps regarding the application of MD simulation technology in the field of bituminous binder still exist. The common-used 12-components molecular models of SARA fractions for virgin bitumen did not consider the existence of the sulfoxide groups [37–39]. Moreover, the current molecular models for aged bitumen were established empirically, and the effects of long-term aging degree on the molecular structure and material composition have not been studied yet. Further, the MD simulation method is essential to explain the long-term aging mechanism and predict the important thermodynamics properties of aged bitumen from the viewpoint of nanoscale, which is difficult to implement with the macroscale experiments. Therefore, this study will develop the molecular models of virgin and different aged bitumen according to their chemical characteristics. Additionally, the molecular models will be verified with the physical properties from laboratory experiments. Further, other important parameters regarding the bulk, interfacial and dynamic properties will be

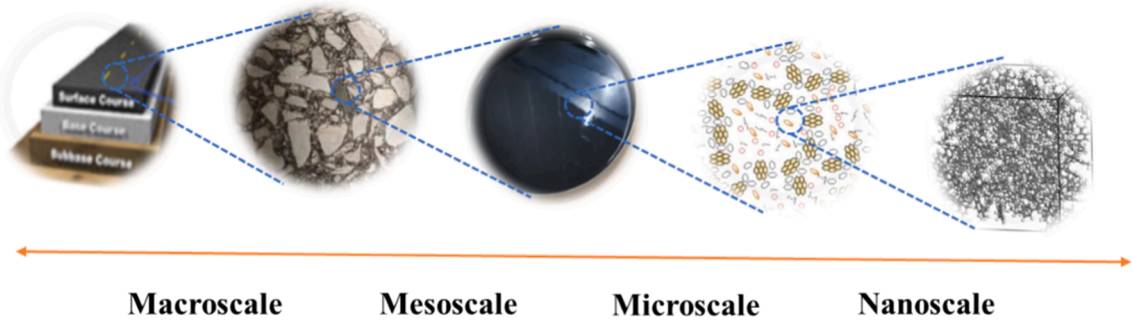


Fig. 1. Multiscale illustration of asphalt materials.

predicted to further fundamentally understand the long-term aging behaviors of bitumen from the perspective of thermodynamics performance.

2. Research objective and protocol

This study aims to investigate the influence of long-term aging of bitumen on the chemical and thermodynamic properties, which are strongly related to the rheological and mechanical performance. To achieve the objective, the experimental and molecular dynamics simulation methods are incorporated. The detailed research protocols are shown in Fig. 2. The molecular models of virgin and different aged bitumen will be established in line with their corresponding chemical properties, including the SARA group constituents, chemical functional groups, elementary composition and molecular weight distribution. Afterwards, MD simulation will be employed to study the effects of long-term aging on the thermodynamic properties of bitumen, which will be further compared with the experimental results. Lastly, the long-term aging mechanism at the molecular level will be explored.

3. Materials and characterization methods

3.1. Material and samples preparation

In this study, one PEN70/100 bitumen from Total Nederland N.V. was used. The physical properties and chemical components of virgin bitumen are shown in Table 1.

In order to understand the fundamental aging influence on the chemical and thermodynamic properties of bitumen binder, the fresh bitumen binder was subjected to short-term and long-term aging processes with different aging durations. In the study, the short-term aged bitumen binder was prepared by using the thin film oven test (TFOT) at

Table 1
The physical properties and chemical components of PEN 70/100 bitumen.

Properties		Value	Test standard
25°C Penetration (1/10 mm)		91	ASTM D5 [40]
Softening point (°C)		48	ASTM D36 [41]
135°C Dynamic viscosity (Pa•s)		0.8	AASHTO T316 [42]
25°C Density (g/cm^3)		1.017	EN 15326 [43]
60°C Density (g/cm^3)		0.996	
Chemical fractions (wt %)	Saturate, S	3.6	ASTM D4124 [44]
	Aromatic, A	53.3	
	Resin, R	30.3	
	Asphaltene, AsColloidal index CI	12.8	
Element compositions (wt%)	Carbon, C	84.06	ASTM D7343 [45]
	Hydrogen, H	10.91	
	Oxygen, O	0.62	
	Sulphur, S	3.52	
	Nitrogen, N	0.9	
Complex shear modulus at 1.6 Hz & 60°C (kPa)		2.4	AASHTO M320 [46]
Phase angle at 1.6 Hz & 60°C (°)		84.5	

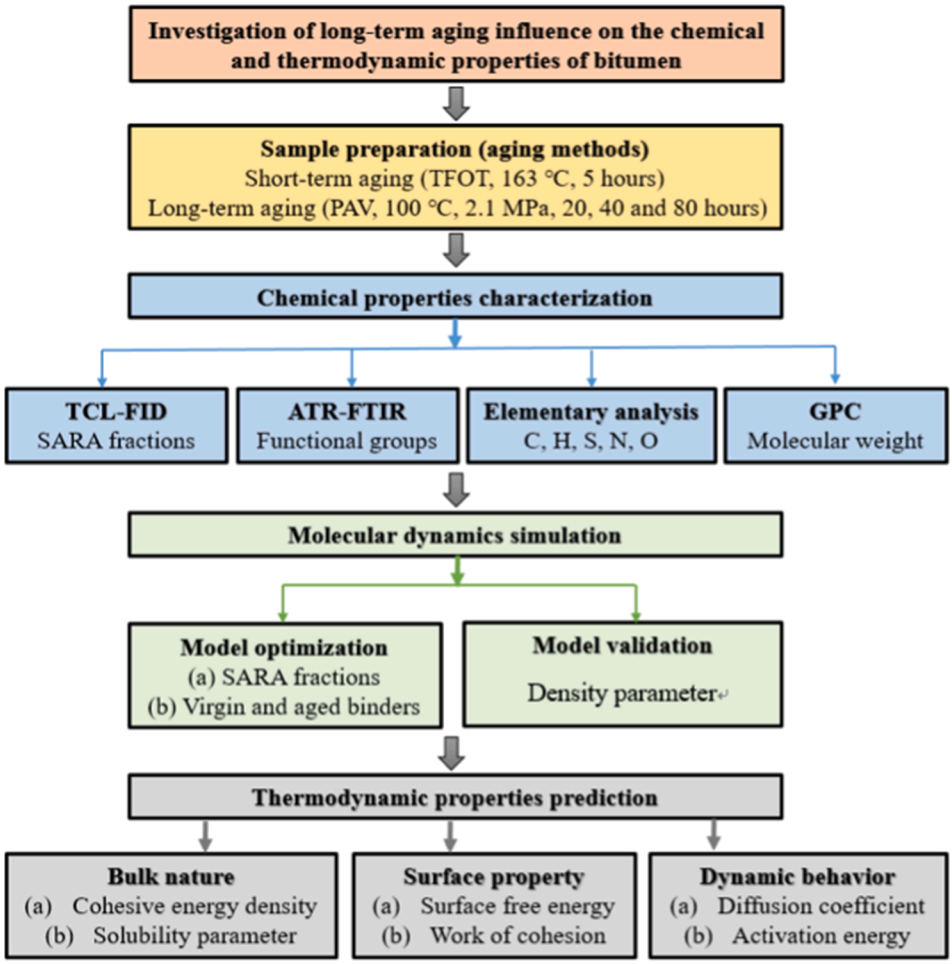


Fig. 2. The research protocol of this study.

163°C for 5 h, which were further transferred to the pressure aging vessel (PAV) device to manufacture the long-term aged binders under the temperature and pressure condition of 100°C and 2.1 MPa, respectively. The long-term aging durations for different aged bitumen binders were selected as 20, 40 and 80 h according to the aging degree of bitumen in the realistic reclaimed asphalt pavement [47,48]. For convenience, the virgin binder, short-aged and long-aged bitumen binders for 20, 40 and 80 h are abbreviated as the VB, SAB, LAB20, LAB40 and LAB80.

3.2. Experimental methods

3.2.1. Thin-layer chromatography with flame ionization detection (TLC-FID)

The TCL-FID method was carried out to measure the mass fractions of SARA components in virgin and aged bitumen with the hydrogen and air flow rate of 160 ml/min and 2 l/min, respectively. About 0.1 g of bitumen sample was dissolved in 10 ml toluene firstly, and the prepared solution was chromatography separated with a silica chrome rod. The fraction weight of saturate component was detected after using the chromatographical separation procedure in n-heptane, while the aromatic and resin fractions were determined in toluene/n-heptane (80:20) and dichloromethane/methanol (95:5) solvents, respectively. Finally, the asphaltene fraction, the heaviest component, was remained at the sampling spot.

3.2.2. Attenuated total reflectance-Fourier-transform infrared (ATR-FTIR) spectroscopy

The chemical functional group information of virgin and aged binders was detected by using the ATR-FTIR spectrometer from the PerkinElmer with a single-point ATR fixture (Waltham, MA, USA). The wavenumbers were set at the region of 600–4000 cm^{-1}. The bitumen sample was scanned 12 times with a fixed instrument resolution of 4 cm^{-1}. To ensure the accuracy of the result, three repetition tests were conducted for each sample.

3.2.3. Elemental analysis

The aging influence on the elemental compositions of bitumen was estimated with an elemental analyzer (Vario EL III, Elementar Corp., Germany). Before the test, the element composition of the reference substance sulfanilamide was examined to calibrate the accuracy of the elemental analyzer device. The 5–10 mg bitumen sample was put in tin capsules to measure the mass percentage of the carbon C, hydrogen H, oxygen O, nitrogen N as well as sulfur S elements.

3.2.4. Gel permeation chromatography (GPC)

In this study, GPC test was conducted to determine the molecular weight distribution of the virgin and different aged binders. The mobile solvent used was the tetrahydrofuran (THF), and the flow rate was selected as 1 ml/min. Before the GPC test, an appropriate 0.05 g bitumen binder was dissolved into the 10 ml THF solvent at 25°C. Then the solution was filtered through a syringe filter before injection. Each sample was measured at least for two times and the average molecular weight values of virgin and aged binders were calculated.

3.2.5. Pyknometer density measurement

To validate the MD simulation results, the density values of virgin and aged bitumen were measured. The capillary-stoppered pyknometer method was performed to determine the density values of bitumen binders at 25°C and 60°C according to the standard of EN 15326 [43].

4. Experimental results and discussion

4.1. Bitumen components

The four-components analysis method was implemented in this study to probe the influence of the short-term and long-term aging on the chemical material compositions of bitumen binders, which significantly influences the chemical, physical and mechanical properties as well as microstructure [37]. Fig. 3 shows the mass weight of the saturate, aromatic, resin and asphaltene fractions in virgin and aged bitumen. The total weight of aromatic and resin fractions in the virgin binder is more than 80 wt%, indicating that the internal colloidal structure of the bitumen shows more stable. Moreover, it can be found that the aging process has no obvious influence on the saturate content of bitumen, which is due to the saturated hydrocarbon structure of saturate with no heteroatom and less reaction potential to oxygen molecules. Thus, the conversion ratio of saturate constitution of bitumen is close to zero during the oxidation aging process. Meanwhile, as the aging degree increasing, the aromatic dosage of bitumen declines dramatically, while the concentration of both resin and asphaltene fractions increases gradually, which results in the physical hardening and colloidal structure instability of bitumen. In other words, the agglomeration of asphaltene nanoparticle in aged bitumen tends to increase, which contributes to the stiffness improvement and the crack phenomenon occurring easily for the aged binder.

In addition, the aging degree of bitumen has a remarkable influence on the mass weight of aromatic, resin and asphaltene fractions. In detail, the aromatic concentration decreases by 1.7%, 9.4%, 14.5% and 20.8%, when the bitumen is subjected to short-term aging and long-term aging 20, 40 and 80 h, respectively. Hence, the compensation of aromatic composition is the main way during the rejuvenation technology of aged binder in reclaimed asphalt pavement (RAP) materials. On the contrary, the corresponding asphaltene content increases by 1.8%, 5.8%, 7.9% and 12.6%, respectively. The increase of asphaltene fraction would reduce the relative distance of the asphaltene molecules and strengthen their molecular interaction, which accelerates the aggravation of the agglomeration phenomenon of asphaltene nanoparticle. It is well-recognized that the bitumen has the typical colloidal structure, where the asphaltene nanoparticle is regarded as the colloidal nucleus. Besides, the asphaltene components are surrounded by the resin fractions, which plays the key role of stabling the colloidal structure and preventing the further agglomeration of the asphaltene nucleus. From Fig. 3, it is illustrated that the short-term aging seems to have no influence on the resin fractions of bitumen, which increases obviously with the long-term aging time prolongs. In detail, the resin fraction weight of bitumen rises from 30.3% to 33.9%, 36.8% and 38.4%, when the long-term aging duration is 20, 40 and 80 h, respectively. In this study, the chemical fractions will be the input parameters of molecular models for the virgin and aged bitumen as the input parameters of following molecular dynamics simulation, which will be used for further investigation of the aging effects on the thermodynamic properties.

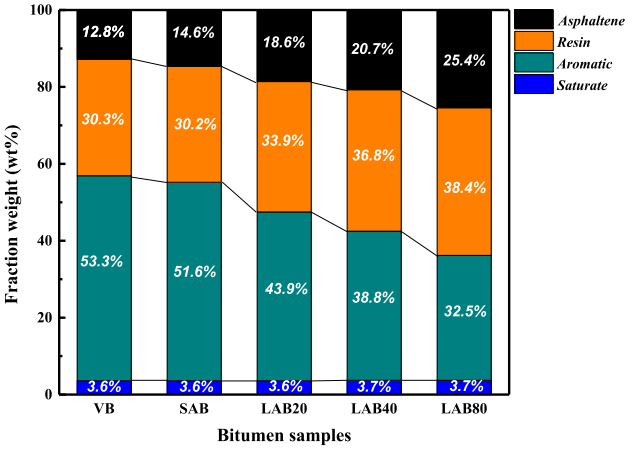


Fig. 3. SARA fractions of virgin and aged bitumen.

4.2. Chemical characteristics

The oxidation reaction is the main aging mechanism of the bitumen binder, which not only affects the SARA fractions distribution, but also alters the molecular structure of each component. Hence, the ATR-FTIR tests were conducted to monitor the chemical functional groups variability during the different aging conditions. Six repetitions of each sample were measured to ensure the accuracy of experimental results.

The FTIR spectra curves of virgin and aged bitumen samples are displayed in Fig. 4. Table 2 displays the main functional groups in bitumen. Regarding the functional groups' characteristics of fresh bitumen, the strong peak at 1030 cm^{-1} can be observed, which shows that the sulfoxide functional groups exist in the fresh bitumen. This finding will be considered during the establishment of molecular models for virgin bitumen. Compared to the virgin binder, aged bitumen shows the strong absorption peaks at 1030 cm^{-1} and 1700 cm^{-1}, which refers to the sulfoxide and carbonyl functional groups.

To quantitatively evaluate the influence of long-term aging on the functional groups' distribution of bitumen, the carbonyl index CI and sulfoxide index SI are calculated as follows [16].

$$\text{CarbonylindexCI} = \frac{A_{1700}}{\sum A} \tag{1}$$

$$\text{SulfoxideindexSI} = \frac{A_{1030}}{\sum A} \tag{2}$$

$$\sum A = A_{(2952,2862)} + A_{1700} + A_{1600} + A_{1460} + A_{1375} + A_{1030} + A_{864} + A_{814} + A_{743} + A_{724}$$

where A_{1700} and A_{1030} refer to the area value of absorption peak at the wavenumber point of 1700 cm^{-1} and 1030 cm^{-1}, respectively. Besides, $\sum A$ is the total area of absorption peaks presented in Fig. 4.

Fig. 5 shows the variations of carbonyl and sulfoxide indexes for virgin and aged bitumen with various aging conditions. It can be found that there is no carbonyl functional group observed in the fresh bitumen, which denotes that the carbonyl functional group is not sensitive to the short-term aging process. On the contrary, the sulfoxide index of virgin bitumen could be monitored, which increases after the short-term aging process. It domenstrates that the sulfoxide functional group exists in the fresh bitumen, which should be considered when the molecular models of bitumen are designed. Meanwhile, the sulfoxide index is invariably larger than the carbonyl index, regardless of the aging degree of bitumen, which may be attributed to the characteristic of the high sulfur concentration in virgin bitumen. This assumption will be validated with the elemental analysis results. In addition, both carbonyl index and sulfoxide index increase with the aging depth strengthens, which is associated with the oxidation and substitution reaction of bitumen aging.

Table 2
Main functional groups of virgin and aged bitumen.

Wavenumber (cm^{-1})	Chemical functional groups
2952 and 2862	Asymmetric and symmetric stretching vibrations of C—H on aliphatic hydrogen
1700	Stretching vibration of C═O group
1600	Stretching vibration of C═C on aromatic ring
1460	Bending vibration of C—H on methylene
1375	Bending vibration of C—H on methyl
1030	Stretching vibration of S═O group
864, 814 and 743	Bending vibration of C—H on the substituents on aromatic rings (One, two or three and four adjacent hydrogen atoms, respectively)

It is interesting to note that the sensitivity of carbonyl and sulfoxide index to the aging time is significantly different. From Fig. 5, the increasing rate of sulfoxide index is faster than carbonyl index in the short-term aging period. Moreover, the carbonyls start to form during long-term aging process and increase with aging time. In other words, the sulfoxides are generated earlier than the carbonyls, because the sulphur is more reactive than the carbon atom in bitumen. On the contrary, the carbonyls increase during long-term aging process, whereas the sulfoxide index stabilizes probably due to the full consumption of sulfur in bitumen. In conclusion, the sulfur oxidation reaction is easier to occur than the carboxylation, which agrees with the previous studies [16,32]. Fig. 6 displays the graphical illustration of main oxidation reactions, including the generation of carbonyl and sulfoxide functional groups. From the perspective of chemical bonding theory, the bond energy of the sulfoxide group (522 kJ/mol) is lower

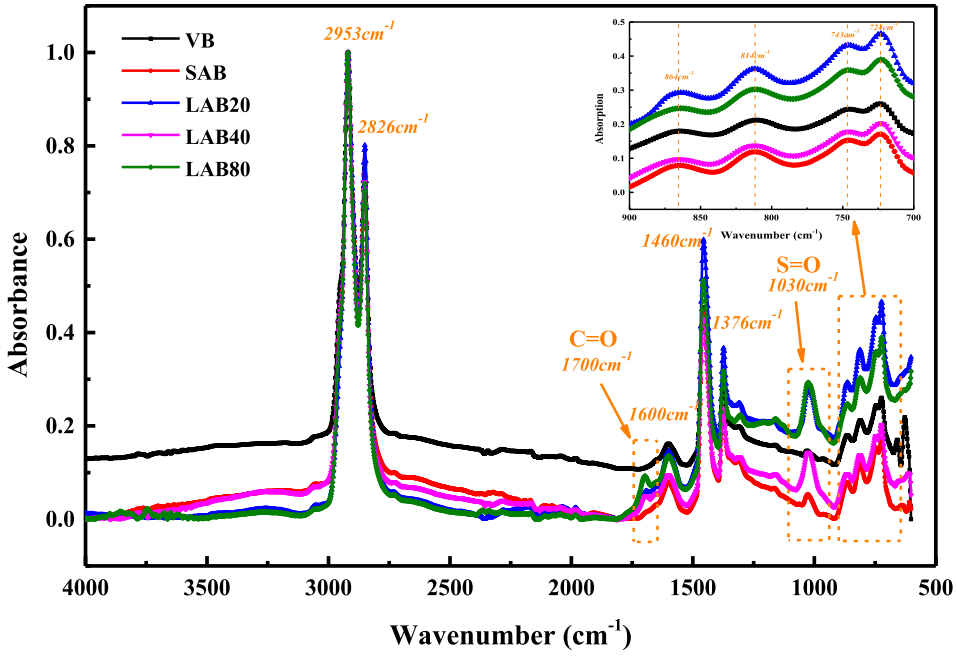


Fig. 4. The detailed FTIR spectra of virgin and aged bitumen.

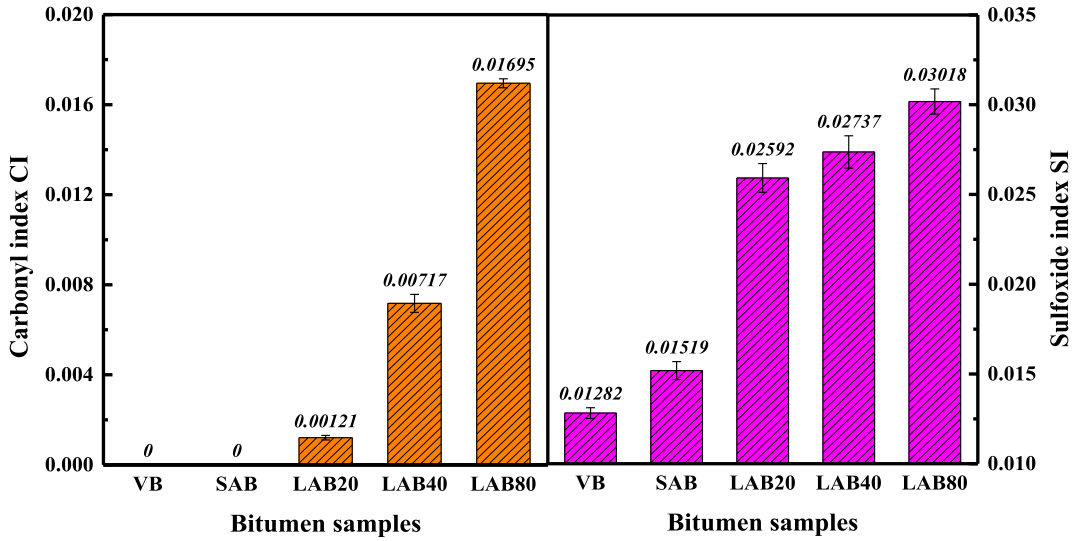


Fig. 5. The carbonyl index CI and sulfoxide index SI of virgin and aged bitumen.

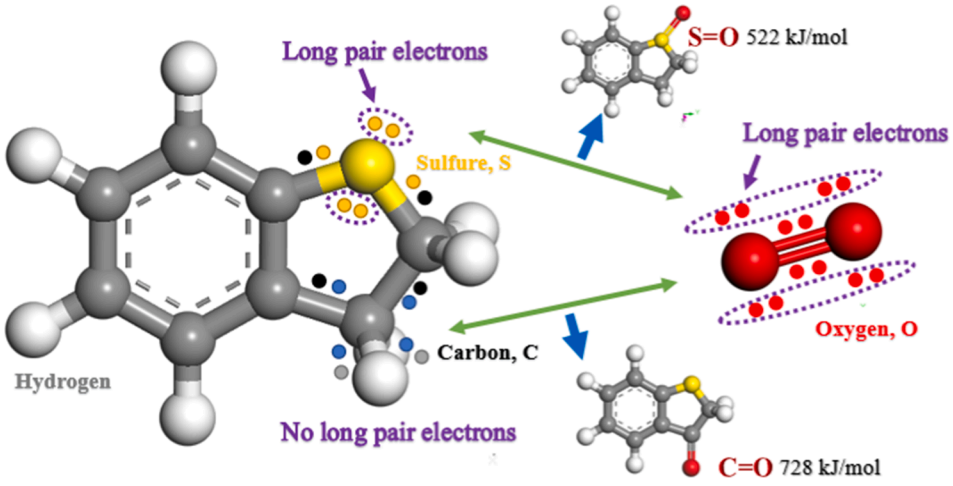


Fig. 6. The graphical illustration of the main reaction during the aging of bitumen.

than that of the carbonyl group (728 kJ/mol).

In addition, from the viewpoint of electronic interaction theory, the sulfur atom has two long-pair electrons, while the carbon atom has no long-pair electrons because all four electrons are occupied to form the covalent bonds with the two adjacent hydrogen and carbon atoms. Thus, it is easy for the sulfur atoms to react with the oxygen molecules and form the peroxide radical, followed by the formation of the sulfoxide functional group. That's why the sulfoxide function groups are easier to form than the carbonyl component. This result is in line with the previous literature [16,17,32], which revealed that the sulfoxide formation would occur earlier than the ketone group. Hence, the aging behavior and mechanism are closely related to the chemical components of virgin bitumen, especially for the sulfur element concentration.

4.3. Elemental analysis

It is well known that the bituminous material is manufactured from the crude oil refinery process, and their main elements contains the carbon C, hydrogen H and other heteroatoms, such as the sulfur S, nitrogen N and oxygen O as well as other heavy metal elements. Table 3 displays the element compositions of virgin and aged bitumen. Overall, the carbon content C% is in the majority, which is more than 80%. Furthermore, the hydrogen concentration H% is larger than 10% for all tested samples. Importantly, it should be mentioned that the sulfur dosage S% is about 3.5%, indicating that the bitumen comes from the high-sulfur crude oil and this result is consistent with the observation of the sulfoxide functional group in the fresh bitumen from the FTIR test. Therefore, the sulfur element cannot be ignored to improve the accuracy of molecular dynamics simulation results. For virgin bitumen, both nitrogen N% and oxygen concentration O% are lower than 1%.

Table 3
The element compositions of virgin and aged bitumen.

Bitumen samples	N (wt%)	C (wt%)	H (wt%)	S (wt%)	O (wt%)
VB	0.90	84.06	10.902	3.52	0.618
SAB	0.91	83.72	10.856	3.51	1.004
LAB20	0.92	83.26	10.748	3.49	1.582
LAB40	0.89	83.02	10.437	3.53	2.113
LAB80	0.91	82.14	10.098	3.54	3.312

It can be found in Table 3 that the aging of bitumen has no obvious influence on the nitrogen and sulfur concentration, which significantly affects the proportions of other elements. With the increase of aging degree, the carbon and hydrogen element contents both reduce, while the oxygen concentration increases dramatically. This indicates that the oxidation degree of the binder deepens gradually as the aging time

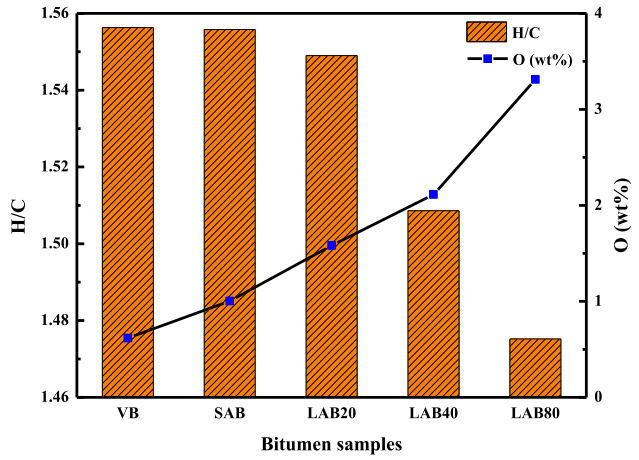


Fig. 7. The aging influence on the H/C ratio and oxygen content in bitumen.

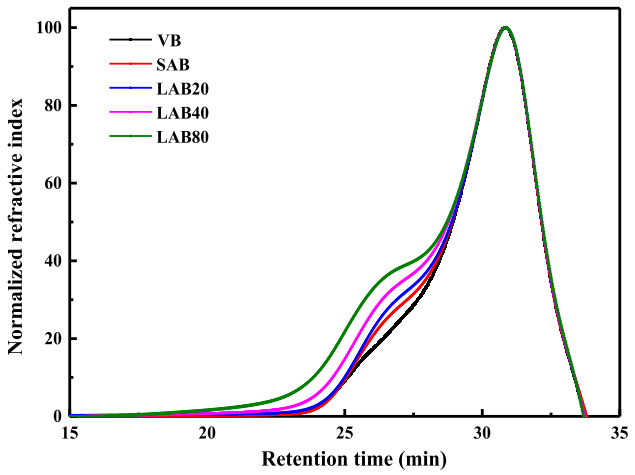


Fig. 8. The GPC results of virgin and aged bitumen.

increasing. To further assess the influence of aging on the molecular structure of bitumen, the ratio of H/C is calculated and shown in Fig. 7. Here, the H/C value refers to the ratio of hydrogen atom number (N_H) to carbon atom number (N_C), which is calculated as equation (3):

$$\frac{H}{C}=\frac{N_H}{N_C}=\frac{\frac{H\%}{M_H}}{\frac{C\%}{M_C}} \tag{3}$$

where H% and C% are the mass fraction of hydrogen and carbon element in bitumen; and M_H and M_c represent the molar weight of C and H atom, which are set as 1 g/mol and 12 g/mol, respectively.

The value of H/C ratio decreases remarkably with the increase of long-term aging time. Compared to the virgin bitumen, the H/C ratio value decreases from 1.556 to 1.475. This phenomenon reveals that the aging of bitumen would strengthen the degree of unsaturation and aromaticity. On the one hand, during the aging of bitumen, light constituents (aromatic fraction with low polarity) would transfer to the heavy components (resin and asphaltene fractions with high aromaticity). On the other hand, the oxidation reaction during bitumen aging would result in the proportion enhancement of the carbonyl and sulfoxide function groups, which increases the unsaturation degree. The phenomena have been validated by the FTIR results. Therefore, the aging mechanism of bitumen is the synergistic effect of components transforming and oxidation reaction. These chemical characterization results provide the data support and theoretical basis to the establishment of the molecular models of virgin and aged binders in following molecular dynamics simulation procedure.

4.4. Molecular weight distribution

From the stand point of polymer science, the molecular weight of material is closely associated with its thermodynamics and mechanical properties, such as the diffusion coefficient, viscosity, stiffness and etc. It is of great importance to track the influence of oxidation aging on the molecular weight distribution of bitumen, which provides the basis for determining the molecular models of aged binders with various aging levels. In this study, the weight-average molecular weight (M_w) and the number-average molecular weight (M_n) of bitumen binders were measured by using the GPC test, and the GPC curves are illustrated in Fig. 8. Previous studies reported that in GPC curve of bitumen, the first peak (3000–19,000 Daltons) refers to the asphaltene fraction, and the second peak (<3000 Daltons) represents the maltene fractions [15,18]. It is worth noting that aging has a great influence on the molecular weight distribution of bitumen, especially for the heavy fractions. With the aging degree deepens, the retention time of heavy fractions decreases, and the refractive index increases dramatically. It indicates that more heavy constituents are generated during the aging process of bitumen, which is related to the polymerization reactions of the light fractions and agglomeration of the heavy molecules. The GPC result is consistent with the SARA fractions distribution, which verifies the fraction conversion process from the light to heavy compositions and provides the essential basis for establishing of molecular models for aged bitumen with various aging degrees.

The number-average molecular weight M_n, weight-average molecular weight M_w, and the dispersion parameter of virgin and aged bitumen D, are calculated as follows:

$$M_w=\frac{\sum_{i=1}^{n} w_i \times M_i}{\sum_{i=1}^{n} w_i} \tag{4}$$

$$M_n=\frac{\sum_{i=1}^{n} N_i \times M_i}{\sum_{i=1}^{n} N_i} \tag{5}$$

$$D=\frac{M_w}{M_n} \tag{6}$$

where w_i and N_i refers to the weight and number of molar mass M_i, respectively.

The influence of aging on the molecular weight and dispersion value of bitumen are found in Table 4. With the aging degree deepening, the values of M_n and M_w of bitumen all strengthen. It is caused by the transformation from the aromatic fractions (light molecular weight and low polarity) into the resin/asphaltenes molecules (heavy molecular weight and high polarity). It is interesting to observe that the weight-average molecular weight is higher than the number-average molecular weight, which is attributed to the large difference in molecular weight distribution, especially for the saturate and asphaltene fractions. The molecular weight distribution difference could be estimated with the dispersion parameter (D), and the aging process significantly increases the D value of bitumen. Hence, it could be summarized that the increase of aging degree would result in the more uneven molecular weight distribution because of the increase of the heavy-weight molecules and decrease of the light-weight fractions. In addition, the D parameter could also be applied to assess the dispersion ability of

Table 4
The average molecular weight (Daltons) of virgin and aged binders.

Samples	Weight average molecular weight M_w	Number average molecular weight M_n	Dispersion parameter D
VB	3879	1290	3.01
SAB	4049	1310	3.09
LAB20	4773	1346	3.40
LAB40	5802	1400	4.15
LAB80	8210	1488	5.52

maltene to asphaltene, and the higher D value represents the lower dispersion ability of maltene. The aging of bitumen weakens the dispersion ability of maltene to asphaltene, while the agglomeration of asphaltene molecules and unstable colloidal structures would occur easily.

5. Molecular simulation methods

Before performing the molecular simulation program, the molecular model of studied matter is the most important input parameter. However, it is difficult to determine the exact molecular model of bitumen, because it is a complex material containing thousands of chemical matters. Different types of alkane, naphthenic hydrocarbon and aromatic hydrocarbon all exist in the bituminous materials based on the results from series of chemical characterizations.

5.1. Establishment of molecular models for virgin bitumen

In this study, the 12-components models of SARA fractions established by Li and Greenfield is adopted as the basis of molecular models for virgin and aged bitumen with different aging levels. As mentioned before, the sulfoxide functional groups exist in the selected bitumen in this study based on the FTIR results. However, this characteristic was not taken into consideration during the establishment of 12-components model. To accurately simulate the high-sulfur bitumen, the sulfoxide functional groups are supplemented in the molecular models of resin fractions, including the Benzobisbenzothiophere and the Thioisorenieratane, because only these two molecules have the sulfur atom. The detailed formation of the sulfoxide functional group is displayed in Fig. 9. Meanwhile, other ten molecular models of SARA fractions in the virgin bitumen keep the same to that in Greenfield's 12-components models. Fig. 10 shows the overall adopted molecular models of SARA fractions for the virgin bitumen in this study. To distinguish the molecular models of SARA fractions in the fresh bitumen and different aged binders, the superscript of "0″ is added into each molecular model of virgin bitumen.

5.2. Establishment of molecular models for different aged bitumen

According to the FTIR and elemental analysis results, it is denoted that aging has great effects on the functional groups and elemental components of bitumen. The oxidation aging of bitumen leads to the remarkable increase of the carbonyl and sulfoxide functional groups. At the same time, the oxygen element, degree of unsaturation and aromaticity of bitumen all show an increasing trend with the deepening of aging degree. Previous studies also revealed that the ketone and sulfoxide are the two main products during the aging of bitumen [49–51].

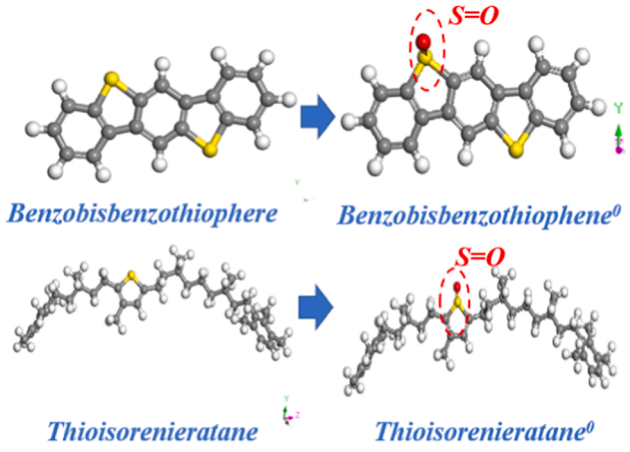


Fig. 9. The formation of the sulfoxide functional group.

Hence, researchers tried to add the carbonyl and sulfoxide functional groups into the fresh SARA fractions molecular structures of virgin bitumen to form the corresponding molecular models for aged bitumen. However, in these models, the carbonyl and sulfoxide functional groups were generated at all potential reaction positions in original molecular models to represent the molecular models for aged bitumen, without considering the influence of the long-term aging level on the molecular structures of aged bitumen.

In this study, different amounts of atomic oxygen were introduced to the molecular structures of the aromatic, resin and asphaltene fractions to represent the molecular structures of aged molecules with different long-term aging degrees. The formation of the oxidized molecules of SARA fractions is shown in Fig. 11, except for the saturate, which is insensitive to oxidation. Apart from the Benzobisbenzothiophene, Trimethylbenzeneoxane and Thiophene molecules, each molecule has two oxidation states, including the half-oxidized and full-oxidized structures. The superscripts of "1″ and "2″ are noted to distinguish the half- and full-oxidized molecules. In addition, there is only one potential oxidation reaction point (the formation of S═O or C═O) in the benzobisbenzothiophene and trimethylbenzeneoxane molecules, and they have no half-oxidized molecular structure. A previous study employed the reaction MD simulation and validated that the sulfoxide was formed earlier than the ketone because the oxygen atoms are more easily adsorbed around sulfur atoms [32]. Regarding the thiophene molecule, the sulfur atom is first oxidized to form sulfoxide, followed by the formation of carbonyl functional groups gradually. The subscript for different oxidized thiophene molecules is from "1″ to "4″, respectively, which rises with the increase of oxidation degree.

Fig. 12 summarizes all 12-components molecular models of SARA fractions for aged bitumen. Tables 5 and 6 list the detailed molecular information of virgin and oxidized molecules for SARA fractions, including the molecular formula, molar mass as well as the number of contained sulfoxide and carbonyl functional groups. The construction of the fresh and aged molecular models of SARA fractions provides the essential elements for constructing the molecular models of the virgin and aged bitumen with different aging degrees, which takes the influence of aging level on the molecular structure of bitumen components into consideration.

5.3. Simulation protocols

The aging behaviors not only influence the molecular structure but also affects the proportion of chemical components in bitumen dramatically. Due to the formation of polar functional groups and free radicals, the aromatic fractions transform to the resin and asphaltene components. The variation of material composition would markedly result in the change of physical and rheological properties of bitumen. In this study, when the virgin and oxidized molecular structures of SARA fractions are determined, the molecular models of virgin and different aged binders could be constructed with the chemical compositions from the SARA analysis results, discussed in section 4.1. Afterwards, the detailed SARA fractions constitution in the molecular models of the virgin, short-term aged, as well as 20, 40 and 80 h long-term aged bitumen, are listed in Tables 7-11, respectively. The SARA fractions in the molecular models of different binders agree well with the experimental results. Due to the integrity of the number of molecules, there is slight difference of SARA fractions distribution in the models and experimental results.

Furthermore, the amounts of ketone and sulfoxide functional groups in the MD simulation systems are calculated to further verify the rationality of molecular models for the virgin and aged binders, which are demonstrated in Fig. 13. Notably, for all bitumen binders, there are linear relationships between the amount of carbonyl and sulfoxide functional groups in the molecular models and the measured values from FTIR tests. Theoretically, the change rate of ketone and sulfoxide functional groups from the MD simulation models should be the same as

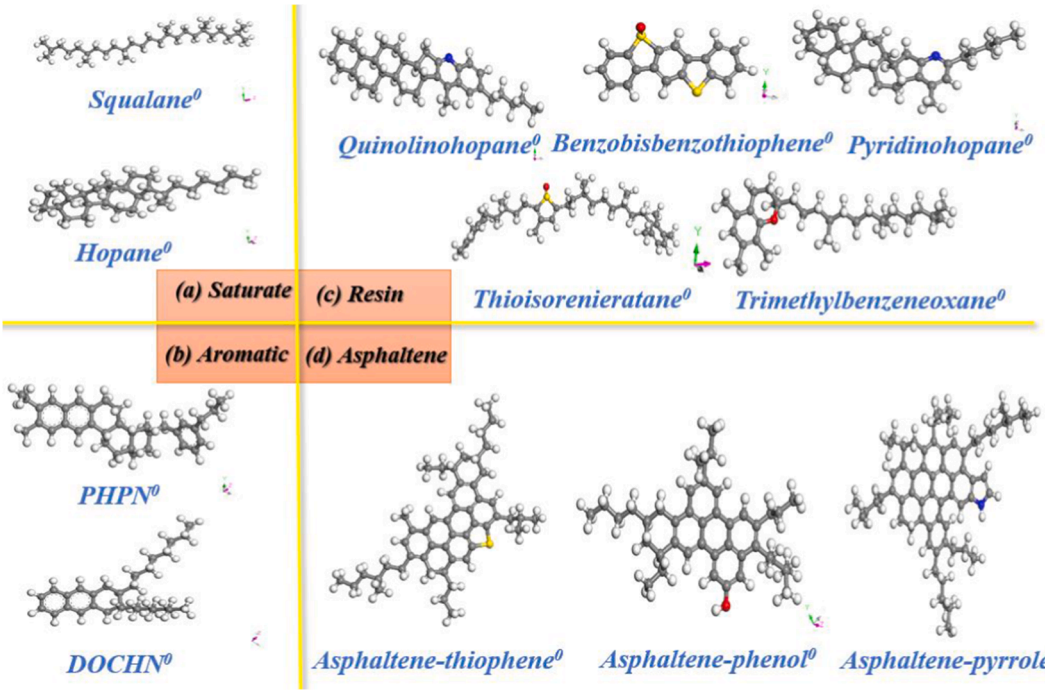


Fig. 10. The molecular models of SARA fractions for virgin bitumen.

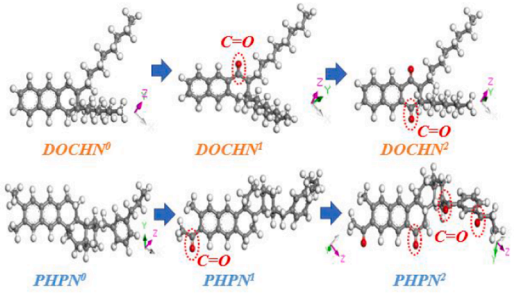
those realistic values in the bitumen. However, the FTIR test results only provide the related intensity of the specific peaks and it is difficult to determine the exact number of functional groups. Hence, the numbers of ketone and sulfoxide in simulation models of aged binders are determined based on the ratio of the carbonyl or sulfoxide indicators. That's why the slope values of the correlation equations between the ketone or sulfoxide number in the MD simulation model and carbonyl or sulfoxide index are not equal to 1.0. According to the linear correlation and FTIR test results, the number of polar functional groups in the molecular models of aged bitumen with an unknown aging degree could be determined.

In addition, Fig. 14 illustrates the correlation curves between the molecular weight values of virgin and aged bitumen models from MD simulation and GPC results. Theoretically, the average molecular weight in MD simulation should be close to the results from GPC tests. However, a significant difference between the MD model and GPC results could be found, and the average molecular weight in the MD model is lower than the experimental values. This phenomenon is associated with the types of initial molecular models of SARA fractions in virgin bitumen. The 12-molecules model from Li and Greenfield's work was chosen as the basis of MD simulation in this study, in which the molecular structures of bituminous molecules were simplified to meet the analog computing capability. For instance, the average molecular weight of asphaltene molecules in the MD model is approximately 900 g/mol. However, it was reported that the average molecular weight of asphaltene fraction was higher than 3000 Dalton from experimental results. In this study, a great linear relationship between the average molecular weight from the MD models and the GPC results for virgin and different aged binders is established. It indicates that the aging influence on the molecular weight of bitumen from the MD models and the GPC test results is similar. Moreover, compared with the weight-average molecular weight, the difference of number-average molecular weight in the molecular model and experimental result is lower. Based on the linear correlation, the average molecular weight of the molecular model for an aged bitumen with uncertain aging degree could be predicted with the GPC test results, which is also beneficial to build the molecular model of aged bitumen from reclaimed asphalt pavement (RAP).

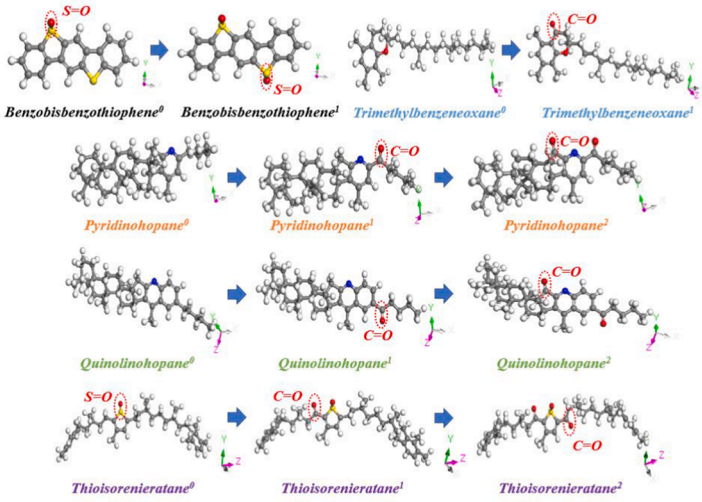
The molecular dynamics simulation procedure for the initial condition includes two stages, the energy minimization and the pre-equilibrium process. The geometry optimization of each molecule is conducted to search for the most stable configuration with the minimum energy. Afterwards, the molecular models of virgin and aged binders are established with the COMPASSII force field, which is the commonly-used force field used to describe the bitumen molecular interaction and has advantages in terms of precisely predicting the thermodynamics properties of bituminous materials. The detailed molecular interaction terms included in the COMPASSII force field could be found in previous literatures [28,36,39]. All molecules are put randomly in a cubic simulation box to obtain the initial bituminous molecular model with the incipient density of 0.1 g/cm^3, followed by the energy minimization to avoid the overlapping of atoms.

And then, the molecular dynamics simulation is performed to obtain the pre-equilibrium molecular models of virgin and aged bitumen under the isothermal-isobaric (NPT) and the canonical ensembles at 25°C for 200 picoseconds (ps), respectively. Each time step of 1 fs (fs) is selected. Moreover, the Andersen barostat and Nose thermostat are adopted to control the pressure and temperature condition during the MD simulation, respectively. Regarding the non-bond molecular interaction, the Van der Waals and electrostatic forces are considered and the Atom-based with a cut-off distance of 12.5 Å and Ewald method are implemented to calculate the two parts of potential energy.

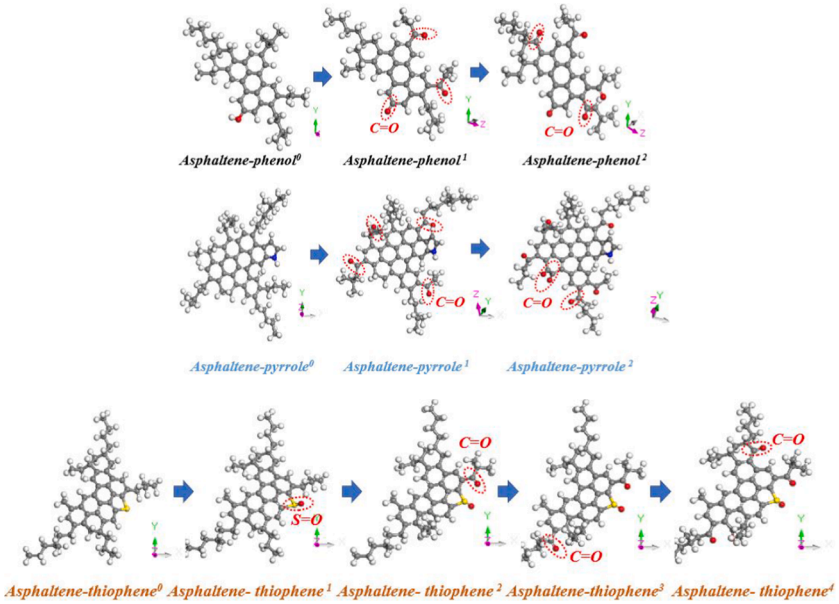
The final equilibrium configurations of the molecular models for the virgin, short-term aged and different long-term aged bitumen after the MD simulation procedure with the NPT and NVT ensembles are illustrated in Fig. 15. From these snapshots, the amount of oxygen atoms (displayed with red color) increases remarkably with the increase of aging degree. Fig. 16 demonstrates the density variety of the whole system as a function of MD simulation time at 293.15 K. As the initial density of all systems is set as 0.1 g/cm^3, the system volume would decrease with the combined influence of the external pressure and molecular interaction, which significantly compresses the system and increases the density. Hence, the density of the bitumen model raises dramatically at the beginning of simulation. When the simulation time exceeds 50 ps, the density values of all bitumen systems keep constant with a slight fluctuation, implying the formation of equilibrium molecular models. The important thermodynamics properties of the virgin and



(a) Virgin and oxidized aromatic molecules



(b) Virgin and oxidized resin molecules



(c) Virgin and oxidized asphaltene molecules

Fig. 11. The virgin and oxidized molecules for aromatic (a), resin (b), and asphaltene (c).

aged binders could be outputted according to the trajectory of molecules and the whole molecular system during MD simulation. Additionally, as the aging depth increases, the density of bitumen markedly strengthens. That is due to the increase of heavy components with high molecular weight and improvement of molecular interaction with the incorporation of polar groups.

6. Validation of MD simulation results

The reasonability of MD simulation results is evaluated by comparing the results from MD simulation and experiments. Density is one of the commonly-used parameters to verify the accuracy of simulation models and force field parameters. The density results of virgin

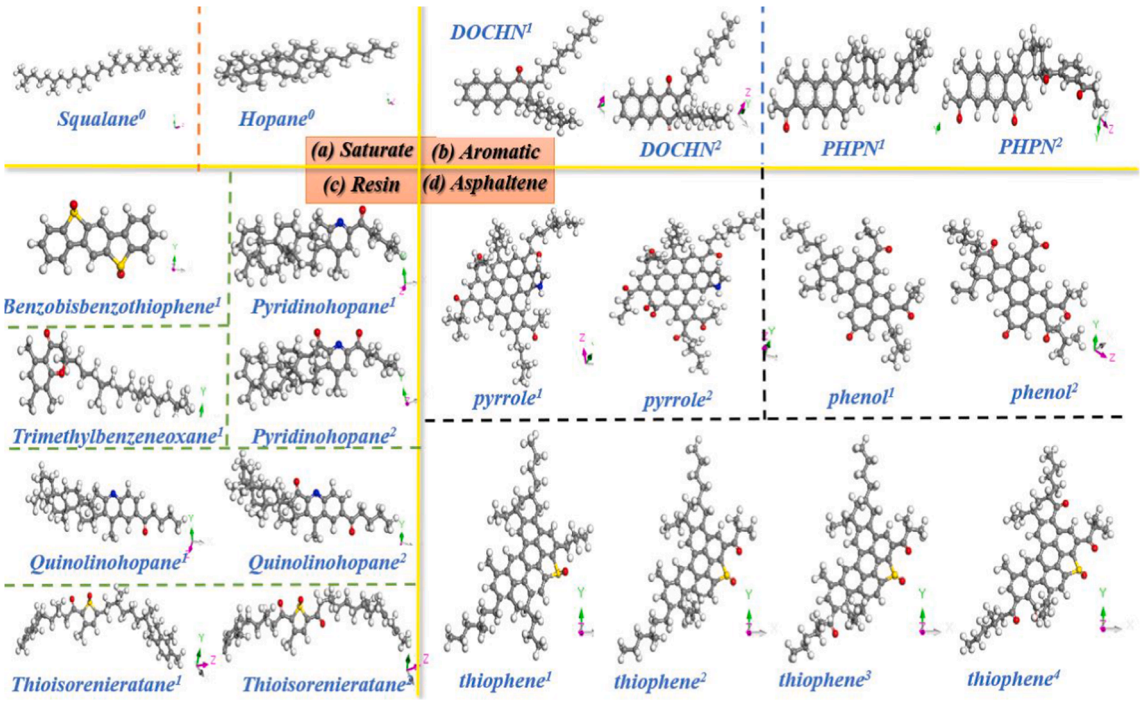


Fig. 12. 12-component molecule models of SARA factions for aged bitumen.

Table 5
The molecular information of virgin and oxidized molecules for SARA fractions.

Chemical fractions	Molecular structure	Chemical formula	Molar mass (g/mol)	Number of C═O	Number of S═O
Saturate	Squalane^0	$C_{30}H_{62}$	422.9	0	0
	Hopane^0	$C_{35}H_{62}$	483.0	0	0
Aromatic	PHPN^0	$C_{35}H_{44}$	464.8	0	0
	PHPN^1	$C_{35}H_{42}O$	478.8	1	0
	PHPN^2	$C_{35}H_{36}O_4$	520.8	4	0
	DOCHN^0	$C_{30}H_{46}$	406.8	0	0
	DOCHN^1	$C_{30}H_{44}O$	420.8	1	0
	DOCHN^2	$C_{30}H_{42}O_2$	434.8	2	0
Resin	Quinolinohopane^0	$C_{40}H_{59}N$	554.0	0	0
	Quinolinohopane^1	$C_{40}H_{57}NO$	568.1	1	0
	Quinolinohopane^2	$C_{40}H_{55}NO_2$	582.0	2	0
	Thioisorenieratane^0	$C_{40}H_{60}SO$	589.1	0	1
	Thioisorenieratane^1	$C_{40}H_{58}SO_2$	603.1	1	1
	Thioisorenieratane^2	$C_{40}H_{56}SO_3$	617.1	2	1
	Benzobisbenzothiophene^0	$C_{18}H_{10}S_2O$	306.4	0	1
	Benzobisbenzothiophene^1	$C_{18}H_{10}S_2O_2$	322.4	0	2
	Pyridinohopane^0	$C_{36}H_{57}N$	503.9	0	0
	Pyridinohopane^1	$C_{36}H_{55}NO$	517.9	1	0
	Pyridinohopane^2	$C_{36}H_{53}NO_2$	531.9	2	0
	Trimethylbenzeneoxane^0	$C_{29}H_{50}O$	414.8	0	0
	Trimethylbenzeneoxane^1	$C_{29}H_{48}O_2$	428.8	1	0

and different aged bitumen at 25 and 60°C are shown in Fig. 17(a and b), respectively. Regarding the virgin bitumen, its density at 25°C measured from simulation and experiment is 0.999 and 1.017 g/cm^3, respectively. Both MD simulation and experimental results agree well with the results in the previous studies, which reported that the 25°C density of virgin bitumen was appropriate 1.0 g/cm^3. The slight difference between the experimental results and simulation predictions might come from the system operation errors. It can be found that the density value of bitumen increases significantly with the aging depth increasing. As mentioned before, the aging of bitumen could lead to the increase of asphaltene and resin fractions and the decrease of the aromatic component. The density values of asphaltene and resin are higher than that of aromatic and saturate components because of the larger molecular weight and polarity. Interestingly, the increasing rate of density from MD simulation and experimental results is different. The rising rate of density from experimental results is slower than that from MD simulation, which may be resulted from errors from molecular models of aged binders.

Fig. 17 illustrates that with the increase of simulation temperature, the density values of virgin and aged bitumen all show the reduction tendency, which is attributed to the increase of molecular distance and volume expansion of the whole system. The aging process results in a remarkable increase of density value for bitumen binder. The correction analysis between the density results from the experiment and MD simulation is performed, which is displayed in Fig. 17(c). It can be found that there is a great linear relationship between the experimental and MD simulation results, which further validate the reasonability of the MD simulation program. Theoretically, the slope and intercept value of

Table 6
The molecular information of virgin and oxidized molecules for SARA fractions (Continued).

Chemical fractions	Molecular structure	Chemical formula	Molar mass (g/mol)	Number of C═O	Number of S═O
Asphaltene	Asphaltene-phenol^0	$C_{42}H_{54}O$	575.0	0	0
	Asphaltene-phenol^1	$C_{42}H_{48}O_4$	617.0	3	0
	Asphaltene-phenol^2	$C_{42}H_{44}O_6$	645.0	5	0
	Asphaltene-pyrrole^0	$C_{66}H_{81}N$	888.5	0	0
	Asphaltene-pyrrole^1	$C_{66}H_{73}NO_4$	944.5	4	0
	Asphaltene-pyrrole^2	$C_{66}H_{67}NO_7$	986.5	7	0
	Asphaltene-thiophene^0	$C_{51}H_{62}S$	707.2	0	0
	Asphaltene-thiophene^1	$C_{51}H_{62}SO$	723.2	0	1
	Asphaltene-thiophene^2	$C_{51}H_{60}SO_2$	737.2	1	1
	Asphaltene-thiophene^3	$C_{51}H_{58}SO_3$	751.2	2	1
	Asphaltene-thiophene^4	$C_{51}H_{54}SO_5$	779.2	4	1

the correlation equation should be 1 and 0, respectively, when the experimental value is equal to the predicted results from MD simulation. However, due to the average molecular models of bitumen and limited computational capacity of MD simulation, a difference between the experimental results and simulation prediction could be observed.

7. MD simulation results and discussion

7.1. Bulk properties of virgin and aged bitumen

The physical characteristics of the bulk bitumen system significantly affect its rheological and mechanical performance due to the influence of the chemical composition and external conditions. In this paper, the effects of short-term and long-term aging time on the cohesion energy density and solubility parameters of bitumen are studied through the MD simulation.

7.1.1. Cohesive energy density

The cohesion energy density is an important parameter to evaluate the molecular attractive interaction degree of the whole bulk system, which examines the mutual attractiveness of all molecules in the per unit volume. The mathematical expression of CED is presented as follows:

$$E_{CED} = E_{coh}/V \quad (7)$$

where E_{CED} represents the cohesive energy density (J/cm^3), E_{coh} refers to the total cohesive energy of the whole system (J), and V is the volume of the molecular system. It should be noted that the E_{coh} value is equal to the energy for separating all molecules of the whole system. Thus, the CED parameter is utilized to assess the stiffness of materials. The larger the CED value, the higher the hardness of the material.

Fig. 18(a) displays the variation of the cohesive energy density of bitumen binders as a function of the aging time. It can be found that the cohesive energy is composed of the Van der Waals and Electrostatic terms, and the non-bond interaction contributes to the intermolecular forces of the bitumen system. In this study, the measured CED value of virgin bitumen is 3.36*10^8 J/cm^3, which is a little larger than the CED value region of 3.19* 10^8-3.22*10^8 J/m^3 reported from previous studies [22,25,28]. It may be related to that the addition of sulfoxide functional

Table 7
The SARA fractions in a molecular model of virgin bitumen.

Chemical fractions	Molecular structure	Chemical formula	Molecule number	Fraction weight (in model)	Fraction weight (in bitumen)
Saturate	Squalane^0	$C_{30}H_{62}$	2	3.9 wt%	3.60 wt%
	Hopane^0	$C_{35}H_{62}$	1		
Aromatic	PHPN^0	$C_{35}H_{44}$	20	52.33 wt%	53.30 wt%
	DOCHN^0	$C_{30}H_{46}$	21		
Resin	Quinolinohopane^0	$C_{40}H_{59}N$	3	31.04 wt%	30.30 wt%
	Thioisorenieratane^0	$C_{40}H_{60}SO$	3		
	Benzobisbenzothiophene^0	$C_{18}H_{10}S_2O$	13		
	Pyridinohopane^0	$C_{36}H_{57}N$	3		
	Trimethylbenzeneoxane^0	$C_{29}H_{50}O$	4		
Asphaltene	Asphaltene-phenol^0	$C_{42}H_{54}O$	2	12.73 wt%	12.80 wt%
	Asphaltene-pyrrole^0	$C_{66}H_{81}N$	2		
	Asphaltene-thiophene^0	$C_{51}H_{62}S$	2		

Table 8
The SARA fractions in a molecular model of short-term aged bitumen.

Chemical fractions	Molecular structure	Chemical formula	Molecule number	Fraction weight (in model)	Fraction weight (in bitumen)
Saturate	Squalane^0	$C_{30}H_{62}$	2	3.86 wt%	3.60 wt%
	Hopane^0	$C_{35}H_{62}$	1		
Aromatic	PHPN^0	$C_{35}H_{44}$	20	50.60 wt%	51.60 wt%
	DOCHN^0	$C_{30}H_{46}$	20		
Resin	Quinolinohopane^0	$C_{40}H_{59}N$	3	30.73 wt%	30.20 wt%
	Thioisorenieratane^0	$C_{40}H_{60}SO$	3		
	Benzobisbenzothiophene^0	$C_{18}H_{10}S_2O$	13		
	Pyridinohopane^0	$C_{36}H_{57}N$	3		
	Trimethylbenzeneoxane^0	$C_{29}H_{50}O$	4		
Asphaltene	Asphaltene-phenol^0	$C_{42}H_{54}O$	2	14.80 wt%	14.60 wt%
	Asphaltene-pyrrole^0	$C_{66}H_{81}N$	2		
	Asphaltene-thiophene^1	$C_{51}H_{62}SO$	3		

Table 9
The SARA fractions in a molecular model of 20 h long-term aged bitumen.

Chemical fractions	Molecular structure	Chemical formula	Molecule number	Fraction weight (in model)	Fraction weight (in bitumen)
Saturate	Squalane[0]	$C_{30}H_{62}$	2	3.78 wt%	3.60 wt%
	Hopane[0]	$C_{35}H_{62}$	1		
Aromatic	PHPN[0]	$C_{35}H_{44}$	12	43.67 wt%	43.90 wt%
	PHPN[1]	$C_{35}H_{42}O$	6		
	DOCHN[0]	$C_{30}H_{46}$	17		
Resin	Quinolinohopane[0]	$C_{40}H_{59}N$	4	33.79 wt%	33.90 wt%
	Thioisorenieratane[1]	$C_{40}H_{58}SO_2$	3		
	Benzobisbenzothiophene[1]	$C_{18}H_{10}S_2O_2$	13		
	Pyridinohopane[0]	$C_{36}H_{57}N$	4		
	Trimethylbenzeneoxane[0]	$C_{29}H_{50}O$	4		
Asphaltene	Asphaltene-phenol[0]	$C_{42}H_{54}O$	3	18.76 wt%	18.60 wt%
	Asphaltene-pyrrole[0]	$C_{66}H_{81}N$	3		
	Asphaltene-thiophene[2]	$C_{51}H_{60}SO_2$	3		

Table 10
The SARA fractions in a molecular model of 40 h long-term aged bitumen.

Chemical fractions	Molecular structure	Chemical formula	Molecule number	Fraction weight (in model)	Fraction weight (in bitumen)
Saturate	Squalane[0]	$C_{30}H_{62}$	2	3.68 wt%	3.70 wt%
	Hopane[0]	$C_{35}H_{62}$	1		
Aromatic	PHPN[1]	$C_{35}H_{42}O$	15	38.54 wt%	38.80 wt%
	DOCHN[1]	$C_{30}H_{44}O$	16		
Resin	Quinolinohopane[1]	$C_{40}H_{57}NO$	5	36.86 wt%	36.80 wt%
	Thioisorenieratane[1]	$C_{40}H_{58}SO_2$	3		
	Benzobisbenzothiophene[1]	$C_{18}H_{10}S_2O_2$	14		
	Pyridinohopane[1]	$C_{36}H_{55}NO$	4		
	Trimethylbenzeneoxane[0]	$C_{29}H_{50}O$	5		
Asphaltene	Asphaltene-phenol[1]	$C_{42}H_{48}O_4$	4	20.92 wt%	20.70 wt%
	Asphaltene-pyrrole[1]	$C_{66}H_{73}NO_4$	3		
	Asphaltene-thiophene[3]	$C_{51}H_{58}SO_3$	3		

Table 11
The SARA fractions in a molecular model of 80 h long-term aged bitumen.

Chemical fractions	Molecular structure	Chemical formula	Molecule number	Fraction weight (in model)	Fraction weight (in bitumen)
Saturate	Squalane[0]	$C_{30}H_{62}$	2	3.48 wt%	3.70 wt%
	Hopane[0]	$C_{35}H_{62}$	1		
Aromatic	PHPN[2]	$C_{35}H_{36}O_4$	13	32.50 wt%	32.50 wt%
	DOCHN[2]	$C_{30}H_{42}O_2$	13		
Resin	Quinolinohopane[2]	$C_{40}H_{55}NO_2$	5	38.79 wt%	38.40 wt%
	Thioisorenieratane[2]	$C_{40}H_{56}SO_3$	3		
	Benzobisbenzothiophene[1]	$C_{18}H_{10}S_2O_2$	15		
	Pyridinohopane[2]	$C_{36}H_{53}NO_2$	5		
	Trimethylbenzeneoxane[1]	$C_{29}H_{48}O_2$	6		
Asphaltene	Asphaltene-phenol[2]	$C_{42}H_{44}O_6$	4	25.23 wt%	25.40 wt%
	Asphaltene-pyrrole[2]	$C_{66}H_{67}NO_7$	4		
	Asphaltene-thiophene[4]	$C_{51}H_{54}SO_5$	4		

groups enhances the polarity and molecular interaction of the virgin bitumen. Moreover, the Van der Waals force contributes more to the cohesive energy of the system than the electrostatic interaction.

The aging duration has a significant effect on the cohesive energy density of bitumen, which increases gradually with the deepening of the aging degree, especially in the period of long-term aging. During the aging process of bitumen, more polar functional groups and the fractions with higher molecular weight are created, promoting the improvement of molecular interaction. Thus, the CED value and hardness of long-term aged binders are both larger than that of virgin or short-term aged bitumen, which are consistent to the chemical properties and previous literature's conclusions [28,39]. It is worth mentioning that the increasing trend of the Van der Waals and electrostatic forces to the aging degree is different distinctly. When the long-term aging time is more than 40 h, the electrostatic interaction enhances more significantly than the Van der Waals force. Compared to the LAB40, the CED improvement of the LAB80 binder mainly comes from the increase of electrostatic interaction, which is associated with the obvious content of polar functional groups, especially for the C═O index in the LAB80 binder. To sum up, the Van der Waals interaction between the bitumen molecules plays a dominant role of enhancing the cohesive energy and stiffness of virgin and aged bitumen. However, as the aging degree increasing, the contribution of the electrostatic force on the energy composition of bitumen models is more obvious. In this study, regarding the case of 80 h long-term aging, the Van der Waals force is still higher than the electrostatic interaction. It can be deduced that the electrostatic force would show a dominating effect when the aging degree continues to prolong, which could be verified in the future study.

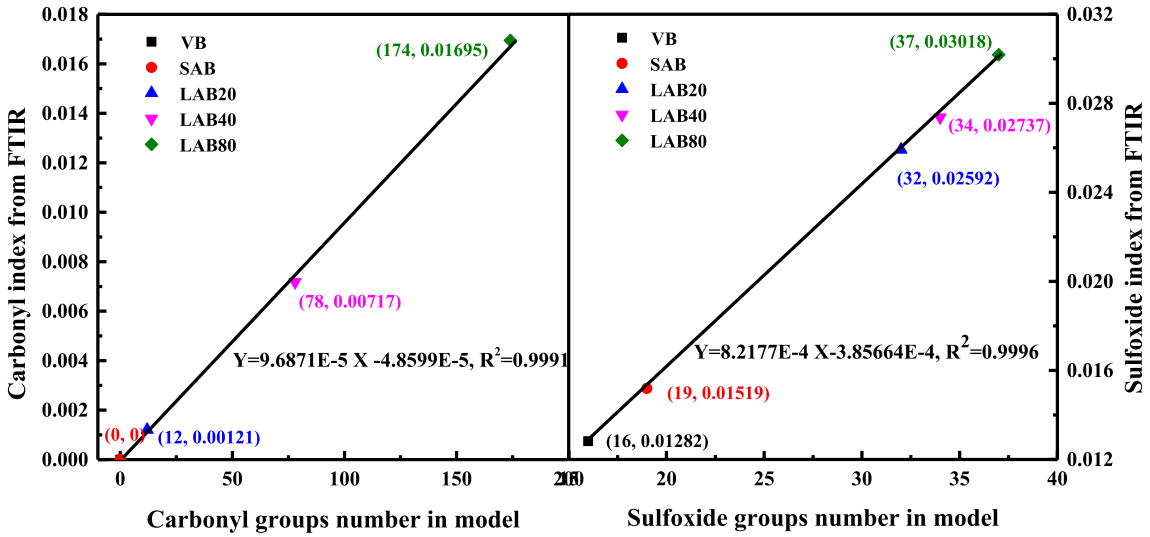


Fig. 13. The correlation between functional groups number in model and FTIR results.

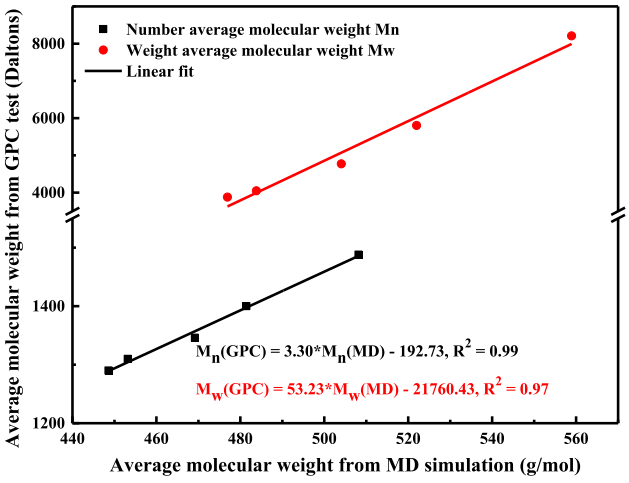


Fig. 14. The correlation between molecular weight in model and GPC results.

7.1.2. Solubility parameter

According to the Flory-Huggins theory, the materials with similar solubility parameter values are likely to be miscible, and the corresponding solubility parameter difference significantly affects the compatibility between different components in a compound system. Therefore, it is of importance to understand the influence of short- and long-term aging on the solubility parameter, which is beneficial to assess the compatibility between aged bitumen and additives, such as the rejuvenators and polymers. The incompatibility of rejuvenated or modified bitumen would result in the phase separation and inhomogeneous binder, which presents a negative influence on the mechanical properties of asphalt pavement, including the resistance to rutting, fatigue and thermal cracking. The solubility parameter of bitumen could be measured by conducting a solubility test with several types of solvents. However, the experimental method is difficult to perform because of lots of solvents required, especially in the pavement engineering laboratory. Hence, it is of great significance to employ the MD simulation to predict the solubility parameter of virgin, aged bitumen or additives.

During the MD simulation procedure, the solubility parameter values of the virgin, short-term aged and long-term aged binders are calculated using Eq.8 and the results are illustrated in Fig. 18(b). It can be seen that the solubility parameter of the virgin bitumen is 18.33 $(J/cm^3)^{1/2}$. From the previous studies [17,28], the recommended range of solubility parameter of bitumen is in 13.30–22.50 $(J/cm^3)^{1/2}$. Thus, the reasonability of bitumen molecular models and MD simulation programs is further validated. The long-term aging has a great influence on increasing the solubility parameter of bitumen, although the effect of short-term aging is not obvious. Like the CED parameter, the Van der Waals force plays a dominant role on determining the solubility parameter of virgin and aged binders, which weakens with the deepening of long-term aging degree. Moreover, the solubility parameter contributed from electrostatic interaction becomes more distinct as the aging time prolonging, which is linked to the generation of polar functional groups during the oxidation aging of bitumen. To sum up, the solubility parameter values of aged binders with various aging degrees are significantly different, which would affect the compatibility between aged binders and rejuvenators. Hence, the selection of rejuvenator type should take the aging degree of aged bitumen into consideration, which not only determines the optimum rejuvenator dosage, but also influences the compatibility and diffusion characteristics of the rejuvenated bitumen. The compatibility and interaction between different types of rejuvenators and various aged bitumen will be explored in future work. It would provide a basis for choosing a proper rejuvenation agent to a long-term aged binder with a specific aging degree. At the same time, the solubility parameter difference between bitumen and polymer modifier or other additives would affect the phase stability of modified bitumen dramatically.

$$\delta = (E_{CED})^{1/2} = (E_{vdw} + E_{ele})^{1/2} \quad (8)$$

7.2. Interfacial properties of virgin and aged bitumen

Asphalt pavement mixture is composed of the bitumen binder, aggregate and filler. The interfacial performance between the aggregates and bitumen binder is of importance to the adhesive property and moisture susceptibility of asphalt road. There are different mechanical and thermodynamics methods to detect the interfacial adhesion of asphalt mixtures, such as the universal tension and contact angle tests. However, these experimental measurements always cost time and money, and the corresponding results cannot help understand the interfacial bonding behaviors from the viewpoint of the microscale. In this study, the influence of long-term aging on the cohesive and adhesive properties of bitumen is investigated with the parameters of surface free energy and work of cohesion outputted from MD simulation. The surface free energy and work of cohesion values of virgin and aged bitumen systems could be calculated by using Eqs.9 and 10, respectively, and results are presented in Fig. 19.

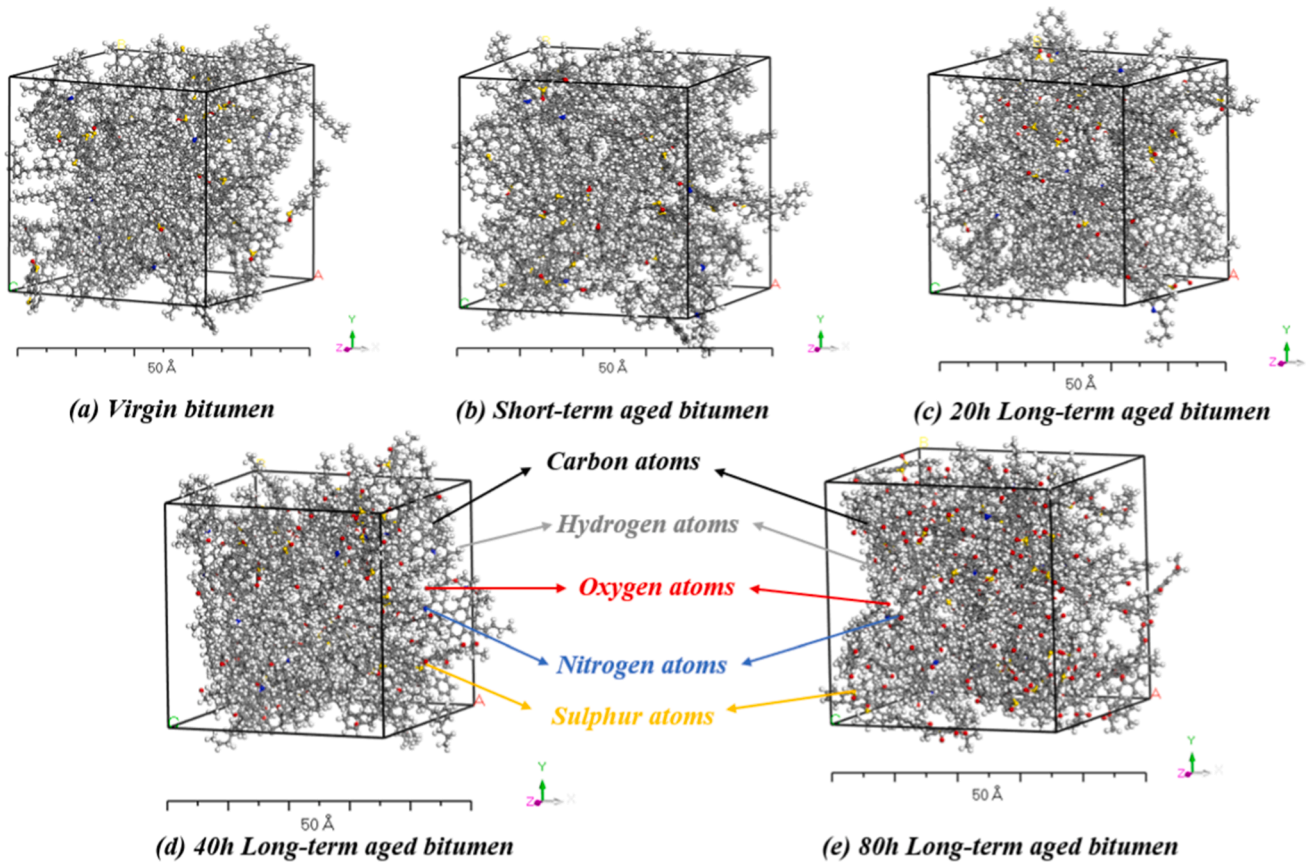


Fig. 15. Molecular models of virgin and aged bitumen with various aging degrees.

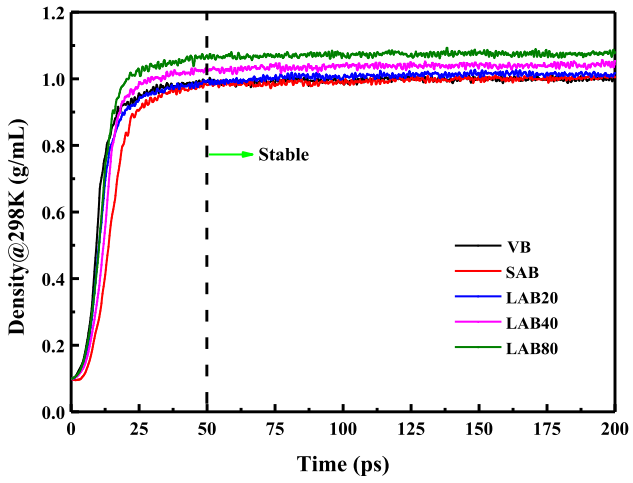


Fig. 16. The density curves of bitumen samples at 298.15 K in the NPT simulation.

$$\gamma = (E_{film} - E_{bulk})/2A \quad (9)$$

$$W_{aa} = 2\gamma \quad (10)$$

where γ and W_{aa} show the surface free energy and work of cohesion (mJ/m^2), E_{film} and E_{bulk} represent the potential energy of the confined bitumen film and bulk bitumen system (mJ), respectively. Besides, parameter A refers to the created new surface area (mm^2).

Regarding the surface free energy, the value of virgin bitumen is approximately 70 mJ/m^2, which agrees well with the recommended range of 39.92–71.56 mJ/m^2 [52]. The aging of bitumen significantly leads to the reduction of surface free energy, indicating that the required external energy for creating a new surface of bitumen decreases remarkably as the aging degree deepening. Therefore, compared to the virgin and short-term aged bitumen, it is easier for the long-term aged binders to occur the temperature cracking disease. The aging process would have an obvious influence on shortening the service life of asphalt pavement. Moreover, the long-term aging time weakens the work of cohesion of bitumen dramatically, which denotes that the fracture resistance of bitumen binder would deteriorate with the increase of aging degree. In detail, compared with the unaged bitumen, the surface free energy and work of cohesion of short-term, 20, 40 and 80 h long-term aged binders decrease by 1.4%, 21.5%, 35.8% and 58.3%, respectively. This study aims at establishing the proper molecular models of virgin and different aged bitumen, and predicting the influence of long-term aging on the cohesive and adhesive properties of bitumen by using MD simulation. The MD simulation results will be further verified and correlated to the macroscale properties in future studies.

7.3. Dynamic behaviors of virgin and aged bitumen

The dynamic properties also play an important role on explaining the aging behavior of bitumen. Moreover, the mobility of molecules has a significant influence on the thermodynamic and rheological properties of bitumen, as well as the mass exchange between the binder and rejuvenator, polymers, or moisture. However, it is difficult for the conventional laboratory experiments to detect the variation of dynamic properties of bitumen molecules as the function of the aging degree. Meanwhile, the synergistic effects of the long-term aging and temperature on the diffusion capacity of bitumen molecules is still unclear. In this study, the MD simulation technology is employed to measure the mean square distance (MSD) of virgin and different aged bitumen sys-

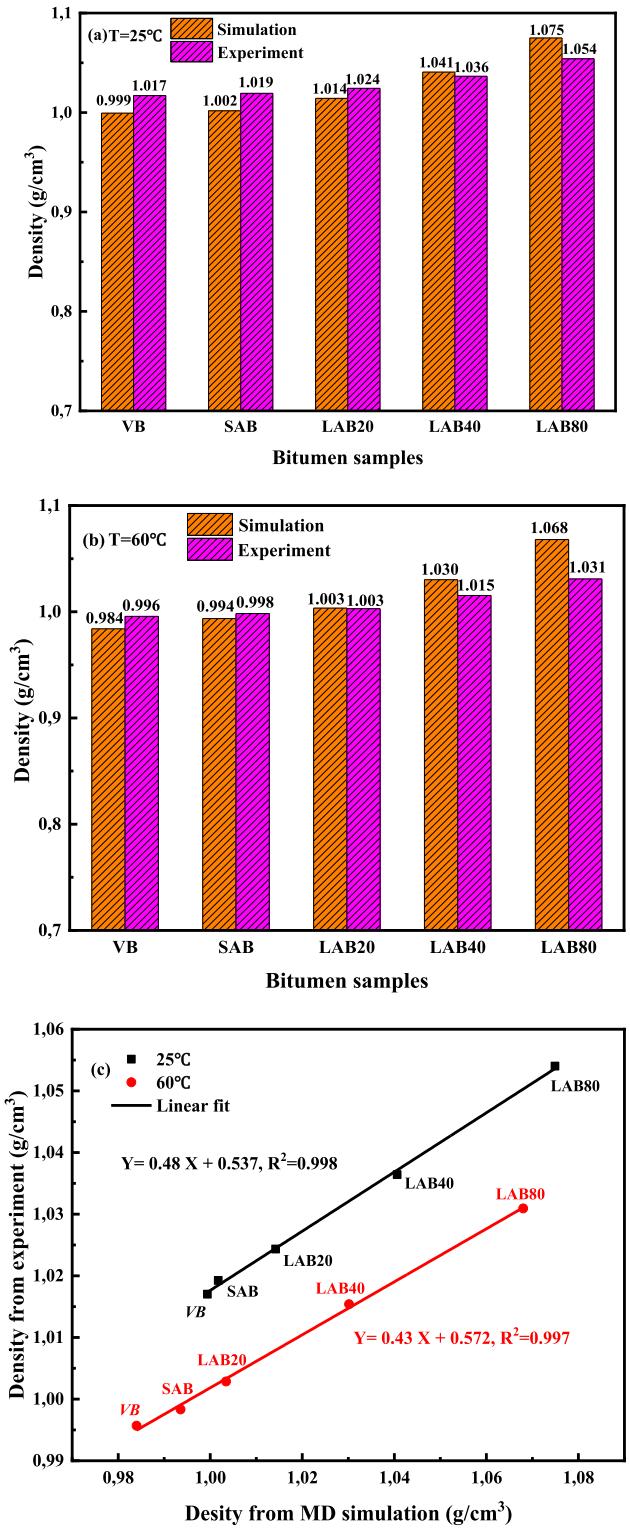


Fig. 17. The result comparison of density parameter of virgin and different aged bitumen from experiments and MD simulation.

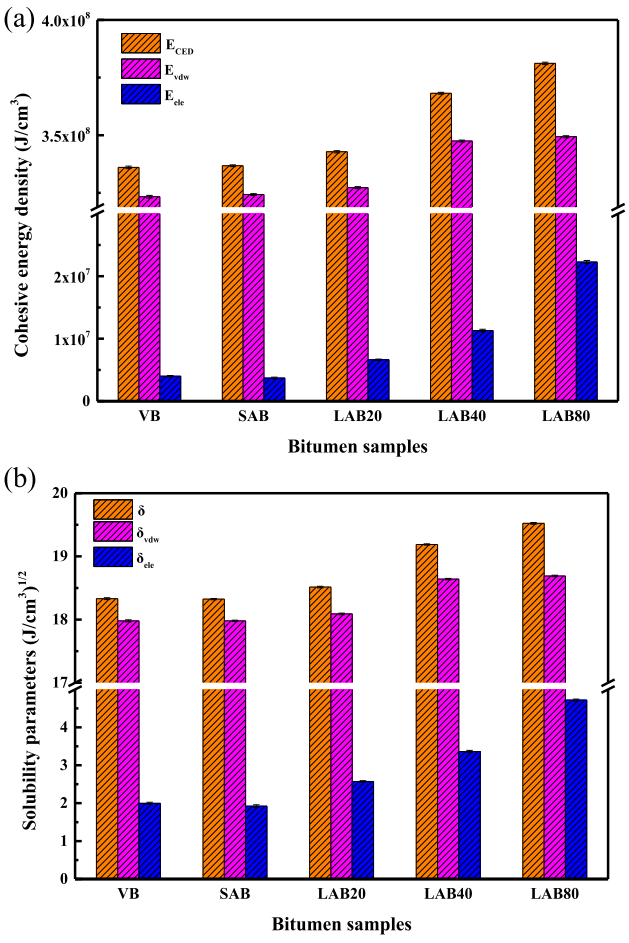


Fig. 18. Influence of long-term aging time on the cohesive energy density(a) and solubility parameter (b) of bitumen.

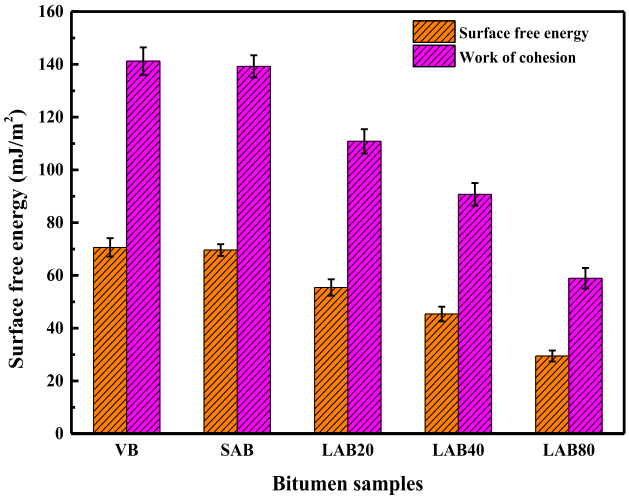


Fig. 19. Influence of long-term aging time on the surface free energy and work of cohesion of bitumen.

tems. The equilibrium molecular models are further subjected to the MD simulation with the NVT ensemble for 200 ps, and the MSD values variation of bitumen systems are recorded as the function of simulation time according to Eq.11 at different temperatures of 248, 273, 298, 333 and 393 K. There is a clear relationship between the diffusion coefficient D and the slope of the MSD curve, shown as Eq.12. The diffusion behaviors of molecules are determined by the Brownian self-movement (kinetic energy) and molecular interactions (potential energy), thus it is also called the inter-diffusion to distinguish with the extra-diffusion resulted from the mass concentration difference.

$$MSD(t) =< \Delta r_i(t)^2 >=< [r_i(t) - r_i(0)]^2 > \quad (11)$$

$$D = \frac{1}{6N}\lim_{t\to\infty}\frac{d}{dt}\sum MSD(t) = \frac{a}{6} \quad (12)$$

where MSD(t) refers to the mean square distance of molecular systems at time t, $r_i(0)$and $r_i(t)$ represent the initial and ultimate coordinate at time t, N means the total number of molecules, and a is the slope value of the correlation curve between MSD and simulation time.

Fig. 20 shows the MSD values of virgin and aged binders at different MD simulation durations and temperatures. It can be found that the MSD parameter of the bitumen system presents a positive linear correlation with the simulation time, indicating that the movement distance of molecules increases gradually during the MD simulation. Meanwhile, the MSD parameter of bitumen decreases as the aging degree deepens dramatically, which is associated with the improvement of molecular interaction due to the increase of polar groups and reduction of system free volume. Hence, the long-term aging would significantly hinder the mobility of molecules and deteriorate the relaxation ability of bitumen. In addition, the increase of temperature is beneficial to enhance the MSD value and improve the mobility of molecules, which contributes to the increase of molecular energy, and results in the expansion of the bitumen system at high temperatures.

The slope ("a" value) of MSD value variation to the simulation time is obviously different at different temperatures, which is related to the diffusion ability of molecules. The calculated diffusion coefficient D values of virgin and aged bitumen are listed in Table 12. It is notable that the inter-diffusion coefficient of the bitumen model has a reduction and improvement trend as the increase of aging degree and temperature, respectively. However, these D values are on the same order of magnitude (10^{-7} cm^2/s), except for the LAB80 binder at 248 K (10^{-8} cm^2/s), which is consistent to the reported diffusion coefficient D value of

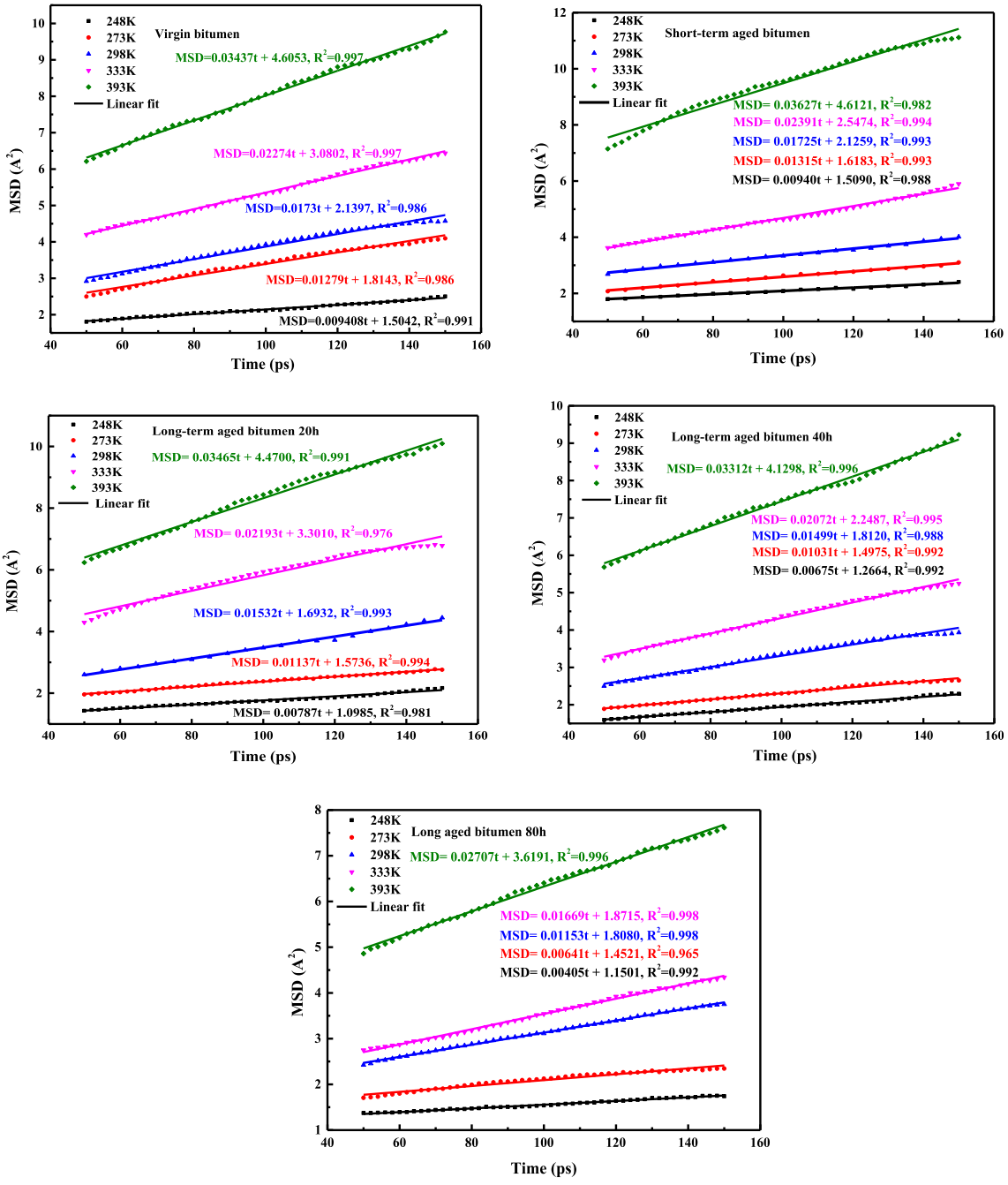


Fig. 20. The relationship between mean square distance with simulation time for virgin and different aged bitumen.

Table 12
The diffusion coefficient of virgin and different aged bitumen.

Bitumen samples	D (393 K) cm^2/s	D (333 K) cm^2/s	D (298 K) cm^2/s	D (273 K) cm^2/s	D (248 K) cm^2/s
VB	$5.73*10^{-7}$	$3.79*10^{-7}$	$2.88*10^{-7}$	$2.13*10^{-7}$	$1.57*10^{-7}$
SAB	$6.05*10^{-7}$	$3.98*10^{-7}$	$2.88*10^{-7}$	$2.19*10^{-7}$	$1.57*10^{-7}$
LAB20	$5.78*10^{-7}$	$3.65*10^{-7}$	$2.55*10^{-7}$	$1.89*10^{-7}$	$1.31*10^{-7}$
LAB40	$5.52*10^{-7}$	$3.45*10^{-7}$	$2.50*10^{-7}$	$1.72*10^{-7}$	$1.13*10^{-7}$
LAB80	$4.51*10^{-7}$	$2.78*10^{-7}$	$1.92*10^{-7}$	$1.07*10^{-7}$	$6.75*10^{-8}$

bitumen from previous studies [20,36,37]. Further, it is interesting that the influence of temperature on the diffusion coefficient of bitumen models is more apparent than that of the aging degree. That's why the workability of aged bitumen in RAP material could be improved by increasing the mixing and compaction temperature. However, this method is energy consuming and then the rejuvenators are added to enhance the mobility of bitumen molecules by weakening the molecular interaction and increasing the free volume.

Fig. 21 illustrates the linear correlation curves between the diffusion coefficient of virgin and aged bitumen and the reciprocal value of temperature. With the increase of temperature, the diffusion coefficient of bitumen systems strengthens dramatically, which is resulted from the improvement of molecular kinetic energy. The Arrhenius equation is used to quantitatively study the effects of aging on the relationship between diffusion coefficient and temperature.

$$D = A\exp\left(\frac{-E_a}{RT}\right) \quad (13)$$

where, A is the pre-exponential factor, E_a represents the activation energy, and R shows the universal gas constant (8.314 $J/mol{\cdot}K^{-1}$). The detailed equations of virgin and aged bitumen are also presented in Fig. 21, and the activation energy E_a value of bitumen markedly improves with the aging degree deepening. It indicates that the bitumen aging would increase the required energy for molecular mobility, especially when the long-term aging time is 80 h. Hence, more rejuvenators are needed to motivate the molecules and reduce the activation energy of the severely aged bitumen, which could save the required external energy to obtain superior workability performance.

8. Conclusions and recommendations

This study investigated the influence of laboratory long-term aging on the chemical and thermodynamic properties of bitumen through the combination of experimental and molecular dynamics simulation methods. The main conclusions can be drawn as follows:

(1) During the long-term aging of bitumen, the aromatic component decreased dramatically, while the resin and asphaltene fractions increased gradually. Besides, the sulfoxide and carbonyl functional groups would generate, and the sulfur oxidation reaction was easier than the carbon oxidation.
(2) The C%, H% and H/C ratio value would decrease during the long-term aging of bitumen, which markedly increased the oxygen dosage and average molecular weight due to the polymerization reaction of light fractions and agglomeration of heavy molecules.
(3) The molecular models of virgin and different aged bitumen were established and validated. The functional groups, average molecular weight and density outputs from the MD simulation agreed well with the laboratory results.
(4) Apart from the chemical properties from experiments, the influence of long-term aging on the thermodynamics properties was predicted through the MD simulation method. The aging of bitumen significantly enhanced the cohesive energy density, solubility parameter and activate energy, while it deteriorated the surface free energy, work of cohesion as well as the molecular mobility of the bitumen system.

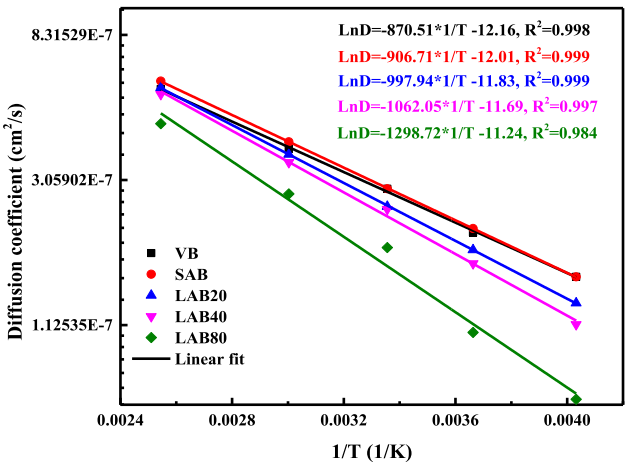


Fig. 21. The correlation curves of diffusion coefficient as a function of temperature for virgin and different aged bitumen.

This study utilized the classical 12-components molecular models to represent the SARA fractions of virgin bitumen with the modification of adding sulfoxide groups. Further works are needed to establish more precise molecular models for bitumen. Moreover, the effects of long-term aging on the rheological properties as well as the oxidation aging kinetics will be taken into consideration. Importantly, the relationships between the microscale characteristics from MD simulation and the macroscale mechanical properties should be explored.

CRediT authorship contribution statement

Shisong Ren: Conceptualization, Methodology, Writing – original draft, Investigation, Validation, Software. **Xueyan Liu:** Methodology, Supervision. **Peng Lin:** Validation. **Sandra Erkens:** Methodology, Supervision. **Yue Xiao:** Software, Writing – original draft.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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