

## Research Article

# Comparative Investigation on the Properties and Molecular Mechanisms of Natural Phenolic Compounds and Rubber Polymers to Inhibit Oxidative Aging of Asphalt Binders

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Using bio-based antioxidants and industrial wastes to inhibit asphalt aging is a sustainable practice in the pavement industry. To investigate the inhibitory effects and potential mechanisms of phenolic compounds and crumb tire rubber on the aging deterioration of asphalt binders, the aging characteristics of base asphalt, catechin modified asphalt, and crumb rubber modified asphalt were evaluated using Fourier transform infrared spectroscopy and reactive molecular dynamics simulations. The results showed that both catechins and crumb rubber exerted resistance to asphalt aging and that the former performed better. Specifically, catechins block asphalt aging at the chemical level by providing active H atoms to react with O<sub>2</sub> and free radicals, thus preventing them from oxidizing asphalt molecules. In contrast, crumb rubber exerts its antiaging properties mainly in physical aspects, firstly by limiting the movement of asphalt molecules to reduce the contact and reaction of asphalt with O<sub>2</sub> and secondly by counteracting the aging-induced asphalt hardening through its own degradation, thus partially restoring the mechanical properties of aged asphalt. This study provides molecular insight into the antiaging mechanisms of natural phenolic compounds and rubber polymers and is expected to provide theoretical guidance for the development of targeted antiaging technologies for asphalt binders.

## 1. Introduction

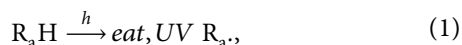
Asphalt is the residue of petroleum fractionation and is widely used as a pavement bonding material due to its unique viscoelastic property and mineral adhesion [1, 2]. According to the Corbett component separation test, asphalt molecules are divided into four components, namely, saturates, aromatics, resins, and asphaltenes (SARA), depending on their polarity and solubility in different solvents [3]. In the natural state, SARA components of asphalt are in thermodynamic equilibrium with the effect of intermolecular interactions, thus maintaining its satisfactory fluidity and functionality [4].

However, asphalt is susceptible to aging during service by reacting with oxygen [5–7]. At high altitude areas, aging of asphalt becomes faster and more severe under UV radiation [8]. Studies based on Fourier transform infrared (FTIR) spectroscopy indicate that a large number of polar oxygen-containing groups, such as carbonyl (mainly ketones and aldehydes) and sulfoxide groups, as well as small amounts of carboxylic acids, dicarboxylic anhydrides, and hydroxyl groups, are produced during asphalt aging [9, 10]. As a result, the molecular polarity and intermolecular agglomeration of aged asphalt increases and the thermodynamic equilibrium between SARA components is irreversibly disrupted, which makes asphalt hard, brittle, and

difficult to flow, resulting in asphalt pavement cracking more easily under load [11–13].

Governments and contractors typically address pavement cracking caused by asphalt aging through preventive maintenance, but it reduces the operational efficiency of the transportation system [14]. Therefore, taking measures to actively inhibit the aging of asphalt is a better choice for building tough and durable road facilities. Current asphalt antiaging technologies, such as the incorporation of layered silicates and layered double hydroxides (LDHs) compounds, face the challenges of high cost and poor compatibility with asphalt, making them difficult to apply in engineering practice on a large scale [15, 16]. In contrast, phenolic antioxidants from natural sources such as catechin, gallic acid, and lignin are widely available and have a similar molecular structure to asphalt, thus avoiding these disadvantages and becoming a promising raw material for the development of efficient asphalt antiaging technology [17].

At the atomic level, the aging of asphalt can be explained by the theory of free radical chain reactions with the steps equations (1)–(3). In the free radical chain reaction, one or more steps are repeated multiple times until the chain is terminated or until one of the reactants is exhausted.



The asphalt molecule ( $R_aH$ ) is dehydrogenated under environmental conditions of heat and UV light to generate an unstable asphalt molecular radical ( $R_a\cdot$ ).  $R_a\cdot$  adsorbs an  $O_2$  molecule to produce the highly reactive  $R_aOO\cdot$  radical, which further attacks another asphalt molecule ( $R_bH$ ) to generate  $R_aOOH$  and an  $R_b\cdot$  radical. Then,  $R_aOOH$  undergoes isomerization to produce ketones, aldehydes, and other groups, while  $R_b\cdot$  drives the reactions equations (2) and (3) to keep repeating, resulting in the continuous aging of asphalt. This process of asphalt aging is supported by the experimental study of Petersen et al. [9].

Fortunately, phenolic hydroxyl groups can capture  $R\cdot$  and  $ROO\cdot$  and block the radical chain reactions by providing protons to transform them to  $RH$  and  $ROOH$  [18], as shown in reactions equations (4) and (5):



The generated  $ArO\cdot$  is also a free radical, but its unpaired electron is conjugated to the delocalized  $\pi$  bond on the neighboring aromatic ring and thus remains stable in the subsequent reactions. Therefore, the addition of phenolic compounds theoretically prevents the asphalt molecules from being attacked by free radicals and aging.

In addition, adding crumb rubber into asphalt binders is also an antiaging technology widely used in engineering practice [19]. This is because the carbon black in the rubber

has antioxidant properties, and the crumb rubber can absorb aromatic components of asphalt to prevent them from evaporating during aging. Furthermore, the crumb rubber can limit the physical hardening of asphalt during aging by reducing the bulk viscosity of asphalt [20]. The crumb rubber is usually recycled from used automobile tires, and its utilization not only improves the performance of asphalt materials but also exerts environmental benefits [21, 22]. The use of crumb rubber modified asphalt (RMA) is mainly used to improve the rutting resistance of asphalt mixtures at high temperatures and cracking resistance at low temperatures, but some studies suggest that the addition of rubber powder also enhances the aging resistance of asphalt, although the mechanism is unclear [23–25]. The main component of crumb rubber from tires is styrene-butadiene rubber (SBR) polymer, which is produced by polymerizing styrene with butadiene and does not contain phenolic structures [26]. This fact suggests that crumb rubber enhances the aging resistance of the asphalt binder by a different mechanism than phenolic compounds.

Understanding the mechanisms by which phenolic compounds and rubber crumbs inhibit asphalt aging is important for the development of targeted antiaging technologies for asphalt but is challenged by the inability to experimentally observe the aging behavior of asphalt molecules and their blocking process at the nanoscale as well as the inability to predict aging-related chemical reactions by classical molecular simulation methods [27]. To address this issue, molecular dynamics (MD) simulations based on the reactive force field (ReaxFF) were carried out in this study to investigate the chemical reaction information of asphalt aging and to comprehensively analyze the inhibition mechanism of phenolic compounds and crumb rubber on asphalt aging in combination with classical MD methods [28]. The specific research steps were as follows:

- (i) conducting attenuated total reflection (ATR)-FTIR tests to evaluate and compare the aging resistance of base asphalt with phenolic compound-modified and crumb rubber-modified asphalt samples;
- (ii) modeling the aging behaviors of various asphalt samples by ReaxFF MD simulations to analyze the potential inhibition mechanisms of phenolic compounds and crumb rubber on asphalt aging from a chemical perspective;
- (iii) determining the molecular diffusion and thermodynamic properties of various asphalt samples by classical MD simulations to analyze the potential antiaging mechanisms of phenolic compounds and crumb rubber from a physical perspective.

## 2. Background on Classical and ReaxFF MD Simulations

MD simulation is a numerical method to predict the state of motion of molecular and atomic systems at a given time by solving Newton's equations of motion by computer [29]. MD simulations can overcome the scale limitations of experimental methods and thus analyze the molecular

mechanisms by which material systems exert their properties. MD was originally conducted in 1957 by Alder and Wainwright to simulate elastic collisions between hard spheres [30]. In 1964, Rahman simulated the system properties of liquid argon using a Lennard-Jones potential and compared them with experimental results [31]. His computer code provided the basic framework for many subsequent MD computing programs. In 2007, Zhang and Greenfield were the first to introduce MD methods to asphalt research, and they proposed a three-component molecular model of asphalt, with each asphalt component represented by a single molecule [32]. Many years later, Li and Greenfield proposed another four-component molecular model of asphalt by summarizing previous studies, in which each asphalt component is represented by multiple molecules [33]. Compared with the three-component model, the simulation results of asphalt properties such as density, polarity, and solubility parameters using the four-component model are closer to the experimental data, so the four-component model was widely accepted as soon as it was proposed.

Subsequently, researchers have conducted numerous studies on the physical and thermodynamic properties of asphalt materials using MD methods [34]. Bhasin et al. and Sun et al. investigated the self-healing mechanism of asphalt based on the diffusion principle and cohesion theory and demonstrated the correlation between the chemical composition and the healing properties of asphalt binders [35, 36]. Xu and Wang et al. performed comprehensive mechanistic analyses of asphalt cohesion and adhesion behaviors based on the interfacial energy theory and considered the effects brought by humidity and oxidation [37, 38]. Guo et al. and Xu et al. investigated the strength formation and debonding mechanisms at the asphalt-aggregate interface, providing theoretical guidance for understanding the cracking resistance of asphalt mixtures [39, 40]. These studies demonstrate that the MD method provides an effective tool for obtaining insight into the microscopic characteristics and mechanical properties of asphalt materials.

However, in these MD methods based on classical force fields (e.g., COMPASS, PCFF, and OLPS), the connectivity between atoms is predefined and remains constant during simulation [27]. In other words, the chemical bonds of the molecule will not be broken or newly generated. Therefore, classical MD simulations cannot be used to study the aging and antiaging behaviors of asphalt related to chemical reactions. Quantum chemistry methods, such as *ab initio* molecular dynamics (AIMD), are able to accurately predict chemical reactions between substances because they calculate electron behaviors based on quantum mechanics (QM), but AIMD is much more computationally expensive than classical MD due to the cost of dealing with electronic degrees of freedom and is typically limited to shorter times and smaller systems [41, 42].

Fortunately, the ReaxFF force field proposed by Senftle et al. bridges this gap [28]. ReaxFF is a bond-order-based force field that can predict the chemical reactions of a system by determining the breakage and formation of chemical

bonds based on the bond-order size. Bond-order refers to the number of chemical bonds that exist between two atoms and determines the type and stability of covalent bonds. If the bond-order is zero, there is no covalent bond between the two atoms. The bond-order is calculated empirically from the interatomic distances and is used to determine the bond connectivity. The model parameters of the ReaxFF force field are obtained by QM calculations, so the accuracy of ReaxFF MD simulations is close to that of quantum chemistry calculations, but its computational cost is only comparable to that of classical MD methods.

The potential energy of the ReaxFF force field is given by

$$E_{\text{system}} = E_{\text{bond}} + E_{\text{over}} + E_{\text{under}} + E_{\text{val}} + E_{\text{pen}} + E_{\text{tors}} + E_{\text{conj}} + E_{\text{vdW}} + E_{\text{Coulomb}}, \quad (6)$$

where  $E_{\text{bond}}$  is the bond energy describing the energy associated with bond stretching;  $E_{\text{over}}$  and  $E_{\text{under}}$  are overcoordination and undercoordination energy corrections according to the valence bond theory;  $E_{\text{val}}$  is the valence angle energy corresponding to valence angle strain;  $E_{\text{pen}}$  is the penalty energy,  $E_{\text{tors}}$  is the torsion angle energy corresponding to torsional angle strain;  $E_{\text{vdW}}$  and  $E_{\text{Coulomb}}$  are van der Waals energy and coulomb energy between atoms that are not connected with covalent bonds.

ReaxFF MD has been successfully applied to the study of oxidation and thermal decomposition of complex organic compounds such as hydrocarbons, coal, and lignin [28]. As for asphalt materials, Pan and Hu et al. performed ReaxFF MD simulations to analyze the thermodynamic and kinetic properties of oxidative aging of asphalt, and the simulated results were well compared with experimental data [11, 43]. Their studies demonstrate that ReaxFF MD is feasible for investigating the aging behavior of asphalt binders and their aging blocking mechanisms.

### 3. Experimental and Modeling Methods

**3.1. Preparation of Crumb Rubber-Modified and Phenolic Compound-Modified Asphalt.** The base asphalt used was a Performance Grade (PG) 64–22 asphalt produced by SK Company (Korea). The crumb rubber was produced by Huangshi Rubber Factory (China), and its size was 40–80 mesh. Catechin purchased from Sigma–Aldrich (Shanghai, China) was selected to represent phenolic compounds for this study. Catechin is a natural phenol and antioxidant widely found in tea leaves and other plants. It is rich in phenolic hydroxyl groups and is therefore expected to have strong antiaging properties. It has a small molecular size, which ensures uniform dispersion when added to asphalt.

First, the base asphalt was heated to a flowing state in an oven at 160°C, and then placed in an oil bath at 180°C to maintain the flowing state. Next, 9 wt.% of crumb rubber and catechin were added to base asphalt, respectively, and stirred manually to make them well dispersed, and then sheared by a high-speed rotary shear at 6000 r/min for 60 min to obtain the RMA sample and the catechin modified asphalt (CMA) sample.

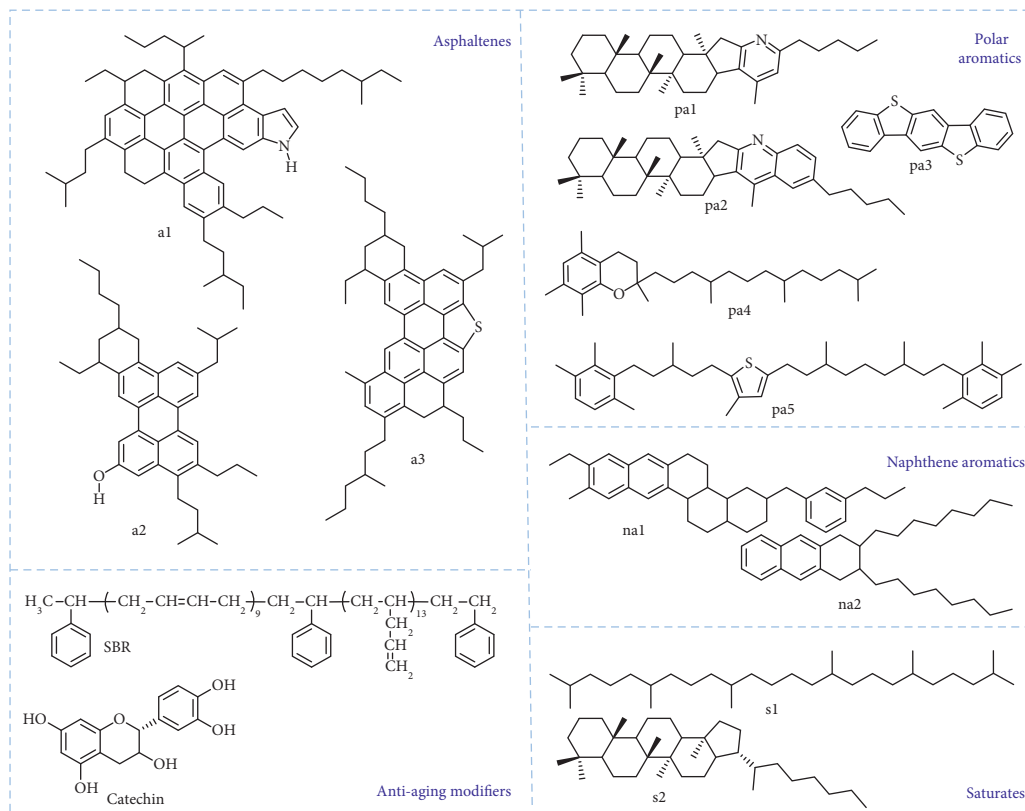


FIGURE 1: Representative molecules of asphalt components and antiaging modifiers.

**3.2. Aging Tests and ATR-FTIR Spectroscopy.** Base asphalt and modified asphalt were subjected to a rolling thin-film oven (RTFO) test according to the AASHTO T240 standard to produce short-term aged samples [44], followed by another pressure aging vessel (PAV) test following the AASHTO R 28 standard to produce long-term aged samples [45]. ATR-FTIR spectroscopy was performed on virgin and long-term aged asphalt samples to assess changes in the characteristics of their oxygen-containing functional groups [46]. The ATR-FTIR tests were conducted on a Thermo Nicolet iS10 spectrometer in the spectral range of  $4000\text{--}400\text{ cm}^{-1}$ .

The carbonyl index (CI) and sulfoxide index (SI) of asphalt samples before and after aging were calculated according to equations (7) and (8) to quantify the abundance of carbonyl and sulfoxide groups and to evaluate the aging degree of asphalt samples.

$$CI = \frac{A(1700)}{A(1460) + A(1375)}, \quad (7)$$

$$SI = \frac{A(1030)}{A(1460) + A(1375)}, \quad (8)$$

where  $A(1460)$ ,  $A(1375)$ ,  $A(1700)$ , and  $A(1030)$  are integrated absorption peak areas of methylene, methyl, carbonyl, and sulfoxide groups, respectively. It is generally assumed that the amount of methylene and methyl groups remains constant during asphalt aging, and thus their

integral areas are used as references in the calculation of CI and SI indexes.

### 3.3. Modeling Details for MD Simulations

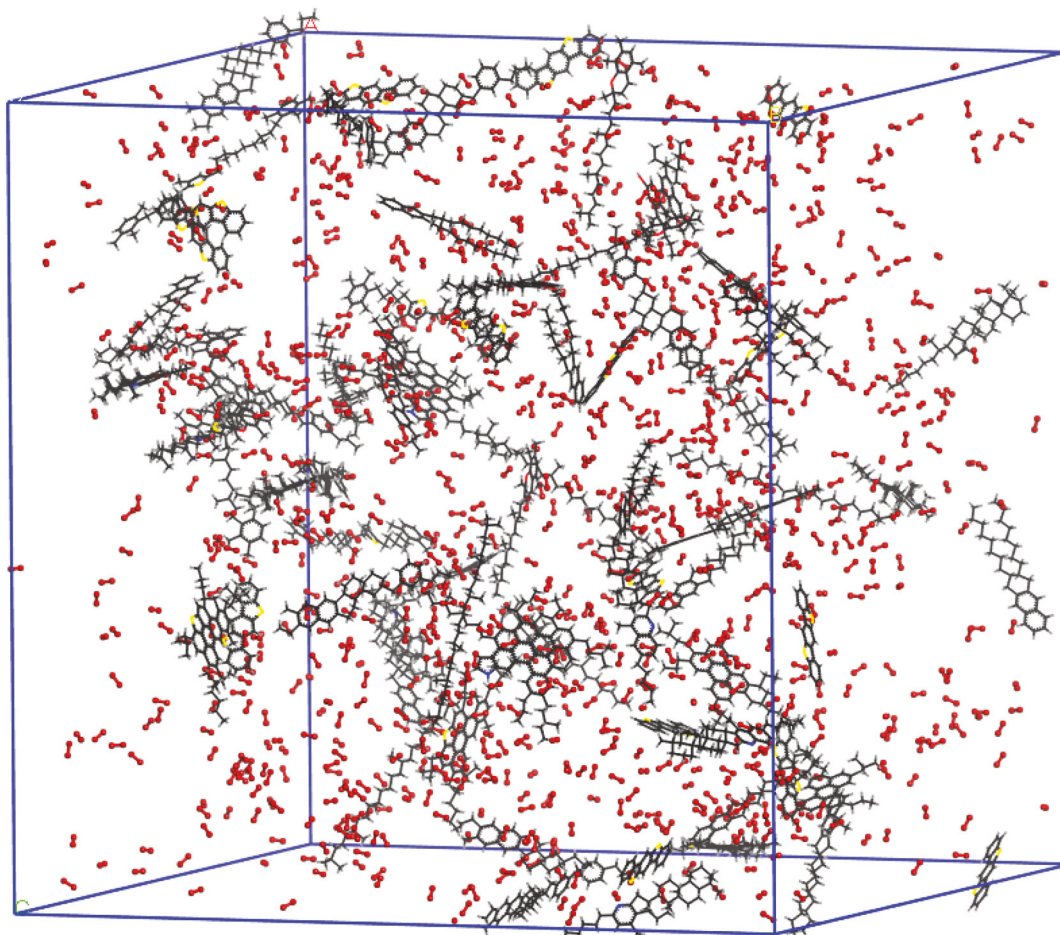
#### 3.3.1. Molecular Models of Asphalt and Modifiers.

Asphalt is composed of a large number of complex hydrocarbons and their nonmetallic derivatives. It is not possible to separate all asphalt molecules and to determine their chemical structures through experimental methods. Therefore, asphalt is usually modeled with a certain proportion of representative molecules in the MD simulation. The asphalt model used in this study was proposed by Li and Greenfield in 2014 by modifying and integrating earlier developed molecular structures [33]. In this model, asphalt was divided into four fractions, namely, asphaltenes, polar aromatics, naphthene aromatics, and saturates, as shown in Figure 1. Each fraction contains multiple representative molecules and is combined into a bulk asphalt model according to the ratios in Table 1.

An SBR polymer chain composed of 13-unit monomers of 1,2-butadiene, 9-unit monomers of 1,4-butadiene, and 3-unit monomers of styrene was used to represent the crumb rubber by reference to the literature [47]. Catechin is a small-sized compound with a clear chemical structure. The molecular models of SBR and catechin are shown in Figure 1 [18]. The number of SBR chain and catechin molecule added to the modified asphalt model was 2 and 10, respectively,

TABLE 1: Chemical information for molecular IDs in Figure 1 and their proportion in the asphalt model.

Component	Molecular ID	Chemical name	Number in the asphalt model
Asphaltenes	a1	1-pyrrole	2
	a2	2-phenol	3
	a3	3-thiophene	3
Polar aromatics	pa1	1-pyridinohopane	4
	pa2	2-quinolinohopane	4
	pa3	3-benzobisbenzothiophe	15
	pa4	4-trimethylbenzeneoxane	5
	pa5	5-thioisorenieratane	4
Naphthene aromatics	na1	1-PHPN	11
	na2	2-DOCHN	13
Saturates	s1	1-squalane	4
	s2	2-hopane	4
Antiaging modifiers	SBR	—	2
	Catechin	—	10

FIGURE 2: Reaction system of base asphalt for ReaxFF simulations ( $102.4 \text{ \AA} \times 102.4 \text{ \AA} \times 102.4 \text{ \AA}$ , black molecules are asphalt, red molecules are  $\text{O}_2$ ).

which was calculated based on a modifier dosage of 9 wt.% of base asphalt.

**3.3.2. ReaxFF MD Simulation of Asphalt Aging Behavior.** ReaxFF MD simulations were carried out in this study using LAMMPS software to predict the chemical reactions that occur during asphalt aging [48]. The VMD procedure was used to postprocess the simulation results for visualization [49]. According to the molecular structures and ratios presented in Figure 1 and Table 1, cubic periodic reaction systems of base asphalt, RMA, and CMA mixed with 1000 O<sub>2</sub> molecules were established, respectively, as shown in Figure 2. The number of O<sub>2</sub> molecules ensures that the asphalt molecules can be seriously oxidized. The reaction system first underwent energy minimization. After that, a 1 ns thermodynamic equilibrium was performed at a canonical ensemble (NVT) and a temperature of 298 K, followed by a 2 ns oxidation simulation at the NVT-ensemble and target temperature.

To accelerate the aging reaction of asphalt in the ReaxFF MD simulation, the simulation temperature should be set higher than the ambient temperature at which the asphalt binder is exposed to in engineering practice. Meanwhile, it should not be set too high, otherwise the oxidation reaction will be too intense and incompatible with the mild aging process of asphalt. To determine the proper temperature condition, aging simulations of base asphalt were performed at different temperatures (1000 K, 1200 K, 1400 K, and 1600 K) in this study. Asphalt is transformed from the solid to gas phase at these simulated temperatures, and its density is much smaller than the real density of around 1.0 g/cm<sup>3</sup>; therefore, the density of the reaction system was set to 0.1 g/cm<sup>3</sup>. The time step of the ReaxFF MD simulation was set to 1 fs, and the cut-off of bond-order used to identify the reaction products was set to 0.3. The ReaxFF parameters used in this study were determined according to the C/H/O/N/S description developed by Van Duin's group [50].

**3.3.3. Classical MD Simulation of Asphalt Molecular Diffusion.** In addition to inhibiting the oxidation reaction activity of asphalt at the chemical level, modifiers may also reduce asphalt aging at the physical level by inhibiting the free diffusion of asphalt molecules and reducing their exposure to oxygen. This is particularly true for polymers such as rubber. Therefore, we simulated the diffusion behavior of asphalt binders and calculated the self-diffusion coefficient of asphalt molecules to evaluate the effect of rubber polymers and catechins on the diffusion property of asphalt molecules. The self-diffusion coefficient ( $D$ ) is calculated as follows [36]:

$$D = \frac{1}{6N} \lim_{t \rightarrow \infty} \frac{d}{dt} \sum_{n=1}^N [x_n(t) - x_n(0)]^2, \quad (9)$$

where  $N$  is the number of particles of the system;  $x_n(0)$  and  $x_n(t)$  are the initial and current positions of the particles.  $D$  is difficult to obtain directly, but it can be calculated from mean square displacement (MSD) of the system particles using the following equation:

$$D = \frac{\text{Slope of the MSD curve with respect to time}}{6}, \quad (10)$$

$$MSD = \frac{1}{N} \sum_{n=1}^N [x_n(t) - x_n(0)]^2. \quad (11)$$

MD simulations based on the COMPASS II force field were carried out using Materials Studio software to obtain the MSD data of asphalt molecules [51]. COMPASS II is a universal ab initio force field suitable for analyzing the physical and thermodynamic properties of organic materials and polymers. Firstly, cubic periodicity simulation systems of base asphalt and modified asphalt were established according to Figure 1 and Table 1, and the initial density of each system was set to 1.0 g/cm<sup>3</sup>, which was consistent with the real density of asphalt at ambient temperature. Then, a 1 ns thermodynamic equilibrium was performed at NVT ensemble and a temperature of 180°C to simulate the mixing of asphalt in engineering practice with a time step of 1 fs and a cut-off of 15.5 Å. After that, a 1 ns isothermal isobaric (NPT) equilibrium was performed at 25°C and the atmospheric (atm) pressure to bring the system density to its true value at ambient temperature. Finally, another 1 ns NPT equilibrium was performed under the same conditions, and the MSD and self-diffusivity coefficients were calculated based on the trajectory of this phase.

**3.3.4. Classical MD Simulation of Hardening-Related Parameters.** The main adverse effect caused by asphalt aging is the hardening of the asphalt binder, namely, an increase in its viscosity and modulus and a decrease in molecular mobility and intermolecular compatibility. Modifiers may enhance the aging resistance of asphalt by reducing the susceptibility of asphalt to aging. Therefore, hardening-related parameters were calculated for aged asphalt models with and without modifiers to analyze whether there is such a potential effect. The molecular structures of the aged asphalt used was obtained according to the ReaxFF simulation in Section 3.3.2. The component ratio of the aged asphalt models was the same as that of the virgin models.

The hardening-related parameters of the asphalt samples were also obtained by conducting MD simulations based on COMPASS II force fields using Materials Studio software. Cubic periodic systems with a density of 1.0 g/cm<sup>3</sup> were first established for various asphalt samples. Then, a 1 ns NVT equilibrium was performed at 180°C to simulate the mixing of asphalt with a time step of 1 fs and a cut-off of 15.5 Å, followed by a 1 ns NPT equilibrium at 25°C and a pressure of 1 atm. The bulk modulus and compatibility parameters were calculated for the obtained system configurations, and the diffusion coefficients related to molecular mobility were calculated according to the procedure in Section 3.3.3. The obtained system configurations were subsequently subjected to another 1 ns NPT equilibrium at 60°C and 1 atm to calculate the shear viscosity. The shear viscosity ( $\eta$ ) was calculated according to the Green-Kubo equation (11) from the



trajectory data of a 10 ns NVT-shear simulation at 60°C and a shear rate of 0.00005/ps [52].

$$\eta = \frac{V}{kT} \int_0^\infty \langle P_{\alpha\beta}(t) P_{\alpha\beta}(0) \rangle dt, \quad (12)$$

where  $V$  is the system volume,  $k$  is the Boltzmann constant,  $T$  is the temperature in thermodynamic scale,  $P_{\alpha\beta}$  is the three off-diagonal elements of the instantaneous pressure tensor, and  $t$  is the time.

## 4. Results and Discussion

**4.1. ATR-FTIR Spectroscopy of Asphalt Samples before and after Aging.** Figure 3(a) displays the ATR-FTIR spectra of base asphalt and modified asphalt before and after aging. The spectra have undergone baseline correction and normalization (by peak height) based on OMSNIC software. The sharp peaks at 1375 and 1460  $\text{cm}^{-1}$  are assigned to methyl and methylene groups, respectively. The moderate peaks at 1700 and 1030  $\text{cm}^{-1}$  correspond to stretching absorption of carbonyl (C=O) and sulfoxide (S=O) groups, respectively. The virgin base asphalt, RMA, and CMA were close in intensity at the peaks corresponding to C=O and S=O, demonstrating the absence of these oxygen-containing groups in the crumb rubber and catechin.

Figure 3(b) shows a significant increase in both CI and SI indices for the aged asphalt samples, manifesting that a large amount of C=O and S=O groups were generated in asphalt during aging, which is consistent with the observation of previous studies [53, 54]. However, the increase in both CI and SI indices of the aged CMA sample is significantly smaller than that of aged base asphalt, indicating that catechins exert considerable antiaging properties. The aged RMA sample also shows less increase in CI and SI indices than base asphalt, although not as significant as the CMA sample.

The FTIR spectroscopy demonstrate that both crumb rubber and catechin can inhibit the degree of aging of asphalt binders, but there are differences in their antiaging ability, which may be attributed to their different antiaging mechanisms. Therefore, the potential antiaging mechanisms of these two modifiers were investigated based on ReaxFF and classical MD simulations.

### 4.2. ReaxFF MD Simulations of Asphalt Aging Behaviors

**4.2.1. Aging Characteristics of Base Asphalt.** FTIR spectra showed that the oxygen-containing groups produced during asphalt aging are mainly carbonyl and sulfoxide, and their corresponding chemical bonds in ReaxFF MD simulations are C–O and S–O bonds (note: the ReaxFF MD simulation cannot distinguish whether the chemical bond is a single or a double bond), respectively. Therefore, based on the results of ReaxFF MD simulations, the number of C–O and S–O bonds in the base asphalt reaction system at each temperature was calculated, and then the oxygen content of base asphalt with time was obtained accordingly, as shown in

Figure 4. Due to the presence of oxygen atoms in the virgin asphalt molecules, the oxygen content in Figure 4 is an increment relative to virgin asphalt rather than an absolute value.

It can be seen that the dependence of the degree of asphalt aging on temperature is very significant. The oxygen content of asphalt at the end of the simulation increases from 8% at 1000 K to 85% at 1600 K. For every 200 K increase in temperature, the oxygen content of asphalt more than doubles. However, the oxygen content of aged asphalt measured in the experiments generally does not exceed 8% [55]. Therefore, the excessive oxygen content observed in the ReaxFF MD simulations at high temperatures (1200, 1400, and 1600 K) suggests that asphalt may have undergone an intense combustion reaction rather than a mild aging process. Consequently, the aging characteristics of asphalt and its influence by rubber polymers and catechins were analyzed hereafter only at a temperature of 1000 K.

The molecular structures of asphalt components at the end of the ReaxFF MD simulation under 1000 K were identified using VMD software to determine the aging products of asphalt. For example, Figure 5 displays the molecular structures of asphaltene-pyrrole (i.e., a1 in Figure 1 and Table 1) before and after aging. It can be seen that the most prominent change on this asphaltene molecule during aging is the production of many carbonyl groups, and most of them are generated on the benzyl C atom (the C atom directly attached to the benzene ring), which is in agreement with the experimental results of Dorrence et al. [56]. This is because the bond dissociation energy of the benzyl C–H bond is relatively small, and the H atom can be easily abstracted from the benzyl C atom by  $\text{O}_2$  and initiate the subsequent oxidation reaction. In addition, a carboxyl (–COOH) group is generated on the asphaltene molecule, which is supported by Petersen's research [9].

The formation of these polar groups leads to an increase in intermolecular binding energy and molecular agglomeration of aged asphalt, increasing the hardness and decreasing the fluidity of the asphalt binder. Another change on the asphaltene molecule is the conversion of two cycloalkanes into benzene rings due to the loss of H atoms. In this process, the bond-order between the carbon atoms on the cycloalkane increases, and the originally distorted carbon ring becomes flat, so aromatization is considered to have occurred. This aromatization reaction was also confirmed by the experimental characterization of Petersen [9]. The well comparison of the simulation results with experimental studies demonstrates that ReaxFF MD is feasible for simulating the aging behavior of asphalt materials.

Figure 6 displays the molecular structures of the various asphalt components at the end of the ReaxFF MD simulation. It can be seen that the main product of asphalt aging is carbonyl, followed by sulfoxide, and a small amount of carboxyl and hydroxyl groups. Because the saturate molecules do not contain benzene rings and thus do not have benzyl groups that are susceptible to oxidation reactions, the saturate molecules (s1 and s2) were generally unreacted at the end of the ReaxFF MD simulation. This is consistent with the observation from the asphalt fraction separation

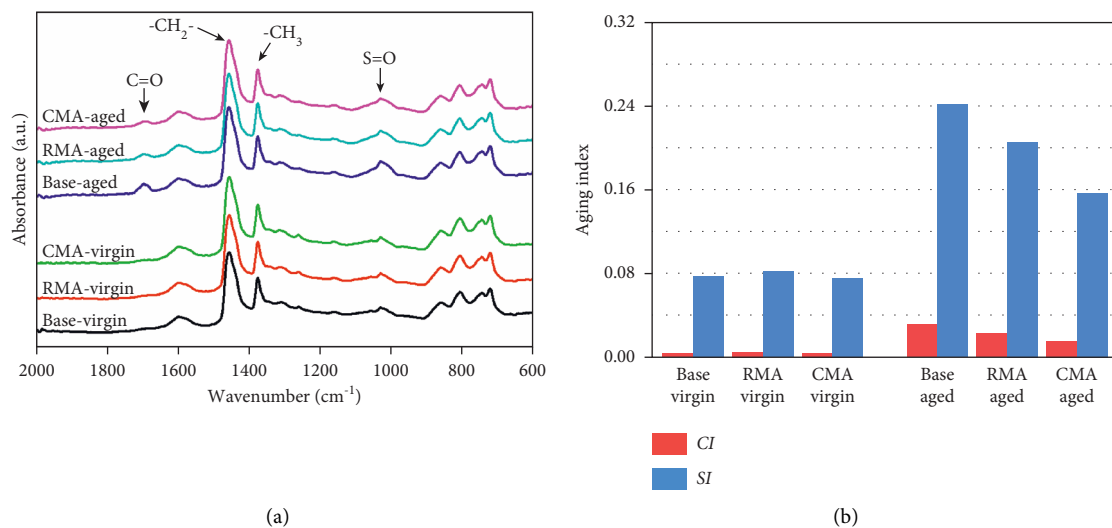


FIGURE 3: ATR-FTIR spectra of virgin and aged asphalt samples.

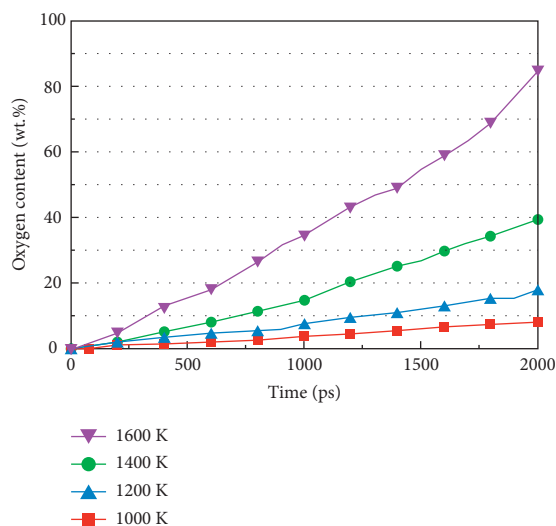


FIGURE 4: Oxygen content of base asphalt at various temperatures observed from ReaxFF MD simulations.

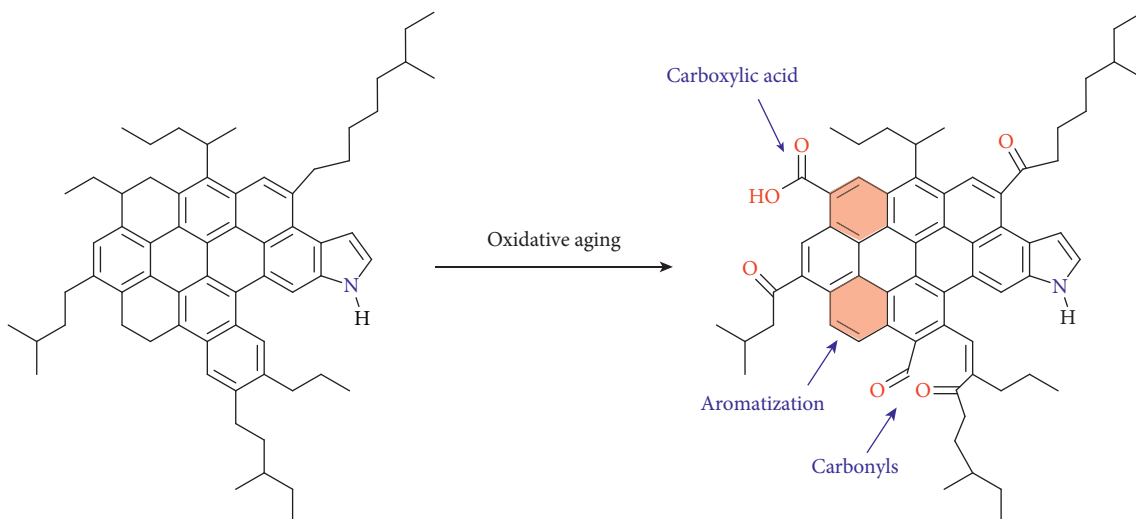


FIGURE 5: Molecular structures of asphaltene-pyrrole before and after aging.



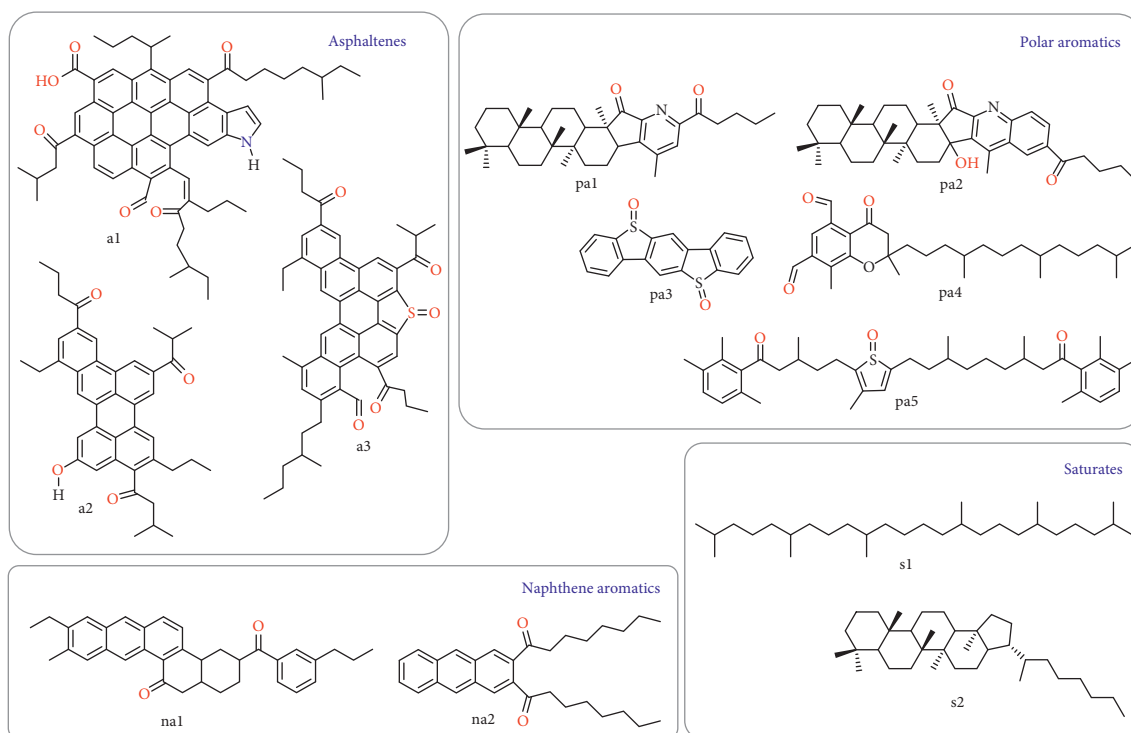


FIGURE 6: Molecular structures of various asphalt components at the end of the ReaxFF MD simulation.

experiments that the percentage of saturate fractions remained essentially unchanged before and after aging [57].

It should be noted that Figure 6 shows representative simulation results of the molecular structures of asphalt after aging; due to the stochastic nature of the chemical reactions, not every simulation will yield the same aging results. For example, there are two asphaltene-a1 molecules in the system, and at the end of the ReaxFF MD simulation, the structure of one molecule is shown in Figure 5, while the carbonyl groups on the other molecule are in different positions, and no carboxyl group is produced. This difference suggests that the aging pathway is not fixed for multiple replicates of the same asphalt molecule. Nevertheless, since these replicates have a similar aging process, the typical representation in Figure 6 was subsequently applied to represent the molecular structures of aged asphalt.

**4.2.2. Antiaging Properties of Rubber Polymers and Catechins.** Figure 7 displays the number of C–O and S–O bonds in the base and modified asphalt with time obtained from the ReaxFF MD simulations. Due to the presence of C–O bonds in the virgin asphalt molecules, the bond amounts in Figure 7(a) are increments relative to the virgin samples rather than absolute values. As shown in Figure 7(a), there is no significant difference in the growth trend of C–O bonds in RMA compared to base asphalt, indicating that rubber polymers cannot inhibit asphalt aging at the chemical level. However, the amount of C–O bond produced in LMA was significantly reduced relative to base asphalt, suggesting that catechins chemically mitigate asphalt aging. This is due to the abundant phenolic hydroxyl

groups on catechins that attract and react with  $O_2$  and free radicals, thus reducing the attack of the latter on asphalt molecules. Figure 7(b) shows that the number of S–O bonds generated during asphalt aging is much smaller than the number of C–O bonds due to the fact that the number of S atoms in the asphalt molecule is much smaller than the number of C atoms. Nevertheless, it can still be observed that rubber polymers cannot but catechins can inhibit the generation of S–O bonds.

Figure 8 displays the changes in chemical structures of rubber polymers and catechins during aging. As can be seen in Figure 8(a), two rubber chains underwent different aging reactions, but they both decomposed into four segments and reacted at the ends of the segments, including the formation of carbonyl, hydroxyl, and unsaturated olefin bonds. For these small-size segments, their molecular structures are similar to that of the saturate molecules of asphalt, except for the oxygen-containing groups at the ends. Therefore, the decomposition of the rubber polymer may exert properties that counteract the degradation of the mechanical performance of aged asphalt, as will be discussed in Section 4.4.

Figure 8(b) shows that the catechin molecule loses the H atoms on its hydroxyl groups after aging, which is the underlying mechanism by which phenolic compounds exert their antiaging properties: phenolic compounds provide active H atoms to consume  $O_2$  and free radicals in the reaction system, thus preventing them from attacking asphalt molecules. Although the catechin molecule exists as a free radical after the loss of H atoms, it remains unreactive due to the conjugation of the phenoxy group to the delocalized  $\pi$  bond of the aromatic ring and therefore does not react with the asphalt molecules.

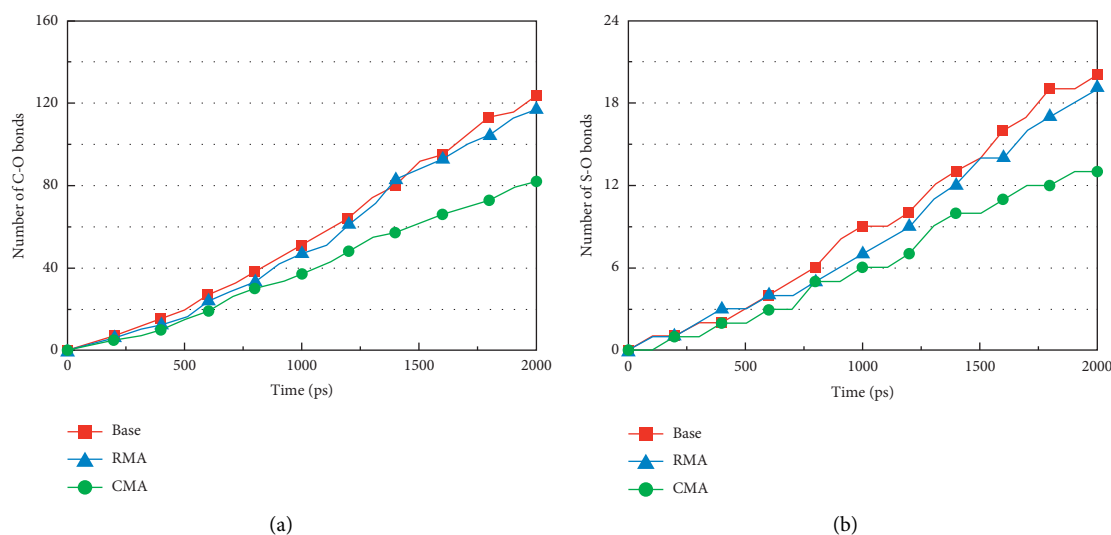


FIGURE 7: Number of C–O and S–O bonds in the base and modified asphalt samples with aging time obtained from ReaxFF MD simulations.

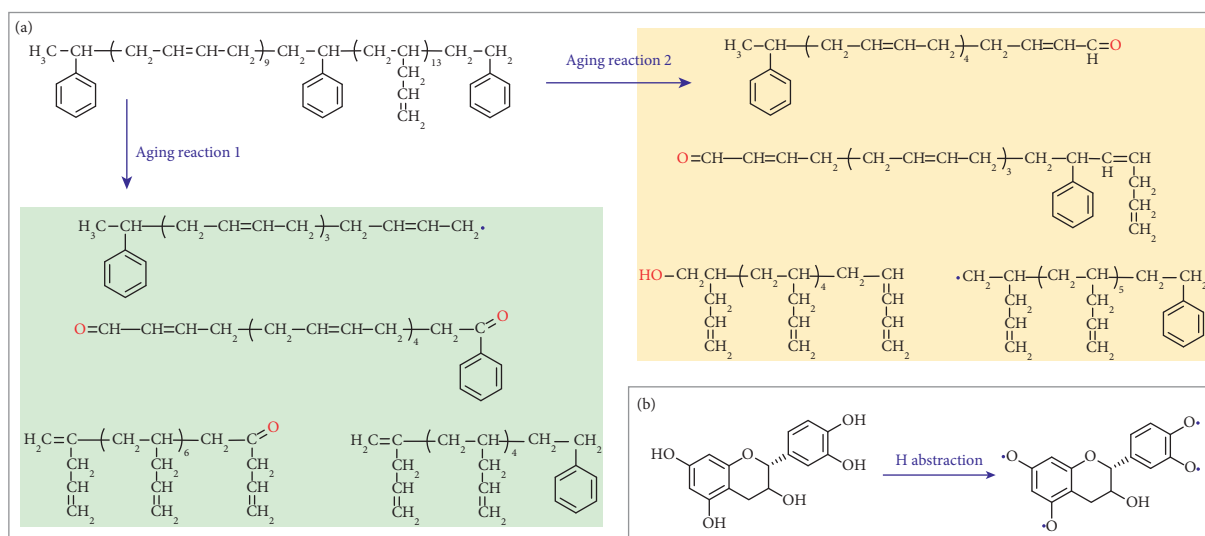


FIGURE 8: Changes in molecular structures of the rubber polymer and catechin during aging.

**4.3. Effects of Rubber Polymers and Catechins on the Diffusivity of Asphalt.** To investigate whether rubber polymers and catechins reduce the contact of asphalt with oxygen and inhibit asphalt aging by restricting the diffusion of asphalt molecules, we calculated and analyzed the diffusivity of base and modified asphalt samples. As described earlier, the self-diffusion coefficient is numerically 1/6 of the slope of the MSD curve. Since the MSD curve is not linearly related to the simulation time in the initial stage of the MD simulation, the first 50 ps of data are not used in the linear fitting of the MSD curve, as shown in Figure 9(a). The self-diffusion coefficients calculated from the MSD curves are shown in Figure 9(b), and they are the average of three replicate simulations.

The self-diffusion coefficient of RMA decreases from 0.021 Å<sup>2</sup>/ps to 0.015 Å<sup>2</sup>/ps compared to base asphalt, indicating that the addition of rubber polymers inhibits the

diffusion of asphalt molecules, which is attributed to the embedding locking effect of the styrene block in the SBR polymer on the asphalt molecules. In contrast, the addition of small-sized catechins does not significantly affect the diffusivity of asphalt molecules. By comparing Figures 7 and 9, it can be seen that both catechins and rubber polymers can exert the property of inhibiting asphalt aging, but their antiaging mechanisms are different: catechins prevent oxidative aging of asphalt by competitively consuming O<sub>2</sub> and free radicals, while rubber polymers exert an antiaging effect by reducing the contact of asphalt molecules with O<sub>2</sub>.

**4.4. Effects of Rubber Polymers and Catechins on the Hardening of Aged Asphalt.** Figure 8(a) reveals that the rubber polymers decompose during aging into small fragments with

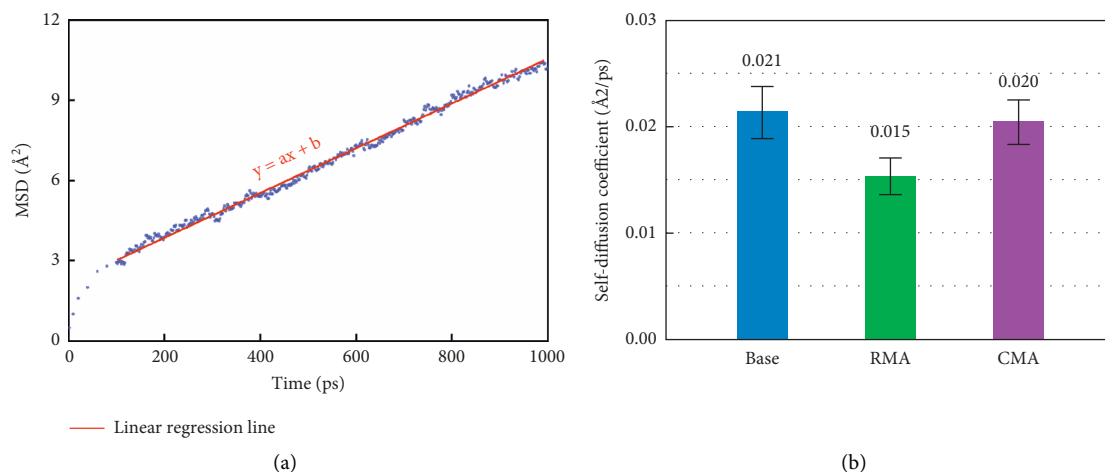


FIGURE 9: Effect of modifiers on the diffusivity of asphalt: (a) linear fitting of the MSD data; (b) self-diffusion coefficients of base and modified asphalt.

similar molecular structures to the saturates of the asphalt binder, which may counteract the hardening caused by asphalt aging to some extent. Therefore, we further analyzed the effect of aging-induced changes in the molecular structures of the modifiers on the hardening-related parameters of the aged asphalt, as shown in Figure 10. The molecular structures of aged asphalt and modifiers presented in Figures 6 and 8 were used here to construct MD models.

Figure 10(a) shows that the shear viscosity of RMA under the virgin condition doubles compared to base asphalt, which is attributed to the enhanced intermolecular friction of the asphalt binder caused by the embedding locking effect of the rubber polymer. The shear viscosity of CMA also increases slightly compared to base asphalt, which may be attributed to the numerous polar hydroxyl groups in catechins that increase the agglomeration of asphalt molecules. After aging, the viscosity of all three asphalt samples increases significantly due to the generation of polar oxygen-containing groups on the asphalt molecules. However, the viscosity of RMA under the aging condition is lower than that of base asphalt due to the breakage of rubber chains into fragments similar to the saturate fraction of asphalt binders. The viscosity of aged CMA also decreases slightly compared to base asphalt, probably because the molecular structure of the catechins was disrupted and their molecular polarity decreased, thus serving to dilute the highly polar aged asphalt molecules.

As displayed in Figure 10(b), the bulk modulus of each sample increases substantially after aging compared to that before aging, which is also attributed to the generation of polar groups that bind the asphalt molecules more tightly and make it difficult for deformation to occur. Compared to base asphalt, the bulk modulus of RMA increases slightly before aging and decreases after aging by the same mechanism as the viscosity change. However, there was no statistical difference in the modulus of CMA before or after aging compared to the matrix asphalt, suggesting that the polar hydroxyl groups of catechins have a different effect on the modulus of asphalt than on the shear viscosity.

The solubility parameter shown in Figure 10(c) is a measure of intermolecular compatibility of the binder samples. The larger the solubility parameter of modified or aged asphalt, the more difficult it is for their respective internal molecules to be compatible, thus exhibiting unfavorable local hardening. In the virgin state, the solubility parameter of RMA increases slightly compared to base asphalt, indicating that the addition of rubber polymers reduced the compatibility of the asphalt components, which is consistent with the lack of storage stability of CRMA in engineering practice [58, 59]. However, the solubility parameter of RMA after aging is smaller than that of base asphalt, indicating that the decomposition products of the rubber polymer become more compatible with the asphalt molecules. The solubility parameters of CMA are not statistically different compared to base asphalt both before and after aging.

Figure 10(d) displays the effects of modification and aging on the diffusivity of the asphalt binder. The lower diffusivity indicates that the asphalt binder is more difficult to flow and is therefore also related to the hardening properties of the asphalt material. The effects of rubber polymers and catechins on the diffusivity of virgin asphalt have been discussed in Section 4. The diffusivity of all samples decreases significantly after aging, indicating that the polar groups produced during aging restricted the movement of asphalt molecules. Compared to aged base asphalt, the diffusivity of RMA increases slightly while that of CMA remains unchanged, suggesting that the cleaved rubber polymers act as a lubricant for the aged asphalt molecules, thus increasing their movement, while catechins do not exert this effect.

According to Figures 9 and 10, it can be concluded that rubber polymers can not only reduce the asphalt aging reaction by limiting the contact of asphalt molecules with oxygen but also restore the mechanical properties of aged asphalt by partially offsetting the aging-induced hardening of the asphalt binder through its own degradation. Therefore, crumb rubber is widely used as antiaging

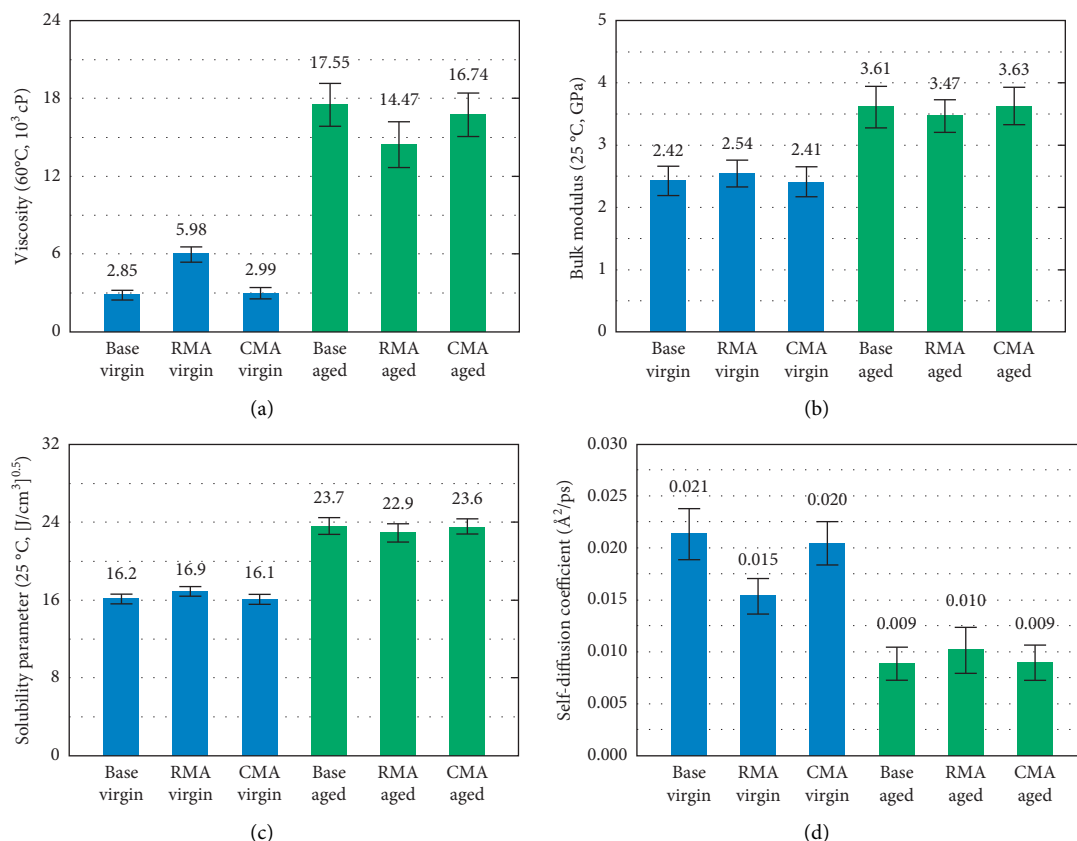


FIGURE 10: Effects of modifiers on the hardening-related parameters of aged asphalt: (a) viscosity; (b) bulk modulus; (c) solubility parameter; (d) self-diffusion coefficient.

agents for asphalt binders, even though it cannot directly block the oxidation reaction of asphalt molecules at the chemical level.

## 5. Conclusions

ATR-FTIR spectroscopy and ReaxFF with classical MD simulations were performed in this study to investigate the inhibitory effects of catechins and crumb rubber on asphalt aging and their potential mechanisms. The following conclusions can be drawn:

- (1) ATR-FTIR analysis showed that both catechins and crumb rubber can inhibit the aging of the asphalt binder to some extent, and catechins have better antiaging properties than crumb rubber.
- (2) ReaxFF MD simulations of asphalt aging behavior demonstrated that catechins can prevent asphalt aging at the chemical level, leading to a reduction of generated S–O and C–O bonds by the mechanism that catechins provide H atoms to react with  $\text{O}_2$  and free radicals, thus preventing them from attacking asphalt molecules.
- (3) Classical MD simulations of diffusion behavior suggested that the addition of rubber polymers

restricts the movement of asphalt molecules, thus reducing their contact and reaction frequency with  $\text{O}_2$  at the physical level.

- (4) MD calculations of the hardening parameters of the aged asphalt binder show that the aging degraded rubber polymer acts as a diluting and lubricating agent, thus partially restoring the aging-induced asphalt hardening.

In conclusion, this study demonstrates that phenolic compounds and rubber polymers enhance the aging resistance of asphalt binders through their respective mechanisms at the molecular scale and is expected to provide theoretical guidance for the development of targeted anti-aging technologies for asphalt. In future studies, we will further analyze the correspondence between the chemical structures of polymers and phenolic compounds and their antiaging properties to guide the selection and development of antiaging agents for asphalt.

## Data Availability

Some or all data that support the findings of this study are available from the corresponding author upon reasonable request.

## Conflicts of Interest

The authors declare that they have no conflicts of interest.

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