The short-term aging effect on the interface and surface wetting behavior of modified asphalt mixtures

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Abstract

In this study, the interface models and nanodroplets wetting models of base asphalt (BA), polyurethane modified asphalt (PU-MA) and polyurethane/graphene oxide composite modified asphalt (PU/GO-MA) with acidic and alkaline aggregates were constructed. The adhesion and debonding effects of modifiers on short-term aged asphalt mixtures were analyzed by molecular dynamics (MD) simulation. The moisture damage resistance of the mixture was evaluated by simulating the wetting characteristics of asphalt and water nanodroplets on the aggregate surface. The contact angle, adhesion work, debonding work and relative concentration distribution can effectively analyse the interface interaction behavior between asphalt and aggregate. The results show that the adsorption effect between aged asphalt and CaCO₃ was stronger, and short-term aging enhanced the interfacial adhesion of asphalt mixtures. Calcite was more hydrophilic, and its resistance to moisture damage was far less than quartz. The difference between the contact angle of water-aggregate and that of asphalt-aggregate can effectively analyze the water sensitivity of asphalt mixture. In addition, different components played different roles in the adsorption of asphalt and different aggregate surfaces. The synergistic analysis of the asphalt-aggregate interface and the asphalt nanodroplet-wetting aggregate surface can more comprehensively reveal the variation principle of asphalt parameters and nanoscale properties of asphalt mixtures.

1. Introduction

Asphalt mixture is made by mixing mineral aggregates and asphalt binder. Because of its low price and excellent performance, it has been widely used in road construction [1–3]. The adhesion of asphalt binder has an important effect on the deformation resistance of asphalt mixture. But the aging of asphalt can affect its adhesion. In the process of storage, transportation of asphalt and mixing, rolling of asphalt mixture, the temperature of asphalt is above 100 °C in order to ensure that it is in a molten state, and even the surface temperature after rolled is not lower than 70 °C [4]. Continuous high temperature accelerates the aging of asphalt, and this short-term aging is inevitable. During the construction process, improper compaction will increase the effective voids and infiltration voids of asphalt [5], which will lead to asphalt long-term aging and moisture damage of asphalt mixture under the impact of wheel loading of cars and trucks, immersion of rainwater, high temperature softening in summer and low temperature cracking in winter [6–9]. In recent years, many scholars have analyzed the pavement properties of asphalt mixture by studying its macroscopic properties such as elastic modulus, creep strength, fracture toughness, adhesion and moisture damage resistance to verify
the effect of modifier, aging of asphalt and mineral species of aggregates on the performance of asphalt mixture [10–13].

Asphaltic modifiers and mineral species have significant impacts on the adhesion and moisture damage resistance of the asphalt mixture interface. Asphalt aging will lead to unstable interface structure of asphalt mixture. Short-term aging mainly affects the adhesion and moisture resistance between asphalt and aggregate interface, while long-term aging may also affect the cohesion inside the asphalt, and the mechanism is more complicated. Many researchers have effectively analyzed the asphalt-aggregate interaction and moisture sensitivity of asphalt mixture by various micro and macro experiments. Jin et al. [14] discovered the adsorption of polyurethane (PU) and rock asphalt composite modified asphalt with various components in minerals by means of x-ray diffraction tests, and found that there are chemical and physical adsorption between alkaline minerals such as calcite. Sun et al. [15] compared the adhesion grades of styrene-butadiene-styrene (SBS) modified asphalt, PU modified asphalt and base asphalt before and after aging with aggregate surfaces of granite, limestone and basalt. It was found that the adhesion between PU modified asphalt and aggregate was higher than SBS modified asphalt and base asphalt due to pressurized aging vessel aging, and the adhesion between asphalt and limestone aggregate surface was the highest in various conditions. Zhu [16] and Wang [17] et al. used droplet method to measure the contact angle between asphalt as well as aggregate and calculated the effect of asphalt on aggregate adhesion characteristics. The contact angle of graphene oxide (GO) modified asphalt decreased and the surface free energy increased with the increase of GO content. Adnan et al. [18] explored the moisture damage resistance of GO modified asphalt mixtures by immersing Marshall test and semicircular bending fracture test. Because GO particles can enhance the cohesion of the asphalt binder, which in turn increases the adhesion between asphalt and aggregate, preventing crack propagation and improving the moisture resistance of the mixture. Xing et al. [19] studied the dependence of the interface interaction parameters on particle size for mineral fillers with different particle shapes and types, and explored the interface interaction between asphalt and mineral fillers with different lithologies. Hamedi et al. [20] found that the nano-modifier used the surface free energy method to reduce the acid-base ratio of asphalt and improved the adhesion between asphalt and the hydrophilic acidic aggregate.

However, macroscopic performance experiments do not provide a comprehensive understanding of how oxidative aging, modifiers or aggregate surface properties inherently affect asphalt-aggregate adhesion. As a nanoscale evaluation method, molecular dynamics (MD) simulations can effectively reveal the change mechanism of the asphalt-aggregate interface [21, 22]. The addition of nanomaterials or polymers to asphalt can affect the asphalt-aggregate interface. Cui et al. [23] calculated adhesion energy to characterize the bond strength of single-walled or multi-walled carbon nanotubes on asphalt-aggregate surface, and the addition of multi-walled carbon nanotubes increased the Van der Waals energy or enhanced electrostatic energy on the surface of asphalt and acidic or basic aggregates. Hu et al. [24] studied the properties of crumb rubber on the asphalt-aggregate interface. High rubber content has a significant effect on the adhesion and moisture stability of the asphalt-Al2O3 interface. Asphalt-aggregate interface adhesion and debonding can reflect the effect of asphalt binder and the influence of moisture. In addition, the aging of asphalt has a greater impact on the adhesion and debonding of the asphalt-aggregate interface. Calculating the relative concentration change of asphalt in asphalt-aggregate model after MD can be used to study the polarity and diffusion factors of different components of asphalt molecules before and after aging [25, 26]. The application of asphalt-aggregate with different mineral categories, different aggregate surface shapes and different moisture content has been increasing gradually [27–30]. It is also very important to study the interfacial adhesion between modified asphalt and aggregate at high temperature. Gong et al. [31] simulated the adhesion of asphalt-quartz interface at different temperatures and in different dry and wet conditions, and quantified the moisture sensitivity of the interface by calculating the adhesion degradation rate. As the temperature increases, the degradation of adhesion decreased and then increased. The adhesion effect of anisotropic mineral surfaces on asphalt mixture was explored by MD simulations. Luo et al. [32] simulated the diffusion process of water nanodroplets on the surface of anisotropic minerals, studied the residual adhesion force and energy ratio between the aggregate surface of different Miller notation systems and asphalt, and obtained the mineral cleavage surface with the best adhesion and moisture damage resistance.

However, limited work has focused on the energy change at the asphalt-aggregate interface, and few studies have combined multiple factors such as oxidative aging, polymer/nanocomposite modifiers, aggregate surfaces with different properties, wet and dry conditions, and high temperature conditions to analyze the interfacial adhesion and debonding capabilities. This paper proposes to apply a common performance experiment, that is, wetting of asphalt on aggregate surface to MD simulations to reveal the contact angle changes of asphalt wetting process on aggregate surfaces with different properties. Therefore, in this paper, the interface models of base asphalt (BA), polyurethane modified asphalt (PU-MA) and polyurethane/graphene oxide composite modified asphalt (PU/GO-MA) as well as aggregates before and after aging were constructed, and then the wetting models of high-temperature liquid asphalt nanodroplets before and after aging and different mineral aggregate surfaces
were also constructed. The effects of modifiers on adhesion and moisture damage resistance of short-term aged asphalt mixtures were analyzed by MD simulation. The adhesion work between asphalt and different aggregates was calculated to analyze the effect of modifiers on asphalt mixtures. By calculating the debonding work of the asphalt and aggregate and simulating the contact angle of high-temperature liquid asphalt on the surface of acid or alkaline aggregate, the moisture damage resistance of asphalt-aggregate adhesive interface was evaluated. Parameters such as relative concentration distribution and contact angle affecting the interface interaction were calculated. The synergistic analysis of the asphalt-aggregate interface and the asphalt nanodroplet-wetting aggregate surface discusses the variation principle of asphalt parameters and nanoscale properties of asphalt mixtures.

2. MD simulation process

2.1. Determination of asphalt and aggregate

The molecular composition ratio and modifier molecular structures of virgin and short-term aged BA, PU-MA and PU/GO-MA used in previous studies were used in this research [33]. The asphalt molecular models adopted the 12-molecule system which was based on AAA-1 proposed by the Strategic Highway Research Program and improved by Li et al [34]. The short-term aged asphalt component model followed the asphalt molecular system model with sulfoxide functional groups presented by Xu et al [35]. All virgin and short-term aged molecular structures of the asphalt SARA components with 12-molecule system and the structure of the modifiers PU and GO are shown in figure 1.

The hydrophilicity and acid-base properties of aggregate are important factors affecting the laying and application of asphalt mixture. Lu et al [36] determined the chemical composition of natural minerals by X-ray fluorescence spectroscopy as follows: SiO\(_2\) > CaO > Al\(_2\)O\(_3\) > MgO > Na\(_2\)O > K\(_2\)O. The two largest components are SiO\(_2\) and CaO, respectively, an acid oxide and an alkaline oxide, which can be used as two typical components for studying the mechanism of asphalt-aggregate interface. In nature, SiO\(_2\) is the most common acid oxide found in the quartz minerals, especially α-quartz, which is at low temperatures [32]. As an alkaline oxide, CaO is unstable, whereas calcium carbonate has more stable properties and is commonly found in minerals, mainly calcite.

2.2. Construction of models

The resulting equilibrium molecular models were used to construct the interface and wetting model. Each crystal has a different cleavage plane, the surface of which is usually described by the Miller notation system (h k l). The most common stable crystal plane of α-quartz in nature is (0 0 1), and due to its hydrophilic characteristics, most studies made its surface hydroxyl into a representative model for acidic aggregates [32], which set the thickness and cleavage plane, as shown in figure 2(a). The most commonly exposed cleavage plane
of calcite is $(1\,0\,4)$, and its surface with thickness and cleavage plane is set as shown in figure 2(b). The surface of the two crystals was relaxed by geometry optimization after constraining the atoms except the surface. SiO$_2$ $(0\,0\,1)$ and CaCO$_3$ $(1\,0\,4)$ aggregate supercells were modeled by extending $U$ and $V$, respectively, and a $10\,\text{Å}$ vacuum layer was added to the upper surface. In addition, moisture can seep into the interface between asphalt and aggregate during undercompaction of the road surface and repeated tire loading, and the phenomenon of moisture damage can occur in asphalt mixtures. A water layer composed of 290 water molecules was established. In order to study the influence of different aggregates and asphalt interface adhesion and water damage, four different asphalt mixture interface models were constructed: asphalt-SiO$_2$, asphalt-CaCO$_3$, asphalt-water-SiO$_2$, and asphalt-water-CaCO$_3$. The temperature was set to $298.15\,\text{K}$ at room temperature. An $80\,\text{Å}$ vacuum layer was set over the asphalt molecule to eliminate periodic interference at the boundary. The thickness of the water was $5\,\text{Å}$. In order to consider the change of the adhesion between asphalt and aggregate as well as the effect of high-temperature on base asphalt and modified asphalt during the process of construction, the asphalt-SiO$_2$ and asphalt-CaCO$_3$ interface models at $408.15\,\text{K}$ were built.

Water-mineral wetting model can indicate hydrophilicity or hydrophobicity of mineral surface, and the wetting model of high-temperature liquid asphalt droplets on the mineral surface can also be used to analyze the wettability of different asphalt and different aggregate surfaces [22, 37]. Nanospheres of virgin and aged base asphalt (VBA and ABA) with a radius of $30\,\text{Å}$ were constructed and placed at the center of quartz-$\alpha$ $(0\,0\,1)$ and calcite $(1\,0\,4)$ surfaces respectively, with side lengths of $145\,\text{Å}$, forming a wetting model with asphalt nanodroplets. Figure 3 shows a schematic diagram of the wetting model of VBA and hydroxylated quartz aggregate surface.

2.3. MD simulation
Molecular models of asphalts and modifiers were built using the Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies II (COMPASS II) force field, which is suitable for liquids such as organic molecules, polymers, inorganic oxides and the interface system of different materials [38]. Thermostat was set to Nose-Hoover-Langevin (NHL) and its algorithm provides a reliable thermostat for systems in the whole process of dynamic equilibrium, which is more efficient in balance and is superior in thermostatting compared to Nosé and Nosé-Hoover dynamics method [39]. Summation methods of electrostatic and van der Waals were set to Ewald and Atom based, respectively, with cutoff distance set to $15.5\,\text{Å}$.

All asphalt were subjected to geometry optimization, annealing, MD simulation under canonical (constant particle number, volume and temperature, NVT) ensemble and constant-pressure, constant-temperature (NPT) ensemble, and finally molecular models of asphalt with stable conformation were obtained. The reliability of the molecule has been proved in several studies. Firstly, the displacement and deformation of
aggregate were constrained, and then the interface models of asphalt-aggregate and asphalt-water-aggregate were geometrically optimized with a maximum iteration number of 5000 steps to obtain an interface model with energy minimization. MD simulation of 100 ps under the NVT ensemble was performed on the asphalt mixture models at different temperatures, and all energies and temperatures of interface models were stable within 10 ps. Using Perl scripts and trajectory files, the average of the last 5 frames was selected as an object for calculation and analysis, because the standard deviation of the adhesion and debonding work in the last 5 frames was small. After MD, the adhesion and debonding energy of asphalt were calculated, and relative concentration distribution of the SARA components and modifiers were analyzed. The concentration distribution selected the (0 0 1) direction. To facilitate analysis and display, the number of bins was set to 2000 and used a smoothing function to plot curves. Width was set to 13.0 bins. MD simulations of 1000 ps under the NVT ensemble were performed on the aggregate wetting model with asphalt droplets. The asphalt was in a molten liquid state at high-temperature, where the temperature was set to 433.15 K. After MD, the contact angles of all asphalt droplets at each moment were calculated.

3. Theoretical calculations

3.1. Calculation of total potential energy
The COMPASS II force field can effectively characterize the energy of asphalt, PU and GO [8, 40–44]. The total energy ($E_{\text{total}}$ kcal mol$^{-1}$) includes Valence energy (diag. terms and cross terms) and non-bond energy. The formula is shown in equation (1):

$$E_{\text{total}} = (E_{\text{Bond}} + E_{\text{Angle}} + E_{\text{Torsion}} + E_{\text{Inversion}}) + (E_{\text{Stretch}} - \text{Stretch} + E_{\text{Stretch}} - \text{Bond} - \text{Stretch}$$

$$+ E_{\text{Torsion}} - \text{Torsion} - \text{Stretch} + E_{\text{Separated}} - \text{Stretch} - \text{Stretch} + E_{\text{Torsion}} - \text{Stretch} + E_{\text{Bond}} - \text{Bond}$$

$$+ E_{\text{Torsion}} - \text{Bond} - \text{Bond} + E_{\text{Bend}} - \text{Torsion} - \text{Bend}) + (E_{\text{van der Waals}} + E_{\text{Electrostatic}} + E_{\text{Long range correction}})$$

(1)

3.2. Calculation of interface adhesion work and debonding work
The size of adhesion work represents the firmness of solid-liquid phases, which can characterize the adhesiveness between asphalt and aggregate. The formula is shown in equation (2):

$$W_{\text{adhesion}} = (E_{\text{asphalt}} + E_{\text{aggregate}} - E_{\text{as,agg}}) / A$$

where $W_{\text{adhesion}}$ represents the adhesion work between asphalt and aggregate, $E_{\text{as,agg}}$ represents the total energy of asphalt and aggregate balanced in vacuum, $E_{\text{asphalt}}$ and $E_{\text{aggregate}}$ represent the energy of asphalt and aggregate separated after stabilization in vacuum, respectively. $A$ represents the area of action between the two-phase at the interface.

Debonding work represents the work required by water to separate the interface between asphalt and aggregate, which can characterize the ability of asphalt against aggregate hydrophilic. The formula is shown in
\[
W_{\text{debonding}} = (\Delta E_{\text{inter-as,w}} + \Delta E_{\text{inter-agg,w}} - \Delta E_{\text{inter-as,agg}}) / A
\]  

where \( W_{\text{debonding}} \) represents the debonding work of asphalt and aggregate, \( \Delta E_{\text{inter-as,w}} \), \( \Delta E_{\text{inter-agg,w}} \) and \( \Delta E_{\text{inter-as,agg}} \) represent the interface binding energy of asphalt-water, aggregate-water and asphalt-aggregate, respectively.

Energy ratio \((ER)\) can characterize the water damage resistance of asphalt, which can evaluate the effect of modifier on water sensitivity of asphalt mixture \([28, 45]\). \( ER \) is calculated by adhesion work and debonding work, as shown in equation (4):

\[
ER = \frac{W_{\text{adhesion}}}{W_{\text{debonding}}}
\]

### 3.3. Calculation of contact angle

When the solid surface comes into contact with the liquid, its free enthalpy will be greatly reduced, resulting in interfacial phenomena. The wetting effect of liquids on the solid surfaces is the interaction of molecules within the interface region, that is, the adhesion work, which can be calculated by the interfacial tension:

\[
W_{\text{adhesion}} = \gamma_{SG} + \gamma_{LG} - \gamma_{LS}
\]

where \( \gamma_{SG} \) represents interfacial tension between solid and gas, \( \gamma_{LG} \) represents interfacial tension between liquid and gas, and \( \gamma_{LS} \) represents interfacial tension between liquid and solid.

Interfacial tension between the solid phase and the liquid phase is usually calculated from the contact angle. At high-temperature, the asphalt becomes a molten liquid state, and when it drops on the mineral surface, incomplete wetting can occur according to different polarities, forming a certain contact angle \( \theta \), as shown in figure 4. The Young equation describes the relationship among the interfacial tensions of the solid-liquid-gas three-phase, as shown in equation (6):

\[
\gamma_{SG} = \gamma_{LS} + \gamma_{LG} \cos \theta
\]

where \( \theta \) is the contact angle between solid and liquid. The wetting models in this research were constructed in a vacuum, so the interfacial tension between solid or liquid and gas is equal to the surface tension of solid or liquid, and the adhesion work is expressed as equation (7). The contact angle ranges from 0° to 180°, and as the contact angle increases, the adhesion work between the asphalt and the aggregate surface decreases.

\[
W_{\text{adhesion}} = \gamma_{LG} (\cos \theta + 1)
\]

The contact angle can be calculated by the droplet height method \([46]\), \( h \) being the height of nanodroplet and \( R \) representing the radius of nanodroplet. The definition of the contact angle is shown in figure 4. There are two cases where the contact angle is greater than 90° and less than 90°. The contact angle can be defined as:

\[
\cos \theta = 1 - \frac{h}{R}
\]
The calculation formula of contact angle is given by Hautman and Klein [47], as follows:

\[
\langle z_{c.m.} \rangle = (2^{-4/3} R_0 \left( \frac{1 - \cos \theta}{2 + \cos \theta} \right)^{1/3} \left( \frac{3 + \cos \theta}{2 + \cos \theta} \right))
\]

where \(z_{c.m.}\) represents the average height of the center of mass of asphalt nanodroplet, \(R_0\) is the radius of asphalt molecules.

4. Results and discussion

4.1. Interaction behavior of virgin and short-term aged asphalt-aggregate interface

The polarity of the aggregate surface and the polarity of the asphalt molecules directly affect their adhesion. Generally, the higher the alkalinity, the more obvious the interaction with acidic substances. Asphalt is a material with low polarity and is rich in asphaltous acid and asphaltic anhydride [29], so its bonding behavior with the acidic aggregates such as SiO\(_2\) is not as good as that with the alkaline aggregates such as CaCO\(_3\). Figure 5 shows the simulations of ABA with SiO\(_2\) and CaCO\(_3\) aggregate surfaces, respectively, as well as snapshots of the relative concentration of ABA. The relative concentration of asphalt before and after MD simulation shows the process of asphalt approaching aggregate. It was obvious that both aggregates can adsorb ABA, but the gradient of the concentration distribution was different. The essence of the concentration curve is the uniformly spaced atomic density curve [48], which can characterize the degree of molecular aggregation at a certain distance [45]. The \(z\)-direction distribution of ABA on the surface of SiO\(_2\) was uniform, while the distribution on the surface of CaCO\(_3\) was uneven, especially the atomic density near the surface of the aggregate was higher, so that the adsorption of asphalt was stronger with CaCO\(_3\). However, the hydroxylated quartz surface formed hydrogen bonds with the sulfoxide groups in the aged asphalt, and the increase of electrostatic attraction enhanced the adsorption of the asphalt to SiO\(_2\) [25].

The interaction behavior of the asphalt-water-aggregate interface was very different from that of anhydrous interface. When moisture invaded the asphalt-aggregate interface, the adsorption between asphalt and aggregate surface was replaced due to hydrophilicity of aggregate. In terms of virgin asphalt, ultra-low polarity kept it away from the water layer and aggregate surface after MD simulation. However, the calcite surface was more hydrophilic than the hydroxylated quartz surface, so water was completely gathered on the calcite surface, and the strong adsorption of water on the aggregate surface prevented asphalt molecules from approaching the aggregate, breaking the bond between asphalt and aggregates. In terms of aged asphalt, the sulfoxide functional group had greater polarity, which can still approach the aggregate surface even with the presence of water. However, the moisture on the surface of SiO\(_2\) was immersed in asphalt, and the cohesive energy among the individual molecules of the asphalt was smaller, which may still lead to the deterioration of the asphalt bonding effect. In conclusion, the asphalt-water-aggregate interface behavior in figure 6 can effectively and intuitively reflect the process and principle of moisture damage to asphalt mixture.
4.2. Adhesion of different asphalt mixtures in dry and wet conditions

By combining the quantification of adhesion with the dynamic behavior of the interface, the adhesion of asphalt mixture in different conditions can be analyzed more reliably. Figure 7 shows the absolute values of adhesion work of different asphalt before and after aging with different aggregate after MD simulation, including VBA, virgin polyurethane modified asphalt (VPU-MA), virgin polyurethane/graphene oxide composite modified asphalt (VPU/GO-MA), ABA, aged polyurethane modified asphalt (APU-MA) and aged polyurethane/graphene oxide composite modified asphalt (APU/GO-MA). All calculated values of adhesion work were negative, indicating that asphalt and aggregate tended to combine. In general, the adhesion work in dry conditions was much greater than that in wet conditions. Obviously, the adsorption of water and aggregate surface hindered the physical adsorption of asphalt and aggregate. The adhesion work between asphalt and CaCO\textsubscript{3} aggregate increased almost after short-term aging, whether in dry or wet conditions. Short-term aging
still plays an enhanced role in the bonding properties of asphalt. In wet conditions, the adhesion work between asphalt and SiO$_2$ also increased significantly after aging. Because the sulfoxide functional groups of short-term aged asphalt increase the electrostatic attraction to the aggregates [24]. Especially in terms of aged asphalt, the addition of PU and PU/GO composites significantly improved the adhesion work between asphalt and SiO$_2$ in wet conditions. This may be that due to the interaction of -NCO, an active group in PU, with the hydroxyl groups on the SiO$_2$ surface, which enhanced the adsorption of asphalt on the SiO$_2$ surface in wet conditions. However, in dry conditions, the adhesion work between aged asphalt and SiO$_2$ surface did not increase, and the change was small. Because the proportion of heavy components such as asphaltene and resin in the asphalt decreased. Overall, in dry condition, CaCO$_3$ as an alkaline oxide, had greater adhesion to aged asphalt than SiO$_2$. However, there was little difference in the adhesion between the virgin asphalt and the two aggregates. Because calcite was weakly alkaline, while hydroxylated quartz adhered more strongly to acid asphalt than unhydroxylated quartz. In wet conditions, SiO$_2$ had greater adhesion to asphalt than CaCO$_3$. Because the hydrophilicity of CaCO$_3$ was stronger than that of SiO$_2$, the effect of water and aggregate hindered the bonding effect of asphalt and aggregate.

4.3. Adhesion of different asphalt mixtures at high temperatures

When asphalt is used, the viscosity and toughness of asphalt should be taken into account, usually hot-mix asphalt and aggregate. When the hot-mix asphalt was paved at higher temperature, the adhesion of asphalt binder varies little with room temperature, as shown in figure 8. The standard deviation of the adhesion work is very small. On the whole, the adhesion work at high temperature was about 1.0–15.0 mJ m$^{-2}$ less than that at room temperature, and the energy of asphalt at high temperature was about 2750 kcal mol$^{-1}$ higher than that at room temperature. High temperature accelerated the movement of asphalt molecules, reduced the tightness among asphalt molecules and decreased its apparent viscosity. There is a certain correlation between viscosity and adhesion. The temperature sensitivity of asphalt increased, which had a weaker affinity and poorer adhesion with aggregate [31, 49]. The addition of modifiers improves the adhesion of virgin asphalt to SiO$_2$ surface, because the modifiers still effectively improve the degree of cross-linking among asphalt molecules at construction temperature. However, dispersion accelerated the movement of asphalt molecules at high-temperature due to the existence of oxygen-containing functional groups in GO [30].

4.4. Influence of modifiers on adhesion of different asphalt mixtures

The addition of modifiers had no significant effect on improving adhesion work between asphalt and different aggregates, which may be due to the low number of PU molecules used in the simulation, lower degree of polymerization and weaker hydrophobicity than actual. However, the effect of modifiers on the adsorption of asphalt on different aggregate surfaces was different. Figures 9(a)–(b) show the process of PU in the VBA and ABA approaching the surface of SiO$_2$ and CaCO$_3$ before and after MD. Obviously, in the case of the same PU position before MD, the relative concentration distribution of PU in the VBA was closer to the surface of SiO$_2$ than that of CaCO$_3$ after MD. The PU plays an important role in enhancing the bonding of virgin asphalt with SiO$_2$ surface. Because -NCO, an active group in the PU, formed a stable hydrogen bond with the hydroxyl group.
on the quartz surface, which improved the bonding effect. Therefore, in dry conditions, there was little difference in the adhesion between the virgin asphalt and the two aggregates, meanwhile, the alkalinity of CaCO₃ was not obvious. However, in terms of aged asphalt, the distance between PU and the two aggregate surfaces were not much different, just the concentration was higher near the SiO₂ surface. Figures 9(c)–(d) show the process of GO approaching the surface of SiO₂ and CaCO₃ before and after MD. In terms of virgin asphalt, similar to the case of PU, GO was closer to the SiO₂ surface after MD. However, the distances of GO in the aged asphalt to the surface of the two aggregates were similar, and the degree of molecular aggregation was also similar.

4.5. Moisture sensitivity of modified asphalt mixtures in terms of the interface models
When asphalt mixtures are used on the road, the moisture damage of asphalt-aggregate is very concerned due to rain, road cleaning and vehicle wheel load. In particular, hydrophilic aggregates can cause water to replace the work required for asphalt and aggregate adhesion, resulting in asphalt to peel off the aggregates. Figure 10 shows the ER of asphalt with different aggregates before and after aging. Asphalt-SiO₂ has a significantly higher ER than asphalt-CaCO₃, regardless of short-term aging or addition of modifiers. In other words, the debonding work of the interface between asphalt and CaCO₃ was very large, because of the strong hydrophilicity of calcite and the great attraction of water, which can easily replace the combination of asphalt and CaCO₃ surface. In addition, in terms of modified asphalt-SiO₂ interface, the debonding work increased after aging, the ER decreased and the moisture damage increased. Due to the hardening of aged asphalt, water was more likely to penetrate into cracks in asphalt and aggregate under the load of wheels, and the moisture damage resistance was reduced. As can be seen from figure 10(b), aged asphalt and CaCO₃ interface had an increased ER value. Because the increased adhesion work of aged asphalt was larger, there is still residual adhesion energy under a certain water content, which offset the increase of the debonding work of some aged asphalt in wet condition. In general, the addition of modifiers had little effect on the moisture damage resistance of asphalt. Since both PU and composite materials are hydrophilic, it is necessary to control the content of modifiers in order to improve the high temperature stability and low temperature crack resistance of asphalt, at the same time to avoid a sharp decrease in moisture sensitivity. In practice applications, the selection of PU/GO composite modifier should take into account the proportion of hydrophilic minerals and hydrophobic minerals, so as to improve the adhesion of the asphalt binder and the aggregate interface, while ensuring increased moisture sensitivity.

Figure 9. The relative concentration distribution of PU (a) and asphalt (b) of the virgin and aged PU/GO-MA and aggregate models before and after MD simulation.
4.6. Moisture damage of asphalt mixtures in terms of the wetting models

Since the moisture damage of the asphalt mixture is due to the adsorption of water on the aggregate surface by replacing the asphalt, the difference between the contact angle of water-aggregate and the contact angle of asphalt-aggregate can be used to evaluate the moisture damage resistance of the asphalt-aggregate adhesion interface. The larger the difference, the worse the moisture damage resistance of the asphalt mixture. Luo et al. [32] calculated the wetting contact angle of water nanodroplets on the surface of two aggregates by using MD simulation. The contact angle of water nanodroplet was 34.5° after fully spreading on the completely hydroxylated quartz-α (0 0 1) surface and 13.8° after spreading on the calcite (1 0 4) surface. Figure 11 shows the gradual wetting of two different aggregate surfaces by VBA and ABA nanodroplets during the MD simulation, and figure 12 shows the change of the contact angle of the asphalt nanodroplets. Obviously, it can be seen that the asphalt droplets gradually spread and the contact angle reached a stable value. The average value of contact angle after stabilization was determined as the contact angle of the VBA and ABA nanodroplets wetting on the quartz and calcite surfaces.

Figure 10. ER of asphalt molecules with different aggregates.

Figure 11. Snapshot of VBA and ABA wetting on two aggregate surfaces.
The contact angles of VBA and ABA nanodroplets with fully hydroxylated quartz surfaces were calculated by droplet height method, which were 55.08° and 36.61°, respectively. The contact angles with calcite surfaces were 59.61° and 62.44°, respectively. It was obvious that the contact angles were all less than 90°, and the surfaces of both aggregates exhibited a certain wetting ability to asphalt droplets. The difference of the contact angle between the VBA-quartz surface as well as the contact angle between the water-quartz surface was 20.58° and between the ABA-quartz surface as well as water-quartz surface was 2.11°. The adsorption capacity of the ABA and quartz surface was comparable to that of water, and the moisture damage resistance was the strongest. The difference of the contact angle between the VBA-calcite surface as well as the contact angle between the water-calcite surface was 45.81° and between the ABA-calcite surface was 48.64°, both of which were much larger than the contact angle difference with the quartz aggregate surface. Evidently, consistent with the analysis results of the interface model, the moisture damage resistance of asphalt and calcite was much lower than that of quartz, regardless of asphalt aging or not. Therefore, it is a reliable method to explore the moisture damage resistance of asphalt mixture from the perspective of wetting, and the intermolecular interaction between high-temperature liquid asphalt and aggregate surface can also be seen.

4.7. Interfacial interaction between aggregates and SARA components in virgin and aged asphalt
Different aggregates with asphalt binders have different bonding properties, which can be reflected in the various components of asphalt. Analysis of the relative concentration distribution of the asphalt SARA components in the z axis direction at the initial stage and the end of MD simulation revealed that different components had different adhesion effects on SiO₂ and CaCO₃. As can be seen from the relative concentration distribution of each component in figure 13(a) and figure 14(a), the distribution of the SARA components at the initial stage in the MD simulation was same for both VBA and ABA. Therefore, the concentration distributions of the SARA components on the different aggregate surfaces only needs to be compared after MD simulation. As shown in
figures 13(b)–(c), the SARA components of the VBA had similar adhesion to CaCO3 and SiO2. This is also illustrated by the aforementioned adhesion. However, the density of aromatic was slightly lower near the quartz surface than far away, while the relative concentration distribution was more uniform regardless of the distance from the calcite surface. Asphaltene and resin as heavy components had a higher atomic density near the SiO2 surface, so the adhesion was slightly higher. This is consistent with the above conclusions and indicates that the relative concentration of the components can effectively reflect the adsorption capacity of asphalt on the aggregate surface. It can be from figures 14(b)–(c) that in terms of the ABA, the differences among the SARA components were more obvious in the asphalt-water-aggregate interface systems. Saturate was further from the quartz surface than calcite. Saturate can be regarded as a non-polar molecule, so in the presence of water layers, it was significantly farther away from the asphalt-water-aggregate interface, where water molecules diffused more widely. Aromatic was located near the aggregate surface, which had a height but slightly narrower peak on the calcite surface. The relative concentration of aromatic on the quartz surface was lower but closer to the surface. Asphaltene was significantly closer to the calcite surface. The adsorption effect of the resin and the two aggregates was not much different.

5. Conclusions

In this study, the synergistic analysis of asphalt-aggregate interface and asphalt nanodroplet-wetting aggregate surface by MD simulation can more comprehensively and effectively reveal the nanoscale effect mechanism of PU/GO composites and short-term aging on asphalt-aggregate interfaces. The following conclusions were drawn:

(1) Through the adsorption process of asphalt with fully hydroxylated α-quartz (0 0 1) and calcite (1 0 4) aggregate surfaces, it was found that the adsorption effect of asphalt with CaCO3 was stronger. The behavior of asphalt-water-aggregate interface confirmed that calcite was more hydrophilic, and the adsorption of water with it was easier to replace the bonding effect between asphalt and calcite aggregate.

(2) Adhesion works of virgin and aged BA, PU-MA and PU-GO-MA with the surfaces of acid and alkaline aggregates in dry and wet conditions and at high-temperature conditions were calculated, which confirmed the positive effect of short-term aging on the adhesion strength of asphalt mixtures. Based on the relative concentrations of PU and GO, the modifiers played a role in the bonding of the virgin asphalt and quartz.

(3) The moisture damage resistance of calcite was much less than that of quartz, and the content of PU should be controlled to prevent hydrophilicity. The calculated difference of contact angle of water-aggregate and asphalt-aggregate can effectively evaluate the water sensitivity of asphalt mixture and the results were consistent with the analysis of the interfacial energy ratio.

(4) The asphaltene and resin in the virgin asphalt can enhance the adhesion with the SiO2 surface, while the saturate as a non-polar molecule in the aged asphalt was further from the aggregate surface with water layer, and the asphaltene was closer to calcite. Different components played different roles in the adsorption of asphalt and different aggregate surfaces.

The research findings provides an effective explanation for the decrease in moisture resistance caused by short-term aging and hydrophilic aggregates. The findings can be used to guide the addition of hydrophilic modifiers and the control of the mineral composition of hydrophilic aggregates. Further work will be focused on...
the adhesion of long-term aged asphalt and aggregates with more mineral components, as well as composite modifiers with high and low temperature properties while avoiding the reduction of moisture resistance.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Conflicts of interest

The authors declared that they have no conflicts of interest to this work.

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