Ultraviolet Aging Mechanism of Asphalt Molecular Based on Microscopic Simulation

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Research Article

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Abstract

In order to reveal the nature of the Ultraviolet aging(UV-aging) behavior of asphalt molecules, simulation by Materials Studio software. The effect of UV aging on the transformation, aggregation and motion state of asphalt microstructure is analyzed by the changes in energy, density of dispersive phase, glass transition temperature and viscosity of the asphalt molecular system. The results show that UV aging enhances the bonding degree of asphalt molecules by increasing the heavy components in the asphalt molecules and increasing the distribution width between the asphalt molecule components, which improves the high-temperature resistance of asphalt. At the meantime, the UV aging causes the asphalt molecular movement state to solidify at low temperature so that the rheological behavior is difficult to occur by reducing the lightweight component and free volume of the asphalt molecule and increasing the glass transition temperature, which reduces the low-temperature resistance of asphalt. In addition, among the factors affecting the viscosity of asphalt molecular, the degree of influence of the molecular structure and molecular weight is significantly greater than the molecular activity. The addition of short branched chain hydrocarbon molecules to the UV-aged asphalt molecules could effectively reduce the viscosity of the asphalt molecules and improve the flowability of the asphalt molecules. The results of the study contribute to the understanding of the characteristics of changes in the microstructural pattern and dynamic behavior of asphalt molecules during UV aging, and achieve interpretation and prediction of changes in asphalt properties at the microscopic level.

1 Introduction

As a binder material in the pavement structure, asphalt is frequently subjected to traffic load and environmental erosion in the process of pavement service, especially under the action of heat, oxygen, water and ultraviolet light, oxidation, polymerization, thixotropic, separation and a series of aging for, resulting in irreversible physical and chemical changes in asphalt, so that the asphalt properties change significantly. Ultraviolet radiation effect is one of the main natural factors affecting the performance and service life of asphalt pavements; therefore, it is significant to systematically investigate the mechanism of ultraviolet aging of asphalt molecules.

The aging process of asphalt mainly exists in two forms of aging: thermal-oxidative aging and ultraviolet aging. Aging causes changes in the structural form and movement state of asphalt molecules, which in turn affects the macroscopic properties of asphalt binders. Thermal oxygen aging process is always in the whole life cycle of asphalt pavement, and thermal oxygen aging is an important cause of premature cracking of asphalt pavement [Ding et al. 2021]. In order to reveal the mechanism of thermal-oxidative aging of asphalt binders, the researchers discuss the effect of thermal-oxidative aging on the evolution of the internal composition of asphalt by tracing the mutational behavior of conversion and degradation between different elements or components based on the variability of molecular polarity and molecular weight within the asphalt [Zhang and Greenfield. 2017]. Research has shown that thermal-oxidative aging of asphalt binders includes degradation of straight-chain hydrocarbons and oxidation of side-chains of hydrocarbons, resulting in a decrease in the internal polar small molecule structure of asphalt, while

sulfur and ketone oxides, as the main products of asphalt oxidation, increase the overall proportion of both elements, and intermediate products in the oxidation of sulfur and ketone promote the oxidation reaction and deepen the thermal-oxidative aging of asphalt [Hu et al. 2020; Yang et al. 2021]. When the microstructure within the asphalt has changed to a certain extent, it would be reflected in the evolution of macroscopic properties. Luo et al. [2021] evaluated the diffusion behavior of asphalt molecules before and after thermal-oxidative aging by mean square displacement (MSD), and found that thermal-oxidative aging slows down the diffusion of asphalt molecules. Omairey et al. [2021] predicted the degree of thermal oxygen deterioration for different pavement depths by using a multi-physical field modeling framework, and the results showed that thermal oxygen deterioration decreases non-uniformly along the depth of the asphalt pavement. Xu and Wang [2017] investigated the effect of thermal-oxidative aging of asphalt using molecular dynamics simulations,analyzed the molecular structure of aging asphalt by mean square displacement (MSD) and radial distribution function (RDF) of molecules. The results showed that thermal-oxidative aging weakens the aggregation behavior between asphalt molecules and reduces the mobility of asphalt. Sahebzamani et al. [2020] evaluated a variety of thermally oxygen-aged asphalt mixtures by dynamic module tests, semicircular bending tests, and indirect tensile strength tests. The results indicated that thermal-oxidative aging leads to increase in stiffness and a decrease in ductility of asphalt mixtures, which remained consistent with the results of the above study. Qin et al. [2021] analyzed the thermal-oxidative aging behavior of SBS modified asphalt and found that thermal-oxidative aging increased the viscosity of asphalt but decreased the fluidity and fatigue resistance of asphalt, while the decrease in the proportion of dispersed medium in the asphalt structure was the primary reason for the weakened fatigue resistance. The above research results explain the reasons for the evolution of the properties of thermal-oxidative aging asphalt from the changes of the microstructure, and the research on the thermal-oxidative aging asphalt binder builds up a complete theoretical system.

Further aging of asphalt binder occurred under the action of UV radiation, deepening the detachment and loosening between asphalt and aggregates, and seriously reducing the service life of asphalt pavement [Gao et al. 2020; Pang 2008]. Researchers have committed to delaying the ultraviolet aging behavior of asphalt binders, and investigated effective measures to enhance the resistance of asphalt to ultraviolet aging by analyzing the effects of additives such as ultraviolet absorber, light shielding agents, hindered amines and antioxidants on the ultraviolet aging performance of asphalt. The research results have formed a complete and reliable ultraviolet aging resistance system [Sun et al. 2021; Liu et al. 2021; Liao et al. 2021; Li et al. 2021; Yang et al. 2021]. At the same time, some studies have been conducted to investigate the ultraviolet aging mechanism of asphalt binders. Zeng et al. [2018] investigated the depth of ultraviolet aging of asphalt by UV spectrometer test and showed that the UV radiation effect can only cause effective depth of aging of asphalt. Lia et al. [2021] tested the rheology and internal structure of asphalt at different depths by using fourier transform infrared spectrometer (FTIR) and dynamic shear rheometer (DSR), and found that the aging effect of high intensity UV light on asphalt was more significant, with the passage of time, the asphalt aging depth gradually increased, different depths of asphalt existed in different degrees of aging, even if the same depth, the aging state of asphalt was not the same. Chen et al. [2020] studied the UV radiation aging gradient phenomenon of asphalt binders, the

results showed that the size of molecules and the content of oxides in the asphalt structure exhibited a vertical gradient distribution with the UV aging time, and the UV aging degree gradually deepened. Yu et al. [2021] evaluated the dynamic mechanical properties of UV-aging asphalt mortars by bending modal and scanning electron microscopy (SEM) tests. The results showed that UV-aging damage extended from the surface layer of the asphalt pavement to the bottom of the mortar. All the above studies on the UV aging mechanism of asphalt binders have unique insights, however, there are controversial conclusions on the effective depth of UV aging of asphalt, while the effect of UV aging action on the morphological characteristics of asphalt microstructure has not been investigated in depth, and the mechanism of UV aging of asphalt molecules is still unclear.

The process of UV aging of asphalt is accompanied by changes in physical properties, which originate from the changes in microstructural morphology and dynamic behavior of UV-aging asphalt. Molecular dynamics simulations can achieve to interpret and predict the changes in UV-aged asphalt properties at the microscopic level. The article use molecular dynamics to simulate the dynamic behavior of asphalt microstructure during UV aging, and obtain the changes of energy, dispersed phase density, glass transition temperature and viscosity of asphalt molecular system, so as to analyze the effect of UV aging on the transformation, aggregation and dynamic behavior of asphalt microstructure, and reveal the essence of the UV aging behavior of asphalt molecules. Finally, the reliability of the kinetic simulation results was verified by comparing the asphalt viscosity test results with the simulation prediction results.

2 Experiment Overview

2.1 Preparation of UV-aged asphalt

In this paper, AC-16 asphalt mixture is selected as the basic experimental material, and the experimental evaluation of asphalt mixture monolithic material is conducted in accordance with the "Test Procedure for Asphalt and Asphalt Mixture for Highway Engineering" (JTG E20-2011), and the evaluation results are shown in Table 1.

Table 1
The basic indicators of asphalt

Projects	Unit	90#Technical specifications of Base Oil	Measurement results
Penetration/25℃,100g,5s	0.1mm	80 ~ 100	86
Ductility/10℃,5cm·min^{-1}	cm	≥ 30	> 100
Softening Point	℃	≥ 44	47
Penetration *PI*	—	-1.5 ~ 1.0	-1.2
Density	g/cm^3	Measurement records	1.013

Reviewing the literature on asphalt mixture aging treatment, heat treatment of loose granules at specific temperatures with different durations can present a realistic state of different UV aging of asphalt mixtures [Wu 2008]. Therefore, AC-16 granules were evenly spread in enamel trays with a loose thickness of about 10kg/m^2 ~ 20kg/m^2 and placed in an oven at 135℃ with forced ventilation for 4h, 8h, 12h and 24h, which stirring was performed periodically until the heating time was set. Referring to the specification, select the best forming grade and the best forming oil ratio for the specimen, and compact each side 75 times to form a 200mm×200mm×150mm Marshall specimen.

2.2 UV aging asphalt viscosity test

Asphalt viscosity is the ability of asphalt materials to resist deformation. Among the technical properties of asphalt, the viscosity of asphalt is one of the properties most closely related to the mechanical behavior of the pavement. Therefore, this paper selected the asphalt viscosity experiment as a representative experiment to investigate the effect of UV aging on the decay of asphalt mixture properties.

A Rotary Viscometer (RV) was used to evaluate the viscosity of 90# base asphalt in the temperature range of 60℃ to 120℃. After auto-zeroing the RV and selecting rotor #4 to connect to the viscometer connector, the asphalt pivot rotor was kept at a constant speed of 10.0 RPM (10 rpm/min). The rotational viscometer measureed the torque at constant speed at different temperatures and converted the torque to the viscosity of the asphalt for automatic display by the rotational viscometer.

3 Molecular Dynamics Simulation

3.1 Asphalt molecules

It is difficult to describe the properties of asphalt by using a single average model of asphalt molecules. Therefore, a four-component model of asphalt (Asphaltene, Resin, Satruate, Aromatic) was chosen to describe the molecular structure of asphalt in a relatively refined way. The study of the molecular averaging formula in the asphalt model has been fairly well established. Li and Greenfield [2011] adjusted the asphalt molecular structure of 3-component through the Hartree-Fock equation, density general function theory and classical force field and other calculation methods. The 4-component, 12-class molecular system of asphalt molecules was proposed, and the asphalt model was constructed by changing the number ratio characterization of each type of molecule. Among them, Asphaltene-1, Asphaltene-2 and Asphaltene-3 molecular structures in asphaltene contained a hydroxyl group, pyrrole functional group and thiophene functional group, respectively, thereby introducing oxygen, nitrogen and sulfur elements. The molecular model of asphalt constructed in article mainly refers to the four-component molecular formula of asphalt in Li's study, in which most of the molecular structures have been experimentally confirmed to exist in petroleum or nature. Therefore, the molecular model of asphalt developed in this paper is reliable.

The structural units of the four components of the asphalt were drawn by the Visualizer module in Material studio (MS) software, and the optimized structure of each component is shown in Fig. 1.

Due to the complexity of asphalt polymer molecules, the structure of each component within the asphalt molecule needs to be energy minimized by Geometry Optimization to eliminate the molecular instability of the system before constructing the asphalt molecular model.

Geometry Optimization in the Forcite module was selected, and the force field was selected as COMPASS II. In order to ensure the computational accuracy and save the computational time as much as possible, Group Based was selected for both the electrostatic algorithm and the van der Waals force algorithm, and the maximum number of iterative steps was 500. Taking the asphaltene molecule a1 as an example, its molecular structure model and energy gradient changes after geometry optimization are shown in Fig. 2.

As seen in Fig. 2, the energy of asphaltene molecule a1 decreased from 621 kcal/mol to 345 kcal/mol after geometrical optimization, and all 12 molecules undergo significant structural changed after optimization, which made their energy and structure will be in a relatively stable state. The comparison of the molecular formula model before and after the geometric optimization of asphalt showed that the molecular structure of asphaltene molecule a1 changed very obviously before and after the geometric optimization, which was more consistent with the reality.

In order to construct a more realistic molecular model of UV-aged asphalt, high-precision design parameters need to be selected for model building. With reference to previous studies, it is known that the wavelength range of UV-A and UV-B is 290–400 nm, and most of the polymer molecular bond energy in asphalt is comparable to the light energy in the wavelength range of 290–400 nm. when the asphalt material is exposed to UV radiation, the molecular structure will be damaged and the percentage of each component of asphalt will keep changing [Sun et al. 2018]. Therefore, the design parameters of the UV-aged asphalt model were determined by changing the molecular mass ratio between each component of the asphalt. The parameters of the mass ratio of each component of asphalt before and after UV aging are shown in Table 2.

Table 2
Parameters of various molecular mass ratios of asphalt models

Component	Mass ratio of molecular (Normal)	Mass ratio of molecular(Ultraviolet aging)
Asphaltene	21.5%	36.4%
Resin	22.3%	32.1%
Saturate	37.3%	14.6%
Aromatic	18.8%	16.9%

Through the Amorphous Cell module in Material studio software, according to the molecular mass ratio of the four components of asphalt before and after UV aging (see Table 2), set the relative density to 1.0g/cm3, set the system temperature to 298K, and select the force field COMPASS II to construct the periodic amorphous normal asphalt molecular model and the UV aging asphalt molecular model (see Fig. 3).

3.2 Force Field, System and Simulation Parameters

The force field in Materials Studio (MS) software calculates the variation of the system energy and the interaction forces between the atoms by providing various parameters for each atom. The COMPASS II force field was selected for this simulation. The COMPASS II force field is a force field that supports atomic-level simulations of condensed materials by incorporating empirical data from a variety of isolated system simulations to enable extremely accurate predictions of the conformational, vibrational, structural, and thermophysical properties of many condensed molecules over a wide range of temperatures and pressures, and is one of the more commonly used force fields in asphalt material simulations. Materials Studio includes four thermodynamic syntheses: NVT, NVE, NPT, and NPH. Depending on the purpose of the simulation, different systems can be selected. In this paper, we focus on the evolutionary behavior of fine microstructures in aged asphalt, so we choose isothermal isobaric (NPT) and canonical (NVT) systems for this research.

Through the Forcite module in MS software, Dynamics dynamics simulation task was performed to select model parameters such as isothermal isobaric system synthesis (NPT), systematic random particle initial velocity, 1.0×e-4 GPa pressure, 1.0 fs time step, 25 ps total simulation time, etc. Kinetic simulations were performed at different temperatures for the normal asphalt molecular model and the UV-aged asphalt molecular model, respectively.

3.3 Model reliability validation

In order to ensure the accuracy of the kinetic simulation results, the reliability of the asphalt molecular model needs to be verified. In this paper, asphalt molecular density and atomic radial distribution function (RDF) are selected as two validation indexes.

3.3.1 Asphalt molecular density

After the geometric optimization of the asphalt molecular model, the density of asphalt molecules is stabilized between 0.93 and 1.05 g/cm^3, while the density of the actual asphalt material is between 1.00 and 1.04 g/cm^3, and its maximum variability is within 6%, which satisfies the control accuracy requirement. Therefore, the molecular model of asphalt can be judged to be reliable and reasonable by molecular density.

3.3.2 Atomic radial distribution function

Asphalt molecules are non-crystalline polymers with atoms arranged in an ordered state within the macromolecule, ordered proximally and disordered remotely, and with intermolecular forces dominated by van der Waals forces. The degree of disorder in its structure can be analyzed by the Forcite module for the radial distribution function g(r) within and between carbon atoms in the asphalt molecular model (see Fig. 4).

The radial distribution function (RDF) is mainly used to analyze the interparticle interaction and microscopic distribution. The action relationship between the central atom and other particles is shown by the fact that there will be two main peaks in the distribution function curve, the first one being the internal action relationship of the central atom and the second one being the distance from the nearest atom to produce the action, while for the long-range action, the RDF curve will gradually flatten out and converge to a constant value 1 as the distances pile up.

As can be seen from Fig. 4, the atomic radial distribution function curve of the carbon atom selected as the central atom of this asphalt model shows the maximum peak at about 1.5 Å and the second peak at about 2.6 Å. 1.4 Å and 2.7 Å are exactly in accordance with the radius and diameter of the carbon atom. Meanwhile, the radius of action of van der Waals force r = 3 ~ 5Å, while the radial distribution function curve of carbon atoms gradually tends to 1 at about 3Å and stabilizes at 1 after 4.5Å, which is consistent with the radius of action of van der Waals force. Thus, the molecular model of asphalt can be judged to be reliable and reasonable by the atomic radial distribution function.

4 Results And Discussion

The changes in macroscopic properties of asphalt during UV aging are all generated by the motion collisions of microscopic particles, which originate from the transfer and transformation of energy between objects. Therefore, the change of system energy is introduced to analyze the effect of UV aging on the motion and aggregation behavior among asphalt components; the change of density and volume is introduced to analyze the effect of UV aging on the four-component structure of asphalt molecules; the glassy transition behavior is introduced to analyze the effect of UV aging on the motion state of asphalt internal chain segments; the WLF model of glass transition temperature was used to predict the viscosity of asphalt molecules in UV aging and compared with the results of the viscosity test to verify the reliability of the results of this simulation.

4.1 System energy variation

The molecular dynamics simulation results of 298K were chosen to establish the total energy variation curves and the energy variation curves at all levels for the molecular systems of normal asphalt and UV-aged asphalt, and the results are shown in Figs. 5 and 6 below.

As can be seen from Fig. 5, only at the beginning of the kinetic simulation had not yet reached equilibrium, the energy excitation inside the molecules of UV-aged asphalt was more than that of normal asphalt, and the excitation of energy inside the molecular model of normal asphalt was generally higher

than that of UV-aged asphalt in the rest of the stage. The results indicated that UV aging reduced the activity of the molecules inside the asphalt and reduced the number of active molecules in the excited state, resulting in a low energy state of the system. Combined with the detailed graphs of energy changes at all levels in Fig. 6, it could be seen that with the increasing simulation time, the total energy fluctuations within the molecular system of normal asphalt and UV-aged asphalt gradually tended to a stable value, and the kinetic simulation reached an equilibrium state. Although the total energy and kinetic energy of the equilibrium normal asphalt molecular system were higher than the UV-aged asphalt molecules, and the overall energy fluctuation was more obvious, the potential energy is lower than that of the UV-aged asphalt molecular system, and the magnitude of the asphalt molecular potential energy was inversely proportional to the distance between the components. This shown that UV aging reduced the activity of asphalt molecules while increasing the distribution width between the components of asphalt molecules.

The properties of polymer molecules are not only related to the relative molecular mass and molecular structure, but also to the aggregation state between molecules. Asphalt is a polymer with light and heavy components blended together. The dispersion of molecular weight means that there is a significant interaction between the light and heavy components, and the high potential energy storage between the components ensures that they have sufficient capacity to resist stripping, giving the asphalt molecules a strong bond. Therefore, although UV aging reduced the activity of asphalt molecules and led to the weakening of the mechanical strength of asphalt, it increased the interaction between the components of asphalt molecules and improved the adhesion of asphalt molecules.

4.2 Density and volume

During molecular dynamics simulations, the density and volume of the dispersed phase are inversely proportional to each other, and density and volume are direct output parameters. However, because the molecular structure and periodic boxes of asphalt nanoaggregates in the simulation are in the same order of magnitude, the molecules of each component of asphalt undergo regional aggregation, resulting in large fluctuations of the dispersed phase density with the simulation step, so the equilibrium state density is chosen as the output with high accuracy. In order to obtained accurate simulation results, the density and volume of the dispersed phase in the last frame of the simulation step (251 frame) were selected as the output results in this paper. The simulation results of density and volume of normal asphalt and UV-aged asphalt molecules at different temperatures are shown in Table 3.

Table 3
Density and volume of asphalt molecules

Temperature(K)	Normal asphalt model		UV-aging asphalt model	
	Density(g/cm^3)	Volume(Å^3)	Density(g/cm^3)	Volume(Å^3)
195K	0.945	17162.174	0.985	13578.59
235K	0.943	17293.988	0.981	13669.431
255K	0.942	17393.866	0.977	13738.832
275K	0.939	17550.733	0.975	13786.749
295K	0.934	17860.281	0.966	13908.804
325K	0.927	18270.985	0.938	14251.773

As shown in Table 3, the kinetic behavior of the equilibrium state of both normal asphalt molecules and UV-aged asphalt molecules showed that the density of the dispersed phase decreased with the increase of the simulation temperature, while the volume gradually increased, and the density and volume of the dispersed phase showed an obvious inverse proportional relationship, which was mainly due to the kinetic simulation of the isothermal isobaric system (NPT) selected, in which the total number of molecules remained constant, the density and volume has an obvious inverse linear relationship, which also illustrates the accuracy of the asphalt model from the side.

Comparing the density and volume of normal asphalt and UV-aged asphalt molecules, it could be seen that the volume of UV-aged asphalt molecules is smaller than normal asphalt molecules at the same temperature, while the density is larger. As can be seen, the internal structural composition of asphalt molecules changed during the UV aging process, which was manifested by the degradation of polar small molecules and aggregation into large molecules, reducing the volume of asphalt molecules while increasing the density of the dispersed phase of asphalt. With the deepening of UV aging, the transformation of lighter components to heavier components in asphalt molecules became more and more obvious, which intensified the aging rate of asphalt.

4.3 Glass state transition behavior

The glassy transition behavior of the asphalt model is characterized by the thermal expansion and contraction of the occupied and free volumes of the polymer as the temperature of the system changes. However, when the temperature of the system reaches a certain temperature, only the occupied volume undergoes thermal expansion and contraction, while the free volume inside the asphalt reaches a critical value and the molecular and chain segment motions are frozen. The glass transition temperature of the asphalt polymer is the critical temperature that describes this change.

Based on the data of density and volume of normal and UV-aged asphalt molecules in Table 3, scatter graphs of density and volume at different temperatures were plotted, and linear regression curves were fitted on each side of the curve inflection point to predict the glass transition temperature of the system

[Du et al. 2012]. Because of the inverse relationship between density and volume, the intersection of the two linearly fitted density scatter curves should be consistent with the intersection of the fitted volume scatter curves, and the intersection point is the glass transition temperature of the asphalt model. The density-volume scatter of normal asphalt and UV-aged asphalt molecules were linearly fitted to obtain the density-volume linear fitting curves of asphalt before and after UV-aging as shown in Fig. 7.

As can be seen from Fig. 7: the glass transition temperature of normal asphalt ($Tg_{,Normal}$=268K) was about 20K lower than that of UV-aged asphalt ($Tg_{,UV}$=288K). Above the glassy temperature, the density-volume variation of normal asphalt and UV-aged asphalt molecules was significant, while on the contrary, below the glassy temperature, the density-volume variation trend was flat and the asphalt molecular model was approximately in a frozen state. As the UV-aged asphalt molecules had a higher glass transition temperature, with the decrease of temperature, the free volume inside the UV-aged asphalt molecules was more likely to reach the critical value, which reduced the active state of each component molecule and chain segment, and the asphalt molecules showed low rheological behavior. Therefore, with the deepening of UV aging, the glass transition temperature of asphalt molecules increased, resulting in the movement state of asphalt molecules gradually being solidified and difficult to occur rheological behavior, reducing the low temperature resistance of asphalt molecules.

In order to present the motion of asphalt molecules more intuitively, the last frame (251 frames) of each simulation stage was selected to construct the free volume visualization of normal asphalt and UV-aged asphalt molecules (see Fig. 8), and the free volume change curves were drawn through the free volume visualization of each stage (see Fig. 9) to deeply explore the nature of the glassy state transition behavior of the asphalt model.

As can be seen from Fig. 8: Surrounding the free volume of asphalt molecules (blue area) were the chain hydrocarbon molecules and aromatic ring molecules. Referring to the structural composition of asphalt molecules, it can be found that the saturated and aromatic of the four components mainly occupy the free volume of asphalt molecules. Compared to asphaltene and resin molecules, saturated and aromatic molecules had large space for movement and high motility, and the molecules behave in an active state, which improved the overall energy of the system. This is an important reason to ensure the mobility of asphalt molecules. Combined with the detailed diagram of the free volume change of asphalt molecules in Fig. 9, the rate of free volume increase of UV-aged asphalt molecules was flatter than that of normal asphalt, indicating that UV-aging caused the reduction of components such as saturated and aromatic in the structural composition of asphalt molecules, which corroborated the conclusion of the previous section.

In summary, UV aging caused the saturated and aromatic of the asphalt molecular structure to degrade and aggregate into asphaltenes and resin, reducing the free volume of asphalt molecules while decreasing the activity of chain segment movement within the asphalt molecule. With the increase of temperature, the low activity of UV-aged asphalt molecules led to low rheological behavior of asphalt molecules, thus it can be seen that UV-aging enhances the high temperature stability performance of

asphalt molecules. However, because the UV-aged asphalt molecules had a higher glass transition temperature, the chain movement inside the molecule was easily frozen, resulting in the UV-aged asphalt molecules in a solid state at low temperatures, while UV aging led to the increase of asphaltenes, resin and other macromolecular components in the asphalt molecules, which aggravated the degree of deterioration in the low-temperature resistance of UV-aged asphalt.

4.4 Viscosity simulation prediction

The viscosity of asphalt, as a characteristic most closely related to the mechanical behavior of asphalt pavements, is one of the main aspects of the research of asphalt road performance. The WLF model based on the glass transition temperature is mainly used in the asphalt molecular model to calculate the viscosity index parameters [He et al. 2020], and the detailed description of the asphalt model viscosity calculation is shown below.

$$\lg \frac{\eta(T)}{\eta(T_g)} = -\frac{17.44(T-T_g)}{51.6+(T-T_g)} \quad (1)$$

Where $\eta(T)$: Polymer viscosity at a temperature of T; $\eta(Tg)$: Viscosity of asphalt polymers at glassy temperature, most amorphous polymers have a viscosity of about 10^{12} Pa·s at glassy temperature; *Tg*: Glass transition temperature of asphalt polymers.

Through the above Eq. (1), the viscosity of normal asphalt and UV-aged asphalt molecules at different temperatures were calculated respectively (see Table 4), and the viscosity change curve was plotted, and the results are shown in Fig. 10.

Table 4
Simulated predicted values of molecular viscosity of asphalt at different temperatures

Temperature(K)	lg(Simulated viscosity value)	
	Normal asphalt model	UV-aging asphalt model
295K	6.009	9.916
305K	4.716	7.678
315K	3.686	6.009
325K	2.846	4.716
335K	2.147	3.686
345K	1.557	2.846

As can be seen from Fig. 10, the viscosity of UV-aged asphalt molecules at the same temperature was higher than that of normal asphalt molecules. Due to UV aging, the saturated and aromatic fractions of

the asphalt molecule were converted into asphaltene and resin. It can be inferred that heavy components such as asphaltene and gums provide viscosity to the asphalt molecules. It can be seen that UV aging enhances the viscosity of asphalt molecules and improves the high temperature stability performance of asphalt by increasing the heavy components in the asphalt molecules and increasing the distribution width between the asphalt molecule components.

Observing the curvature of the change of molecular viscosity of UV-aged asphalt in Fig. 10, it can be found that the rate of decrease of viscosity of UV-aged asphalt molecular gradually flattens out with the increase of temperature. If the change in viscosity is predicted from the rheological behavior of asphalt molecules, as the temperature increases, the asphalt molecules become more and more reactive, so the rate of decrease in the viscosity of the asphalt molecules should be more and more dramatic, but this assumption is the opposite of the results in Fig. 10. The factors that effect the change of viscosity of asphalt molecules are not only the activity of asphalt molecular, but also related to the structure and molecular weight of asphalt molecules. The increase in temperature leads to the activation of asphalt molecular energy, the molecular system energy is higher than the bond energy of branched chain hydrocarbon molecules, resulting in the degradation and aggregation of branched chain hydrocarbon molecules into heavy molecules, and the presence of heavy molecules is conducive to increasing the viscosity of asphalt molecules, thus delaying the rate of sharp decrease in viscosity of asphalt molecules due to the increase in temperature, presenting the simulation results in Fig. 10. Among the factors affecting the viscosity of asphalt molecular, the degree of effect of the molecular structure and molecular weight is significantly greater than the molecular activity. The addition of short branched chain hydrocarbon molecules to the UV-aged asphalt molecules could effectively reduce the viscosity of the asphalt molecules and improve the flowability of the asphalt molecules, thus enhancing the low-temperature resistance of UV-aged asphalt.

4.5 Experimental validation

The viscosity range that can be measured by rotational viscometer (RV) is 0.002 ~ 10000 Pa·s. The viscosity of 90# base asphalt before and after UV-aging in the temperature range of 60 ~ 120℃ was determined by using RV, and the results are shown in Fig. 11.

As shown in Fig. 11, the viscosity of UV-aged asphalt was significantly higher than that of normal asphalt, indicating that UV-aging increased the viscosity of asphalt, which is consistent with the conclusions obtained from the previous kinetic simulations. With the increase of temperature, the viscosity of both UV-aged asphalt and normal asphalt decreased, and the rate of decrease gradually leveled off, and the trend of the test viscosity change curve was similar to the simulated viscosity. This verified the accuracy of the previous kinetic simulation results and conclusions.

5 Conclusion

(1) UV aging reduces the activity of asphalt molecules, resulting in a low energy state of the internal system of asphalt, which is the main reason for the weakening of the mechanical strength of asphalt. At

the same time, UV aging increases the distribution width between the components of asphalt molecules, which enhances the interaction between the components and improves the adhesion of asphalt molecules.

(2) Under the action of UV radiation, the molecular bonds of polar small molecules break, the structure degrades and aggregates to form large molecular structures. With the passage of UV aging time, the transformation of light components to heavy components in asphalt molecules becomes more and more significant, which increases the degree of aging of asphalt molecules.

(3) UV aging increases the glass transition temperature of asphalt molecules, resulting in the low temperature state of asphalt molecular movement solidification and difficult to occur rheological behavior, which is an important factor in reducing the low temperature resistance of asphalt.

(4) The saturated and aromatic molecules in the four components of asphalt have a large space for movement and strong motility, providing the overall active force for asphalt molecules, which is an important reason to ensure the flowability of asphalt molecules. Asphaltene and resin molecules have strong interaction forces between them, providing bonding force for asphalt molecules.

(5) Among the factors affecting the viscosity of asphalt molecular, the degree of effect of the molecular structure and molecular weight is significantly greater than the molecular activity. The addition of short branched chain hydrocarbon molecules to the UV-aged asphalt molecules could effectively reduce the viscosity of the asphalt molecules and improve the flowability of the asphalt molecules, thus enhancing the low-temperature resistance of UV-aged asphalt.

(6) By comparing the simulation prediction results of asphalt viscosity with the experimental results, it was found that the change trend of the simulated predicted viscosity was similar to the experimental results, which verified the reliability of using molecular dynamics to simulate the nature of the UV aging behavior of asphalt molecules. The results help to understand the changes characteristics in microstructural morphology and dynamic behavior of asphalt molecules during UV aging, while molecular dynamics can achieve the interpretation and prediction of macroscopic properties from the microscopic level, which is an effective method to reveal the mechanism of material changes.

Declarations

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CONFLICT OF INTEREST

We declare that we have no financial and personal relationships with other people or organizations that can inappropriately influence our work.

DATA AVAILABILITY STATEMENT

All data and models generated or used during the study appear in the submitted article.

CODE AVAILABILITY

All code generated or used during the study appear in the submitted article.

AUTHORS' CONTRIBUTIONS

Xiao Minmin is responsible for the initial idea of the article, draft review and check, and the final decision of the article. FanLin is responsible for the experimental arrangement, simulation computing, and draft writing.

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Figures

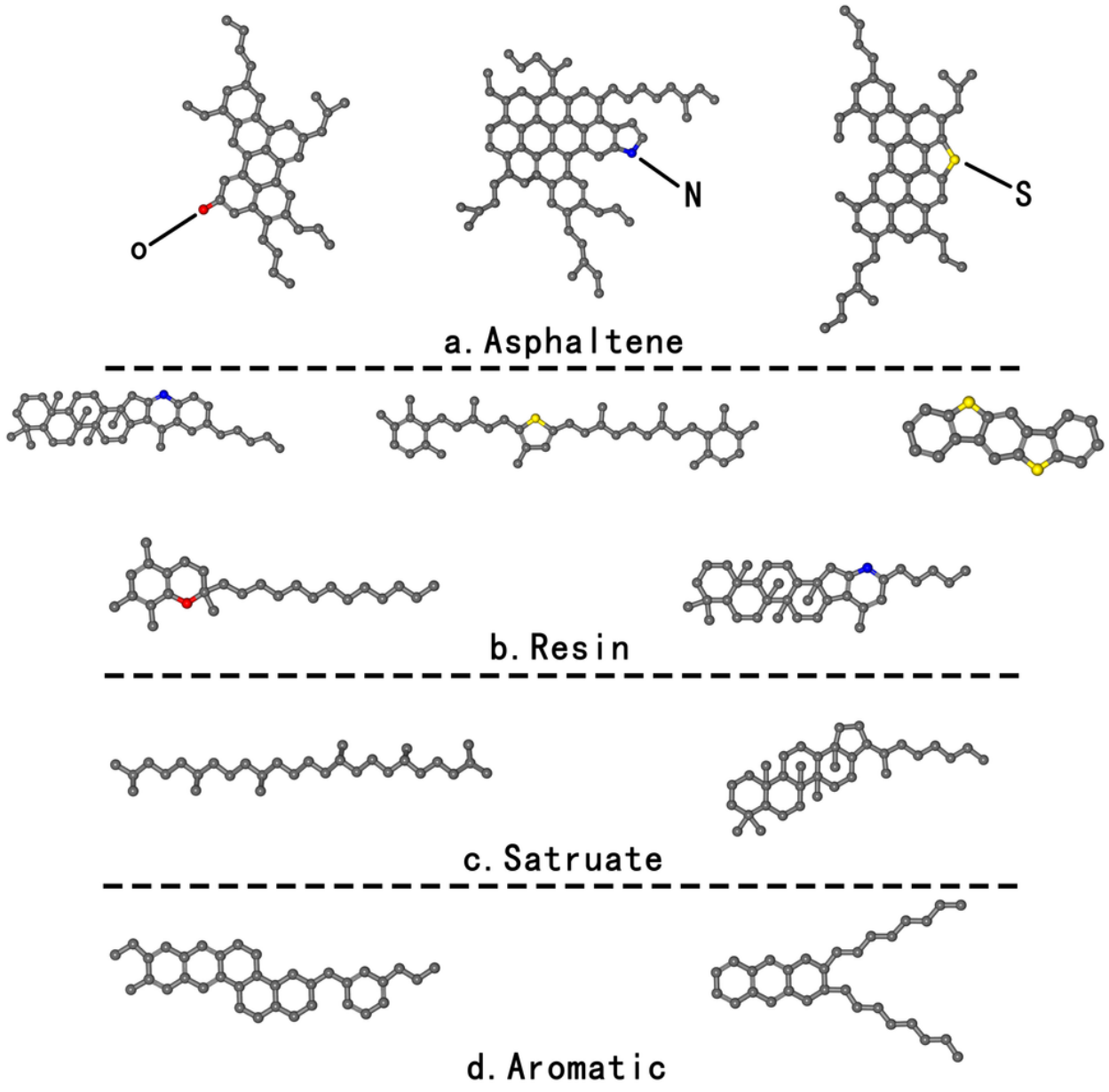
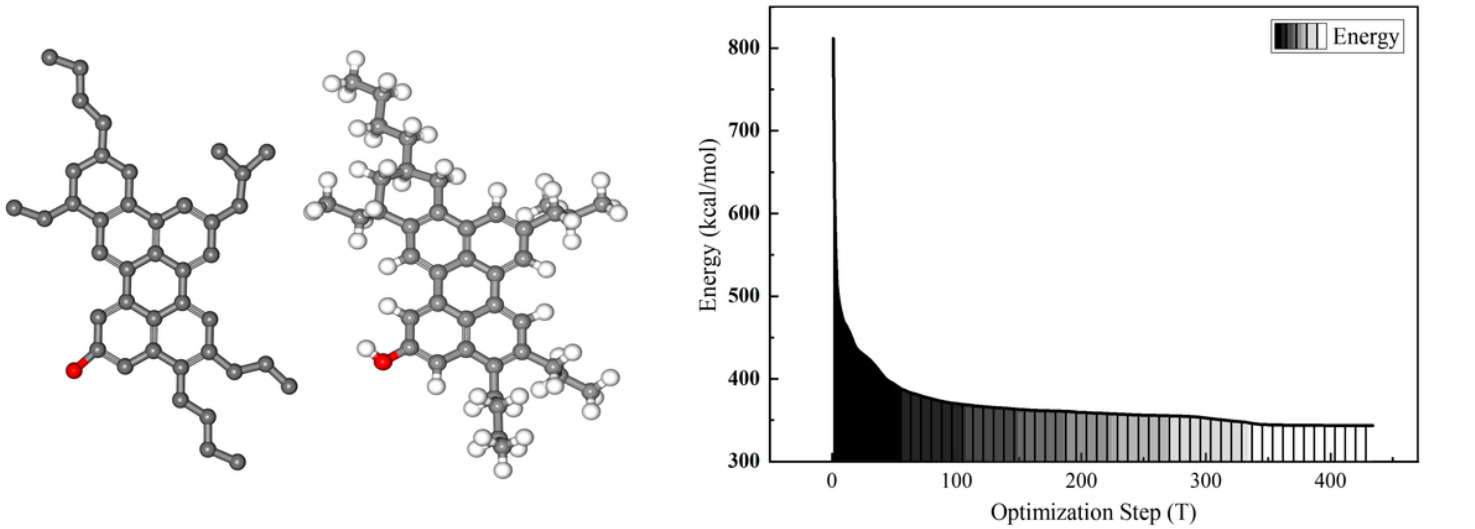


Figure 1

Molecular structure of asphalt four-component: a.Asphaltene; b.Resin; c.Satruate; d.Aromatic.

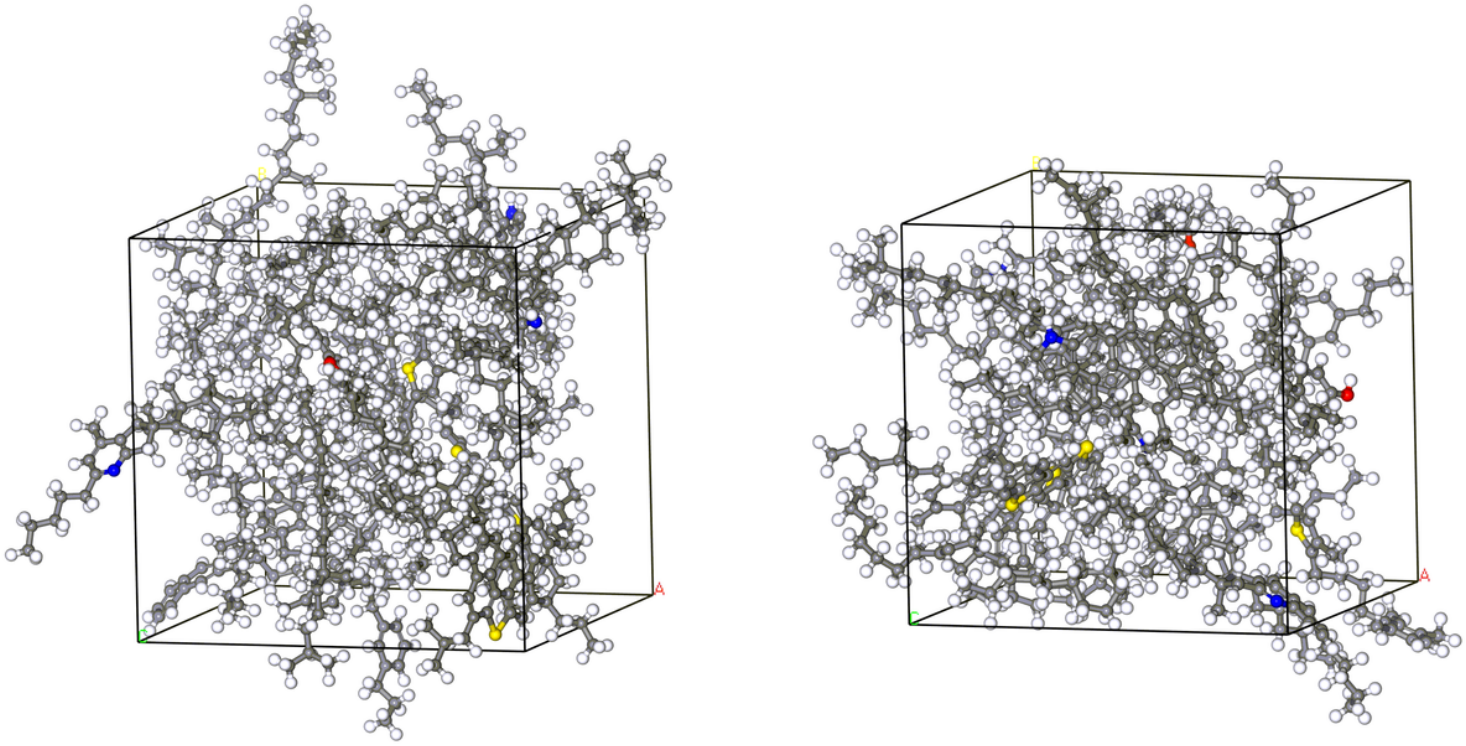


a.Asphaltene molecular optimization model

b.Asphaltene molecular geometry optimized energy profile

Figure 2

Geometrically optimized asphaltene molecular structure model and energy gradient variation



a.Normal asphalt molecules

b.UV-aged asphalt molecules

Figure 3

Molecular model of asphalt

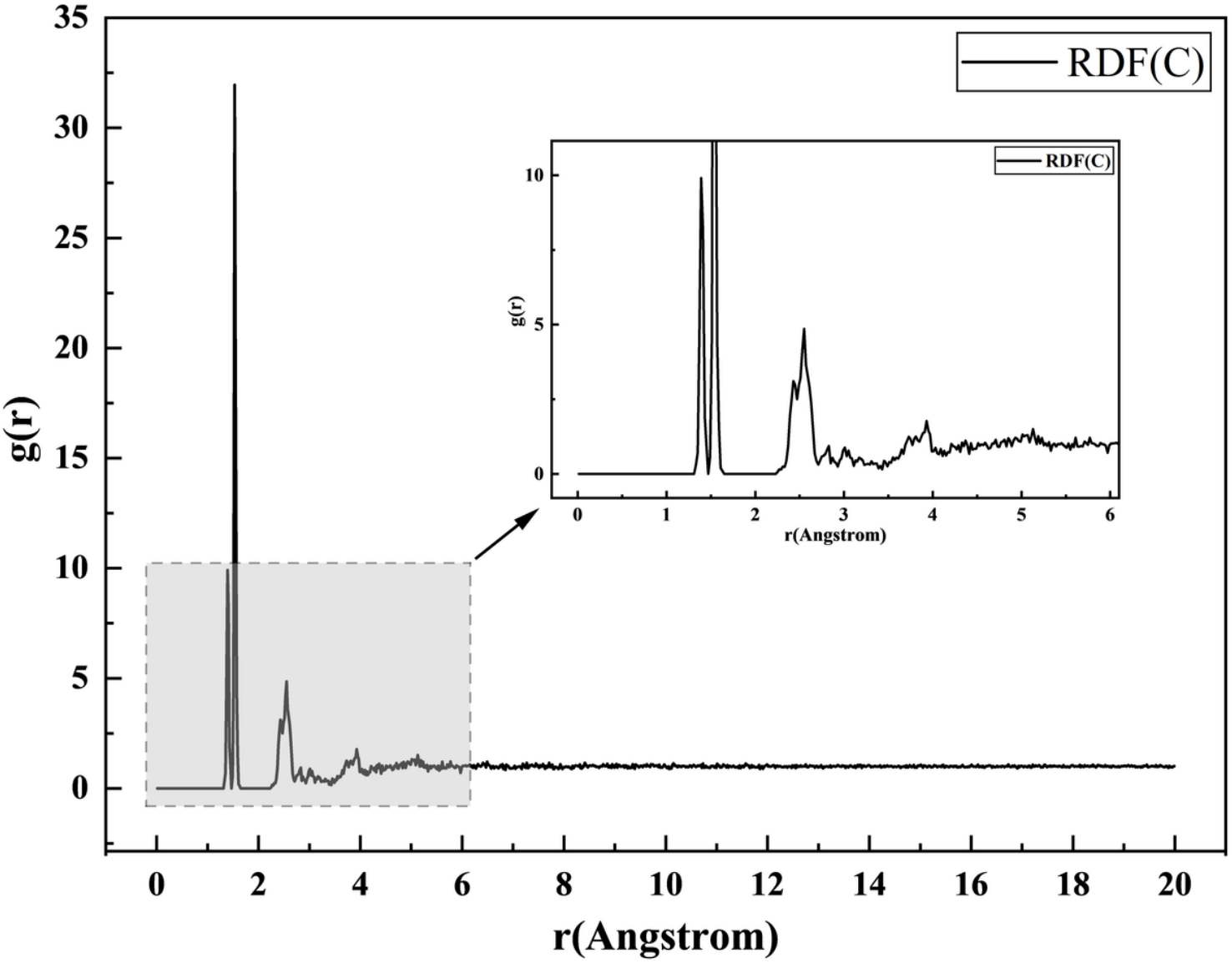


Figure 4

Radial distribution function of carbon atoms

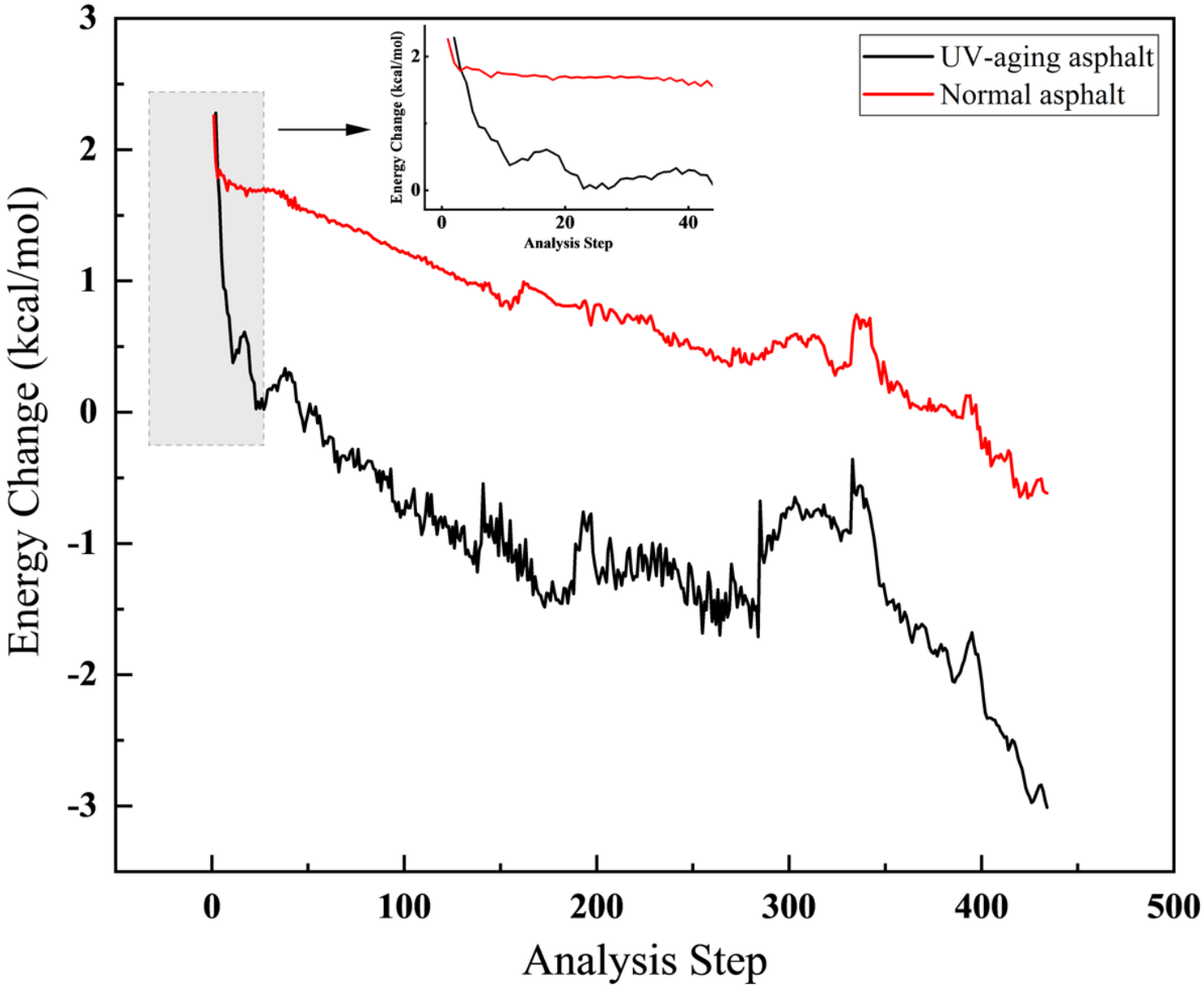


Figure 5

Total energy change curve of asphalt molecular system

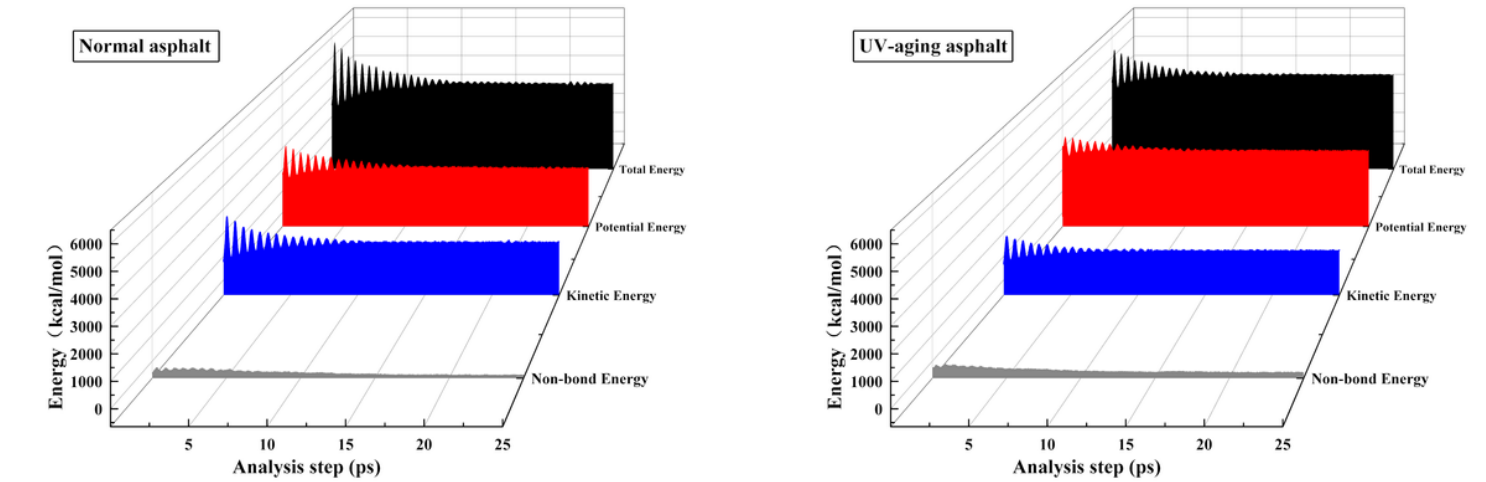


Figure 6

Energy of asphalt molecular system at all levels Change curve

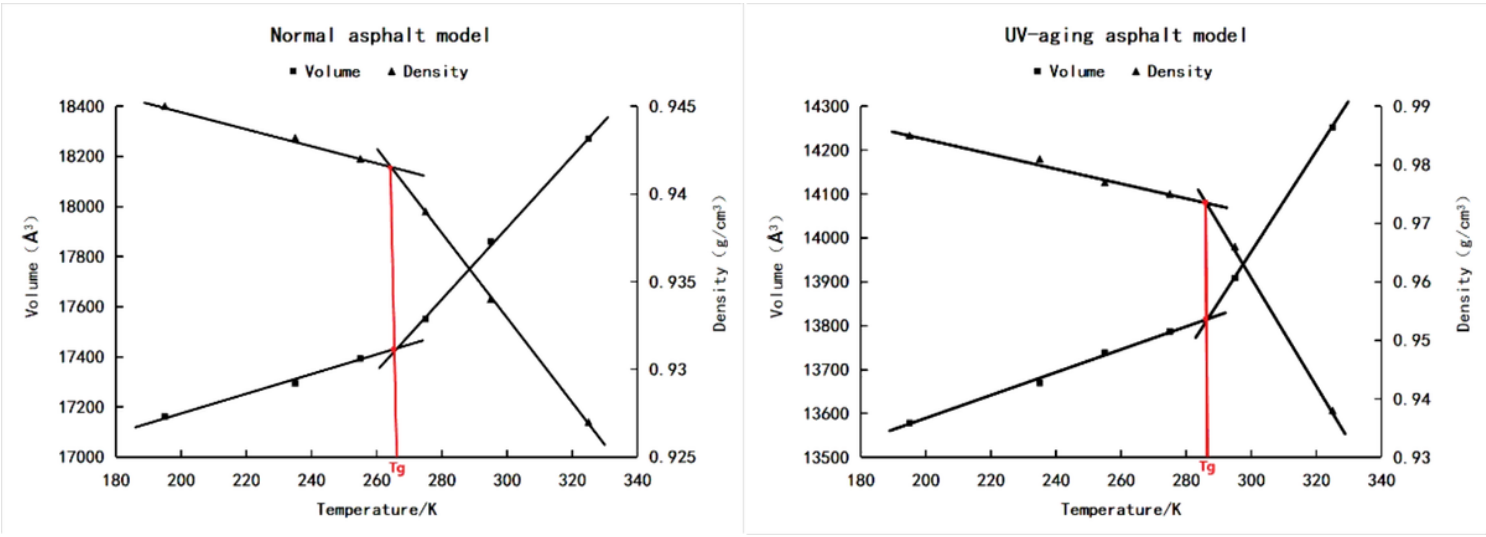


Figure 7

Density-volume fitting curve of asphalt molecules

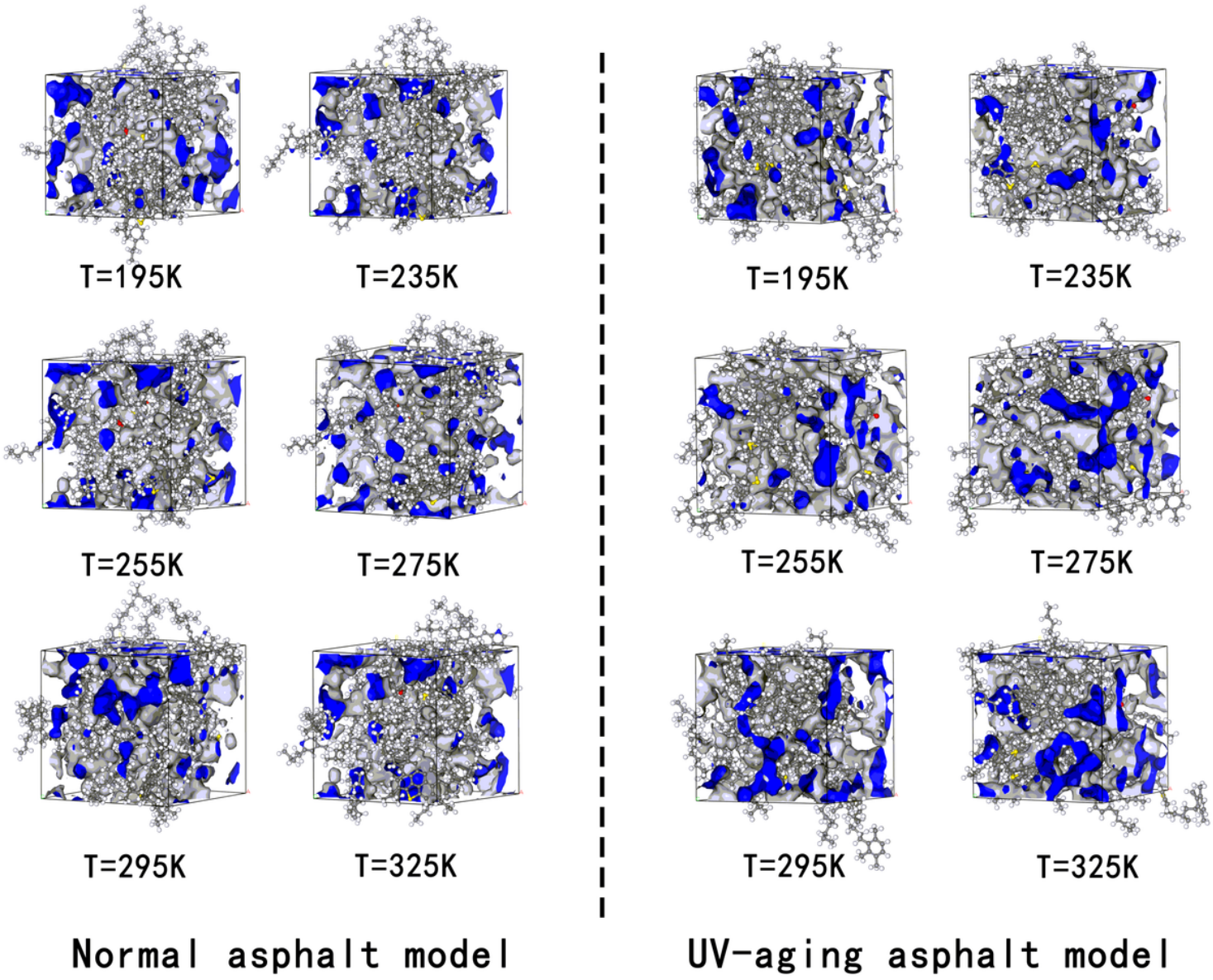


Figure 8

Visualization of the free volume of asphalt molecules at different temperatures

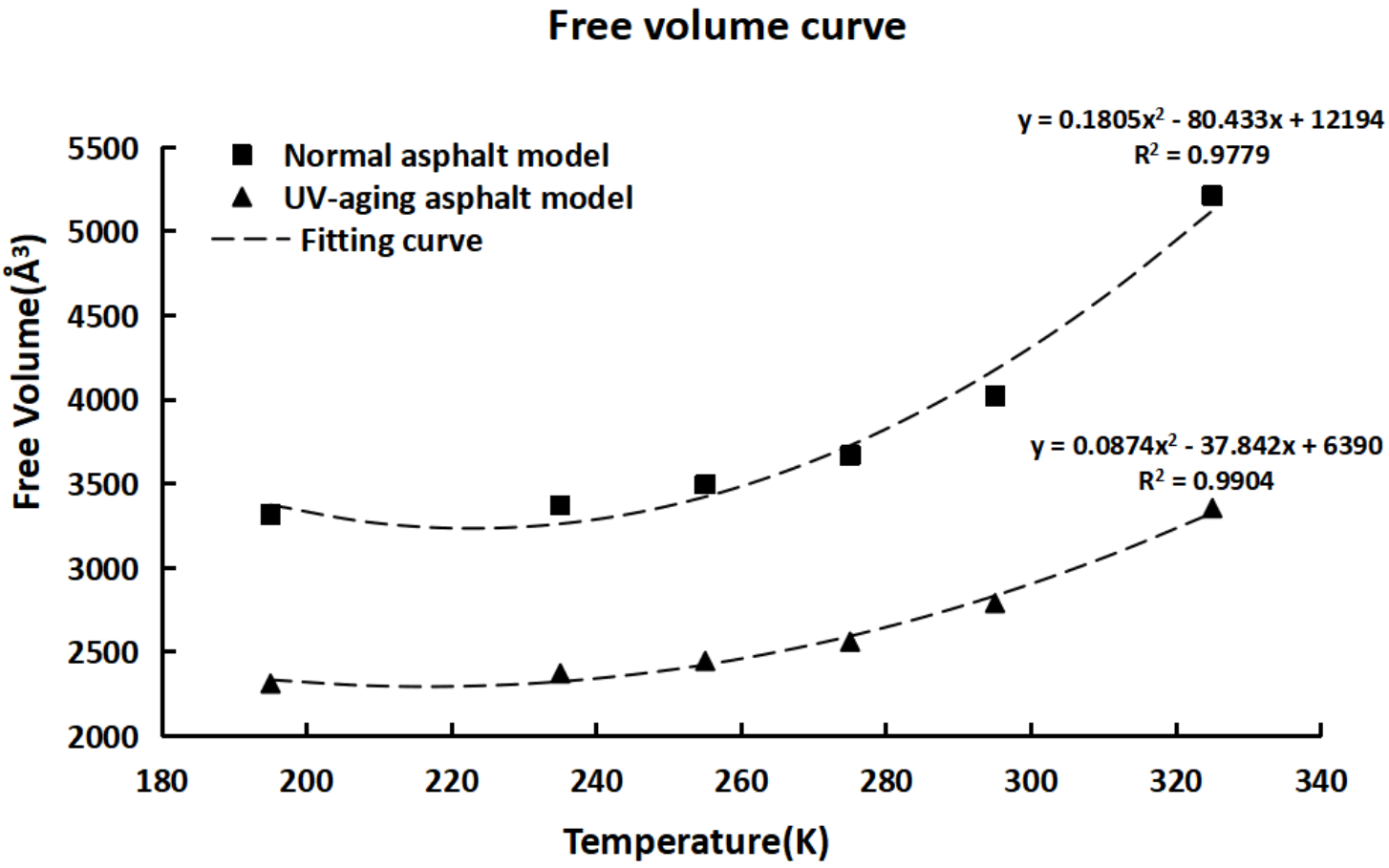


Figure 9

Free volume change curve of asphalt molecules at different temperatures

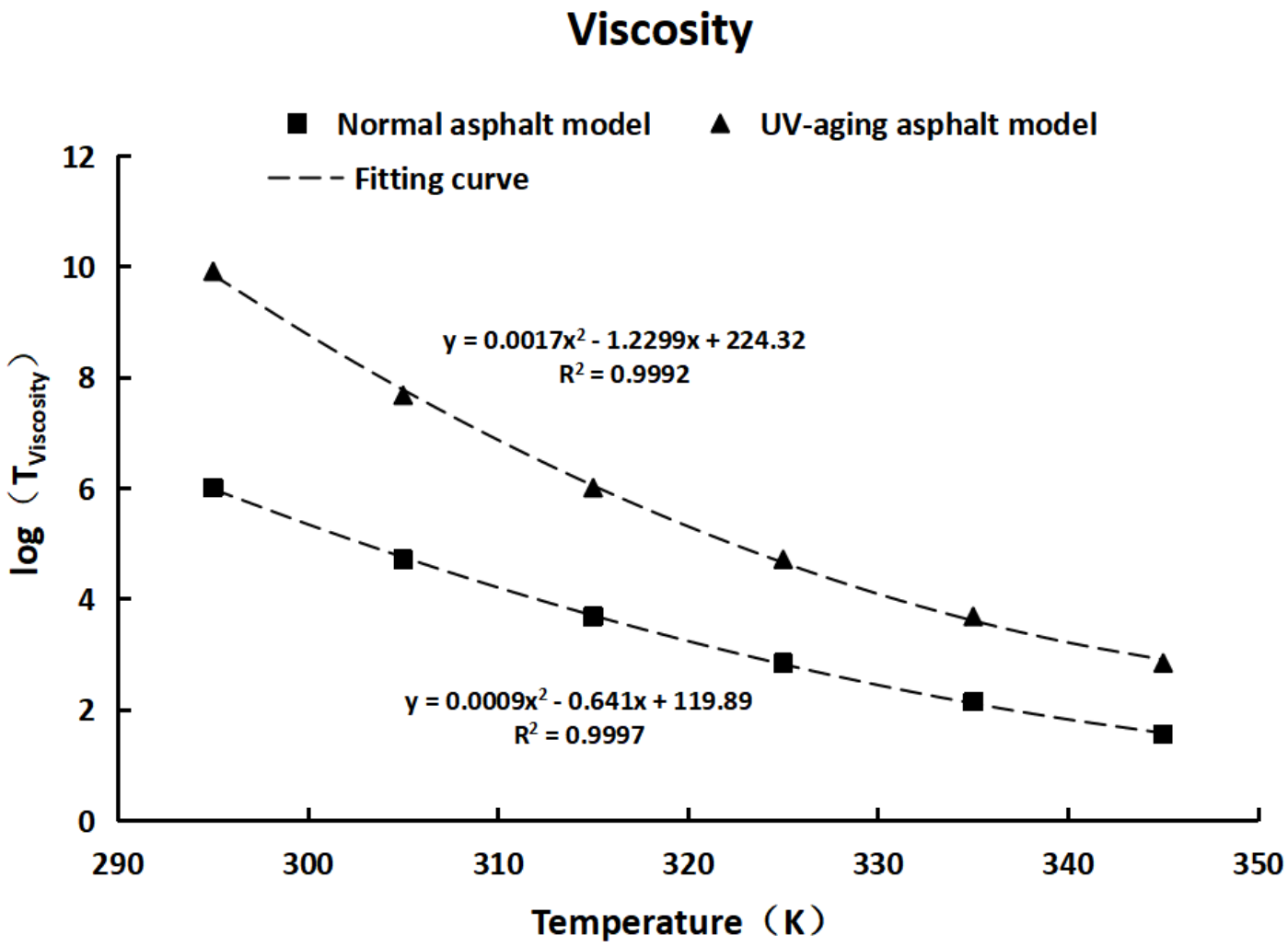


Figure 10

Predicted viscosity change curve of asphalt molecules at different temperatures

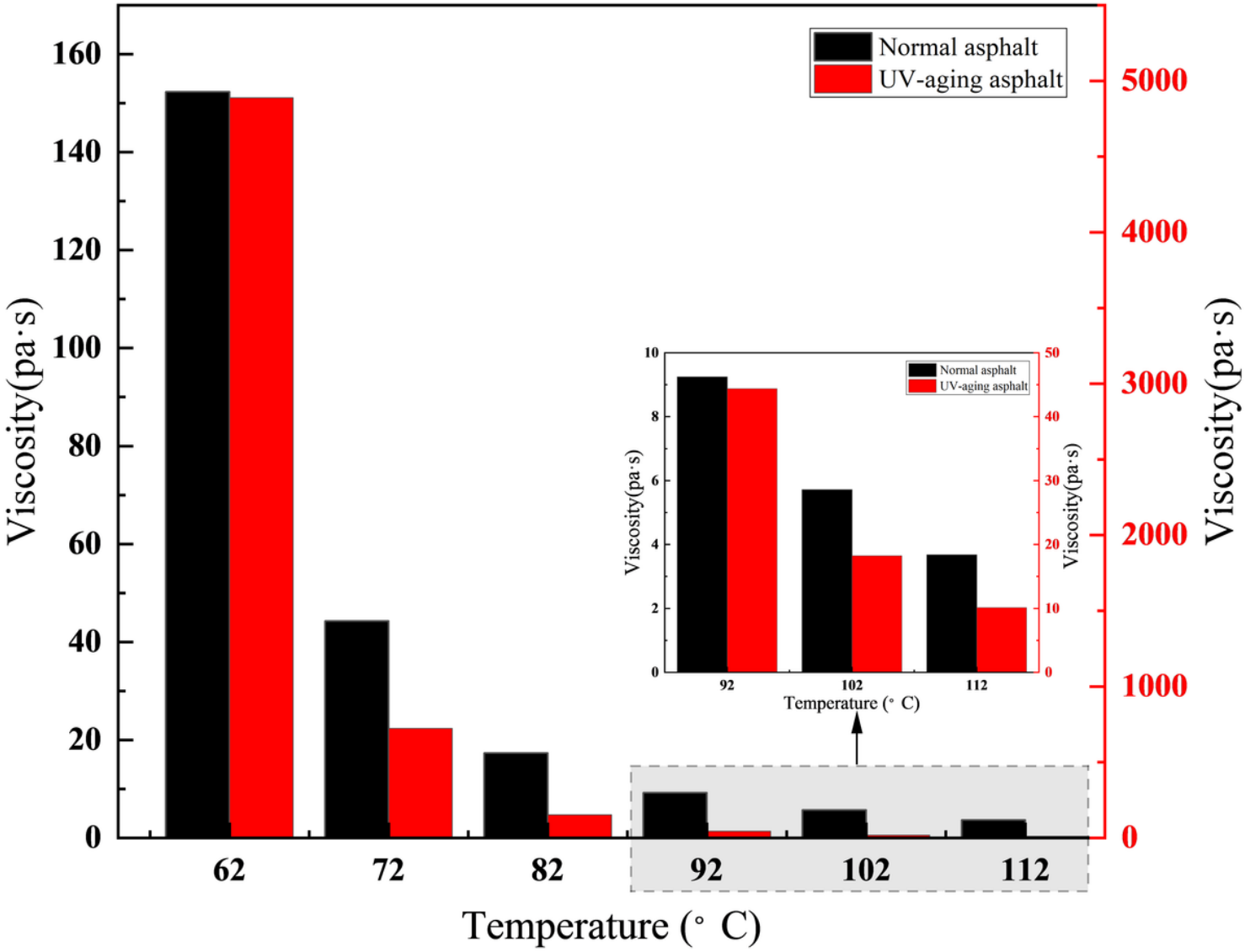


Figure 11

Test viscosity change graph of asphalt at different temperatures