


Article

Using Molecular Dynamics Simulation to Analyze the Feasibility of Using Waste Cooking Oil as an Alternative Rejuvenator for Aged Asphalt

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Abstract: The purpose of this study was to investigate the regeneration effect of waste cooking oil (WCO) on aged asphalt with molecular dynamics (MD) simulation, comparing it with a rejuvenator. Firstly, the molecular models of virgin and aged asphalt were established by blending the four components of asphalt (saturate, aromatic, resin, and asphaltenes). Then, different dosages of the rejuvenator and WCO (6, 9, and 12%) were included in the aged asphalt model for its regeneration. After that, MD simulations were utilized for researching the mechanical and cohesive properties of the recycled asphalt, including its density, viscosity, cohesive energy density (CED), shear modulus (G), bulk modulus (K), and elastic modulus (E). The results show that the density values of the asphalt models were relatively lower than the existing experimental results in the literature, which is mostly attributed to the fact that the heteroatoms of the asphalt molecules were not considered in the simulation. On the other hand, the WCO addition decreased the viscosity, the shear modulus (G), the bulk modulus (K), and the elastic modulus (E) of the aged asphalt, improving its CED. Moreover, the nature of the aged asphalt was gradually restored with increasing rejuvenator or WCO contents. Compared with the rejuvenator, the viscosity of the aged asphalt was more effectively restored through adding WCO, while the effect of the CED and the mechanical properties recovery of the aged asphalt was relatively low. This implies that WCO could restore partial mechanical properties of aging asphalt, which proves the possibility of using WCO as an asphalt rejuvenator. Additionally, the MD simulation played an important role in understanding the molecular interactions among the four components of asphalt and the rejuvenator, which will serve as a guideline to better design a WCO rejuvenator and optimize its content.

Keywords: molecular dynamics simulations; waste cooking oil; rejuvenator; mechanical properties; cohesive properties



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1. Introduction

In recent years, a mass of Reclaimed Asphalt Pavement (RAP) materials have been produced, which is mostly attributed to the reconstruction and expansion of old asphalt pavements. The use of high percentages of RAP is becoming a new trend in the process of the reconstruction of old roads; this means sparing huge amounts of asphalt materials to facilitate sustainable development of the economy and the environment [1–3]. However, because of the presence of aged asphalt in RAP materials, the high RAP contents used in road construction still need to deal with many concerns, including fatigue cracking and low temperature cracking [4,5]. Oxidation and volatilization of the light components are major contributors to asphalt aging. The above factors could make aging asphalt harder and more brittle, which in turn results in asphalt that is more prone to cracking in low-temperature conditions [6,7]. Therefore, to realize the secondary use of aging asphalt, researchers found

that the addition of rejuvenators could effectively restore the nature of aged asphalt binders in RAP materials.

Rejuvenators are usually defined as softening additives that contain a high proportion of light components. Rejuvenators are beneficial for improving rheological and mechanical properties when these additives are added to aged asphalt [8,9]. Recently, rejuvenators in the market have been mainly petroleum-based, organic-based, or engineered products. These rejuvenators have different structures and compositions due to these different sources. Moreover, after years of research, various rejuvenators have been successfully employed to restore various properties of aged asphalt. For instance, Zaumanis et al. [10] studied the effect of six rejuvenators (waste vegetable oil, waste vegetable grease, organic oil, distilled tall oil, aromatic extract, and waste engine oil) on the rheological properties of aged asphalt, and found that this recycled asphalt still had excellent rutting resistance and prolonged fatigue life. In addition, the effectiveness of bio-based rejuvenators was greater than petroleum-based rejuvenators. Borghi et al. [11] found that a rejuvenator derived from pine trees added to aging asphalt restored the physical and rheological properties of the aged asphalt. Taziani et al. [12] found that the chemical, rheological, and physical behaviors of aged asphalt were improved when virgin asphalt and rejuvenators were added to the aged asphalt. In previous studies, it has been proved that the regeneration effect of bio-based rejuvenators is greater than that of petroleum-based rejuvenators. What is more, petroleum-based binders are detrimental to sustainable development, which is mostly attributed to their high cost and environmental effects. Various other products (such as engineered binders and bio-based binders) are treated as rejuvenators to improve the pavement performance of the aged binders in RAP materials [13]. However, traditional bio-based binders, which are made from plants or other organisms, are still expensive. Furthermore, some engineered binders are made from non-renewable natural resources. Thus, alternative and sustainable bio-based rejuvenators could play an important role in rejuvenating asphalt [14–16].

Waste cooking oil (WCO) is generated by cooking edible vegetable and animal oils [17]. The global WCO consumption in 2020 has reached 208.98 million metric tons, and this figure is increasing each year [18]. The existence of a large amount of WCO, if not properly disposed of, will seriously threaten sustainable global development. Given that, with the treatment technology of WCO at present, only a small amount of WCO is recycled or reused, while the rest fails to be well-managed and is randomly discarded into land and rivers, this could threaten human health and the environment [19,20]. Thus, it is necessary to find an effective way to treat WCO. A recent study indicated that WCO contains a lot of unsaturated fatty acids, which are similar to the light oil components of asphalt. The light oil components of asphalt are reduced by the influence of high temperatures when the asphalt pavement is in service. WCO was added to aged asphalt to supplement the lost light oil components in the aged asphalt. Thus, due to the primary components of WCO, which are similar to the light oil components of asphalt, this makes it a potential material for asphalt rejuvenation [21]. In recent years, Bailey et al. [22] provided a theoretical basis for the utilization of WCO as an asphalt rejuvenator. After that, various researchers explored the regeneration effect of WCO on various properties of asphalt, including physical, rheological, chemical, and microscopic properties. It was found that the additive amount increases with the aging degree of the asphalt. Furthermore, the physical, rheological, chemical, and micro natures of recycled asphalt are notably influenced by the content of WCO [18,23,24].

Currently, most studies are focused on investigating the effect of WCO on the macroscopic performance of recycled asphalt [25]. Only a few studies have analyzed the effect of WCO on microscopic performance. Moreover, the employment of some micro tests is a time-consuming and cost-intensive process. With the advancement of molecular dynamics simulation technology, MD simulation has played an essential role in characterizing material behaviors at the molecular level and has helped describe the mechanism of interaction between the chemical composition of the material and the admixture [26–28]. Recently, a

growing number of researchers have used MD to research recycled asphalt material. Xu et al. [29] evaluated the effect of rejuvenator on the molecular structure of asphalt by establishing the virgin/aged asphalt molecular model. Xiao et al. [30] employed MD simulation techniques to investigate the diffusion behavior of rejuvenators in aged asphalt. The results showed that rejuvenators were more beneficial to recover the pavement performance of the long-term aged asphalt than that of short-term aged asphalt. Sun et al. [31] researched the diffusion mechanism of bio-oil-regenerated asphalt with MD simulation. Cui et al. [32] used MD simulation to investigate a multi-physics evaluation of the rejuvenator effects on aged asphalt. The results showed that adding rejuvenators into aged asphalt still failed to entirely restore the colloidal structure of the aged asphalt.

To date, MD simulation has been widely used to establish molecular models for asphalts or aggregates and calculate their density, diffusivity, and viscosity. However, the mechanical properties of recycled asphalt have rarely been investigated using MD simulation. Remarkably, in previous work, we studied the diffusion behavior of WCO recycled asphalt. Therefore, the purpose of this study was to investigate the mechanical properties of WCO recycled asphalt by MD simulation and prove that WCO possesses a regeneration potential for aged asphalt. Molecular models before and after asphalt aging and regeneration were established through MD simulation. Then, the mechanical properties, such as the density, viscosity, viscosity elasticity, shear modulus (E), elastic modulus (G), and volume modulus (K), were calculated. Finally, the regeneration effect of different doses of the WCO and rejuvenator on aged asphalt was evaluated.

2. Molecular Models and Simulation Method

2.1. Molecular Models of Virgin and Aged Asphalt

Asphalt contains various hydrocarbons, such as alkanes, cycloalkane, aromatic hydrocarbon, and so on, which makes its chemical molecular structures and compositions extremely complex. However, asphalt is divided into four compositions, including saturate, aromatics, resins, and asphaltenes, in terms of asphalt solubility. In this study, the molecular structure of asphaltene and resin proposed by Dong and Qi [33,34] and the saturated and aromatic molecular model proposed by Zhang [22] were selected to establish the virgin asphalt. Thus, the molecular model of each asphalt component was established by the Visualizer module of the Materials Studio software. The results are shown in Figure 1.

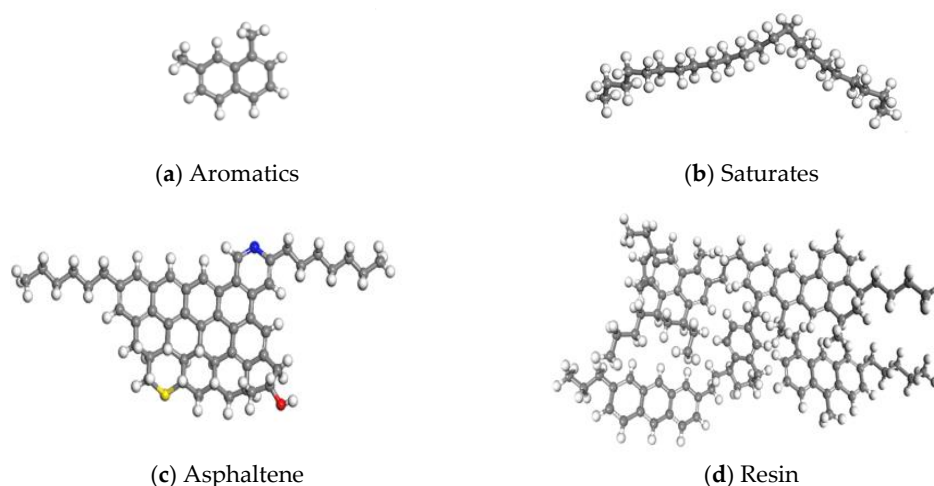


Figure 1. Molecular structure of asphaltic components.

As we know, the four components of asphalt change with the increase of aging degrees. While the asphaltene and resin content increase, the aromatics and saturate content decrease. In this study, the ratios of the four components of asphalt before and after aging were confirmed by using the results of Zhou and Wang et al.'s study [35,36]. The results are given in Table 1.

Table 1. The ratios of the four components of virgin and aged asphalt.

Models	The Ratios of the Four Components
	As/Sa/Ar/Re
Virgin asphalt	5:11:42:3
Aged asphalt	14:6:18:2

Note: As = Asphaltene. Sa = Saturates. Ar = Aromatics. Re = Resin.

2.2. Molecular Model of Rejuvenator and WCO

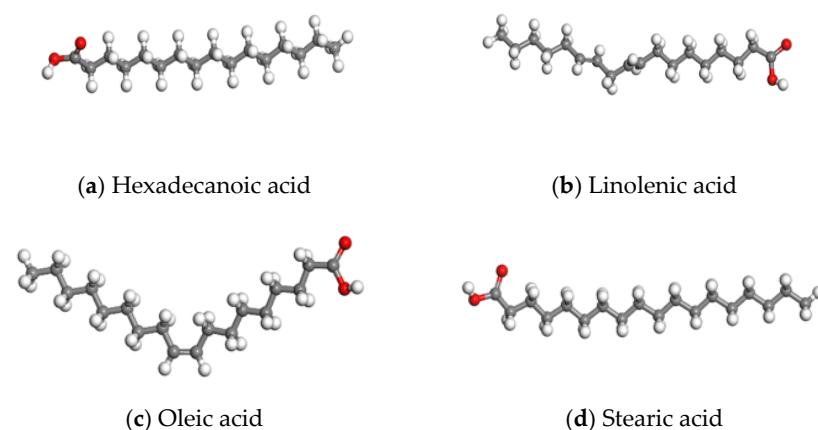
The working mechanism of the rejuvenator is to restore the properties of the aged asphalt by supplementing the light components that have been lost as the asphalt aged. Some of the resins were shifted into asphaltenes during aging. Therefore, in this study, the molecular number ratios of the different components in the rejuvenator were obtained by the test results of Xu [29]. The results are shown in Table 2.

Table 2. Molecular number ratios of rejuvenator and WCO.

Models	Molecular Number Ratios
Rejuvenator	Sa/Ar/Re = 50:105:2
WCO	HA/LA/OA/SA = 18:27:37:12

Note: HA = Hexadecanoic acids. LA = Linoleic acids. OA = Oleic acids. SA = Stearic acids.

Liu [37] obtained the dominating chemical compositions of WCO by utilizing gas chromatography–mass spectrometry (GC–MS). Firstly, in the study, the main molecular structures of the WCO were randomly distributed based on the results of Liu [37]. Then, the chemical compositions of the WCO were obtained by searching and analyzing the NIST (National Institute of Standards and Technology) standard spectra. Finally, a relatively high content and high matching degree of the compounds were selected for the study. The dominating molecules of the WCO in the study included hexadecanoic, oleic, and stearic acids, and confirmed the molecular number ratios of the different components in WCO. The results are presented in Table 2. Similarly, the method of creating their molecular models agreed with that of the asphalt molecular models. The results are presented in Figure 2.

**Figure 2.** Molecular structure of WCO components (grey globes are carbon atoms; red globes are oxygen atoms; white globes are hydrogen atoms).

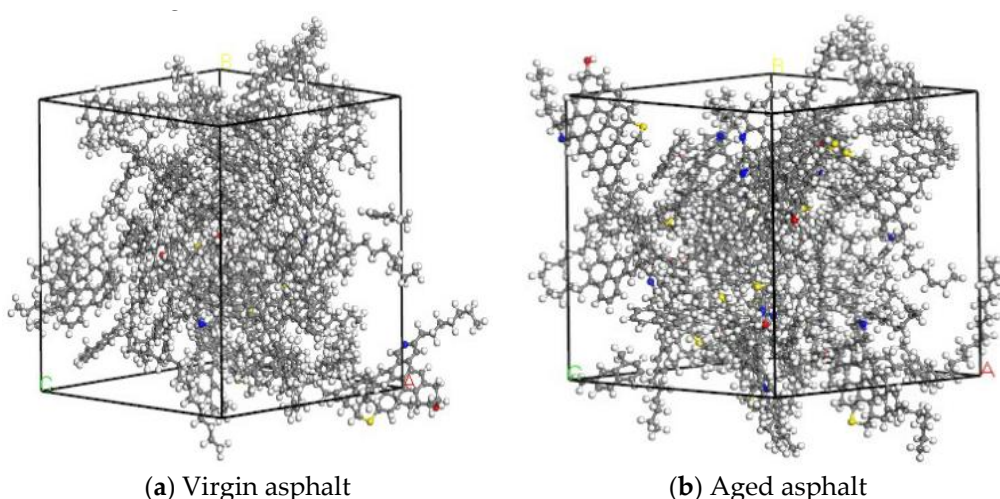
2.3. MD Simulation Method

To characterize the regeneration effect of WCO, a rejuvenator was selected as a reference. The rejuvenator and WCO contents were set at 6%, 9%, 12%, respectively (by the weight). Detailed contents of the rejuvenator and WCO are shown in Table 3.

Table 3. Molecular components of the rejuvenator and WCO.

Content	WCO				Percent of the Total Mass	Rejuvenator		
	HA	LA	OA	SA		Sa	Ar	Percent of the Total Mass
	Number of Molecules					Number of Molecules		
6%	1	1	1	1	5.8%	2	4	6.4%
9%	1	2	1	2	8.4%	3	6	9.4%
12%	2	2	3	1	11%	4	8	12.1%

In this study, all the simulation results were obtained by using the commercial software Material Studio. Firstly, the above molecular model of each component was built in the Visualizer module. Then, amorphous cell modules were used to build a virgin asphalt system, an aged asphalt system, a recycled asphalt system, and a WCO recycled asphalt system. The initial density of these asphalt systems was set as 0.1 g/cm^3 , which was intended to allow the random arrangement of these molecules. After that, these models were optimized through the Forcite module to ensure that the calculated models were in accordance with the actual asphalt system. The first step was to conduct the 5000 iterations of the geometry optimization process in the Geometry Optimization module, and then the system reached an energy-minimized state. The second step was to perform an annealing process in the Anneal module. The number/volume/temperature (NVT) ensemble (N represents the number of molecules; V represents the volume; T represents the temperature) was used to run a 100 ps simulation process and then run an anneal with 300–500 K for 5 cycles, which in turn obtained a stable molecular structure model of the equilibrium state with global energy minimization. The third step was to bring the system to a stable state. The number/pressure/temperature (NPT) ensemble was used to run 100,000 steps with a time step of 1 fs. Taking into account that the actual test was carried out at room temperature, the temperature was set at 298 K (25 °C) and the pressure was set at 1.0 atm in this step of the simulation process. Meanwhile, to improve the accuracy of simulation results, a time step of 1.0 fs was selected to carry out the simulation [33]. The eight asphalt systems are shown in Figure 3.

**Figure 3.** Cont.

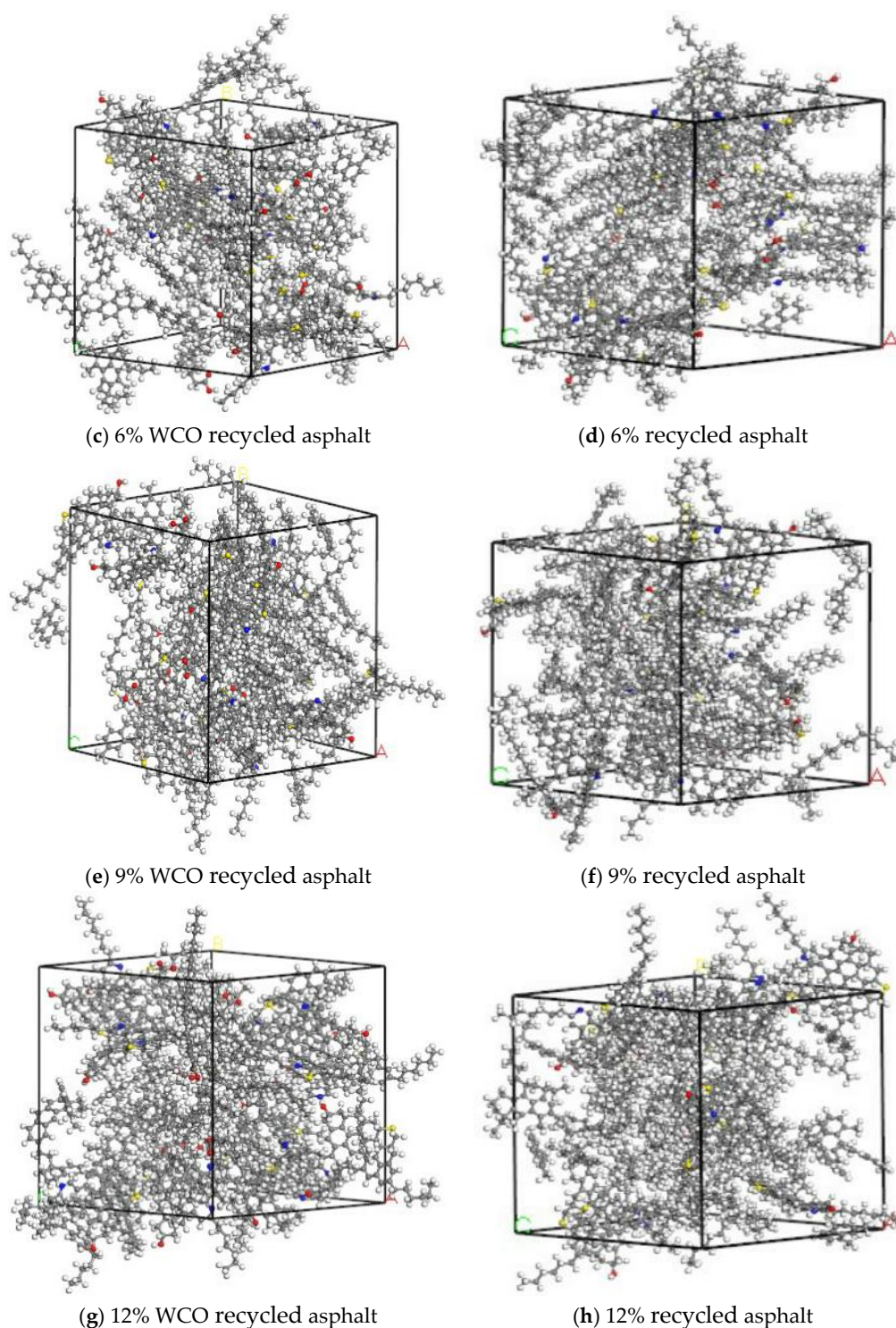


Figure 3. Models of asphalt systems.

Based on the above method, all the asphalt systems met the conditions that can be used for molecular dynamics calculation. Therefore, different modules in the MS (Materials Studio) software were applied to calculate the properties of the asphalt. For the viscosity, the Shear module was used to perform an MD simulation. The relevant parameters of the simulation process were set to a temperature of 298 K and pressure of 1.0 atm. After which, a timestep of 1 fs was used to enact NVE (N represents the number of molecules; V represents the volume; E represents the energy) simulation. For the cohesive properties,

cohesive energy density (CED) was used to characterize the cohesive properties in the study. The CED option in the Forcite module was used to calculate the CED per unit volume of the molecular structure of a single asphalt system. For mechanical properties, in this study, the Mechanical Properties module in the MD software was employed to characterize the mechanical properties of all asphalt systems. A given state of stress was applied to the asphalt systems using the Mechanical Properties module. Next, the energy of the whole asphalt system gradually was tended to the minimizing state during the iterative process. Afterward, the stiffness matrix and flexibility matrix were calculated by using the Mechanical Properties module, and then the mechanical properties were obtained, including the shear modulus (G), the bulk modulus (K), and the elastic modulus (E).

The elastic modulus (E) is a stiffness measurement for elastic materials. The bulk modulus (K) is the ratio of the increment in pressure to decrement in volume. The shear modulus (G) is the ratio of shear stress to the shear strain. Hence, in this study, E and K were used to characterize the deformation resistance of the asphalt system under external compressive stress. G was used to characterize the shear deformation resistance of the asphalt system under external shear stress. E, K, and G were obtained by the following formulas, Equations (1)–(3):

$$K = \frac{\mu(3\lambda + 2\mu)}{\lambda + \mu} \quad (1)$$

$$G = \mu \quad (2)$$

$$E = \lambda + \frac{2}{3}\mu \quad (3)$$

where E is the elastic modulus; B is the bulk modulus; G is the shear modulus; λ and μ are Lamé coefficients, which were obtained through referring to the reported data in the literature [38].

3. Results and Discussion

3.1. Density of Asphalt

The density of a material is often considered a significant symbol for confirming the accuracy of simulation results [39]. Therefore, density values under different dosages or states were calculated for virgin asphalt models, aged asphalt models, WCO recycled asphalt models, and rejuvenator asphalt models. Based on the simulation method above, the density values of these asphalt models are shown in Figure 4.

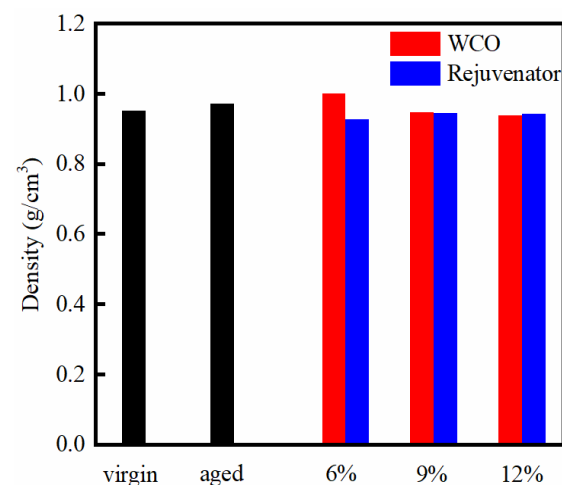


Figure 4. Density values of asphalt models.

From Figure 4, it is obvious to note that the density value of the aged asphalt (0.97 g/cm^3) was slightly greater than that of the virgin asphalt (0.95 g/cm^3). The density of the WCO recycled asphalt was $0.900\text{--}1.000 \text{ g/cm}^3$, and the recycled asphalt was $0.900\text{--}0.950 \text{ g/cm}^3$.

These data were a bit lower than the test data in the literature (1.01–1.04 g/cm³) [40]. A possible reason for this is that too few sulfur atoms were added into these molecular models, as well as there being a lack of heteroatoms.

3.2. Effect of WCO and Rejuvenator on the Viscosity of Aged Asphalt

When the asphalt was subjected to external forces, its deformation resistance was represented by the value of viscosity [41]. In this study, the viscosity of all the asphalt systems was obtained by the Shear module in the MS software. The simulation results are shown in Figure 5.

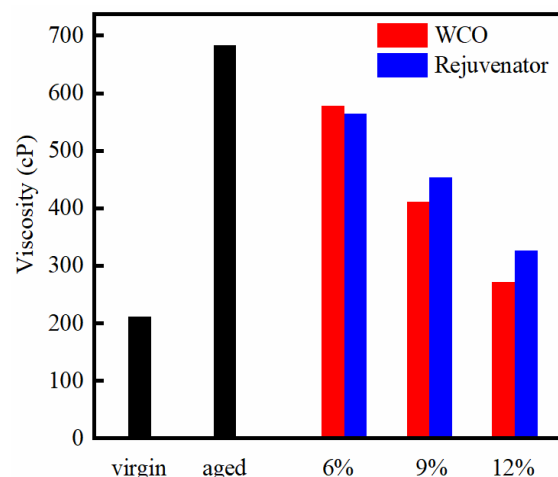


Figure 5. Viscosity values of all asphalt systems.

As shown in Figure 5, the viscosity value of the aged asphalt was much higher than that of the virgin asphalt. After rejuvenator or WCO was added to the aged asphalt, it was found that the viscosity value of the aged asphalt declined. This result is in line with the experimental results reported by Ding et al. [42]. From Figure 5, 6% rejuvenator decreased the viscosity by 17.4% and WCO reduced the viscosity by 15.4%. When the WCO or rejuvenator content was 9%, the viscosity decreased by 39.9% and 33.7%, respectively. However, when the WCO or rejuvenator content was 12%, the viscosity decreased by 60.3% and 52.2%, respectively. The results indicate that the viscosity of the aged asphalt gradually recovered with increasing WCO and rejuvenator dosages, and the recovery effect of the WCO was better than that of the rejuvenator on the viscosity of the aged asphalt. This also implies that aged asphalt would have a better softening effect with the appropriate addition of WCO.

3.3. Effect of WCO and Rejuvenator on the Cohesive Properties of Aged Asphalt

The cohesive energy density (CED) is used to measure the intermolecular bonding strength of an asphalt model by calculating the cohesive energy per unit volume. In general, the greater the molecular force, the greater the CED in a substance. Thus, cohesive properties of the asphalt were characterized through CED in this study. The CEDs of all the asphalt systems were calculated by the CED option of the Forcite module in the MS software. The calculation results are presented in Figure 6.

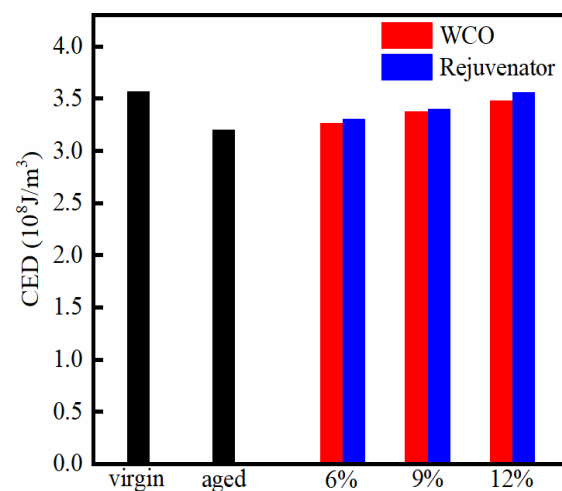


Figure 6. The cohesive energy density (CED) of all asphalt systems.

It can be seen in Figure 6 that the CEDs of the virgin and aged asphalt were $3.565 \times 10^8 \text{ J/m}^3$ and $3.202 \times 10^8 \text{ J/m}^3$, respectively, which are in good agreement with the literature [43]. The reason for this is that the heavy components increased with the degree of age, which in turn resulted in the cohesive properties of asphalt being changed.

Furthermore, it was found that there was an incremental trend in the value of CED with increasing rejuvenator or WCO dosages. The recovery effect of the WCO on the cohesive properties of the aged asphalt was lower than that of the rejuvenator. Specifically, when the content of the WCO and the rejuvenator was 12%, their CEDs recovered by 77.41% and 97.80%, respectively. The asphalt rejuvenator based on WCO had a great recovery effect on the cohesive properties of the asphalt, but there was still some gap between the WCO and the rejuvenator.

3.4. Effect of WCO and Rejuvenator on the Mechanical Properties of Aged Asphalt

Mechanical properties, which mainly include the elastic modulus (E), the bulk modulus (K), and the shear modulus (G) in this paper, are some of the essential indicators for evaluating the deformation resistance of a material. The mechanical properties of all the asphalt systems were obtained by the Mechanical Properties module in the MD software. The results are shown in Figure 7, where W and R were represented as waste cooking oil and rejuvenator, respectively.

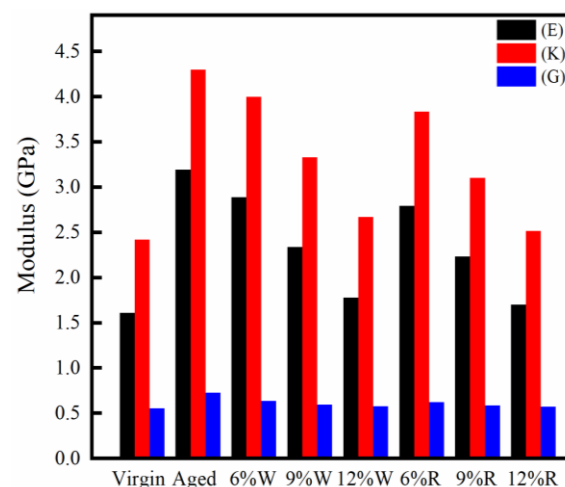


Figure 7. Three kinds of moduli of asphalt systems at different dosages.

As can be observed in Figure 7, three moduli of asphalt increased after asphalt aging. This indicates that the hardness of the asphalt had improved after aging. After the WCO or the rejuvenator was added into the aged asphalt, the shear modulus (G), the bulk modulus (K), and the elastic modulus (E) of the aged asphalt decreased. The E and K values decreased significantly, while the change in the G value was not significant. This means that the WCO or rejuvenator can soften the aged asphalt. Moreover, the results are approximately consistent with the experimental results reported in the literature [44,45].

In this study, the change rate of the modulus indices applied before and after regenerating was utilized as the regeneration indices to evaluate the regeneration effects of WCO and rejuvenator and it was calculated by Equation (4). The lower the regeneration indices, the better the recovery effect of the asphalt. The results of the calculations are shown in Figure 8.

$$RI = \frac{AM - RAM}{AM - UAM} \times 100\% \quad (4)$$

where RI is regeneration indices; AM is aged asphalt modulus; RAM is recycled asphalt modulus; UAM is unaged asphalt modulus.

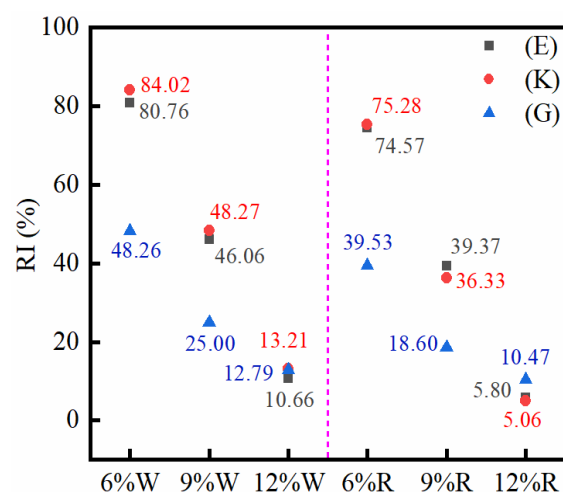


Figure 8. Regeneration indices of recycled asphalt.

As can be seen in Figure 8, the values of the RI gradually decreased with increasing dosages. It was suggested that the mechanical properties of the aged asphalt gradually recovered with increasing WCO or rejuvenator content. Furthermore, the regeneration effect of the WCO on the mechanical properties of the aged asphalt was slightly lower than that of the rejuvenator when their dosages were the same, but the WCO still played a vital role in restoring the mechanical properties of the aged asphalt. It was further implied that WCO is feasible as an alternative rejuvenator for aged asphalt.

4. Conclusions

In this study, MD simulations were employed to analyze the feasibility of WCO as an asphalt rejuvenator. The study mainly included density, viscosity, cohesive properties, and mechanical properties. Based on the analysis of the simulation results, the conclusions are summarized as follows:

- (1) The density values of all asphalt systems lower than the reported experimental data, due to an appropriate amount of sulfur atoms or heteroatoms, were not taken into account during the modeling process. Therefore, in future work, it is suggested that an appropriate number of heteroatoms or sulfur atoms are added into the asphalt model to ensure that the density of the modeled asphalt is closer to the values of the asphalt.
- (2) The viscosity of the aged asphalt was higher than the viscosity of the original asphalt. When the aged asphalt was supplemented with different contents of WCO or reju-

venator, the viscosity of the aged asphalt could decrease with increased rejuvenator content. Specifically, with 12% WCO and rejuvenator, the viscosity was reduced by 60.3% and 52.5%, respectively. These results indicate that WCO has an obvious regeneration effect on the viscosity of aged asphalt.

- (3) After the asphalt aged, its CED value decreased from $3.565 \times 10^8 \text{ J/m}^3$ to $3.202 \times 10^8 \text{ J/m}^3$. These results show that the cohesive properties of the asphalt decreased with the increase of aging. The cohesive properties of the asphalt gradually recovered with the addition of WCO or rejuvenator. When the content of the WCO or rejuvenator was 12%, its cohesive properties could be restored by 77.41% and 97.80%, respectively. This indicates that the regeneration effect of WCO on the cohesive properties of aged asphalt is less than that of the rejuvenator.
- (4) The shear modulus (G), the bulk modulus (K), and the elastic modulus (E) of the aged asphalt were greater than those of the virgin asphalt. It was implied that the asphalt hardened after aging. The mechanical properties of the recycled asphalt could also partially recover to those of the virgin asphalt with increasing rejuvenator content. Although the regeneration effect of the WCO on the mechanical properties of the aged asphalt was slightly smaller than that of the rejuvenator, the WCO was still beneficial to rejuvenate the aged asphalt.

The findings of this study may be useful for studying the regeneration effect of the WCO rejuvenator. Furthermore, the simulation method developed can be further applied to accelerating the WCO rejuvenator design and determining the optimal WCO dosages. It should be noted that four molecules were used to represent WCO, which are the four most abundant in WCO. However, whether the other components influence the regeneration effect of WCO is not certain. Thus, for further research on rejuvenation, other components of WCO will be considered to design a more durable WCO rejuvenator.

Author Contributions: L.L. designed the research method; C.X. executed the molecular dynamics simulation and improved the method of molecular dynamics simulation; M.G. (Mingyang Guan) wrote the paper; M.G. (Meng Guo) supervised the research and made suggestions regarding the research. All authors have read and agreed to the published version of the manuscript.

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