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Study on the Physical, Chemical and Nano-Microstructure Characteristics of Asphalt Mixed with Recycled Eggshell Waste

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Abstract: Green economy is a major them of sustainable development. The application of biological waste in engineering is conducive to green development. This study reveals the effect of recycled eggshell waste on the physical and chemical properties as well as nano-microstructure characteristics of asphalt. The hardness, thermal stability and ductility of asphalt were explored by the penetration, softening point and ductility tests. The distribution and relative content of protons in asphalt were revealed by nuclear magnetic resonance hydrogen spectrum (^{1}H-NMR). The microscopic characteristics of the particle morphology and surface structure of the eggshell powder were explored by scanning electron microscopy (SEM). An atomic force microscope (AFM) was used to analyze the evolution laws of asphalt nano-microstructures. The experiment results indicate that (1) the eggshell waste increases the hardness, thermal stability and reduces the ductility of asphalt; (2) the chemical environment in which the protons of the eggshell waste asphalt are located and the H index have no obvious changes; (3) the eggshell powder is characterized by a rough, wrinkled, porous and loosened structure; (4) the nano-microstructure of eggshell waste asphalt exhibits "bee-like structures", and the different proportion of eggshell waste changes the maturity, size and quantity of the "bee-like structures" and roughness, which can be attributed to the interaction of the asphaltene-waxiness system.

Keywords: eggshell waste; asphalt materials; physical and chemical properties; nano-microstructure

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Citation: Ji, G.; Wang, X.; Guo, Y.; Zhang, Y.; Yin, Q.; Luo, Y. Study on the Physical, Chemical and Nano-Microstructure Characteristics of Asphalt Mixed with Recycled Eggshell Waste. *Sustainability* **2021**, *13*, 11173. https://doi.org/10.3390/su132011173

Academic Editor: Antonio D'Andrea

Received: 13 September 2021
Accepted: 6 October 2021
Published: 10 October 2021

1. Introduction

With the development of road engineering, the demand for asphalt materials is increasing [1]. In recent years, the consumption of petroleum asphalt in China has been increasing. According to the statistics, from 2014 to 2019, the apparent consumption of petroleum asphalt in China increased by 63.28% and continued to maintain a trend of growth [2]. Asphalt is a complex petroleum-based material, and petroleum is a non-renewable resource [3–5]. For these reasons, the properties of conventional petroleum asphalt need to be upgraded urgentlyand there is a great demand for substitutes [6–8]. At the same time, many new technologies and materials are also widely used [9,10]. Bioenergy is widely available, produces high yields and is sustainable; thus, it has attracted increasing attention from researchers [11]. As the transformation from fossil energy to bio-energy can improve the performance and environmental friendliness of materials, bio-waste is gradually becoming more widely used in the asphalt industry [3]. According to previous research, municipal waste, sawdust, animal manure, crop straw, waste engine oil and waste bio-oil have been widely used in asphalt materials [12]. In addition, biological shell wastes, such as crayfish shells and oyster shells, can also be used to improve asphalt performance [13–15].

Among all types of biological shell waste, eggshell waste has received continuous attention [16–18]. According to the statistics, about 7 million tons of eggshell waste are produced every year around the world [19]. Eggshell waste is dumped as garbage, which causes many environmental problems and has serious impacts on the sustainable development of society [20–22]. Eggshell, as a low-cost biological waste, has been used in asphalt materials. Asphalt mixed with eggshell powder was demonstrated to increase the high-temperature performance of asphalt materials [23]. The eggshell waste and low-density polyethylene improved the rheological properties of natural asphalt [24]. Therefore, advocating for the application of eggshell waste in asphalt has remarkable economic and environmental benefits.

Because of the development of testing technology, research on asphalt properties has become focused on the micro-scale step by step [25]. For analyzing the effect of C, H, O and N on the properties of bio-asphalt, an elemental analysis method was adopted. The results showed that the O content in bio-oil was significantly higher than that of conventional asphalt [26]. Microscopic characteristics of fish scale powder asphalt were characterized using Fourier transform infrared spectroscopy. The results indicated that the mixing of fish scale powder and asphalt was a physical process, and the chemical reaction was not obvious [27]. The micro-molecular distribution of asphalt at different aging circumstances was analyzed by gel permeation chromatography. The results showed that the SBS was degraded into small molecules step by step during aging, and the SBS-modified network structure failed step by step [28]. Micro-figures of direct-to-plant SBS-modified asphalt were gained using a fluorescence microscope. As increase in EVA/SBS or naphthenic oil/SBS, the effect of dispersion and swelling in asphalt using SBS were upgraded [29]. Additionally, the chemical composition of petroleum asphalt and neat asphalt was tested by nuclear magnetic resonance spectroscopy. The results showed that the two types of asphalt showed similar spectra, and the concentration of aliphatic H of neat asphalt was higher than that in the petroleum asphalt [30]. Morphological changes in the new and old asphalt after melting were observed by AFM. The results showed that as the increase in neat asphalt proportion size of the "bee-like structure" decreases, the quantity increases, the roughness index gradually decreases and the microstructure becomes more similar to that of the neat asphalt [31].

At present, some research on eggshell powder asphalt generally focuses on macro-performance [23,24]. This study is to reveal the effect of recycled eggshell waste on the physical and chemical properties as well as the nano-microstructure characteristics of asphalt. For exploring the physical, chemical and nano-microstructure properties of eggshell waste asphalt, three kinds of eggshell waste asphalt with 5, 10 and 15% (mass ratio) were made. The hardness, thermal stability and ductility of asphalt were explored by the penetration, softening point and ductility tests. Based on ^{1}H-NMR, the chemical characteristics of eggshell wasteasphalt were evaluated, and the distribution and relative content of protons before and after adding the eggshell waste were analyzed. At the same time, the microstructure of the eggshell powder and the evolution laws of the eggshell waste asphalt nano-microstructure were studied using SEM and AFM. These results provide further theoretical support for the use of eggshell waste in bio-roads, which is of great significance for the sustainable development of society and the economy.

2. Materials and Methods

2.1. Materials

The ordinary 70# asphalt was selected as the neat asphalt, and its penetration at 25 °C is 60–80 (0.1 mm) [32,33].

Its conventional properties indexes are shown in Table 1.

Table 1. Conventional properties indexes of 70# asphalt.

Properties	Experimental Values	Requirements [34]
Penetration (25 °C, 100 g, 5 s, 0.1 mm)	67.6	60–80
Softening point (°C)	49	≥46
Ductility (5 cm/min, 5 °C, mm)	79	—

The eggshell waste came from Anhui, China. The treatment process of eggshell waste is as follows: clean the eggshell with clean water, dry it in an oven at 80 °C for 12 h, grind it into powder with a grinder, pass it through a 0.125 mm sieve, and finally put the eggshell powder (ESP) in a drying container for later use. This process is shown in Figure 1.

(**a**) (**b**)

Figure 1. Appearance of eggshell material: (**a**) crushed eggshell; (**b**) eggshell powder.

2.2. Sample Preparation

In these experiments, samples were prepared using the FM300 high-speed shearing machine produced by Shanghai Frank Company. The specific process used for the preparation of eggshell waste asphalt is as follows: First, 70# neat asphalt was heated and melted in an oven at 135 °C. Second, 5, 10 and 15% (mass ratio) ESP was uniformly and slowly added to the neat asphalt, and it was stirred at a shear stirring speed of 2000 r/min for 10 min at 160~170 °C; then, at a speed of 3000 r/min, it was stirred continuously for 30 min. Finally, the eggshell waste asphalt was prepared.

2.3. The Hardness, Thermal Stability and Ductility of Asphalt

According to the experiment standards [35–38], the penetration test at 25 °C and the softening point and ductility test at 5 °C of asphalt materials were carried out. Six parallel tests were conducted in each group to analyze the effect of eggshell waste on hardness, thermal stability and ductility of asphalt.

2.4. Chemical Properties of Asphalt

The structure and chemical composition of asphalt have an important effect on the service quality of pavement, thus determining the service life of pavement [39]. The eggshell waste asphalt was analyzed using ^{1}H-NMR in this paper based on previous literatures [39–45] and operating procedures of the instrument. The experiment was carried out with a Bruker 400 M liquid NMR instrument, and the solvent used was $CDCl_3$. $CDCl_3$ (Deuterated chloroform) is the most commonly used solvent for nuclear magnetic resonance detection. The main production method is that trichloroacetophenone and other materials react with heavy water under the catalysis of alkali [40]. The 70# asphalt and 5, 10 and 15% (mass ratio) eggshell waste asphalt were dissolved in $CDCl_3$ to prepare solutions; then, the prepared solutions were dripped into the sample tubes. Tetramethylsilane (TMS) was used as the internal standard. Additionally, three parallel tests were conducted for each dosage. The tests are shown in Figure 2.

(**a**) (**b**)

Figure 2. ^{1}H-NMR test: (**a**) dissolve sample; (**b**) NMR equipment.

Nuclear magnetic resonance (NMR) uses the nucleus with nuclear magnetic moment as a magnetic probe to test the local magnetic field inside the molecule and study the internal structure of the molecule by analyzing the change in the magnetic field [41]. NMR is related to the spin motion of nucleus. When electromagnetic waves with a certain frequency radiate the spin nucleus, this causes the resonance transition of magnetic energy level in the spin nucleus and produces absorption signals. This phenomenon is called NMR [42]. In this paper, taking the absorption peak of tetramethylsilane as the origin, the relative distance between the characteristic absorption peak of H on other structures and the origin is measured, which is called chemical shift and is expressed in δ (ppm) [43]. It is closely related to the chemical environment in which hydrogen nuclei are located. Therefore, the changes in asphalt molecular structure before and after adding eggshell waste can be further analyzed by studying the chemical shift [44]. NMR is a powerful tool that can be used to study the influence of internal structure and environment on molecules [45].

According to the different chemical shifts, the types of hydrogen in the spectrum can be classified into four groups: H_a, H_α, H_β and H_γ. The attribution of H in the ^{1}H-NMR is shown in Table 2 [43].

Table 2. The classification of H in ^{1}H-NMR.

Classification	Meaning	Chemical Shift (ppm)
H_a	Hydrogen directly linked to aromatic carbon	6.0~9.0
H_α	Hydrogen linked to α-carbon of aromatic ring	2.0~4.0
H_β	Hydrogen on β carbon of aromatic ring and hydrogen on CH_2CH group far away from β	1.0~2.0
H_γ	Hydrogen on γ-position of aromatic ring and hydrogen on CH_3 group far away from γ-position	0.5~1.0

For further comparing and analyzing the evolution laws of the chemical characteristics of asphalt before and after adding eggshell waste, the relative content of H in asphalt was quantitatively analyzed. In ^{1}H-NMR, the area below the peak represents the relative content of H in different structures [46]. In this paper, the H index is used to judge the relative content of H; each absorption peak in ^{1}H-NMR is integrated separately; and the proportion of the integrated area of all kinds of H absorption peaks in relation to the sum of the integrated areas—that is, the H index—is calculated. The chemical characteristics of asphalt before and after adding the eggshell waste are analyzed through the change in the H index in ^{1}H-NMR.

$$PI_H = \frac{P_{ab}}{\sum p} \tag{1}$$

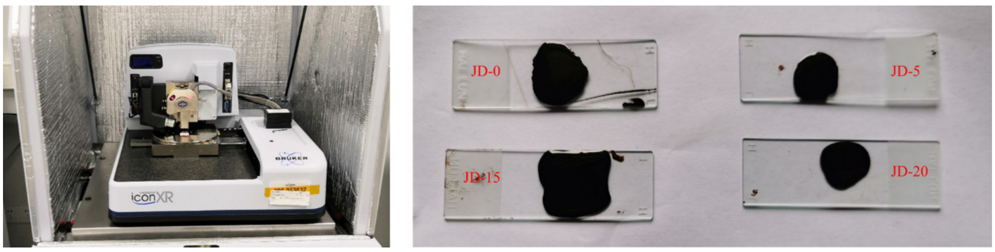
where P_{ab} is the integral area of the absorption peak in the ^{1}H-NMR; $\sum P$ is the sum of the integrated areas of absorption peaks in the ^{1}H-NMR; PI_H is the H index.

2.5. Microscopic Characteristics of Eggshell Powder

A small amount of eggshell waste powder dried in an oven at 80 °C is evenly coated on the conductive adhesive of the sample test bench. In order to ensure that the sample had a good electrical conductivity, the sample was treated with an E-1045 gold spraying instrument to enhance its electrical conductivity before the test; then, the microscopic characteristics of the eggshell powder were observed by an S-4800 cold field emission scanning electron microscope based on previous literatures [15,27] and operating procedures of the instrument. The microscopic characteristics of the particle shape and surface structure of the eggshell waste powder were revealed, which laid a foundation for exploring the law of interaction between the eggshell waste powder and asphalt.

2.6. Nano-Microstructure of Asphalt

AFM is usually applied to reflect the nano-microstructure of asphalt [47]. A nano-microstructure analysis of asphalt with different contents of eggshell waste was carried out using a Dimension Icon atomic force microscope (as shown in Figure 3a) produced by the BRUKER Company based on previous literatures [47–51] and operating procedures of the instrument. The AFM test adopted tapping mode, the probe used was RFESP-75, the elastic constant was 3 N·m^{-1}, and the scanning range was 10 µm × 10 µm. All test samples were prepared at the same time and observed at room temperature (25 °C). Three parallel tests were conducted for each condition.

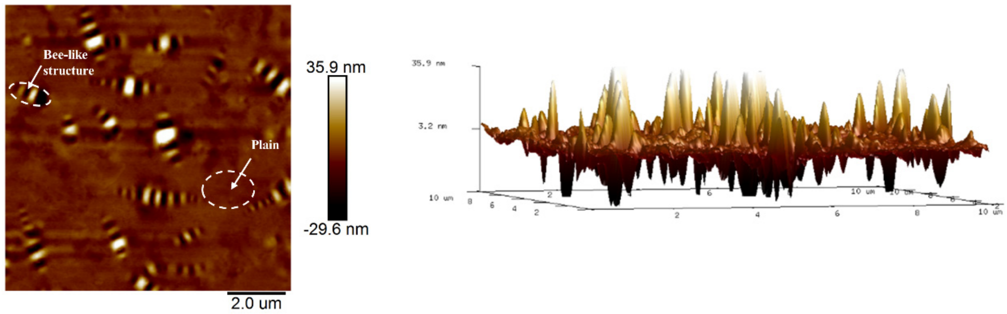


(**a**) (**b**)

Figure 3. AFM test: (**a**) AFM instrument; (**b**) asphalt samples.

The quality of samples used in the AFM test directly affects the results found for the nano-microstructure of asphalt, referring to previous studies [31,48]. we adopted the hot melt method for the sample preparation in this paper. Additionally, the specific method was carried out as follows: we heated the asphalt sample in an oven at 145 °C to make it flow, stirred the asphalt sample properly with a glass rod, took a proper amount of asphalt and dropped it on a glass slide of 25.4 × 76.2 mm, put the glass slide with the asphalt into the oven, heated it at the same temperature for about 10 min, let the asphalt naturally flow and disperse to form a smooth film (as shown in Figure 3b), took out the glass slide to cool it, and sealed it for the test.

The nano-microstructure of the sample was obtained by AFM. Combined with the typical nano-microstructure of asphalt in Figure 4, nano-microstructure indexes applied in the study were explained.



(**a**) (**b**)

Figure 4. AFM figures of asphalt: (**a**) two-dimensional height of asphalt; (**b**) three-dimensional height of asphalt.

Figure 4 shows the AFM figures of asphalt. It is able to be seen from Figure 4a that there are many "bee-like structures" and the nano-microstructure area of the asphalt is able to be divided into a "bee-like structure" area and a "plain" area. It is able to be seen from Figure 4b that the asphalt is composed of high and low undulating peaks and valleys. The three-dimensional "bee-like structure" area is obviously different from the "plane" area, and the overall degree of this high and low undulating three-dimensional fluctuation reflects the roughness of the nano-microstructure of the asphalt [49,50].

For the purpose of further exploring the nano-microstructure characteristics of the asphalt, these nano-microstructure parameters were used to comprehensively reflect the state of the nano-microstructure. The roughness parameters of the "bee-like structure" area can include both the area and amplitude characteristics [51]. Thus, root mean square roughness (R_q) and arithmetic average roughness (R_a) were applied to quantitatively analyze the overall degree of three-dimensional fluctuation of the asphalt [31]; the calculation formulas are as follows:

$$R_q = \sqrt{\frac{\Sigma_1^N Z_i^2}{N}} \quad (2)$$

$$R_a = \frac{1}{N}\Sigma_1^N |Z_j| \quad (3)$$

where R_q is the root mean square roughness, nm; R_a is the arithmetic average roughness, nm; N is the number of scanning points; Z_i and Z_j are the adhesion deviation.

3. Results and Discussion

3.1. The Hardness, Thermal Stability and Ductility of Asphalt

The penetration, softening point and ductility of asphalt respectively reflect the hardness, thermal stability and resistance to plastic deformation of asphalt materials [52]. Figure 5 shows the relationship between penetration, softening point and ductility of asphalt materials with different contents of eggshell waste. In Figure 5, the maximum value of each test result is selected, and then the test result is compared with the maximum value so as to obtain the relative performance of asphalt material with each eggshell waste content [53]. It can be seen from Figure 5 that with the increase of eggshell waste content, the penetration of asphalt decreases and the softening point increases, indicating that eggshell waste improves the hardness and thermal stability of asphalt materials. And the ductility index of asphalt materials gradually decreases, which is mainly related to stress concentration caused by eggshell waste particles.

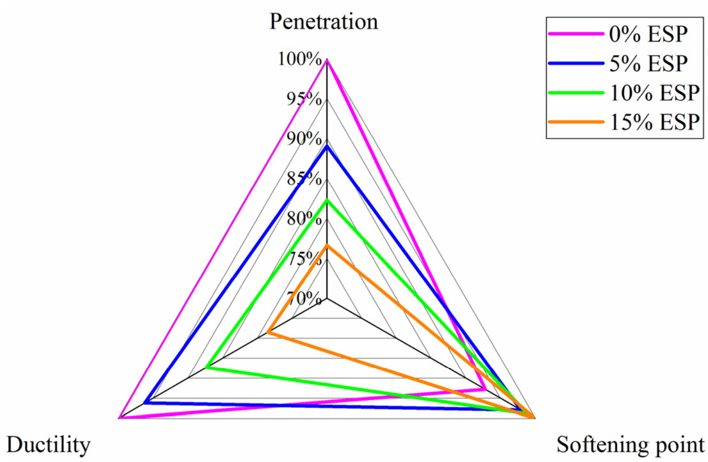


Figure 5. The hardness, thermal stability and ductility of asphalt with different contents of eggshell waste.

3.2. Chemical Properties of Asphalt

^{1}H-NMR in structural analysis of asphalt materials has been widely applied for identifying the chemical structure of compounds [54]. In ^{1}H-NMR, the number of absorption peaks indicates the type of protons, the position of the absorption peaks indicates the chemical environment in which protons are located and the integral area ratio of absorption peaks reflects the relative number of protons. Therefore, the chemical characteristics of compounds can be studied according to the number, position and area of absorption peaks in the NMR spectra [55]. For the purpose of studying changes in chemical characteristics between the neat asphalt and asphalt with different contents of eggshell waste, the distribution and relative content of H in the asphalt before and after adding eggshell waste were studied by ^{1}H-NMR. Figure 6 shows the ^{1}H-NMR of neat asphalt and asphalt with 5, 10 and 15% eggshell waste.

3.2.1. Chemical Shift

Figure 6 shows that ^{1}H-NMR of asphalt with different contents of eggshell waste is mainly composed of two parts—namely, aromatic region on the left side of the spectrum and aliphatic region on the right side of the spectrum, in which the aromatic region H is mainly on the aromatic ring and the aliphatic region H is on the saturated carbon bond [39]. In Figure 6a, the absorption peaks of the neat asphalt appear near 0.87914, 1.07837, 1.25101, 1.70722, 2.28566, 2.53776, 2.87907 and 7.25388 ppm. Additionally, the 5% ESP asphalt in Figure 6b shows obvious absorption peaks near 0.87885, 1.08113, 1.25225, 1.72282, 2.28751, 2.53869, 2.88551 and 7.25298, which correspond to the absorption peaks of the neat asphalt at these positions. This is because the frequency of NMR is not only related to the magnetic spin ratio and the external magnetic field intensity but also the chemical environment around the nucleus. The frequencies absorbed by different kinds of H are different—that is, the positions of spectral lines are different. Chemical shift is closely related to the density of the extranuclear electron cloud. Different densities of the extranuclear electron cloud may result in different shielding and de-shielding effects and cause the chemical shift of H to move to high field or low field, meaning that the chemical shift is slightly different [56]. Therefore, Figure 6 indicates that the absorption peaks of asphalt are slightly offset. However, the absorption peaks of asphalt are basically consistent, indicating that the addition of eggshell waste has not caused great changes to the chemical environment of H. The same rule applies to Figure 6c,d.

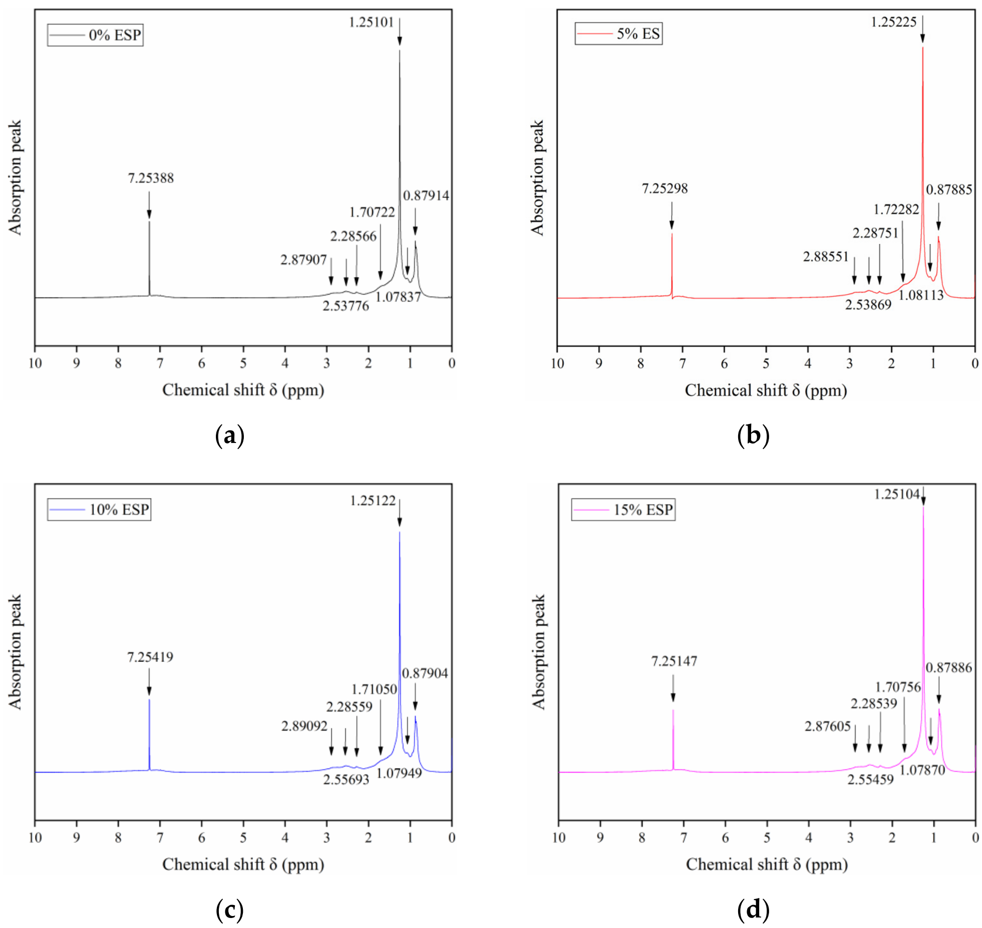


Figure 6. The ^{1}H-NMR of asphalt with different contents of eggshell waste: (**a**) neat asphalt; (**b**) 5% ESP; (**c**) 10% ESP; (**d**) 15% ESP.

The analysis of the ^{1}H-NMR chemical shift in Figure 6 shows that, compared with the neat asphalt, the quantity and position of absorption peaks of eggshell waste asphalt are basically the same—that is, proton type and chemical environment have not changed greatly. It is preliminarily indicated that the eggshell waste does not have an obvious chemical reaction with asphalt, the proton type does not change obviously, and the interaction between the eggshell waste and asphalt is a physical miscible process.

3.2.2. Hydrogen Atom Index

The absorption peak intensity in ^{1}H-NMR can reflect the relative number of various protons [55]. For the purpose of further studying changes of the asphalt chemical characteristics before and after adding eggshell waste, the relative content of H in asphalt was quantitatively analyzed. Additionally, the proportion of the integrated areas of various H absorption peaks to the sum of the integrated areas—namely, the H index—was calculated according to the classification standard of H. A distribution diagram of the H index of asphalt with different eggshell waste contents is shown in Figure 7.

Asphalt is composed of a large number of aromatic rings and naphthenes. Figure 7 shows that H on carbon at the β position of the aromatic ring and H on CH_2 and CH groups far away from β are the majority groups in asphalt. There is no great change in the H index of four hydrogens between the asphalt with eggshell waste and the neat asphalt, and the error is small. Therefore, the H index further reflects that the interaction between eggshell waste and asphalt is a physical process, and the H index test results are consistent with the chemical shift results for various H before and after adding eggshell waste.

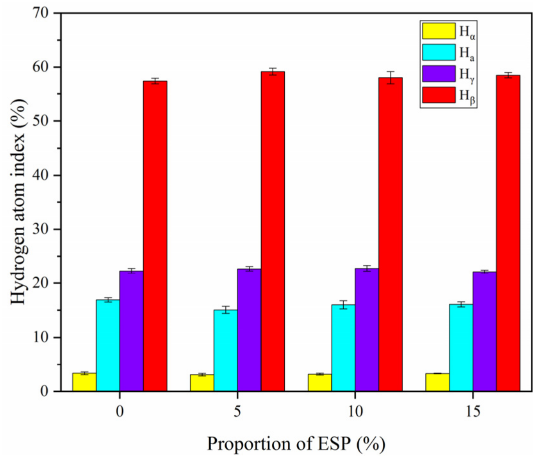


Figure 7. H-index distribution diagram of asphalt with different contents of eggshell waste.

3.3. Microscopic Characteristics of Eggshell Powder

For the purpose of revealing the microscopic characteristics of the particle morphology and surface structure of waste eggshell powder and further explore the law of interaction between eggshell powder and asphalt, the eggshell powder samples were tested by SEM. To study the microstructure characteristics of eggshell powder more clearly and deeply, the observation method of gradually enlarging a certain particle and a certain area of the eggshell powder was adopted in the experiment, and figures with 200×, 600×, 1000× and 3000× magnifications were obtained, as shown in Figure 8.

Figure 8 points out that the microstructure of the eggshell powder mainly consisted of four parts: particle morphology, particle surface structure, pores and adhesion between particles. The 200× image in Figure 8a indicates that eggshell powder contains mainly angular particles, with a small amount of flaky particles. The eggshell powder particles were distributed in a disorderly way after pulverizing, and the samples were filled with particles with obvious angular characteristics. Figure 8b–d can be observed according to the direction indicated by the red arrow, and each part shows a gradually enlarged image of the red dotted line particle surface in Figure 8a, which was used to further observe the microstructure characteristics of the particle surface. Figure 8b–d shows that the surface of eggshell powder is rough, and there are some obvious fold structures on the facade. When the image is enlarged to 3000×, Figure 8c shows that the fold structure on the surface of the eggshell powder is more prominent, and there are many pore structures with different sizes and shapes on the surface of the eggshell powder particles. Moreover, a large number of debris particles are attached to the surface which may fall off from large particles during crushing. This rough, wrinkled, porous and loosened surface structure may make the contact area between the eggshell powder and asphalt larger, which is conducive to consistency between eggshell powder and asphalt.

The microscopic characteristics of eggshell powder particles are the material basis of various physical and mechanical properties that are closely related to the role of eggshell powder in asphalt and are very important for studying the law of interaction between eggshell powder and asphalt. The microstructure of eggshell powder is rough, wrinkled, porous and loosened and can usually show good adsorption performance [57–59]. This special surface morphology and particle structure may allow it to be more closely combined with asphalt materials. In this mixing process, the physical properties of eggshell powder will have a great impact on the properties of asphalt, which may help them to form a whole with a good structure.

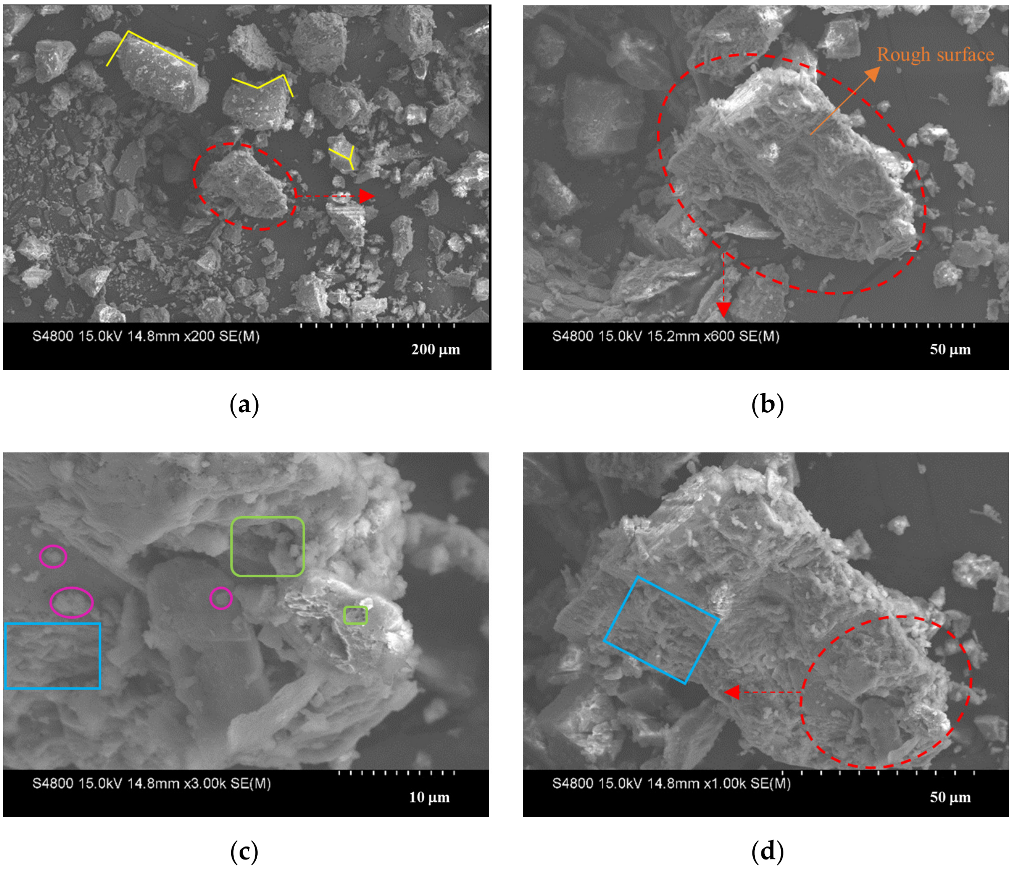


Figure 8. Microstructure of eggshell powder under scanning electron microscope: (**a**) 200×, (**b**) 600×, (**c**) 3000×, (**d**) 1000×. The red dotted line indicates the observation area, the red arrow indicates the observation according to the trend of increasing multiples, the yellow solid line indicates the edges and corners of particles, the blue area indicates the fold structure, the green area indicates the pore structure, and the pink area indicates the attachment of particles.

3.4. Evolution of Nano-Scale Microstructure Characteristics of Asphalt

3.4.1. Characteristics of Nano-Scale Microstructure of Asphalt

The AFM samples were obtained using the hot melt method, and AFM figures of the neat asphalt and eggshell waste asphalt with different contents were measured at room temperature. Figures 9 and 10 show the AFM nano-micro morphology of the neat asphalt and the asphalt with different contents of eggshell waste, respectively.

Asphalt is a complex material with concomitant multi-phases, and nano-scale folds and undulations of asphalt samples are represented by nano-morphology AFM figures. It can be seen from the AFM 2D nano-morphology images in Figure 9 that both the neat asphalt and the asphalt with eggshell waste present a "bee-like structure" which is black and white, relatively dispersed and locally aggregated at the nano-micro-scale. In the AFM 3D diagrams in Figure 10, the peak features a bright white peak bulge, representing the bright stripe of the white area in the "bee-like structure", while the trough features a black columnar bulge in the opposite direction, representing the dark stripe in the "bee-like structure" close to the black area, which is intuitively reflected in the 3D diagrams.

By further comparing the AFM figures of the neat asphalt and asphalt with different contents of eggshell waste, it can be seen that the "bee-like structure" of the two asphalts are different. Figure 9a shows that the "bee-like structure" of the neat asphalt was relatively small in shape and evenly dispersed and contains many immature bees. Additionally, the white area in Figure 9a with a two-dimensional morphology shows a relatively thin convex structure in Figure 9a of three-dimensional morphology figures. When the contents of eggshell waste is 5% and 10%, as shown in Figure 9b,c, as the addition of eggshell waste, the "bee-like structure" gradually matures, the number of "bee-like structure" decreases, the size of some "bee-like structure" increases, the size of some "bee-like structure" becomes significantly larger than others, and the originally thin protrusions in Figure 10b,c gradually become thicker, especially in the 10% eggshell waste asphalt. When the content of eggshell waste reaches 15%, as shown in Figure 9d, the "bee-like structure" changes obviously. The size of some "bee-like structure" decreases, the quantity of small-sized "bee-like structure" increases, and the bulge becomes thinner in Figure 10d. Obviously, the nano-micro morphology of the asphalt changes greatly after adding the eggshell waste.

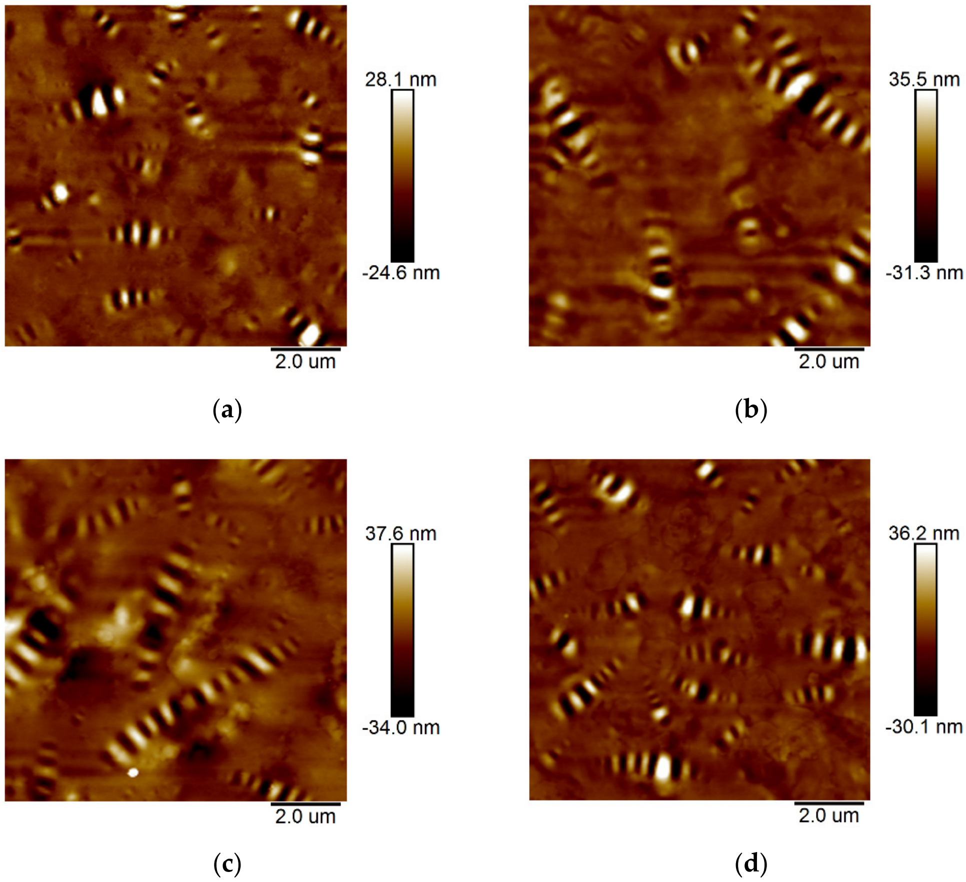


Figure 9. Two-dimensional nano-morphology AFM figures of asphalt with different eggshell waste contents: (**a**) neat asphalt, (**b**) 5% ESP, (**c**) 10% ESP, (**d**) 15% ESP.

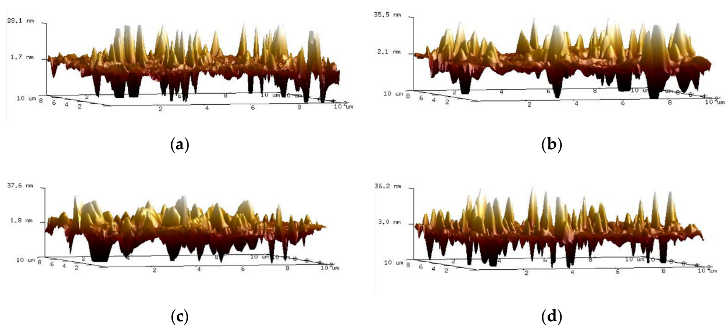


Figure 10. Three-dimensional nano-morphology AFM figures of asphalt with different eggshell waste contents: (**a**) neat asphalt, (**b**) 5% ESP, (**c**) 10% ESP, (**d**) 15% ESP.

Both the neat asphalt and eggshell waste asphalt are rich in nano-microstructures, and the "bee-like structure" is randomly distributed. There are differences in the maturity, size, and quantity of the "bee-like structure" between the two asphalts in the AFM figures. Therefore, eggshell waste does induce the evolution of the nano-micro morphology of asphalt.

3.4.2. Quantification of Nano-Scale Microstructure Characteristics of Asphalt

From the above evolution analysis of asphalt nano-microstructure characteristics, it can be seen that there are obvious differences in the nano-microstructures of the asphalt due to the addition of biological eggshell waste. For the purpose of further analyzing the evolution characteristics of the nano-microstructure of asphalt, the R_q and R_a were selected to quantify the differences between the nano-micro morphology. Figure 11 is a nano-micro roughness parameter diagram of asphalt with different contents of eggshell waste.

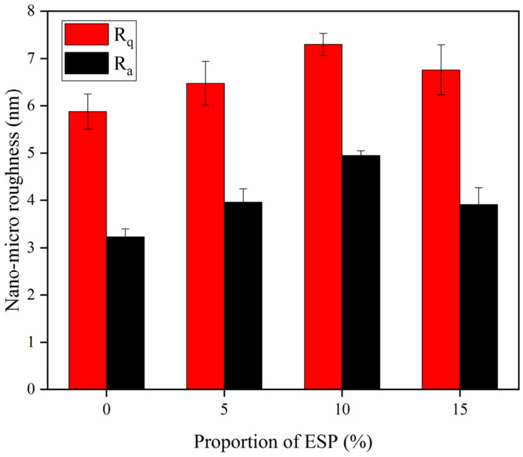


Figure 11. Nano-micro roughness of asphalt with different contents of eggshell waste.

Figure 11 points out that the R_q and R_a of the neat asphalt are both small, and the nano-micro roughness of the asphalt changes greatly with the increase in the content of eggshell waste. Compared with the neat asphalt, when the content of eggshell waste is 5% and 10%, the R_q and R_a values of the eggshell waste asphalt increase, which indicates that the roughness of asphalt increases obviously after adding the eggshell waste, which is consistent with phenomenon of the "bee-like structure" of asphalt in Figures 9 and 10. When the content of eggshell waste increases from 10–15%, the R_q and R_a values of the eggshell waste asphalt decrease, which indicates that the roughness of the eggshell waste asphalt decreases when the content of eggshell waste reaches 15%. This phenomenon is the same as that seen in Figure 9d. Obviously, with the addition of eggshell waste, the nano-micro roughness index of asphalt changes greatly. Asphalt is a type of mixture, and there are many components. The difference of components in asphalt reflects the difference in the microstructure characteristics [60]. Therefore, the addition of eggshell waste may change the relative content of each component in asphalt, causing the two kinds of asphalt to have great differences in terms of nano-microstructure.

To sum up, the addition of eggshell waste changed the nano-micro roughness of the asphalt, and the variation trend of the nano-micro roughness parameters R_q and R_a of asphalt with the content of eggshell waste was similar to the maturity and size of the "bee-like structures" in the AFM figures.

3.4.3. The Relationship between Nano-Micro Indexes of Asphalt and Proportion of Eggshell Waste

By studying the evolution of the nano-microstructure characteristics of asphalt, it can be seen that the nano-microstructure characteristics of asphalt are closely related to the contents of eggshell waste. For the purpose further analyzing the quantitative relationship between them, the regression analysis method is used to construct the functional relationship between nano-micro indexes of asphalt and the proportion of eggshell waste.

Based on the above analysis of evolution of nano-microstructure characteristics of asphalt, a functional relationship model between the nano-micro indexes of asphalt and proportion of eggshell waste is proposed, as shown in Equation (4).

$$I_{nano} = aP^2 + bP + c \tag{4}$$

where I_{nano} is the nano-micro indexes; P is the eggshell waste proportion; a, b, c are the regression parameters.

According to Equation (4), the analysis results are shown in Table 3.

Table 3. The fitting equation of the relationship between nano-micro indexes of asphalt and proportion of eggshell waste.

I_{nano}	P	a	b	c	R^2
R_q	Eggshell Waste	−0.01328	0.27363	5.80242	0.92127
R_a	proportion	−0.02034	0.37530	3.16000	0.93266

Figure 12 shows the fitting effect of the nano-micro indexes of asphalt at different contents of eggshell waste.

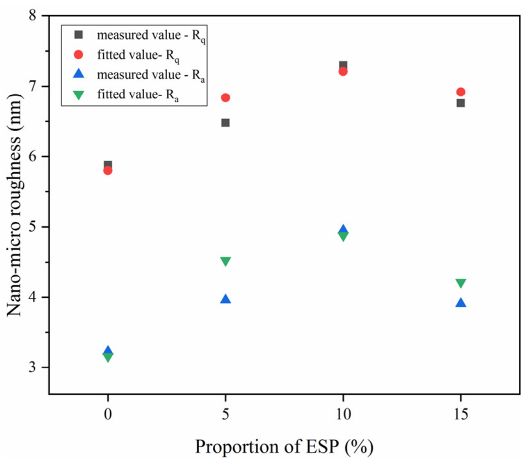


Figure 12. The fitting effect of the nano-micro indexes of asphalt at different contents of eggshell waste.

Table 3 and Figure 12 show that there is a significant correlation between the nano-microstructure characteristics of asphalt and contents of eggshell waste. By establishing a functional relationship model, the quantitative relationship between the eggshell waste asphalt and proportion of eggshell waste is further clarified, which provides an important support for further research on the microscopic performance of the interaction between eggshell waste and asphalt.

3.4.4. Evolution Analysis of Nano-Scale Microstructure Characteristics of Asphalt

According to the AFM test results, "bee-like structure" exist in the nano-scale morphology of asphalt with different eggshell waste contents, so the effect of different contents of eggshell waste on the nano-microstructure characteristics of asphalt can be reflected by the evolution of the micro-morphology characteristics.

Based on the above analysis, both the neat asphalt and eggshell waste asphalt are rich in microstructure. With the increase in the eggshell waste content, the maturity, size and quantity of the "bee-like structure" and roughness in the two kinds of asphalt become different, and the eggshell waste greatly influences the nano-microstructure of asphalt. According to Loeber et al., asphaltene micelle plays an important role in the appearance of "bee-like structure"; moreover, the increase in the asphaltene content is the main reason for the formation of "bee-like structure" [61]. Wu Shaopeng et al. believed that the emergence of more asphaltenes with large molecular weights has caused larger "bee-like structure" to be found [62]. Pauli et al. held the view that that the interaction between the asphalt component and the wax crystal structure is the main reason for the formation of "bee-like structure" [63]. Asphalt contains a variety of components in a complex mixture. The change in the microstructure of asphalt is caused by the different interactions between the internal components, which further affects the performance of the asphalt [64]. Therefore, this paper analyzes the reason for the evolution of the nano-microstructure characteristics of asphalt with different eggshell waste contents from the interaction between the asphaltene—waxiness system.

Based on the theory of asphalt colloids, most asphalt belongs to the colloidal system, which is formed by dispersing asphaltenes with relatively large molecular weights and high aromaticity in a soluble medium with a relatively low molecular weight [65]. When the temperature is below 56 °C, the wax molecules contained in asphalt will be separated from the asphaltene and colloid in the form of wax crystals to produce a "bee-like structure" [66]. Wax crystals are often surrounded by asphaltenes and colloids, which surround and disperse wax crystals. When the relative content of asphaltene is small, wax molecules will coagulate. As the relative content of asphaltene increases, the size of the structure formed by the wax crystals also gradually increases. When the relative content of asphaltene continues to increase, the dispersive effect of asphaltene on the wax crystal structure will be enhanced, and asphaltene micelles will destroy the structure formed by wax crystals. Therefore, different relative contents of asphaltenes can promote or hinder wax crystallization, thus affecting the structure of the wax crystals connected with each other. In addition, it is not known whether the "bee-like structure" of asphalt occurs in the whole material or is only a surface phenomenon [51,64].

According to the test results in this paper, the maturity, size, quantity and roughness of "bee-like structures" on asphalt surfaces are changed by different amounts of eggshell waste. Based on the above analysis, this phenomenon can be attributed to the complex action of asphaltene and wax crystals due to the change in their relative content. ^{1}H-NMR tests of asphalt with different contents of eggshell waste indicate that there is no obvious chemical reaction between eggshell waste and asphalt, and the physical blending between eggshell waste and asphalt plays an important role. The SEM test results show that the structural characteristics of eggshell waste are rough, wrinkled, porous and loosened, and they usually show a good adsorption performance. This special surface morphology and particle structure may cause it to experience a closer combination with asphalt in the asphalt system. Eggshell waste may gradually absorb more light components, so the addition of eggshell waste will cause the light components to gradually decrease, resulting in a gradual increase in the relative proportion of asphaltenes. This phenomenon is similar to the principle of SBS-compound-modified asphalt with nano-sulfur. SBS absorbs the light components of asphalt, and the relative content of asphaltene and colloid increases, which destroys the balance of the neat colloidal structure [67]. With the increase in the relative content of asphaltene, the adsorption of wax crystals is dominant at first, the wax crystals will adsorb more asphaltenes, and the size of the structure of the wax crystals will gradually increase. At this time, the reflection of the nano-micro morphology structure is that the "bee-like structure" of AFM figures gradually matures, the size increases, the number decreases, and the roughness increases. As content of eggshell waste continues to increase, the relative content of asphaltene continues to increase, and asphaltene micelles will play a leading role in the dispersion of the wax crystal structure. This may destroy the connection between the structures of wax crystals, meaning that the wax crystal structure is dispersed into small structures. At this time, the reflection of the nano-micro morphology structure is that the size of "bee-like structures" in AFM figures decreases, the number increases, and the roughness decreases. Therefore, the addition of eggshell waste may affect the interaction of the asphaltene—waxiness system, causing the two kinds of asphalt to have great differences in terms of nano-microstructure.

4. Conclusions

This study reveals the effect of recycled eggshell waste on the physical and chemical properties as well as nano-microstructure characteristics of asphalt. The results provide further theoretical support for the use of eggshell waste in bio-roads, which is of great significance for the sustainable development of society and the economy. The main conclusions are as follows:

1. The penetration, softening point and ductility tests indicates that the eggshell waste increases the hardness, thermal stability and reduces the ductility of asphalt.
2. ^{1}H-NMR test points out that there is no obvious chemical reaction between the eggshell waste and asphalt, and the interaction between eggshell waste and asphalt is a physical miscible process.
3. The SEM test of the eggshell powder microstructure shows that eggshell powder is rough, wrinkled, porous and loosened and can usually show good adsorption performance.
4. The AFM test of the asphalt shows that a “bee-like structure” exists in the nano-microstructure of asphalt with different contents of eggshell waste. In addition, adding different contents of eggshell waste changes the maturity, size, quantity of the “bee-like structure” and roughness of asphalt, which can be attributed to the interaction of the asphaltene—waxiness system.

At present, green economy is a major theme in sustainable development and has become a common concern across the whole world. Under the premise of the increasing demand for the application of asphalt materials in engineering, the combination of the biological waste of eggshells with asphalt can not only reduce the production of solid waste and “reduce the burden” on the Earth but also turn waste into wealth and realize the comprehensive recycling of resources. This is conducive to green production and is of great significance to the sustainable development of society and the economy. eggshell waste has a great effect on the physical properties, chemical properties and nano-microstructure characteristics of asphalt.

However, there are no further studies on the performance of the eggshell waste asphalt mixture such as the high temperature, low temperature, water stability and anti-aging properties.And the dynamic modulus of asphalt mixture at different temperatures and frequencies should be obtained so as to better evaluate the road performance of eggshell waste asphalt. Moreover, the recycling scheme of eggshell waste will be optimized. In addition, at the same scale, the similarities and differences between eggshell waste and other materials on asphalt properties can be further explored.

Author Contributions: Conceptualization, G.J. and Y.G.; methodology, G.J. and Y.G.; validation, G.J., Y.Z. and Y.G.; formal analysis, G.J., Y.Z. and Q.Y.; investigation, G.J., Y.G. and Q.Y.; writing—original draft preparation, G.J.; writing—review and editing, G.J., Y.G. and Y.Z.; supervision, X.W. and Y.L.; project administration, X.W. and Y.L. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data are not be shared due to restrictions eg privacy and regulation.

Acknowledgments: This research was supported by the project of China Communications Construction Second Highway Engineering (QHTJ01-QT-80).

Conflicts of Interest: The authors declare no conflict of interest.

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