Treatment on Crumb Rubber Modifier towards Enhanced Storage Stability of Asphalt Rubber

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Abstract

Breaking waste tires into crumb and adding it to asphalt as modifier to prepare asphalt rubber (AR) is an effective method to solve the waste tire problem and improve the performance of matrix asphalt. The modified asphalt has better high and low temperature performance. However, the segregation of the crumb rubber modifier (CRM) causes storage instability of the AR. At present, studies have been conducted that improving the solubility of the CRM or adding some macromolecular polymer can improve the storage stability of the AR. However, the structure and polarity of the CRM surface are rarely explored for its correlation with the storage stability of AR. In this paper, the surface structure and polarity of the CRMs was changed by four different reagents, and the properties of the ARs prepared by the CRM were measured to analyze the adhesion between the CRM and the asphalt. It is concluded that the CRM with rough porous and non-polar surface has higher storage stability due to the better interfacial adhesion, which provides a research direction for improving the storage stability of rubber asphalt.

Keywords: *storage stability; asphalt rubber; interfacial adhesion; polarity*

1. Introduction

The development of the automobile transportation industry has promoted economic and social progress, but considerable waste tires have hindered social development [1]. The irrational treatment of waste tires can lead to serious problems for society and human health [2]. The recycling of waste tires is the key to solve this problem. Among it, the preparation of asphalt rubber (AR) by crushing waste tires into crumb rubber modifier (CRM) and then adding it to matrix asphalt is the main market for recycling waste tires.

As early as 180 years ago, CRM began to be tested on asphalt pavement. In the 1960s, "dry process" and "wet process" were successively invented, and AR began to be widely used and studied [3]. Compared with matrix asphalt, AR has high-temperature stability, low temperature crack resistance, and also better aging resistance. The asphalt mixture produced by AR is also so superior in performance that it is the most important binder in road construction, especially for the flexible pavement. [4].

However, due to the instability of thermodynamics, the CRM as a modifier always exhibits segregation during storage, which destroys the modification effect of the CRM. Especially when the binder is stored at high temperatures, the expanded CRM settles rapidly due to the higher initial density than asphalt [5]; In addition, some studies have shown that the density of the CRM after swelling is reduced and migrates to the top of the asphalt [6] . Ghavibazoo analyzed the effect of the dissolution of the CRM on the final properties of the binder and found that the percentage of dissolution affected the storage stability of the AR [7]. However, the dissolved CRM will lose the effect of the modification. At present, there is little research on the correlation between the adhesion of CRM and asphalt interface to the storage stability of AR.

In order to solve the storage instability in the process of compatibility between CRM and asphalt, this paper proposes the correlation between the surface structure and polarity of CRM in the process of modifying asphalt according to the principle of “similar compatibility”. The surface of the wet-crushed 80-mesh waste tire CRM was treated with four different reagents including sodium hydroxide, carbon tetrachloride, silane coupling agent (KH-Si69) and sodium hypochlorite. Measurements are carried to characterize the surface of CRM by scanning electron microscopy, infrared spectrometer and surface contact angle tester. Then the CRM before and after treatment is prepared to make AR, and the modification effect is obtained by various performance indexes before and after Rolling Thin Film Oven (RTFO). The evaluation was carried out to evaluate the interfacial adhesion characteristics of CRM and asphalt.

The conclusion is drawn that the adhesion between the CRM and the asphalt interface is not only related to the polarity of the CRM surface, but also the microstructure of the CRM. In addition, different chemical agents also affect the performance of AR. It is initially believed that a rough porous and hydrophobic non-polar surface facilitates an increase in adhesion between CRM and asphalt. The improvement of surface structure and polarity of CRM can be used as a research direction to improve the storage stability of AR.

2. Material and Experiment Design

2.1 Material

Compared with ambient shredding[8] and cryogenic grinding, the wet-processed CRM is the most suitable to modify asphalt for its rough surface and uniform small size [3]. Therefore, the wet-processed CRM with a size of 80 mesh was used in this study. The penetration of the matrix asphalt is 7.0mm, which is commonly used in Guangdong. In addition, four chemical reagents including 5 mol•L^{-1} sodium hydroxide solution, carbon tetrachloride, KH-Si69, and sodium hypochlorite solution were used.

The KH-Si69 solution is prepared according to the ratio of coupling agent: water: absolute ethanol = 1:1:20, and standing for 2 hours to ensure sufficient hydrolysis of the coupling agent.

The sodium hydroxide solution, carbon tetrachloride, KH-Si69 solution and sodium hypochlorite solution were respectively reacted with CRM in an oven at 50℃ for 2 hours, and the obtained CRMs were labeled as RA, RB, RC, and RD. The untreated CRM is recorded as RO.

The AR was prepared by the "wet process". The specific operation process was as follows: 800 g of matrix asphalt was preheated in an oven at 180℃ for 40 min, and then slowly mixed up with 144 g of RO, RA, RB, RC, and RD respectively under the stirring of the shearing machine for 20 min with the 1400 r / min of rotation speed; and then the rotation speed of the shearing machine slowly increased to 4500 r / min and keep shearing for 40 min; finally the rubber swelled in the asphalt at 180-185℃ for 4 h, and the AR obtained is recorded as O, A, B, C and D.

2.2 Test methods

2.2.1 CRM test

The scanning electron microscope (SEM) test utilizes the high-energy electron beam obtained by the aggregation to bombard the surface of the CRM, and the physical signals obtained after the interaction is used to characterize the microscopic morphology of the surface of the CRM. In this study, SEM test was carried out with a scanning electron microscope S-3700N at Hitachi Company in Japan with an operated voltage of 10 kV. Before tested, the sample should be placed on a metal stage for gold spraying.

When the substance is irradiated with infrared light, if the frequency of the infrared light is consistent with the vibration frequency of the functional group of the material molecule, a resonance effect occurs, and the substance absorbs infrared light of a specific frequency, and then the transmittance of the infrared light is reduced at that frequency. The functional group is analyzed by the transmittance of infrared light of the sample. In this study, a Fourier transform infrared spectrometer (FTIR) VERTEX 70 manufactured by Bruker Company in Germany was used under a wavelength of 400 ~ 4000 cm^{-1}. The samples were compressed by KBr tableting method.

The contact angle can be used to judge the wettability of the solid as well as the polarity of the solid surface. In this study, the surface contact angle tester OCA40 Micro produced by the German Dataphysics Company was used. The test liquid was distilled water with a droplet volume of 4 µL and a droplet velocity of 1µL/s.

2.2.2 AR test

The physical properties of AR were tested by penetration, softening point and ductility test. Workability was characterized by the rotational viscosity measured using a Brookfield digital viscometer at 135℃ and 165℃ to provide a reference for asphalt mixing and compaction temperatures.

The penetration was determined by the inserting depth caused by a 100 g stylus inserted into a pitch at 25℃ for 5 s, and the viscosity of the asphalt could be further evaluated by this value. The softening point was represented by the temperature at which the small steel ball slides down to the bottom with the asphalt sample on the small steel ring from 5℃ , and this could also evaluate the high temperature stability of the asphalt. Further, the asphalt was stretched at a stretching speed of 5 mm/min at 5℃ until fracture, and the tensile length at the time of breaking was the ductility of the asphalt, evaluated for the deformation resistance and low temperature performance. The aging resistance of asphalt was evaluated by the physical properties including penetration and ductility which had been aged by RTFO.

For storage stability, an isolation experiment was used for evaluation. During the experiment 50 g of AR was poured into the sample aluminum tube, sealed and placed in an oven at 163℃ for 48 h, and then placed in a refrigerator for freezing. After the asphalt solidification, it was divided into two sections, and the difference between the softening points of the top and down section was measured. This value was used to evaluate the segregation of the AR, and further used as a basis for evaluating the compatibility between CRM and matrix asphalt.

3. Result and Discussion

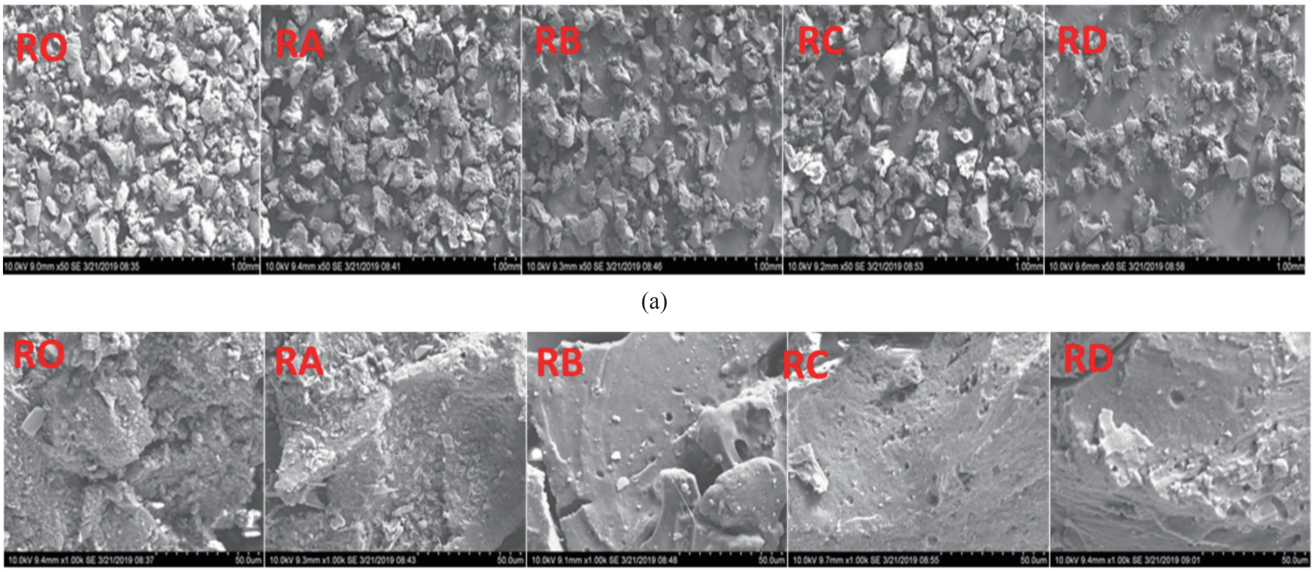
3.1 CRM

3.1.1 SEM test result

The change in shape, size, and aggregation of the CRM with and without the treatment can be seen from figure 1.

It can be seen in figure 1(a) that with the treatment by sodium hydroxide, the size of the CRM is obviously increased, and the degree of aggregation becomes larger. Compared with the CRM without treatment, those treated by carbon tetrachloride and KH-Si69 seem that there is no obvious change; while the CRM treated by sodium hypochlorite was obviously reduced both in size and the degree of aggregation.

In figure 1(b), the CRM treated with sodium hydroxide has pin-like particles gathered on the surface of the CRM. The one treated with carbon tetrachloride has a smoother surface for the guess that carbon tetrachloride is related to the dissolution of impurities on the surface of the CRM. The surface of the CRM treated by the KH-Si69 is rough and porous. It is because some of the hydroxyl groups of the coupling agent are dehydrated into bonds with the hydroxyl groups on the surface of the CRM after hydrolysis, and adhered to the surface of the CRM. For the CRM treated with sodium hypochlorite, due to the strong oxidizing property which can completely oxidize some unsaturated groups, the surface becomes smoother and have fewer holes.



(a)

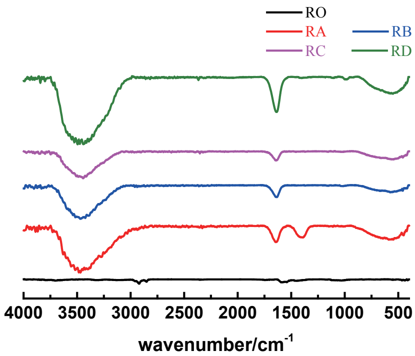
(b)

Figure 1. SEM evaluation: (a) 50 times; (b) 1000 times.

3.1.2 FITR test result

Figure 2.(a) is the infrared spectrum peak of CRM, and Figure 2.(b) is the analysis of the main peak position. After chemical treatment, the CRM was decolorized to some extent, making the infrared spectrum peak more obvious. At the wave numbers of 3500cm^{-1} and 1636cm^{-1}, the peak intensity of the infrared spectrum is: RD>RA>RB>RC. Therefore it is

speculated that the surface polarity of the CRM treated with sodium hypochlorite becomes the largest while the one treated by KH-Si69 has the smallest polarity. A similar pattern exists in the fingerprint area of about 600 cm^{-1}.



(a)

Main functional groups in CRM:

3500 cm^{-1} (O-H the stretching vibration of hydroxyl group),

1636 cm^{-1} (C=O stretching vibration of carbonyl group),

1400 cm^{-1} (O-H in-plane bending vibration of alcoholic hydroxyl group).

(b)

Figure 2. FTIR evaluation of CRM: (a) spectrum; (b) analysis.

3.1.3 contact anger test result

By measuring the contact angle of the interface, the hydrophilicity or hydrophobicity of the CRM can be known and the polarity change of the CRM can be estimated. It can be seen from table 1 that the surface change effect of the CRM is different after different treatment. The surface of the CRM treated with carbon tetrachloride and KH-Si69 becomes more hydrophobic than the original CRM while those treated with sodium hydroxide and sodium hypochlorite have a hydrophilic surface. For RD, the water droplets are completely extended on the surface of it as long as it contacts with the water droplets. So the contact angle with water cannot be accurately measured by this method.

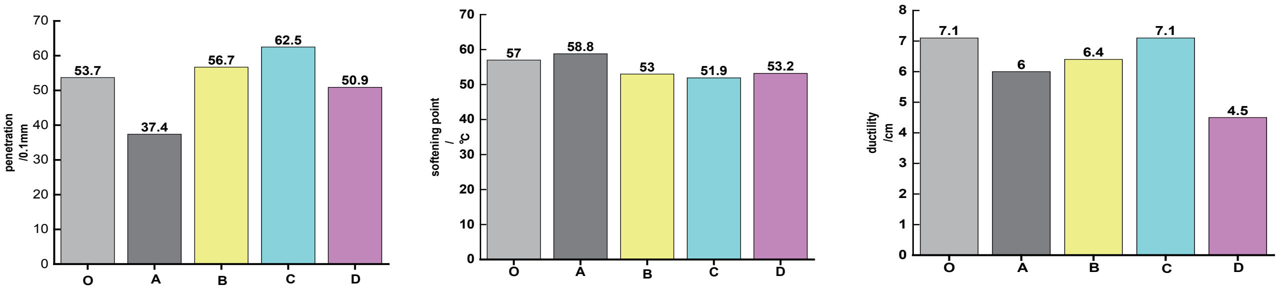
Table 1. Interface contact angle between CRM and water.

-	RO	RA	RB	RC	RD
test 1	128.7°	82.17°	133.5°	139.9°	-
test 2	129.8°	81.3°	135.0°	140.4°	-
test 3	129.6°	77.0°	134.1°	139.1°	-
average	129.4°	80.2°	134.2°	139.8°	-

This is also consistent with the above infrared analysis results. The more -OH , more hydrophilic, and the more polarity. The CRM treated with carbon tetrachloride or KH-Si69 has a significantly larger interface angle with water than the untreated one , which indicated a smaller polarity.

3.2 AR

3.2.1 Physical properties before RTFO



(a) (b) (c)

Figure 3. Physical properties before RTFO: (a) penetration; (b) softening point; (c) ductility.

As the penetration shown in Figure 3 (a), after the sodium hydroxide treatment, the penetration of A is significantly reduced, followed by D. The penetration of the B or C is improved, and the increase in the C is the most obvious, increased by 16%. It shows that the CRM treated with carbon tetrachloride and coupling agent has better compatibility with the matrix asphalt.

As shown in Figure 3 (b), except for the group treated with sodium hydroxide, the softening points of the other groups has decreased. But overall, the change in softening point is not significant. It shows that different reagent has little effect on the high temperature stability of AR.

The ductility is basically reduced as shown in Figure 3 (c), the magnitude of the decrease is D>A>B>C=O. Note that in addition to the KH-Si69 treatment group, other treatment methods will reduce the low temperature performance of the AR.

3.2.2 Workability

As shown, the viscosities at 135℃ and 165℃ show the same pattern, i.e. A > O > B > C > D. That is to say, in addition to the fact that the sodium hydroxide treated sample increases the viscosity of the AR while other agents lowers the rotational viscosity of the AR at 135℃ and 165℃. The decrease in viscosity indicates that the workability of the AR prepared by the treated CRM is improved.

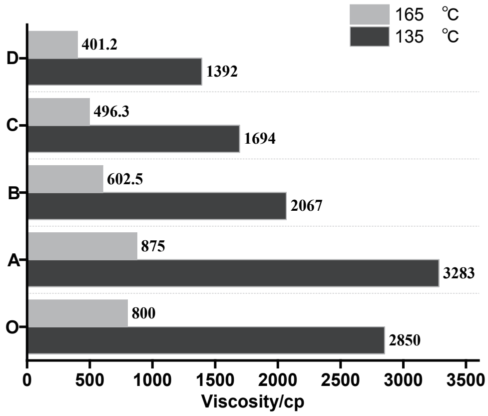


Figure 4. Rotational viscosity test results.

3.2.3 Storage stability

The storage stability of the AR was evaluated by the separation test of the asphalt binder. Figure 5 shows the softening point difference between the top and bottom section of the sample. It can be seen that the AR treated by the KH-Si69 can significantly improve the storage stability, and other treatment methods are generally effective. As known before, the surface of the CRM treated by KH-Si69 is rough and porous, and the specific surface area is relatively large so that the contact area with the matrix asphalt is larger. At the same time, the surface of the CRM treated by KH-Si69 is less polar as the asphalt, which makes the CRM treated by this reagent is better compatible with the matrix asphalt and has better interfacial adhesion properties.

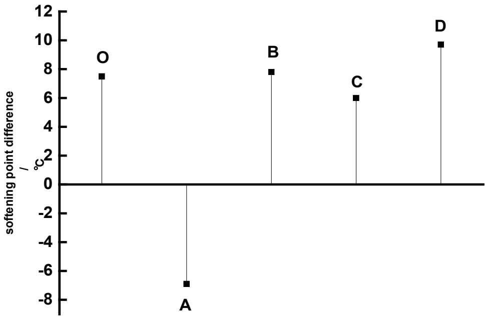
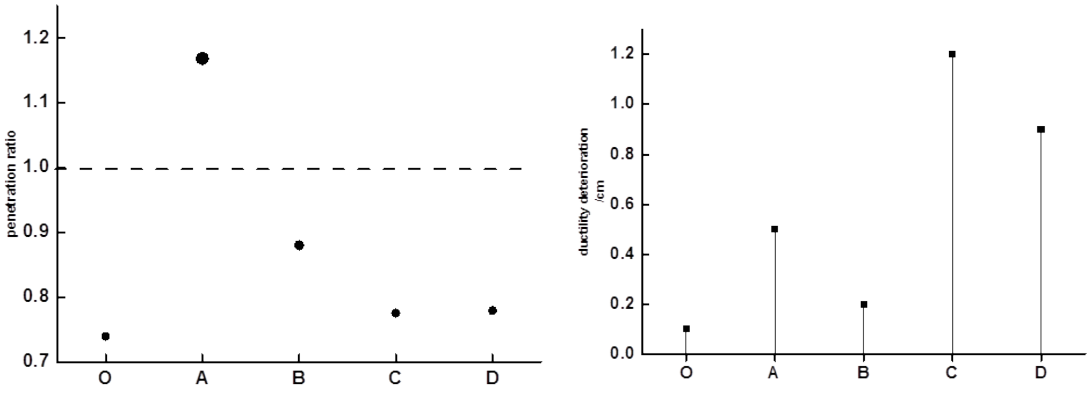


Figure 5. Storage stability of AR.

3.2.4 Physical properties after RTFO

The penetration ratio of various ARs before and after RTFO is shown in Figure 6(a). It shows that the penetration ratio of the AR treated with the reagent is higher than that of the untreated one.

Figure 6(b) is a comparison of the 5 °C ductility before and after RTFO. After RTFO, all the ARs showed a decrease in ductility, and the AR prepared by the untreated CRM had the smallest degree of decline, among which the AR treated with KH-Si69 had the largest decrease in ductility. From the perspective of ductility, the aging resistance of various ARs is as follows, O>B>A>D>C.



(a) (b)

Figure 6. Physical properties before RTFO: (a) penetration ratio; (b) ductility deterioration.

4. Conclusions

In order to solve the problem of storage instability in the process of compatibility between CRM and asphalt, this paper proposes the correlation between the surface structure and polarity of CRM in the process of AR according to the principle of “similar compatibility”. The treatment method makes the CRM have different surface structure and polarity, and then the following conclusions by measuring the physical properties are obtained.

- The CRM treated with sodium hydroxide or sodium hypochlorite reagent has an increased surface polarity, becomes more hydrophilic, increases the degree of aggregation, which is not compatible with asphalt.
- The surface of the CRM treated with carbon tetrachloride or KH-Si69 becomes more hydrophobic and non-polar. Among them, the surface of the KH-Si69 -treated CRM is rough and porous, and the storage stability of the AR prepared by this CRM is significantly improved. While the surface of the carbon tetrachloride treated CRM is smooth and less porous, making the interface adhesion effect with the asphalt not ideal.
- The CRM treated with sodium hydroxide and sodium hypochlorite exhibits a modification effect different from that of other reagents, and its mechanism needs further investigation.

The adhesion between the CRM and the asphalt is not only related to the polarity of the surface of the CRM, but also the microstructure. It is initially believed that a rough porous and hydrophobic non-polar surface facilitates an increase in adhesion between CRM and asphalt. In addition, different chemical agents will also affect the performance of the modified asphalt, and the influence mechanism of different chemical reagents will be further explored. How to improve the storage stability of AR, and how to reduce odor and optimize the working environment by improving the interface adhesion of CRM and asphalt, will become a major development direction of AR.

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