Effect of Thermal-Oxygen Aging of the Waste Tire Rubbers on the Interfacial Bond Strength of Porous Elastic Road Surface

Binfang Lan[1], Jing Gu[1], Sheng Cheng[1], Yuchun Li[2*]

[1] Taizhou Highway Development Center, Taizhou, Jiangsu, 225300 China
[2]Research Institute of Highway Ministry of Transport, Beijing, 100088 China

*Corresponding author's e-mail: yc.li@rioh.cn

Abstract. Porous elastic mixture is a kind of functional pavement, which possess the noise reduction ability, energy saving and carbon reduction, waste resource utilization and other composite functions. In the mixture, the polyurethane as binder, aggregates mixed with 15%-25% waste rubber particles. Compared with new rubber, the broken molecular chain structure is more prone to further aging degradation and "sulfur return" in a short time after being subjected to different intensities of hot oxygen in the road service environment. The elasticity decreases rapidly, and the thermal oxygen aging rate is significantly faster than that of the adhesive of the mixture, which affects the interfacial bond strength of the mixture. In the aging process, polar groups are generated, surface free energy is increased, adhesion with polyurethane is increased, and interface drawing strength is increased. However, with the extension of aging time, the cemented structure formed by holes on the surface of waste rubber and polyurethane is more likely to be the stress concentration point after being subjected to force, so the drawing strength gradually decreases after 35 days of aging.

Keywords: porous elastic road surface, thermal- oxygen aging, waste tire rubbers

1 Introduction

Porous elastic mixture is a kind of functional pavement, which possess the noise reduction ability, energy saving and carbon reduction, waste resource utilization and other composite functions [1]. The combination of polyurethane adhesive and waste rubber particles not only solves the reuse of waste rubber, but also makes the porous elastic mixture have good vibration and noise reduction performance, as well as excellent road performance such as high temperature stability and water stability[2].

However, as a recycled material, waste rubber has been subjected to various effects such as light heat and load during its early use as a tire, and its molecular chain structure has been partially broken[3]. Compared with new rubber, the broken molecular chain structure is more prone to further aging degradation and "sulfur return" in a short time

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after being subjected to different intensities of hot oxygen in the road service environment. The elasticity decreases rapidly, and the thermal oxygen aging rate is significantly faster than that of the adhesive of the mixture, which affects the road performance and functional characteristics of the mixtures[4]. Thermal degradation is a key process of rubber aging, especially in the high temperature environment, the break of rubber molecular chain will lead to changes in physical and chemical properties[5].

In the aging process, hydroxy-containing groups are generated in waste rubber, which results in increased surface polarity, decreased non-polarity, increased surface free energy, decreased intermolecular force, and changes in bonding strength with polyurethane cement materials, thus affecting the performance of the mixture. In order to further study the changes in bonding strength between waste rubber and polyurethane at different aging times, interface drawing test was used to analyze the boundary Surface drawing strength, according to the same method 3.5, according to the waste rubber used to form the mixture, select the same waste rubber, cut into 4cm4cm, and aging at different times.

2 Method

2.1 Materials

The single-component PU with long curing time was selected by Wanhua Chemical, co. ltd, which is used as the binder of PERS mixture, the technical indexes of single-component PU adhesive are shown in the **Tab.1**.

Table 1. Technical indexes of single PU adhesive

Sample Color	NCO group content (%)	viscosity (30°C)	Surface drying time	Curing time
Pale yellow	10.2	1590	1.8h	3h

Waste rubbers were selected as nature rubbers, which provided by Xinchen Chemical Co. Ltd, China. The metal, fibers and other additives in the waste rubbers were removed, which were crushed into particles with sizes of 1.18 mm and 2.36 mm. the technical indexes of rubber particles are shown in the **Tab.2**.

Table 2. Technical indexes of rubber particles

Index	Unit	Test value
Relative density	/	1.14
Moisture content	%	0.2
Metal content	%	0.5
Slender and flat particles content	%	4.1

2.2 Contact Angle test

The contact Angle of the sample was determined when the residence time of different reagents was 3s. The existing waste rubber sample was 1.18 mm and 2.36mm, and the particle size was too small to conduct contact Angle test. Therefore, the same sample of waste rubber used in the above-mentioned test was selected and cut into 2cm×2cm for the same thermal oxygen aging treatment as the aforementioned waste rubber, and the contact Angle test was carried out through optical contact. The waste rubber of 2cm×2cm is shown in the **Fig. 1.** The solvents used to determine the contact Angle of waste rubber samples before and after thermal oxygen aging included deionized water and dimethyl iodide, both at concentrations of 2μL.

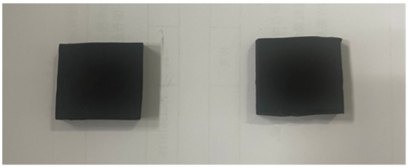

Fig. 1. The waste rubbers

2.3 Surface Free Energy Calculation method

In order to further study the influence of the intermolecular forces on the surface of waste rubber and the generation of hydroxyl groups on the surface properties of waste rubber, the surface free energy was introduced. The OWRK model is highly regarded for its practicality and has become a commonly used model in the field of surface free energy research. The polar and non-polar liquids in OWRK model were chosen to water and Diiodomethane (CH_2I_2), the interfacial tension is shown in the **Tab.3.**

Table 3. The interfacial tension of water and CH_2I_2

Liquid	γ_{lv}(mJ/m^2)	γ_{lv}^{d}(mJ/m^2)	γ_{lv}^{p}(mJ/m^2)
Water	72.8	22.1	50.7
CH_2I_2	50.8	50.8	0

2.4 Pull-out Test

During the drawing test to evaluate the adhesion between the polyurethane binder and the rubber, the waste rubber is first cut into a 4cm× 4cm cross-section cube, and then the surface of the waste rubber is cleaned and dried in the oven. Then, a quantitative polyurethane adhesive is evenly applied on one side, and the two pieces of the cut waste rubber are quickly bonded. In order to enhance the bonding effect, a quantitative amount of AB glue is applied on the spindle, and it is respectively glued to the contact surface of the polyurethane binder and rubber. Finally, the whole structure is placed on the indoor silicone paper, waiting for its natural curing. The whole operation process is strict to ensure the accuracy of the test results. The sample of pull-out is shown in the **Fig. 2.**

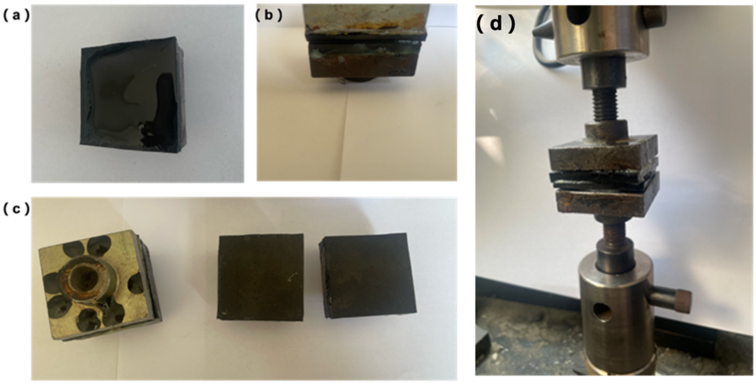

Fig. 2. The mold of pull test of waste rubbers and polyurethane

3 Results and Discussion

3.1 Change of Surface Free Energy

For waste rubber aged for different times, the surface contact angle of the two solvents presents different laws. The surface contact angle of waste rubbers after being aged for different times is shown in the **Fig. 3**. For water solvents, when the sample does not continue to age, the surface of waste rubber is hydrophobic, the water contact angle is 120.2 °, with the occurrence of re-aging, the water contact angle gradually decreases, in the aging 7 days, the contact angle decreases by about 10 ° to 109.2 °, which is due to the fact that in the process of thermal and oxidative aging, the molecular structure of waste rubber is broken to produce more polar groups containing hydroxyl groups. Until 35 days of aging, the water contact angle is 106.9°, but it is still hydrophobic. The contact angle of diiodomethane is small, and when the sample does not continue to age, the contact angle is only 16°, indicating that the surface of waste rubber is non-polar, with the occurrence of re-aging, the contact angle of diiodomethane gradually increases, and in the 7 days of aging, the contact angle rises to 20.1°, until the aging 35 days, the contact angle increases by 2 times to 34.1°. Therefore, the contact angle of diiodomethane gradually increases. In order to further study the influence of intermolecular forces and hydroxyl groups on surface properties on the surface properties of waste rubber, surface free energy was introduced, which explored by Fowkes theory, the results of surface free energy are shown in the **Tab.4**.

Table 4. The results of solid surface free energy

	0 day	7 days	14 days	35days
solid surface free energy (mJ/m^2)	5.01	7.90	8.08	12.86

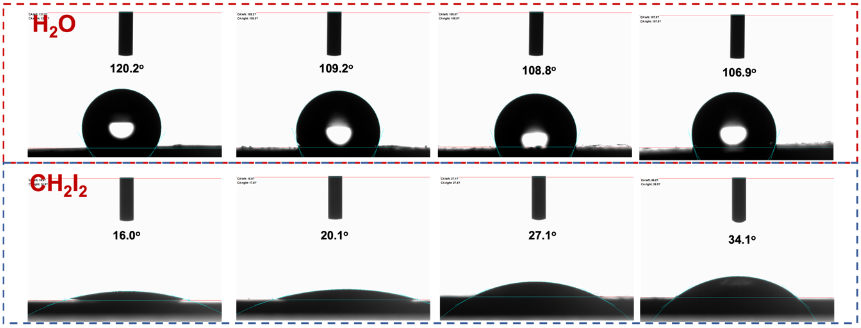

Fig. 3. The results of contact angle

The solid surface free energy of waste rubber is 5.01 mJ/m^2 when there is no re-aging, and the solid surface free energy gradually increases with the occurrence of thermal-oxidative aging, which is due to the production of more hydroxyl groups on the surface during the thermal-oxidative aging process, which improves the surface polarity, and the increase of surface free energy indicates that the waste rubber is more unstable and more prone to decomposition after thermal-oxidative aging. After 35 days of thermal-oxidative aging, the surface free energy increased to 12.86 mJ/m^2, which was 2.5 times that of waste rubber, indicating that the waste rubber after 35 days was unstable and more prone to thermal-oxygen degradation, which was the same as the results of the above-mentioned surface morphology test.

3.2 Change of Pull-out Strength

The pull-test results of waste rubbers after being aged for different times is shown in the **Tab. 5.** In the aging 0 days, the interfacial tensile strength of waste rubber and polyurethane cementing material is 0.97MPa, with the increase of aging time, the interfacial tensile strength, which is due to the generation of polar groups on the surface of waste rubber in the process of thermo-oxidative aging, from the test results of the above-mentioned 3.5 surface free energy and structural change, the surface polarity of waste rubber gradually increases with the thermo-oxidative aging. Because the terminal isocyanate group in polyurethane is polar and has better adhesion to the polar group generated on the surface of waste rubber, the interfacial pull-out strength gradually increases with the increase of aging time, but due to the serious degradation of waste rubber after 35 days of thermal and oxidative aging, it can be seen from the test results of the above-mentioned surface free energy and surface morphology that the surface free energy after 35 days of aging indicates that the waste rubber is very easy to degrade, and the surface presents a large number of unstable structures that are easy to peel off and void.

Table 5. The results of pull-test

	0day	7days	14days	35days
Interfacial pull-out strength (MPa)	0.97	1.45	1.72	1.20

4 Conclusions

In this word, the rubber thermo-oxidative aging test method is used to subject to the thermo-oxidative aging of waste rubber particles with particle sizes of 1.18-2.36 mm and 2.36-4.75 mm at different times. Calculating the surface solid free energy from the contact angle, it can be obtained that the surface of waste rubber produces more polar groups during the thermal-oxidative aging process, and the surface free energy increases, but after 35 days of aging, the surface free energy increases to 2.5 times, which is very easy to undergo aging degradation. According to the interfacial tensile strength of waste rubber and polyurethane cementing materials with different aging days, it can be seen that due to the increase of the adhesion between polar groups and polyurethane during the aging process, the interfacial tensile strength is increased, but with the extension of aging time, there are cavities on the surface of waste rubber and the cemented structure formed by polyurethane is more likely to be used as a stress concentration point after being subjected to force, so the tensile strength gradually decreases after 35 days of aging.

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