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STUDY ON THE EFFECT OF THERMAL-OXYGEN AGING ON THE ADHESION PROPERTIES OF WASTE RUBBER POWDER MODIFIED ASPHALT AGGREGATE BASED ON SURFACE FREE ENERGY THEORY

ŠTUDIJ VPLIVA TERMIČNO-KISIKOVEGA STARANJA NA ADHEZIJSKE LASTNOSTI ASFALTNEGA AGREGATA MODIFICIRANEGA Z ODPADNIM GUMI PRAHOM, NA PODLAGI TEORIJE PROSTE POVRŠINSKE ENERGIJE

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Waste rubber powder modified asphalt (WRMA) has attracted considerable attention due to its environmental friendliness and excellent road performance. However, WRMA is susceptible to thermal-oxygen aging during long-term service, which causes changes in the adhesion between asphalt and aggregates. It can lead to water damage and other defects in an asphalt mixture. The present study was conducted to elucidate the mechanism, with which thermal-oxygen aging affects the adhesion properties of WRMA-aggregate systems, comprising aggregates of limestone and diabase. A thin film oven and a pressure aging vessel (PAV) were utilized in the simulation of various aging conditions of WRMA to systematically evaluate the adhesion energy, peeling energy, and the pull-off tension strength (POTS) in dry conditions of a WRMA-aggregate system, based on the surface free energy (SFE) theory, combined with pull-off tests and WRMA rheological properties. The results indicate that thermal-oxygen aging increases the surface free energy and adhesion energy of WRMA in dry conditions but decreases the peeling energy in wet conditions; thermal-oxygen aging weakens the water damage resistance of WRMA. In addition, the adhesion energy ratio (ER) of acidic diabase is lower than that of alkaline limestone, indicating that it is more susceptible to the influence of moisture. The pull-off tests showed that in dry conditions, a pull-off failure occurred within WRMA, while thermal-oxygen aging increased the complex viscosity and cohesion energy of WRMA, enhancing its resistance to failure and improving adhesion to aggregates in dry conditions. A strong positive correlation was observed between the complex viscosity, cohesion energy, and POTS of WRMA. The V&C index proposed in this paper exhibits a high linear correlation with tensile strength, indicating that the V&C index can effectively predict the adhesion performance of WRMA-aggregate systems in dry conditions. This study provides a theoretical basis for optimizing the anti-aging design of WRMA pavement and evaluating the water stability of asphalt mixtures.

Keywords: thermal-oxygen aging, WRMA, surface free energy, adhesion, water damage

Asfalt modificiran s prahom iz odpadne gume (WRPMA; angl.: Waste Rubber Powder Modified Asphalt) je zanimiv zaradi tega, ker je to okolju prijazen material in se odlično obnaša med obremenitvijo cest. Vendar pa je WRPMA občutljiv na termično staranje v kisiku (TOA; angl.: thermal-oxygen aging) med dolgotrajno uporabo. Ta povzroča spremembe oprijemljivosti med asfaltom in agregati, kar povzroča poškodbe zaradi vode in druge defekte v asfaltni mešanici. V tem članku avtorji opisujejo študijo mehanizmov, ki vplivajo na adhezijo WRMA-aggregatnega sistema zaradi termičnega staranja v kisiku. V študiji so uporabili kot agregat apnenec in diabaz. V peči za tanke filme in visokotlačni posodi (PAV; angl.: pressure aging vessel) so izvajali simulacije staranja WRMA pri različnih pogojih ter sistematično ovrednotili energijo adhezije, energijo luščenja (lupljenja) in natezno trdnost (POTS; angl.: pull-off tension strength). Ovrednotenja so izvajali v suhih in mokrih pogojih WRMA-aggregatnega sistema na osnovi teorije proste površinske energije (SFE; angl.: surface free energy) v kombinaciji s POTS testi in reološkimi lastnostmi WRMA. Rezultati analiz so pokazali, da termično staranje v kisiku povečuje prosto površinsko energijo in energijo adhezije WRMA v suhih pogojih. Vendar pa zmanjšuje energijo njegovega luščenja v mokrih pogojih. Termično staranje v kisiku slabi odpornost WRMA proti vodnim poškodbam. Dodatno je razmerje energij za adhezijo v primeru uporabe kislega diabaza manjše kot je pri bazičnem agregatu iz apnenca, kar kaže na to, da je le-ta bolj občutljiv na vlago. POTS testi v suhih pogojih so pokazali, da je prišlo do odtrgavanja materiala znotraj asfaltnega sloja WRMA, in da termično-kisikovo staranje poveča kompleksno viskoznost in kohezijsko energijo WRMA. To povečuje njegovo odpornost proti odlomu (odtrgavanju) in izboljša adhezijo agregatov v suhih pogojih. Avtorji so opazili tudi močno pozitivno korelacijo med kompleksno viskoznostjo, kohezijsko energijo in natezno trdnostjo WRMA. Indeks V&C, predlagan v tem članku, kaže visoko linearno korelacijo z natezno trdnostjo. Zato ta indeks lahko učinkovito napove oprijemljivost izbranega sistema WRMA-agregat v suhih pogojih. Ta študija zagotavlja tudi teoretično osnovo za optimizacijo zasnove asfaltnih zmesi WRMA proti staranju in oceno stabilnosti asfaltnih mešanic v vodi.

Ključne besede: temično staranje v kisiku, asfalt modificiran z odpadno gumo, prosta površinska energija, adhezija, poškodbe zaradi vode

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1 INTRODUCTION

With the rapid development of the automotive industry, there is an increasing annual global generation of waste tyres.[1] In the highway engineering industry, crushing waste tires into rubber powder for use in asphalt modification not only improves the performance and durability of asphalt pavements but also effectively alleviates the pollution caused by waste tires to the human living environment and the natural environment.[2–4] Waste rubber powder swells and blends in the base asphalt, enhancing the performance of the base asphalt and improving the elasticity, high-temperature stability, low-temperature performance, and fatigue resistance of traditional asphalt mixtures.[5–10] However, WRMA inevitably undergoes thermal-oxygen aging during long-term service, resulting in significant changes to its chemical composition and physical properties, which in turn affect the adhesion characteristics between asphalt and aggregates. The deterioration of adhesion performance is a key factor causing water damage in asphalt mixtures. Therefore, it is of great significance to thoroughly investigate the mechanism of thermal-oxygen aging on the adhesion properties of a WRMA-aggregate system for improving the long-term performance of waste rubber powder modified asphalt pavements.[11,12]

In recent years, surface free energy (SFE) theory has been widely applied in evaluating asphalt-aggregate adhesion performance due to its ability to quantify asphalt-aggregate interface interactions from a thermodynamic perspective, thereby predicting the water damage resistance of asphalt mixtures.[13–18] Researchers used the SFE theory to establish the relationship between the adhesion properties of the asphalt-aggregate system and the macro-scale test results of asphalt mixtures, such as the freeze-thaw splitting strength ratio. They verified the reliability of the SFE method in characterizing the moisture sensitivity of asphalt mixtures.[19–22] However, existing studies have primarily focused on base asphalt or SBS-modified asphalt. There is a lack of systematic research on the evolution patterns of SFE components during thermal-oxygen aging in WRMA, as well as on the adhesion mechanisms for different aggregates. Yang et al.[23,24] believe that the surface free energy and rheological properties of asphalt have a certain impact on the adhesion between asphalt and aggregate. On the one hand, the decrease in surface free energy of asphalt means an increase in interfacial tension between asphalt and aggregate, which may weaken the adhesion between asphalt and aggregate. On the other hand, by optimizing the rheological properties of asphalt (such as viscosity and elasticity), the adhesion between asphalt and aggregate can be improved. Rheological properties can be indicative of the cohesion force of asphalt, as well as the molecular interaction ability of the asphalt-aggregate system. The alteration in the viscosity-elasticity ratio of asphalt can also effectively elucidate the adhesion trend between asphalt and aggregate. The pull-off test is the most commonly used method for evaluating adhesion strength mechanically, and researchers widely recognize its results as reliable. Some researchers have investigated the effect of aging on the adhesion strength of an asphalt-aggregate system using pull-out tests, yielding differing conclusions: Guo et al.[25] demonstrated that as the degree of asphalt aging increases, the POTS of the asphalt-aggregate system decreases, while Xu et al.[26] observed the opposite phenomenon, indicating that the POTS of the asphalt-aggregate system increases. These contradictory conclusions indicate that the mechanism, with which aging affects the asphalt-aggregate adhesion requires further investigation.

This study systematically investigated the influence of thermal-oxygen aging on the interfacial adhesion characteristics of waste rubber powder modified asphalt-aggregate systems. Case studies included waste rubber modified asphalt (WRMA), limestone aggregates, and diabase aggregates. The study obtained WRMAs with different thermal-oxygen aging degrees using a thin film oven test (TFOT) and pressure aging vessel (PAV). The SFE parameters of asphalt and aggregates were determined using the sessile drop method, and parameters such as the adhesion energy in dry conditions and the peeling energy in wet conditions of the asphalt-aggregate system were calculated. Combined with pull-off tests and a rheological performance analysis of WRMA, the adhesion failure mechanism between WRMA and aggregates during aging was revealed.

2 RAW MATERIALS AND EXPERIMENTAL DESIGN

2.1 Raw materials

2.1.1 Waste rubber powder modified asphalt

Ordinary waste rubber powder modified asphalt (O-WRMA) is obtained by adding 22 % of waste rubber powder (30–80 mesh) to the base asphalt. The preparation steps for ordinary waste rubber powder modified asphalt are as follows:

- Heat the base asphalt to 180 °C, and add waste rubber powder; stir them for 20 min at a stirring rate of 300 min^{-1};
- A high-speed shearing machine cuts the mixture of base asphalt and waste rubber powder for 20 min at a shear rate of 5000 min^{-1};
- After shearing, the mixture is stirred at 180 °C for another 60 min to obtain ordinary waste rubber powder modified asphalt.

According to Chinese technical specification (JTG E20-2011), the fundamental properties of O-WRMA are shown in **Table 1**.

WRMAs with different degrees of aging were obtained through different aging methods. For the thin film oven test (TFOT), the prepared O-WRMA was placed in a thin film oven at 163 °C for 5 h to obtain short-term aged waste rubber powder modified asphalt. This asphalt

Table 1: Performance of O-WRMA

Properties	Unit	Test value	Test method
Penetration (25 °C)	0.1 mm	42	T0604-2011
Softening point	°C	67.5	T0606-2011
Ductility (5 °C, 1 cm/min)	cm	9.0	T0605-2011
Elastic recovery (25 °C, 5 cm/min)	%	87	T0662-2000

was then placed in a PAV, with the temperature set to 100 °C and the pressure set to 2.1 MPa. It was aged for 20 h and 40 h to obtain long-term aged waste rubber powder modified asphalt. The aging methods for WRMA are shown in **Table 2**.

Table 2: Types of aged waste rubber powder modified asphalt and the aging methods

Asphalt type	Aging equipment and parameters
Short-term aged waste rubber powder modified asphalt (TFOT-WRMA)	Thin film oven, 163 °C, 5 h
PAV-20h long-term aged waste rubber powder modified asphalt (PAV-20hWRMA)	PAV, 100 °C, 2.1 MPa, 20 h
PAV-40h long-term aged waste rubber powder modified asphalt (PAV-40hWRMA)	PAV, 100 °C, 2.1 MPa, 40 h

2.1.2 Aggregates

In this study, limestone aggregate and diabase aggregate were used, and their basic properties, including density and water absorption, were tested, as shown in **Table 3**. The chemical compositions of limestone and diabase are shown in **Table 4**.

Table 3: Basic properties of limestone and diabase

Aggregate type	Density (g/cm^3)	Water absorption rate (%)
Limestone	2.702	0.22
Diabase	2.797	0.78

The high content of calcium oxide (CaO) and low content of silicate (SiO_2) in limestone aggregates indicate that limestone is an alkaline aggregate. Diabase is a basic rock with a SiO_2 content of 48 %, and belongs to acidic aggregates.

2.1.3 Liquid for contact angle testing

The sessile drop method is based on measuring the contact angle between a liquid with known surface free energy parameters and asphalt/aggregate and then calculating the surface free energy parameters of the asphalt/aggregate. The number of liquids selected for testing is generally three or more, and they do not react with asphalt/aggregate. In this experiment, the liquids were distilled water, glycerol, and formamide. **Table 5** shows the surface free energy parameters of the three liquids at a temperature of 25 °C.

Table 5: Surface free energy of liquids at 25 °C and its components (contact angle test)

Liquid type	Surface free energy γ (mJ/m^2)	Dispersion component γ^d (mJ/m^2)	Polar component γ^p (mJ/m^2)
Distilled water	72.3	18.7	53.6
Glycerol	65.2	28.3	36.9
Formamide	59	39.4	19.6

2.2 Test methods and design

2.2.1 Testing of free surface energy parameters of asphalt and aggregates

The sessile drop method is an optical measurement technique used to determine the contact angle and evaluate the wettability of solid surfaces. **Figure 1** shows a schematic diagram of liquid wetting and contact angles on solids.

Surface free energy is defined as the energy required to separate a liquid or solid under vacuum. Owkes and van Oss[27–29] developed a method for indirectly measuring the surface free energy of asphalt/aggregate through contact angles. The surface free energy of liquids (γ_l) and the surface free energy of solids (γ_s) include polar and dispersion components, as shown in Equations (1) and (2).

$$\gamma_l = \gamma_l^d + \gamma_l^p \quad (1)$$

$$\gamma_s = \gamma_s^d + \gamma_s^p \quad (2)$$

Where γ_l^d and γ_l^p represent the dispersion component and polar component of the surface free energy of the liquid, respectively; γ_s^d and γ_s^p represent the dispersion and polar components of the surface free energy of the solid, respectively.

Fowkes[27] pointed out that the dispersion forces between the liquid-solid interface could be characterized by the geometric mean of the dispersion components of

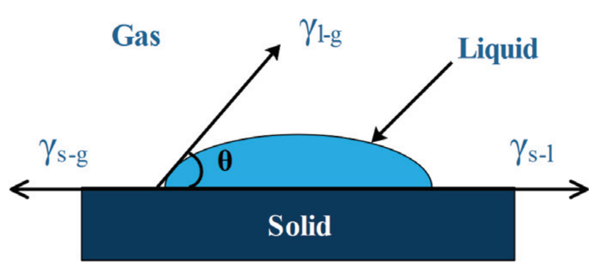

Figure 1: Schematic diagram of liquid wetting on solids

Table 4: Chemical compositions of limestone and diabase

Aggregate	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	K_2O	Na_2O	Ti_2O
Limestone	12.34	1.14	2.45	79.39	1.56	0.67	1.56	0.89
Diabase	48.16	2.68	17.24	18.67	7.57	1.9	3.2	0.58

the liquid and solid. 0wens[30] extended this method to make it applicable to polar components. Consequently, the liquid-solid interface free energy (γ_{s-l}) can be expressed by Equation (3).

$$\gamma_{s-l} = \gamma_s + \gamma_l - 2\sqrt{\gamma_s^d \gamma_l^d} - 2\sqrt{\gamma_s^p \gamma_l^p} \tag{3}$$

The Young equation[31] describes the relationship between the contact angle of the liquid on solid and the surface free energy, as shown in Equation (4).

$$\gamma_l \cos\theta = \gamma_s - \gamma_{s-l} \tag{4}$$

Fowkes[28] and Owens[31] derived expressions for calculating surface free energy using dispersion components, polarity components, and contact angles based on Equations (3) and (4), as shown in Equation (5).

$$1+\cos\theta = 2\sqrt{\gamma_s^d}\left(\frac{\sqrt{\gamma_l^d}}{\gamma_l}\right) + 2\sqrt{\gamma_s^p}\left(\frac{\sqrt{\gamma_l^p}}{\gamma_l}\right) \tag{5}$$

Based on Equation (5), the surface free energy of a solid can be calculated using the contact angle, as shown in Equation (6).

$$\frac{1+\cos\theta}{2}\frac{\gamma_l}{\sqrt{\gamma_l^d}} = \sqrt{\gamma_s^p} \times \sqrt{\frac{\gamma_l^p}{\gamma_l^d}} + \sqrt{\gamma_s^d} \tag{6}$$

Linear fitting is performed with Equation (6), which can be expressed as $y = mx + b$, $\sqrt{\gamma_l^p / \gamma_l^d}$ as the independent variable, and $\gamma_l(1+\cos\theta)/2\sqrt{\gamma_l^d}$ as the dependent variable. The square of the slope of the linear equation is the polar component of the asphalt/aggregate, and the square of the intercept is the dispersion component of the asphalt/aggregate.

2.2.2 Preparation of asphalt/aggregate samples

2.2.2.1 Preparation of asphalt samples

The contact angle between the liquid and the WRMA was measured using the sessile drop method. During the experiment, the WRMA was heated to the molten state. Then, a glass slide was inserted vertically into the liquid asphalt and placed in a baking oven at 180 °C for three minutes to form a smooth surface. Once the specimen had cooled to room temperature, the contact angles between the WRMA and distilled water, glycerol, and formamide were measured using a contact angle measuring instrument (HARKE-SPCA) manufactured by Beijing Hake Testing Instrument Factory.

2.2.2.2 Preparation of aggregate samples

A polishing machine was used to polish limestone or diabase circular rock samples, achieving a smooth surface. Then, the sessile drop method was used to measure the contact angle between distilled water, glycerol, formamide, and limestone/diabase aggregates.

2.2.3 Evaluation indicators for asphalt-aggregate adhesion

There are two types of adhesion failure in asphalt mixtures: 1) failure of the asphalt material itself and 2) failure of the interface between the asphalt and the aggregate. The former is referred to as cohesion failure, while the latter is referred to as bond failure.

2.2.3.1 Cohesion energy

Cohesion energy is defined as the energy required to create two new surfaces within a homogeneous material. Its value is equal to twice the material's surface free energy. The cohesion energy values of asphalt ($C_{\text{l-cohesion}}$) and aggregate ($C_{\text{s-cohesion}}$) are given by Equations (7) and (8), respectively.

$$C_{l-\text{cohesion}} = 2\gamma_l \tag{7}$$

$$C_{s-\text{cohesion}} = 2\gamma_s \tag{8}$$

2.2.3.2 Adhesion energy and peeling energy

Failure of the interface between asphalt and aggregate can occur in both dry and wet conditions. In dry conditions, the adhesion energy between asphalt and aggregate (W_{dry}) can be calculated using Equation (9). In wet conditions, water damage occurs at the asphalt-aggregate interface. According to the surface free energy theory, this process can be regarded as the separation of asphalt and aggregate, forming new asphalt-water and water-aggregate interfaces. Equation (10) can be used to calculate the peeling energy (W_{wet}) between asphalt and aggregate:

$$W_{\text{dry}} = 2\sqrt{\gamma_s^d \gamma_l^d} + 2\sqrt{\gamma_s^p \gamma_l^p} \tag{9}$$

$$W_{\text{wet}} = 2\Big(\gamma_w + \sqrt{\gamma_s^d \gamma_l^d} + \sqrt{\gamma_s^p \gamma_l^p} - \\ -\sqrt{\gamma_s^d \gamma_w^d} - \sqrt{\gamma_s^p \gamma_w^p} - \sqrt{\gamma_l^d \gamma_w^d} - \sqrt{\gamma_l^p \gamma_w^p}\Big) \tag{10}$$

where W_{dry} represents the adhesion performance of aggregate and asphalt in dry conditions, while W_{wet} characterizes their ability to resist stripping in wet conditions. The larger the W_{dry} value, the stronger the adhesion performance of the asphalt mixture in dry conditions, and the larger the W_{wet} value, the stronger its water damage resistance in wet conditions. **Figure 2** shows a schematic diagram of adhesion failure in the asphalt-and-aggregate system in wet conditions.

2.2.3.3 Adhesion energy ratio

$$ER = \frac{W_{\text{wet}}}{W_{\text{dry}}} \tag{11}$$

Here, ER is the adhesion energy ratio used to evaluate the moisture sensitivity of the asphalt-aggregate system. The higher the ER, the lower the moisture sensitivity of the mixture and the stronger its resistance to water damage.

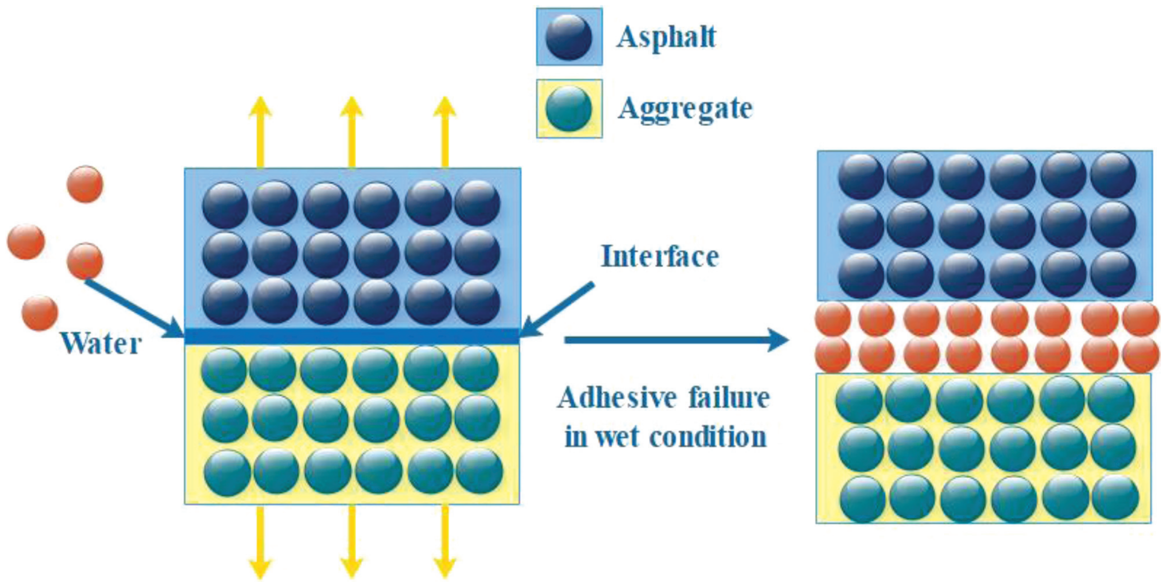

Figure 2: Schematic diagram of adhesion failure of the asphalt-aggregate system in wet conditions

2.2.4 The binder bond strength (BBS) test

The BBS test is the standard test specified by AASHTO for evaluating the bond performance of an asphalt-aggregate interface. The loading rate tested in this study is 0.7 MPa/s. The preparation of the pull-off test specimens is as follows: First, the WRMA is heated to 185 °C; approximately 2 g of WRMA is dropped onto the aggregate substrate, and covered with the stub. Then, pressure is applied to the stub by placing a 2.25 kg weight on it. A specimen is cured in a 25 °C environment for two hours to allow for the formation of the asphalt-aggregate bond strength. Finally, the specimen is cured for a further 24 h at 25 °C; then a Posit Test AT-T pull-off tester is used to perform a vertical pull-off test on the stub adhering to the aggregate substrate and the pull-off tensile strength (POTS) is measured. The BBS test process is shown in **Figure 3**.

2.2.5 Viscosity testing of WRMA

A DHR-2 Dynamic Shear Rheometer (DSR), manufactured by the American company TA Instruments, was used to measure the complex viscosity of WRMA at room temperature, with the test mode set to temperature scanning.

Basic parameters of the temperature scanning mode:

Parallel plate dimensions: diameter of 25 mm;

Strain: 1 %;

Frequency: 10 rad/s;

Temperature: 16–34 °C, with a temperature interval of 6 °C.

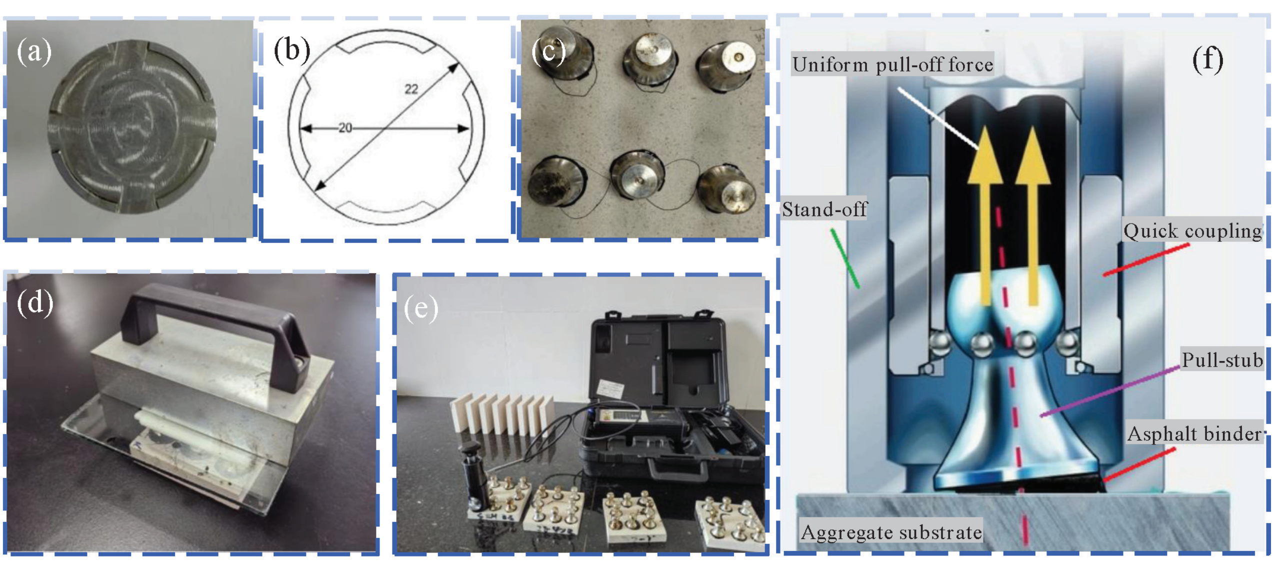

Figure 3: BBS test process: a) the stub surface, b) schematic view of the stub surface, c) the stub bonded to the aggregate substrate, d) applying a certain pressure to the stub, e) pull-off test, f) BBS test schematic diagram

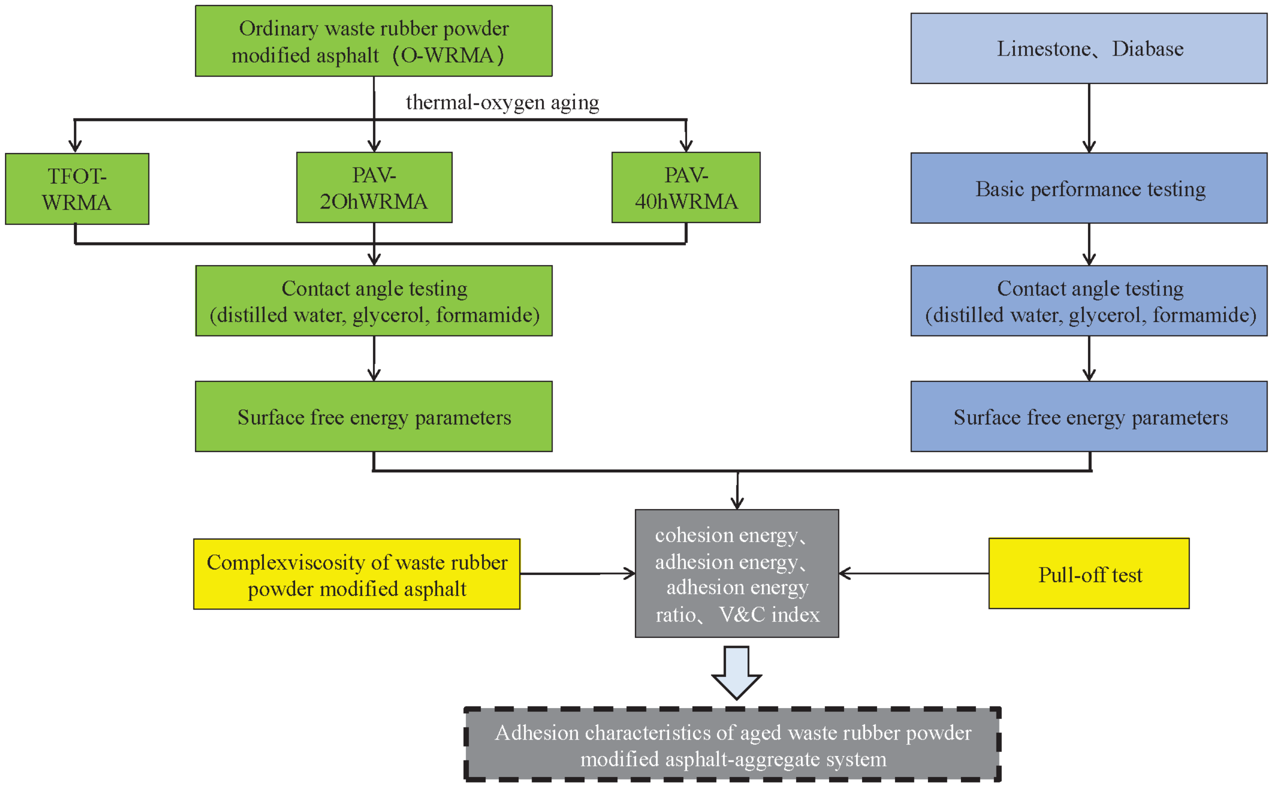

Figure 4: Workflow diagram

3 RESULTS AND DISCUSSION

3.1 Analysis of the surface free energy parameters of WRMA

The contact angles of distilled water, glycerol, formamide, and WRMA were measured using the sessile drop method. The results are shown in **Table 6**. The surface free energy parameters of WRMA were also calculated. As shown in **Table 6**, the contact angles between WRMA and distilled water are all greater than 90°. In contrast, the contact angles between glycerol, formamide, and WRMA are less than 90°, indicating that the surface of WRMA is more easily wetted by glycerol and formamide and thus it has higher hydrophobicity. Thermal-oxygen aging has little effect on the contact angle between WRMA and distilled water, indicating that it has a low impact on the hydrophobic properties of WRMA.

Table 6: Contact angles between WRMA and liquids and coefficients of variation

Asphalt type	Distilled water		Glycerol		Formamide	
	Θ (°)	CV (%)	*θ* (°)	CV (%)	Θ (°)	CV (%)
O-WRMA	96.0	1.42	89.2	1.56	83.7	2.86
TFOT-WRMAA	95.9	1.37	84.9	2.31	80.6	2.14
PAV-20hWRMA	97.6	1.31	87.9	2.45	79.9	2.89
PAV-40hWRMA	91.0	1.56	84.2	2.54	76.9	2.71

Figure 5 shows the surface free energy parameters of WRMA, calculated using Equation (6).

As shown in **Figure 5**, the surface free energy of WRMA increases gradually with aging, which is conducive to improving the adhesion of asphalt. Compared with O-WRMA, thermal-oxygen aged WRMA exhibits larger dispersion and polar components, with the dispersion component being significantly higher than the polar component, indicating that the dispersion component dominates. The increase in dispersion components is at-

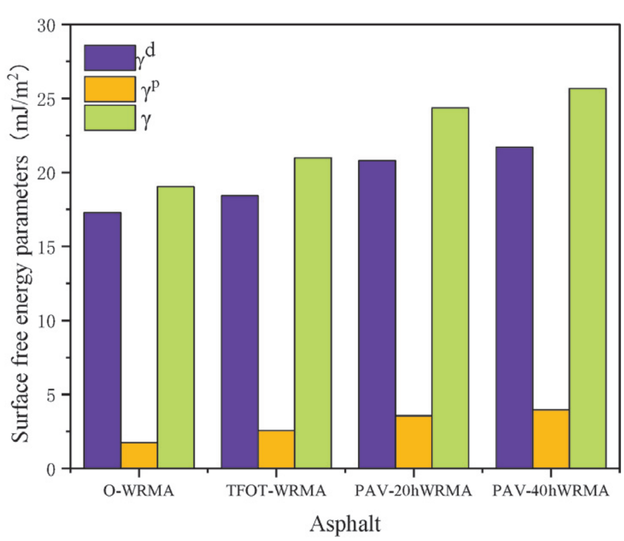

Figure 5: Surface free energy parameters of WRMA

tributed to the thermal-oxygen aging, resulting in a certain degree of desulfurization and degradation of the waste rubber powder, a reduction in the particle size of the waste rubber powder and the formation of a sol-gel layer on its surface, thereby improving its compatibility with the base asphalt. The polar components account for a relatively small proportion of the surface free energy. As the degree of aging increases, the polar components in WRMA tend to rise due to desulfurization and degradation that promote the activation of waste rubber powder, causing it to swell in the base asphalt and absorb more light components, such as saturated and aromatic fractions. The reduction in saturated and aromatic components leads to a relative increase in the content of polar substances, such as asphaltenes in the base asphalt. Therefore, thermal-oxygen aging increases the polar components in WRMA.

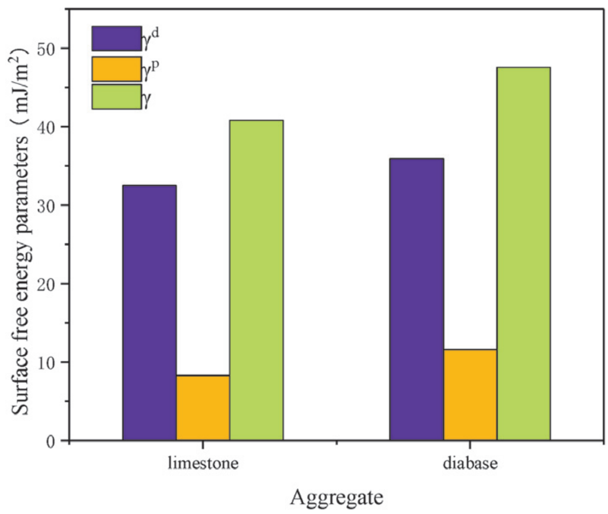

Figure 6: Surface free energy parameters of limestone and diabase

3.2 Analysis of the surface free energy parameters of aggregate

The contact angle between distilled water, glycerol, formamide, and aggregate was tested using the sessile drop method, and the results are shown in **Table 7**. As shown in this table, the contact angles between limestone/diabase and distilled water, glycerol, and formamide are all less than 90°. Compared with WRMA, the contact angles between aggregates and distilled water, glycerol, and formamide are significantly reduced, indicating that liquids more easily wet the aggregate surface. Compared to limestone, diabase has a smaller contact angle with water, indicating that water is more easily absorbed by acidic diabase, which can easily cause water damage to the diabase-asphalt system.

Table 7: Contact angles between aggregates and liquids and coefficients of variation

Aggregate type	Distilled water		Glycerol		Formamide	
	Θ (°)	CV (%)	θ (°)	CV (%)	Θ (°)	CV (%)
Limestone	82.1	1.34	76.4	2.34	53.6	2.03
Diabase	60.2	1.67	49.0	2.56	30.1	2.26

Figure 6 shows the surface free energy parameters of limestone/diabase, calculated using Equation (6).

As shown in **Table 7**, the surface free energy, dispersion component, and polarity component of diabase are all greater than those of limestone, with the dispersion component contributing significantly to the surface free energy. The differences in surface free energy parameters between different types of aggregates are mainly related to their mineral composition. Compared with WRMA, the surface free energy values of the aggregates are higher. Rocks are composed of minerals, which are substances with high surface free energy, while asphalt is composed of non-polar hydrocarbons, resulting in differences in surface free energy parameters between aggregates and asphalt.

3.3 Analysis of cohesion energy of WRMA and aggregates

The cohesion energy is twice the surface free energy of a material. The cohesion energy values of WRMA and aggregates are shown in **Table 8**.

Table 8: Cohesion energy of WRMA and aggregates

Material type	Cohesion energy (mJ/m^2)
O-WRMA	38.08
TFOT-WRMA	41.96
PAV-20hWRMA	48.72
PAV-40hWRMA	51.34
Limestone	81.66
Diabase	95.10

The greater the cohesion energy of a material, the greater the energy required to separate it. An increase in the cohesion energy of asphalt and aggregates enhances their resistance to internal damage, thereby improving the water stability of asphalt mixtures. As thermal-oxygen aging progresses, the cohesion energy of WRMA exhibits an upward trend, indicating that thermal-oxygen aging enhances the resistance of WRMA to internal damage.

3.4 Analysis of adhesion parameters of WRMA-aggregate system

The adhesion energy and peeling energy of an asphalt-aggregate system are closely related to the surface free energy parameters of asphalt and aggregate. The adhesion energy and peeling energy of the asphalt-aggregate system can be calculated using Equations (9) and (10), respectively. The calculation results are shown in **Table 9**.

According to **Table 9**, an increase in the surface free energy of WRMA leads to an increase in the adhesion energy between the asphalt and limestone/diabase, indi-

Table 9: Adhesion energy and peeling energy of *WRMA*-aggregate system

Aggregate type	Asphalt type	Surface free energy of asphalt (mJ/m^2)	Adhesion energy (mJ/m^2)	Peeling energy (mJ/m^2)
Limestone	O-WRMA	19.04	55.04	52.83
	TFOT-WRMA	20.98	58.18	50.75
	PAV-20hWRMA	24.36	62.90	48.91
	PAV-40hWRMA	25.67	64.61	48.28
Diabase	O-WRMA	19.04	58.86	46.61
	TFOT-WRMA	20.98	62.36	44.70
	PAV-20hWRMA	24.36	67.54	43.32
	PAV-40hWRMA	25.67	69.42	42.86

cating that thermal-oxygen aging enhances the adhesion between WRMA and aggregates in dry conditions. In road environments, asphalt mixtures are always affected by moisture. In wet conditions, water molecules can easily penetrate an asphalt-aggregate system. Under the combined effects of vehicle loads and dynamic water pressure, the asphalt-aggregate interface gradually transforms into separate aggregate-water and water-asphalt interfaces. Ultimately, this leads to water damage. In wet environments, as the aging degree of WRMA increases, the peeling energy between asphalt and aggregate becomes smaller, and water molecules are more likely to invade the WRMA-aggregate system, indicating that thermal-oxygen aging can weaken the adhesion between WRMA and aggregate in wet conditions. Compared to limestone, the peeling energy of WRMA and diabase is lower, and the WRMA-diabase system is more susceptible to water damage.

Figure 7 shows the adhesion energy ratio of the WRMA-aggregate system. As the degree of thermal-oxygen aging increases, the adhesion energy ratio of the WRMA-aggregate system gradually decreases, indicating that the water damage resistance of the WRMA-aggregate system decreases. Thermal-oxygen aging reduces the water stability of the waste rubber powder modified asphalt mixture. The adhesion energy ratio of the WRMA-diabase system is lower than that of limestone, meaning that the diabase mixture is more moisture sensitive.

3.5 Analysis of complex viscosity of WRMA

The complex viscosity is a comprehensive reflection of the dynamic balance between the elasticity and viscosity of WRMA, characterizing its deformation resistance and fluidity. **Figure 8** illustrates the complex viscosity of WRMA at temperatures ranging from 16 °C to 34 °C.

As shown in **Figure 8**, the complex viscosity of WRMA gradually increases with the aggravation of thermal-oxygen aging. On the one hand, thermal-oxygen aging causes waste rubber powder to form a sol-gel layer, enhancing its compatibility with the base asphalt. On the other hand, during the aging process, light oil components such as aromatic and saturated fractions in the base asphalt continuously decrease, leading to an increase in the viscosity of the entire WRMA system and a corresponding decrease in its flow properties. Roads usually serve at room temperature. This investigation analyzes the relationship between the complex viscosity and surface free energy of WRMA at room temperature and studies the influence of rheological parameters on sur-

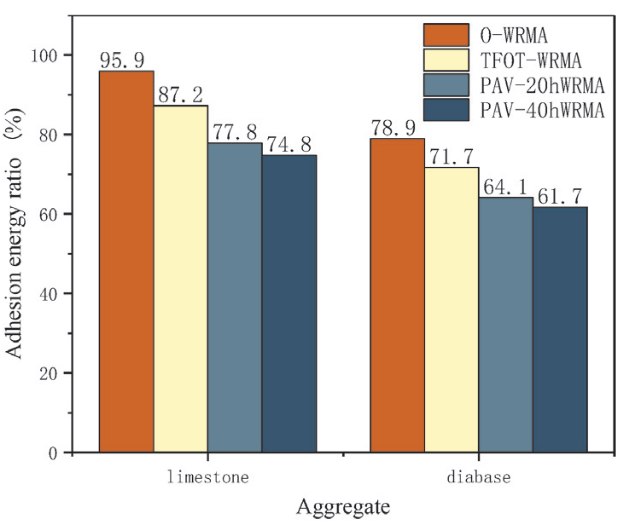

Figure 7: Adhesion energy ratio of WRMA-aggregate system

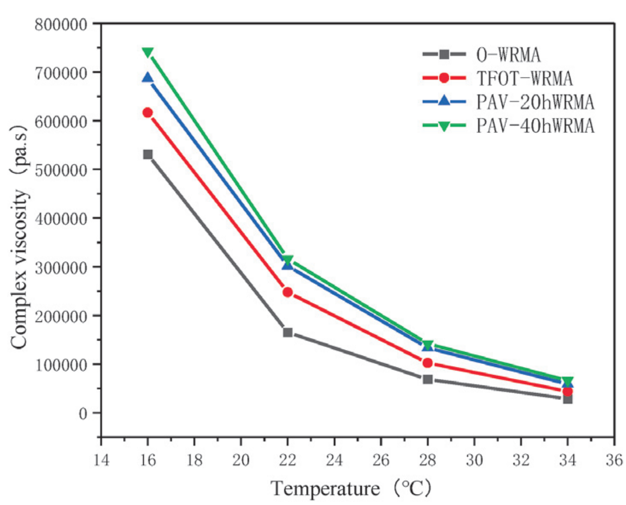

Figure 8: Complex viscosity of WRMA

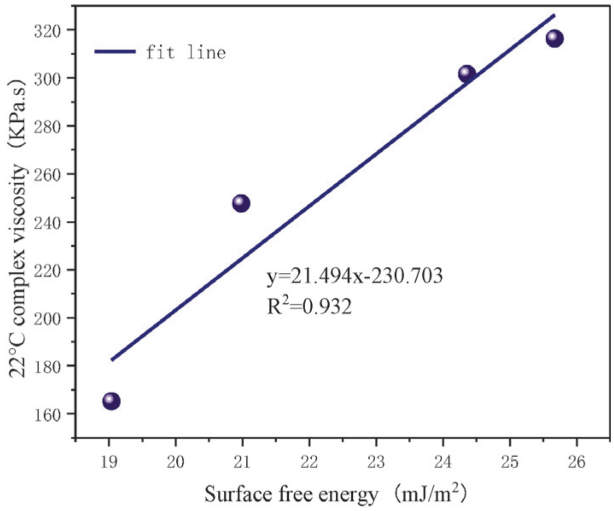

Figure 9: Fitting of 22 °C complex viscosity and surface free energy of WRMA

face free energy. The complex viscosity of WRMA at 22 °C was selected, and a linear regression analysis was performed between the complex viscosity at 22 °C and the surface free energy. **Figure 9** shows a high linear correlation between the complex viscosity at 22 °C and the surface free energy, with an R^2 value of 0.932.

3.6 Analysis of POTS and adhesion of WRMA-aggregate system

The POTS in the pull-off test can reflect the adhesion strength of the WRMA-aggregate system. The room temperature POTS values of WRMA with limestone and diabase are shown in **Figure 10**.

As shown in **Figure 10**, the POTS values of WRMA and aggregate gradually increase as the degree of thermal-oxygen aging increases. The difference in the POTS between WRMA-limestone and WRMA-diabase is relatively small. In the pull-off test, it was found that all tensile failures occurred within the WRMA, as illustrated in **Figure 11**, indicating that the bond strength between the WRMA and aggregate is greater than that of the WRMA itself. Based on this, it can be concluded that the POTS is primarily related to the cohesion energy and viscosity of WRMA and is less influenced by the adhesion energy and peeling energy of the WRMA-aggregate system. As the degree of thermal-oxygen aging increases, the complex viscosity of WRMA gradually increases, and the energy required to disrupt its internal structure also increases. Therefore, the POTS of the WRMA-aggregate system gradually increases. As the types of asphalt are the same and the POTS is less affected by adhesion at the asphalt-aggregate interface in dry conditions, the POTS for the WRMA-limestone system is essentially the same as for the WRMA-diabase system.

In dry conditions, due to the absence of moisture erosion, the interface of pull-out failure is cohesive failure, and there is basically no adhesive failure area. This indicates that pull-out failure occurs inside the waste rubber powder modified asphalt in dry conditions, and the pull-out strength is less affected by the type of aggregate and more affected by the properties of asphalt. To analyze the relationship between the adhesion of WRMA-aggregate system and asphalt properties in dry conditions, a linear correlation analysis was conducted on the POTS, complex viscosity, and surface free energy parameters of WRMA. **Table 10** shows the POTS, 22 °C complex viscosity, and cohesion energy of WRMA.

According to **Table 10**, in dry conditions, the pull-out strength of WRMA is greatly affected by viscosity and cohesive work. The pull-out failure interface only exhibits cohesive failure, and there is no adhesive failure area. To analyze the relationship between the POTS of WRMA and its complex viscosity and cohesion energy, a new parameter was developed: the V&C index, composed of the complex viscosity and cohesion energy of WRMA. The V&C index includes dimensionless parameters derived from viscosity and cohesion energy. The

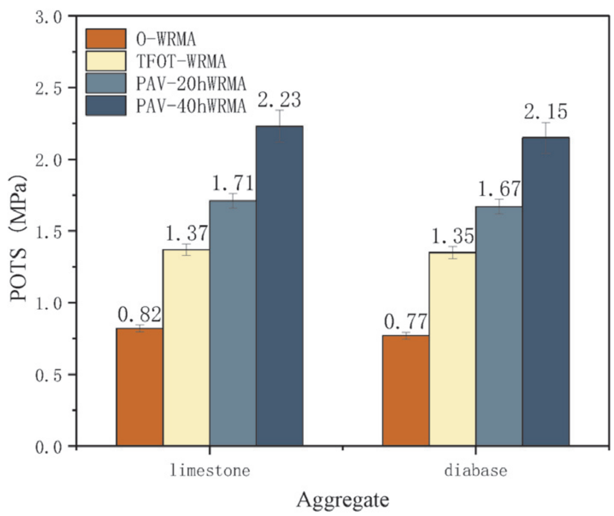

Figure 10: POTS of WRMA-aggregate system

Figure 11: Failure morphology of the pull-off interface in the BBS test

Table 10: POTS, 22 °C complex viscosity, and cohesion energy of WRMA

Aggregate type	Asphalt type	POTS (MPa)	22 °C Complex viscosity (pa.s)	Cohesion energy (mJ/m^2)
Limestone	O-WRMA	0.82	165203	38.08
	TFOT-WRMA	1.37	247652	41.96
	PAV-20hWRMA	1.71	301567	48.72
	PAV-40hWRMA	2.23	316371	51.34
Diabase	O-WRMA	0.77	165203	38.08
	TFOT-WRMA	1.35	247652	41.96
	PAV-20hWRMA	1.67	301567	48.72
	PAV-40hWRMA	2.15	316371	51.34

dimensionless treatment (averaging treatment) of the complex viscosity and cohesion energy of WRMA, as well as the calculation steps for the V&C index, are as follows:

(1) Listing the true values of the complex viscosity or cohesion energy of WRMA.

$$X_i = \{X_i(k) | k = 1,2,3,4\} \quad (i = \text{viscosity, cohesion}) \qquad (12)$$

(2) By calculating the mean of the sequence of the numbers presented above, denoted by X_i, and assuming that the mean value is $\bar{x}_i$, it is possible to obtain the dimensionless values of complex viscosity and cohesion work.

$$Y_i(k) = \{X_i(k) / \bar{X}_i | k = 1,2,3,4\} \qquad (13)$$

(3) Calculation of the V&C index.

$$V\&C = Y_{viscosity}(k) + Y_{cohesion}(k), \; k = 1,2,3,4 \qquad (14)$$

Numerals 1, 2, 3 and 4 are used to denote O-WRMA, TFOT-WRMA, PAV-20hWRMA and PAV-40hWRMA, respectively.

The V&C index of WRMA is obtained using Equation (15). The V&C index of WRMA and its tensile strength are shown in **Table 11**.

The V&C index and POST of WRMA were fitted. **Figure 12** shows that the V&C index and POST of WRMA exhibit a high linear correlation. When the aggregate is limestone, the R^2 of the linear regression equation is 0.936. When the aggregate is diabase, the R^2 of the linear regression equation increases to 0.946, indicating that the V&C index can effectively predict the POST of WRMA in dry conditions. The larger the V&C index, the greater the adhesion energy between WRMA and aggregate, which means that the adhesion between WRMA and aggregate is stronger.

Table 11: V&C index and POST of WRMA

Aggregate type	Asphalt type	V&C index	POST (MPa)
Limestone	O-WRMA	1.49	0.82
	TFOT-WRMA	1.89	1.37
	PAV-20hWRMA	2.26	1.71
	PAV-40hWRMA	2.37	2.23
Diabase	O-WRMA	1.49	0.77
	TFOT-WRMA	1.89	1.35
	PAV-20hWRMA	2.26	1.67
	PAV-40hWRMA	2.37	2.15

4 CONCLUSIONS

Based on the surface free energy theory, combined with pull-out tests and an asphalt rheological analysis, this study systematically investigates the effect of thermal-oxygen aging on the adhesion properties of WRMA-aggregate systems. The main conclusions are as follows:

Thermal-oxygen aging increases the surface free energy of WRMA, with the dispersion component dominating. During thermal-oxygen aging, waste rubber pow-

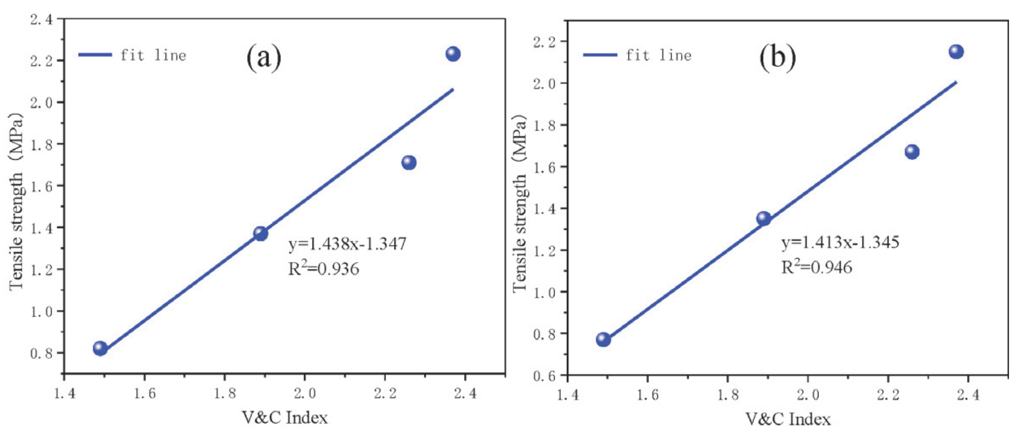

Figure 12: Fitting between the V&C index and the POST of WRMA: a) limestone, b) diabase

der undergoes desulfurization and degradation, and the light components of the base asphalt decrease, leading to an increase in both the dispersion component and the polar component of the asphalt. After 40 h of PAV aging, the surface free energy of O-WRMA increased from 19.04 mJ/m^2 to 25.67 mJ/m^2, thereby enhancing its resistance to external damage.

As the degree of thermal-oxygen aging increases, the adhesion energy of the WRMA-aggregate system gradually increases in dry conditions, but the peeling energy decreases in wet conditions.

Thermal-oxygen aging is beneficial for the adhesion between WRMA and aggregate in dry conditions, increasing the POTS of the WRMA-aggregate system. In wet conditions, as the degree of aging of WRMA increases, water molecules become more easily absorbed into the WRMA-aggregate system, and aging weakens the water damage resistance of the WRMA-aggregate system.

Compared to alkaline limestone, the WRMA-diabase system exhibits lower peeling energy and adhesion energy ratio (ER), confirming that acidic aggregates are more susceptible to water erosion. The WRMA-diabase system is relatively sensitive to water and has relatively low resistance to water damage.

In dry conditions, tensile failure occurs exclusively due to the failure of asphalt cohesion. The V&C index, which is based on the complex viscosity and cohesion energy of WRMA, demonstrates a high linear correlation with the POTS. The V&C index was shown to effectively predict the POTS of WRMA in dry conditions, thereby reflecting the adhesion between the WRMA and the aggregate.

Acknowledgments

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5 REFERENCES

[1] X. Jin, D. Ren, H. Wu, H. Kong, Q. Yang, T. Zhou, Z. Zhao, J. Li, Enhancing compatibility of waste tire rubber powder in asphalt: A comparative study of acid surface activation and molecular dynamics insights, Construction and Building Materials, 478 (**2025**), 141417, doi:10.1016/j.conbuildmat.2025.141417

[2] D. Li, Z. Leng, S. Zhang, J. Jiang, H. Yu, F. Wellner, S. Leischner, Blending efficiency of reclaimed asphalt rubber pavement mixture and its correlation with cracking resistance, Resources Conservation and Recycling, 185 (**2022**), 106506, doi:10.1016/j.resconrec.2022.106506

[3] H. Li, Y. Hu, X. Shi, M. Zhang, G. Zhao, X. Zou, Y. Sheng, Influence of Rubber Powder Movement on Properties of Asphalt Rubber from the Mesoscopic View, Journal of Wuhan University of Technology-Materials Science Edition, 38 (**2023**), 312–324, doi:10.1007/s11595-023-2700-x

[4] Y. Zhou, G. Xu, H. Wang, X. Chen, Y. Fan, J. Yang, Z. Leng, W. Huang, Investigation of the rheological properties of devulcanized rubber-modified asphalt with different rubber devulcanization degrees and rubber contents, Road Materials and Pavement Design, 25 (**2024**), 1950–1963, doi:10.1080/14680629.2023.2287714

[5] F. Dong, X. Yu, S. Liu, J. Wei, Rheological behaviors and microstructure of SBS/CR composite modified hard asphalt, Construction and Building Materials, 115 (**2016**), 285–293, doi:10.1016/j.conbuildmat.2016.04.057

[6] K. Duan, C. Wang, J. Liu, L. Song, Q. Chen, Y. Chen, Research progress and performance evaluation of crumb-rubber-modified asphalts and their mixtures, Construction and Building Materials, 361 (**2022**), 129687, doi:10.1016/j.conbuildmat.2022.129687

[7] H.-S. Kim, S.-J. Lee, S. Amirkhanian, Rheology investigation of crumb rubber modified asphalt binders, KSCE Journal of Civil Engineering, 14 (**2010**), 839–843, doi:10.1007/s12205-010-1020-9

[8] P. Lin, W. Huang, N. Tang, F. Xiao, Performance characteristics of Terminal Blend rubberized asphalt with SBS and polyphosphoric acid, Construction and Building Materials, 141 (**2017**), 171–182, doi:10.1016/j.conbuildmat.2017.02.138

[9] N. Tang, C. Xue, G. Hao, W. Huang, S. Liu, H. Zhu, Evaluation of Physicochemical and Rheological Properties of Terminal Blend Rubberized Asphalt Incorporating Polymer, Journal of Materials in Civil Engineering, 36 (**2024**), 18125, doi:10.1061/jmcee7.Mteng-18125

[10] Y. Zhang, P. Xiao, P. Qian, X. Deng, A. Kang, Z. Wang, Y. Li, Probe the properties of SBS/CR composite modified asphalt with CR directional distribution, Construction and Building Materials, 411 (**2024**), 134475, doi:10.1016/j.conbuildmat.2023.134475

[11] Z. Chen, X. Wang, G. Huang, D. Yi, S. Zhou, J. Pei, S. Zhang, Effect of aging on asphalt-aggregate adhesion properties and its correlation with interfacial interaction, Construction and Building Materials, 479 (**2025**), 141519, doi:10.1016/j.conbuildmat.2025.141519

[12] J. Yi, S. Shen, D. Wang, Y. Huang, D. Feng, Characterization of the Bonding Fracture Properties of the Asphalt-Aggregate System Using a Thin-Film Interface Test, Journal of Testing and Evaluation, 44 (**2016**), 450–460, doi:10.1520/jte20140409

[13] S. A. Ali, M. Zaman, R. Ghabchi, M. A. Rahman, S. Ghos, S. Rani, Effect of additives and aging on moisture-induced damage potential of asphalt mixes using surface free energy and laboratory-based performance tests, International Journal of Pavement Engineering, 23 (**2022**), 285–296, doi:10.1080/10298436.2020.1742335

[14] R. Bionghi, D. Shahraki, M. Ameri, M. M. Karimi, Correlation between bond strength and surface free energy parameters of asphalt binder-aggregate system, Construction and Building Materials, 303 (**2021**), 124487, doi:10.1016/j.conbuildmat.2021.124487

[15] C. DeCarlo, E. V. Dave, J. E. Sias, G. D. Airey, R. Mallick, Comparative Evaluation of Moisture Susceptibility Test Methods for Routine Usage in Asphalt Mixture Design, Journal of Testing and Evaluation, 48 (**2020**), 88–106, doi:10.1520/jte20180908

[16] X. Wang, J. Liu, Z. Wang, H. Jing, B. Yang, Investigations on Adhesion Characteristics between High-Content Rubberized Asphalt and Aggregates, Polymers, 14 (**2022**), 14245474, doi:10.3390/polym14245474

[17] H. Xiang, Z. Wang, M. Deng, S. Tan, H. Liang, Adhesion Characteristics of an Asphalt Binder-Aggregate Interface Based on Molecular Dynamics, Materials, 18 (**2025**), 18050981, doi:10.3390/ma18050981

[18] M.-X. Zhang, Y.-M. Wang, W.-K. Zhang, W. Du, X. Li, X.-N. Wang, X.-C. Liu, Adhesion characteristics of montmorillonite modified asphalt unveiled by surface free energy and AFM, International Journal of Adhesion and Adhesives, 132 (**2024**), 103699, doi:10.1016/j.ijadhadh.2024.103699

[19] G. H. Hamedi, F. Moghadas Nejad, Using energy parameters based on the surface free energy concept to evaluate the moisture suscepti-

bility of hot mix asphalt, Road Materials and Pavement Design, 16 (**2015**), 239–255, doi:10.1080/14680629.2014.990049

[20] J. E. Kliewer, Development of performance based test procedures for asphalt mixtures, Oregon State University 1994

[21] A. S. Mohamed, F. Xiao, C. Hettiarachchi, T. Abdel-Wahed, Bond Strength in Dry Condition of Reclaimed Asphalt Modified by Crumb Rubber Modified Binder, Journal of Adhesion, 99 (**2023**), 691–720, doi:10.1080/00218464.2022.2046561

[22] H. Rahmani, H. Shirmohammadi, G. H. Hamedi, Effect of Asphalt Binder Aging on Thermodynamic Parameters and Its Relationship with Moisture Sensitivity of Asphalt Mixes, Journal of Materials in Civil Engineering, 30 (**2018**), 0002453, doi:10.1061/(asce)mt.1943-5533.0002453

[23] F. Yang, L. M. Yang, H. R. Gong, Q. Zhou, L. H. He, Q. Chen, C. H. Cen, M. Zhou, Investigating on the composite modification process and pavement performance of emulsified asphalt by styrene-butadiene latex/waterborne epoxy resin, Construction and Building Materials, 487 (**2025**), 142134, doi:10.1016/j.conbuildmat.2025.142134

[24] F. Yang, Q. Zhou, L. M. Yang, L. H. He, Q. Chen, S. G. Tang, Preparation and performance evaluation of waterborne epoxy resin modified emulsified asphalt binder, Case Studies in Construction Materials, 21 (**2024**), e03548, doi:10.1016/j.cscm.2024.e03548

[25] M. Guo, X. Yin, X. Du, Y. Tan, Effect of aging, testing temperature and relative humidity on adhesion between asphalt binder and mineral aggregate, Construction and Building Materials, 363 (**2023**), 129775, doi:10.1016/j.conbuildmat.2022.129775

[26] N. Xu, H. Wang, Y. Chen, M. Kamani, H. Wang, Microscopic Analysis of Aging Effects on the Adhesion Properties between Asphalt and Mineral Aggregate, Journal of Materials in Civil Engineering, 35 (**2023**), 15381, doi:10.1061/jmcee7.Mteng-15381

[27] F. M. Fowkes, Attractive forces at interfaces, Ind. Eng. Chem., 56 (**1964**), 40–52

[28] R. J. Good, Contact angle, wetting, and adhesion: a critical review, J. Adhes. Sci. Technol., 6 (**1992**), 1269–1302

[29] C. Van Oss, R. J. Good, M. K. Chaudhury, Additive and nonadditive surface tension components and the interpretation of contact angles, Langmuir, 4 (**1988**), 884–891

[30] D. K. Owens, R. Wendt, Estimation of the surface free energy of polymers, J. Appl. Polym. Sci., 13 (**1969**), 1741–1747

[31] T. Young, III. An essay on the cohesion of fluids, Philos. Trans., R. Soc. London, 95 (**1805**), 65–87