



Article Water Damage Resistance of Tuff Asphalt Mixtures with Admixtures Based on Surface Energy Theory

Xiaoyuan Zhang ^{1,2,3,*}, Yunfei Ma⁴, Zongkai Zhu⁵, Jingyi Xu³, Yu Zhang² and Boming Tang¹

- ¹ College of Traffic & Transportation, Chongqing Jiaotong University, Chongqing 400074, China
- ² Zhejiang Communication Construction Group Co., Ltd., Hangzhou 310051, China
- ³ School of Civil Engineering and Architecture, Zhejiang Sci-Tech University, Hangzhou 310018, China; lucky6669990@163.com
- ⁴ Pan'an County Road and Transportation Management Center, Jinhua 322300, China
- ⁵ Chongqing Municipal Research Institute of Design, Chongqing 400020, China
- * Correspondence: xyzhang@zstu.edu.cn

Abstract: At present, tuff aggregates as asphalt pavement mixtures have insufficient water damage resistance; hence, modifying and evaluating the related properties of tuff asphalt mixtures are necessary. In this study, cement and a liquid antistripping agent were selected as admixtures, and tuff and limestone mixtures without admixtures were selected as control. The surface energy for the SBS-modified asphalt polymers and aggregates in the mixtures was evaluated by using surface energy theory. The adhesion work and the spalling work of the polymer–aggregate interface was calculated, and a factor *k* was proposed to predict the water damage resistance of the tuff mixture with admixtures. The prediction values were compared with those of the macroscopic water stability test for the mixture. The results of this research showed that the factor *k* after adding admixtures was improved, and the increase range was from 7.14% to 47.62%. The admixture scheme with the best improvement was that with 2% cement content, in which the *k* value increased by 21.57% and 47.62% compared with that of the limestone and tuff mixtures without admixtures, respectively. The tested water stability indexes and the predicted factor *k* under different admixture schemes exhibited a good positive correlation, and the correlation equations were obtained by linear fitting. Thus, it was feasible to use the factor *k* characterizing the water damage resistance of tuff mixtures using surface energy theory.

Keywords: tuff asphalt mixture; surface energy; water damage resistance; adhesion work; spalling work

1. Introduction

With the continuous development of China's road network construction, a large amount of tunnel slag is produced in the process of highway tunnel excavation in mountainous areas, and tuff gravel is one of them, which is a kind of widespread stone material in the Zhejiang area of China. However, owing to the complex composition of tuff, great differences in tuff characteristics exist in diverse regions. Especially, the adhesion between acidic tuff as an aggregate and asphalt is poor, resulting in the lack of water damage resistance of asphalt pavement. Thus, tuff as an aggregate in asphalt pavement has not been widely applied. If local tuff can be used, it will not only effectively alleviate the shortage of high-quality stone materials in asphalt mixtures but will also reduce the cost of aggregate procurement and transportation. Therefore, research on the improvement of the water damage resistance for tuff asphalt mixtures is of great significance.

To enhance the water damage resistance of acidic aggregate–asphalt mixtures, some scholars have carried out a series of related tests and evaluations of the effect of improving the performance of asphalt to increase the adhesion with acidic aggregates [1,2]. For instance, Huang et al. [3] mixed hydrated lime into a granite asphalt mixture to study the water stability of the mixture through laboratory tests. The results indicated that adding hydrated lime could clearly enhance the water damage resistance of the granite



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). mixture. Qian et al. [4] evaluated the performance of adding cement to a granite asphalt mixture through water stability test. The results showed that the water damage resistance could be improved by adding cement instead of mineral powder, and the improvement effect was best with the 2% cement content. Meanwhile, scholars have also evaluated the effect of organic antistripping agents on improving the adhesion property of aggregatesasphalts [5–9]. Nazirizad et al. [10] investigated the water stability of a sandstone aggregateasphalt mixture through indoor experiments, and the results indicated that adding a liquid antistripping agent could significantly enhance the water damage resistance of the mixture. Park et al. [11] added aliphatic amine antistripping agents to an asphalt mixture and conducted road performance tests. The antistripping agents could effectively improve the rutting resistance of the mixture and the adhesion between modified asphalt binder and aggregate. Liu et al. [12] screened the optimal content of a TR-500S antistripping agent using adhesion tests and then evaluated the performance of a granite asphalt mixture under the optimal antistripping agent content. The results indicated that the antistripping agent could improve the water stability of the granite mixture and had good road performance. Zhang et al. [13] investigated the effects of three different antistripping agents on rubber powder-modified asphalt, and the antistripping agent of LOF-6500 exerted a good effect on the adhesion property of rubber powder-modified asphalt to aggregate. At present, minimal research exists on the use of tuff as an asphalt pavement aggregate, and few modification studies on related properties have been performed for reference to other acidic aggregate–asphalt mixtures. For instance, Goual et al. [14] investigated the strength of tuff-limestone sand mixtures with different cement contents through laboratory tests, and the results indicated the possibility of the development on asphalt pavement materials containing tuff in Algeria. Zhang et al. [15] evaluated the performance of a tuff asphalt mixture after adding cement and a liquid antistripping agent through laboratory tests, and the results indicated that the addition of admixtures could improve the adhesion property and water stability of the tuff mixture.

Furthermore, researchers at home and abroad have studied the adhesion mechanism of asphalt binders to aggregates and evaluated the water damage of corresponding mixtures with admixtures. Commonly used adhesion evaluation methods include water boiling and water immersion methods, which are qualitative evaluation methods with the advantages of simple operation and easy to understand. However, the results of the adhesion property require people to judge the stripping degree of asphalt films by naked eye, and the results vary from person to person, failing to meet the objective and uniform requirements. Accordingly, some scholars have studied the adhesion property between asphalts and aggregates using surface energy theory and quantitatively evaluated the adhesion property of asphalt-aggregate interfaces from a microscopic perspective to make test results highly accurate. For example, Elphingstone et al. [16] investigated the water damage resistance of an asphalt mixture using surface free energy theory. When the asphalt mixture was added with water, the Gibbs free energy and adhesion property of the asphalt-aggregate interface decreased. Hefer et al. [17] improved the contact angle measurement method to estimate the surface energy of asphalt binder, which provided great help for predicting the water stability of asphalt mixtures. Liu et al. [18] measured the surface energy of asphalt binder and aggregate before and after immersion via the insert plate method and columnar wick method and calculated the work at the interface of styrene-butadiene-styrene (SBS)modified asphalt binder with amphibolite gneiss aggregate. Peng et al. [19] measured the surface free energy of asphalt-aggregate with a warm mixing agent, and the results indicated that the warm mixing agent increased the polarity of asphalt binder, thus enhancing the adhesion of asphalt binder with granite and improving the water damage resistance of the mixture. Geng et al. [20] calculated the work of asphalt and broken pebbles on the basis of surface energy theory and verified them through water stability tests. The calculated results for the surface energy were similar to the water stability test results.

In summary, the exploration of the adhesion property of asphalt–aggregate mixtures from the perspective of surface energy theory and the evaluation of the water damage resistance of the mixtures have become research hotspots. However, in view of the insufficiency of the adhesion of tuff as aggregates to asphalt after water contact, although the water damage of tuff common asphalt mixtures as the lower asphalt course of pavement has been evaluated by macroscopic tests [15], the improvement evaluation of the water damage resistance of tuff SBS-modified asphalt mixtures as the other asphalt course of pavement using surface energy theory has not been conducted owing to the difference in the origin of tuff stone and its properties. In this regard, this study took the typical graded tuff mixture in the middle asphalt course of pavement as the object and planned to enhance the adhesion property of tuff aggregates to SBS-modified asphalt polymers with admixtures, including cement and liquid antistripping agents. The improvement effect and action mechanism of the tuff mixture were also investigated by using surface energy theory to predict the water damage resistance of tuff mixtures with admixtures. Furthermore, the predicted and test results for the water damage of corresponding mixtures were compared in order to verify the validity of the theoretical results.

2. Raw Materials and Mix Design

The raw materials for the asphalt mixture included asphalt binder, mineral powder, aggregate, and admixtures. The specific indicators and related characteristics of each raw material are as follows.

2.1. Asphalt Binder

SBS-modified asphalt was selected as the binder of the asphalt mixture, which came from the Zhejiang Transportation Resources Investment Co., Ltd., Hangzhou, China [15]. The technical indexes of SBS-modified asphalt binder were tested by referring to the test methods of the JTG E20-2011 specifications [21]; they are provided in Table 1, indicating that the SBS-modified asphalt binder conformed to the requirements of the JTG F40-2004 specifications [22,23].

	Technical Indexes	Values	Requirements	Methods
Penetrat	tion (25 °C, 100 g, 5 s) (0.1 mm)	58	60–80	T0604
Ductilit	y index (5 cm/min, 5 $^{\circ}$ C) (cm)	40	≥ 30	T0605
Softening point (°C)		85	≥55	T0606
Flash point (°C)		250	≥230	T0611
Density (g/cm ³)		1.036	-	T0603
	Mass loss (%)	-0.026	± 1.0	T0609
RTFOT	Penetration ratio (25 $^{\circ}$ C) (%)	72.4	≥ 60	T0609
	Ductility (5 cm/min, 5 °C) (cm)	25	≥ 20	T0605

Table 1. Properties of SBS-modified asphalt binder.

2.2. Aggregates

Two types of aggregates, tuff and conventional limestone, were used for comparative investigation. The coarse and fine tuff aggregates in the mixture all came from the tunnel slag of the Wentai Highway Project in Zhejiang Province. The typical tuff samples are seen in Figure 1. Moreover, the chemical components of three groups of tuff samples obtained via an X-ray diffractometer are listed in Table 2. The mean weight ratio of SiO₂ in the three groups of aggregates was 75.17%, which was more than 65%. Therefore, the lithology of the selected tuff samples was acidic. The properties of the coarse and fine aggregates are presented in Table 3, indicating that they met the requirements of the specifications [22,24].



Figure 1. Tuff samples.

Table 2. Chemical components of tuff samples.

Compone	nts	SiO ₂	Al ₂ O ₃	K ₂ O	Fe ₂ O ₃	MgO	CaO	Na ₂ O	Other
Weight	1#	75.62	15.33	4.64	2.31	1.19	0.37	0.16	0.38
percentage (%)	2#	71.58	16.68	5.35	3.27	1.95	0.49	0.28	0.40
	3#	78.32	12.62	4.11	2.45	1.52	0.36	0.22	0.40

Table 3. Basic properties of the coarse and fine aggregates.

Technical Indexes			t Results	D o guinom on to	
			Limestone	Requirements	
	Crushing value index (%)		23.1	≤ 28	
Coarse	Flat particle content (%)	8.5	7.0	≤ 18	
aggregates	Los Angeles abrasion value (%)	15.9	14.2	≤ 30	
	Soundness (%)	2	5	≤ 12	
	Less than 0.075 mm particle content (%)	0.2	0.3	≤ 1	
	Sand equivalent (%)	80	74	≥ 60	
Fine	Grain angularity (%)	51.2	45.6	\geq 30	
aggregates	Methylene blue value (g·kg ⁻¹)	2.0	3.6	≤ 25	
	Silt content (less than 0.075 mm particles) (%)	2.6	2.5	<u>≤</u> 3	

2.3. Mineral Powder and Admixtures

The limestone mineral powder selected as filler in the asphalt mixture was produced in Fuyang District of Zhejiang Province, and its basic properties of mineral powder met the relevant specification requirements [22,24]. In addition, two admixtures, XT-2 liquid antistripping agent and cement, were selected to improve the adhesion property of asphalt–tuff in the asphalt mixture. The XT-2 liquid antistripping agent was produced by Changzhou Xintuo Pavement Material Co., Ltd., Changzhou, China. It was a non-amine antistripping agent with a relative density of 1.0 and its failure temperature could exceed 260 °C. Meanwhile, common Portland cement P.O42.5 adopted as another additive was manufactured by Jiangshan South Cement Company Co., Ltd., Jiangshan, China. and its density was 3.05 g/cm^3 . The technical indexes of cement conformed to the requirements of the GB175-2007 specifications [25].

2.4. Mix Design

SUP20 was adopted in the study for mixture gradation in the middle asphalt layer of pavement. The grading curves of two types of mixtures are presented in Figure 2.



Figure 2. Grading curves for the SUP20 mixtures.

On the basis of the engineering experience, the initial asphalt content P_b for tuff and limestone asphalt mixtures was selected as 4.7% and 4.2%, respectively. Then, Marshall asphalt mixture samples with four different asphalt contents, P_b , $P_b + 0.5$ %, $P_b - 0.5$ %, and $P_b + 1$ %, were prepared using a gyratory compactor. Five parallel samples in each asphalt content were selected, and the sample thickness was 63.5 mm \pm 1.3 mm. After the molded Marshall samples were cooled for about 24 h, the volume properties of the asphalt mixtures under four asphalt contents were tested and obtained [26]. The test results of the tuff and limestone mixtures are listed in Table 4, where *VV* is the void ratio in the sample, %; *VMA* is the void in the mineral aggregate of the sample, %; *VFA* is the effective asphalt saturation of the sample, %; r_t is the maximum theoretical specific density of the sample; r_f represents the bulk-specific density.

Aggregate Types	Asphalt Content/%	r_t	r_{f}	<i>VV</i> /%	VMA/%	VFA/%
	4.2	2.481	2.342	5.6	13.5	58.5
Tuff	4.7	2.463	2.364	4.0	13.0	69.2
Tull	5.2	2.455	2.369	3.1	13.3	76.4
	5.7	2.427	2.359	2.8	13.5	79.0
	3.7	2.564	2.426	5.4	13.1	58.9
Limestone	4.2	2.544	2.443	4.0	13.0	69.1
Linestone	4.7	2.525	2.449	3.0	13.2	77.4
	5.2	2.506	2.456	2.0	13.4	84.8

Table 4. Volume properties of two types of mixtures.

According to the parameter results in Table 4, when the design target void ratio of the mixture was 4.0%, the optimal asphalt contents of tuff and limestone mixtures could be 4.70% and 4.20%, respectively; thus, the respective optimum oil–stone ratio was 4.93% and 4.38%. Furthermore, the schemes of the admixtures used to modify the adhesion property

of the mixture were determined. The mixing schemes of the admixtures were as follows: (1) cement was mixed in the mixture to replace part of the filler, which accounted for 1%, 2%, 3%, and 4% of the mineral materials' weight composed of the filler and aggregate; (2) the XT-2 antistripping agent was mixed with asphalt, which accounted for 0.3%, 0.6%, and 0.9% of the asphalt weight; (3) the tuff and limestone mixture had no additive and served as control.

3. Basic Theory and Test Method

3.1. Basic Theory of Surface Energy

(1) Surface energy and its components

The total surface energy γ consists of the van der Waals component γ^d and the polar component γ^p . γ^d is generated by the electrostatic force between molecules or atoms, and γ^p is formed by the intermolecular hydrogen bond force. γ^p includes acidic and alkaline components and is expressed as follows:

$$\gamma^p = 2 \times \left(\gamma^+ \gamma^-\right)^{\frac{1}{2}},\tag{1}$$

where γ^p is the polar component of a liquid or solid (mJ/m²), γ^+ is the acidic component of a liquid or solid (mJ/m²), and γ^- is the alkaline component of a liquid or solid (mJ/m²).

(2) Gas–solid–liquid interface

The change in surface energy usually occurs in the three-phase system of solid, liquid, and gas. When liquid drops on a solid surface, owing to the excess energy on the solid surface, the solid will maintain a stable state by absorbing liquid molecules to reduce the surface potential energy. At this time, the liquid begins to wet the solid surface. The degree of liquid wetting is generally reflected by the change ΔG in the Gibbs surface free energy. When the change ΔG is negative, the liquid can wet the solid; the greater the negative value, the easier the liquid wets the solid. Meanwhile, the change ΔG will be converted into the work carried out by the adhesion force between the solid and liquid interfaces. Solid–liquid contact includes the processes of expansion and wetting, where wetting means that after solid and liquid phases combine to form a solid–liquid phase, the gas–solid and gas–liquid interfaces transform into a solid–liquid interface. ΔG in this process is shown in Equation (2), and the corresponding work carried out by the system W_a is shown in Equation (3).

$$\Delta G = \gamma_{sl} - \gamma_{gs} - \gamma_{gl},\tag{2}$$

$$W_a = -\Delta G = \gamma_{gs} + \gamma_{gl} - \gamma_{sl},\tag{3}$$

where ΔG is the change in surface free energy in the wetting process (mJ/m²); W_a is the wetting work (mJ/m²); γ_{sl} , γ_{gs} , and γ_{gl} are the surface energies of the solid–liquid, gas–solid, and gas–liquid interfaces (mJ/m²), respectively. When the work $W_a > 0$, the wetting process occurs spontaneously; the greater W_a , the stronger the adhesion of the solid–liquid interface.

(3) Contact angle and Young's equation

In the interface of the solid, liquid, and gas phase, a straight line is drawn, which is tangent to the gas–liquid interface. The angle formed between the straight line and the solid–liquid interface is called contact angle θ . When $\theta < 90^\circ$, the liquid can wet the solid; when $\theta > 90^\circ$, the liquid cannot wet the solid completely, as shown in Figure 3. In the case of incomplete wetting, if droplet has a very small change, the corresponding displacement will have a small change. Suppose that the area *A* of the droplet wetting the solid surface has changed at this time, as shown in Equation (4), ΔG can be shown as Equation (5).

$$\Delta A = 2\pi R dR, \tag{4}$$

$$\Delta G = \Delta A \times \left(\gamma_{sl} - \gamma_{gs}\right) + \Delta A \times \gamma_{gl} \cos(\theta - \Delta \theta), \tag{5}$$

Through sorting out Equation (5), Young's equation can be obtained by simplifying the above equation:

$$\gamma_{sl} - \gamma_{gs} + \gamma_{gl} \cos \theta = 0. \tag{6}$$

Young's equation applies to the solid–liquid equilibrium state, where no chemical reaction occurs. Through substituting Young's Equation (6) into Equation (3), the equation of wetting work can be obtained as:

$$W_a = \gamma_{ql} \times (1 + \cos \theta). \tag{7}$$

From the above equation, the wetting work can be obtained by measuring the surface energy γ_{gl} and the contact angle θ of the solid–liquid interface.



Figure 3. Two states of liquid wetting on solid. (a) Wetting, (b) incomplete wetting.

3.2. Surface Energy Determination Methods

(1) Surface energy for aggregates

In this study, the columnar wick method was selected to determine the surface energy of aggregates. This method uses a suitable probe liquid to wet solid particle powders, then the contact angle θ can be calculated indirectly by observing the height and time of wetting. The relevant surface energy and parameters of the selected probe liquids in the columnar wick method are shown in Table 5, where η is the viscosity of the probe liquids (mPa·s).

Probe Liquids	γ	γ^d	γ^p	γ^+	γ^-	η
Distilled water	72.8	21.8	51	25.5	25.5	0.89
Hexane	18.4	18.4	0	0	0	0.3
Diiodomethane	50.8	50.8	0	0	0	2.8
Formamide	58.0	39.0	19	2.3	39.6	4.6

Table 5. Surface energy and parameters of probe liquids.

For the process of the columnar wick method, the limestone and tuff aggregates were washed and then dried in an oven for 24 h. After cooling to room temperature, the aggregates were crushed and screened using a 0.15 mm sieve to obtain limestone and tuff particles with sizes not exceeding 0.15 mm. A glass tube with an inner diameter of 3 mm and a length of 10 cm was selected, and 0.2 g of the aggregates were weighed and placed into the glass tube. The glass tube was gently shaken to even out the aggregates. Next, 1 mL of a probe liquid (a hexane liquid with low surface energy) was placed into a glass container, and the wetting height X (mm) and time T(t) were measured. To reduce the errors of X and T, three parallel tests were conducted on each aggregate, then the average of the results was obtained. A schematic of the test device is shown in Figure 4.



Figure 4. Schematic of the test device for the columnar wick method.

In accordance with the Washburn wetting Equation (8), the wetting height *X* and time *T* were substituted into the equation, and the relationship between X^2 and *T* were calculated and fitted. The effective radius *r* was obtained through the fitted result. Owing to the low surface energy of the hexane liquid selected in the test, the aggregate could be completely wetted, and the contact angle θ between the probe liquid and aggregate was 0° ; thus, $\cos\theta$ was equal to 1, and Equation (8) could be simplified to Equation (9).

$$\frac{X^2}{T} = \frac{\gamma_L \times \cos\theta \times r}{2\eta},\tag{8}$$

$$\frac{X^2}{T} = \frac{\gamma_L \times r}{2\eta} \tag{9}$$

where γ_L is the surface energy of the probe liquid (mJ/m²), and *r* is the effective radius of the glass tube (mm).

On the basis of surface energy combination theory of van Oss–Chaudhury–Good, the wetting work was obtained as Equation (10). This equation was combined with Equation (7), resulting in Equation (11). If the acidic and alkaline components of the selected probe liquid in the test were all equal to 0, Equation (11) could be simplified to Equation (12).

$$W_a = 2\sqrt{\gamma_L^d \gamma_S^d} + 2\sqrt{\gamma_L^- \gamma_S^+} + 2\sqrt{\gamma_L^+ \gamma_S^-}, \tag{10}$$

$$\gamma_L(1+\cos\theta) = 2\sqrt{\gamma_L^d \gamma_S^d} + 2\sqrt{\gamma_L^- \gamma_S^+} + 2\sqrt{\gamma_L^+ \gamma_S^-},\tag{11}$$

$$\gamma_L(1+\cos\theta) = 2\sqrt{\gamma_L^d \gamma_S^d},\tag{12}$$

where γ_L^a and γ_S^d are the van der Waals component in the surface energy of the probe liquid and aggregate, respectively (mJ/m²); γ_L^- and γ_L^+ are the alkaline and acidic components in the surface energy of the probe liquid, respectively (mJ/m²); γ_S^- and γ_S^+ are the alkaline and acidic components in the surface energy of the aggregate, respectively (mJ/m²).

Therefore, this test first wetted the aggregate using the hexane liquid to obtain the effective radius *r*. Then, the diiodomethane liquid with high surface energy was selected, but alkaline and acidic components having zero value obtained $\cos\theta$ values between those of the probe liquid and the measured aggregate. Thus, the van der Waals component γ_S^d in the surface energy of the aggregate was generated using Equation (12). Next, the distilled water and formamide liquid with the alkaline and acidic components having nonzero values were chosen, and the alkaline and acidic components γ_S^- , γ_S^+ in the surface energy of the aggregate using Equation (11).

(2) Surface energy for asphalt polymer

The surface energy of asphalt polymers with different admixture schemes was determined under the ratio of mineral powder to asphalt of 1. The content of admixtures in asphalt polymers corresponded to the mixture results. For the surface energy measurement of polymers, the sessile drop method was selected. This method dropped the probe liquid on a smooth solid surface and then determined the θ value of the contact interface through a contact angle tester to calculate the surface energy components. Because the texture of polymers was relatively viscous, the phenomenon of wire drawing would occur in the dripping process, and a completely smooth surface was difficult to form, which affected the measurement results of surface energy. Thus, distilled water and ethylene glycol were selected as the probe liquid to conduct testing on the solid polymer film, and the surface energy of the polymer film with admixtures was calculated. The surface energy of the ethylene glycol liquid including γ , γ^d , γ^p , γ^+ , and γ^- was 48, 29, 19, 4.0, and 30.1 mJ/m², respectively.

For the sample preparation of the solid polymer film, the polymer was heated to a flowing state. A glass sheet of 2 mm \times 2 mm was placed into the polymer and then taken out after it was fully wetted. The excess asphalt was let to drip off at room temperature for 15 min. When only a smooth polymer film was left on the glass sheet surface, it was placed in a dryer for 10 h to complete the sample preparation. To reduce the error of test results, five parallel samples for each polymer were made, as shown in Figure 5.



Figure 5. Samples of solid polymer film.

The contact angle θ between probe liquids and the polymer film was tested using the contact angle instrument, and the test data were substituted into the Owens–Wendt Equation (13) [27]; thus, the components γ_S^d , γ_S^p of the solid polymer were further obtained. According to Equation (11), the other surface energy components of the polymer were calculated:

$$\gamma_L(1+\cos\theta) = 2\sqrt{\gamma_S^d \gamma_L^d} + 2\sqrt{\gamma_S^p \gamma_L^p}.$$
(13)

3.3. Evaluation Model of Interface Adhesion Characteristics

(1) Adhesion model for polymer–aggregate interface

The mutual adhesion between asphalt polymer and aggregate occurs when the asphalt mixture is fully mixed. At this time, the two contact each other, and the two independent phases bond to form a new phase of polymer–aggregate. In the adhesion process, the aggregate–gas and polymer–gas interfaces are transformed into a polymer–aggregate interface. When the change in the surface free energy $\Delta G < 0$, the energy is transformed into the adhesion work *W*, i.e., *W* > 0. The adhesion work of the polymer–aggregate interface is derived from the van der Waals force and polar force. In this regard, Equation (14) was chosen to calculate the adhesion work of the polymer–aggregate interface.

$$W_{AB} = W^d_{AB} + W^p_{AB'} \tag{14}$$

where *AB* is the adhesive interface of polymer–aggregate; W_{AB} is the adhesion work of the polymer–aggregate interface (mJ/m²); W_{AB}^d and W_{AB}^p are the adhesion work generated by the van der Waals force and polar force at the polymer–aggregate interface (mJ/m²), respectively.

The adhesion work W_{AB}^d can be calculated using Equation (15). Given that $\gamma_{AB}^d = \left[\left(\gamma_A^d\right)^{\frac{1}{2}} - \left(\gamma_B^d\right)^{\frac{1}{2}}\right]^2$, substituting this formula into Equation (15) can yield Equation (16).

$$W_{AB}^{d} = \gamma_{A}^{d} + \gamma_{B}^{d} - \gamma_{AB}^{d}, \tag{15}$$

$$W_{AB}^{d} = 2 \times \left(\gamma_{A}^{d} \gamma_{B}^{d}\right)^{\frac{1}{2}},\tag{16}$$

where γ_A^d , γ_B^d , and γ_{AB}^d are the van der Waals components in the surface energy for the polymer, aggregate, and polymer–aggregate interface (mJ/m²), respectively.

Similarly, the adhesion work W_{AB}^{p} can be calculated as

$$W_{AB}^{p} = \gamma_{A}^{p} + \gamma_{B}^{p} - \gamma_{AB}^{p}.$$
(17)

In this equation,

$$\gamma_A^p = 2 \times \left(\gamma_A^+ \gamma_A^-\right)^{\frac{1}{2}},\tag{18}$$

$$\gamma_B^p = 2 \times \left(\gamma_B^+ \gamma_B^-\right)^{\frac{1}{2}},\tag{19}$$

$$\gamma_{AB}^{p} = 2 \times \left[\left(\gamma_{A}^{+} \right)^{\frac{1}{2}} - \left(\gamma_{B}^{-} \right)^{\frac{1}{2}} \right] \times \left[\left(\gamma_{A}^{-} \right)^{\frac{1}{2}} - \left(\gamma_{B}^{+} \right)^{\frac{1}{2}} \right], \tag{20}$$

where γ_A^+ , γ_A^- , and γ_A^p are the acidic, alkaline, and polar components in the surface energy for the polymer (mJ/m²), respectively; γ_B^+ , γ_B^- , and γ_B^p are the acidic, alkaline, and polar components in the surface energy for the aggregate (mJ/m²), respectively; γ_{AB}^p is the polar component in the surface energy for the polymer–aggregate interface (mJ/m²).

Substituting Equations (18)–(20) into Equation (17) yields

$$W_{AB}^{p} = -\Delta G_{AB}^{p} = 2 \times \left[\left(\gamma_{A}^{+} \gamma_{B}^{-} \right)^{\frac{1}{2}} + \left(\gamma_{A}^{-} \gamma_{B}^{+} \right)^{\frac{1}{2}} \right].$$
(21)

Through substituting Equations (16) and (21) into Equation (15), the total adhesion work can be obtained as

$$W_{AB} = 2 \times \left[\left(\gamma_A^d \gamma_B^d \right)^{\frac{1}{2}} + \left(\gamma_A^+ \gamma_B^- \right)^{\frac{1}{2}} + \left(\gamma_A^- \gamma_B^+ \right)^{\frac{1}{2}} \right].$$
(22)

The adhesion work produced by polymer and aggregate bonding can be calculated from the van der Waals and acidic–basic components of the polymer and aggregate. The interface adhesion work between tuff aggregates and asphalt polymer under different admixture schemes can be obtained by substituting the surface energy component results into Equations (16)–(22).

(2) Spalling model for polymer–aggregate interface

Spalling theory generally states that two substances with minimal polar difference are likely to bond to each other; conversely, substances with large polar difference are likely to peel off each other. When the asphalt mixture meets water, the asphalt polymer and water molecules on the aggregate surface can undergo displacement reaction, and the polymer–aggregate interface is transformed into the polymer–water phase, aggregate–water phase, and polymer–aggregate system. Therefore, in the water environment, the balance of the water, aggregate, and asphalt polymer three-phase system is a key to the adhesion property

between the polymer and aggregate. In the spalling process of the polymer–aggregate interface, the change value ΔG of the surface free energy in the whole system is negative, whereas the spalling work is positive; nevertheless, both values are the same. In this study, Equation (23) was chosen to calculate the spalling work W_{ABW} of the polymer–aggregate interface with water.

$$W_{ABW} = W^d_{ABW} + W^p_{ABW}, (23)$$

where *ABW* is the spalling interface of the polymer–aggregate with water; W_{ABW}^d and W_{ABW}^p are the spalling work generated by the van der Waals force and polar force of the polymer–aggregate interface with water (mJ/m²), respectively.

The spalling work W_{ABW}^d was calculated as

$$W^d_{ABW} = \gamma^d_{AW} + \gamma^d_{BW} - \gamma^d_{AB} - 2\gamma^d_{W}, \tag{24}$$

where γ_{AW}^d , γ_{BW}^d , γ_{AB}^d , and γ_w^d are the van der Waals component in the surface energy for the polymer–water interface, aggregate–water interface, polymer–aggregate interface, and water (mJ/m²), respectively.

Specifically,

$$\gamma_{AW}^{d} = \left[\left(\gamma_{A}^{d} \right)^{\frac{1}{2}} - \left(\gamma_{W}^{d} \right)^{\frac{1}{2}} \right]^{2}, \tag{25}$$

$$\gamma_{BW}^{d} = \left[\left(\gamma_{B}^{d} \right)^{\frac{1}{2}} - \left(\gamma_{W}^{d} \right)^{\frac{1}{2}} \right]^{2}, \tag{26}$$

$$\gamma_{AB}^{d} = \left[\left(\gamma_{A}^{d} \right)^{\frac{1}{2}} - \left(\gamma_{W}^{d} \right)^{\frac{1}{2}} \right]^{2}.$$
(27)

Substituting the above three equations into Equation (24) led to

$$W_{ABW}^{d} = 2 \times \left[\left(\gamma_{A}^{d} \gamma_{B}^{d} \right)^{\frac{1}{2}} - \left(\gamma_{A}^{d} \gamma_{W}^{d} \right)^{\frac{1}{2}} - \left(\gamma_{B}^{d} \gamma_{W}^{d} \right)^{\frac{1}{2}} \right].$$
(28)

Similarly, the spalling work W_{ABW}^p was calculated as

$$W_{ABW}^{p} = \gamma_{AW}^{p} + \gamma_{BW}^{p} - \gamma_{AB}^{p} - 2\gamma_{W}^{p}, \tag{29}$$

where γ_{AW}^p , γ_{BW}^p , γ_{AB}^p , and γ_W^p are the polar components in the surface energy for the polymer–water interface, aggregate–water interface, polymer–aggregate interface, and water (mJ/m²), respectively. The polar component can be further expressed by the acidic and alkaline components, such as Equations (30)–(32), where γ_W^- and γ_W^+ represent the alkaline and acidic components of water, respectively.

$$\gamma_{AW}^{p} = 2 \times \left[\left(\gamma_{A}^{+} \right)^{\frac{1}{2}} - \left(\gamma_{W}^{-} \right)^{\frac{1}{2}} \right] \times \left[\left(\gamma_{A}^{-} \right)^{\frac{1}{2}} - \left(\gamma_{W}^{+} \right)^{\frac{1}{2}} \right], \tag{30}$$

$$\gamma_{BW}^{p} = 2 \times \left[\left(\gamma_{B}^{+} \right)^{\frac{1}{2}} - \left(\gamma_{W}^{+} \right)^{\frac{1}{2}} \right] \times \left[\left(\gamma_{B}^{-} \right)^{\frac{1}{2}} - \left(\gamma_{W}^{-} \right)^{\frac{1}{2}} \right], \tag{31}$$

$$\gamma_{AB}^{p} = 2 \times \left[\left(\gamma_{A}^{+} \right)^{\frac{1}{2}} - \left(\gamma_{B}^{+} \right)^{\frac{1}{2}} \right] \times \left[\left(\gamma_{A}^{-} \right)^{\frac{1}{2}} - \left(\gamma_{B}^{-} \right)^{\frac{1}{2}} \right], \tag{32}$$

Through substituting the above three equations into Equation (29), the following equation was obtained:

$$W_{ABW}^{p} = 2 \times \left[\left(\gamma_{A}^{+} \gamma_{B}^{-} \right)^{\frac{1}{2}} + \left(\gamma_{A}^{-} \gamma_{B}^{+} \right)^{\frac{1}{2}} - \left(\gamma_{A}^{+} \gamma_{W}^{-} \right)^{\frac{1}{2}} - \left(\gamma_{A}^{-} \gamma_{W}^{+} \right)^{\frac{1}{2}} - \left(\gamma_{B}^{+} \gamma_{W}^{-} \right)^{\frac{1}{2}} - \left(\gamma_{B}^{-} \gamma_{W}^{+} \right)^{\frac{1}{2}} \right].$$
(33)

Furthermore, through substituting Equations (28) and (33) into Equation (23), the total spalling work at the interface of polymer–aggregate with water under each admixture scheme could be calculated from the van der Waals component and acidic–basic components.

3.4. Test Methods for Water Stability of Mixtures

With the selected admixtures and the obtained optimum asphalt content for the mixture under the corresponding admixture scheme, the Marshall samples of the mixture were formed, and water stability tests, including Marshall immersion and freeze–thaw splitting tests, were selected with reference to the standard test methods of [21].

(1) Marshall immersion test

For the Marshall immersion test, the prepared Marshall samples were divided into two groups, and three parallel samples were tested in each group. The first group of samples was kept in a water bath of 45 $^{\circ}$ C for about 30 min and then taken out, and their stability was measured. The second group of samples was soaked in a water bath of 45 $^{\circ}$ C for about 48 h before the stability index was tested. In accordance with the stability results of the samples before and after immersion, the residual stability of samples in a water environment could be calculated as

$$MS_0 = (MS_1/MS) \times 100,$$
 (34)

where MS_1 is the stability of Marshall samples after 48 h immersion (kN), MS is the stability of Marshall samples after 30 min immersion (kN), and MS_0 is the residual stability of Marshall samples after 48 h immersion (%).

(2) Freeze-thaw splitting test

For the freeze–thaw splitting test, the samples were divided into two groups, and four parallel samples were made in each group. The first group of samples was stored at room temperature. The second group was treated with vacuum water preservation, then 10 mL of water was injected into a bag containing the samples. The bag was sealed tightly, and the samples were frozen in a freezer at a constant temperature of -18 ± 2 °C, as seen in Figure 6. After the samples were frozen for 16 h, they were soaked in a water bath of 60 °C about 8 h. After the insulation, the two groups of samples were simultaneously soaked in a water bath of 25 °C about 2 h, and the samples were loaded when the specified time was reached.



Figure 6. Treatment of samples before freezing–thawing. (a) Samples' vacuum treatment, (b) low-temperature frozen samples.

After the splitting testing before and after freezing–thawing, the splitting tensile strength of the first and second groups of samples was obtained in accordance with the sample size and load value, shown as follows:

$$R_{T1} = 0.006287 P_{T1} / h_1, \tag{35}$$

$$R_{T2} = 0.006827 P_{T2} / h_2, \tag{36}$$

where R_{T1} and R_{T2} are the splitting tensile strengths of individual samples in the first and second groups, respectively (MPa); P_{T1} and P_{T2} are the test load values of individual samples in the first and second groups, respectively (N); h_1 and h_2 are the heights of individual samples in the first and second groups, respectively (mm).

The freeze-thaw splitting strength ratio TSR was calculated as

$$TSR = (\overline{R_{T2}}/\overline{R_{T1}}) \times 100, \tag{37}$$

where $\overline{R_{T1}}$ and $\overline{R_{T2}}$ are the average splitting tensile strengths of the first and second groups of samples (MPa), respectively.

4. Test Results and Discussion

4.1. Results of Surface Energy

(1) Surface energy of aggregates

Through the columnar wick method, the surface energy of the limestone and tuff aggregates was tested and calculated. The results of three parallel samples for each aggregate were obtained. The wetting height X and time T were determined using the hexane probe liquid, and the results of the relationship between X^2 and T are shown in Figure 7. A linear relationship existed between X^2 and T; thus, the fitted results could indicate the corresponding ratio of X^2 to T, then the effective radius r could be calculated via Equation (9). In this study, the mean effective radius of tuff and limestone aggregates was 5.03 and 3.6 µm, respectively. The surface energy of tuff and limestone aggregates was obtained through related tests under other probe liquids mentioned above, as shown in Table 6.



Figure 7. Relationship between X^2 and T under hexane liquid. (a) Limestone aggregate, (b) tuff aggregate.

Types	γ	γ^d	γ^p	γ^+	γ^-
Limestone	75.76	29.34	44.42	18.51	26.65
Tuff	66.25	18.93	47.32	36.14	15.49

Table 6. Surface energy of two kinds of aggregates.

From Table 6, the polar component and total surface energy of the tuff aggregate were 47.32 and 66.25 mJ/m², respectively; the corresponding values for the limestone aggregate were 44.42 and 75.76 mJ/m². The polar component of the tuff and limestone aggregates accounted for 71.43% and 58.63% of the respective total surface energy, indicating that the polarity of the tuff aggregate was stronger. The smaller the polarity difference between the two substances, the easier they are adsorbed. Therefore, given that water molecule is a substance with strong polarity, it is more likely to bind tuff aggregate than limestone

aggregate. In addition, Table 6 presents that the alkaline component γ^- of the limestone aggregate was greater than its acidic component γ^+ , and γ^+ of the tuff aggregate was greater than its γ^- . That is, the limestone aggregate was alkaline stone, whereas the tuff aggregate was acidic stone, which was consistent with the results of the chemical composition of tuff stone in Table 2.

(2) Surface energy of asphalt polymers

The surface energy and related parameters of polymers under different admixture schemes were obtained using the sessile drop method, as shown in Table 7. The expression of the admixture content in polymers was generated in accordance with the content in asphalt mixtures. The contact angles θ between the two kinds of probe liquid, distilled water and ethylene glycol, and the polymer without admixture were 100.3° and 79.4°, respectively. Meanwhile, the θ value decreased to different degrees after cement and XT-2 antistripping agent were added. Thus, the wetting ability of the probe liquid on the polymer after admixture addition was improved, and the admixture could increase the compatibility between the polymer and the probe liquid.

Polymer Types	θ		Ŷ	. d	o.p	o/ †	o/
Torymer Types	Distilled Water	Ethylene Glycol	1	Ŷ	Υ	Ŷ	·γ
0% admixture	100.3°	79.4°	20.95	16.79	4.16	3.83	1.13
1% cement	97.2°	79.2°	21.22	15.21	6.01	2.83	3.19
2% cement	90.6°	72.2°	24.29	15.17	9.12	4.73	4.40
3% cement	91.8°	75.9°	22.94	16.02	6.92	3.27	3.66
4% cement	93.3°	77.4°	22.37	16.32	6.05	2.80	3.27
0.3% XT-2	98.2°	78.8°	21.15	16.20	4.95	3.83	1.6
0.6% XT-2	93.6°	78.1°	21.31	15.64	5.27	3.02	2.3
0.9% XT-2	89.4°	76.0°	22.56	16.56	6.00	3.75	2.4

Table 7. Surface energy and its parameters for asphalt polymers.

For the surface energy of polymers, Table 7 presents that the polar component of the polymer without admixture was 4.16 mJ/m^2 , accounting for 19.86% of the total surface energy, in which the proportion of the polar component increased after adding admixture. For instance, although the total surface energy of the polymer with 2% cement and 0.9% antistripping agent increased by 15.94% and 7.68%, respectively, the proportion of polar components in the total surface energy reached 37.55% and 26.60%; thus, the corresponding proportion with admixture increase was 89.07% and 33.94% compared with that of the polymer without admixture. For the effect of admixture contents on the polar component, when the cement content. However, when the content was greater than 2%, the polar component decreased with the increase in cement content. With regard to the ratio of acidic–basic components in the polar component of polymers, the acidic component was significantly higher than the alkaline component under the polymer without admixture, and the alkaline component increased after adding admixture,

The reasons for the change in polarity component of polymers after mixing cement is that with the increase in cement content, cement could react with asphalt to form polar salt compounds and water and adsorb the polar groups such as sulfoxide and 2-quinoline in asphalt. Thus, it could increase the polarity of polymers. However, when the cement content was higher than 2% and continued to increase, the reaction of admixtures to acidic substances in asphalt became sufficient, resulting in the formation of a large amount of salt substance. As the proportion of soluble media in polymers decreased, the polymers became viscous with reduced fluidity, such that the polarity component of the polymers decreased.

In the range of 0–0.3%, the polarity of polymers increased rapidly with the increase in antistripping agent content because the antistripping agent is a non-amine active agent with polar groups; hence, it could increase the polarity component of polymers.

4.2. Prediction of Water Damage Resistance for Tuff Asphalt Mixtures

Based on the results of surface energy for aggregates and polymers, the results of the water damage resistance of the polymer–aggregate interface were predicted to evaluate that of tuff mixtures under different admixture schemes.

(1) Adhesion work of the polymer–aggregate interface

Through the calculation of the adhesion model, the adhesion work of the polymer– aggregate interface under different admixture schemes were obtained, as shown in Figure 8. In the horizontal coordinate of Figure 8, limestone and tuff represent the limestone and tuff mixtures without admixture; 1%C, 2%C, 3%C, and 4%C represent the tuff mixtures with 1%, 2%, 3%, and 4% cement contents, respectively; and 0.3%L, 0.6%L, and 0.9%L represent the tuff mixtures with 0.3%, 0.6%, and 0.9% XT-2 antistripping agent contents, respectively.



Figure 8. Adhesion work of the polymer-aggregate interface under different admixture schemes.

Figure 8 depicts that, compared with the results of the tuff mixture without admixture, the total adhesion work after adding admixtures increased by 6.86–43.47%. Some results (such as adding 2%, 3% cement and 0.6%, 0.9% XT-2 antistripping agent) were even higher than those of the limestone mixture. In addition, after admixtures were added, the adhesion work in the van der Waals component did not change significantly, whereas the adhesion work in the polar component was significantly increased. For example, the total work with 2% cement and 0.9% XT-2 increased by 43.47% and 32%, respectively, compared with the result of the tuff mixture without admixture. The work in the polar component increased by 104.65% and 81.45%, but the work in the van der Waals component decreased by 3.09% and 7.02%. That is, when the polarity difference between polymers and tuff aggregates decreased, asphalt fully infiltrated the aggregate, thus improving the adhesion between the two phases. In short, from the perspective of surface energy theory, the total surface energy of polymers with admixtures increased, and their polarity was enhanced. That is, the polarity difference between polymer and tuff decreased, so that the polymer could fully wet the tuff aggregate, improving the interface adhesion of the polymer–aggregate.

(2) Spalling work of the polymer–aggregate interface

Through the calculation of the spalling model, the spalling work of the polymeraggregate interface under different admixture schemes was obtained, as shown in Figure 9.



Figure 9. Spalling work of the polymer-aggregate interface under different admixture schemes.

Figure 9 illustrates that, compared with the result of the tuff mixture without admixture, the total spalling work after adding admixtures decreased to a certain extent, but the results were larger than those of the limestone mixture. The work in the van der Waals component did not change significantly, while the work in the polar component decreased to different degrees. The polarity of polymers after adding admixtures was enhanced, the polarity difference between polymers and water was reduced, and the difficulty of water molecules replacing asphalt on the surface of tuff aggregates increased; thus, the toll spalling work at the interface was reduced.

(3) Water damage resistance of the polymer–aggregate interface

To achieve stability for the water-damaged mixture, the polymer–aggregate interface will reduce part of surface energy, and the reduced energy produces spalling work. Therefore, the lower the spalling work, the less water damage is likely to occur at the interface. However, judging the water damage resistance of the polymer–aggregate interface only on the basis of the reduction value of spalling work is not comprehensive and objective, and the adhesion work at the interface needs to be evaluated. To quantify the water damage resistance of the polymer–aggregate interface, a factor *k* was introduced to evaluate the water damage resistance of the mixture. Specifically, *k* is the absolute value of the ratio between the adhesion work W_{AB} at the polymer–aggregate interface after encountering water. The relationship between *k* and W_{AB} , W_{ABW} , is shown as follows:

$$k = \left| \frac{W_{AB}}{W_{ABW}} \right| \tag{38}$$

Owing to the condition in which great adhesion work leads to a strong bond of the polymer–aggregate interface minimal spalling work results in a low stripping degree of

the interface, a large value of the factor k was obtained from Equation (38); thus, a strong water damage resistance of the interface could be characterized. Furthermore, k values of the mixtures without and with admixtures were obtained, as shown in Figure 10.



Figure 10. Effect of admixtures on the water damage resistance factor.

Figure 10 demonstrates that the factor k was improved after admixture addition, and the increase range was from 7.14% to 47.62%. The admixture scheme showing the best improvement was that with 2% cement content, in which the k value increased by 21.57% and 47.62% compared with that of the limestone and tuff mixtures without admixture, respectively. The improvement effect for the 0.9% XT-2 scheme was the second. The least improvement effect was that from the 1% cement content scheme, which showed only 7.14% more than that of the tuff mixture without admixture.

4.3. Verification of Water Damage Resistance for Tuff Mixtures

To verify the feasibility of the predicted result for surface energy theory, it was further compared with the laboratory result of water damage resistance for asphalt mixtures.

(1) Test results of water damage resistance

For the Marshall immersion test, the stability of samples was measured, and corresponding residual stability MS_0 was calculated, as shown in Figure 11. The error range of the stability was controlled within 5%. MS_0 of the limestone and tuff mixtures without admixtures was 82.94% and 74.39%, respectively. Thus, the water damage resistance of the tuff mixture was poor, and the stability decreased obviously. The performance of the tuff mixture was not as good as that of the limestone mixture. In addition, compared with the MS_0 of the tuff mixture without admixture, the results of the tuff mixtures with admixtures all increased. That is, the results for 2%, 3% cement contents and 0.9% XT-2 content increased by 15.10%, 11.41%, and 13.40%, respectively; thus, the improvement effect was good. However, MS_0 of 1%, 4% cement contents and 0.3% XT-2 content was insignificantly improved.

For the freeze–thaw splitting test, the splitting tensile strength before and after freeze–thaw cycles and the splitting strength ratio *TSR* of the mixture are shown in Figure 12. The error range of the splitting strength was controlled within 5%. The splitting strength of

the mixture decreased after freeze–thaw cycles, but the decreasing degree differed among the admixture schemes. The *TSR* of the limestone and tuff mixtures without admixture was 0.85 and 0.79, respectively, indicating that the tuff mixture was more susceptible to water damage, similar to the results of the Marshall immersion test. The *TSR* of the tuff mixture after adding admixtures increased to different degrees; thus, the water damage resistance was improved. However, differences in the improvement range were observed. For instance, compared with that of the tuff mixture without admixture, the *TSR* for 2% cement and 0.9% XT-2 schemes was 0.88 and 0.86, respectively, which exceeded the result of the limestone mixture by 11.39% and 8.86%. Meanwhile, the results of 3% cement and 0.6% XT-2 schemes were increased by 6.33% and 5.06%, respectively. On the contrary, the improvement effect under 1%, 4% cement and 0.3% XT-2 schemes was not obvious.



Figure 11. Results of the Marshall immersion test.



Figure 12. Results of the freeze-thaw splitting test.

A comparative analysis of the test and predicted results was conducted to determine the relationship between the test indexes MS_0 , TSR of the mixture and the surface energy index of the polymer–aggregate interface under admixture schemes, as shown in Figure 13.





Figure 13 indicates that the tested indexes MS_0 , TSR and the predicted factor k under different admixture schemes had a positive correlation. When the indexes MS_0 , TSR of the tuff mixture without admixture were poor, the corresponding water damage resistance factor k was also small; when the MS_0 , TSR of the tuff mixture with admixtures increased, the corresponding k value also increased. With the increase in the polymer's polarity after adding admixtures to the mixture, the adhesion work of the polymer–aggregate interface increased, whereas the corresponding spalling work decreased, thereby increasing the water damage resistance of the tuff mixture.

Through linear fitting of the relationship between k and MS_0 , TSR, the correlation equations were obtained as follows:

$$MS_0 = 56.8k + 51.8, (39)$$

$$TSR = 0.438k + 0.61, \tag{40}$$

where the correlation coefficient R^2 of k with MS_0 and TSR was 0.9136 and 0.9118, respectively, indicating that the water stability indexes had a good correlation with k. Thus, the factor k could be used to quantitatively characterize the water damage resistance of tuff mixtures using surface energy theory.

5. Conclusions

Taking a tuff asphalt mixture as the research object, combined with laboratory test and surface energy theory, this study evaluated and verified the improvement effect of the mixture under different admixture schemes on water damage resistance. The main conclusions are as follows:

- 1. Through the columnar wick method, the surface energy of aggregates was obtained, from which the polarity of the tuff aggregate was stronger than that of the limestone aggregate, i.e., the polar component accounted for 71.43% and 58.63% of the corresponding total surface energy. Meanwhile, through the sessile drop method, the surface energy of asphalt polymers was generated. The total surface energy of asphalt polymers after adding admixture increased, but the van der Waals component did not change much. The proportion of polar components in the total surface energy also increased.
- 2. The total adhesion work after adding admixtures increased by 6.86–43.47%, and some results were even higher than that of the limestone mixture. The work in the van der Waals component did not change significantly, whereas the work in the polar component was significantly increased. For instance, when the total work with 2% cement increased by 43.47% compared with that of the tuff mixture without admixture, the work in the polar component increased by 104.65%, whereas the work in the van der Waals component decreased by 3.09%. Meanwhile, the total spalling work after adding admixtures decreased to a certain extent, but the results were larger than that of the limestone mixture. The work in the van der Waals component did not change significantly, whereas the work in the polar component decreased to a certain extent, but the results were larger than that of the limestone mixture. The work in the van der Waals component did not change significantly, whereas the work in the polar component decreased to different degrees.
- 3. Through comparative analysis of the test and predicted results, the relationship between the tested water stability indexes and the surface energy index of the mixture under admixture schemes was obtained. They exhibited a positive correlation, and the correlation equations were further obtained by linear fitting. Thus, the factor *k* could be used to characterize the water damage resistance of tuff mixtures using surface energy theory. With the increase in the asphalt polymer's polarity after adding admixture to the mixture, the adhesion work of the polymer–aggregate interface increased, and the corresponding spalling work decreased, thereby improving the water damage resistance of the tuff mixture.

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