Article

Study on Factors Influencing Moisture Susceptibility of Warm Mix Asphalt Using the Surface Free Energy Approach

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Abstract: The application of warm-mixing technology brings considerable economical and environment benefits by decreasing the mixing temperature during warm asphalt mixture(WMA) production. However, the possible water residue also generates concerns in moisture susceptibility. For deep investigation on the influencing factors and mechanism of the moisture susceptibility of WMA, surface free energy(SFE) test and laboratory tests are applied in this research. A novel indicator based on SFE namely effective adhesion work is proposed to assess the asphalt-aggregate adhesion with different moisture contents. Then, given the mixing procedure of dry mixing method, an advanced three-phase model as form of asphalt-aggregate-warm mixing additive is introduced improving from the conventional two-phase asphalt-aggregate model for better reflecting the separate addition of warm mixing additive during mixing. Afterwards, the influence of aggregate types, asphalt type, aggregate moisture contents, warm-mixing agent types and warm-mixing process on the moisture susceptibility of WMA is analyzed utilizing the models and indicators proposed. Finally, the validity of the SFE indicator is verified by comparing the calculation of effective adhesion work with freeze-thaw splitting test result. The results show that all of the above factors impact the moisture susceptibility of WMA by influencing the interfacial adhesion, with the effect of moisture content being the most significant. Meanwhile, effective adhesion work and the three-phase model brought out in this research are proven to be feasible to characterize the adhesion properties of WMA, offering theoretical support to the research on warm mixing technology.

Keywords: Warm Mix Asphalt; Moisture Susceptibility; Surface Free Energy; Three-phase Model; Effective Adhesion Work

1. Introduction

The warm mixing technology allows the asphalt to reach the viscosity needed for mixing at lower temperature and therefore is able to reduce the mixing temperature by 30~40℃ during the asphalt mixture production, resulting in less energy consumption, better construction convenience and less ageing of asphalt[1~4]. Whereas, problems also arise that moisture susceptibility may deteriorate as a consequence of lower mixing and compacting temperature[5~7]. Relative studies have pointed out that the moisture damage of mixture is attributed to the adhesion failure between asphalt and aggregate and therefore researchers have introduced various methods as well as indicators to characterize the adhesion properties[812]. Currently, methods such as boiling method, photoelectric colorimetry, surface free energy(SFE) test and atomic force microscopy (AFM) have been applied to the investigation of the adhesion between asphalt and aggregate, among which the SFE obtains more attention because of its unnecessity of compacted specimen preparation, simplicity of test process and the economic advantage[13].

Elphingstone introduced SFE to asphalt mixture research for the first time to studied the interfacial cracking prediction in hot mix asphalt(HMA) mixture[14]. Cheng measured the SFE indexes of different asphalts and aggregates and calculated the cohesion work of asphalt and the adhesion work of asphalt-aggregate interface. The comparison between SFE test and conventional moisture susceptibility test confirms the feasibility of SFE indicators to evaluate the moisture susceptibility[15].

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Zhang et al. compared the SFE test result with adhesion grade and TSR obtained from laboratory test of 6 different WMA and the relevance among them were studied[16].

There are more factors impacting the moisture susceptibility of WMA compared to HMA[17]. In addition to the commonly accepted factors of HMA, the involvement of warm mixing additives and the mixing procedure applied also attracted attentions of researchers on their impact to moisture susceptibility of WMA. Hurley et al. found that the influence of different warm mixing additives on different aggregates is distinct[18-20]. Zaumanis noted that the poor adhesion between asphalt and aggregates may occur due to the unevaporated water remained during some warm mixing process, thus leading to negative performance of WMA[21].

Present researches have made remarkable investigation on the SFE theory and the influencing factors of moisture susceptibility of WMA, while it still can be noticed that few researches draw concerns on the influence of moisture content and the mixing process. In this research, on the basis of SFE theory, a novel indicator for evaluating the asphalt-aggregate adhesive property with different moisture contents is proposed. At the meantime, a three-phase model of aggregate-asphalt-warm mixing additive is introduced enhanced from the conventional two-phase model by taking the process of dry mixing method into consideration. The influence of several factors on the moisture susceptibility is analyzed using the advanced indicator and model put forward in this paper and the freeze-thaw splitting test is applied for the verification of SFE test.

2. Surface Free Energy Theory

The SFE theory provides a quantitative measurement method for adhesion properties between aggregates and asphalt. Having the SFE components of asphalts and aggregates contributes to an insight prediction of moisture susceptibility.

2.1. Two-phase model

In the traditional two-phase model, the adhesion process of asphalt and aggregate can be expressed as asphalt + stone → asphalt-stone. The amount of energy change per unit area of the adhesion interface is the adhesion work(W_{as}). The larger the W_{as} is, the stronger the asphalt-stone interface is. The adhesion work without moisture can be calculated according to **Eq. 1**. When water related damage appears in the asphalt pavement, water enters the void, and then gradually adheres with aggregate by replacing asphalt. This process requires work by external forces, which is called the adhesion work with moisture(W_{asw}), the physical meaning of which is the energy change per unit after two contacted materials is separated by water[22]. The larger the W_{asw} is, the weaker the asphalt-stone interface is. The adhesion work with moisture can be calculated according to **Eq. 2**.

$$W_{as} = \gamma_a + \gamma_s - \gamma_{as} = 2\sqrt{\gamma_s^{LW}\gamma_a^{LW}} + 2\sqrt{\gamma_s^+\gamma_a^-} + 2\sqrt{\gamma_s^-\gamma_a^+} \quad (1)$$

$$W_{asw} = \gamma_{sw} + \gamma_{aw} - \gamma_{as} = 2\gamma_w + 2\sqrt{\gamma_a^{LW}\gamma_s^{LW}} + 2\sqrt{\gamma_a^+\gamma_s^-} + 2\sqrt{\gamma_a^-\gamma_s^+} - 2\sqrt{\gamma_a^{LW}\gamma_w^{LW}} - 2\sqrt{\gamma_s^{LW}\gamma_w^{LW}} - 2\sqrt{\gamma_a^+\gamma_w^-} - 2\sqrt{\gamma_a^-\gamma_w^+} - 2\sqrt{\gamma_s^+\gamma_w^-} - 2\sqrt{\gamma_s^-\gamma_w^+} \quad (2)$$

Where, γ_a, γ_s and γ_w represent the surface free energy of asphalt, stone and water respectively, mJ·m^{-2}; γ_{sw}, γ_{sw} and γ_{aw} represent the stone-water, stone-water and asphalt-water interface energy, mJ·m^{-2}; γ^{LW} is the van der Waals component, mJ·m^{-2}; γ^+ and γ^- is the Lewis acid term and base term, mJ·m^{-2}.

In addition, some researchers have proposed some comprehensive indicators by considering the adhesion work with/without moisture and cohesion work of asphalt, such as ER_1, ER_2, ER_1·SSA, ER_2·SSA, etc. Among them, ER_2 is proved to be well-correlated with indicator of moisture susceptibility, and furthermore, a threshold value is recommended in a NCHRP report[23-24]. Therefore, in this paper, ER_2 is used as the comprehensive indicator, noted as ER. The larger the ER value, the better the moisture susceptibility of corresponding asphalt mixture. ER can be calculated as **Eq. 3**.

$$ER = \left|\frac{W_{as}\text{-}2\gamma_a}{W_{asw}}\right| \tag{3}$$

2.2. Three-phase adhesion model

In the conventional two-phase adhesion model, only asphalt(or warm mix additive modified asphalt) and aggregate are considered, as shown in **Figure 1a)**, which is suitable for wet mixing process. However, in the engineering practice of WMA, the dry mixing is also widely used during which the aggregates are first mixed with warm mix additives and afterwards with asphalt, as shown in **Figure 1b)**. This process is absolutely inconsistent with the original two-phase model. Hence, a corresponding three-phase model needs to be established which takes warm mix agent into account. The adhesion in dry mixing method can be expressed as asphalt + extra agent + stone → asphalt-extra agent-stone. According to its energy change, the corresponding formula of adhesion work without moisture(W_{ase}) can be introduced, as shown in **Eq. 4**.

$$\begin{aligned} W_{ase} &= \gamma_{ae} + \gamma_{se} - \gamma_a - 2\gamma_e - \gamma_s \\ &= 2(\sqrt{\gamma_e^{LW}\gamma_a^{LW}} + \sqrt{\gamma_s^{LW}\gamma_e^{LW}} + \sqrt{\gamma_e^{+}\gamma_a^{-}} + \sqrt{\gamma_e^{-}\gamma_a^{+}} + \sqrt{\gamma_e^{+}\gamma_s^{-}} + \sqrt{\gamma_e^{-}\gamma_s^{+}} \end{aligned} \tag{4}$$

Where, γ_{ae} and γ_{se} denote the interfacial energy of asphalt-extra agent and aggregate-extra agent, respectively, mJ·m^{-2}; γ_e is the surface free energy of extra agent.

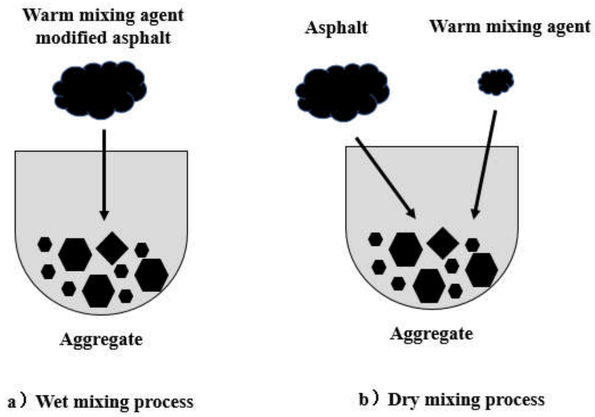

Figure 1. Wet and dry mixing process.

The adhesion failure process with moisture of three-phase model is complex. The interfacial failure caused by water may occur at two interfaces. One is the warm mixing agent-asphalt interface, and the other is the warm mixing agent-aggregate interface, as shown in Figure 2. Assuming a 50/50 split between the two scenarios, then the formula of adhesion with moisture is calculated as Eq.5, and ER can be calculated as Eq.6.

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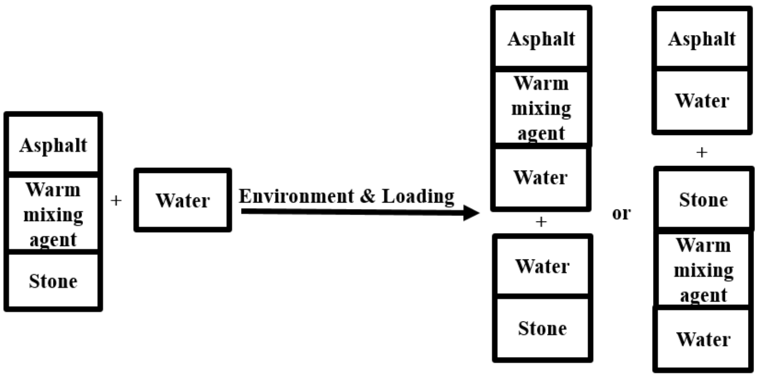

Figure 2. The adhesion failure process with moisture in dry mixing.

$$\begin{aligned} W_{asew} &= \frac{1}{2}(2\gamma_{ew} + 2\gamma_{sw} - \gamma_{ae} - \gamma_{se}) \\ &= \sqrt{\gamma_a^{LW}\gamma_e^{LW}} + \sqrt{\gamma_e^{LW}\gamma_s^{LW}} + \sqrt{\gamma_a^{+}\gamma_e^{-}} + \sqrt{\gamma_a^{-}\gamma_e^{+}} + \sqrt{\gamma_e^{+}\gamma_s^{-}} \\ &\quad + \sqrt{\gamma_e^{-}\gamma_s^{+}} - 2\sqrt{\gamma_e^{LW}\gamma_w^{LW}} - 2\sqrt{\gamma_s^{LW}\gamma_w^{LW}} - 2\sqrt{\gamma_e^{+}\gamma_w^{-}} \\ &\quad - 2\sqrt{\gamma_e^{-}\gamma_w^{+}} - 2\sqrt{\gamma_s^{+}\gamma_w^{-}} - 2\sqrt{\gamma_s^{-}\gamma_w^{+}} + 4\gamma_w + \gamma_s - \gamma_a \end{aligned} \quad (5)$$

$$ER = \frac{1}{2}\left|\frac{W_{as}\text{-}2\gamma_a}{W_{asw}} + \frac{W_{as}\text{-}2\gamma_a}{W_{asw}}\right| = \left|\frac{W_{as}\text{-}\gamma_a - \gamma_e}{W_{asw}}\right| \quad (6)$$

The three-phase model can characterize the process of dry mixing method and the corresponding adhesion indicators can be calculated. It enables the SFE theory to study the effect of mixing process on water stability of WMA.

3. Materials and Methods

3.1. Materials

In this research, two kinds of asphalt are involved including base asphalt with penetration 60/80 and I-D linear SBS modified asphalt. Each index of both asphalt meets the requirement of *Technical Specification for Construction of Highway Asphalt Pavements standards*, a Chinese standard[25]. The specific properties are shown in **Table 1**.

Table 1. Properties of Asphalt.

Indicator	Penetration (25°C, 100g)	Ductility (cm, 5cm/min)	Softening Point (°C)
	70# Base asphalt		
Properties	64.1	78.8	50.7
Requirement	60-80	≥40	≥43
	SBS modified asphalt		
Properties	57	28.5	85
Requirement	40-60	≥20	≥60

*The test temperature of ductility for 70# base asphalt and SBS modified asphalt is 15°C and 5°C respectively.

Additionally, five kinds of warm mixing agents shown in **Figure 3** are employed in this study. Among them, agent A and B are fine and course white particles respectively. Agent C and D are both brown viscous liquids. Agent E is white latex. The mixing content is summarized in **Table 2**.

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Figure 3. Five kinds of warm-mixing agents.

Table 2. Mixing content of warm mixing agents.

Additives	Mixing content
A	3 wt.% to the aggregate
B	3 wt.% to the bitumen
C	6 wt.% to the bitumen
D	6 wt.% to the bitumen
E	10 wt.% to the bitumen

Three kinds of aggregates, including limestone, basalt and granite, which are commonly used in the field of road engineering, are selected for further research. The density indexed are shown in **Table 3**.

Table 3. Density indexes of aggregates.

Aggregate type	Limestone	Basalt	Granite
Bulk Density/g·cm^{-3}	2.692	2.815	2.721
Apparent Density/g·cm^{-3}	2.720	2.933	2.784

In order to study the factor of aggregate moisture content, limestone with different moisture contents is obtained by soaking limestone in water for three hours and placing it in a 145°C oven for different time. The quality is recorded every half an hour and therefore the relationship between the moisture content of the aggregate and the drying time can be acknowledged, which is shown in **Table 4** and **Figure 4**.

Table 4. Moisture content of limestone at different drying time.

Drying time	0	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5
Moisture content	4.8	3.8	2.9	2.1	1.5	0.9	0.4	0.1	0.01	0

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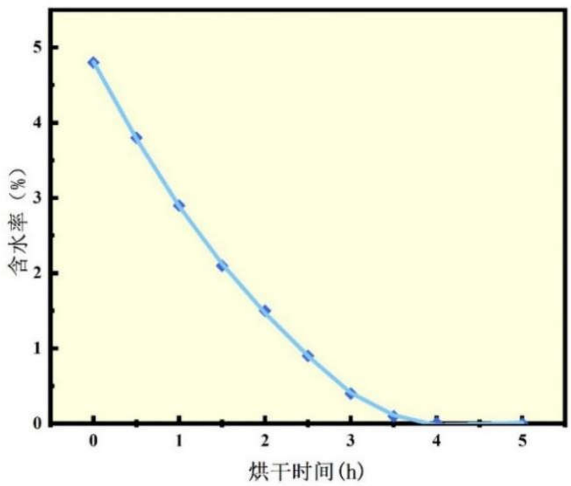

Figure 4. The moisture content of limestone at different drying time.

3.2. Experimental methods

3.2.1. Surface free energy testing technology

The sessile drop method is employed in this research to test the surface free energy of asphalt and aggregates. The instrument used is the contact angle system OCA as shown in **Figure 5**, of which the theoretical basis is the Young's equation (**Eq. 7**) deduced in **Figure 6**. Combining it with the LW-AB model (Lewis Acid/Base Model) of **Eq. 8**, **Eq. 9** can be obtained. Regarding the solid as the object to be measured, by increasing the number of known liquids, the linear equation set shown in **Eq. 10** can be established and the surface free energy parameters can be obtained when the equation is solved.

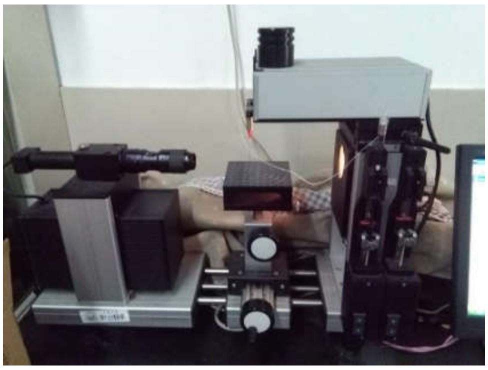

Figure 5. Contact angle system OCA.

$$\gamma_s = \gamma_l \cos\theta + \gamma_{sl} \tag{7}$$

$$\gamma = \gamma^{LW} + \gamma^{AB} = \gamma^{LW} + 2\sqrt{\gamma^+\gamma^-} \tag{8}$$

$$\gamma_l(1+\cos\theta) = 2(\sqrt{\gamma_s^{LW}\gamma_l^{LW}} + \sqrt{\gamma_s^+\gamma_l^-} + \sqrt{\gamma_s^-\gamma_l^+}) \tag{9}$$

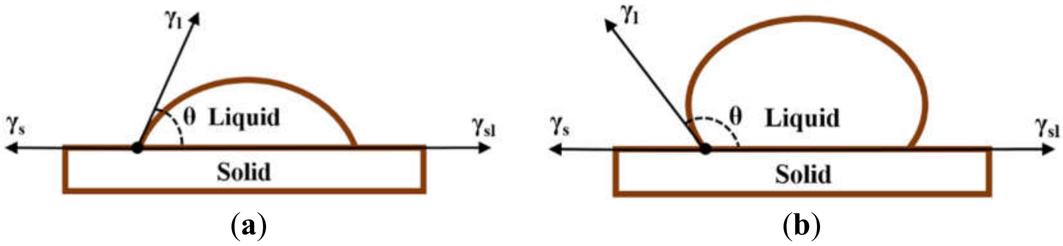

Figure 6. Experimental Principle (a) θ<90°, (**b**） θ>90°.

$$\begin{bmatrix} \sqrt{\gamma_{l_1}^{LW}} & \sqrt{\gamma_{l_1}^{+}} & \sqrt{\gamma_{l_1}^{-}} \\ \sqrt{\gamma_{l_2}^{LW}} & \sqrt{\gamma_{l_2}^{+}} & \sqrt{\gamma_{l_2}^{-}} \\ \sqrt{\gamma_{l_3}^{LW}} & \sqrt{\gamma_{l_3}^{+}} & \sqrt{\gamma_{l_3}^{-}} \end{bmatrix} \begin{bmatrix} \sqrt{\gamma_{s}^{LW}} \\ \sqrt{\gamma_{s}^{-}} \\ \sqrt{\gamma_{s}^{+}} \end{bmatrix} = \begin{bmatrix} \frac{\gamma_{l_1}(1+\cos\theta_1)}{2} \\ \frac{\gamma_{l_2}(1+\cos\theta_2)}{2} \\ \frac{\gamma_{l_3}(1+\cos\theta_3)}{2} \end{bmatrix} \quad (10)$$

Where, θ represents the contact angle between the test solid and known liquid; γ_s and $\gamma_l$represent the surface free energy of solid and liquid respectively, mJ·m^{-2}; γ_{sl} represents the solid-liquid interface energy, mJ·m^{-2}; l_1, l_2 and l_3 represent different known liquids.

In the NCHRP report, the surface energy parameters of five known liquids suitable for testing asphalt and aggregates are given, which are listed in **Table 5**[24]. Some preliminary researches have been done to select proper liquids based on conditional number(CN) to reduce the impact of parameters on test results. As a consequence, distilled water, diiodomethane and glycerin are chosen for the following test.

Table 5. The surface energy parameters of five liquids.

Liquid type	γ(mJ/m²)	γ^{LW}(mJ/m²)	γ^{-}(mJ/m²)	γ^{+}(mJ/m²)
Distilled water	**72.8**	**21.8**	**25.5**	**25.5**
Glycol	**48.0**	**29.0**	**47.0**	**1.92**
Glycerin	**64.0**	**34.0**	**57.4**	**3.92**
Formamide	**58.0**	**39.0**	**39.6**	**2.28**
Diiodomethane	**50.8**	**50.8**	**0**	**0**

3.2.2. Freeze-thaw splitting test

According to corresponding standard of China, the moisture susceptibility is evaluated using freeze-thaw splitting test[26]. The test requires two groups of four specimens prepared by 50 times of Marshall compaction in each side and one group, namely the freeze-thaw group, needs to undergo freeze-thaw conditioning while the other group is the control group stored in ambient environment. Both groups are tested at 25℃ and the splitting strength can be obtained by **Eq.11**. The tensile strength ratio(TSR) can be calculated as **Eq. 12**.

$$S_{T1} \ or \ S_{T1} = \frac{0.006287P_T}{h} \quad (11)$$

$$TSR = \frac{S_{T2}}{S_{T1}} \times 100 \quad (12)$$

Where, TSR is tensile strength ratio (%); S_{T1} and S_{T2} are splitting tensile strength (kPa) under dry and freeze-thaw conditioning, respectively; P_T is the maximum load (N); h is the height of the specimen, mm.

4. Results and Discussion

The factors affecting the moisture susceptibility of WMA, which are complicated, can be studied by using SFE theory. The characteristics of raw materials, the mixture design, and the mixing temperature will all make a difference[27]. In this paper, the influence of aggregate type, aggregate moisture content, warm mix additives, asphalt type and mixing method on the water stability of WMA is studied utilizing SFE theory.

4.1. Surface free energy components

The test samples and the testing procedures are shown in **Figure 7**. The parameters based on surface free energy can be calculated after contact angles are measured and the results are shown in **Table 6**.

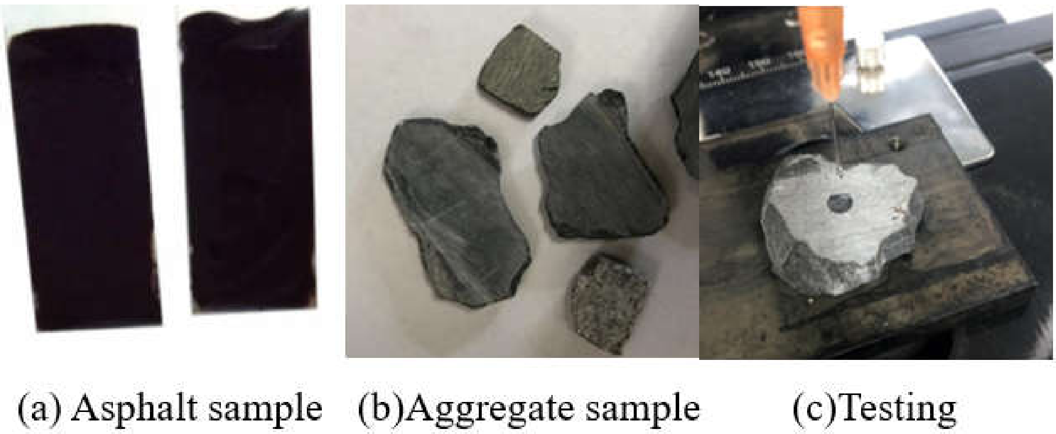

Figure 7. Testing samples and procedure.

Table 6. SFE parameters.

Items	γ(mJ/m²)	γ^{LW}(mJ/m²)	γ^{-}(mJ/m²)	γ^{+}(mJ/m²)
Base asphalt	34.84	33.26	1 .04	0.60
Agent A modified asphalt	43.04	41.04	0.69	1.45
Agent B modified asphalt	33.03	32.98	0.01	0.05
Agent C modified asphalt	34.84	32.59	2.00	0.64
Agent D modified asphalt	37.21	35.77	0.74	0.70
Agent E modified asphalt	34.60	33.32	0.85	0. 48
SBS modified asphalt	33.70	31.28	2.60	0.57
Agent A modified SBS	35.06	33.15	2.31	0.39
Agent B modified SBS	34.34	32.13	2.60	0.47
Agent C modified SBS	39.68	34.61	5.96	1.08
Agent D modified SBS	32.29	31.10	1.39	0.25
Agent E modified SBS	37.11	34.11	2.95	0.76
Basalt	42.8	36.9	18.04	0.48
Granite	40.57	35.49	14.66	0.44
Limestone	49.68	40.40	24.85	0.87
Agent E	30.09	25.05	0.67	9.45

4.2. The effect of aggregate type

In order to explore the effect of aggregate type on the water stability of WMA, the adhesion parameters of basalt, granite, limestone with agent A modified base asphalt are calculated and shown in **Figure 8**. The TSR test values of corresponding mixtures are prepared and tested for verification. The mixture gradation is AC-20. Results are shown in **Table 7**.

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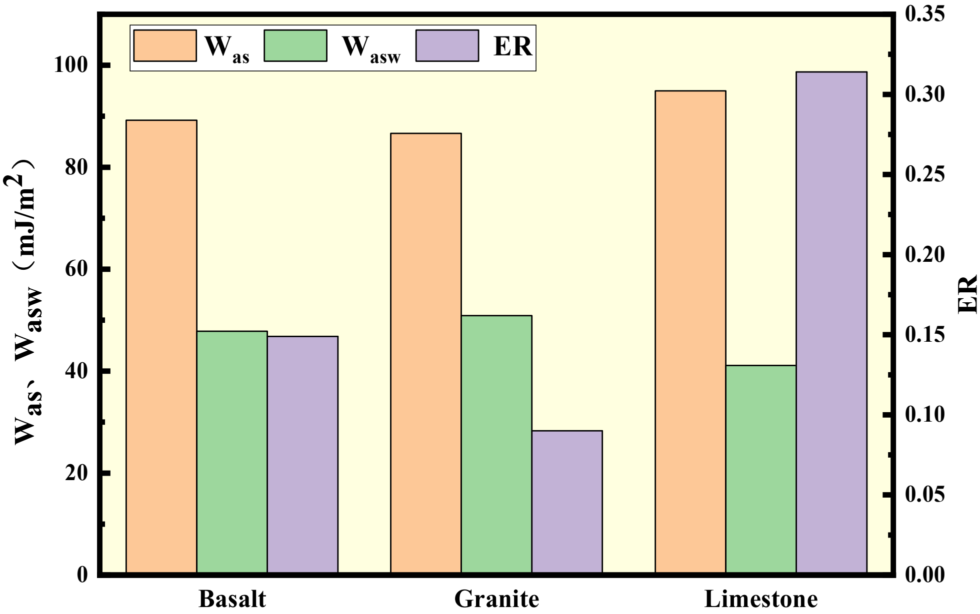

Figure 8. Values of Adhesion indicators of different aggregates and agent A.

Table 7. TSR test results of different aggregates.

Aggregate	Basalt	Granite	Limestone
TSR/%	80.1	76.9	81.4

It can be seen from the viewpoint of adhesion indicators that the type of aggregate has a significant influence on the asphalt-aggregate adhesion. The ranking result is limestone > basalt > granite ordered by W_{as}, W_{asw} as well as *ER*. The ranking of TSR results shows favorable consistence with the adhesion indicators.

4.3. The effect of aggregate moisture content

None of the existing adhesion indicators consider the effect of aggregate moisture content. Calculation models of adhesion work with and without moisture respectively simulate conditions of no water and adequate water. In this paper, the effective adhesion work is proposed based on the moisture content of aggregate in the mixtures. The physical meaning of effective adhesion is the value of the surface energy change on a unit area of the aggregate after the adhesion among water, asphalt and aggregate. The value is positively correlated with asphalt content and adhesion work without moisture, and negatively correlated with moisture content and adhesion work with moisture as shown in **Eq. 13**. The larger the effective adhesion work, the better the adhesion between asphalt and aggregate.

$$W_{as,eff} = W_{as} \times \frac{p_a}{p_a + w} - W_{asw} \times \frac{w}{p_a + w} \quad (13)$$

Where, $W_{as,eff}$ is the effective adhesion work, mJ/m^2; ω and P_a represent the aggregate moisture content and asphalt content, respectively.

The adhesion work with and without moisture between warm-mixing agent A modified asphalt and different aggregates are calculated as shown in **Table 8**. Analysis of the results shows that for all combinations of asphalts and aggregates, W_{asw} is less than W_{as}, meaning that water is more prone to achieve adhesion to aggregate than asphalt. This indicates that the presence of water influences the adhesion between asphalt and aggregate thus creating weakened adhesion areas at the interface of asphalt and aggregates, which can result in easier water invasion into the asphalt-aggregate interface and moisture damage.

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Table 8. Value of W_{as} and W_{asw}

Asphalt type	W_{as} (mJ/m²)			W_{asw} (mJ/m²)		
	Basalt	Granite	Limestone	Basalt	Granite	Limestone
Agent A modified asphalt	89.210	86.652	94.992	47.819	50.880	41.100

Meanwhile, specimens using warm mixing additive agent A and limestone with moisture contents of 0%, 0.01%, 0.4%, and 1.5% respectively are prepared for freeze-thaw splitting test. The mixing temperature is 135℃, the gradation is AC-13, and the asphalt content is 5.0%. The TSR results and effective adhesion work of mixtures with different moisture contents are summarized and then subjected to linear regression analysis shown in **Figure 9**.

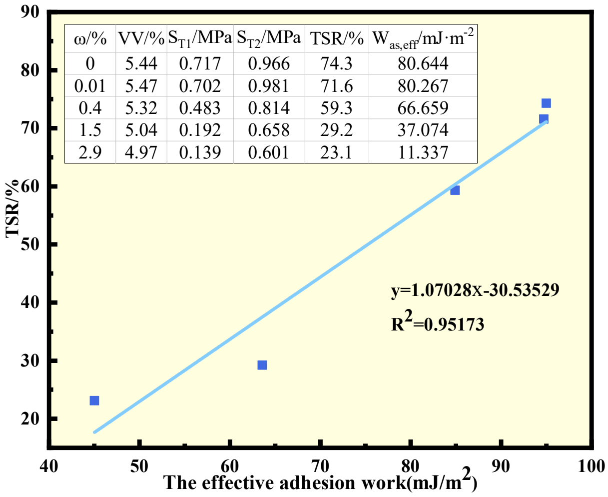

Figure 9. TSR、$W_{as,eff}$ and Linear regression analysis

From the figure, it can be seen that the effective adhesion work decreases significantly as the moisture content of aggregate increases, indicating that the presence of water in the aggregate significantly degrades the adhesion of the asphalt to the aggregate. The TSR values verified this phenomeno. As the moisture content of the aggregate increases, the splitting strength without freeze-thaw cycles decreases slightly, while that with freeze-thaw conditioning decreases sharply, leading to a dramatic decline in TSR.

Linear regression analysis shows that the correlation coefficient between TSR and $W_{as,eff}$ calculated reaches 0.95 which means strong correlation. This proves the validity of the effective adhesion work in evaluating the water stability of the WMA.

4.4. The effect of warm-mixing agent type

It has been researched that warm-mixing agents have an important effect on the performance of WMA[18,20]. In this section, the adhesion indicators of different warm-mixing modified base asphalts to limestone are calculated. The results are shown in **Table 8** and **Figure 10**.

Table 8. Adhesion indicators of asphalts and limestone.

Asphalt type	**W_{as} (mJ/m²)**	**W_{asw} (mJ/m²)**	**ER**
Base asphalt	82.938	37.442	0.4385
Agent A modified asphalt	94.992	41.100	0.3142
Agent B modified asphalt	82.007	38.276	0.4015
Agent C modified asphalt	75.420	45.005	0.2102
Agent D modified asphalt	83.185	33.994	0.5297
Agent E modified asphalt	85.975	39.468	0.3657

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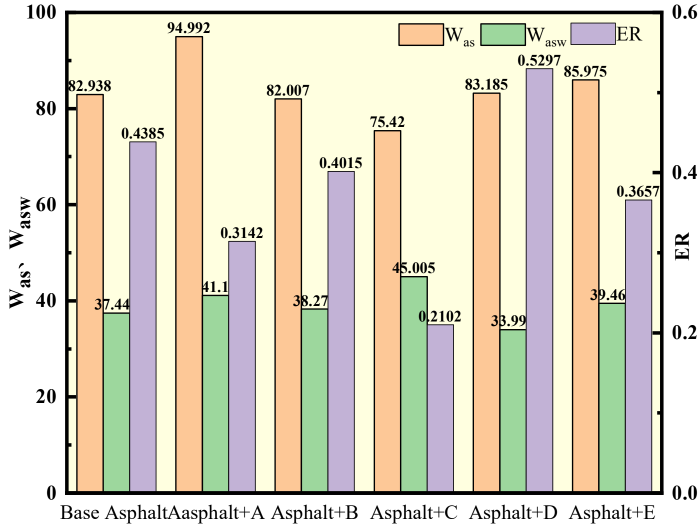

Figure 10. Adhesion indicators of asphalts and limestone.

The ranking based on calculation of the three adhesion indicators are different. The result ranked by the W_{as} is A>E>D>B>C while W_{asw} and ER D>B>E>A>C. The difference emerges due to the consideration of the effect of moisture. When lacking the consideration of water, agent A and D are able to promote the adhesion as the W_{as} value announces while all the agents deteriorate the adhesion when moisture is taken into account as W_{asw} and ER, with oil-based warm-mixing agent D having the least effect.

To verify the above findings, WMA samples using warm-mixing agent A, D and E are compacted and the TSR test is conducted. The mixture gradation is AC-20, aggregate is limestone. Results are shown in the **Table 9**.

Table 9. TSR of WMA using different warm-mixing agents.

Agent	HMA	Agent A	Agent D	Agent E
TSR/%	**91.9**	**81.3**	**86.6**	**81.5**

From the view of TSR, all the warm-mixing agent degrade the moisture susceptibility among which mixture with agent D is least affected. The ranking by TSR test result is consistent with and the calculation of W_{asw} and ER. The reason may be the possible introduction of moisture brought by agent A and E. Agent A is a kind of water soluble solid and thus can easily absorb water while agent E is in a form of emulsion containing water. Agent D is oil-based thus hydrophilic, and will not be a cause for the introduction of water. Overall, all the indicators except W_{as} come to consensus that the water stability of WMA with oil-based warm-mixing agent is better.

4.5. The effect of asphalt type

To investigate the effect of asphalt type on the moisture stability of WMA, the adhesion indicators are calculated based on the SFE parameters of base asphalt, SBS modified asphalt and limestone aggregates, and the result is shown in **Figure 11**. The freeze-thaw splitting test is conducted for verification on the hot mix and warm mix simultaneously with limestone and base asphalt or SBS modified. The warm mix additive is agent C and the mixing temperature is 30℃ lower than HMA. The test result is shown in **Table 10**.

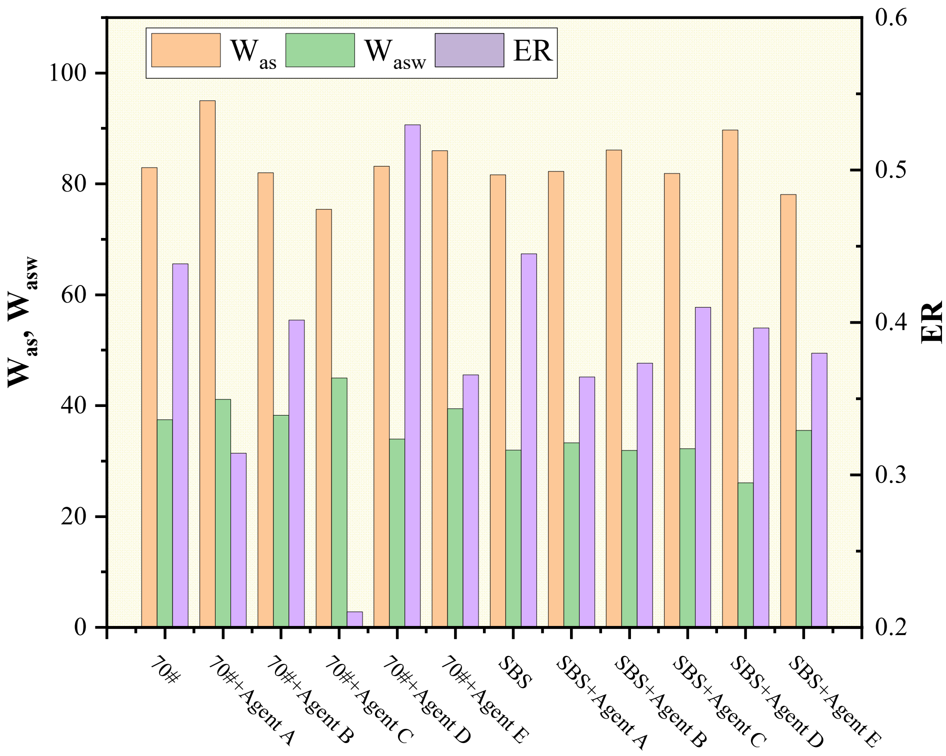

Figure 11. Adhesion indicators of different asphalt with different warm mix additives.

Table 10. TSR of mixture with different asphalt and warm mix additive C.

Asphalt type	Mixture type	TSR/%
SBS	HMA	91.0
	WMA-C	93.4
70#	HMA	76.7
	WMA-C	68.9

It can be inferred from the result that when different warm mix additive is applied to different asphalt, the adhesion properties between asphalt and aggregate are distinct. In other words, there is compatibility between asphalt and warm mix agents. From the calculation result of ER, agent D is the best among the 5 agents for base asphalt while agent C for SBS modified asphalt. The choice of asphalt can determine the application of warm mix agents and therefore result in distinct performances of WMA mixture.

In the meantime, when applying different asphalt to warm mixing, the effect on the moisture susceptibility is distinct. To take the combination of asphalt + agent C as an example, the introduction of it results in an extreme decrease in ER for base asphalt while the ER for SBS modified asphalt is almost equivalent to original asphalt and is much higher than agent C modified base asphalt. This is verified by the TSR result. Also, it is worthy to notice that the TSR result of base asphalt mixture is consistent with ER value which both shows a sharp decrease while that of SBS modified asphalt shows a slight enhancement and is not consistent with ER. There may be other more sophisticated mechanism for the interaction between polymer modified asphalt and warm mix agent that compensates the slight decline in SFE parameters.

4.6. The effect of mixing process

As interpreted above, the conventional two-phase asphalt-aggregate adhesion model is suitable for the wet mixing method, in which the warm mixing additives are added into asphalt to modified asphalt first and then mixed with aggregates. When confronting with additives needing dry mixing method, the adhesion of asphalt, aggregate and warm-mixing agent should be characterized by the three-phase model proposed in previous sections. In this article, the adhesion indicator ER of agent

E with base asphalt based on two- and three-phase model is calculated and shown in **Figure 12**. Dry mixing and wet mixing WMA mixture specimens using AC-13 gradation for TSR test are prepared with agent E, limestone and base asphalt for validation. The mixing temperature is 135°C. The freeze-thaw splitting test result is shown in **Table 11**.

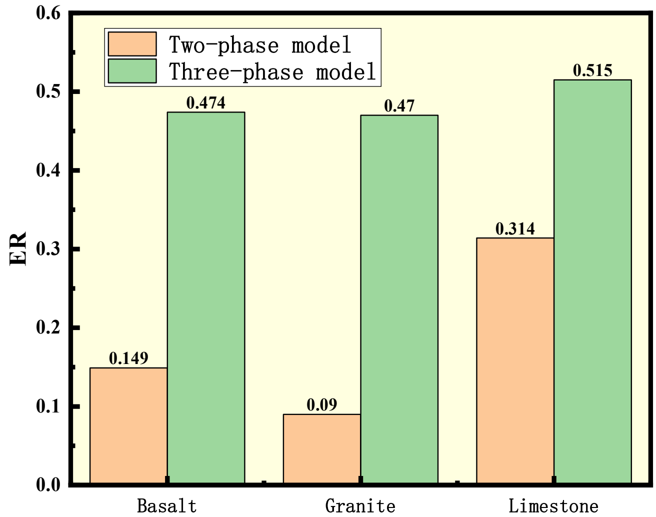

Figure 12. Adhesion indicators ER based on different models.

Table 11. TSR values of different mixing method.

Mixing method	VV/%	S_{T1}/MPa	S_{T2}/MPa	TSR/%
Dry	5.44	0.717	0.966	81.7
Wet	5.47	0.567	0.850	74.3

For different types of aggregates, the ER values of the three-phase model are greater than those of the two-phase model, indicating better adhesion prepared by dry mixing method. The TSR result demonstrates the theoretical calculation, with mixture prepared by dry mixing method superior to that by wet mixing method. This consistency also indicates that the three-phase model proposed in this paper is effective for predicting the water stability of the WMA prepared by the dry mixing method.

5. Conclusion

Using surface free energy theory, the influence of several factors on the moisture susceptibility of WMA focusing on the adhesion properties of asphalt-aggregate interface is studied, and the following conclusions can be drawn:

1. Aggregate type, moisture content of aggregate, warm-mixing agent type, asphalt type and mixing process have significant effects on the water stability of WMA. And the conclusions of adhesion indicators based on SFE and conventional moisture susceptibility test method result are consistent. Specifically, water content of aggregate state as the most significant factor affecting the moisture susceptibility. The presence of water greatly affects the performance of the mixture. Therefore, the dryness of aggregate should be strictly controlled in WMA.
2. Based on the surface free energy theory, the effective adhesion work considering the water content of the aggregate is proposed to characterize the aggregate-asphalt adhesion condition under different water contents. This indicator is highly correlated with TSR value and can be used as a convenient index to predict the moisture susceptibility of WMA.
3. The three-phase model of asphalt-warm mixing agent-aggregate is proposed according to the production process of dry mixing method. The corresponding calculation equations of adhesion indicators are also derived. The consistency between the adhesion indicator and TSR indicates that the three-phase model is applicable to the adhesion process of WMA prepared by the dry mixing method.

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