

RELATIONSHIP BETWEEN FOAMING BEHAVIOR AND SURFACE ENERGY OF ASPHALT BINDER

Jian-ping Xu^{1,2}, Kai Zhang³ and Yao-ting Zhu³

1. *College of Traffic and Transportation, Chongqing Jiaotong University, Chongqing, No. 66 university avenue, nankiang district, China; 318661112@qq.com*
2. *Jiangxi Provincial Expressway Investment Group Co.Ltd, Nanchang, No. 367 chaoyang road, China*
3. *Department of Road and Material, Jiangxi Transportation Institute, Nanchang, No. 809 sands avenue, China; kaizhang@whut.edu.cn, 12322756@qq.com*

ABSTRACT

To solve the problem of insufficiency in microscopic performance of foamed asphalt binder, surface energy theory was utilized to analyze the foaming behavior and wettability of asphalt binder. Based on the surface energy theory, the Wilhelmy plate method and universal sorption device method were employed to measure the surface energy components of asphalt binders and aggregates, respectively. Combined with the traditional evaluation indicator for foamed asphalt, the relationship between the foaming property and surface energy of asphalt binder was analyzed. According to the surface energy components, the wettability of asphalt binder to aggregate was calculated to verify the performance of foamed asphalt mixture. Results indicate that the foaming behavior of asphalt will be influenced by surface energy, which will increase with the decline of surface energy. In addition, the surface energy of asphalt binder significantly influences the wettability of asphalt binder to aggregates. Meanwhile, there is an inversely proportional relationship between surface energy of asphalt binder and wettability. Therefore, it can be demonstrated that surface energy is a good indicator which can be used to evaluate the foaming behavior of the asphalt binder. And it is suggested to choose the asphalt binder with lower surface energy in the process of design of foamed asphalt mixture.

KEYWORDS

Foamed asphalt mixture, Surface energy theory, Foaming behavior, Surface energy, Wettability

INTRODUCTION

As a stabilizer and regenerative, foamed asphalt has extremely wide applicability. In many countries, foamed asphalt technology has been used for road substrate materials (including recycled asphalt mixture). Foamed asphalt for cold recycling technology can not only solve the stacking problem of asphalt recycling material (RAP), which is conducive to protecting the environment and saving energy, but also has less impact on the environment in the construction process [1~2]. In the application process of foamed asphalt technology, the foaming property of the asphalt binder directly influences on the performance of the foamed asphalt mixture [3]. A good foaming performance can obviously improve the mechanics and road performance of cold recycled asphalt mixture [4~5]. Therefore, it is necessary to carry out in-depth research and analysis on the foaming performance of asphalt in the study of cold recycled asphalt pavement.

At present, the characteristics of foamed asphalt can be characterized by the expansion rate (ER) and half-life (HL), which can be mainly affected by many factors [6~7]. Meanwhile, many researches have been conducted for foaming property of asphalt at home and abroad. Brennen et al. studied the influence of water content and temperature on expansion rate and half-life [8]. Maccarone et al. used the additive agent to improve the foaming performance of foamed asphalt [9]. Yang et al. discussed the effect of viscosity on the performance of asphalt foaming in terms of main indicators of asphalt [10]. It can be seen that researches on the performance of asphalt foaming mainly focused on the external influencing factors, such as temperature, water content, additive, without the in-depth conducting of microscopic performance analysis. In addition, based on the macroscopic nature of asphalt binder, a few researches have shown that foaming performance mainly depends on the components of asphalt binder [11~13]. However, different categories of asphalt have different internal components, so that it is hard to accurately judge advantages and disadvantages of asphalt foaming in terms of the main technical indexes of asphalt [14~15]. Based on the foaming mechanism of asphalt, the foaming process is a kind of surface physical chemistry which can mainly divided into four consecutive stages including cooling, expansion, film-formation and metastability. These series of surface physical chemistry are the keys to promote the foaming of asphalt binder. Meanwhile, grasping the foam stability of asphalt is an effective way to improve the foaming property of asphalt and road performance of foamed asphalt mixture. In addition, how to use surface energy of the asphalt binder to evaluate the performance of foamed asphalt mixture is another key issue in this study.

As the basis of surface physical chemistry theory, surface energy theory is widely used in many important fields, which can well explain the physical chemistry on surface or interface of materials [16~17]. Meanwhile, the property of surface expansion and contraction of materials can be accurately characterized through surface energy which is a subsistent contraction force on the surface of a material. Therefore, the purpose of this paper is to utilize the surface energy theory to analyze the relationship between the foaming performance and surface energy of asphalt binder, with reasonably forecasting the foaming performance of asphalt binder through conducting foaming test and Wilhelmy plate method. Finally, the wettability of asphalt binder to aggregate was used to verify the performance of foamed asphalt mixture based on the relationship between the foaming performance and surface energy of asphalt binder.

FOAMING PERFORMANCE OF ASPHALT

Materials

In this study, 4 kinds of representative asphalt binders were used to manufacture foamed asphalt. According to standard test methods of bitumen and bituminous mixtures for highway engineering [18], the main indexes of asphalt were measured, as shown in Table 1.

Tab. 1 - Results of indexes test

Type	KLMY-70	Guo Chuang AH-70	SHELL-70	China Offshore AH-70	Requirement
Penetration (100g, 5s, 25°C) (0.1mm)	69.6	66	66.7	70.5	60-80
Ductility(5 cm/min, 5°C)(cm)	156	125	161	120	≥100
Softening Point (°C)	48.9	47.5	49.5	47.1	≥46

Theoretical limit for the water content

The influence of water on the foamed asphalt cold recycled pavement can be divided into two aspects: the effect on the foaming performance of asphalt; and the effect on the performance of foamed asphalt mixture. Firstly, the foaming process of asphalt is a series of physical reactions, including the following process:

- Thermal exchange occurs on the surface of hot asphalt and cold moisture droplets, accompanied by evaporation of water vapor.
- The steam bubbles are pressed into the continuous phase of the asphalt under a certain pressure to form asphalt foam.
- During the rapid expansion of the foam, the surface tension of the asphalt film is resisted with the vapor pressure. As the foam expands, the vapor pressure decreases gradually until it forms a balance with the surface tension. But if the steam bubble expands beyond the tensile limit of the asphalt during this process, the foam will burst.
- Due to the low thermal conductivity of asphalt and water, the asphalt foam can be maintained for several seconds, but the amount of bubbles formed during the foaming process is in a steady state and prone to burst.

Researches have shown that the increase of water content will reduce the HL and improve the ER [19~20], as shown in Figure 1. The limit of water content is decided by the intersection or the adjacent points of two curves to obtain the best foaming property.

Secondly, the limit of water content will significantly influence the performance of foamed asphalt mixture [21~22]. Excessive water content will affect the compaction effect and the strength of the mixture, so the appropriate amount of water must be determined during the mixing and compaction process to optimize the performance of the foamed asphalt mixture. As a medium, water provides a channel for the dispersion of foamed asphalt in aggregates. If the amount of water is too small, it will affect the uniform dispersion of the asphalt. If the water is too much, it will cause the debonding of asphalt from the surface of aggregates. Many researches have been conducted on the determination of the optimal water content for the foamed asphalt mixture [23]. Lee has studied the water content under different grades of foamed asphalt mixtures and found that there was an optimum water content for each mixture [24]. Meanwhile, the optimum water of mixture should be 65% to 85% of the corrected AASHTO optimum water content. Sakr has obtained the optimum water consumption formula (1) from the researches of different gradation asphalt mixture, with using the statistical methods [25].

$$MMC = 8.92 + 1.48OMC + 0.4PF - 0.39BC \quad (1)$$

Where MMC = the optimum water content; OMC = the corrected AASHTO optimum water content; PF = the mass fraction of fine aggregate; BC = asphalt content.

In addition, Wirtgen found the relationship between the optimum water content and the amount of water reduction, as shown in formula (2). For the purpose of optimum mixing, the water content can be calculated according to Equation (2). Subsequently, the quality of the water to be added is calculated according to Equation (3).

$$w_{add} = w_{OMC} - w_{moist} - w_{reduce} \quad (2)$$

$$m_{water} = \frac{w_{add}}{100} \times (m_{aggregate} + m_{cement}) \quad (3)$$

Where w_{add} = added water consumption in the aggregate; w_{OMC} = the optimum water content; w_{moist} = water content in the aggregate; w_{reduce} = reduction of water; m_{water} = mass of the water; $m_{aggregate}$ = dry mass of the aggregate; m_{cement} = quality of cement.

At present, few researches are aimed to address the optimum water content in foamed asphalt and its mixture [23]. There are no relevant conclusions according to the range of water content. Therefore, this paper will determine the optimum water content in the foamed asphalt and its mixture through the follow-up performance test.

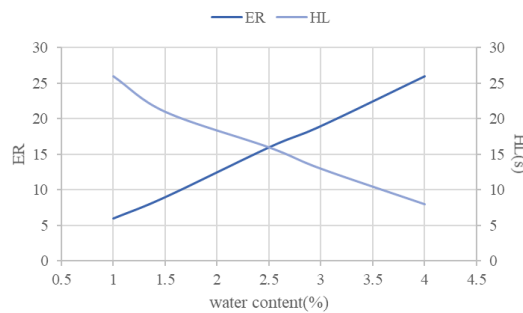


Fig. 1 - Determination method of water content for the best foaming property

Foaming test

According to the physical facilities of asphalt foaming applied in the engineering, the small equipment was employed in this study, called Wirtgen WLB 10S made in Germany, shown in Figure 2. During the process of foaming, the foaming temperature was 165°C and the water consumption was 2.5%. Meanwhile, the environment conditions such as temperature, relative humidity, water pressure, air pressure were controlled for 20 °C, 83%, 0.4 MPa and 0.55 MPa, respectively. The results of asphalt foaming tests were shown in Table 2.



(a) Asphalt foaming device



(b) Foamed asphalt

Fig. 2 - Foaming test

Tab. 2 - Results of asphalt foaming tests

Type							
KLMY-70		Guo Chuang AH-70		SHELL-70		China Offshore AH-70	
Expansion rate (%)	Half-life (s)	Expansion rate (%)	Half-life (s)	Expansion rate (%)	Half-life (s)	Expansion rate (%)	Half-life (s)
11.7	11.8	12.0	10.9	8.2	10.5	10.9	12.7

Generally, the ER and HL are used to evaluate the performance of foamed asphalt. On the one hand, the greater ER is in favor of sufficient contact and coating between foamed asphalt and aggregates. On the other hand, the longer HL can promote the mixing effect between foamed asphalt and aggregates. Generally speaking, the great expansion and long half-life can ensure good foaming property of asphalt [26~27]. Therefore, as seen in Table 2, under the same test conditions, the sequence of foaming performance for various types of asphalt was China Offshore AH-70> KLMY-70> Guo Chuang AH-70> SHELL-70.

SURFACE ENERGY THEORY

In a vacuum, there is a kind of force occurred on the material surface, which is used to balance the internal and external force, called surface energy and denoted by the Greek letter γ [28]. The surface energy of any material is mainly composed of two parts which respectively are the non-polar van der Waals component (LW) and polar acid-base component (AB), and can be represented by the formula (4):

$$\gamma = \gamma^{LW} + \gamma^{AB} = \gamma^{LW} + 2\sqrt{\gamma^+ \gamma^-} \quad (4)$$

Where γ^{LW} = Lifshitz-van der Waals component; γ^{AB} = acid-base component; γ^+ = Lewis acid component; γ^- = Lewis base component.

Simply put, the foaming of asphalt binder is mainly due to the steam bubble pressed into the continuous phase of asphalt under the certain condition, causing the asphalt foam. At the same time, the expansion of compressed vapor will lead to form a kind of asphalt film which takes advantage of its own surface energy to coat the bubble. In the process of expansion, the surface energy of asphalt film will resist to steam pressure until a state of balance, namely metastable state.

Researchers considered that the reason caused the collapse of asphalt foam in the process of expansion is a pressure difference [29]. A bubble has a nearly stable gas cell like a cellular structure, both sides of which are foam film. When three or more bubbles gather each other, the Plateau boundary is formed due to the curved asphalt film and concaving toward the gas cell. At the Plateau junction consisted of multiple bubbles, the greater curvature radius will create the pressure difference between the gas phase and the liquid phase, as shown in the Laplace equation:

$$\Delta p = \frac{2\gamma}{r} \quad (5)$$

Where r = curvature radius.

The pressure difference between the gas phase and the liquid phase will decrease with the increase of curvature radius of bubbles, therefore the hydraulic pressure in the Plateau junction is less than the place which has a small curvature. Subsequently, the liquid will flow from the place with a small curvature to the Plateau boundary with a great curvature. In addition, the pressure difference will increase with the increase of surface energy. Similarly, the increase of surface energy will promote the flow of asphalt film towards the Plateau boundary. If the asphalt film becomes thinner and reaches a certain extent, usually is from 5 to 10nm for thickness, the foam of asphalt binder will fracture, as shown in Figure 3.

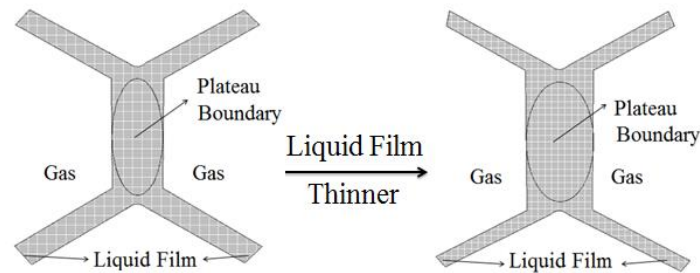


Fig. 3 - Micro structure of foamed asphalt binder

Generally, the increase of surface energy will force the fracture of asphalt foam, which is the disadvantage of property of foamed asphalt [16]. Therefore, it should be tried to choose the asphalt with lower surface energy during the preparation of foamed asphalt binder.

In addition, the better wetting property of asphalt to aggregate is more beneficial to promote the pavement performance of foamed asphalt mixture [30]. The formation of the wetting is a complex physical and chemical process. According to the surface energy theory, wettability refers to the ability of a material spreading on the surface of another material. For asphalt mixtures, a good wetting property of asphalt is favorable to wrap the aggregate and wet up the surface micro texture of aggregates, with improving the performance of asphalt mixtures. The appearance of the wetting mainly depends on the value of adhesion energy between foamed asphalt and aggregates and cohesion energy of foamed asphalt, respectively termed as W_{AB} and W_{BB} . Meanwhile, the wetting property of asphalt to aggregate can be expressed by formula (6) [31]:

$$R_s = W_{AB} - W_{BB} \tag{6}$$

Where R_s = wettability; W_{AB} = adhesion work between foamed asphalt and aggregates; W_{BB} = cohesion work of foamed asphalt.

The adhesion work is defined that when two materials are in touch with each other to form a new interface, the surface free energy of these materials will cause them to physically adhere to each other. Meanwhile, the work required to separate these two materials is defined as the adhesion work. Similarly, the cohesion energy occurs inside of the material. As a matter of fact, the adhesion energy and cohesion energy both are the results of molecular interaction, which can be described well by the surface energy theory. Finally, the adhesion work and cohesion work are explained by the formula (7) and (8), respectively [32].

$$W_{AB} = 2\sqrt{\gamma_A^{LW} \gamma_B^{LW}} + 2\sqrt{\gamma_A^+ \gamma_B^-} + 2\sqrt{\gamma_A^- \gamma_B^+} \tag{7}$$

$$W_{BB} = 2\gamma_B^{LW} + 4\sqrt{\gamma_B^+ \gamma_B^-} \tag{8}$$

Where γ_A^{LW} , γ_A^+ , and γ_A^- = surface energy components of aggregate; γ_B^{LW} , γ_B^+ , and γ_B^- = surface energy components of asphalt binder.

Generally speaking, when the cohesion work of asphalt is significantly greater than the adhesion between foamed asphalt and aggregates, the intermolecular forces in asphalt binder will be stronger than the acting force between asphalt and aggregate, leading to the reduction of the wetting property of asphalt to aggregate. However, when the cohesion work is significantly lower than the adhesion, good wetting effect will occur [33]. Subsequently, the performance of asphalt mixture will be improved obviously.

RELATIONSHIP BETWEEN THE FOAMING PERFORMANCE AND SURFACE ENERGY

Wilhelmy plate method

Based on Wilhelmy plate method, the automatic surface tensiometer was utilized to measure the surface energy components of asphalt binders, shown as in Figure 4. Based on kinetic force equilibrium, the Wilhelmy plate method can be described that when a glass slip uniformly coated with asphalt is immersed in a probe liquid solvent at a slow and constant speed of 20 μm/s, the stable and dynamic contact angle between the asphalt and the probe liquid is measured. Figure 5 shows the loading process of the glass slip. The following Equation (9) is used to calculate the contact angle from all the parameters that are determined during testing.

$$\cos \theta = \frac{\Delta F + V_{im}(\rho_L - \rho_{air}g)}{P_i \gamma_L} \quad (9)$$

Where ΔF = buoyancy difference between mass of a plate measured in air and partially immersed in a probe liquid; V_{im} = the volume immersed in the liquid; P_i = the perimeter of the bitumen coated plate surface; ρ_L = the density of the probe liquid; ρ_{air} = the air density; g = the local gravitational force; γ_L = the surface energy of the probe liquid.

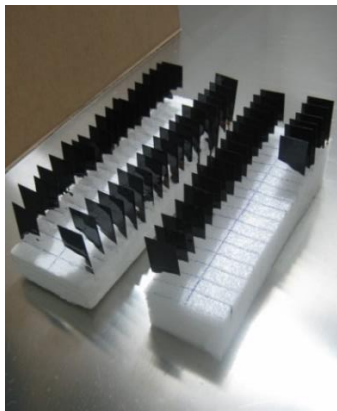


Fig. 4 - Automatic surface tensiometer

Under the environment of 20 °C, place the glass slides coated with asphalt binder into the operating chamber and conduct the test, as shown in Figure 5. On the basis of the Young-Dupre and Good-van Oss-Chaudhury equation, the surface energy components of asphalt were obtained by using the following equation [34]:

$$\gamma_i(1 + \cos \theta) = 2\sqrt{\gamma_s^{LW} \gamma_i^{LW}} + 2\sqrt{\gamma_s^- \gamma_i^+} + 2\sqrt{\gamma_s^+ \gamma_i^-} \quad (10)$$

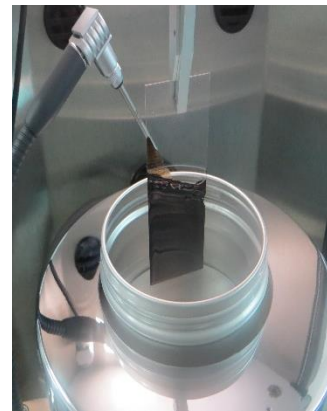
Where γ_s^{LW} 、 γ_s^+ 、 γ_s^- = three unknown components of surface energy; γ_i^{LW} 、 γ_i^+ 、 γ_i^- = surface energy components of probe liquid; γ_i = total surface energy of probe liquid; θ = the contact angle between the glass slip and the probe liquid.



(a) Asphalt sample



(b) Size measurement



(c) Measurement of contact angle

Fig. 5 - Wilhelmy plate method

Analysis of surface energy

To improve the test accuracy, four solvent liquids whose surface energies were known must be used to produce three simultaneous equations. Water, formamide, glycerin and ethanediol were used as probe liquid solvents, due to their relatively large surface energy, immiscibility with asphalt binder and differing surface energy components. The surface energy components of the four solvent liquids were listed in Table 3. According to the contact angles between the asphalt and the probe solvents, the surface energy components of the asphalt binders were calculated with Formula (7), shown as in Table 4. Figure 6 graphically illustrates the proportion of non-polar and polar component of surface energy.

Tab. 3 - Surface energies of solvents

Probe solvents	Surface energy components, (ergs/cm ²)				
	γ^{Total}	γ^{LW}	γ^+	γ^-	γ^{AB}
Distilled Water	72.8	21.8	25.5	25.5	51.0
Glycerin	64.0	34.0	3.92	57.4	30.0
Formamide	58.0	39.0	2.28	39.6	19.0
Ethanediol	48.0	29.0	1.92	47.0	19.0

Tab 4. Surface energy components of asphalt binders

Type	Surface energy components, (ergs/cm ²)					W^{BB}
	γ^{LW}	γ^+	γ^-	γ^{AB}	γ^{Total}	
KLMY-70	6.53	3.27	1.17	3.91	10.44	20.88
Guo Chuang AH-70	7.64	3.15	1.91	4.91	12.55	25.10
SHELL-70	12.17	2.19	0.79	2.63	14.80	29.60
China Offshore AH-70	6.71	4.50	0.64	3.39	10.10	20.20

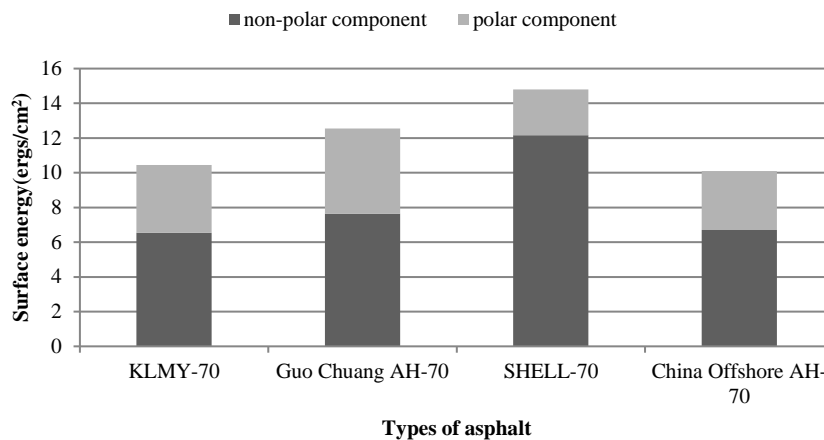


Fig. 6 - Surface energies of asphalt binders

Data in Figure 6 indicates that the order of the total surface energy of different asphalt binders is SHELL-70 > Guo Chuang AH-70 > KLMY-70 > China Offshore AH-70. The non-polar LW component of the total surface energy accounts for the largest proportion. Hence, the four materials present non-polar interaction on their surface. Moreover, according to the value of the polar acid and base composition, the surface of four kinds of asphalt mainly presents a polar base interaction, with showing acidic property in nature.

According to the influence of surface energy on foaming property of asphalt, it can be decided that the use of China Offshore AH-70 will improve the asphalt foaming and the mixing with aggregates, due to its lowest surface energy. Combined with the results of foaming test of asphalt, shown as in Table 2, the evaluation results for asphalt foaming property used surface energy theory have a good coincidence with the using of conventional method. It is reasonable to consider that the surface energy as a key index can be used to effectively evaluate the foaming property of the asphalt binder.

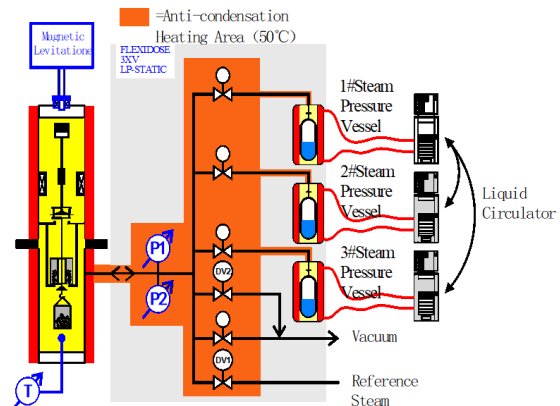
WETTABILITY OF FOAMED ASPHALT TO AGGREGATE

Measurement of surface energy components of aggregates

In this study, the surface energies of two kinds of aggregates were measured with the universal sorption device (USD) method by using the magnetic suspension weight analysis system, as shown in Figure 7. Similar to the calculation of surface energy components of the asphalt binder, the USD method utilized the gas adsorption characteristics of selected solvent, whose surface energy components were known, to indirectly measure the surface energy components of aggregates at 20 °C [35~36]. Table 5 shows the surface energy components of aggregates obtained in this study.



(a) Physical diagram



(b) Schematic diagram

Fig. 7 - Magnetic suspension weight analysis system

Tab. 5 - Surface energy components of aggregates

Type	Surface energy components, (ergs/cm ²)				
	γ^{LW}	γ^+	γ^-	γ^{AB}	γ^{Total}
Basalt	82.42	1.09	392.93	41.43	123.85
Granite	100.36	7.75	169.42	72.47	172.83

Analysis of wettability

Table 6 illustrates the adhesion work between asphalt binders and the selected aggregates. Subsequently, the wettability of asphalt binders to aggregates was calculated by using formula (3), shown as in Table 7. Figure 8 and 9 show the adhesion work between asphalt binders and aggregates and wettability of aggregates by asphalt binders, respectively.

Tab. 6 - Adhesion work between asphalt binders and the selected aggregates

Type	Adhesion work, (ergs/cm ²)			
	KLMY-70	Guo Chuang AH-70	SHELL-70	China Offshore AH-70
Basalt	120.38	123.44	118.43	132.80
Granite	104.30	109.28	107.37	111.58

Tab. 7 - Wettability Rs of asphalt to aggregates

Type	Wettability, (ergs/cm ²)			
	KLMY-70	Guo Chuang AH-70	SHELL-70	China Offshore AH-70
Basalt	99.50	98.34	88.83	112.6
Granite	83.42	84.18	77.77	91.39

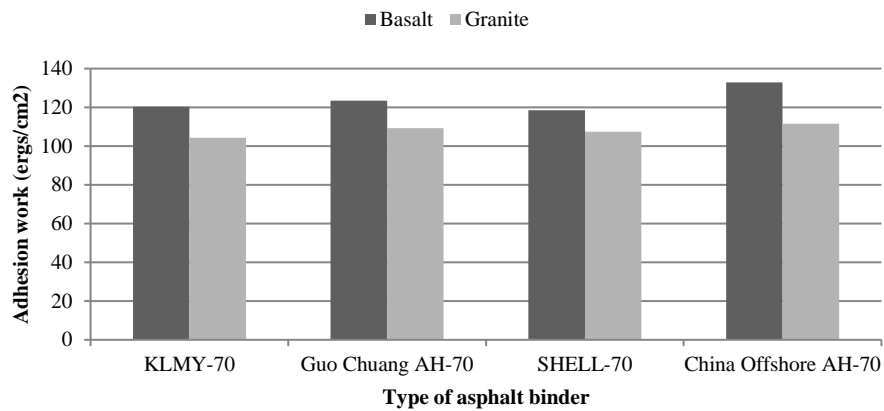


Fig. 8 - Adhesion work between asphalt binders and aggregates

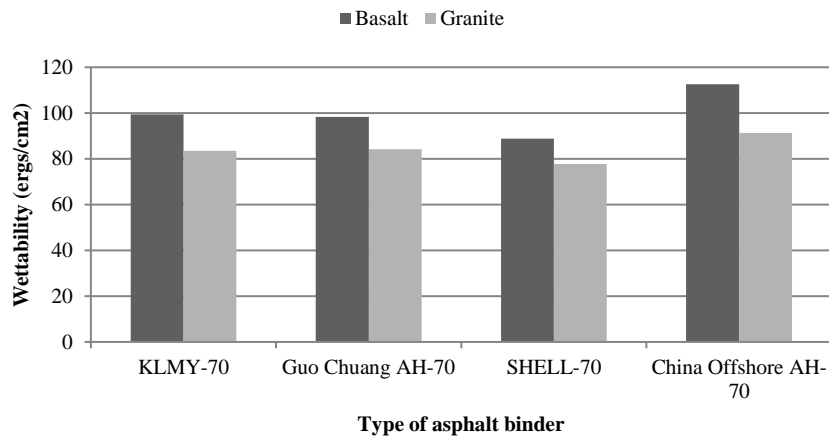


Fig. 9 - Wettability of aggregates by asphalt binders

As a very important factor in foamed asphalt mixture, the more positive the adhesive work, the better the bonding between asphalt binder and aggregate. It can be seen from the data in Figure 4 that compared with other asphalt binders, the asphalt binder of China Offshore AH-70 has greatest adhesion work with basalt. And compared with granite, the adhesion work between asphalt binders and basalt is greater. As noted above, good wettability is in favor of improving the pavement performance of foamed asphalt mixture. It can be observed from Figure 5 that the wettability of basalt by China Offshore AH-70 is greatest, which is the same as the results of adhesion work. The foamed asphalt mixture prepared by China Offshore AH-70 and basalt has the best performance in these combinations of mixtures.

Combined with the surface energies of asphalt binders, it is concluded that the lower the surface energy of asphalt binder, the better the foaming property of asphalt binder. During the process of calculation including adhesion work between asphalt binders and aggregates and cohesion work of asphalt binders, the lower surface energy facilitates the lower cohesion work of asphalt binder, which can improve the wettability of asphalt binder to aggregate. Therefore, for the foamed asphalt mixture, the surface energy of the asphalt binder not only can influence on the foaming property, but also has an impact on the wettability of asphalt binder to aggregate. In order to improve the foaming property of the asphalt binder and the pavement performance of foamed asphalt mixture, it should be suggested to choose the asphalt binder with the lower surface energy in the design process of foamed asphalt mixture.

CONCLUSIONS

This research focused on using a method to analyze the relationship between foaming behavior and surface energy of asphalt binder from a key point of view based on the influence of surface energy of asphalt binder on the foaming property and wettability of asphalt to aggregates. Based on the surface energy theory, the surface energy components of asphalt binders and aggregates were measured by utilized Wihelmy plate method and universal sorption device method, respectively. Subsequently, the surface energies of asphalt binders and wettability of asphalt binders to aggregates were calculated to evaluate and verify the property of foamed asphalt mixture, respectively.

The following conclusions can be drawn from the present research:

- Through mechanism analysis of foaming of the asphalt binder, it can be found that the surface energy will significantly influence the foaming property of asphalt. The lower the surface energy of selected asphalt binder, the greater the foaming property.
- Combining the expansion rate (ER) with the half-life (HL), it can be seen from the macroscopic perspective that the asphalt binder of China Offshore AH-70 has a greatest foaming property among four kinds of asphalt under the same experimental conditions.
- The calculation results of surface energies of asphalt binders demonstrate that the surface energy used to evaluate the foaming property has a good consistency with the indicators of expansion rate and half-life.
- Based on surface energy theory, surface energy as a good index can be used to effectively evaluate the foaming property of asphalt. Results of the traditional asphalt foaming test validated the results of the surface energy method.
- The surface energy of the asphalt binder significantly influences the wettability of asphalt binder to aggregate. Under a certain condition, there is an inversely proportional relationship between surface energy of the asphalt binder and wettability.
- To optimize the foaming behavior of asphalt binder and the pavement performance of foamed asphalt mixture, it is suggested to choose the asphalt binder with lower surface energy in the design process of foamed asphalt mixture.

This paper has a few limitations. The research is mainly based on surface energy theory to analyze the influence of surface energy on foaming behavior of asphalt and wettability of asphalt binder to aggregate. The performance test of mixture has not been conducted. In the future study, it is necessary to research the influence of surface energy of asphalt as well as the effects of water susceptibility and thereby the adhesion on the foamed asphalt mixture. In addition, a kind of approach based on the influence of surface energy method was developed to evaluate the asphalt foaming property and pavement performance of foamed asphalt mixture, which can provide the theoretical basis for the development of performance of foamed asphalt mixture.

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STATEMENT

The authors declare that there is no conflict of interest regarding the publication of this paper.

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