Technical Paper

ISSN 1997-1400 Int. J. Pavement Res. Technol. 7(6):456-460
Copyright @ Chinese Society of Pavement Engineering

Asphalt-Aggregate Adhesion Work of Natural Asphalt Modified Asphalt

Ma Feng[1+], Fu Zhen[1], and Wang Lilong[1]

Abstract: The surface free energy is an important parameter that can be used to estimate the adhesion work of asphalt binder and aggregates system. Based on the theory of surface physical chemistry, the surface free energy of the base asphalt and asphalt modified by natural asphalt is determined by measuring contact angles with the sessile drop method. The adhesion grade of asphalt and aggregate is obtained by the boiled water method. The method of calculating adhesion work is studied first. Then, the adhesion work of asphalt aggregate systems and asphalt aggregate water systems are determined, respectively. Test results show that by increasing the additive of natural asphalt, the adhesion work of natural asphalt modifier asphalt and aggregate elevates distinctly, and the adhesion work of the modified asphalt, aggregate and water system decreases. There is a good relation between the adhesion grade and the adhesion work of dry and the adhesion work in the presence of water. The additive of natural asphalt improves the moisture damage resistance.

DOI: 10.6135/ijprt.org.tw/2014.7(6).456

***Key words**: Asphalt aggregate adhesion; Contact angle; Natural asphalt modified asphalt; Surface free energy.*

Introduction

Asphalt pavements are often subjected to damage induced by water. Moisture damage in asphalt mixes can be defined as early loss of strength and durability caused by moisture penetrating the asphalt-aggregate mixture. Moisture damage in asphalt mixes has become a prevalent problem in most highways in China. The phenomenon is referred to as stripping. And it occurs when moisture causes a loss of bond between the aggregate and the asphalt binder [1-4]. And natural asphalt can effectively improve the adhesion of asphalt and aggregate system. Natural asphalt can be found in different forms, such as asphalt deposits, lake asphalt or rock asphalt, and in different degrees of purity (i.e., the proportions of bitumen and other mineral matter). Trinidad Lake Asphalt is perhaps the most famous source of natural asphalt. It occurs as a semi-solid emulsion of soluble bitumen, mineral matter, and other minor constituents. Mined from the world famous Pitch Lake in the south west of Trinidad, West Indies, it has enjoyed continuous use in asphalt products for well over 100 years. Trinidad lake asphalt is added to base asphalt to improve the road performances of the modified asphalt [5-6]. And the mix technology of lake asphalt and base asphalt is analyzed by different researchers.

Adhesion is a thermodynamic phenomenon related to the surface energy of the materials, asphalt, water, air, and aggregate. Usually the adhesion tension for asphalt-aggregate interface is much lower than the adhesion tension for water-aggregate interface. This shows that most aggregates have a higher affinity for water than for asphalts. Thus water can rupture the bond between asphalt and aggregate if the water comes in contact with it. The rate of stripping depends upon the magnitude of the free energies involved. Chen [7] measured the surface free energy of aggregate and asphalt using the universal gas adsorption and the Wihlelmy plate, respectively.

The measurement of the surface free energy of the solid is not straightforward. It cannot be measured directly. In this study, indirect methods are used and the surface energies of asphalt are inferred from the known surface energy vales of three probe liquids. Although this approach is theoretically correct, improper choice of liquids combined with small experimental errors can result in inaccurate estimates of surface energy characteristics of asphalt. These inaccuracies are inherited in calculations of wet and dry adhesive bond energies and prediction of moisture resistance. The objective of this paper is to estimate the asphalt-aggregate adhesion work of modified asphalt by natural asphalt.

Materials

Properties of Natural Asphalt

Natural asphalts, which are produced from various places, have different characteristics. Natural asphalts have experienced high temperature and pressure within rocks for long periods of time. The natural asphalt used in this study is manufactured from Si-chun Province, China. The natural asphalt contains main chemistry elements, such as, C (82.1%), H (7.5%), O (2.3%), N, and some metal elements. It is black and block-shaped. Before being blended into base asphalt, the natural asphalt is grinded into powder. The natural asphalt is made up of aromatics (54.11%), resins (11.01%), saturates (2.43%), and asphaltenes (32.45%). There is no wax in the natural asphalt. The main composition of natural asphalt is asphaltene which molecular weight exceeds 10,000. The R&B softening point is 119^{o}C, and the penetration in 25^{o}C is 0.1 mm. The density is 1.04 g/cm^3 at 15^{o}C. The flashing point is 350^{o}C above.

Properties of Asphalt Binders

The base asphalt, domestic 70A, is used in the western part of China. The base asphalt is mixed with natural rock asphalt with different dosages, such as 2%, 4%, 6%, and 8% respectively. At first, the natural rock is grinded into power. The powder is put into the 1.18

[1] Key Laboratory for Special Area Highway Engineering of Ministry of Education, Chang'an University, Xi'an 710064, China.
[+] Corresponding Author: E-mail mafeng@chd.edu.cn
Note: Submitted March 9 2014; Revised July 27, 2014; Accepted September 12, 2014.

Table 1. Properties of Asphalt Binders.

	Base Asphalt	2%	4%	6%	8%
25°C Penetration(0.1mm)	65.5	54.8	45.4	36.8	32.5
15℃ Ductility (cm) (5cm/min)	>150	>100	85.7	31.6	14
Softening Point (℃)	58.5	62.5	67.2	74.2	79.1
Penetration Index	-0.88	-0.02	0.32	0.79	0.81

Table 2. Adhesion Grade between Asphalt Binders and Aggregate.

	Base Asphalt	2%	4%	6%	8%
Limestone	5	5	5	5	5
Granite	3-	3+	4	5-	5

mm screen. The base asphalt is heated to about 165°C. The natural asphalt of certain dosage, calculated by the mass ratio of base asphalt, is put into the base asphalt. With the help of a high speed blending machine, the modified asphalt is obtained after stirring for 20 minutes. The properties of base asphalt and natural asphalt modified asphalt binders are shown in Table 1.

The adhesion grade test of asphalt binders and aggregate is conducted in accordance with the Chinese specifications. The method specifies adding the several aggregate particles coated with asphalt into boiling water for 3 minutes. The adhesion grade is obtained by the size of the visible area of the aggregate that retains its original coating of asphalt. The adhesion grade of asphalt binders test result is shown in Table 2. The adhesion grade is used to rank the performance of resisting moisture damage. The highest grade is 5, which means the asphalt and aggregate pair possesses wonderful adhesion ability. The lowest grade is 1, which means the asphalt and aggregate pair is affected significantly by the moisture. In asphalt mixture design process, the basic criterion of adhesion grade of an asphalt and aggregate pair is more than 3.

For limestone, the adhesion grade is satisfactory. All base asphalt and different dosage nature asphalt modified asphalt can get a grade 5. For granite, the adhesion grade is not good as limestone. The adhesion grade of granite and base asphalt pair is only 3. But with additive of natural asphalt augments, the adhesion grade increases.

Experimental and Methods

The important role of adhesion between asphalt and aggregate to resist debonding in the presence of moisture has been recognized for long time. In order to measure the surface free energy, many researchers have contributed their efforts to this area [8-12]. And Eqs. (1) to (5) are used to describe the interaction between the asphalt and aggregate in this literature [7, 8]. With the development in physical chemistry, the surface free energy of a liquid or a solid is described as Eq. (1).

$$\gamma_l = \gamma_l^d + \gamma_l^p \quad ; \quad \gamma_s = \gamma_s^d + \gamma_s^p \tag{1}$$

In Eq. (1) γ_l^d and γ_l^p is referred as dispersion component and polar component of a liquid surface free energy separately. In this equation, the surface free energy is divided into two components based on the forces that are responsible for forming adhesive bonds at the interface. The dispersion component refers to the Lifshitz-Van der Waals force. The polar component refers to total Lewis acid force and Lewis alkali force.

Applied the theory of two liquids into the liquid and solid system, the interfacial surface free energy between the liquid and solid is described as,

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

By combining the Young's equations, the relation is described as

$$\frac{(1+\cos\theta)}{2}\frac{\gamma_l}{\sqrt{r_l^d}} = \sqrt{\gamma_s^p}\sqrt{\frac{\gamma_l^p}{\gamma_l^d}} + \sqrt{\gamma_s^d} \tag{3}$$

For different liquids, a linear best fit line was generated between $\frac{(1+\cos\theta)}{2}\frac{\gamma_l}{\sqrt{r_l^d}}$ versus $\sqrt{\frac{\gamma_l^p}{\gamma_l^d}}$ for each asphalt binder. The slope and intercept of the fit line can be determined. The square of the slope is polar component of asphalt binder surface free energy. The square of the intercept is dispersion component of asphalt binder surface free energy. The surface free energy of the asphalt binder equals the total of the polar component and dispersion component.

From a thermodynamic point of view, the free energy of adhesion is the creation of an adhesive unit area between two substances. The work of adhesion between the asphalt and aggregate at their interface in a dry condition, or absolute value of bond energy is given by Eq. (4), by replacing the surface energy of liquid with asphalt and solid with aggregate.

$$W_{ls} = \Delta G_{ls} = \gamma_s + \gamma_l - \gamma_{sl} = 2\sqrt{\gamma_s^d \gamma_l^d} + 2\sqrt{\gamma_s^p \gamma_l^p} \tag{4}$$

The subscripts *l* and *s* refers to asphalt and aggregate in the asphalt aggregate system. The surface free energy components are as described earlier. A higher magnitude of W_{ls}, the absolute value of bond energy, indicates a stronger adhesion between the asphalt and aggregate system.

When the asphalt and aggregate system is in the presence of water, the adhesion work is described as Eq. (5). The tendency of the asphalt to strip from the aggregate surface is quantified as the amount of free energy released when water displaces asphalt at the asphalt aggregate system.

$$\begin{aligned} W_{ls,w} &= \Delta G_{ls,w} = \gamma_{lw} + \gamma_{sw} - \gamma_{ls} \\ &= 2(\gamma_w + \sqrt{\gamma_l^d \gamma_s^d} + \sqrt{\gamma_l^p \gamma_s^p} - \sqrt{\gamma_l^d \gamma_w^d} - \sqrt{\gamma_l^p \gamma_w^p} - \sqrt{\gamma_s^d \gamma_w^d} - \sqrt{\gamma_s^p \gamma_w^p}) \end{aligned} \tag{5}$$

The subscript *w* refers to the water. A higher magnitude of $W_{ls,w}$ represents a higher amount of free energy released when the water displaces asphalt at the asphalt-aggregate interface and, hence, a greater tendency for water to displace asphalt at the asphalt-aggregate interface.

Results and Discussion

Surface Free Energy of Asphalt and Aggregate

a. Gycerol sessile drop on base asphalt b. Distilled water sessile drop on 8% natural asphalt modified asphalt

Fig. 1. Sessile Drop on the Surface of Asphalt.

Table 3. The Contact Angles between Test Liquids and Asphalt.

	Distilled Water		Glycerol		Formamide	
	Average(°)	CV(%)	Average(°)	CV(%)	Average(°)	CV(%)
Baes Asphalt	105.2	0.8	103.6	0.96	102.9	0.54
2%	102.7	0.65	102.6	0.59	101.2	0.97
4%	96.5	0.6	96.1	0.81	94	0.49
6%	92.2	0.54	91.27	0.63	86.4	0.86
8%	89.4	0.79	89.6	0.55	80.8	0.90

In this study, indirect methods are used and the surface energies of asphalt are inferred from the known surface energy values of three probe liquids. The contact angle is measured by the OCA20 Video Optics Contact Instrument produced by the Dataphysics. The OCA 20 is equipped with a micro syringe with needle, a camera, and image analysis software, which is used to reduce the deviation in determining the contact angle. The sessile drop method is used to measure contact angles of asphalt binders.

The microscope glass slide is cleaned with distilled water and dried in an oven at 60°C. The asphalt binder is heated to 160°C. The microscope glass slide is immerged into hot asphalt. Excess asphalt is allowed to drain from the plate until a very thin and uniform layer remains on the plate, making the microscope glass slide smoothly coated with hot asphalt. The sample is cooled to the room temperature in a desiccator. Distilled water, glycerol, and formamide are selected as probe liquids. The surface free energy components for the probe liquids are listed in the surface free energy theory literature.

A sessile drop of the probe liquid is dispensed on a horizontal, flat surface of the asphalt binder being tested using a syringe. The examples are shown in Fig. 1, and the test results are listed in Table 3. The contact angle measurement can be conducted by software equipped with the instrument.

The surface free energies of different asphalt binders are shown in Table 3. From the thermodynamics theory, there is a criterion that for different liquids with a certain solid there is a linear relation between $\gamma_l \cos\theta$ and γ_l. This method can be used to evaluate the validity of the contact angle results. In this study, a good linear fit between $\gamma_l \cos\theta$ and γ_l was observed, as shown in Figs. 2 and 3. Following the contact angles results, the dispersion components and polar components of asphalt binders are obtained.

The test results in Table 4 show that asphalt binder has a lower

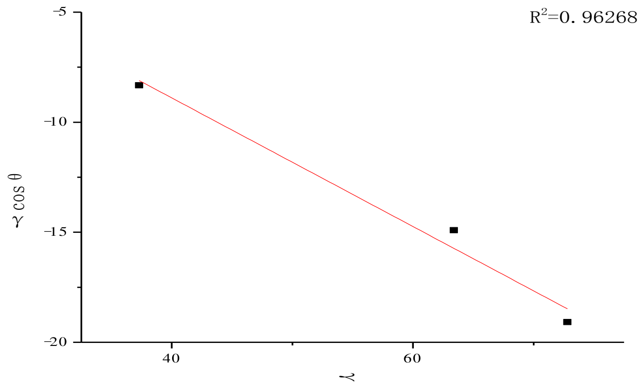

Fig. 2. Relation $\gamma_l \cos\theta$ and γ_l of Base Asphalt.

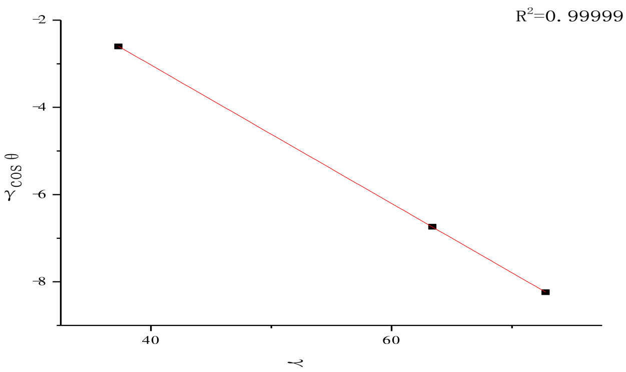

Fig. 3. Relation between $\gamma_l \cos\theta$ and γ_l of 4% Modified Asphalt.

surface free energy than the distilled water has. When the addition natural asphalt is 8%, both the dispersion component and the polar component augment distinctly. The total surface free energy of 8% natural asphalt modified asphalt increases from the 10.60 mJ/m^2

Table 4. Surface Free Energies of Different Asphalt Binders.

	γ (mJ/m^2)	γ^d (mJ/m^2)	γ^p (mJ/m^2)
Base Asphalt	10.60	8.49	2.11
2%	11.87	9.83	2.04
4%	15.17	12.31	2.87
6%	17.21	12.93	4.28
8%	18.60	12.97	5.64

of base asphalt to 18.60 mJ/m^2. For the increasing trend, the magnitude of the polar component is larger than that of the dispersion component. For all modified asphalt binders, the addition of natural asphalt increases the surface free energies of asphalt's binder.

In order to evaluate the adhesion work of asphalt and aggregate system, it is necessary to obtain the surface free energy components of aggregates. The aggregate properties, the surface texture, and chemical composition are very complex. At present, it is difficult to measure the aggregate surface free energy. Chen [7] obtained the surface free energy through a universal adsorption method. Wei [13] obtained the surface free energy of grinded aggregates with the contact angles method. The microcalorimeter method is researched to characterize the adhesion between asphalt and aggregate. There is an obvious difference between a typical aggregate surface and a grinded aggregate surface.

In this study, Eqs. (4) and (5) are used for calculating the adhesion work of natural asphalt modified asphalt and different types of aggregate. The surface free energy data of granite and limestone are introduced by the literature [13]. The surface free energy of grinded aggregate shows the influence of the chemical compositions. At the same time, the surface texture is weakened significantly.

Adhesion Work of Asphalt and Aggregate System

Putting the surface free energy component of asphalt and aggregate into Eq. (4) will obtain the adhesion work of asphalt and aggregate system for the dry situation. The adhesion work results are shown in Table 6.

The adhesion work without the presence of water corresponds to the creation of a unit crack area at the interface between the asphalt and aggregate in a vacuum condition. The results in Table 5 are derived from ideal situation. The value of the adhesion work is positive; it means that the asphalt and aggregate tend to bind together. And the higher magnitude of the adhesion work dictates a stronger adhesion between the asphalt and aggregate. Test results shows that adhesion work of asphalt and aggregate system increases obviously after adding natural asphalt into base asphalt, as shown in Fig. 4.

For adhesion grade of limestone and asphalt binder, test results of all asphalt binders are 5. That is to say, the adhesion grade method is not able to show the difference of the adhesion work. The adhesion work of asphalt and aggregate system increases with the increasing natural asphalt content for both limestone and granite. This trend is in agreement with the adhesion grade of the asphalt binder and granite pair. The adhesion work of granite and 6% natural asphalt modified asphalt is 45.86 mJ/m^2. Meanwhile, the

Table 5. Surface Free Energy Components of Aggregates [13].

	γ (mJ/m^2)	γ^d (mJ/m^2)	γ^p (mJ/m^2)
Limestone	43.44	21.67	21.77
Granite	30.88	25.34	5.45

Table 6. The Adhesion Work of Asphalt and Aggregate System (mJ/m^2).

	Base Asphalt	2%	4%	6%	8%
Limestone	40.45	42.74	48.45	52.78	55.68
Granite	35.87	38.23	43.22	45.86	47.34

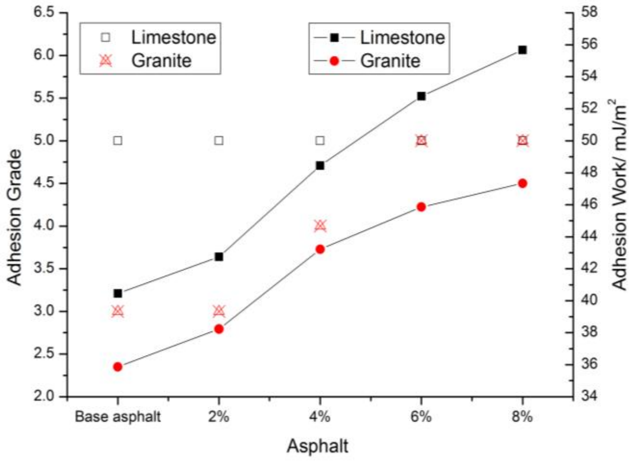

Fig. 4. Adhesion Work of Asphalt and Aggregate System.

adhesion grade is 5. But for limestone and base asphalt binders, the adhesion work is 40.45 mJ/m^2. At the same time, the adhesion grade is 5. The absolute value of adhesion work is not in accordance with the adhesion grade. This result may be connected to the inaccuracy of aggregate surface free energy. The aggregate texture and grinded process may influence the result of aggregate surface free energy. But for the same type aggregate, there is a good relation between the adhesion grade and the adhesion work of asphalt and aggregate system.

Adhesion Work of Asphalt, Aggregate, and Water System

When the asphalt and aggregate system is in the presence of water, the adhesion work of the asphalt, aggregate, and water system is calculated by Eq. (5). The adhesion work results are shown in Table 7 and Fig. 5. It is important to obtain the adhesion work in the presence of water because moisture damage is very deteriorative to asphalt pavement.

For the asphalt, aggregate, and water system, the tendency of the asphalt to strip from the aggregate surface is quantified as the amount of free energy released when water displaces asphalt at the asphalt aggregate interface. A higher magnitude of $W_{ls,w}$ represents a higher amount of free energy released when water displaces asphalt at the asphalt-aggregate interface and, hence, a greater tendency for water to displace asphalt at the asphalt-aggregate interface.

When the asphalt and aggregate system is in the presence of water, there is an obviously difference between the limestone and

Table 7. The Adhesion Work of Asphalt-aggregate-water System (mJ/m^2).

	Base Asphalt	2%	4%	6%	8%
Limestone	23.50	23.72	21.91	20.32	19.13
Granite	45.65	45.94	43.41	40.14	37.52

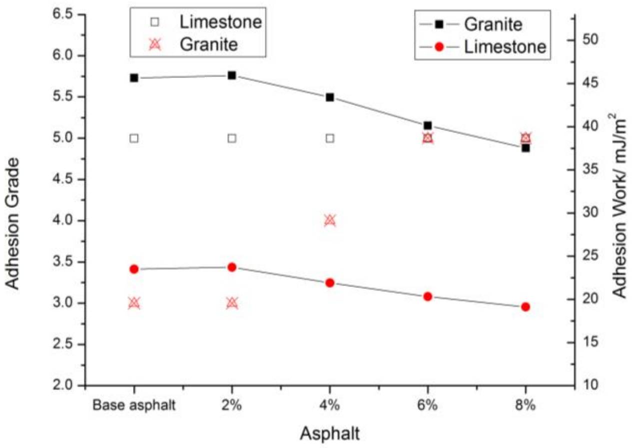

Fig. 5. Adhesion Work of Asphalt-aggregate-water System.

granite. For granite, a higher natural asphalt content improves the adhesion grade from the 3 for base asphalt to 5 for 6% and 8% natural asphalt modified asphalt. The adhesion work of the asphalt aggregate and water system decreases slightly. The result shows that the adding of natural asphalt improves the ability of resisting moisture damage for the asphalt and granite system. There is a good relation between the adhesion grade and the adhesion work in presence of water.

Conclusions

The surface free energies of base asphalt and natural asphalt modified asphalt binders are measured by contact angles through the sessile drop method.

Based on the contact angles method and surface free energy theory, the adhesion work of asphalt aggregate system with and without presence of water is quantified. There is a good relation between adhesion work and adhesion grade. The adhesion work is used to evaluate the adhesion performance of asphalt aggregate system.

The additive of the natural asphalt helps to improve the surface free energy of the asphalt binders. At the same time, it increases the adhesion work between natural asphalt modified asphalt and aggregate system. The adhesion work of modified asphalt, aggregate, and water system decreases.

For limestone and granite, the adding of natural asphalt improves the performance of resisting the moisture damage.

Acknowledgments

This work is supported by the National Natural Science Foundation of China, No.51108038 and No.51108039, Shannxi Science and Technology Research Development Project, No. 2013KJXX94 and No. 2013KW24.

Reference

1. Mccann, M. and Sebaaly, P. (2001). Quantitative Evaluation of Stripping Potential in Hot-mix Asphalt, Using Ultrasonic Energy for Moisture-accelerated Conditioning. *Transportation Research Record*, No. 1767, pp. 48-59.
2. Hefer, A., Bhasin, A., and Little, D. (2006). Bitumen Surface Energy Characterization Using a Contact Angle Approach. *Journal of Materials in Civil Engineering*, 18(6), pp. 759-767.
3. Bhasin, A. and Little, D.N. (2009). Application of Microcalorimeter to Characterize Adhesion between Asphalt Binders and Aggregates. *Journal of Materials in Civil Engineering*, 21, pp. 235-243.
4. Han, S., Liu, Y., and Xu, O. (2010). Influence of Material Characteristics on Adhesion at Interface between Asphalt and Aggregate. *Journal of Chang'an University (Natural Science Edition)*, 30(03), pp. 6-9+70.
5. Widyatmoko, I. and Elliott, R. (2008). Characteristics of Elastomeric and Plastomeric Binders in Contact with Natural Asphalts. *Construction and Building Materials*, 22(3), pp. 239-249.
6. Ni, F., Lai, Y., Shen, H., and Zhan, Q. (2005). Research on Pavement Performance of Composite Modified Asphalt mixture with Trinidad Lake Asphalt (TLA). *Journal of Highway and Transportation Research and Development*, 22(1), pp. 13-16 (in Chinese).
7. Cheng, D. (2002). Use of Surface Free Energy Properties of the Asphalt-Aggregate System to Predict Damage Potential. *Proceedings of Association of Asphalt Paving Technologists*, 71, pp. 59-88.
8. Owens, D.K. and Wendt, R.C. (1969). Estimation of the Surface Free Energy of Polymers. *Journal of Applied Polymer Science*, 13(8), pp. 1741-7.
9. Jaroslaw, D., Krishna, B., and Miller, J.D. (1994). Surface Tension of Toluene-extracted Bitumens from Utah oil Sands as Determined by Wilhelmy Plate and Contact Angle Techniques. *Energy and Fuels*, 8(3), pp. 700-4.
10. Lin, M.-S., Chaffin, J.M., and Liu, M. (1996). Effect of Asphalt Composition on the Formation of Asphaltenes and their Contribution to Asphalt Viscosity. *Fuel Science and Technology International*, 14(1-2), pp. 139-62.
11. Volpe, C.D. and Siboni, S. (1997). Some Reflections on Acid-base Solid Surface Free Energy Theories. *Journal of Colloid and Interface Science*, 195(1), pp. 121-36.
12. Tan, Y. and Guo, M. (2013). Using Surface Free Energy Method to Study the Cohesion and Adhesion of Asphalt Mastic. *Construction and Building Materials*, 47, pp. 254-60.
13. Wei, J. (2008). Study on Surface Free Energy of Asphalt Aggregate and Moisture Diffusion in Asphalt, Ph D. Dissertation, China University of Petroleum, Dong Ying, Shang Dong, China (in Chinese).