Primljen / Received: 18.10.2017.
Ispravljen / Corrected: 2.5.2018.
Prihvaćen / Accepted: 4.7.2018.
Dostupno online / Available online: 25.10.2018.

Estimating moisture susceptibility of asphalt modified with alumina trihydrate

Authors:

Assist.Prof. Shengjie Liu, PhD. CE
Hohai University, China
College of Civil and Transportation Engineering
lsjwork@126.com

Sheng Bo Zhou, PhD. CE
Guangxi Transportation Research Institute
China
zhoushengbo2005 @163.com

Yinshan Xu, MCE
Zhejiang Scientific Research Institute of Transport
China
xys0613@126.com

Original scientific paper

Shengjie Liu, Sheng Bo Zhou, Yinshan Xu

Estimating moisture susceptibility of asphalt modified with alumina trihydrate

The moisture susceptibility of asphalt containing alumina trihydrate (ATH) was assessed through the surface free energy. Physical properties and flame retardancy of ATH samples were also investigated. For research purposes SBS modified asphalt samples with different dosages (0-14 %) of ATH were prepared. Increased viscosity, softening point limiting oxygen index and lower penetration ductility, were investigated for the ATH modified samples. ATH has a significant negative effect on the moisture-induced damage potential of asphalt mixture from the view of micromechanisms.

Key words:
asphalt binder, alumina trihydrate, moisture susceptibility, surface free energy

Izvorni znanstveni rad

Shengjie Liu, Sheng Bo Zhou, Yinshan Xu

Ocjena osjetljivosti asfalta modificiranog aluminijevim trihidratom na vlagu

U radu je na temelju slobodne površinske energije (SFE), ocijenjena osjetljivost asfalta s aluminijevim trihidratom (ATH) na vlagu. Analizirana su fizikalna svojstva i zapaljivost uzoraka s dodatkom aluminijeva trihidrata. Za potrebe istraživanja izrađeni su uzorci asfalta modificiranog stiren-butadien-stirenom (SBS) s različitim udjelima ATH-a (0-14 %). Na uzorcima s dodatkom ATH-a analizirano je povećanje viskoznosti, točka razmekšanja, otpornost bitumena prema kolotraženju, granični indeks kisika i indeks penetracije. Iz aspekta mikromehanizama, ATH u velikoj mjeri nepovoljno utječe na oštećenje asfaltne mješavine uslijed djelovanja vlage.

Ključne riječi:
asfaltno vezivo, aluminijev trihidrat, osjetljivost na vlagu, slobodna površinska energija

Wissenschaftlicher Originalbeitrag

Shengjie Liu, Sheng Bo Zhou, Yinshan Xu

Bewertung der Empfindlichkeit des Asphalts, der durch Aluminiumtrihydrat gegen Feuchtigkeit modifiziert wurde

In der Abhandlung wurde, basierend auf der freien Oberflächenenergie, die Empfindlichkeit des Asphalt mit Aluminiumtrihydrat auf die Feuchtigkeit bewertet. Analysiert wurden die physikalischen Merkmale und die Entflammbarkeit der Proben des Bindemittels mit Zusatz von ATH. Für Forschungszwecke, wurden Asphaltproben angefertigt, die mit Styrol-Butadien-Styrol (SBS) mit unterschiedlichen Anteilen von ATH (0-14 %) modifiziert wurden. An den Proben mit Zusatz von ATH wurde Folgendes analysiert: Erhöhung der Viskosität, Aufweichepunkt, Beständigkeit des Bitumens auf Spurbildung Grenzindex des Sauerstoffs und Penetrationsindex. Unter dem Aspekt der Mikromechanik wirkt sich ATH auf die Beschädigung der Asphaltmischung aufgrund der Wirkung von Feuchtigkeit stark negativ aus.

Schlüsselwörter:
Asphaltbindemittel, Aluminiumtrihydrat, Empfindlichkeit auf Feuchtigkeit, freie Oberflächenenergie

1. Introduction

Many road tunnels have been built in mountainous areas in the scope of rapid development of highway construction incentives in China. Thus, over 15,000 highway tunnels, with a total length of 14,039.7 km, have been built in China by the end of 2016 [1]. Out of this total tunnel length, long tunnels (L ≥ 1000 m) account for as many as 740 km. Although tunnel construction brings convenience to transport sector, a problem that cannot be ignored is the semi-closed space, which is highly detrimental with regard to rescue efforts in case of fire [2]. In fact, many high-profile road tunnel fires have occurred in tunnels over the past decades, and the consequences of such fires have been quite serious [3]. To counter this problem, flame-retardant materials should be used in tunnels.

Asphalt pavements have been used widely in road and tunnel construction owing to their superior performance and long service life. However, such pavements can easily be ignited in case of traffic accidents involving outbreak of fire. In such cases, asphalt can catch on fire and, while burning, it releases large amounts of smoke and toxic gases, impeding the traffic and hampering rescue operations [4]. A growing attention is currently paid to possible improvements of flame retardancy of asphalt pavements in tunnels, and adding flame retardants into asphalt has proven to be a successful popular measure to inhibit asphalt combustion and/or pyrolysis [5]. In recent years, many flame retardants such as magnesium hydroxide, decabromodiphenyl oxide, decabromodiphenyl ethane, alumina trihydrate, antimonous oxide, ammonium polyphosphate, and pentaerythritol, have been used as additives to asphalt [6]. Due to its cost effectiveness, safe handling, and environmental friendliness, alumina trihydrate (ATH) has become a popular flame retardant for reducing or preventing asphalt combustion.

The issues such as flame retardant properties, ageing characteristics of flame retardant asphalts, asphalt mixture design methods, and the effect of flame retardant on pavement performance, are currently studied, and the thermal degradation behaviour and modification mechanism of flame retardant (FR) asphalt materials are investigated by thermogravimetric and infrared analyses [7, 8]. However, some researchers have placed emphasis on the moisture-induced damage potential of asphalts containing FRs, especially from the point of view of micro-mechanisms. Actually, this is very necessary because some tunnel environments are very humid. At present, many theories and methods have been developed to estimate and explain damage that could result from moisture. Surface free energy (SFE) has proven to be an effective and successful method for evaluating moisture susceptibility of asphalt mixtures, as it can characterize the cohesive strength and adhesion strength of asphalt and asphalt-aggregate from the point of view of micro-mechanisms [9, 10]. In general, the surface free energy of a material could be considered as a capacity needed to create a unit area of new surface of such material. The SFE has been successfully used to evaluate moisture susceptibility of asphalt materials.

The objective of this study is to examine the moisture-induced damage potential of the ATH modified asphalt using the SFE theory. The penetration, ductility and softening point, rutting resistance performance, and flame retardancy of the ATH modified asphalt, are investigated. The SFE components of asphalt are determined by static contact angle measurement. The cohesion energy, debonding work, adhesion work, and energy ratio, are calculated to explore the moisture susceptibility of the ATH modified asphalt.

2. Materials and methods

2.1. Asphalt and flame retardant

SBS (I-C) modified asphalt, widely used in China, was chosen as the matrix asphalt in the test. Its basic physical properties are presented in Table 1. Aluminium trihydrate (ATH) consisting of micro AH-2 was used as the flame retardant in this study. Its basic technical index is presented in Table 2.

2.2. Aggregate and probe liquids

Three types of aggregate provided from Jiansu Province, China, were used in this study. Their basic physical properties and surface free energy components are listed in Table 3.

The formamide, distilled water, and glycerol, were selected as probe liquids to measure the contact angle with the tested binders. The SFE parameters of the above liquids are listed in Table 4.

Table 1. Basic physical properties of SBS modified asphalt

Test items	Penetration (100 g. 5 s. 25 °C)/0.1 mm	Ductility (15 °C)/cm	Softening point / °C	(Residue after RTFOT) Mass loss [%]	(Residue after RTFOT) Penetration ratio (25 °C)/ [%]
Results	53.6	34.3	68.7	-0.02	69.4

Table 2. Basic technical index of ATH

Items	Al_2O_3	Na_2O	SiO_2	Fe_2O_3	pH	Particle diameter
Results	64 %	0.3 %	0.03 %	0.01 %	8.5	3 μm

Table 3. Physical properties and SFE components of aggregates

Aggregates	Density [g/cm^3]	SiO_2 content [%]	pH	γ^{LW} (Lifshitz-Van der Waals)	γ^{AB} (Acid Base)	γ (Total SFE)
Limestone	2.720	4.8	8.8	8.01	48.17	56.19
Basalt	2.952	48.7	7.9	7.86	44.98	52.84
Granite	2.861	67.5	6.5	7.07	48.55	55.62

Table 4. SFE parameters of probe liquids (mJ/m^2)

Probe liquids	γ^{LW}	γ^{AB}	γ
Formamide	39.4	19.6	59.0
Distilled water	18.7	53.6	72.3
Glycerol	28.3	36.9	65.2

2.3. Preparation of ATH modified bitumen

The ATH modified bitumens were prepared using a high shear mixer at a rotational speed of 4,000 rpm at 165 °C. First, the matrix binder was heated in an iron container to make it fluid. Then the 6-14 wt % of ATH was added into the binder and sheared for 30 min to produce the ATH modified asphalt. Finally, the asphalt samples were used for the follow-up tests.

2.4. Test methods

2.4.1. Measuring performance of ATH modified asphalts

Physical and mechanical properties of the ATH-modified asphalts were determined using a series of tests. The penetration at 25 °C, ductility at 5 °C, softening point, and viscosity at 135 °C of the asphalt samples, were determined on the basis of the Chinese standard JTG E20-2011 [11]. The anti-rutting performance of ATH modified asphalt was evaluated by the rutting factor (G*/sinδ), measured using DSR at the 10 rad/s frequency in the temperature range from 58 to 82 °C according to ASTM D 7175 [12].

2.4.2. Measuring flame retardancy of ATH modified asphalts

The flame retardancy of the ATH modified asphalt was characterized by the limiting oxygen index (LOI), which is the minimal oxygen concentration allowing asphalt to burn as per ASTM D-2863 [13]. The sample size of the ATH modified asphalt was 110 × 6.5 × 3 mm^3.

2.4.3. Measuring contact angles

Surface energies of asphalt were measured by contact angle, which is the simplest and the most common approach for measuring the surface energy. The Drop Shape Analyser 10 was used for measuring contact angles of the ATH modified asphalt. The distilled water, glycerol, and formamide liquids were used in this analysis.

2.4.4. SFE parameters and fundamentals

Based on earlier literature surveys [14-16], the moisture susceptibility of the ATH modified asphalt was evaluated by the SFE components, as well as the cohesion energy of asphalt, the work of adhesion (under dry conditions), work of debonding (under wet conditions), wettability, and energy ratio.
The relationships between the contact angle (θ), SFE of liquid or solid (γ_l or γ_s), and interaction energy of liquid-solid (γ_{ls}) was determined using the Young equation expressed by Eq. (1) [17]:

$$\gamma_{ls}\cos\theta = \gamma_s - \gamma_{ls} \quad (1)$$

where γ is the surface free energy of the material, while l and s denote the liquid and solid, respectively.
γ_{ls} is the interaction energy between liquid and solid materials. It can be calculated from Eq. (2) based on the Owens and Wendt method [18]:

$$\gamma_{ls} = \gamma_s + \gamma_l - 2\sqrt{\gamma_s^{LW}\gamma_l^{LW}} - 2\sqrt{\gamma_s^{AB}\gamma_l^{AB}} \quad (2)$$

where γ^{LW} is the Lifshitz-van der Waals component and γ^{AB} is the acid base component.
It should be noted that SFE is composed of two components: Lifshitz-van der Waals (nonpolar component) and acid-base component [19]. The total surface free energy was obtained by combining these components as follows, when the material is liquid and solid.

$$\gamma_l = \gamma_l^{LW} + \gamma_l^{AB} \quad (3)$$

$$\gamma_s = \gamma_s^{LW} + \gamma_s^{AB} \quad (4)$$

The above analysis was used to establish the relationship between the contact angle and SFE components as shown by Eq. (5):

$$\frac{1+\cos\theta}{2}\frac{\gamma_l}{\sqrt{\gamma_l^{LW}}}=\sqrt{\gamma_s^{AB}}\cdot\sqrt{\frac{\gamma_l^{AB}}{\gamma_l^{LW}}}+\sqrt{\gamma_s^{LW}} \quad (5)$$

Furthermore, the cohesive energy (W_{ll}^{c}) providing the energy of materials to attract each other due to the nature of mutual attraction was calculated from Eq. (6):

$$W_{ll}^{c}=2\gamma_l \quad (6)$$

The work of adhesion is considered as the energy for asphalt stripping from the aggregate, and this could characterize the bond strength of the asphalt-aggregate system. The work of adhesion (W_{dry}^{a}) under dry conditions, and the work of debonding (W_{wet}) under wet conditions, can be calculated by means of Eqs. (7) and (8), respectively:

$$W_{dry}^{a}=\gamma_l+\gamma_s-\gamma_{ls}=2\sqrt{\gamma_l^{LW}\gamma_s^{LW}}+2\sqrt{\gamma_l^{AB}\gamma_s^{AB}} \quad (7)$$

$$W_{wet}^{a}=\gamma_{wl}+\gamma_{ws}-\gamma_{ls}=2(\gamma_{water}+\sqrt{\gamma_l^{LW}\gamma_s^{LW}}+\sqrt{\gamma_l^{AB}\gamma_s^{AB}}-\sqrt{\gamma_l^{LW}\gamma_w^{LW}}-\sqrt{\gamma_l^{AB}\gamma_w^{AB}}-\sqrt{\gamma_s^{LW}\gamma_w^{LW}}-\sqrt{\gamma_s^{AB}\gamma_w^{AB}}) \quad (8)$$

According to the research of Akvarez *et al.* [20], the wettability can be represented by the Spreading Coefficient as shown by Eq. (9):

$$SC=W_{dry}^{a}-W_{ll}^{c} \quad (9)$$

Howson *et al.* [21], and Little *et al.* [22] combined cohesive and adhesive energies into a single term as shown by Eq. (10).

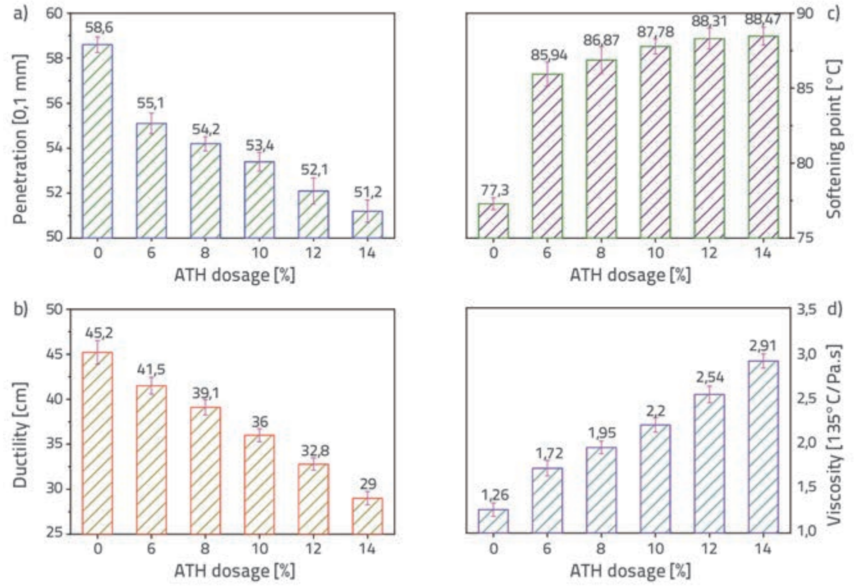

Figure 1. Physical performance of ATH modified asphalt

$$ER=\frac{SC}{W_{wet}^{a}} \quad (10)$$

3. Results and discussion

3.1. Physical properties

The results of penetration, ductility, softening point, and viscosity of ATH modified asphalt are shown in Figure 1. It can be seen in that figure that the penetration 25 °C and ductility 5 °C decrease with an increase in ATH dosage, while the softening point and viscosity 135 °C significantly improve in comparison with the neat (base) asphalt. For instance, when the 6 % ATH was mixed into asphalt, the penetration and ductility was reduced by 6 % and 8 %, respectively. This result indicates that ATH additives increase the stiffness of asphalt. Furthermore, the softening point and viscosity increased by 11.18 % and 36.51 %, respectively, for asphalt samples with 6 % of ATH. This also proves that stiffness increases with the addition

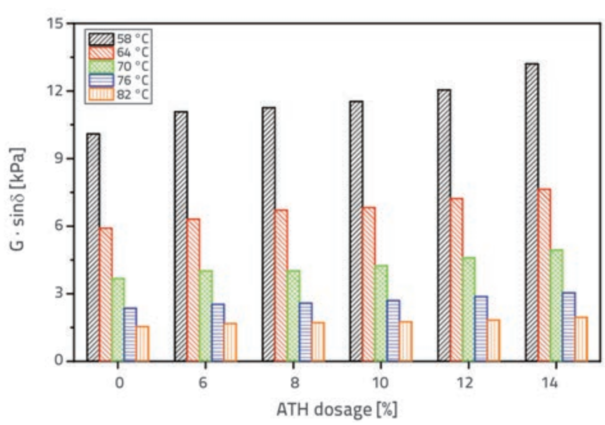

Figure 2. G*/sinδ of ATH modified asphalt

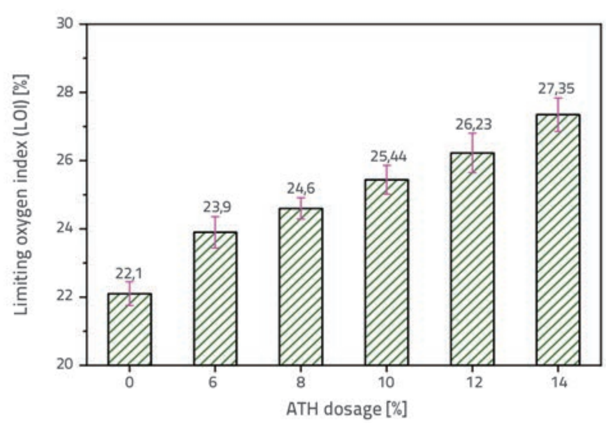

Figure 3. Limiting oxygen index of ATH modified asphalt

of ATH to asphalt. As a result, the ATH modified asphalt is more stable at high temperatures and may also be more resistant to permanent deformation (rutting) compared to matrix asphalt.

3.2. Rutting resistance

In order to better characterize the high-temperature rutting resistance, the G*/sinδ of asphalt with or without ATH was analysed, as shown in Figure 2. It can be seen that the G*/sinδ increases when ATH is added to the matrix asphalt at different temperatures. For instance, the G*/sinδ of asphalt at 58 °C, with 6 % ATH dosage, increased by 19.15 %. In general, the greater the G*/sinδ, the better the rutting resistance performance of asphalt. The results indicate that the high-temperature performance of the ATH modified asphalt improves with an increase in ATH content. Furthermore, the change of amplitude of asphalt at different temperatures reveals a great difference when the ATH content is increased. For matrix asphalt, the G*/sinδ decreased by 41.4 % when the temperature increased from 58 °C to 9 °C, while for the modified asphalt containing 6 % ATH, the G*/sinδ decreased by 43 % when the temperature increased from 58 °C to 64 °C. The difference in the changed G*/sinδ also shows that the high-temperature performance of asphalt alters with the addition of ATH.

3.3. Flame retardancy

The limiting oxygen index (LOI) was selected as the indicator to evaluate the flame-retardant capability of the ATH modified asphalt. Asphalt with different dosages of ATH was investigated to illustrate the effect of ATH on flame retardancy in the similar test environment. Figure 3 presents the LOI test results of asphalt samples. The results illustrate that the LOI of the ATH modified asphalt was greater than that of the matrix asphalt. Meanwhile, the LOI shows an increasing trend with an increase in ATH dosage. It was identified that the addition of ATH enhanced the flame retardant performance of the modified asphalt. In addition, as shown in Figure 4, the incremental of LOI was similar when the LOI increased in the same range. To be specific, the LOI increased by 2.93 %, 3.41 %, 3.11 %, and 4.27 %, when ATH dosage increased from 6 % to 8 %, 8 % to 10 %, 10 % to 12 %, and 12 % to 14 %, respectively.

3.4. Contact angle, SFE, and cohesive energy

Measured contact angles of the unmodified and ATH-modified bitumen with formamide, distilled water, and glycerol under different ATH dosages are presented in Figure 4.a. The van der Waals component of (γ^{LW}) of SFE and Lewis acid-base component (γ^{AB}) of the surface free energy of each asphalt were calculated using the contact angle based on Eq. (5). The corresponding results are shown in Figure 4.b. The cohesive energy results were calculated based on Eq. (6). The corresponding results are presented in Figure 4.c.

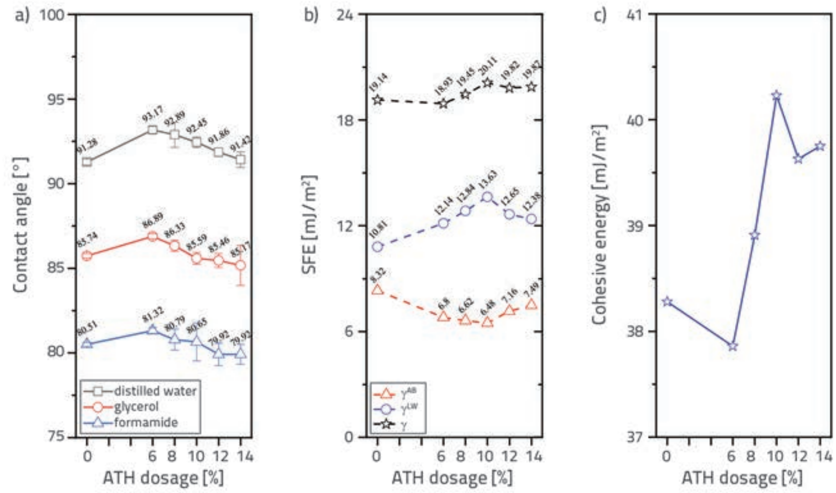

Figure 4. Effect of ATH content on cohesive energy

Figure 4.a shows that the contact angle of asphalt increases first and then decreases at 6 % ATH. In the case of water, for 6 % ATH, the contact angle of asphalt increased from 91.28° to 93.47°. A contrary decreasing trend was observed when the ATH dosage increased from 6 % to 14 %, and the contact angle of asphalt decreased to 91.42°. The contact angle could directly indicate the wetting ability of the probe liquid with a solid. Generally, if the contact angle is close to zero, the solvent spreads completely on the surface; conversely, the contact angle > 90° indicates that the solvent is not wetting, or is poorly wetting the surface; and if it is in the range from 0° to 90°, it nicely wets the surface of the material. The contact angles were > 90° when the water was taken as the probe liquid for all ATH dosages, indicating that the water cannot wet them well. Furthermore, the use of higher amounts of ATH was found to possibly reduce the contact angle. In particular, the asphalt with 14 % ATH has the contact angle similar to that of the unmodified asphalt.

Figure 4.b shows that the van der Waals component (γ^{LW}) of asphalt increases first and then decreases at the turning point of 10 % ATH. A reverse trend was observed, showing the decrease of the acid-base component (g^{AB}), followed by an increase in the ATH content up to 10 %. However, the trend of total SFE was found to be similar to γ^{LW}. This indicates that the van der Waals component is the most significant contributing factor to the total SFE, and that the total SFE slightly improves with an increase in ATH content. The van der Waals component (γ^{LW}), which corresponds to nonpolar molecules, is usually considered as solvent for polar molecules in asphalt. Therefore, an increase in the total SFE of asphalt could be deemed to provide a higher potential for bonding with aggregates in the presence of moisture.

In particular, the acid-base component (γ^{AB}), or polar molecules within the asphalt binder, play a vital role in the adhesion to aggregate surface, because of high polarity of aggregate surface. Therefore, if the content of polar molecules in asphalt is lower, water can easily displace the asphalt binder from the aggregate surface in the absence of a strong bond, as the polarity of water is higher than that of the asphalt binder. In this study, the acid-base component of asphalt decreased first and then increased at 10 % ATH. This may be explained based on the fact that the ATH has both acidic and alkaline characteristics. When ATH (< 10 %) is added into the asphalt (almost acidic), it may lead to neutral reaction, reducing the acid-base component. Furthermore, the acidity of ATH increases with an increase in ATH dosage, causing the acid-base component to increase. Therefore, the change trend of the adhesion of asphalt-aggregate system may be similar to the acid base component. However, the potential moisture damage to asphalt should still be analysed in depth as the moisture damage causes the loss of the strength and stiffness at the binder aggregate interface.

Estimated cohesive energies of the tested binder samples are shown in Figure 4.c. As the cohesive energy is twice of the total SFE, it can be found that the cohesive energy exhibits an increase similar to the SFE. Furthermore, the cohesive energy of asphalt at all ATH dosages is higher than that of the unmodified asphalt, although it increases first and then decreases at the turning point of 10 % ATH. Because a higher cohesive energy will lead to greater external energy for crack propagation, it suggests higher resistance to the moisture damage for the ATH modified binder.

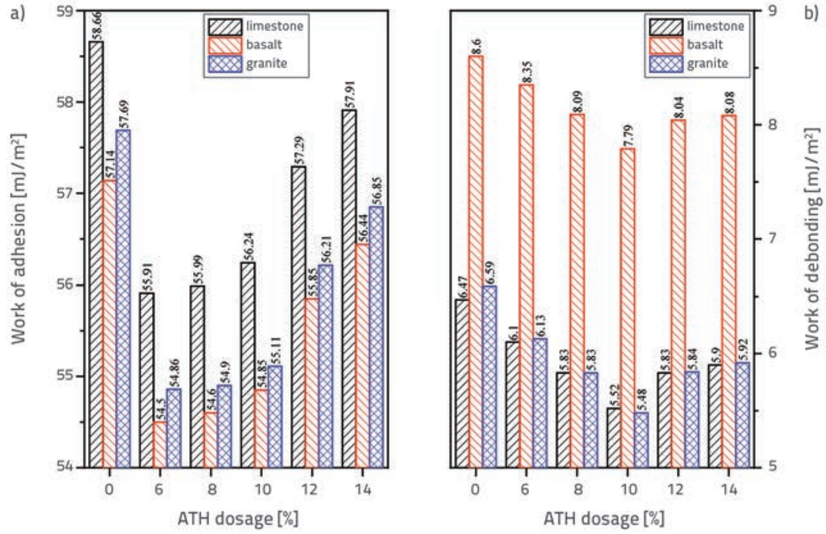

Figure 5. Work of adhesion and work of debonding

3.5. Work of adhesion and work of debonding

The indexes of work of adhesion and work of debonding for the asphalt samples are shown in Figure 5. There it can be seen that the work of adhesion decreases at 6 % to 10 % of ATH content, while it increases at higher ATH contents (12 % and 14 %) compared to the control asphalt, as shown in Figure 5.a. This is similar to the changing trend of acid components. Especially, all the studies of adhesion of the ATH modified binders are lower compared to control asphalt. These results illustrate that the addition of ATH reduces both indexes for the three aggregates. The decrease of adhesion will cause an exponential increase in fracture energy [23]. Therefore, this finding points to a higher moisture damage resistance of the ATH modified asphalt mixture. Furthermore, the limestone-asphalt system has been shown to have the highest adhesion energy, while the basalt-asphalt system has the lowest adhesion energy at different ATH contents. Thus, it is much harder to induce adhesive fracture at the limestone-asphalt interface under the same wheel load and environmental stresses.

Figure 5.b also shows that the work of adhesion was slightly reduced by the addition of ATH. This reduction increased for the granite aggregate compared to other aggregates. For example, when ATH dosage increased from 0 % to 10 % for the asphalt-limestone, asphalt-basalt and asphalt-granite systems, the

Table 5. Variance analysis result of work of adhesion and work of debonding

Source	Work of adhesion				Work of debonding			
	SS	MS	F	P	SS	MS	F	P
Factor A	19.23	3.85	1468.08	< 0.01	1.562	0.312	113.771	< 0.01
Factor B	6.67	3.33	1272.55	< 0.01	19.450	9.725	3540.607	< 0.01
Model	25.9	3.85	1468.08	< 0.01	1.562	0.312	113.771	< 0.01
Intercept	6.67	3.7	1412.21	< 0.01	21.012	3.002	1092.867	< 0.01
Error	0.026	0.003			0.027	0.003		
Corrected total	25.926				21.040			

Note: DF = degrees of freedom; F = value F; MS = mean squares; SS = sum of squares. Similarly hereinafter.

reduction of adhesion amounted to 14.6 %, 9.4 %, and 17.16 %, respectively. It is noteworthy that, for all the aggregates, the work of adhesion is the lowest at the 10 % ATH dosage. Out of the three aggregates, the basalt aggregate has the highest work of debonding, indicating it has the best resistance to moisture damage.

The sensitivity was analysed in order to further explore if ATH and aggregate have significant effects on the adhesion and debonding. The independent variables were designed as factor A: ATH content (0 %, 6 %, 8 %, 10 %, 12 %, and 14 %); factor B: aggregate type (limestone, basalt and granite), while dependent variables were designed as the work of adhesion and debonding. The sensitivity results are listed in Table 5. The results show that the ATH dosage and aggregate type have significant effects on the adhesion and debonding at the level of $P < 0.05$. This analysis indicates the ATH will significantly reduce the adhesion and debonding work.

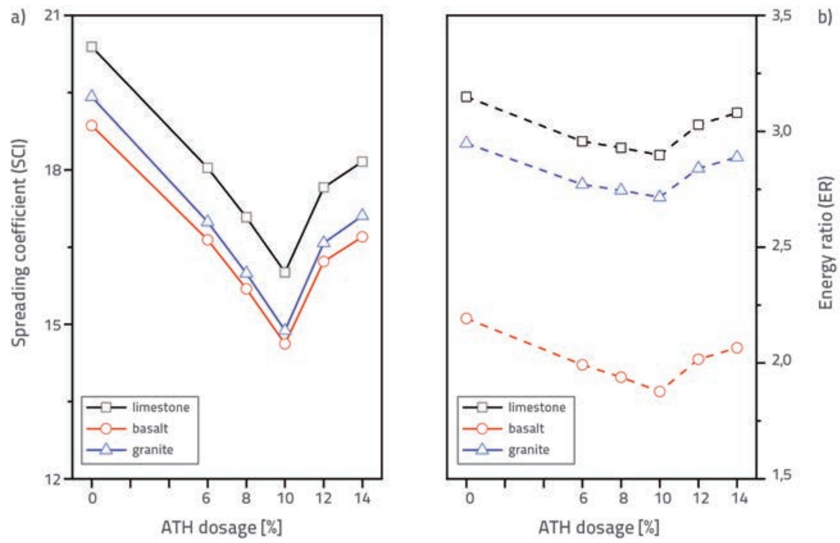

Figure 6. Spreadability coefficient and energy ratio

3.6. Spreading coefficients and energy ratio

The spreadability coefficient (SC) of asphalt samples over aggregate surface is calculated using Eq. (9). The results calculated and determined for bitumen blends and aggregates are presented in Figure 6.a. It can be seen in that figure that the spreadability of matrix asphalt reduced after addition of ATH, although it slightly improved at the ATH dosage >10 %. In general, a higher SC value indicates better wettability of asphalt with aggregate. If the wettability is higher, the aggregate surface can easily be coated by asphalt. This result indicates that ATH negatively affects the aggregate coating with asphalt, especially as physical and chemical properties of asphalt and aggregates are originally different. Furthermore, as to various asphalt-aggregate systems, the limestone clearly showed the highest SC, while the granite exhibited the lowest SC. Therefore, the asphalt-limestone system has the best wettability and moisture resistance damage potential.

The energy ratio (ER) calculated based on Eq. (10) is presented in Figure 6.b. This figure shows that the ER decreases at the 6 % to 10 % ATH content, while it increases at higher ATH contents (12 % and 14 %). The ER values for the ATH modified asphalt are lower than those for the matrix asphalt, although they increase at ATH dosage >10 %. A higher ER value represents better moisture resistance for the asphalt-aggregate system. This result shows that ATH has a negative effect on the resistance of the moisture-induced damage potential. Furthermore, the ER values for granite aggregate combinations are lower than those for the limestone aggregate and basalt aggregate combinations, while the ER values for the limestone aggregate are the highest. This indicates that the resistance to moisture damage is the lowest for granite combinations, and the one for limestone combinations is the highest.

The sensitivity was also measured to analyse if ATH and aggregate have significant effects on the SC and ER. The independent variables were also designed as factor A: ATH content (0 %, 6 %, 8 %, 10 %, 12 %, and 14 %), and factor B: aggregate type (limestone, basalt and granite), while dependent variables were designed as SC and ER. The sensitivity results are listed in Table 6. The results show that the ATH dosages and aggregate types have significant effects on the SC and ER at the level of $P < 0.05$. The above analysis indicates the ATH reduces the Spreadability Coefficient and ER significantly.

Table 6. Variance analysis result of spreadability coefficient and energy ratio

Source	Spreadability coeficient				Energy ratio			
	SS	MS	F	P	SS	MS	F	P
Factor B	31.829	6.366	2258.283	< 0.01	0.141	0.028	111.894	< 0.01
Model	6.651	3.326	1179.805	< 0.01	3.340	1.670	6621.960	< 0.01
Intercept	38.481	5.497	1950.146	< 0.01	3.482	0.497	1971.913	< 0.01
Error	5237.420	5237.420	1857973.228	< 0.01	123.036	123.036	487806.960	< 0.01
Greška	0.028	0.003			0.003	0.000		
Corrected total	38.509				3.484			

4. Summary and conclusions

In this study, SFE components, work of cohesion of the matrix asphalt and ATH modified asphalt, the work of adhesion, work of debonding, wettability, and energy ratio of various asphalt and aggregate systems, were investigated by means of the SFE approach. The static contact angles were measured to calculate the SFE parameter. Physical properties and flame retardancy of ATH binder samples were also measured to study their performance. The experimental results of this study leads to the following conclusions:

- Increased viscosity, softening point, G*/sinδ, LOI, and lower penetration and ductility, were observed because of addition of the ATH modifier.
- The addition of ATH increased the contact angle, van der Waals component, total SFE, and cohesion energy, but decreased the acid base component for all binder samples.
- The work of adhesion of all asphalt aggregates increased due to addition of ATH additive, but the work of debonding decreased. All the adhesion and debonding values of ATH binders were lower than those of the matrix asphalt for various aggregates.
- The addition of ATH decreased the spreading coefficients and energy ratio, which also shows that the ATH reduced moisture resistance of asphalt mixes.
- The limestone-asphalt system has the highest adhesion work and the lowest adhesion work among all the tested aggregates-asphalt systems. Therefore, the asphalt-limestone system has the best moisture resistance damage potential.
- 10 % ATH dosage is a turning point for the cohesion energy, work of adhesion, work of debonding, wettability, and energy ratio. At this dosage, the moisture resistance damage potential of asphalt and asphalt-aggregates system reached the lowest value.

Acknowledgements

The research presented in this paper was sponsored by the Fundamental Research Funds for the Central Universities (2015B11614) and by the Foundation of Guangxi Key Laboratory of Road Structures and Materials (2015gxjgclkf-005).

REFERENCES

[1] Ministry of Transport of the People's republic of China.Statistical communique of the development of transportation industry in 2017, http://zizhan.mot.gov.cn/zfxxgk/bnssj/zhghs/201704/t20170417_2191106.html.

[2] Bendelius, A.G.: Tunnel fire and life safety within the world road association (PIARC), Tunnelling & Underground Space Technology, 17 (2002) 2, pp.159-161.

[3] Wangdan, W.: Analysis of highway tunnel fire accidents and study on countermeasures, Sciencepaper Online, Beijing, 2009.

[4] Borghetti, F., Derudi, M., Gandini, P., Frassoldati, A., Tavelli, S.: Tunnel Fire Testing and Modeling: The Morgex North Tunnel Experiment, Springer, 2017, https://doi.org/10.1007/978-3-319-49517-0

[5] Schartel, B., Bahr, H., Braun, U., Recknagel, C.: Fire risks of burning asphalt , Fire & Materials, 34 (2010) 7, pp. 333-340.

[6] Cong, P., Yu, J., Wu, S., Luo, X.: Laboratory investigation of the properties of asphalt and its mixtures modified with flame retardant, Construction and Building materials, 22(6) , pp.1037-1042, 2008, https://doi.org/10.1016/j.conbuildmat.2007.03.012

[7] Lei, Z., Shaofei, W., Hui, L.: Fire disaster reduction and emergency management of long highway tunnels, Chinese journal of underground space and engineering, 8 (2012) S1, pp.1584-1590.

[8] Cong, P., Chen, S., Yu, J., Wu, S.: Effects of aging on the properties of modified asphalt binder with flame retardants, Construction & Building Materials, 24 (2010) 12, pp. 2554-2558.

[9] Moraes, R., Velasquez, R., Bahia, H.: Using bond strength and surface energy to estimate moisture resistance of asphalt-aggregate systems. Construction & Building Materials, 130 (2016), pp. 156-170, https://doi.org/10.1016/j.conbuildmat.2016.10.043

[10] Tan, Y., Guo, M.: Using surface free energy method to study the cohesion and adhesion of asphalt mastic,Construction & Building Materials, 47 (2013) 5, pp. 254-260.

[11] Ministry of Transport of the People's republic of China. Standard test methods of bitumen and bituminous mixtures for highway engineering, JTG E20-2011, 2011.

[12] ASTM. Standard test Method for Determining the Rheological Properties of Asphalt Binder Using a Dynamic Shear Rheometer, ASTM D 7175, 2008.

[13] ASTM. Standard test method for measuring the minimum oxygen concentration to support candle-like combustion of plastics (Oxygen index) ASTM D 2863, 2013.

[14] Abandansari, H.F., Modarres, A.:. Investigating effects of using nanomaterial on moisture susceptibility of hot-mix asphalt using mechanical and thermodynamic methods, Construction and Building Materials, 131 (2017), pp. 667-675, https://doi.org/10.1016/j.conbuildmat.2016.11.052

[15] Liu, S., Yu, X., Dong, Y.: Evaluation of moisture susceptibility of foamed warm asphalt produced by water injection using surface free energy method, Construction and Building Materials, 131 (2017), pp. 138-145, https://doi.org/10.1016/j.conbuildmat.2016.11.072

[16] Hefer, A., Little, D., Lytton, R.: A Synthesis of Theories and Mechanisms of Bitumen-Aggregate Adhesion Including Recent Advances in Quantifying the Effects of Water, Association of Asphalt Paving Technologists, 2005.

[17] Oss, C.J.V., Chaudhury, M.K., Good, R.J.: Interfacial Lifshitz-van der Waals and polar interactions in macroscopic systems, Chemical Reviews, 88 (1988) 6, pp. 927-941.

[18] Owens, D.K., Wendt, R.C.: Estimation of the surface free energy of polymers, Journal of Applied Polymer Science, 13 (1969) 8, pp. 1741-1747.

[19] Van Oss, C.J., Good, R.J.: Interfacial Forces in Aqueous Media, New York, Marcel Dekker, 1994.

[20] Alvarez, A.E., Ovalles, E., Martin, A.E.: Comparison of asphalt rubber-aggregate and polymer modified asphalt-aggregate systems in terms of surface free energy and energy indices, Construction & Building Materials, 35 (2012) 10, pp. 385-392.

[21] Howson, J., Masad, E.A., Bhasin, A., Branco, V.C., Arambula, E., Lytton, R.L., Little, D.N.: System for the evaluation of moisture damage using fundamental material properties, Texas Transportation Institute, Texas A&M University, 2007.

[22] Little, D.N., Bhasin, A.: Using surface energy measurements to select materials for asphalt pavement, Transp. Res, Board NCHRP Project, pp. 9-37, 2006.

[23] Fini, E.H., Alqadi, I.L., Abulebdeh, T., Masson, J.: Use of Surface Energy to evaluate Adhesion of Bituminous Crack Sealants to Aggregates, American Journal of Engineering and Applied Sciences, 4 (2011) 2, pp. 244-251.