Investigation of moisture susceptibility of SBS modified asphalt containing Alumina Trihydrate by static contact angle measurements

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ABSTRACT: Although several studies have been carried to discover the asphalt mixture performance when Alumina Trihydrate (ATH) as a flame retardant was added into, the moisture susceptibility of asphalt mixture containing ATH is still not fully clear. In this study, the moisture susceptibility of binders containing ATH were assessed through the surface free energy (SFE) obtained by the sessile drop method. A commonly used SBS modified asphalt with different dosages (0%, 6%, 8%, 10%, 12%, and 14%) of ATH were prepared to determine the physical properties, flame retardancy and SFE parameters. Experimental results indicated that the addition of ATH increased the viscosity, softening point, $G^*/\sin\delta$ and limiting oxygen index, but decreased the penetration and ductility. What's more, increases in total SFE, cohesive energy and work of adhesion were observed with the addition of ATH. Conversely, the work of debonding, wettability and energy ratio decrease due to the addition of ATH. It is concluded that the ATH has a significant negative effect on the moisture-induced damage potential of asphalt mixture from the view of micromechanisms. The recommended percentage of ATH was 6-8% in consideration of physical properties, flame retardation and moisture susceptibility.

Key words: Asphalt binder, flame retardant, contact angle, surface free energy, moisture susceptibility.

1 Introduction

Tunnels have become one of the most effective methods to shorten the travel mileage and reduce the pressure on ground transportation, which are vital to maintain the transport infrastructure. In China, a growing number of tunnels have been built to connect the networks from the purpose of environmental protection or reduce the destruction of the mountain [1]. Based on the data of the Comprehensive Planning Division of Transportation Department, China [2-3], in the last decade, the development of the tunnel construction are quickly,
furthermore, the length and number of tunnel in the 2015 have arrived 14000 km and 12000, respectively. As the semi-enclosed space of long highway tunnel, many catastrophic fires have occurred in tunnels in the past years all over the world, which led to important structural damages and even loss of lives, due to the toxic smoke production and hard to rescue. Inevitably, the tunnel fire is also difficult to avoid in China, according to the survey, many high-profile road tunnel fires have taken place in the tunnel over the past decades [4-6]. So in consideration of the high risk of fire, it is necessary to improve material properties or choose suitable materials when the tunnel pavement is building [7].

Because the disadvantages of slow construction, difficulty maintenance, and high noise level for rigid pavements, asphalt pavements have been used widely in the roads and tunnels. Especially in China, with the rapid increase of the tunnel number and mileage, many large-scale road tunnels gradually adopte asphalt mixture as the paving material [8-9]. However, due to the asphalt is a hydrocarbon, it is easy to be ignited if an accident occurs in a tunnel, especially one involving a fire [10-12]. This causes asphalt to burn and release large amounts of smoke and toxic gases, which will impede the traffic and hampered the rescue operations. The technologies to improve the flame retardant of asphalt have gradually attracted the attention of researchers and become a widely accepted concept [13-14]. In the recent years, adding flame retardants into asphalt have proven to be a success popular measure to inhibit the asphalt to burn or pyrolyzate [15]. There are many flame retardant types currently, such as magnesium hydroxide (MH), decabromodiphenyl oxide (DBDPO), decabromodiphenyl ethane (DBDPE), alumina trihydrate (ATH), antimonous oxide (Sb₂O₃), ammonium polyphosphate (APP), pentaerythritol (PER) [16]. In consideration of cost-effectiveness, safe
handling and environmental, alumina trihydrate (ATH) has become the most widely used flame retardant to weaken or avoid the burning behavior of asphalt in the word [17].

Previous studies have carried to study the evaluated the flame retardant properties, including the flame retardant performance [18-19], the aging characteristic of flame retardants asphalt [20], the design method of asphalt mixture [21], the effect of flame retardant on the pavement performance[2, 22]. In addition, the thermal gravimetric analysis and infrared spectrum (IR spectrum) were also carried to discover the thermal degradation behaviors of flame retardant (FR) asphalt materials [23-25]. In short, most of the FR asphalt tests have carried out to analyze the properties of rheological behaviors, pavement performance, and reaction mechanism. Although several studies also have reported that FR additives could weaken the water stability of asphalt mixture through the marshall stability, loss of marshall stability test and freeze-thaw split test [26-27]. However, according to the existing reported, the correlation between field observations and above evaluation methods of water stability are not very well. Especially, the evaluation methods of water damage from the view of asphalt mixture could not reflect the water damage mechanism [28-29]. So it is not very clear how the FR influences on the moisture damage of asphalt and asphalt mixture.

In general, moisture damage of asphalt mixture is regarded to be induced by the cohesive failure and adhesive failure, which are caused by the reduction of bond strength of asphalt, and the bonding failure of the asphalt-aggregate system under wet condition [30]. Many theories were carried to explain and evaluate the water damage mechanism [31-32], one of the theories used widely and successful to evaluate the moisture susceptibility of asphalt mixture is surface free energy (SFE), which could determine the asphalt binders’ cohesive strength and adhesion strength of asphalt-aggregate from the point of micro-
mechanisms [33-34]. The purpose of this research is to investigate the moisture-induced damage potential of binders containing ATH flame retardants through the SFE method. The physical and flame-retardant properties were first tested to analyze the characteristics of asphalt containing ATH. Then the components of SFE of tested binders were obtained through sessile drop method. Finally, the SFE parameters of asphalt-aggregate systems containing different ATH contents and aggregate types were calculated to evaluate the moisture susceptibility.

2 Material and methods

2.1 Raw materials

In this experimental, a SBS modified asphalt was selected as the matrix asphalt to blend with flame retardants additive. The conventional test was carried to characterize the properties of the matrix asphalt, and its results are shown in Table 1. The Aluminum trihydrate (ATH) of mico AH-2 was selected used in this study as the flame retardant, whose related properties are illustrated in Table 2.

<table>
<thead>
<tr>
<th>Table 1 Properties of the asphalt binders</th>
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<th>Table 2 Properties of the flame retardant ATH</th>
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In order to estimate the moisture susceptibility of asphalt-aggregate system containing various dosages of ATH, three widely used aggregates for asphalt mixture in Jiansu Province, China, were collected and tested in this study. Table 3 shows the SFE components of the selected limestone, basalt and granite.

| Table 3 Surface free energy components of aggregates (mJ/m²) |
Three common used probe liquids such as distilled water, glycerol, and formamide, were used to measure and calculate the contact angle with the tested binders. Table 4 shows the SFE components of the selected probe liquids.

Table 4 SFE components of probe liquids (mJ/m²)

2.2 Preparation of binders

To prepare the flame resistant asphalt binders, the SBS modified bitumen was heated to 165 °C in an iron container to make it flowed first. Then different dosages of ATH (0% wt., and 6%-14% wt. with 2% incensement) were poured into the liquid matrix asphalt to prepare tested samples using a high shear mixer. The shear time lasted for 20min at 165 °C at a rotational speed of 4000 rpm to promote the interaction between ATH additive and binders. Finally, the asphalt samples are placed in the air to cool them back to ambient temperature for the follow-up tests.

2.3 Experimental program

2.3.1 Performance test of asphalt

In this study, conventional tests including penetration, ductility and softening point were performed out in accordance with the procedure of T0604-2011, T0606-2011 and T0605-2011 in JTG E20-2011 [35]. The viscosities of the binders were also evaluated at 135°C by a Brookfield Rotational Viscometer (RV) according to T0625-2011 in JTG E20-2011 [35].

The rutting resistance performances of the asphalt samples were characterized by the rutting factor (G'/sinδ) at the frequency of 10 rad/s (almost 1.6 Hz) using the Dynamic Shear Rheometer (DSR). The test temperatures were set at a range of 58-82°C, with 6°C increment according to ASTM D 7175.
The flame retardant property of asphalt can be evaluated using the minimum oxygen concentration which allows the asphalt to burn, while the limiting oxygen index (LOI) was determined as the characteristic index. According to ASTM D-2863, the samples size for LOI is 11 cm × 6.5 cm × 0.3 cm.

### 2.3.2 Fundamentals of surface free energy and contact angle test

In general, the SFE is constituted by a sum of Lifshitz-Van der Waals component and Acid-Base component based on the acid-base theory, which is also called Van Oss Chaudhury-Good approach [36]. According to the research of Chen et al. [37], the SFE can be expressed as the Eq. (1) and Eq. (2), when the material is liquid and solid.

\[
\gamma = \gamma^LW + \gamma^{AB} \\
\gamma_s = \gamma^LW_s + \gamma^{AB}_s
\]  

Where \( \gamma \) is the total SFE; The subscripts \( l \) and \( s \) stand the test materials are solid and liquid, respectively; the superscript \( LW \) and \( AB \) stand the SFE components are Lifshitz-Van der waals component and Acid-Base component for the test materials, respectively.

Owens and Wendt [38] put forward the Eq. (3) to determine the interaction energy (\( \gamma_{ls} \)) between liquid and solid materials, as follows:

\[
\gamma_{ls} = \gamma_s + \gamma_l - 2\sqrt{\gamma^LW_s \gamma^LW_l} - 2\sqrt{\gamma^{AB}_s \gamma^{AB}_l}
\]  

The relationships among the contact angle (\( \theta \)), SFE of liquid or solid (\( \gamma_l \) or \( \gamma_s \)) and interaction energy of liquid-solid (\( \gamma_{ls} \)) can be determined using the Young equation, as the Eq. (4).

\[
\gamma_l \cos \theta = \gamma_s - \gamma_{sl}
\]  

Recalling Equations (1)-(4), the Eq. (5) could establish the relation between the contact angle and SFE components. So if the SFE components of probe liquids are known, each
component of the binders can be calculated through the measured contact angle with probe liquids.

\[
\frac{1 + \cos \theta}{2} \cdot \frac{\gamma_i L}{\sqrt{\gamma_i W}} = \sqrt{\gamma_s^A} \times \sqrt{\gamma_s^B} + \sqrt{\gamma_s^L}
\]

Base the previous surveys [39], the SFE components and cohesion energy of asphalt, the work of adhesion (under dry condition), work of debonding (under wet condition), wettability and energy ratio were adopted to evaluate moisture susceptibility of asphalt binders containing ATH additive.

In this study, the sessile drop method was used to obtain the contact angles with the help of distilled water, glycerol, and formamide liquids by the equipment of Drop Shape Analyze 10. The samples were prepared used 25 × 50 mm glass slides (Fig. 1), after the asphalt was heated to fluid, the glass slide was inserted and withdrawn quickly into the tested asphalt.

**Fig.1.** Asphalt binder samples prepared using glass slides

To obtained reliable experimental results, three replicates were measured and compared in the laboratory. The average value was computed to represent the experimental result. The experimental organization and structure of this study are illustrated in Fig. 2.

**Fig.2.** Flow chart of the experimental organization

### 3. Results and discussions

#### 3.1 Physical properties and flame-retardant data

The values of penetration, softening point, ductility and viscosity of asphalt samples are plotted versus the ATH contents, and the results are shown in Fig. 2 (a)-(d), respectively. It can be found that the penetration and ductility of binders decrease by the increasing of ATH content. For instance, the penetration value of the SBS modified binder (control binder) was
found to be 58.6, while it decreases by about 6%, 7.5%, 8.9%, 11.1%, and 12.9%, respectively, when the 6%, 8%, 10%, 12%, and 14% ATH was added into binders. Similarly, the ductility had an 8% decrement. This indicates that ATH modification of asphalt caused an increase in the asphalt stiffness. From the fig. 3 (c) and (d), it is found that the softening point and 135℃ viscosity increase as the ATH participated in, for example, when the 6% ATH added into the matrix asphalt, the softening point and viscosity value increased by 11.1% and 26.7%, respectively. Such increase in softening point and viscosity also indicate that the stiffness will increase due to the incorporation of ATH.

**Fig.3.** Physical properties and flame-retardant data, (a) penetration, (b) ductility, (c) softening point, (d) viscosity, (e) G*/sinδ, (f) limiting oxygen index.

Furthermore, G*/sinδ was also measured and calculated through the DSR to characterize the high-temperature rutting resistance. From the Fig 3 (e), the ATH modified asphalt has a more G*/sinδ than that of control asphalt, while the G*/sinδ of all asphalt samples show a trend of increase at different temperatures following the ATH contents increase. For example, when the temperature is 58℃, the G*/sinδ of ATH modified asphalt and control asphalt are 13.19 kPa and 11.07 kPa, respectively. This means that the ATH is helpful to enhance the high-temperature stability.

In addition, although the G*/sinδ are different at various test temperatures, it is interesting found that the G*/sinδ variation range is similar at the same temperature range. For instance, when the temperature increase from 58 ℃ to 82 ℃ by 6 ℃ increment, the G*/sinδ of 6% ATH modified asphalt decrease by 43 % (58 ℃ to 64 ℃), 36.4% (64 ℃ to 70 ℃), 37.1% (70 ℃ to 76 ℃) and 33.5% (76 ℃ to 82 ℃), respectively. While for the control asphalt, the G*/sinδ decrease by 41.4% (58 ℃ to 64 ℃), 37.9% (58 ℃ to 70 ℃), 35.9% (58
°C to 76 °C) and 33.4% (58 °C to 82 °C), respectively. This indicates that although the ATH increase the G*/sinδ of asphalt, the thermal property of asphalt seems not change.

Meanwhile, the flame-retardant of ATH modified asphalt was checked and the Limiting oxygen index (LOI) was used as the evaluation index. From the Fig 3 (f), it can be found that the LOI has an obvious increase owing to the addition of ATH. For the control asphalt, the LOI is nearly 22%, when the 14% ATH added into, the LOI value of the samples increases to 27%. Because the flame retardance will be better if the LOI is higher, this result means that ATH makes the asphalt better has a better flame retardancy.

3.2 SFE components and cohesive energy of asphalt binder analysis

Contact angle could direct indicate the wetting ability of the probe liquid with a solid. Table 5 and Fig.4 show the asphalt samples’ contact angles measured with the probe liquids. The results in the Fig.4 reveal that the contact angles increased when the 6% ATH added into the asphalt. However, the contact angles decreased for three probe liquids, with the ATH contents increasing. When the ATH content is 14%, the contact angles are almost the same with that of control asphalt, for example, the contact angle between control asphalt and distilled water is 91.28°, while it is 91.42° for the 14% ATH binder. The results are similar for the other probe liquids. Therefore, using of higher amounts of ATH seems not obviously affect the contact angle.

Table 5 Contact angle of SBS modified binders containing ATH.

<table>
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<tr>
<th>Fig.4. ATH content on contact angle</th>
<th>Fig.5. ATH content on SFE</th>
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Fig.5 shows the results of the surface layer energy of asphalt samples investigations, obtained from the calculation result using the Eq. (5). The non-polar SFE component (γ^LW) value of asphalt increase with the addition of 6% to 10% ATH, however, when the ATH
content is above 10%, its value reduce. A reverse trend has been observed that the acid-base
component (\(\gamma^{AB}\)) decreased following the ATH content increasing up to 10%. The nonpolar
molecules (\(\gamma^{LW}\)) of asphalt is considered as a solvent for polar molecules, which has a
related relationship with the elastic properties of asphalt, in general, a higher \(\gamma^{LW}\) will lead
to higher work of adhesion. From the results in Fig.4, the \(\gamma^{LW}\) has an increase with the ATH
content increasing up to the 10% ATH, while the \(\gamma^{LW}\) decrease at the higher ATH contents
(12% and 14%). Thus, it can be inferred that the asphalt with lower ATH contents (<10%)
has a better adhesion. Overall, the total surface free energy has a little improvement with an
increase in ATH content.

**Fig.6.** ATH content on cohesive energy

The work of cohesion (\(W_{ll}^c\)) provides the energy of material to attract each other due to
the nature of mutual attraction. In general, a higher cohesive bond energy will lead more
difficulty for the crack propagating. Because the cohesive energy is the double value of the
total SFE, it can be calculated from the Eq. (6).

\[ W_{ll}^c = 2\gamma_l \]  

Fig.6 illustrates the work of cohesion of the binders containing different ATH
contents. Similar to the change trend of total SFE, it can be found that the work of cohesion
has a slight increase due to the addition of ATH agents. As a higher of work of cohesion will
lead to a more external energy for the crack propagating, this results means that ATH agents
will increase the interfacial adhesion of binders, although the improvement may be very
slightly.
3.3 Work of adhesion and debonding analysis

The work of adhesion is considered as an energy for asphalt stripping form the aggregate interface, which could characterize the bond strength of asphalt-aggregate system. In general, to obtain a better bond for the asphalt-aggregate system, a higher adhesion is desired. In terms of the SFE theory, the work of adhesion under dry condition can be calculated as Eq. (7).

\[ W_{\text{dry}}^a = \gamma_1 + \gamma_s - \gamma_{ls} = 2\sqrt{\gamma_{lw} \gamma_{lw}} + 2\sqrt{\gamma_{ab} \gamma_{ab}} \]  

(7)

Fig.7 shows the adhesion work of the asphalt-aggregate system with different ATH contents. As can be seen in the Fig.7, for all tested aggregates, the work of adhesion for the binder samples decreases at 6% to 10% ATH contents, while increase at higher ATH contents (12% and 14%), comparing with the control asphalt. In addition, all work of adhesion of ATH modified binders is lower than that of control asphalt. Therefore, it can be conclude the addition of ATH may weaken the work of adhesion, especially the low amounts of ATH (6%-10%). Furthermore, among three tested aggregates, the limestone-asphalt system has the highest adhesion energy and the basalt-asphalt system has the lowest adhesion energy at different ATH contents, which means that the bond strength of the limestone-asphalt system is highest in absence of water. From previous studies, the fracture energy is associated with work of adhesion of asphalt mixture, and a decrease of adhesion will lead to an exponential increase for the fracture energy [40]. Therefore, the results of this study show that the addition of ATH will weaken the fracture resistance and further reduce the moisture damage resistance of asphalt mixture.
The work of debonding ($W_{wet}$) is another designation of adhesion work in presence of moisture, which characterizes the energy for the binder to separate from aggregate interface under wet condition.

From the view of thermodynamics, it is prone to strip when debonding work is higher. So in order to pursuit a better resistive to moisture for the asphalt mixture, a low $W_{wet}$ is desired. On the basis of the Young–Dupre equation and SFE theory, the work of debonding can be estimated through the Eq. (8).

$$W_{wet}^{l} = \gamma_{wl} + \gamma_{ws} - \gamma_{ls} = 2(\gamma_{water} + \sqrt{\gamma_{LW}^{LW} \gamma_{s}^{LW}} + \sqrt{\gamma_{AB}^{AB} \gamma_{s}^{AB}} - \sqrt{\gamma_{LW}^{LW} \gamma_{w}^{LW}} - \sqrt{\gamma_{s}^{AB} \gamma_{w}^{AB}}$$

(8)

Fig. 8 shows the work of debonding of the asphalt-aggregate system with different ATH contents. It is seen that the results of debonding work are similar with the adhesion work, the work of debonding for the asphalt samples decreases at 6% to 10% ATH contents, while increase at higher ATH contents (12% and 14%), compared with the control asphalt. In addition, all work of debonding of ATH modified binders is lower than that of control asphalt. In addition, basalt showed the highest value of Wwet and limestone and granite showed the similarWwet, for example, the Wwet for bastle is 8.08 mJ/m$^2$, whereas for limestone is 5.9 mJ/m$^2$ for 14% ATH binder.

Fig. 8. ATH content on work of debonding

Table 7 ANOVA Analysis for work of debonding at confidence level of 95%

The analysis of variance (ANOVA) was performed through the SPSS program to verify whether significance difference existed among the test binders. The primary independent variables included the ATH contents (0%, 6%, 8%, 10%, 12%, and 14%), aggregate types...
(limestone, basalt and granite) and the dependent variable was the work of adhesion and debonding. Using ANOVA, the statistical significance of the change in the work of adhesion and debonding were examined and the results showed in Table 6 and Table 7, respectively. Based on the p-values for the significant variables, both ATH contents and the aggregate types are the significant factors. It can thus be stated that the addition of the ATH significantly reduced the adhesion and debonding work.

3.4 Wettability and energy ratio analysis

The wettability of a liquid is considered as the property to wet a solid surface, and it also reflects the energy of a solid surface to reduce the surface tension of a liquid. In general, the asphalt is easy to coat the aggregate surface if the wettability is higher. As the physical and chemical properties of the asphalt and aggregates are different, it is not very easy to wet each other. When the ATH is added, the asphalt may be more difficult to wet the aggregate surface, so it is necessary to assess the wettability between aggregate and asphalt with different amount of ATH. According to the research of Akvarez et.al [41], the wettability can be represented by the Spreading Coefficient ($SC$) as Eq. (9):

$$ SC = W_{ac}^{\text{dry}} - W_{ll}^{\text{ac}} $$

(9)

Fig. 9 illustrates the spreading coefficients ($SC$) of asphalt-aggregate systems with different ATH contents and aggregate types. The $SC$ of asphalt samples first decrease at lower ATH contents (<10%), and then increase at higher ATH contents (12% and 14%), for three test aggregates. In addition, all spreading coefficients of asphalt samples with ATH are lower than the control asphalt, which means using an amounts of ATH will have negative effects on the aggregate coating with a binder. So it can be inferred that the addition of ATH
leads to an adverse effect on the bond strength of the asphalt-aggregate system, which will cause high moisture damage potential for asphalt mixture. Furthermore, limestone and basalt have the highest and lowest spreading coefficient values, respectively.

**Fig.9.** ATH content on spreading coefficients

**Table 8** ANOVA Analysis for spreading coefficient at confidence level of 95%

Considering the comprehensive of wettability and work of debonding, the energy ratio (ER) the parameter was put forward under NCHRP 9-37 research project as a parameter to assess the compatibility of asphalt-aggregate system considering moisture or water participated in. Then Howson et al [42], and Little et.al [43] combined the cohesive and adhesive energies into a single term as shown in Eq. (10). In general, a higher ER value represents a better moisture resistance for an asphalt-aggregate system.

\[
ER = \frac{SC}{W_{wet}}
\]

(10)

The ER values were determined for different combinations of ATH contents (0%, 6%, 8%, 10%, 12% and 14%), and different aggregate types (limestone, basalt, and gravel). It is evident from Fig.10 that the ER value decrease following ATH content increase, for all tested aggregates. Furthermore, the control asphalt has higher ER than that of binders containing different contents of ATH. Therefore, it can be inferred that the ATH additive has a negative effect on the resistance of the moisture-induced damage potential. The addition of 10% ATH causes the lowest ER value for all tested aggregates. For instance, the ER value of basalt aggregate with control asphalt and 10% ATH binder are 3.15 and 2.89, respectively. Moreover, the ER of asphalt with limestone is higher than other aggregate types, while the ER of asphalt with basalt is the lowest. This means limestone has the best resistance to moisture-induced damage.
The ANOVA is also used to examine the statistical significance of wettability and energy ratio for tested asphalt samples. Based on the p-values for the significant variables in Table 8 and Table 9, the amount of ATH content is the significant factors influencing spreading coefficient and energy ratio. So it can be stated that the addition of the ATH significantly reduced the moisture damage resistance potential. These results of wettability and energy ratio are consistent with the discussion of the adhesion and debonding work.

### 4 Summary and conclusions

In this research, the moisture susceptibility of the asphalt with flame retardant was evaluated. SBS modified asphalt was used as the matrix asphalt to prepare the samples with a set percentage of ATH (0%, 6%, 8%, 10%, 12%, and 14%). Then the penetration test (25 °C), softening point, ductility (5 °C), viscosity, G*/sinδ and limiting oxygen index were tested to inspect the physical and flame-retardant properties, while the surface free energy characteristics included SFE components, cohesion energy, work of adhesion, work of debonding, wettability and energy ratio were selected to evaluate moisture damage resistance. From the experiment results and following discussions, the conclusions can be drawn as:

1. The results of physical and flame-retardant tests show that adding ATH to asphalt could increase the viscosity, softening point, G*/sinδ and limiting oxygen index, indicating ATH modified binder has better rut resistance and flame resistance. However, the decrease of penetration and ductility means ATH will reduce the low-temperature performance of asphalt.

2. The contact angles of ATH modified binders exhibited an increase in the lower amounts (i.e., 6% ATH) and then decreased with increasing ATH content, while the acid
SFE component (polar component) total SFE component had an incensement with the addition of ATH. These changes of SFE components showed the addition of ATH will influence the moisture sensitivity of asphalt.

(3) Results obtained from work of cohesion, work of adhesion and work of debonding show that ATH could improve the interfacial adhesion of binders, but reduce the bond strength between aggregates and asphalt binder systems under dry and wet conditions. This shows that the addition of ATH may decrease the water resistance of asphalt.

(4) It was observed that the spreading coefficients and energy ratio of ATH modified asphalt were lower than the control binders, although these values had a slight increase in in higher amounts of ATH, (i.e., 12% and 14% ). Such decrease shows a high moisture induced damage potential in the mix as the addition of ATH.

(5) The results of this study proved that the addition of ATH will weaken the moisture resistance of asphalt from the view of micromechanisms. Moreover, the recommended percentage of ATH was 6-8% in consideration of physical properties, flame retardation and moisture susceptibility for the test asphalt and aggregates.

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References


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### Tables

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### Table 1 Properties of the asphalt binders

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<th>Test Properties</th>
<th>SBS modified bitumen</th>
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<tr>
<td>25°C Penetration</td>
<td>53.6 (0.1mm)</td>
</tr>
<tr>
<td>15°C Ductility</td>
<td>34.3 (cm)</td>
</tr>
<tr>
<td>Softening point (TR&amp;B)</td>
<td>68.7 (°C)</td>
</tr>
<tr>
<td>15°C Density</td>
<td>1.033 (g/cm³)</td>
</tr>
<tr>
<td>Solubility (trichloroethylene)</td>
<td>99.7 (%)</td>
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### Table 2 Properties of the flame retardant ATH

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<tr>
<th>Test Properties</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>Fe₂O₃</th>
<th>Na₂O</th>
<th>loss on ignition</th>
<th>Particle size</th>
<th>PH</th>
<th>Adhesive water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Results</td>
<td>64%</td>
<td>0.03%</td>
<td>0.01%</td>
<td>0.3%</td>
<td>34±0.5 %</td>
<td>3μm</td>
<td>8.5</td>
<td>0.5%</td>
</tr>
</tbody>
</table>

### Table 3 Surface free energy components of aggregates (mJ/m²)

<table>
<thead>
<tr>
<th>aggregates</th>
<th>γ&lt;sub&gt;LW&lt;/sub&gt; (Lifshitz-Van der waals)</th>
<th>γ&lt;sub&gt;AB&lt;/sub&gt; (Acid Base)</th>
<th>γ (Total SFE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>limestone</td>
<td>8.01</td>
<td>48.17</td>
<td>56.19</td>
</tr>
<tr>
<td>basalt</td>
<td>7.86</td>
<td>44.98</td>
<td>52.84</td>
</tr>
<tr>
<td>granite</td>
<td>7.07</td>
<td>48.55</td>
<td>55.62</td>
</tr>
</tbody>
</table>

### Table 4 SFE components of probe liquids (mJ/m²)

<table>
<thead>
<tr>
<th>Probe</th>
<th>γ&lt;sub&gt;LW&lt;/sub&gt; (Lifshitz-Van der waals)</th>
<th>γ&lt;sub&gt;AB&lt;/sub&gt; (Acid Base)</th>
<th>γ (Total SFE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distilled water</td>
<td>18.7</td>
<td>53.6</td>
<td>72.3</td>
</tr>
<tr>
<td>Formamide</td>
<td>39.4</td>
<td>19.6</td>
<td>59.0</td>
</tr>
<tr>
<td>Glycerol</td>
<td>28.3</td>
<td>36.9</td>
<td>65.2</td>
</tr>
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</table>

### Table 5 Contact angle of SBS modified binders containing ATH

<table>
<thead>
<tr>
<th>Samples sources</th>
<th>contact angle (°) in liquid</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>distilled water</td>
</tr>
</tbody>
</table>

23
### Table 6 ANOVA Analysis for work of adhesion at confidence level of 95%

<table>
<thead>
<tr>
<th>Sources of variance</th>
<th>Sum of squared</th>
<th>DF</th>
<th>Mean square</th>
<th>F statistic</th>
<th>P value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model corrected</td>
<td>25.900</td>
<td>7</td>
<td>3.700</td>
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<td>.000</td>
</tr>
<tr>
<td>Intercept</td>
<td>56784.500</td>
<td>1</td>
<td>56784.500</td>
<td>21673473.282</td>
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</tr>
<tr>
<td>ATH content</td>
<td>19.232</td>
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<td>3.846</td>
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<td>Aggregate type</td>
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<td>Errors</td>
<td>.026</td>
<td>10</td>
<td>.003</td>
<td></td>
<td></td>
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<tr>
<td>Total</td>
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<td></td>
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<tr>
<td>Total corrected</td>
<td>25.926</td>
<td>17</td>
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</tr>
</tbody>
</table>

### Table 7 ANOVA Analysis for work of debonding at confidence level of 95%

<table>
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<tr>
<th>Sources of variance</th>
<th>Sum of squared</th>
<th>DF</th>
<th>Mean square</th>
<th>F statistic</th>
<th>P value</th>
</tr>
</thead>
<tbody>
<tr>
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<td>805.208</td>
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<td>9.725</td>
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<tr>
<td>Errors</td>
<td>.027</td>
<td>10</td>
<td>.003</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>826.248</td>
<td>18</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total corrected</td>
<td>21.040</td>
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</table>

### Table 8 ANOVA Analysis for spreading coefficient at confidence level of 95%

<table>
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<tr>
<th>Sources of variance</th>
<th>Sum of squared</th>
<th>DF</th>
<th>Mean square</th>
<th>F statistic</th>
<th>P value</th>
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</thead>
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<tr>
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<td>5.497</td>
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<td>Sum of squared</td>
<td>DF</td>
<td>Mean square</td>
<td>F statistic</td>
<td>P value</td>
</tr>
<tr>
<td>--------------------------</td>
<td>----------------</td>
<td>-----</td>
<td>---------------</td>
<td>-------------</td>
<td>---------</td>
</tr>
<tr>
<td>Model corrected</td>
<td>3.482</td>
<td>7</td>
<td>.497</td>
<td>1971.913</td>
<td>.000</td>
</tr>
<tr>
<td>Intercept</td>
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<td>123.036</td>
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<td>6621.960</td>
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<tr>
<td>Errors</td>
<td>.003</td>
<td>10</td>
<td>.000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
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<td></td>
<td></td>
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<tr>
<td>Total corrected</td>
<td>3.484</td>
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</tr>
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</table>

**Table 9** ANOVA Analysis for energy ratio at confidence level of 95%

**Figures**

**Fig.1.** Asphalt binder samples prepared using glass slides

**Fig.2.** Flow chart of the experimental organization

**Fig.3.** Physical properties and flame-retardant data, (a) penetration, (b) ductility, (c) softening point, (d) viscosity, (e) G*/sinθ, (f) limiting oxygen index.

**Fig.4.** ATH content on contact angle

**Fig.5.** ATH content on SFE
Fig. 1. Asphalt binder samples prepared used 25×50 mm glass slides
**Fig. 2.** Flow chart of the experimental organization

**Fig. 3.** Physical properties and flame-retardant data, (a) penetration, (b) ductility, (c) softening point, (d) viscosity, (e) G*/sinδ, (f) limiting oxygen index.
**Fig. 4.** ATH content on contact angle  
**Fig. 5.** ATH content on SFE  

**Fig. 6.** ATH content on cohesive energy  

**Fig. 7.** ATH content on work of adhesion
Work of debonding \( W_{\text{wet}} \) (mJ/m\(^2\))

- **Limestone**
- **Basalt**
- **Granite**

<table>
<thead>
<tr>
<th>ATH content (%)</th>
<th>0</th>
<th>6</th>
<th>8</th>
<th>10</th>
<th>12</th>
<th>14</th>
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<tbody>
<tr>
<td>4.5</td>
<td>6.47</td>
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<td>5.83</td>
<td>5.52</td>
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<td>5.83</td>
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<td>6.0</td>
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<td>5.83</td>
<td>5.52</td>
<td>5.67</td>
<td>5.83</td>
<td>5.9</td>
</tr>
<tr>
<td>7.5</td>
<td>5.83</td>
<td>5.52</td>
<td>5.67</td>
<td>5.83</td>
<td>5.9</td>
<td>6.1</td>
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<tr>
<td>9.0</td>
<td>5.9</td>
<td>6.1</td>
<td>5.83</td>
<td>5.9</td>
<td>6.1</td>
<td>6.47</td>
</tr>
</tbody>
</table>

Fig. 8. ATH content on work of debonding

Spreading coefficient (SC)

- **Limestone**
- **Basalt**
- **Granite**

<table>
<thead>
<tr>
<th>ATH content (%)</th>
<th>0</th>
<th>6</th>
<th>8</th>
<th>10</th>
<th>12</th>
<th>14</th>
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<tbody>
<tr>
<td>9</td>
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<td>17.11</td>
<td>17.11</td>
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</tbody>
</table>

Fig. 9. ATH content on spreading coefficients

Energy ratio (ER)

- **Limestone**
- **Basalt**
- **Granite**

<table>
<thead>
<tr>
<th>ATH content (%)</th>
<th>0</th>
<th>2</th>
<th>4</th>
<th>6</th>
<th>8</th>
<th>10</th>
<th>12</th>
<th>14</th>
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</thead>
<tbody>
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<td>2.7</td>
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<td>2.5</td>
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<td>2.7</td>
<td>2.6</td>
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</tr>
<tr>
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<td>2.6</td>
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<td>2.3</td>
<td>2.2</td>
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</tr>
<tr>
<td>8</td>
<td>2.7</td>
<td>2.6</td>
<td>2.5</td>
<td>2.4</td>
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<td>2.2</td>
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</tbody>
</table>

Fig. 10. ATH content on energy ratio
Fig. 10. ATH content on energy ratio