Laboratory evaluation of the effect of nano-organosilane anti-stripping additive on the moisture susceptibility of HMA mixtures under freeze–thaw cycles

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HIGHLIGHTS

- Addition of both anti-stripping additives significantly increased the ITS and TSR values of all asphalt mixtures.
- Effects of anti-stripping additives on mixtures made with siliceous aggregate are more noticeable than limestone mixtures.
- The fracture energy area under the load–deflection curve, for the Zycosoil-modified mixtures is higher than other mixtures.
- Generally, influence of freeze–thaw cycling on resilient modulus and fracture energy was in accordance with TSR results.

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ABSTRACT

The objective of this research study was to evaluate moisture susceptibility of hot mix asphalt (HMA) with and without Zycosoil as a nano-organosilane anti-stripping additive and hydrated lime in the form of slurry. Moisture resistance was evaluated on mixtures prepared with two sources of aggregate: limestone and siliceous. The base bitumen used was AC 60–70 grade, and two anti-stripping additives. The functional characterization of the base bitumen with and without Zycosoil was analyzed by means of Fourier Transform Infrared Spectroscopy (FTIR). The performance of HMA mixtures under multiple freeze–thaw cycles was evaluated through the following tests: resilient modulus; indirect tensile strength; tensile strength ratio and fracture energy. The findings of this research indicate that use of both additives enhanced the resilient modulus ratio of the mixtures. It was also observed that the effects of anti-stripping additives on specimens made by siliceous aggregate are more pronounced than those prepared with limestone aggregates. Fracture energy results also proved that use of Zycosoil additive will increase adhesion bond between the aggregates and asphalt binders, and in turn influences the moisture resistance of the mixture to moisture damage.

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1. Introduction

The moisture damage of asphalt mixtures is defined as the progressive loss of functionality of the material due to loss of the adhesive bond between the asphalt binder and the aggregate surface [1]. Penetration of moisture in asphalt mixtures reduces strength and stiffness of asphalt mixtures and prone the mixtures to develop various forms of premature pavement distress. The premature deterioration of asphalt pavements caused by moisture in asphalt mixtures includes stripping, raveling, and hydraulic scour. Additional distresses provoked by moisture in asphalt mixtures are: rutting, alligator cracking, and potholes [2]. The presence of water in pavements can be detrimental if combined with other environmental factors such as freeze–thaw cycling [3].

The chemical and physical interactions that occur between bitumen and aggregate at the interface are influenced by freeze–thaw cycling over extended periods of time. Among these interactions affected by freeze–thaw cycling are those influencing adhesive strength [4].

To alleviate or to control the deformations due to water damage, various researches were performed leading to the utilization of anti-stripping additives. Anti-stripping additives are used to increase physico-chemical bond between the bitumen and aggregate and also to improve wetting by lowering the surface tension of the bitumen. The additives that are used in practice or tested in the laboratory include: (i) traditional liquid additives, (ii) metal ion surfactants, (iii) hydrated lime and quick lime, (iv) silane coupling agents, and (v) silicone. Among them, hydrated lime...
and quicklime are the most commonly used solid type anti-stripping agents [5]. When lime is added to HMA, it reacts with aggregate and strengthens the bond between the bitumen and the aggregate interface. The ability of hydrated lime to make an asphalt mix stiffer, tougher, and resistant to rutting, is a reflection of its superior performance as active mineral filler [5].

It should be noted that an effective anti-stripping agent must improve both the unconditioned and moisture conditioned properties of asphalt mixtures in order to ensure long term performance of asphalt pavements [6].

Even though engineers are interested in the material properties at the macro- and meso-scales, the phenomena at nano- and micro-scales provide fundamental insight for the underlying interactions defining the physico-chemical behavior of materials [7].

In the last decade or so, nanotechnology has emerged as the potential solution to greatly enhance the performance and durability of construction materials. Nanomaterials are defined as materials with at least one dimension that falls in the length scale of 1–100 nm. Due to the small size and high surface area, the property of nanomaterials is much different from normal size materials [8]. Therefore, research engineers tried to apply the nanomaterials into the asphalt technology. Some research showed that fatigue cracking, rutting and moisture resistance of asphalt binders and mixtures are improved with the addition of nanomaterials [6–9].

Arabani in 2012 focused on evaluating the moisture susceptibility of warm mix asphalt (WMA) with and without Zycosoil as a nano-organosilane additive by determining the micromechanisms that affect the adhesion bond between the aggregates and asphalt binders and the cohesion strength of the asphalt binder. The results of the surface free energy (SFE) method indicate that addition of Zycosoil into asphalt binders of WMA mixtures increase the surface energy of adhesion between aggregate and asphalt in dry and wet condition. Thus, the energy released in mixes modified by Zycosoil is lower than other mixes, and therefore their stripping resistance is higher [9]. In another study conducted by Moghadas Nejad et al. it was shown that addition of Zycosoil in hot mix asphalt containing limestone and granite aggregates will increase tensile strength ratio (TSR) as compared to the control mixtures [6].

In recent years, several studies focusing on use of nano-scale organosilane as anti-stripping additives in asphalt mixtures have been conducted; however, the effects of these additives on moisture susceptibility of asphalt mixture under freeze–thaw cycles are still not fully understood [9].

2. Materials

2.1. Aggregate

In this research study, two types of widely used aggregates in the country namely siliceous and limestone were used for evaluation of asphalt mixtures against moisture damages. These aggregates represent a substantial range in mineralogy and associated degree of stripping. The chemical compositions are determined with an electron microprobe analyzer (EMPA). The results of chemical compositions are given in Table 1. The physical and engineering properties of the aggregates are shown in Table 2. The gradation of the aggregates employed in the study (mean limits of ASTM specifications for dense aggregate grading) is presented in Table 3. The nominal size of this grading was 19.0 mm.

2.2. Asphalt binder

In this experimental investigation, an asphalt binder of 60/70 penetration grade from Isfahan mineral oil refinery was used. To characterize the properties of the asphalt binder, conventional tests including the penetration, softening point and ductility were carried out. Table 4 summarizes the basic properties of the asphalt binder.

2.3. Additives

Zycosoil is a water soluble reactive organo-silicon compound that is specially designed to improve the adhesion between bitumen and aggregates [9]. In this study, as recommended by the manufacturer, Zycosoil was added in quantity equal to 0.5% by weight of the asphalt binder. The properties of the Zycosoil are presented in Table 5.

2.4. Hydrated lime

Lime slurry was added to aggregates in an attempt to improve asphalt mixture resistance to moisture damage, whereby optimum content of hydrated lime added to aggregate was obtained after preliminary tests. The percent of hydrated lime that showed the best strength against moisture damage was 1% by weight of aggregate that was selected as optimum content of hydrated lime.

2.5. Sample preparation and test methods

The asphalt mixtures were designed by using the standard marshal mix design procedure with 75 blows on each side of cylindrical samples in accordance with ASTM D1559 standard [10]. Marshall tests were carried out to find the optimum asphalt binder content of mixtures. The optimum asphalt binder content of asphalt mixture with siliceous and limestone aggregate was 5.3% and 4.8%, respectively.

2.6. Fourier Transformed Infrared Spectroscopy (FTIR)

From the infrared spectra of test, the material information about chemical bonding and materials structure would be obtained [11]. Zycosoil were applied to modify the base bitumen, and the FTIR test were employed to determine the functional characteristics of bitumens in wave numbers ranging from 4000 to 400 cm⁻¹ [12]. The FTIR test was implemented in the central Chemical Engineering Research Laboratory of the country.

2.7. Resilient modulus test

The resilient modulus is directly affected by the loss of adhesion and cohesion [13]. It is believed that resilient modulus is more sensitive to changes in asphalt binder properties and a mixture’s sensitivity to damage by water than the tensile strength of the mixture [14]. In this study, the ratio of resilient modulus test in wet-to-dry conditions was used to assess the effect of additives on the rate of stripping in HMA. This test is a non-destructive test, and in this research, it is undertaken in accordance with the ASTM D 4123 [10] using an assumed Poisson’s ratio of 0.35. The samples were tested with Universal Testing Machine (UTM) at 25 °C by applying a haversine load consists of 0.1-s load application followed by a 0.9-s rest period. The sample preconditioning of resilient modulus test was similar to ITS test. The load and deformation were continuously recorded and resilient modulus were calculated using the following equation:

\[
M_R = \frac{P}{(t \times \Delta h)}
\]

where P is the peak value of the applied vertical load (N), \( \Delta h \) is the mean amplitude of the horizontal deformation obtained from five applications of the load pulse (mm), t is the mean thickness of the test specimen (mm), and v is the Poisson’s ratio (assumed 0.35) [15–17].

The ratio of resilient modulus is used for evaluating of the moisture susceptibility of asphalt mixtures. The resilient modulus ratio is defined by the following equation:

\[
\text{Resilient Modulus Ratio (MRR)} = \frac{M_{R \text{ of conditioned specimen}}}{M_{R \text{ of dry(control)specimen}}}
\]

where \( M_R \) is the resilient modulus of mixtures [13]. A resilient modulus ratio (MRR) of 70% or above has typically been utilized as a minimum acceptable value for HMA mixtures [1,13].
2.8 Indirect tensile strength test

The tensile strength of an HMA mixture is generated by the cohesive strength of the asphalt binder and the bond strength at the binder–aggregate interface [6]. The influence of water in the reduction of the strength of HMA mixtures has been reported as one of the main issues that need to be evaluated for moisture damage [6, 18]. Thus, in this study the tensile strength of five subsets of specimens compacted with 7.0 ± 0.5% air voids were obtained using the indirect tensile strength (ITS) test according to AASHTO T283 [19]. The purpose of this test is to determine the effect of saturation and accelerated water conditioning on the indirect tensile strength (ITS) of cylindrical specimen [20].

The first subset was tested in a dry condition, and the other four subsets subject to vacuum saturation (55–80% of the air voids volume), followed by one freeze-thaw (F–T) cycle, two F–T cycles and up to four F–T cycles, respectively, prior to being tested. In the ITS test, a compressive load applied to the cylindrical specimens, which act parallel to the vertical diametral plane by using the Marshall loading equipment. This type of loading produces a relatively uniform tensile stress, which acts perpendicular to the applied load plane. The maximum load that the samples can sustain prior to cracking and also the deformations of them were continuously recorded.

Parameters from the indirect tensile strength test that have been correlated to actual cracking values include indirect tensile strength, tensile strength ratio (TSR), and fracture energy to failure. These indirect tensile strength parameters are defined as follows:

1. The indirect tensile strength \( (S_t) \) is the maximum stress developed at the center of the specimen in the radial direction during the loading by the following equation:

\[
S_t = \frac{2 \times P_{\text{max}}}{\pi \times d \times t}
\]

where \( S_t \), tensile strength of conditioned or unconditioned specimens, kPa; \( P_{\text{max}} \), maximum applied load, kN; \( t \), thickness of the specimens, meter; \( d \), diameter of the specimens, m [21].

2. A tensile strength ratio (TSR) which is the ratio of the average tensile strength of the conditioned specimens (1 F–T, 2 F–T, 3 F–T and 4 F–T) to the average tensile strength of the unconditioned specimens was then calculated. The TSR represents a reduction in the mixture integrity due to moisture damage. A minimum ratio of 80% has been typically used for TSR as a failure criterion [22].

3. The energy at onset of failure is calculated from the results of the ITS test as shown in Fig. 1 [15].

A higher ITS and TSR values typically indicate that the mixture will perform well with a good resistance to moisture damage. At the same time, mixtures that are able to tolerate higher deformation prior to failure are more likely to resist cracking than those unable to tolerate high deformation [23].

### Table 2

Physical and engineering properties of the aggregate.

<table>
<thead>
<tr>
<th>Test Standard</th>
<th>Siliceous Limestone</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific gravity (coarse agg.)</td>
<td>ASTM C 127</td>
<td>2.649</td>
</tr>
<tr>
<td>Bulk</td>
<td>2.671</td>
<td>2.643</td>
</tr>
<tr>
<td>SSD</td>
<td>2.689</td>
<td>2.659</td>
</tr>
<tr>
<td>Apparent</td>
<td>2.689</td>
<td>2.659</td>
</tr>
<tr>
<td>Specific gravity (fine agg.)</td>
<td>ASTM C 128</td>
<td>2.669</td>
</tr>
<tr>
<td>Bulk</td>
<td>2.652</td>
<td>2.633</td>
</tr>
<tr>
<td>SSD</td>
<td>2.692</td>
<td>2.651</td>
</tr>
<tr>
<td>Apparent</td>
<td>2.669</td>
<td>2.618</td>
</tr>
<tr>
<td>Specific gravity (filler)</td>
<td>ASTM D854</td>
<td>2.663</td>
</tr>
<tr>
<td>Los Angeles abrasion (%)</td>
<td>ASTM C 131</td>
<td>20.1</td>
</tr>
<tr>
<td>Flat and elongated particles (%)</td>
<td>ASTM D 4791</td>
<td>6.8</td>
</tr>
<tr>
<td>Sodium sulfate soundness (%)</td>
<td>ASTM C 88</td>
<td>1.7</td>
</tr>
<tr>
<td>Fine aggregate angularity</td>
<td>ASTM C 1252</td>
<td>57.5</td>
</tr>
</tbody>
</table>

### Table 3

Gradation of the aggregates used in the study.

<table>
<thead>
<tr>
<th>Sieve (mm)</th>
<th>Lower–upper limits</th>
<th>Passing (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>19</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>12.5</td>
<td>90–100</td>
<td>88</td>
</tr>
<tr>
<td>4.75</td>
<td>44–74</td>
<td>75</td>
</tr>
<tr>
<td>2.36</td>
<td>28–58</td>
<td>56</td>
</tr>
<tr>
<td>0.3</td>
<td>5–21</td>
<td>40</td>
</tr>
<tr>
<td>0.25</td>
<td>2–10</td>
<td>20</td>
</tr>
<tr>
<td>0.106</td>
<td>7–18</td>
<td>9</td>
</tr>
<tr>
<td>0.075</td>
<td>4–10</td>
<td>6</td>
</tr>
</tbody>
</table>

### Table 4

Results of the experiments conducted on 60/70 penetration grade asphalt binder.

<table>
<thead>
<tr>
<th>Test Standard</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Penetration (100 g, 5 s, 25 °C), 0.1 mm</td>
<td>ASTM D5-73</td>
</tr>
<tr>
<td>Penetration (200 g, 60 s, 4 °C), 0.1 mm</td>
<td>ASTM D5-73</td>
</tr>
<tr>
<td>Penetration ratio</td>
<td>ASTM D5-73</td>
</tr>
<tr>
<td>Ductility (25 °C, 5 cm/min), cm</td>
<td>ASTM D113-79</td>
</tr>
<tr>
<td>Solubility in trichloroethylene (%)</td>
<td>ASTM D2042-76</td>
</tr>
<tr>
<td>Softening point (°C)</td>
<td>ASTM D36-76</td>
</tr>
<tr>
<td>Flash point (°C)</td>
<td>ASTM D92-78</td>
</tr>
<tr>
<td>Loss of heating (%)</td>
<td>ASTM D1754-78</td>
</tr>
<tr>
<td>Properties of the TFOT residue</td>
<td>ASTM D5-73</td>
</tr>
<tr>
<td>Penetration (100 g, 5 s, 25 °C), 0.1 mm</td>
<td>ASTM D70-76</td>
</tr>
<tr>
<td>Specific gravity at 15 °C, cSt</td>
<td>ASTM D2170-85</td>
</tr>
</tbody>
</table>

### Table 5

Properties of the Zycosoil.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Zycosoil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Form</td>
<td>Solid</td>
</tr>
<tr>
<td>Color</td>
<td>Colorless–pale yellow</td>
</tr>
<tr>
<td>Flash point</td>
<td>80 °C</td>
</tr>
<tr>
<td>Viscosity (at 25 °C)</td>
<td>0.2–0.8 Pa s</td>
</tr>
</tbody>
</table>

Fig. 1. Typical load–deformation curve for calculation of fracture energy at onset of failure [19].
3. Test results and discussion

3.1. Fourier Transformed Infrared Spectroscopy (FTIR) analysis

Figs. 2 and 3 provide Infrared spectroscopy analysis master curves of the Zycosoil modified and original base asphalt binder at 25 °C.

According to the report by Bukka, the bands at 2923 and 1376 cm\(^{-1}\) are characteristic of C–H asymmetrical stretching and C–H deformation in –CH\(_3\), respectively; the two bands at 2852 and 1460 cm\(^{-1}\) are associated with C–H asymmetrical stretching and C–H deformation in –CH\(_2\), respectively [24]. From the infrared spectroscopy data, peaks in the region of 1710–1690 cm\(^{-1}\) corresponding to carbonyl stretch were used to characterize bitumen. This region is characteristic of functional groups like carboxylic acids, 2-quinolones, anhydrides and ketones, some of which could be crucial as regards to moisture damage. Plancher in 1977 found that carboxylic acids in the bitumen were strongly adsorbed by siliceous aggregates, but were present in very small amounts. At the same time, carboxylic acids tend to be displaced first from the aggregate in presence of moisture [25]. The positions of bands in the curves of Zycosoil modified binder and original base binder are nearly the same. The differences is the stretching vibration band of Si–OH and Si–O appears at 3360, 1038 cm\(^{-1}\).

3.2. Resilient modulus result

Figs. 4 and 5 present the resilient modulus results for the dry and conditioned HMA mixtures from the two aggregates sources at 25 °C. In order to more accurately assess the effect of lime slurry and Zycosoil on the resistance of asphalt mixtures to moisture damages, four freeze–thaw cycles are applied to the samples. As seen in Figs. 4 and 5, generally, resilient modulus decreased after freeze–thaw (F–T) conditioning for all mixtures. Siliceous control mixtures were lasted until the fourth F–T cycle. While mixtures with anti-stripping additives after F–T conditioning. As depicted in Fig. 5, the resilient modulus of the siliceous mixture containing Zycosoil relative to control mixture was greater than containing lime slurry.

The results of the FTIR test performed on asphalt binder modified with Zycosoil are shown in Fig. 3, indicates the points related to the Si–O bonds in organosilane compounds of the Zycosoil. In the presence of water, this bonds turn into Si–OH silanoles, and through reacting with silanols on aggregate surface creates the Si–O–Si film structure over the surface. Since the covalent bonds are stronger than hydrogen bonds, the Si–O–Si film structure acts as a hydrophobic layer and covers the aggregates surface [27]. Finally, this hydrophobic layer avoids water penetration and prevents the establishment of hydrogen bonds between water and aggregate surface at binder–aggregate interfaces.

3.3. Resilient modulus ratio (MRR)

Fig. 6 shows the change of resilient modulus ratio versus the number of F–T cycles. The MRR was used to evaluate the propensity of the mixtures to stripping potential. Mixtures with resilient modulus ratios of less than 70% are considered prone to stripping potentials [1,13]. The siliceous control mixtures did not perform as adequately as the limestone control mixtures did in the freeze–thaw cycles. The MRR values of all of the siliceous control mixtures were less than 70% and thus these mixtures are more sensitive to moisture damage. Fig. 6b shows that Zycosoil and lime slurry have enhanced the MRR of siliceous mixtures in all freeze–thaw processes. As can be seen in Fig. 6a and b both siliceous and limestone mixtures with Zycosoil additives have better resistance during freeze–thaw cycles than the control mixtures and also the mixtures containing lime slurry.

3.4. Indirect tensile strength (ITS) result

The ITS and TSR test are often used to evaluate the moisture susceptibility of an asphalt mixture [23]. A higher ITS and TSR values typically indicate that the mixture will have better resistance to moisture damage. At the same time, mixtures that are able to tolerate higher strain prior to failure are more likely to have better resistance to environmental cracking [23,28].
Figs. 7 and 8 show the indirect tensile strength of specimens. As shown in these figures, F–T cycles have reduced the indirect tensile strengths of the mixtures, specifically the mixture containing siliceous aggregate. Siliceous control mixtures were deteriorated at the third F–T cycle but limestone control mixtures could resist the detrimental F–T effects, indicating limestone aggregate mixture has better resistant to moisture damage relative to siliceous aggregate.

According to Figs. 2 and 3, the FTIR test shows the existence of carboxylic acids in the virgin base bitumen and also modified binder. During the mixing of binder with aggregate, carboxylic acid is quickly absorbed by aggregates [27]. At binder–aggregate interface, the bonds between carboxylic acids and Si–OH compounds on the aggregate surface are unstable against water [27].
reduction in the indirect tensile strengths of the samples by increasing number of F–T cycles can be attributed to the loss of adhesion bond between the aggregates and the asphalt binders and also the loss of cohesive strength of the asphalt binder due to F–T cycles effects.

Based on the South Carolina Department of Transportation (SCDOT) criterion, moisture resistant mixtures should have wet ITS value more than 448 kPa. All of the control siliceous and limestone aggregates mixtures failed the SCDOT requirement under the F–T conditioning with the exception of the limestone samples in the first F–T cycle.

As can be seen from Figs. 7 and 8, addition of both anti-stripping additives significantly increased the indirect tensile strengths values of all asphalt mixtures. It is noteworthy that the effects of anti-stripping additives on specimens made by siliceous aggregate are more pronounced than those on mixture made by limestone aggregate.

From Figs. 7 and 8, it is evident that addition of Zycosoil to the limestone mixtures improves the indirect tensile strengths of the mix more than the lime slurry. However, test results demonstrated that the influence of lime slurry on increasing the indirect tensile strengths of siliceous mixtures was higher than Zycosoil until the second F–T cycle. In terms of ITS, the Zycosoil showed better effect than lime slurry at the third and fourth F–T cycle.

3.5. Tensile strength ratio (TSR)

TSR of wet group to dry group specimens was computed from the results of the indirect tensile strength test at 25 °C. The higher the TSR value, the higher the resistance of the mixture to moisture damage. According to the research conducted by Little and Jones in 2003 [29], hydrated lime ties with carboxylic acids in the bitumen, with the formation of insoluble calcium organic salts, which prevent these functionalities from reacting with a siliceous surface to form water sensitive bonds. This leaves important active sites on the siliceous surface to form strong water resistant bonds with nitrogen groups in bitumen.

Besides Zycosoil produces a hydrophobic nano-layer on aggregates since it converts the hydrophilic silanol groups to hydrophobic siloxane groups. So Zycosoil can eliminate water sensitive surface permanently and makes it oil-loving [6].

The test results of the mixtures studied in this research indicated that the effect of both anti-stripping additives on increasing the TSR values of specimens was similar. By taking both ITS and TSR results into account, although, the differences between the effects of Zycosoil and lime slurry are not significant, but the results confirm the tendency of the Zycosoil additive to increase the moisture damage resistant of limestone mixtures.

3.6. Fracture energy result

This stage of analysis focused on computing the fracture resistance of modified and unmodified HMA mixtures exposed to accelerated moisture damage process based on the load–displacement curves obtained from ITS test which presented in Fig. 1. Figs. 11 and 12 show the fracture energy of HMA specimens fabricated with two aggregate types and two kinds of anti-stripping additives.

3.6.1. Limestone mixtures

According to ITS test results presented in Fig. 11, it was found that the average mean dry fracture energy values of limestone control mixtures were not higher than the modified limestone mixtures. Comparison of wet fracture energy values indicated that it can be concluded that the siliceous aggregates are more susceptible to moisture damage than the limestone aggregates.

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the mean wet fracture energy values of all Zycosoil modified limestone mixtures were greater than the control limestone mixtures and mixtures containing lime slurry.

The area under the load–deflection curve for the Zycosoil-modified mixtures is also higher than control mixture and mixtures containing lime slurry.

As can be seen in Table 1, the limestone aggregate has small percentage of Silica (SiO2). In the case of control limestone mixtures, a small percentage of bitumen and aggregate bonding functional groups are sensitive to moisture during F–T conditions [26]. As a result, the fracture energy values of these specimens in wet conditions are somewhat lower than the fracture energy values of these specimens in dry condition. In addition, according to the results, it appears that the adhesion between binder and aggregate in the mixtures containing additives, particularly the specimens modified by Zycosoil, is higher than the mixtures without anti-stripping additives. Thus, when a mixture is modified with Zycosoil, more energy is needed to break the bonds between aggregate and bitumen in both dry and wet conditions. Therefore it can be concluded that if an asphalt mixture sustains more load and also more deformation at the onset of failure it will have more resistance to moisture damage.

3.6.2. Siliceous mixtures

From Figs. 11 and 12, it is clear that the mixtures prepared with the siliceous aggregate have higher fracture energy than the mixtures prepared with the limestone aggregate. The siliceous control mixtures had lower fracture energy values in the wet condition than modified siliceous mixtures. Thus it is deduced that use of additives has increased fracture energy values of siliceous mixtures followed by F–T conditions. Although the indirect tensile strengths of asphalt mixtures containing Zycosoil additive in the first and second cycles of F–T were somewhat lower than asphalt mixtures containing lime slurry, but conversely, the fracture energy of mixtures containing Zycosoil were higher than those mixtures containing lime slurry.

Siliceous aggregates predominantly comprised of SiO2 and produce unstable bonds with bitumen against water. Upon exposure to moisture conditions, water is rapidly absorbed by the siliceous aggregate. Due to existence of the high percentage of hydroxyls on the surface of siliceous aggregate, the Zycosoil has a very good effect in combination with siliceous aggregate.  

As can be seen from Figs. 11 and 12, the fracture energy values of both modified and unmodified mixtures decrease as the number of F–T cycles increases. However, according to Figs. 13 and 14, at the same F–T cycle, the Zycosoil-modified mixture always has higher fracture energy as compared to the mixtures that are modified with or without slurry lime. Also from Figs. 11 and 12 it is deduced that use of Zycosoil will produce a more cohesive binder with a better adhesion to aggregate surface, this is evident from the higher residual strength and also higher displacement value at maximum load for specimens containing Zycosoil.

The fracture energy obtained from the area under the load–displacement curve is the amount of work required for breaking the sample. In fact, the failure of the specimen in the indirect tensile strength test depends on two parameters namely: friction, and adhesion of mixture. Since the fracture energy of the Zycosoil mixtures is higher than those mixtures modified with hydrated lime slurry, it can be deduced that the Zycosoil additive improves the adhesion between binder and aggregate and thus enhanced the resistance of the mixture to the moisture damage.

4. Conclusion

To investigate the moisture damage susceptibility of asphalt mixtures under freeze–thaw cycles, two anti-stripping additives namely Zycosoil and hydrated lime slurry with two different kinds of aggregate and one grade of bitumen were used. Control mixtures were produced with AC60–70 using the same aggregate sources and gradation, for comparison purposes. Various laboratory tests were conducted to evaluate the characteristics of using Zycosoil as a nano-organosilane additive, and hydrated lime slurry in the hot mix asphalt under freeze–thaw cycles. The following conclusions...
were drawn based upon the experimental results obtained from this research study:

- In the resilient modulus test, although mixtures with siliceous aggregate have higher $M_R$ values than mixtures with limestone aggregate in dry condition, but siliceous control mixtures were failed in the fourth F–T cycle whereas limestone control mixtures lasted until the fourth cycle.
- Use of anti-stripping additives improves the MRR of the mixtures. Both Zycosoil and lime slurry have obvious effects on MRR for siliceous mixtures in all freeze–thaw cycles.
- Addition of both anti-stripping additives significantly increased the indirect tensile strength values and tensile strength ratio of all asphalt mixtures. It is worthy to note that the effects of anti-stripping additives on mixtures made with siliceous aggregate are more noticeable than those mixtures made with limestone aggregates.
- Regardless of the aggregate source, the mean wet ITS values of all the Zycosoil modified mixtures were higher than the control mixtures and mixtures containing hydrated lime slurry. Also the deflection of modified mixtures increased due to the addition of Zycosoil. Consequently, the area under the load–deflection curve (fracture energy) for the Zycosoil-modified mixtures is also higher than other mixtures.
- Based on fracture energy results, the fracture energy of the Zycosoil mixtures is higher than hydrated lime slurry mixtures.
- In the light of current research findings from laboratory investigations conducted in this research study, it is found that addition of Zycosoil additive improves HMA mixture resistance to moisture damage.
- Generally, influence of freeze–thaw cycling on resilient modulus and fracture energy was in accordance with TSR results. It can be concluded that these tests are useful for evaluation of moisture sensitivity of hot mix asphalt.
- It is recommended to conduct a field study to investigate the performance of HMA mixtures modified by Zycosoil.

References

[29] Little D, Jones D. Chemical and mechanical mechanisms of moisture damage in hot mix asphalt pavements. National Seminar in Moisture Sensitivity, San Diego, California; 2003.