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Investigating of the Effects of Nano-materials on the Moisture Susceptibility of Asphalt Mixtures Containing Glass Cullets

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ABSTRACT: The pavement industry is one of the industries that has considered using waste to partially replace the aggregates in asphalt mixtures. Despite its many environmental and technical benefits, the use of crushed glass increases the moisture damage potential of asphalt mixtures. Therefore, in the present study, the aim was to investigate the effects of two nano anti-stripping additives called nano iron oxide (Fe_2O_3) and nano aluminum oxide (Al_2O_3) on the moisture susceptibility of hot mix asphalt (HMA) mixtures containing crushed glass. The glass asphalt mixtures were made by replacing 0, 5, 10, 15, and 20% of the fine aggregates with glass cullets. In order to investigate the effects of nano-materials on the moisture susceptibility of glass asphalt mixtures, the modified Lottman test (AASHTO T283) and the surface free energy (SFE) method were used. The results showed that the addition of nano-materials improved the adhesive force between asphalt binders and aggregates (crushed glass and aggregates with acidic properties) by reducing the acidic and increasing the basic properties of the modified asphalt binder. Moreover, asphalt modification with nano-materials increased the initial energy required to separate asphalt binder from the aggregate surface and reduced the risk of moisture damage by increasing the total SFE of asphalt binder.

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1- Introduction

Glass and glassware are widely used in industries and everyday life, and the growing trend of this use has turned glass into one of the most important waste materials that are collected on a daily basis [1]. The glass is a crisp, fragile, non-metallic, and inorganic material that is made by heating raw materials such as silicates and other oxides. It is a hard substance with a specific gravity of 2.5 g/cm^3 and a high chemical resistance. According to statistics, in 2005, the total global waste glass production estimate was 130 Mt [2]. In the construction of roads, waste glass is mainly used as a substitute for a part of the coarse or fine aggregates of asphalt mixes. Hot mix asphalt containing glass cullet is termed “Glasphalt” or glass asphalt [3]. Many studies have been carried out on the use of glass cullets as an aggregate substitute in varying portions. Su and Chen [3] investigated the properties of asphalt mixtures containing 0 to 15% glass cullet (as aggregates). The results of their investigation showed a decrease in the optimum binder content, Marshall Stability, de-bonding resistance and moisture resistance and an improvement in roadway light reflection, water permeability, and frictional coefficient of the glass specimens compared to the control ones. Arabani et al. [4] surveyed the dynamic properties of asphalt mixes containing various percentages of waste glass at different temperatures and proved that the glass samples had a higher stiffness modulus, longer fatigue life, and lower thermal sensitivity than the control specimens. The glass aggregates had a maximum size of 4.75 mm and 3 to 5% hydrated lime was added to increase the resistance of the samples against water. In a study by Jassim [5], the effects of using glass aggregates as a partial replacement for raw aggregates on the Marshall stability of HMA mixtures was perused. The results revealed an increase in the Marshall stability of the specimens containing glass size No.8 and No.200. Shafabakhsh and Mirabdolazimi [6] and Shafabakhsh and Sajed [7] conducted a study on the performance of HMA mixtures containing different percentages of glass cullet at different temperatures and gradations and presented behavioral models to predict the stiffness modulus of the mixtures as a function of temperature, aggregate gradation, and glass cullet percentage. They also found that glass mixtures exhibited a better dynamic behavior than conventional ones. An investigation performed by Androjic´ and Dimter [8] on the use of glass cullet in asphalt mixtures indicated a reduced stability, density, void content and voids filled with asphalt in these mixtures. A study on the Marshall properties of glass specimens by Issa [9] revealed that glass-asphalt concretes with a lower binder content (4.5%) showed a higher Marshall ratio and the best result belonged to the sample with 10% glass content. Lachance-Tremblay et al. [10] examined the effects of using 5, 10, 15, and 20% glass cullet as a partial replacement for natural aggregates and found that the use of crushed glass reduced the binder content and rutting resistance of the mixtures and increased

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their workability. The evaluation of using 10% recycled glass in asphalt mixtures (as the optimum content) showed that it did not affect the thermal cracking resistance and stiffness of the mixtures. However, their moisture susceptibility had increased.

As mentioned in previous studies, despite the positive effects of the use of waste glass as secondary aggregates in asphalt mixtures such as lower optimum binder content and thermal sensitivity and improved light reflection, water permeability, dynamic behavior, and frictional coefficient, in some aspects, glass asphalt has shown a weak performance especially in its resistance against moisture [1, 5]. Moisture damage or stripping is defined as the loss of strength and durability due to the presence of water in the asphalt mixture. Moisture damage or stripping can cause the pavement to fail in a short time period, especially in rainy areas [11] and can lead to other types of distresses such as fatigue, rutting, potholes, and raveling [12]. The most common mechanisms of moisture damage are the mastic cohesion loss and the asphalt-aggregate adhesion loss at the contact surface, both of which occur due to water absorption [11].

There are various anti-stripping additives that improve the resistance of asphalt mixtures against water through two main methods; one improves the asphalt binder cohesion and the asphalt-aggregates adhesion (liquid anti-stripping additives from the family of amines), and the other changes the properties of the aggregate surface and reduces its tendency to water (hydrophilic) (hydrated lime) [11, 12]. The anti-stripping additives are also widely used in glass asphalt mixtures to improve their moisture resistance and other characteristics [13-21]. Despite their positive effects, the use of anti-stripping materials brings about a number of complications leading to the introduction of nano-additives [22]. So far, various nano-materials, including calcium carbonate [11, 12], iron oxide and aluminum oxide [22], zycosil [19, 23, 24], zinc oxide [11, 25], zycotherm [26], clay and lime [27, 28], and styrene-butadiene-styrene (SBS) nano-composite [29] have been used to improve the moisture susceptibility of asphalt mixtures. Nano Fe2O3 and Al2O3 are basic nano-materials [30, 31] whose addition to asphalt binder lead to a decrease in acidic properties of asphalt binder and results in stronger adhesion force between asphalt binder and acidic aggregates. The base metals for the production of these nanoparticles are aluminum and iron which are the most abundant metals in the Earth's crust. Furthermore, the production process of nano-materials from these two mineral aggregates is also not complicated. Extensive existence of iron and aluminum mines and easy production of nano Fe2O3 and Al2O3 result in lower preparation cost of these nano-materials compared to other nano-materials. The effect of these nanoparticles as anti-stripping agents on the moisture damage of conventional HMA was assessed in a previous study and showed that using nano additives increased the asphalt mixture resistance against moisture damage [22].

2- Problem Statement and Objective

In glass asphalts, hydrated lime is mainly used as an anti-stripping agent. However, its utilization is associated with many implementation problems. Therefore, in this research, two types of nano-materials namely nano Fe_2O_3 and Al_2O_3 were used as asphalt binder modifiers to reduce the moisture sensitivity of glass asphalts. The main objectives of this study are as follows:

1. Investigating the effects of waste glass on the moisture sensitivity of asphalt mixtures
2. Investigating the effects of nano Fe_2O_3 and Al_2O_3 on the moisture sensitivity of glass asphalts using laboratory tests
3. Investigating the effects of asphalt modification with nano-materials on the moisture sensitivity of glass asphalts using thermodynamic concepts
4. Determining the equation-ship between mechanical and thermodynamic methods

3- SFE Theory

Various SFE theories describe the materials based on their molecular structures. One of the most important theories used extensively to describe the components of SFE is the Lewis acid-base theory [32]. According to this theory, the total SFE of each material is divided into three components based on the type of surface molecules forces: 1) The Lifshitz-van der Waal or non-polar component (Γ^{LW}), 2) The Lewis acid component (Γ^{+}), and 3) The Lewis base component (Γ^{-}).

The total SFE of asphalt binders and aggregates can be determined by applying Equation 1:

$$\Gamma=\Gamma^{LW}+\Gamma^{AB} \tag{1}$$

Where Γ is the total SFE, Γ^{LW} is the non-polar component of SFE and ΓAB is the polar component of SFE. The polar component of SFE is composed of the acid (Γ^{+}) and base (Γ^{-}) components of SFE:

$$\Gamma^{AB}=2\sqrt{(\Gamma^{+}\,\Gamma^{-})} \tag{2}$$

From a thermodynamic point of view, free energy of cohesion (ΔG_i^c) is defined as the energy needed to create a crack in a material and make two interfaces from one. Based on this definition, the work of cohesion (W^{AC}) is simply defined as follows:

$$W^{AC}=2\Gamma \tag{3}$$

The work of cohesion is an important parameter used in some of the basic equations of fracture mechanics, which determines the energy required for the growth of fine cracks in the asphalt binder or mastic.

The free energy of adhesion (ΔG_a) has two main components: the polar or the acid-base component and the non-polar component, or the Lifshitz-van der Waals. The following equation is used to determine the free energy of adhesion between asphalt and aggregates.

$$G^{a}=-W^{a}=\Delta G_a^{LW}+\Delta G_a^{AB}=-2[(\sqrt{(\Gamma_2^{lw}\,\Gamma_1^{lw})})+(\sqrt{(\Gamma_2^{+}\,\Gamma_1^{-})})+(\sqrt{(\Gamma_2^{-}\Gamma_1^{+})})] \tag{4}$$

Where, ΔG_i^{a} is the free energy of adhesion, ΔG_i^{aLW} is the nonpolar component of free energy of adhesion, ΔG_i^{aAB} is the polar component of the free energy of adhesion, and Γ_1^{LW}, Γ_1^{+}, and Γ_1^{-} are the SFE components of asphalt binder and Γ_S^{LW}, Γ_S^{+}, and Γ_S^{-} are the SFE components of aggregates.

Equation 5 is used to calculate the work of adhesion between asphalt binders and aggregates in the presence of water. Indices 1, 2, and 3, represent asphalt, aggregate and water respectively. Positive values of SFE values indicate the materials (aggregate and asphalt) tendency to adhere to each other. The larger the value, the more work is required to remove the adhesion between them.

$$\Delta G_a^{132} = \Gamma_{12} - \Gamma_{13} - \Gamma_{23} = -\begin{bmatrix} (2\Gamma_3^{LW}) + \left(4\sqrt{\Gamma_3^{+}\Gamma_3^{-}}\right) - \left(2\sqrt{\Gamma_1^{LW}\Gamma_3^{LW}}\right) \\ -\left(2\sqrt{\Gamma_3^{+}\Gamma_1^{-}}\right) - \left(2\sqrt{\Gamma_1^{+}\Gamma_3^{-}}\right) - \left(2\sqrt{\Gamma_2^{LW}\Gamma_3^{LW}}\right) \\ -\left(2\sqrt{\Gamma_3^{+}\Gamma_2^{-}}\right) - \left(2\sqrt{\Gamma_2^{+}\Gamma_3^{-}}\right) + \left(2\sqrt{\Gamma_1^{LW}\Gamma_2^{LW}}\right) \\ +\left(2\sqrt{\Gamma_1^{+}\Gamma_2^{-}}\right) + \left(2\sqrt{\Gamma_2^{+}\Gamma_2^{-}}\right) \end{bmatrix} \tag{5}$$

4- Materials and Methods

4- 1- Aggregates

In this research, granite aggregates were used. Granite aggregates contain a large amount of silica and thus are susceptible to moisture. Mineral compounds of the aggregates and their physical properties are presented in Tables 1 and 2, respectively. Figure 1 shows the gradation of the aggregates used in this research.

Table 1. Mineral compounds of the aggregates used in this research

SiO_2 (%)	R_2O_3 (Al_2O_3+ Fe_2O_3) (%)	Al_2O_3 (%)	Fe_2O_3 (%)	MgO (%)	CaO (%)
68.1	16.2	14.8	1.4	0.8	2.4

Table 2. Physical properties of the aggregates used in this research

Test	Standard	Values	Regulation limits
Coarse aggregates			
Bulk specific gravity (g/cm^3)	ASTM C 127	2.654	-----
Saturated surface dry specific gravity (g/cm^3)		2.667	-----
Apparent specific gravity (g/cm^3)		2.692	-----
Fine aggregates			
Bulk specific gravity (g/cm^3)	ASTM C 128	2.659	-----
Saturated surface dry specific gravity (g/cm^3)		2.661	-----
Apparent specific gravity (g/cm^3)		2.688	-----
Specific gravity (filler) (g/cm^3)	ASTM D854	2.656	-----
Los Angeles abrasion (%)	ASTM C 131	19	At most 45
Flat and elongated particles (%)	ASTM D 4791	6.5	At most 10
Crushed content (two faces) (%)	ASTM D 5821	94.5	At least 90
Fine aggregate angularity (%)	ASTM 1252	56.3	At least 40

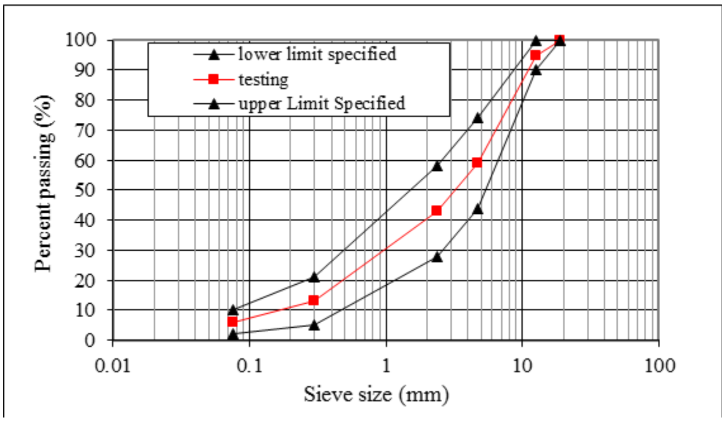

Figure 1. Gradation of the aggregates used in this research

4- 2- Glass cullets

Figure 2 shows the gradation of the glass aggregates used in this research. The maximum size of glass aggregates is 4.75 mm [33]. Mineral compounds of the waste glass used in this study are presented in Table 3.

Table 3. Mineral compounds of the glass cullets used in this research

SiO_2	K_2O	Al_2O_3	Na_2O	MgO	CaO	Oxide
70.5	1.2	2.6	16.3	2.9	5.7	(%)

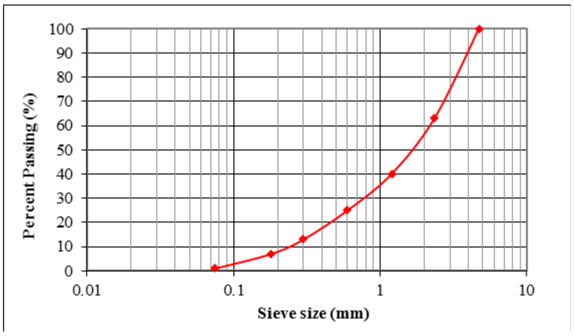

Figure 2. Gradation of the glass aggregates used in this research

In this research, 5, 10, 15 and 20 % of the fine aggregates were replaced with glass cullets, because, according to previous studies, the substitution of coarse aggregates with glass cullets may result in lower friction coefficient, higher abrasion, flat tires and other problems.

4- 3- Nano-materials

The most commonly used nano-materials are ceramic nano-particles that are divided into metal oxide ceramics and silica nano-particles. All three dimensions of metal nano-particles or metal oxides are almost the same size and they range from two or three nm to 100 nm. These nano-particles stick to each other by electrostatic forces and are observed in a very fine powder form. The smaller the size of nano-particles, the higher the effective surface to particle size ratio, the surface effects, and the catalytic properties.

In this study, two types of basic nano-materials, named nano iron oxide and aluminum oxide were used. These nano-materials are widely available and are more easily and cheaply produced compared to other nano-materials. The physical properties of the nano-materials used in this study are presented in Table 4.

Scanning electron microscopy (SEM) images of nano Fe_2O_3 and Al_2O_3 with a magnification of 60,000 times are shown in Figure 3. As it is obvious, the apparent shape of these nano-particles is nearly spherical. Iron oxide nanoparticles are in a more dispersed mode due to their higher weight and dimension, and aluminum oxide nanoparticles have a more filling characteristic owing to their higher specific surface area.

Table 4. Physical characteristics of the nanomaterials used in this research

Fe_2O_3	Al_2O_3	Characteristic
Cubic Cristal	alpha, gamma	Particle structure
2.6-2.9	5.9-6.4	Specific gravity (gr/cm^3)
1.5-1.8	3	Reflection index
38±2	45±5	Specific surface area (m^2/gr)
40≈	≈ 24	Average particle size (nm)
0.38-0.45	0.22-0.40	Bulk specific gravity (gr/cm^3)
8.4-10.6	8.7-9.9	Degree of acidity
262	112	Water percentage

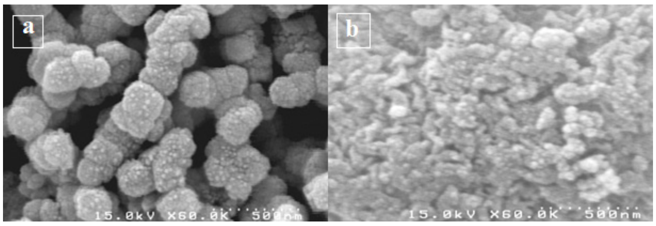

Figure 3. SEM images of a) nano Fe_2O_3 and b) nano Al_2O_3 used in this research

4- 4- Asphalt binder

In this research, a 60-70 penetration grade asphalt binder from Isfahan Refinery was used. Basic properties of the base asphalt binder are presented in Table 5.

Table 5. Basic properties of the base asphalt binder

Property	Standard	Value
Penetration (25 °C, 100 g, 5s; 0.1 mm)	ASTM-D5	66
Softening point (°C)	ASTM-D36	51
Ductility at (25 °C; cm)	ASTM-D113	112
Flash point (°C)	ASTM-D92	262
Solubility in trichloroethylene	ASTM D2042	99
Loss of heating (%)	ASTM D1754	0.75
Specific gravity (25°C; g/cm^3)	ASTM-D70	1.02

4- 5- Sample preparation

The Marshall mix design method was used to prepare the samples and determine the optimum binder content. For the preparation of modified asphalt binders, nanomaterials were added to asphalt binders at 0.5% and 1% in terms of asphalt binder weight. In order to achieve the homogeneous dispersion of nano-materials in the binders, they were blended with the asphalt binders in a controlled temperature chamber with a high shear mixer at the speed of 14000 rpm for 20-

30 min at the temperature of 120-150 °C. The SEM images of nano-modified binders are depicted in Figure 4. The efficiency of blending method and proper dispersion of nano-particles in the binders can be inferred from these images. It should be noted that in the case of asphalt samples containing nano Al2O3, samples with 1% nano Al_2O_3 were not produced due to the satisfying performance of the 0.5% Al_2O_3 modified specimens. 20 different types of asphalt mixtures (5 different types of aggregates and 4 different types of asphalt binders) were produced and tested in this research, as shown in Table 6.

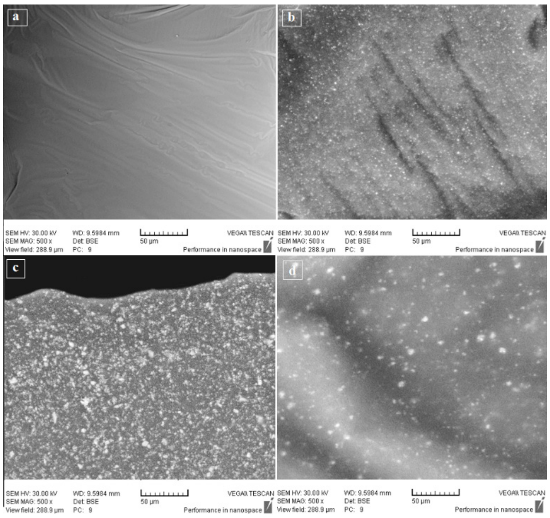

Figure 4. SEM images of neat and modified asphalt binders with nanoparticles. (a) neat asphalt binder, (b) 0.5% nano-Fe_2O_3 modified asphalt binder, (c) 1% nano-Fe_2O_3 modified asphalt binder, and (d) 0.5% nano-Al_2O_3 modified asphalt binder

4- 6- Hot storage stability test

The storage stability test is conducted to evaluate the stability of modified asphalt binders during hot storage according to the ASTM D7173 standard. For this test, the modified asphalt binder is poured into an aluminium tube of 25 mm in diameter and 125 to 140 mm in length and placed in an oven at 163±5 °C for 48 h. Next, the specimen is cooled down to −10±10 °C for 4 h and divided into 3 parts to measure the difference between the softening point of upper and lower parts of the specimen. Results can be considered satisfactory and the mixture will be stable when this value is 10% or less (2.2 °C or less).

4- 7- Modified Lottman test (AASHTO T283)

The asphalt mixtures' resistance to stripping has been evaluated using the reduced indirect tensile strength (ITS) under freeze-thaw cycles according to the AASHTO T283. This is the most common method used to investigate the effects of anti-stripping materials and to study the asphalt mixtures' resistance to moisture damage. In this study, to clearly investigate the effect of additives, 1, 3, and 5 freeze–thaw cycles were applied to the specimens.

4- 8- Measuring the SFE components of asphalt binders

The contact angle between asphalt and a liquid can be obtained by the Wilhelmy plate (WP) method based on the balance of kinetic energies of a very thin plate while being immersed or pulled out of a liquid at a constant and very low speed. When a plate is suspended in the air, Equation 8 is used to determine the force needed to keep it in a balance position:

$$F=Wt_{plate}+Wt_{asphalt}-V.\rho_{air}.g \tag{8}$$

Table 6. Different types of asphalt mixtures produced in this research

Mix	Asphalt type	Aggregate type	Mix	Asphalt type	Aggregate type
1	Base asphalt	Granite	11	Asphalt+1% Fe_2O_3	Granite + 10% Glass
2	Asphalt+ 0.5 % Fe_2O_3	Granite	12	Asphalt+ 0.5% Al_2O_3	Granite + 10% Glass
3	Asphalt+1% Fe_2O_3	Granite	13	Base asphalt	Granite + 15% Glass
4	Asphalt+ 0.5% Al_2O_3	Granite	14	Asphalt+ 0.5 % Fe_2O_3	Granite + 15% Glass
5	Base asphalt	Granite + 5% Glass	15	Asphalt+1% Fe_2O_3	Granite + 15% Glass
6	Asphalt+ 0.5 % Fe_2O_3	Granite + 5% Glass	16	Asphalt+ 0.5% Al_2O_3	Granite + 15% Glass
7	Asphalt+1% Fe_2O_3	Granite + 5% Glass	17	Base asphalt	Granite + 20% Glass
8	Asphalt+ 0.5% Al_2O_3	Granite + 5% Glass	18	Asphalt+ 0.5 % Fe_2O_3	Granite + 20% Glass
9	Base asphalt	Granite + 10% Glass	19	Asphalt+1% Fe_2O_3	Granite + 20% Glass
10	Asphalt+ 0.5 % Fe_2O_3	Granite + 10% Glass	20	Asphalt+ 0.5% Al_2O_3	Granite + 20% Glass

Where, F is the force needed to keep the plate in a balance position, Wt_{plate} is the weight of the metal plate, $Wt_{asphalt}$ is the asphalt binder weight, V is the volume of the asphalt binder plate, g is the local gravitational acceleration, and ρ_{air} is the specific weight of air.

When the plate soaked in asphalt binder is immersed into a liquid, Equation 8 turns into the Equation 9.

$$F=Wt_{plate}+Wt_{asphalt}+P_t \Gamma_L \cos\theta-V_{im}.\rho_L.g-(V-V_{im}).\rho_{air} \tag{9}$$

In Equation 9, Pt is the perimeter of the asphalt binder-soaked plate, Γ_L is the total SFE of the liquid, θ is the dynamic contact angle between the asphalt binder and liquid, V_{im} is the volume of the immersed part of the asphalt binder-soaked plate, V is the total volume of the asphalt binder plate, and ρ_L is the liquid's specific weight.

By combining the two above-mentioned equations, the following is obtained:

$$\Delta F=P_t \Gamma_L \cos\theta-V_{im}.\rho_L.g+V_{im}.\rho_{air}.g \tag{10}$$

By rewriting the above equation in terms of contact angle, all the unknowns on the right side of the equation can be obtained using the WP method:

$$\cos\theta=((\Delta F+V_{im}.(\rho_L-\rho_{air}).g))/(P_t \Gamma_L) \tag{11}$$

Equation 12 is the equation between the contact angle and the SFE components:

$$\Gamma_{L1} (1+\cos\theta)=2[(\Gamma_{Li}^{LW} \Gamma_2^{LW})^{0.5}+(\Gamma_{Li}^{-} \Gamma_2^{+})^{0.5}+(\Gamma_{Li}^{+} \Gamma_2^{-})^{0.5}] \tag{12}$$

To measure the SFE components of asphalt binders, at least three liquids with specific SFE components are needed. Water, glycerol and formamide liquids were used as probe materials in this study.

5- Results and Discussion

5- 1- Marshall test results

The evaluation of Marshall design parameters of asphalt mixtures with different combinations of aggregates at their optimum binder content are presented in Table 8. It is clear that the optimum binder content (OBC) and percent binder absorbed (Pba) of the glass specimens are lower than the conventional mixtures due to the lower porosity and asphalt absorption of glass aggregates compared to natural aggregates. Previous studies have also shown similar results about the asphalt absorption of glass aggregates [3, 7, 10, 19, 34]. It can also be understood from Table 8 that by increasing the glass cullet, Marshall flow, voids filled with asphalt (VFA), voids in mineral aggregate (VMA) and unit weight of mixtures have decreased while Marshall stability has increased. In fact, all-round crushed face and higher angularity of glass aggregates compared to natural aggregates and dispersion of glass particles in all directions enhance the internal friction angle and interlocking of the aggregates and as a result, improve the Marshall stability of glass mixtures. This trend has continued up to 15% of the glass cullet and after that, the smooth surface of the glass aggregates and high brittleness of the mixtures led to a decrease in stability of the mixtures. Furthermore, the observed decrease in voids filled with asphalt (VFA), voids in mineral aggregate (VMA) and unit weight of glass containing mixtures can be justified by lower porosity and specific gravity of glass cullet compared to natural aggregates.

5- 2- Hot storage stability test results

If additive particles are not well dispersed or are chemically opposed to asphalt binder, long or hot storage and transportation may negatively affect the homogeneity of the mixture and these two phases may eventually be separated. Therefore, the storage stability test is required for most modified asphalt binders. The hot storage stability of the nano-modified asphalt binders was measured, with results illustrated in Table 9.

It was observed that, as the additive content in the asphalt binder increased, the difference between the softening point of upper and lower parts of the samples (ΔS) increased, showing the higher possibility of separation in high-temperature storage. Although, for all the samples prepared and tested in this study, the ΔS values remained below the allowable value of 2.2 °C and separation may not occur.

Table 8. Marshall mix design parameters at optimum binder content

Glass content (%)	OBC (%)	Marshall stability (Kg)	Marshall flow (mm)	VFA (%)	VMA (%)	Unit weight (g/cm^3)
0	5.5	1023	2.7	73.3	14.6	2.357
5	5.5	1112	2.6	71.8	14.49	2.349
10	5.4	1166	2.4	71.4	14.33	2.340
15	5.3	1205	2.3	70.9	14.2	2.335
20	5.1	1137	2.3	70.5	14	2.331

Table 9. Hot storage stability of nano modified asphalt binders

Mixture type	Neat binder	Asphalt+ 0.5 % Fe_2O_3	Asphalt+ 1 % Fe_2O_3	Asphalt+ 0.5 % Fe_2O_3
Softening point of upper part (°C)	51	52.05	52.62	52.14
Softening point of lower part (°C)	50.9	53.13	54.1	53.37
ΔS (°C)	0.1	1.08	1.48	1.23

5- 3- Modified Lottman test results

The ITS test results of control and modified asphalt mixtures containing different percentages of glass cullets and nanomaterials under different freeze-thaw cycles are depicted in Figures 5 to 8. As can be seen, by increasing the glass cullet content, the ITS of dry specimens has increased, and this trend has continued to an optimum content of 15% glass. The all-round crushed face and the higher angularity of glass aggregates enhance the internal friction angle and interlocking of the aggregates and as a result, enhance the tensile strength of glass samples. Furthermore, the dispersion of glass particles in all directions can also lead to a higher resistance to shear deformations. The ascending trend of the ITS gradually slowed down by increasing the glass content and it began to decrease at levels higher than 15%. This might be due to the presence of high amounts of glass cullets which leads to the high brittleness of the mixtures and the inability of the glass aggregates' smooth surfaces to maintain the asphalt binder. In the case of wet specimens, it was observed that with the presence and increase of the glass cullet percentage, the ITS of the samples started to decrease. This was predictable according to previous studies. This fact can be attributed to the effect of chemical characteristics of different aggregates surfaces. As can be seen in Tables 1 and 3, glass contains more SiO_2 than granite which makes it more hydrophilic. Therefore, glass containing mixtures show more tendency towards water than the control mixtures. In addition, due to the crushed glass' lack of asphalt absorption, asphalt is more easily separated from the surface of glass aggregates compared to natural aggregates. These effects grow higher by increasing the glass content and result in lower values of ITS. As the number of freeze-thaw cycles increased, a greater reduction in the strength of the specimens was observed due to the longer exposure of the samples to moisture and the greater loss in asphalt cohesion or mixture adhesion.

Moreover, the test results showed that the use of nano Fe_2O_3 and Al_2O_3 as anti-stripping materials boosted the ITS of the modified samples compared to the control ones in both dry and wet conditions. This improves the cohesion of the asphalt binder, the adhesive force between asphalt and aggregates and, the asphalt binder's ability to cover the aggregates and it reduces the voids in mineral aggregates. A decrease in the acidic properties of the asphalt binder and glass cullets caused by the nano-materials can be another factor that improves the adhesion characteristics of the mixture and its resistance against moisture damage. By increasing the freeze-thaw cycles, the tensile strength of the specimens decreased. However, the reduction rate in the modified specimens is lower than that of the control ones.

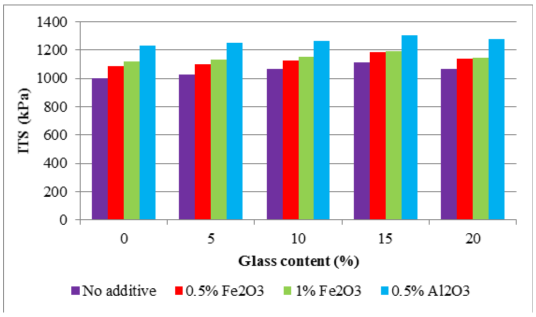

Figure 5. The ITS test results of unconditioned samples containing different glass contents

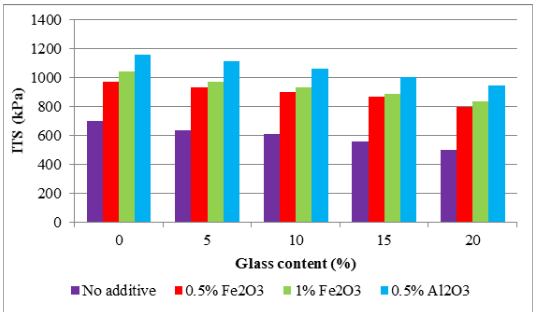

Figure 6. The ITS test results of samples containing different amounts of glass under 1 freeze-thaw cycle

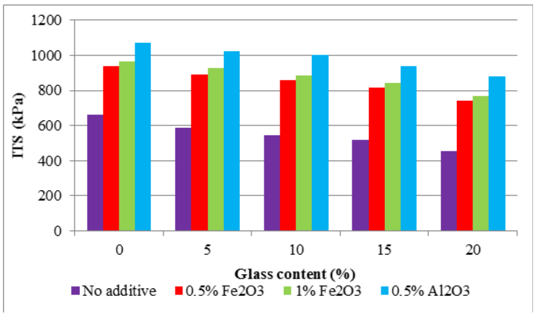

Figure 7. The ITS test results of samples containing different amounts of glass under 3 freeze-thaw cycles

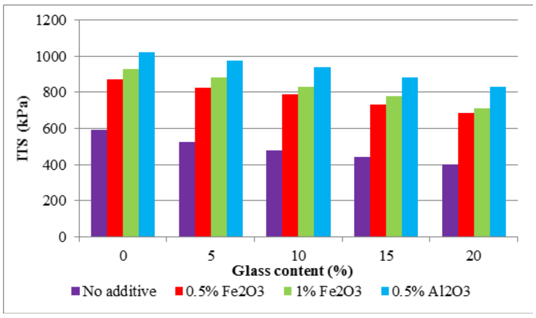

Figure 8. The ITS test results of samples containing different amounts of glass under 5 freeze-thaw cycles

Figures 9 to 11 show the tensile strength ratio (TSR) or, in other words, the moisture resistance of asphalt mixtures containing different contents of glass cullets and nanomaterials.

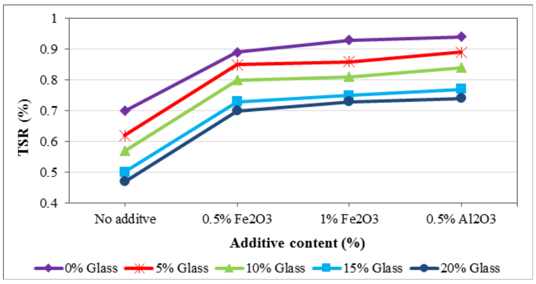

Figure 9. The TSR test results of samples containing different amounts of glass under 1 freeze-thaw cycle

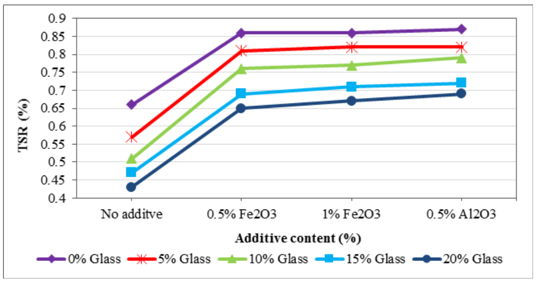

Figure 10. The TSR test results of samples containing different amounts of glass under 3 freeze-thaw cycles

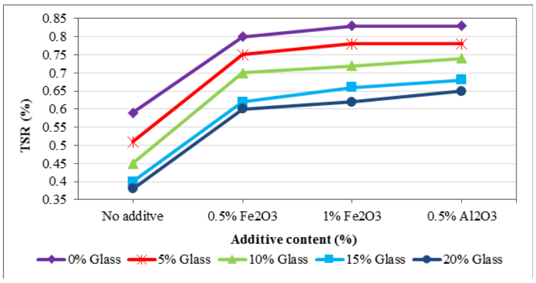

Figure 11. The TSR test results of samples containing different amounts of glass under 5 freeze-thaw cycles

It is clear that as the number of freeze-thaw has cycles increased, the TSR of the samples has decreased. The trend of the TSR curves shows that by increasing the percentage of the glass cullets, the TSR value of the mixtures has declined. In fact, the higher the glass aggregate's content, the lower the failure stress and the adhesion between the aggregates (granite and glass) and the asphalt binder. This can be attributed to the effect of chemical characteristics of different aggregates surfaces. The chemical composition of granite and glass aggregates used in this research are presented in Tables 1 and 3, respectively. As can be seen, glass contains more SiO2 than granite which makes it more hydrophilic. Therefore, the presence of glass cullets in the mixtures results in the higher moisture susceptibility of the mixtures. In addition, due to the crushed glass' lack of asphalt absorption, asphalt is more easily separated from the surface of glass aggregates compared to natural aggregates. By increasing the glass content in the samples, the moisture sensitivity of the samples increased, which is due to the exacerbation of the abovementioned conditions.

It was also observed that the glass asphalt samples with no additives exhibited a lower TSR than the conventional specimens (no glass and no additive). However, with the addition of nanomaterials, the TSR values of the glasphalt samples grew higher than the conventional samples. For instance, in the specimen containing 15% glass that was exposed to 3 freeze-thaw cycles, the addition of 0.5% Fe_2O_3, 1% Fe_2O_3, and 0.5% Al_2O_3 increased the TSR by 51, 56 and 60% compared to the non-modified specimens (15% glass+no additive) and by 4.5, 7.6 and 9.1% compared to the conventional specimens (no glass and no additive). In fact, these materials have been able to prevent the rapid separation of asphalt binder from the aggregate surface and have increased the resistance of the mixtures to freeze-thaw cycles by improving the adhesion and cohesion forces in asphalt mixtures. Different additives have different effects on the performance of asphalt mixtures. The test results revealed that the addition of nano Fe_2O_3 to asphalt binders had a positive effect on the TSR of the modified mixtures. 0.5% of nano Fe_2O_3 increased the TSR of the mixes significantly, while the effect of 1% nano Fe_2O_3 was not considerable. The stronger adhesion between the nano Al_2O_3 modified asphalt binders and aggregates caused a lower reduction in their TSR values under freeze-thaw cycles compared to the nano Fe_2O_3 modified samples. This means that 0.5% of nano Al_2O_3 had a more significant effect on the moisture resistance of glass asphalt mixtures compared to nano Fe_2O_3.

5- 4- SFE components of asphalt binders

The results of the SFE components measurement are presented in Table 10. These tests were carried out at the Polymeric Biomaterials Lab of the Iran Polymer and Petrochemicals Institute using the Wilhelmy plate method. As can be seen, the acidic component of the base asphalt binder is 3.18 (ergs/cm^2) which is higher than its base component (1.16 ergs/cm^2) that shows the acidic properties of the asphalt binder. This proves that no good adhesion is going to occur between the asphalt binder and acidic aggregates. This is one of the main reasons for moisture damage in asphalt mixtures containing acidic aggregates.

It is also observed that the use of nano-materials has decreased the acidic property of asphalt binders and increased its base component. For example, the acidic component of the base binder dropped from 3.18 ergs/cm^2 to 3.15 ergs/cm^2 and to 3.14 ergs/cm2 in the 0.5% nano Al_2O_3 and the 1% nano Al_2O_3 modified binders, respectively. A roughly similar trend was observed in the addition of nano Fe_2O_3. Also, the base component of the base asphalt dropped from 1.16 ergs/cm^2 to 1.45 ergs/cm^2 and to 1.45 ergs/cm^2 in the 0.5 and the 1% nano Fe_2O_3 modified asphalt binders, respectively. This increase was also observed in the asphalt binders modified with nano Al_2O_3. An increase in the base component of modified asphalt binders improves the adhesive force between asphalt binders and acidic aggregates such as granite. This also increases the initial energy needed for stripping and asphalt binder separation from the aggregate surface.

Furthermore, the use of nano-materials led to an increase in the total SFE of the modified asphalt binders. This causes asphalt binder to better cover and coat the aggregate surface. Although the coating is different from adhesion, in most of the previous studies, the requirement for a good adhesion in the first place is a good coverage [35-37].

As it is shown in Table 10, asphalt binder modification with nanomaterials has increased the acid-base (polar) component of modified binders. This results in an improved adhesion between asphalt binders and aggregates that have high polar characteristics. The use of nano-materials also has led to a slight increase in the non-polar component of the binders. The only exception is the asphalt binder modified with 1% nano Fe_2O_3, whose nonpolar SFE component was significantly increased. It is clear from Table 10 that the non-polar component of the asphalt binder is much larger than its polar component. In fact, the asphalt binder exhibits weak polar characteristics, and most of its bonds with aggregates are of a non-polar type (covalent), which provides more stability in the presence of water.

5- 5- Statistical analysis

To evaluate the effect of nano-materials on the moisture sensitivity tests, a statistical test was conducted. The results related to statistical analysis of the TSR values are presented in the Table 11. In statistical hypothesis testing a result has statistical significance when it is very unlikely to have occurred given the null hypothesis. More precisely, the significance level defined for a study, α, is the probability of the study rejecting the null hypothesis, given that it was true. The significance level (sig.) for a study is chosen before data collection, and typically set to 5%. The Levene's test uses an F-test to test the null hypothesis that the variance is equal across groups. The test statistic F is approximately F-distributed. In Table 11, if the sig. value of the Levine test is considered to be greater than the confidence level (0.05), it can be said that the variances of the two groups of samples are equal and the first row data should be used. Otherwise, the second row data must be used. The difference between these two rows of output lies in the way the independent samples t-test statistic is calculated. When equal variances are assumed, the calculation uses pooled variances; when equal variances cannot be assumed, the calculation utilizes un-pooled variances and a correction to the degrees of freedom. Based on the t-test of each row, if the sig. value is less than the confidence level (0.05), then the assumption of the difference between the mean of the two groups of samples can be confirmed and the type of coating has a significant impact on the results of the moisture sensitivity test. Fractional degrees of freedom are generally used when they provide a better approximation to something than would integer degrees of freedom (if the sig. value of the Levine test is lower than 0.05). The results indicate that the use of nano-materials has had a significant impact on the results of the wet to dry strength ratio in all glasphalt samples made in this study.

Table 10. SFE components of base and modified asphalt binders

SFE components	SFE components (ergs/cm^2)				
	Total SFE	Lifshitz-van der Waal	Acid-Base	Acidic	Basic
Base asphalt	17.86	14.02	3.84	3.18	1.16
Asphalt+ 0.5% Fe_2O_3	19.25	15.02	4.23	3.09	1.45
Asphalt+ 1% Fe_2O_3	20.89	16.73	4.16	2.90	1.49
Asphalt+ 0.5% Al_2O_3	18.74	14.56	4.18	3.15	1.39
Asphalt+ 1% Al_2O_3	19.28	14.98	4.30	3.14	1.47

Table 11. Statistical analysis of the effects of asphalt binder modification on TSR of glasphalt samples

Coefficientsa							
Mixture Type	Conditions	Equal variance	Levene's Test for Equality of Variances		Standardized Coefficients		
			F	Sig.	t	df	Sig. (2tailed)
With 0.5% Fe_2O_3	Under1 freeze-thaw cycle	Equal variances assumed	0.070	0.798	-4.067	8	.004
		Equal variances not assumed				7.832	.004
With 1% Fe_2O_3		Equal variances assumed	0.064	0.807	-.339	8	.002
		Equal variances not assumed				7.879	.002
With 0.5% Al_2O_3		Equal variances assumed	0.040	0.847	-4.757	8	.001
		Equal variances not assumed				7.899	.001
With 0.5% Fe_2O_3	Under 3 freeze-thaw cycles	Equal variances assumed	0.008	0.932	-4.066	8	.004
		Equal variances not assumed				7.979	.004
With 1% Fe_2O_3		Equal variances assumed	0.111	0.747	-4.474	8	.002
		Equal variances not assumed				7.829	.002
With 0.5% Al_2O_3		Equal variances assumed	0.198	0.668	-4.813	8	.001
		Equal variances not assumed				7.681	.001
With 0.5% Fe_2O_3	Under 5 freeze-thaw cycles	Equal variances assumed	0.000	1.000	-4.232	8	.004
		Equal variances not assumed				7.832	.004
With 1% Fe_2O_3		Equal variances assumed	0.001	0.977	-4.729	8	.001
		Equal variances not assumed				8	.001
With 0.5% Al_2O_3		Equal variances not assumed	0.181	0.681	-5.366	8	.001
		Equal variances assumed				7.805	.001

6- Conclusions

In this research, the effects of using glass aggregates as a partial replacement for natural fine aggregates on moisture damage of hot asphalt mixtures was explored. To improve the resistance of glass asphalt mixtures against water, the use of nano-materials (nano Fe_2O_3 and Al_2O_3) was investigated through mechanical and thermodynamic methods. The following conclusions can be drawn from the present study:

1. Using waste glass cullets as a secondary aggregate in the structure of asphalt mixtures reduced the optimum binder content due to the glass' lack of asphalt absorption.
2. All-round crushed face and angularity of glass aggregates improved the aggregates interlocking and increased the internal friction angle of glass containing mixtures. This trend continued up to 15% of the glass cullet and after that, the slippage of the glass particles caused the ITS of the mixtures to be reduced.
3. The use of glass aggregates increased the moisture susceptibility of asphalt mixtures due to the poorer bonding of secondary aggregates with asphalt binder due to the higher hydrophilic property of glass compared to granite, as well as its lack of asphalt absorption.
4. The ITS of nano Fe_2O_3 and Al_2O_3 modified mixtures was improved in both wet and dry conditions.
5. The addition of nanomaterials improved the moisture resistance of glass asphalt mixtures. Nanomaterials reduced the acidic properties of asphalt and glass cullet and enhanced the adhesion and cohesion forces in modified asphalt mixtures under freeze-thaw cycles. The use of nanoparticles was more effective in glass containing mixtures and increased their TSR to a higher degree compared to the conventional ones.
6. The statistical analysis of the effects of asphalt binder modification on TSR of glasphalt samples indicated the significant impact of nano-materials on the results of the wet to dry strength ratio in this study.
7. Nano-materials increased the base and reduced the acidic components of SFE of asphalt binders and resulted in a good adhesion between the acidic aggregates (glass+granite) and the modified asphalt binders
8. The use of iron and aluminum oxide nanoparticles led to a slight increase in the non-polar component of modified asphalt binders. In fact, the major adhesion between asphalt binders (that are materials with weak polar characteristics) and aggregates is caused by the non-polar or covalent bonds that remain stable in the presence of water.
9. The total SFE of modified asphalt binders was higher than that of the base binder which indicates an increase in the energy required for stripping in modified asphalt mixtures and, consequently, a reduction in moisture damage caused by cohesion failure.
10. Nano Al_2O_3 had a greater effect on the ITS of modified asphalt mixtures compared to nano Fe_2O_3, while the effects of nano Fe_2O_3 on the SFE components of asphalt binder was more significant than that of the nano Al_2O_3.

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