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Evaluation of Nano Hydrated Lime on the Moisture Susceptibility of Asphalt Mixtures Using Surface Free Energy

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ABSTRACT: Moisture damage is one of the common causes of asphalt pavement failure in moisture presence. To reduce this damage, different additives such as lime, liquid anti stripping, etc. is conventionally added to mix. In this study, the effect of nano hydrated lime (Nano-HL), on the moisture susceptibility of asphalt mixtures was investigated by applying surface free energy principals, indirect tensile strength and resilient modulus tests. The asphalt specimens were prepared with granite aggregate and neat bitumen of 60/70 penetration grade containing 0%, 3% and 6% Nano-HL by bitumen weight. The results of this study indicate that modification of bitumen with Nano-HL decreases the acidic component of surface free energy and increases its basic components. So these changes improve the adhesion between the bitumen and aggregate. Also, cohesion free energy of bitumen is improved by an increase in a nonpolar component of bitumen. Furthermore, the results of the indirect tensile strength test and resilient modulus test indicate that the addition of Nano-HL in mixtures causes an increase in ITS and Mr values of modified HMA. On the other hand, the de-bonding energy of bitumen-aggregate for bitumen modified with this Nano material was decreased. This led to an increased resistance to moisture damage.

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1. INTRODUCTION

Moisture presence can have a negative effect on bonding properties of asphalt mixtures and cause moisture damage in the mix. This has been a topic of interest for many researchers due to its significant effect on the pavement management, maintenance system and its subsequent costs [1]. Moisture damage affects the pavement durability as a desirable property of asphalt mixtures. This is more challenging in rainy regions due to moisture penetration in mix microstructure [2]. The other types of damages which occur as a result of this phenomenon are shoving, ravelling, etc. which increase the road maintenance cost. Therefore, evaluation of asphalt mixtures' resistance against this damage can be an effective approach for the pavement management system to be considered [3]. Two types of factor can increase the moisture susceptibility of the asphalt mixture: external and internal factors. External factors include climatic condition, construction of the asphalt mixture. External factors initiate bitumen removal from the aggregate surface in moisture presence which increases the potential for early failure. Internal factors are the parameters related to the properties of asphalt mixture materials e.g. bitumen and aggregate and their combination [4].

In recent decades, several studies have been devoted to evaluating moisture damage implementing various methods. Considering the internal factors affecting moisture damage, cohesion and adhesion are important properties which should be determined and analyzed based on thermodynamic theory. Surface free energy (SFE) and its relevance with contact energy were found to be an appropriate index for measuring cohesion and adhesion of materials and hence evaluation of moisture damage. The surface free energy typically denoted by Γ is the amount of work needed to create a unit surface of new material in the vacuum condition. Actually, moisture resistance of the asphalt mixture depends on basic properties of material such as acid-base and Lifshitz-van derWaals intermolecular forces [5]. According to this theory, thermodynamic changes in adhesion properties cause crack in aggregate and bitumen interface while thermodynamic changes in cohesion can cause crack creation in bitumen structure [6]. Therefore, it is necessary to evaluate SFE components for determining cracking potential in the asphalt mixture.

Although there are many approaches for preventing moisture damage in asphalt mixture, but using additives as a modifier of HMA properties is the most common solution. Nano materials are among these additives which have been considered recently by researchers. On the other hand, surface free energy is a proper method to determine the HMA resistance against moisture damage. Therefore, the effect of the Nano material on moisture damage can be assessed by applying SFE principals. Also, the optimum value of Nano-

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HL can be determined for maximum resistance of asphalt mixture against moisture damage.

1.1 Literature Review

Traditionally moisture susceptibility of mixtures was studied as a whole, and it was not possible to quantitatively evaluate the contribution of each of the mixture's components to this phenomenon. Such information could be important in material selection with economic factors in mind [1]. Some researchers evaluated moisture damage by applying SFE principals which has a practical advantage over other approaches. They have asserted that there is a direct relationship between the bitumen cohesion and adhesion in the contact surface of aggregate-bitumen with HMA moisture damage. Bashin et al. indicated that SFE principals can be used to derive fundamental indices to determine moisture susceptibility potential and is useful in selection of material properties to decrease this damage [1]. Also in recent decades, different approaches such as using additive have been implemented to improve rheological properties of bitumen and asphalt mixture performance. Nano materials as an additive have caused a revolution in pavement industry due to their rapid progress and good performance [7].

In another study, Ghaffarpour and Khodaii added Nano clay to bitumen and performed Marshal strength test, ITS test and Mr test. The authors have concluded that Marshal strength, resilient modulus and indirect tensile strength of modified HMA increased [8]. In another research, Hamedi et al. investigated the effect of Styrene-Butadiene Rubber (SBR) Polymer on HMA moisture damage. The results of this study show that use of SBR polymer cause to increasing in the strength of asphalt mixture against moisture damage especially in mixtures made with granite aggregate. Also, SBR polymer increased the free energy of cohesion and reduced the released energy of system in stripping event, decreasing the rate of moisture damage. Moisture damage index, which is the percentage of aggregate surface exposed to water as calculated by using the measured SFE and module of asphalt mixture in different cycles. The Results of this index show that SBR cause to significant decreasing in the stripping percentage of control asphalt mixtures [9]. Furthermore, in order to modify bitumen, Moghadas Nejad et al. incorporated Nano zycosoil in HMA and used the surface free energy method to evaluate their effects and concluded that bitumen modification decrease de-bounding energy and thus HMA resistance against moisture damage has increased significantly [10]. Akbari and Modares have investigated the effect of utilizing Nano clay (NC) and Nano Limestone (NL) on asphalt mixtures durability during freeze-thaw cycles. The result of this study revealed that the addition of NC and NL increased the indirect tensile strength and resilient modulus of HMA. Therefore, moisture susceptibility potential of modified HMA was decreased [11]. In another study, Azarhoosh et al. investigated the effect of Nano-TiO_2 on aggregate-bitumen adhesion of asphalt mixtures by applying surface free energy method. The SFE results of this study indicated that Nano material addition increases aggregate-bitumen adhesion and this adhesion will be stronger through an increase in the basic component and a decrease in an acidic component of bitumen [12].

Table 1. Aggregate chemical composition

Component	Value
Silicon dioxide, SiO_2 (%)	65.3
R_2O_3 (Al_2O_3 + Fe_2O_3) (%)	21.4
Aluminum oxide, Al_2O_3 (%)	18.1
Calcium oxide, CaO (%)	3.3
Ferric oxide, Fe_2O_3 (%)	1.5
Magnesium oxide, MgO (%)	2.1

1.2 Objective and Statements

In the recent decades the moisture susceptibility of asphalt mixture has been investigated by applying SFE principals. However, the effect of Nano-HL and repeated Freeze-thaw cycles on HMA moisture damage using SFE principals hasn't received much attention. In this study, the effect of Freeze-thaw cycles on moisture damage in modified HMA with Nano-HL using surface free energy and indirect tensile strength test (ITS) and resilient modulus test (Mr) is investigated. Therefore, the SFE component of aggregate, neat bitumen and modified bitumen were obtained and compared to the experimental test results of asphalt mixture prepared with these materials. Hence, the effect of Nano-HL on HMA moisture damage was studied by applying repeated Freeze-thaw cycles. The objectives of this study were:

· Determination of the SFE component of aggregate, neat bitumen and modified bitumen by Nano-HL,

· Evaluation of HMA moisture susceptibility according to the SFE parameters

· Comparison of the indirect tensile strength test results of modified and unmodified HMA by considering various Freeze-thaw cycles,

· Comparison of the resilient modulus test result of modified and unmodified HMA by considering various Freeze-thaw cycles,

· Blend selection of Aggregate and bitumen and modifier which has maximum resistance to moisture damage at various Freeze-thaw cycles.

2. MATERIALS

2.1 Aggregate and Bitumen

Hydrophilic granite aggregate with relatively high moisture susceptibility was used to study the effect of Nano-HL. Granite aggregate was brought in from a local quarry. The chemical composition of the aggregate was obtained using XRF test and presented in Table 1.

Physical properties of aggregates used in this study are shown in Table 2. Aggregates gradation was selected according to ASTM D3515-01 [13] as shown in Fig. 1. Bitumen with a 60/70 penetration grade (PG 58-16), supplied from a local

Table 2. Aggregates physical properties

Test	Standard	Quantity	Specification limit
Specific gravity (coarse aggregate)	ASTM C127	—	—
Bulk	—	2.65	—
Apparent	—	2.71	—
Specific gravity (fine aggregate)	ASTM C128	—	—
Bulk	—	2.63	—
Apparent	—	2.70	—
Specific gravity (filler)	ASTM D854	2.59	—
Los Angeles abrasion (%)	ASTM C131	21	Max 30
Flat and elongated particles (%)	ASTM D4791	7	Max 15
Sodium sulfate soundness (%)	ASTM C88	9	Max 12
Fractured faces(two-fractured face)	ASTM D5821	95	Min 90

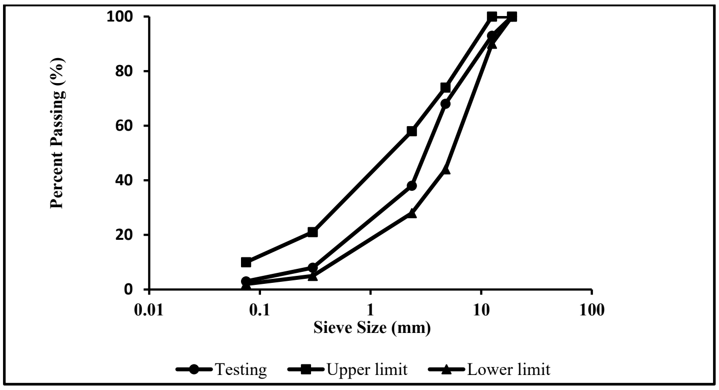

Fig. 1. Aggregate gradation used in this study

Table 3. Classical properties of neat and modified bitumen

Test		Standard	bitumen (60/70)	3% Nano-HL	6% Nano-HL
Penetration (100 g, 5 s, 25°C), 0.1 mm		ASTM D5-73	68	61	59
Ductility (25°C, 5 cm/min), cm		ASTM D113-79	114	>150	>150
Softening point (°C)		ASTM D36-76	51	55	57
Flash point (°C)		ASTM D92-78	265	274	276
Viscosity (m Pa s)	115°C	ASTM D2171-07	0.729	0.887	0.913
	135°C		0.311	0.426	0.435
	150°C		0.156	0.203	0.218

petroleum company, was utilized. The Classical test was performed to derive neat and modified bitumen properties, and results are presented in Table 3.

2.2 Nano-HL

In order to produce hydrated lime nanoparticles, a planetary ball mill has been used. In this type of mill, four parameters of rotational speed, rotational time, the ratio of bullet to hydrated lime and process control agent (PCA) are the process variables of milling. Process control agent refers to a group of additives that are used in the milling process. These materials keep balance between breaking the bonds of materials and re-connecting them in the milling process and create a sTable structure, ultimately [14]. In this study, isopropanol was used as PCA. Isopropanol is a member of the family of alcohols, and by repelling between particles of

Table 4. Chemical composition of Nano- HL

Properties	Silicon dioxide, SiO_2 (%)	R_2O_3 (Al_2O_3+Fe_2O_3) (%)	Aluminum oxide, Al_2O_3 (%)	Ferric oxide, Fe_2O_3 (%)	Magnesium oxide, MgO (%)	Calcium oxide, CaO (%)
Value	0.936	0.560	0.245	0.315	0.537	76.42

Nano-HL prevents them from sticking together. The milling operation was also performed by applying PCA as 5% by weight of hydrated lime. Also, the chemical characteristics of Nano-HL used in this study are determined using X-ray fluorescence analysis and are shown in Table 4. Also, physical properties of Nano-HL are given in Table 5.

3. EXPERIMENTAL PROCEDURE

The experimental program in this study comprised of: (i) measurement of the SFE component of neat bitumen, modified bitumen with Nano-HL and aggregate (ii) obtaining the optimum bitumen percentage to prepare the asphalt mixture sample according to Marshall Design method (iii) evaluation of moisture susceptibility potential of all types of HMA (with and without Nano-HL), after applying various Freeze-thaw cycles and using ITS and Mr tests. Furthermore, three HMA samples were prepared for each test condition and combination of bitumen and aggregate and average of three values were reported.

3.1 Bitumen and Mix Preparation

Previous studies have shown that the proper dosage of Nano-HL to be used in HMA is between 1% and 8% by bitumen weight [12, 15]. In this study, bitumen was modified with 3% and 6% Nano-HL. Nano-HL was mixed with bitumen using a high shear mixer with 8000 rpm velocity and for 1 hour at 135-140°C. The pure bitumen is also placed in the mixer at the same temperature and time to experience the same aging effect as modified bitumen. The optimum bitumen content was derived to be 6% according to the Asphalt Institute Manual (MS-2) and used both for neat and modified bitumen.

In this regard, in order to investigate the appearance of nanoparticles and their mixing method inside a 'nanoparticle distributor' device, scanning electron microscopy (SEM) was used. This image was obtained from scanning the sample by the concentrated loads of the electron. As can be seen in Fig. 2, the image was taken with the magnification of 500X and 30 kV voltage. The appearance of these nanoparticles was nearly spherical and the following image demonstrated the validity of the size and appearance of these nanoparticles.

3.2 SFE Measurement

Thermodynamic is a science concerned with the assessment of energy change, and on that basis, there are two kinds of tendency likely to occur in the case of energy change: 1- Enthalpy (internal energy change of a system) and 2- Entropy (irregularity or randomness change of a system). The relationship between these tendencies can be defined by considering Gibb's free energy in constant temperature and pressure as follows:

$$\Delta G = \Delta H - T.\Delta S = U + P.\Delta V - T.\Delta V - T.\Delta S \quad (1)$$

In which ΔG = Gibb's free energy or the difference between the initial and final system states, ΔH = Enthalpy or the total released or absorbed energy during the process, ΔS = Entropy or the irregular change of the system, T = System temperature, P = System pressure and U = System internal energy.

The oldest methods of determining the surface free energy based on molecule structure are two-component theory and acidic- basic theory. The acidic-basic theory has been utilized in this study, and on that basis, surface free energy includes the following components: 1- Nonpolar SFE component (Lifshitz-van der Waals SFE component), 2- Lewis acid SFE component and 3- Lewis base SFE component. According to this theory, Cheng et al. illustrated the nonpolar and polar components of SFE as follows [16]:

Table 5. Properties of Nano- HL used in this study

Specification	Result
SSA (m^2/g)	10-45
Color	White
Particle size (nm)	20
Bulk density (g/cm3)	0.46
Purity (%)	+99
Morphology	Spherical

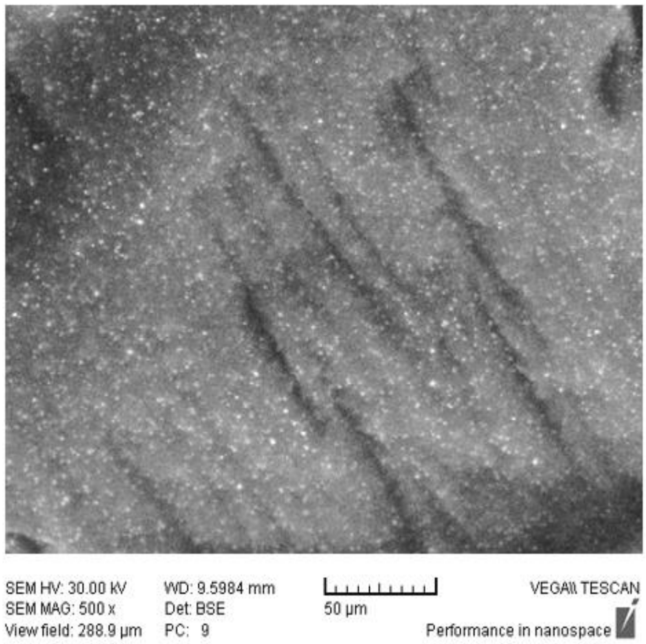

Fig. 2. Nano hydrated lime particles mixed in the bitumen

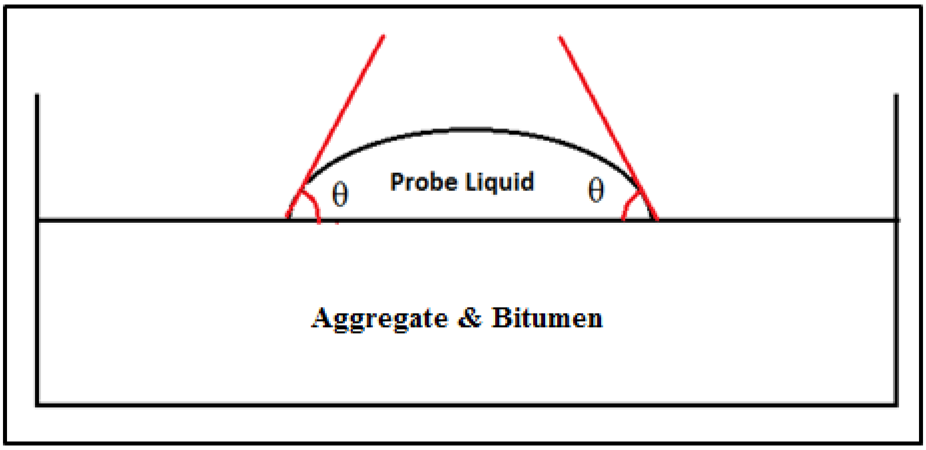

Fig. 3. Sessile drop technique for measurement of the contact angle

$$\Gamma=\Gamma^{LW}+\Gamma^{AB} \tag{2}$$

In which Γ = the total free energy of the material, Γ^{LW} = Nonpolar SFE component (Lifshitz-van der Waals SFE component) and Γ^{AB} = Polar SFE component.

Γ^{AB} was expressed as a combination of the acidic and basic Lewis components as follows:

$$\Gamma^{AB}=\Gamma^{\pm}=2\sqrt{\Gamma^{+}\Gamma^{-}} \tag{3}$$

In which Γ^{+} and Γ^{-} are the acidic and basic components respectively.

It should be noted that there is a need for at least 3 liquids with known SFE components to determine the SFE components of bitumen and aggregate. These liquids are named Probe Liquids, the functions of which will be illustrated in the next section. The common SFE measurement methods are the Atomic Force Molecular (AFM), the Inverse Gas Chromatography (IGC), the Sessile Drop (SD), Universal Sorption Device (USD), Micro Calorimeter (MC) and the Wilhelmy Plate (WP). In this study, the SD method was used to determine the aggregate and bitumen SFE components.

The sessile drop method is used to measure the probe liquid static contact angle with the surface of any type of solid material. By setting the temperature, camera and light, a drop of the probe liquid is released by a micro syringe from the 5 mm height above the horizontal surface of the material tested. A photograph of the drop is taken after it reaches the steady state. By analyzing this image, 2 angles are obtained, the mean of which is considered as the angle of contact. Three angles are obtained for each probe liquid in 3 repetitions of the test, the average of which is reported. The standard deviation for the measured contact angle for each probe liquid and the surface of the tested material based on the results obtained with three repetitions should be less than 5 degrees. Fig. 3 shows a schematic of the sessile drop technique and the contact angle between the probe liquid and bitumen or aggregate flat surface.

These probe liquids have known SFE components (e.g . , Γ_L^{LW} , Γ_L^{+} and Γ_L^{-}), so the unknown bitumen SFE component can be computed (e.g. Γ_b^{LW} , Γ_b^{+} and Γ_b^{-}), by a simultaneous solution of three equations like Eq. (4).

$$W_{Lb}=\Gamma_{L}^{Total}(1+\cos\theta) = 2[(\sqrt{\Gamma_{b}^{LW}\Gamma_{L}^{LW}})+(\sqrt{\Gamma_{b}^{+}\Gamma_{L}^{-}}+\sqrt{\Gamma_{b}^{-}\Gamma_{L}^{+}})] \tag{4}$$

Note: Index "b" concerns the bitumen component, and "L" concerns the probe liquid component. W_{Lb} = work between the bitumen surface and probe liquid and Γ_L^{Total} =the total free energy of the probe liquid.

This test method will not reveal precise results for aggregates with large polar components. On the other hand, the aggregate used in this study has a large polar component, so it will be unsuiTable to apply this test method to determine the SFE component [17].

According to the definition, surface free energy of the material is the amount of work needed to increase a unit surface to the surface of material in vacuum condition. Also, adhesion free energy of two materials is equal to the amount of energy needed to create two new surfaces in the material's interface. Similarly, the amount of needed energy to create a crack with a unit surface in the materials is named cohesion free energy. Since Gibbs's free energy is equal to the system free energy on the surface, it can be concluded that it is the same as adhesion free energy which can be defined for two materials. If two materials are the same, this energy would be cohesion free energy.

As it was previously mentioned, bitumen cohesion and aggregate-bitumen adhesion are important to calculate the moisture damage and cracking of HMA. So these energy components must be determined to find the precise behavior of HMA.

$$-\Delta G= W= 2\Gamma \tag{5}$$

Also, adhesion free energy between two materials which have nonpolar and polar component can be determined using Eq. 6:

$$\Delta G^{a} = \Delta G^{aLW} + \Delta G^{aAB} = 2\left[\left(\sqrt{\Gamma_1^{aLW}\Gamma_2^{aLW}}\right) + \left(\sqrt{\Gamma_1^{+}\Gamma_2^{-}} + \sqrt{\Gamma_1^{-}\Gamma_2^{+}}\right) \right] \tag{6}$$

In which ΔG^{a} = adhesion free energy, ΔG^{aLW} = adhesion nonpolar component, ΔG^{aAB} = adhesion polar component Γ_1^{+}, Γ_1^{-} and Γ_1^{LW} = acidic, basic and nonpolar component of material 1 and Γ_2^{+}, Γ_2^{-} and Γ_2^{LW} = acidic, basic and nonpolar component of material 2.

When mixtures are in contact with water, system energy has negative value which is called De-bounding energy. The negative value indicates that energy is given off and it means that the energy releasing process will be performed spontaneously. Hence de-bounding energy occurs on its own [18]. In other words, moisture presence leads to a spontaneous separation of bitumen from aggregate. By adding water components into equations, according to presented relationships by Cheng et al. [19], the adhesion free energy of aggregate-bitumen (or de-bounding energy) can be calculated using Eq. (7). Increasing the absolute value of this energy will cause an increase in the separation potential of bitumen and aggregates.

$$\Delta G_i^{a} = \Delta G_i^{aLW} + \Delta G_i^{aAB} = -\begin{pmatrix} (2\Gamma_w^{LW}) + (4\sqrt{\Gamma_w^{+}\Gamma_w^{-}}) - (2\sqrt{\Gamma_L^{LW}\Gamma_w^{LW}}) \\ -(2\sqrt{\Gamma_w^{+}\Gamma_L^{-}}) - (2\sqrt{\Gamma_L^{+}\Gamma_w^{-}}) - (2\sqrt{\Gamma_S^{LW}\Gamma_w^{LW}}) \\ -(2\sqrt{\Gamma_w^{+}\Gamma_S^{-}}) - (2\sqrt{\Gamma_S^{+}\Gamma_w^{-}}) + (2\sqrt{\Gamma_L^{LW}\Gamma_S^{LW}}) + (2\sqrt{\Gamma_L^{+}\Gamma_S^{-}}) + (2\sqrt{\Gamma_S^{+}\Gamma_S^{-}}) \end{pmatrix} \tag{7}$$

It should be noted that the symbols are as defined previously and the indices “W”, “S” and “L” refers to the water, bitumen, and liquid, respectively.

3.3 Moisture Susceptibility Determination of HMA

Indirect tensile strength test (AASHTO T283) and resilient modulus test (ASTM D7369) has been used to determine the indirect tensile strength (ITS) and resilient modulus (Mr) of asphalt mixtures, respectively. These test methods determine the HMA moisture damage in a certain temperature and damage mechanism based on the mechanical loading applied to three different freeze-thaw cycles (1, 3 and 5) on asphalt mixture samples.

The wet samples are first saturated with relative vacuum conditions (absolute pressure of 13-67 kPa) for five minutes. Then they are kept in a submerged state and without vacuum conditions for 5-10 minutes. The samples are then taken out and their mass is measured and percentage of saturation of the samples is obtained. If the saturation percentage is less than 70%, the samples should be placed under vacuum conditions again. If sample saturation is more than 80%, the sample is considered to be damaged and a new sample should be made instead. Lower vacuum times must be considered for the new samples so that their saturation to be between 70 and 80%. Saturated samples are placed inside plastic bags and 10 ml of water are poured inside the bags. The samples are stored inside the freezer at -18 °C for 16 hours. Then, the samples were taken to a hot water bath at 60 °C, then they are taken out of the plastic bags and allowed to remain at this temperature for 24 hours. At the end, the samples are brought to room temperature (25 ° C); in this way, they are called wet samples.

The tensile strength ratio (TSR) index which is calculated from Eq.8 can be used to determine the moisture damage potential of HMA. It is believed that the higher value of this ratio corresponds to higher resistance against moisture damage.

$$TSR = \left(\frac{ITS_{Wet}}{ITS_{Dry}}\right) \times 100 \tag{8}$$

In which, ITS_{Wet} = the average ITS value of the wet set samples that are subjected to freeze-thaw cycles, and ITS_{Dry} = the average ITS value of the dry set samples.

Also the resilient modulus ratio (RMR) can be determined from Eq. (9), as an indicator of the HMA moisture susceptibility:

$$RMR = \left(\frac{Mr_{Wet}}{Mr_{Dry}}\right) \times 100 \tag{9}$$

Where Mr_{Wet} = the average Mr value of the wet set samples, and Mr_{Dry} = the average Mr of the dry set samples.

Although it has remained a challenge for researchers to present a practical test procedure to determine moisture damage of asphalt mixture, these mentioned tests (ITS and Mr) has been accepted and widely used [20].

4. RESULT AND DISCUSSION

4.1 Surface Free Energy theory

4.1.1 SFE of Bitumen and aggregate

As it was previously mentioned, the SD method was used to measure the bitumen and aggregate SFE component. The probe liquids used in this study were, Ethylene glycol, Diiodomethane, and Water which are monopolar, nonpolar and bipolar materials, respectively and their SFE components were known. Finally, the bitumen and aggregate SFE components can be calculated by applying SD method to these probe liquids and obtaining contact angles for each of them and simultaneously solving three equations like Eq. (4). Probe liquids SFE components are presented in Table 6.

According to Table 7, addition of 3 and 6% of Nano-HL to neat bitumen will increase the total free energy value of neat bitumen from13.62 mJ/m^2 to 18.18 and 19.70 mJ/m^2, respectively. Therefore, the cohesion fracture potential of modified bitumen is smaller than neat bitumen. The decrease in bitumen acidic property and increase in its basic property lead to an increase in adhesion of aggregate to bitumen in

Table 6. SFE component of probe liquids (mJ/m²)

Type of liquid	Total SFE (Γ)	Nonpolar component (Γ^{LW})	Polar component (Γ^{AB})	Acidic component (Γ^{+})	Basic component (Γ^{-})
Water	72.8	21.8	51	25.5	25.5
Diiodomethane	50.8	50.8	0	0	0
Ethylene glycol	48.29	29	19.29	3	31

Table 7. SFE Components of Bitumen (mJ/m²)

Bitumen types	Neat bitumen	Bitumen with 3% Nano-HL	Bitumen with 6% Nano-HL
Total SFE (Γ)	13.62	18.18	19.70
Nonpolar component (Γ^{LW})	11.80	14.92	16.21
Polar component (Γ^{AB})	1.82	3.26	3.49
Acidic component (Γ+)	2.95	2.55	2.50
Basic component (Γ^{-})	0.28	1.04	1.22

Table 8 . SFE Components of Aggregate (mJ/m²)

Aggregate types		SFE components			
	Total SFE (Γ)	Nonpolar component (Γ^{LW})	Polar component (Γ^{AB})	Acidic component (Γ^{+})	Basic component (Γ^{-})
Quantity	365.62	50.77	314.85	57.24	432.95

Table 9. Components of SFE of Adhesion and De-bounding

Type of Bitumen	SFE of Adhesion, (mJ/m²)		De-bonding Energy, (mJ/m²)	
	Values	Percentage change (%)	Values	Percentage change (%)
Base	128.43	-	173.01	-
Base + 3% Nano-HL	136.93	6.62	166.36	3.84
Base + 6% Nano-HL	139.89	8.92	165.81	4.16

water presence. Change in the acidic and basic parameters of modified bitumen occurs because of the basic property of Nano-HL (8<PH<10) which affect the alkaline property of bitumen and increase this property. Since the aggregate-bitumen bond is non-polar, it can be said that the increase in non-polar SFE component causes this bond to be stronger.

Table 8 shows the result of calculated SFE components of aggregate. As it was mentioned previously, during the moisture damage occurrence, rupture appearance in the aggregate's bulk is rare and this damage normally occurs in the bitumen film and aggregate-bitumen contact. Thus, the total surface free energy of aggregate does not have significant effect on moisture damage. Since it is essential to change the acidic-basic component of aggregate to improve aggregate-bitumen adhesion in the water present, the aggregate effect on moisture damage potential can be investigated based on the change of these parameters.

4.1.2 Thermodynamic Parameters

The cohesion free energy of the neat bitumen and modified bitumen with 3% and 6% of Nano-HL were calculated from Eq. (5) to be 27.24, 36.36 and 39.40 mJ/m², respectively. These results show that the addition of Nano-HL will cause an increase in cohesion free energy, and therefore the bitumen resistance against cracking will increase. Based on presented results, it can be concluded that the reason for this resistance enhancement is an increase in bitumen SFE non-polar component. Considerable point in results is that the effect of 3% of Nano-HL addition is more significant as compared to 6% of this Nano material. On the other hand, the polar components (acidic-basic) were not found to have an important role in resistance change against the cohesion rupture.

The adhesion SFE components of aggregate-bitumen, water-bitumen and water-aggregate are calculated using Eq.

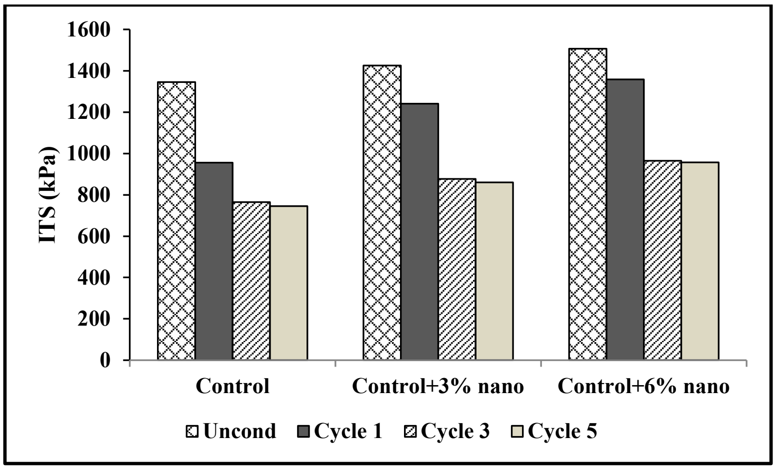

Fig. 4. ITS values for Mixtures Made with and without Nano-HL

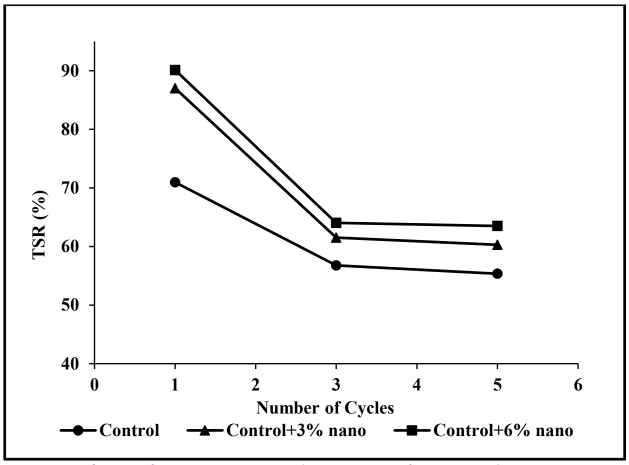

Fig. 5. Effect of Nano-HL and Freeze–Thaw Cycles on TSR of Mixtures

6 and the energy which is released in water presence (or De-bounding energy) is calculated using Eq. 7. These results are shown in Table 9.

Modifying bitumen with Nano-HL decreases its acidic SFE component and increases its basic SFE component. Therefore, the polar component of modified bitumen increases and leads to an increase in aggregate-bitumen adhesion (Table 10). It should be noted that the de-bounding energy values are negative, but the absolute values are reported in Table 10. The results indicate that modifying bitumen with Nano-HL, decreases the de-bounding energy and therefore striping occurrence potential will be decreased and asphalt mixture durability will subsequently be increased.

According to the results of this section and comparing it with various types of HMA, it can be understood that the addition of 3% of Nano-HL has relatively more significant effect on HMA thermodynamic stability as compared to 6% addition of Nano-HL. According to Table 10, the increase in the percentage of adhesion free energy for 3% and 6%of Nano-HL is 6.62% and 8.92% respectively. Also according to this Table, the decrease in the percentage of de-bounding energy for 3% of Nano-HL is 3.84% and for 6% of Nano-HL is 4.16%. Thus, maximum improvement in these properties is associated with 3% of Nano-HL.

4.2 Asphalt Mixture Result

4.2.1 ITS Test Results

The ITS values of asphalt mixtures are determined according to AASHTO T283 standard test, and results are presented in Fig. 4. This Fig. presents ITS values for un-conditioned and conditioned samples under various freeze-thaw cycles. It can be concluded that the ITS value of samples subjected to freeze-thaw cycle are decreased as compared to dry set samples. The increase in number of freeze-thaw cycles has a similar effect on ITS values of samples as shown in Fig. 4.

According to Fig. 4, using Nano-HL cause an increase in the ITS values of HMA (dry and wet condition). Two main reasons can interpret this change: firstly in bitumen modified with Nano-HL, aggregate-bitumen adhesion will be increased and secondly the increase in SFE of bitumen will decrease the rupture potential in the mastic. Considering the increase in ITS value for modified samples as compared to control samples, Nano-HL can be used as a modifier to prevent the reduction of aggregate-bitumen adhesion and bitumen cohesion in water presence.

Due to high moisture resistance of asphalt mixtures, TSR values for mixtures must be at least 70-80% after first cycle of freeze-thaw; otherwise, moisture damage is likely to happen [20]. TSR values for control and the modified mix with 3% and 6% modifier after three different number of freeze-thaw cycles are presented in Fig. 5.

Addition of 3% Nano-HL causes an increase in TSR value of samples (from 71% to 87%) while adding 6% of Nano-HL led to a smaller increase in TSR value (from 87% to 90%). Also, it should be noted that percent of the TSR decrease in modified HMA during various freeze-thaw cycles is smaller than control samples. In other words, TSR values of modified HMA decrease is lower as compared to control samples when the number of freeze-thaw cycle increases. For example, the TSR percentage reduction of HMA containing 3% and 6%

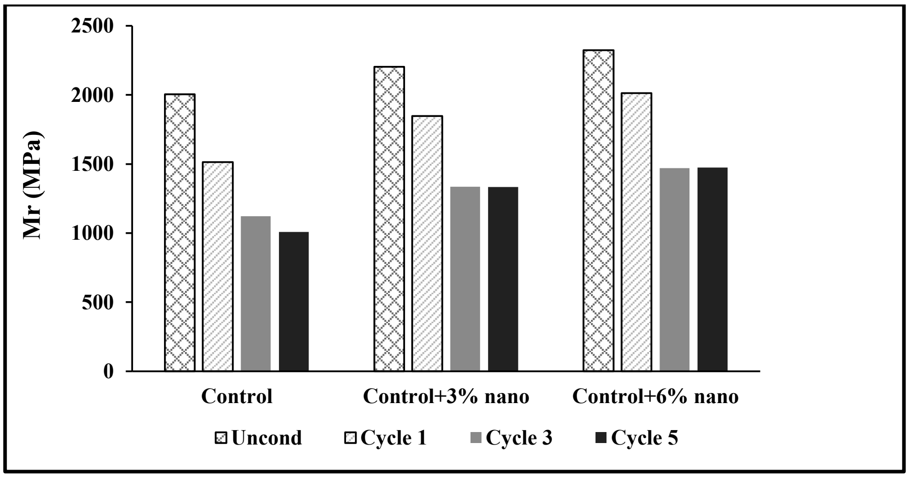

Fig. 6. Mr for mixtures made with and without Nano-HL

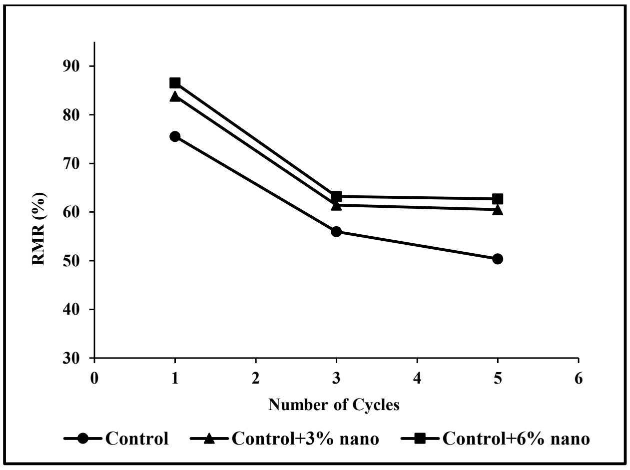

Fig. 7. Effects of Nano-HL and Freeze–Thaw Cycles on RMR in Mixtures

of Nano-HL is 0.98% and 0.50%, respectively when freeze-thaw cycle is increased from 3 to 5. While the TSR percentage decrease of control samples is 2.33%. So it can be said that modified HMA has better moisture resistance compare with control samples under various freeze-thaw cycles. Since the bitumen percentage and gradation and type of aggregate were constant in this study, comparison of control and modified samples show that bitumen modifying led to TSR increase.

This can be interpreted by the fact that TSR increase occurred in the samples with higher calculated adhesion and cohesion free energy (e.g. HMA contain 3% and 6% of Nano-HL). Adding Nano-HL to bitumen in all of the dosages helped the asphalt mixture resistance against moisture damage. It was also concluded that increased resistance due to the addition of 6% of Nano-HL wasn't significant as compared to 3% of Nano-HL when compared with the controlled mix.

4.2.2 Resilient Modulus Test Results

ASTM D7369 standard test was conducted to determine Mr values and the results are shown in Fig. 5. In this method similar to ITS test, HMA samples are subjected to various freeze-thaw cycles.

The results show that using Nano-HL causes an increase in asphalt mixtures Mr (both in dry and wet condition). Also, when the number of freeze-thaw cycles increases the reduction in RMR percentage of modified mix is smaller than control samples (Fig. 7). For instance, applying 3 and 5 cycles to samples containing 3% and 6% of Nano-HL cause a decrease of 0.9% and 0.49% in RMR percentage, respectively. While the RMR reduction percentage of control samples is 5.57%. This indicates that under various freeze-thaw cycles, the modified samples have higher moisture resistance compared to the unmodified samples. Also, the effect of 3% of Nano-HL on RMR value improvement is more as compared to 6% of this modifier. For example, the addition of 3% of Nano-HL causes an increase in RMR value from 59% to 62.4% when the 3 cycles of freeze-thaw was applied. While, the addition of 3% to 6% of Nano-HL, cause an increase in RMR value from 62.4% to 63.2% during the 3 cycles of freeze-thaw. So it can be concluded that using 3% of Nano-HL is obviously more cost effective.

The analysis of the Nano-HL effect on various cycles of freeze-thaw was performed using ANOVA method. According to previous analysis, critical P-Value was selected to be 0.05 and this analysis was performed for both mean of values. The results of this analysis are presented in Tables 10 and 11 for TSR and RMR values respectively.

According to these results, the addition of 3% of Nano-HL to neat bitumen causes P-value to become lower than 0.001 in all of the freeze-thaw cycles while by the addition of 6% of Nano-HL, P-value was found to be higher. Therefore, by an increase in Nano-HL dosage from 3% to 6%, P-value becomes closer to the critical value (0.05). It can be concluded that it is not cost effective to use more than 3% of Nano-HL for bitumen modification. Furthermore, in all cases, the total P-value is lower than 0.05. Controlling F-value indicates that the calculated F-values are bigger than critical F-value ($F_{critical}$=5.14). This mean that the average of TSR (and also Mr) of modified and control samples aren't equal and have a significant difference.

Table 10. ANOVA Analysis for Means of TSR Values

Condition	Bitumen (i)	Bitumen (j)	df	P-Value	F	F_{crit}	Total P-Value
Un conditioned	Base	Base	2	-	39.5	5.14	<0.001
	Base	Base+3% Nano		0.006			
	Base+3% Nano	Base+6% Nano		0.028			
Cycle 1	Base	Base	2	-	74.3	5.14	<0.001
	Base	Base+3% Nano		0.001			
	Base+3% Nano	Base+6% Nano		0.009			
Cycle 3	Base	Base	2	-	54.2	5.14	<0.001
	Base	Base+3% Nano		0.003			
	Base+3% Nano	Base+6% Nano		0.012			
Cycle 5	Base	Base	2	-	424.3	5.14	<0.001
	Base	Base+3% Nano		<0.001			
	Base+3% Nano	Base+6% Nano		<0.001			

Table 11. ANOVA Analysis for Means of Mr Values

Condition	Bitumen (i)	Bitumen (j)	df	P-Value	F	F_{crit}	Total P-Value
Un conditioned	Base	Base	2	-	31.2	5.14	0.001
	Base	Base+3% Nano		0.009			
	Base+3% Nano	Base+6% Nano		0.063			
Cycle 1	Base	Base	2	-	116.0	5.14	<0.001
	Base	Base+3% Nano		<0.001			
	Base+3% Nano	Base+6% Nano		0.008			
Cycle 3	Base	Base	2	-	104.0	5.14	<0.001
	Base	Base+3% Nano		<0.001			
	Base+3% Nano	Base+6% Nano		0.004			
Cycle 5	Base	Base	2	-	496.1	5.14	<0.001
	Base	Base+3% Nano		<0.001			
	Base+3% Nano	Base+6% Nano		<0.001			

5. CONCLUSION

The effect of Nano-HL as a modifier was investigated in this study by applying SFE principals and thermodynamic concept. In the second step, moisture resistance of HMA was evaluated using indirect tensile strength (ITS) and resilient modulus in various cycles of freeze-thaw. Finally, a comparison was performed between the experimental results of HMA and SFE principals. Moisture resistance of HMA was assessed by considering the effect of the freeze-thaw cycle. According to the obtained results, these conclusions can be made:

· Using Nano-HL causes an increase in the total bitumen surface free energy. So cohesion of modified bitumen will be increased.

· Using Nano-HL causes an increase and decrease in a basic and acidic component of modified bitumen, respectively. Therefore, adhesion SFE of modified bitumen in surfaces in contact with an aggregate increase in water presence.

· The addition of Nano-HL to bitumen decreases de-bounding energy in water presence. So moisture susceptibility potential of the asphalt mixture containing this bitumen is reduced.

· The moisture resistance of modified HMA is increased by the Nano-HL addition. Since the TSR and Mr values of modified HMA were larger than control samples, significantly.

· Applying three different freeze-thaw cycles on the asphalt mixture show that modified HMA with Nano-HL has more resistance as compared to control samples.

· ANOVA analysis results of contact angles, TRS values, and RMR values compared to means of modified and unmodified samples show that the means of these samples pair aren't equal and have a significant difference.

· Dosage comparison of 3% and 6% of Nano-HL indicate that usage of 3% of this Nano material is more cost effective for increased moisture resistance and durability against various freeze-thaw cycles.

· According to surface free energy method and mechanical tests, using Nano-HL as additive increase moisture resistance of HMA. So it can be concluded that the mixture tests (ITS and Mr) validate the SFE method.

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