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Investigation of the Moisture Susceptibility of Nanocomposite-Modified Asphalt Mixture Using Surface Free Energy Theory

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ABSTRACT: Moisture damage is a form of distress of asphalt pavement due to the presence of water and its impact on the mechanical characteristics of the asphalt mixture. One of the strategies delaying this event is to use a polymer-nanocomposite as an additive. In the present study, the effect of polyethylene (PE)/montmorillonite nanocomposite (NC) on the moisture susceptibility of asphaltic mixtures has been investigated using surface free energy (SFE) theory and indirect tensile strength (ITS) test. The results of SFE tests indicated that the acid component of SFE was decreased and its base component was increased through modifying the asphalt cement with PE/NC, and this increased the adhesion between asphalt cement and aggregates in the presence of water. In addition, the de-bounding energy between asphalt cement and aggregates has been decreased in modified mixtures, hence it can be expected the resistance of these mixtures to improve against stripping. Moreover, the cohesion-free energy and thus the resistance to rupture of the modified asphalt cement increased by increasing the nonpolar component. Furthermore, the results of experiments on asphalt samples indicated that the addition of PE/NC to asphalt mixtures has increased the tensile strength ratio, which increases the durability of the asphalt pavement.

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1- Introduction

Water can negatively affect the mechanical characteristics of the asphalt pavement and cause moisture damage to this structure. This issue has been of interest to many researchers since it has significant effects on the pavement management system (PMS) and its costs [1]. Moisture damage affects the durability of asphaltic pavement, which is one of its most important features. This type of damage occurs when the tendency of aggregates to absorb water is higher relative to their tendency to be coated with asphalt cement [2]. Other damages, including fatigue cracking, rutting, bleeding, pothole, and shoving, are created due to moisture damage in asphalt pavements, increasing the operation and maintenance costs. Therefore, evaluation of resistance of asphalt pavements to moisture damage as a factor affecting the PMS must be carefully considered [3].

The potential for moisture damage depends on the internal conditions of the asphalt mixture and the external factors affecting them. External factors include climatic conditions and the construction of hot mix asphalt (HMA). The main causes of moisture damages regarding the internal factors are cohesion rupture in the asphalt film and adhesion rupture at the interface between asphalt cement and aggregates in the presence of water, which increases the potential for early failure in asphalt pavements [4]. In the past several decades, numerous studies have been carried out to identify moisture damage and its analytical methods. Due to the effective internal factors mentioned in the moisture damage, adhesion and cohesion are concepts analyzed based on the theory of thermodynamics. Surface free energy (SFE) and its relation with bonding energy were accepted as indicators for measuring the adhesion and cohesion of materials. Therefore, moisture damage can be investigated in HMAs by quantifying the stripping potential through SFE.

The SFE designated by the Greek letter Γ is equal to the amount of work required to create a unit area of the new material surface in vacuum conditions. In this theory, the asphalt mixture resistance against the loss of asphalt cement cohesion and asphalt cement-aggregate adhesion is measured in wet and dry conditions; this strength of materials is naturally dependent on the basic characteristics of the materials [5]. The molecular Lifshitz-van der Waals force and the acid-base force are among these basic characteristics of materials. Based on the thermodynamics theory, thermodynamic changes in free energy of adhesion will create cracks and notches at the interface of aggregates and asphalt cement. In addition, the cause of cracking in asphalt cement will also be due to thermodynamic changes in free energy of cohesion [6]. Therefore, according to this theory, the determination of SFE components is necessary to evaluate the potential of cracking in asphalt cement and the aggregates-asphalt cement interface.

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There are several methods to prevent moisture damage in asphalt mixtures; using additives as a modifier of their characteristics is one of the prevalent solutions. Nano-materials are of these additives which have been recently considered by researchers. Moreover, the improvement in the strength of a modified asphalt mixture against moisture damage can be determined using the SFE theory. According to this approach, the effect of nanomaterials and their optimal content can be determined to prevent moisture damage in the asphalt mixture.

The moisture susceptibility of asphalt mixtures has been studied using SFE theory in the last decade. However, the effect of repetition of freeze-thaw cycles on moisture damage of polyethylene (PE)/montmorillonite nanocomposite (NC) modified asphalt mixtures has not been investigated using SFE theory. In this study, the effect of freeze-thaw cycles on the modified asphalt mixtures has been investigated using SFE theory and the ITS test. Therefore, the components of SFE of aggregates, pure and modified asphalt cement were calculated and compared with the results of experiments performed on asphalt mixtures. In summary, the objectives of the present research are as follows:

- Determination of the components of SFE of aggregates, pure and PE/NC modified asphalt cement,
- Evaluation of moisture susceptibility of asphalt mixtures based on SFE parameters,
- Comparison of ITS test results in modified and control mixtures and studying the effect of freeze-thaw cycles on it,
- Relationship between mechanical and thermodynamic methods in terms of determining moisture damage.

In recent decades, numerous studies have been conducted to determine the potential for moisture susceptibility of asphalt mixtures and to provide solutions to reduce it. Elphingstone [7] from the Texas Transportation Institute, was the first who indicate that SFE measurement could be used as a suitable tool to predict fatigue cracking and moisture damage in asphalt mixtures. Cheng et al. [8] in their study investigated the concepts of SFE measurement and its application in asphalt mixtures. The results obtained from this study indicated that thermodynamic changes in SFE of adhesion and cohesion are directly related to de-bonding at the asphalt cement-aggregate interface and crack occurrence in mastic. In addition, Bhasin and Little [9] stated that the SFE theory could be used as an essential indicator to determine the potential for moisture damage and help in selecting suitable materials to prevent this failure.

Moreover in the last few decades, many approaches have been presented to improve the rheological characteristics of asphalt cement and the asphalt mixture, including the use of additives. Nano-materials are of these additives, which have revolutionized the pavement industry due to their rapid development and effective application [10]. Golestani et al. [11] evaluated the physical and rheological properties of asphalt modified with SBS/NC. In this study, the base binder was modified separately with a linear SBS polymer and nanoclay at different proportions. As a result, three modified binders: nano-modified asphalt (NMA), polymer-modified asphalt (PMA), and nanocomposite modified asphalt (NCMA) were made. Test results have shown that nanoclay can enhance the physical and rheological properties of the PMA binder as well as its storage stability. With these enhanced binder characteristics, the asphalt concrete specimens showed an increase of tensile strength and resilient modulus and also improved rutting resistance over conventional asphalt concrete.

In another study, Hamedi et al. [12] investigated the effects of Nano-$CaCO_3$ on the moisture damage of HMAs. The results of this study indicated that the use of Nano-$CaCO_3$ increases the asphalt cement-aggregate adhesion, in addition, the asphalt mixture containing this additive showed greater resistance to moisture damage compared to the control mixture. In addition, Hamedi et al. [13] in another study, with the use of Nano-ZnO to modify asphalt cement and using the SFE theory, concluded that modified asphalt cement reduces de-bounding energy and, hence, the resistance of asphalt mixtures to moisture damage increases significantly. Moreover, Azarhoosh et al. [14] evaluated the effect of nano-TiO_2 on the adhesion between aggregate and asphalt binder in hot mix asphalt. The results of the SFE method indicate that nano-TiO_2 increases the wettability of the asphalt binder on the aggregate and promotes the adhesion between the asphalt binder and aggregate. Also, adding nano-TiO_2 leads to the decrease of the acid component of SFE and increases the basic component of SFE of the asphalt binder leading to an increase of adhesion between the asphalt binder and aggregate.

Derun and Luo [15] were investigated the effects of additives on moisture susceptibility of asphalt mixtures using the SFE method. This study proposes an SFE method to investigate the effects of various additives on the moisture susceptibility of asphalt mixtures. For this purpose, 6 commonly-used additives: a warm mix asphalt additive, two nano-materials, a hydrated lime, a Portland cement, and a non-amine liquid asphalt anti-stripping agent were selected. The results showed that the ranking of the moisture damage resistance of asphalt mixtures measured from the mixture moisture susceptibility tests is consistent with that of the energy ratio results determined from the proposed SFE method. This validates that the proposed SFE method can be used to accurately quantify the effects of additives on the moisture susceptibility of asphalt mixtures. In another study, the SFE and moisture sensitivity of warm mix asphalt binders was evaluated using a dynamic contact angle. The results showed that the Cecabase improved the spread ability of the asphalt cement over limestone compared to the granite aggregate substrate. Nevertheless, the Ceca base-modified asphalt cement improved the work of adhesion. In terms of moisture sensitivity, it is also evident from the compatibility ratio indicator that, unlike granite aggregates, the limestone aggregates were less susceptible to moisture damage [16]. Furthermore, a polypropylene nanocomposite was used for improving the moisture susceptibility of the asphalt mixtures. The experimental design included one base asphalt binder, two types of aggregates (granite and limestone), and 2% of the nanocomposite. The test results showed that the tensile-strength-ratio values of the asphalt

Table 1. Properties of aggregates and PE was used in this study.

Materials	Properties	Quantity (Limestone/Granite)
Aggregates	Physical	
	Specific gravity (coarse agg.), ASTM C 127	
	Bulk	2.68/2.65
	SSD	2.70/2.68
	Apparent	2.72/2.71
	Specific gravity (fine agg.), ASTM C 128	
	Bulk	2.66/2.63
	SSD	2.69/2.67
	Apparent	2.71/2.70
	Specific gravity (filler), ASTM D854	2.61/2.59
	Los Angeles abrasion (%), ASTM C 131	33/21
	Flat and elongated particles (%), ASTM D 4791	9/7
	Sodium sulfate soundness (%), ASTM C 88	6/9
	Fine aggregate angularity (%), ASTM C 1252	54.3/61.2
	Chemical	
	Silicon dioxide, SiO_2 (%)	4.96/65.3
	R_2O_3 (Al_2O_3+Fe_2O_3) (%)	15.73/21.4
	Aluminum oxide, Al_2O_3 (%)	13.57/18.1
	Ferric oxide, Fe_2O_3 (%)	2.16/3.3
	Magnesium oxide, MgO (%)	3.52/1.5
	Calcium oxide, CaO (%)	70.44/2.1
HDPE	Density(g/cm^3)	0.97
	Water Absorption, 24 hours (%)	0
	Tensile Strength (MPa)	23.6
	Tensile Elongation at Yield (%)	820-850

mixtures containing nanocomposite had improved. In addition, the results of the surface free energy test indicated that the nanocomposite could be used to improve the moisture susceptibility of the asphalt mixtures [17].

2- Materials

In this study, two types of aggregates (granite and limestone) have been used, which have acidic and basic characteristics, respectively. The main reason for using these materials is the different chemical composition of aggregates, which provides them with different susceptibility to moisture damage. The chemical characteristics of these aggregates have been obtained using the x-ray fluorescence spectroscopy (XRF) test, the results of which are presented in Table 1. Also, the physical characteristics of the aggregates are shown in Table 1. The grading used in this study is shown in Fig. 1.

PE is the most popular plastic in the world. This material is a semi-crystalline material with excellent chemical resistance, good fatigue and wears resistance, and a wide range of properties. It has a very simple structure. A molecule of PE is a long chain of carbon atoms, with two hydrogen atoms attached to each carbon atom. They are light in weight and provide good resistance to organic solvents with low moisture absorption rates [18]. One type of PE grade was used in this research, the properties of which are shown in Table 1. All the high-density polyethylene (HDPE) particles passed a No.10 (2 mm) sieve and were retained on a No.40 (0.42 mm) sieve in powder form. HDPE offers excellent impact resistance, and it is lightweight, has low moisture absorption and high tensile strength [18].

In addition, the asphalt cement with 60/70 penetration grade produced by Pasargad Oil Refinery, Tehran, Iran, has been used in this study. Moreover, conventional experiments were carried out to describe the characteristics of pure and modified asphalt cement, the results of which are presented in Table 2.

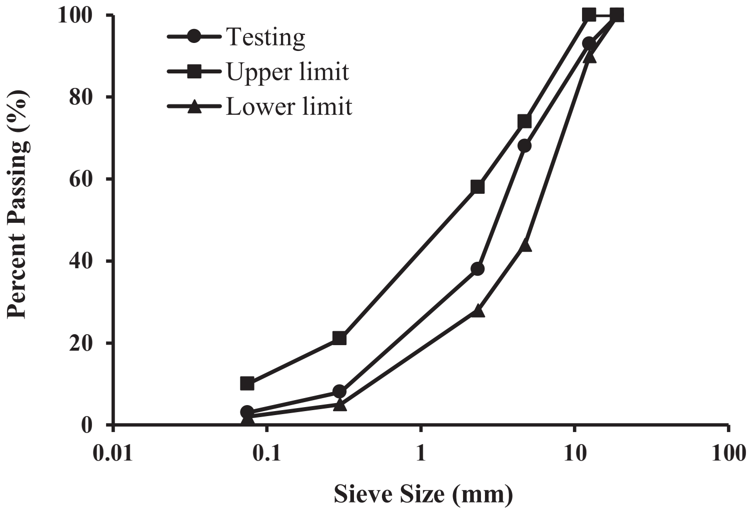

Fig. 1. Three limits of aggregates gradation.

Table 2. Results of the experiments conducted on three types of asphalt cement.

Test	Standard	Neat asphalt cement (AC) (60/70)	Modified asphalt cement	
			3% PE/NC	6% PE/NC
Penetration (100 g, 5 s, 25 ºC), 0.1 mm	ASTM D5-73	68	53	42
Ductility (25 ºC, 5 cm/min), cm	ASTM D113-79	>150	109	79
Softening point, ºC	ASTM D36-76	51	65	84
Flash point, ºC	ASTM D92-78	265	274	282
Viscosity, mPa.s (135 ºC)	ASTM D2171-07	0.311	1.114	1.723

3- Experimental Setup and Procedure

Experimental stages of this study include: 1) modifying the asphalt cement with different amounts of PE/NC; 2) Obtaining optimum asphalt cement content for making asphalt mixtures according to Marshall Mix design method; 3) Determination of SFE components of aggregates and asphalt cement with and without PE/NC; 4) Obtaining the moisture damage of different types of asphalt mixtures using ITS test with different freeze-thaw cycles. It is worth noting that in this research, 3 asphalt samples were made for each asphalt cement-aggregate combination and the type of test conditions to take into account the reproducibility of the results [19].

3- 1- Preparation of modified asphalt cement

Previous studies indicate that the use of nanocomposites as asphalt cement modifiers is limited to 1 to 6% asphalt cement weight [20, 21]. Therefore, 3 and 6% PE/NC was used as asphalt cement modifier in this study. The following blending procedure was employed for preparing the nanocomposites: Asphalt cement was heated in an iron container at a temperature of 180 ± 5 ºC, and the required amount of HDPE (3 and 6 wt.%) was then added into the asphalt cement in a high shear mixer at the speed of 10000 rpm for 1 h (for homogenous blending). The organophilic montmorillonite (OMMT) was then added into PE-modified asphalt cement with a ratio of PE/OMMT = 100/25 at 180 ºC, and the mix was blended at the fixed speed of 6000 rpm for 30 min. The pure asphalt cement is also placed in the mixer at the same temperature and time to experience the same aging effect as modified asphalt cement.

3- 2- Mix design

In this study, Marshall mixing design method has been used according to ASTM D6927-15 standard to determine the optimum asphalt cement ratio [22]. Therefore, three series of 1200 gr mixtures with five different asphalt cement percentages were prepared for the production of Marshall samples. 75 impacts were hit on each side of the cylindrical samples to provide them for simulation of heavy traffic. Using the temperature-viscosity graph, the temperature ranges of 163-169 °C and 150-155 °C were obtained for mixing and compaction temperatures, respectively.

To determine the optimum asphalt cement content, the graphs of stability, flow, unit weight, void mineral aggregate (VMA), and air voids of the compacted samples were first plotted for various percentages of asphalt cement. Since the air void content of the compacted samples is the main factor in the design of asphalt mixtures, the amount of 4% air void

Table 3. SFE 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

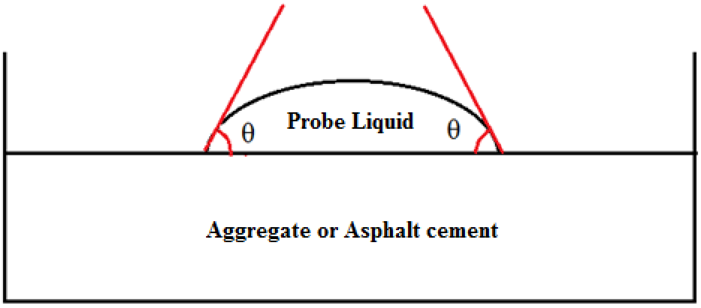

Fig. 2. Contact angles measured in the sessile drop method.

was considered to determine the optimum asphalt cement. In addition, the other parameters in optimum asphalt cement were controlled. Therefore, due to the above issues, the optimum asphalt binder contents were found to be 5 and 5.5% for granite and limestone, respectively. The optimal contents of asphalt binder, i.e., 5 and 5.5%, were accepted for the modified mixtures containing granite and limestone.

3- 3- Theory of SFE

The two-component theory and the acidic-basic theory are the most common theories used to specify the SFE of the materials based on the molecular structure. In this study, the acidic-basic theory is used based on which; the SFE includes nonpolar components (the Lifshitz-van der Waals component), Lewis acid SFE component, and Lewis base SFE component. Therefore, the total SFE is obtained by combining these components using Eq. (1):

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

Where Γ^{Total} represents total SFE of asphalt or aggregate; Γ^{LW}, Lifshitz–van der Waals component of the SFE; and Γ^{AB}, acid–base component of the SFE.

According to the principles provided by Van Oss et al. [23], the polar part consists of the Lewis acid and Lewis base parameters.

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

Where Γ^{+} is Lewis acid component of surface interaction, and Γ^{-} is Lewis base component of surface interaction.

3- 3- 1- Measurement of the SFE components of asphalt cement and aggregates

Various methods can be used to measure the components of SFE of aggregates and asphalt cement. The sessile drop method has been used in this study. The sessile drop method is used to measure the probe liquid (material with specific SFE components) 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 microsyringe 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. In the present study, 3 probe liquids were used including, water, Diiodomethane, and ethylene glycol. The SFE components of these liquids are shown in Table 3. Fig. 2 shows the schematic of the sessile drop technique and the contact angle between the probe liquid and the smooth surface of the tested material (asphalt cement or aggregate).

After finding the angle θ at the contact surface of the tested material and three different probe liquids, three equations can be formed as Eq. (3) and, by simultaneously solving 3 equations, determine the SFE components of the tested material [8].

$$\Gamma^{Total}\left(1+\cos\theta\right)=2\left(\sqrt{\Gamma_S^{LW}\Gamma_L^{LW}}+\sqrt{\Gamma_S^{+}\Gamma_L^{-}}+\sqrt{\Gamma_S^{-}\Gamma_L^{+}}\right) \quad (3)$$

Where S and L indices show the surface free energy components of tested materials and probe liquids, respectively.

3- 3- 2- SFE parameters

Based on the definition, the SFE of a material is equal to the amount of work required to increase a unit area to the surfaces of the material under vacuum conditions. In addition, the adhesion-free energy between two materials is equal to the amount of energy required to create two new surfaces at the interface of the two materials. Similarly, the energy required to create a crack with a unit area in a material is called cohesion-free energy. As mentioned earlier, the cohesion-free energy of the asphalt cement and also the asphalt cement-aggregates adhesion-free energy in HMAs are of importance for the assessment of moisture damage and fatigue cracking. Therefore, the above parameters must be determined to properly understand the performance of asphalt mixtures.

According to the definition of SFE, the cohesion free energy for various materials can be calculated as follows [8]:

$$W=2\Gamma^{Total} \quad (4)$$

Where W represents cohesion free energy of materials.

Similarly, the adhesion free energy between objects 1 and 2, which have two polar and nonpolar components, can be specified as follows [8]:

$$W_{12}=2\left[\left(\sqrt{\Gamma_1^{LW}\Gamma_2^{LW}}\right)+\left(\sqrt{\Gamma_1^{+}\Gamma_2^{-}}\right)+\left(\sqrt{\Gamma_1^{-}\Gamma_2^{2}}\right)\right] \quad (5)$$

Where W_{12} is the free energy of adhesion, Γ_1^{lw} , $\tilde{A}_1^{+}$, and Γ_1^{-} a re SFE components of material 1, and Γ_2^{lw} , Γ_2^{+} , and Γ_2^{-} are SFE components of material 2.

When the asphalt mixture is in contact with water, the energy of the system is freely released; this is called the de-bonding energy. Since the de-bonding energy is released from the system, it will always be negative. By adding another substance (water) to Eq. (5), the asphalt cement-aggregate adhesion-free energy in the presence of water can be obtained according to the relation proposed by Van Oss et al. [23], which equals the same de-bounding energy with a negative value. (Eq. (6)). The higher this negative value, the potential of the asphalt cement-aggregate de-bounding will increase, and hence, the possibility of stripping will increase in the asphalt mixture.

$$W_{123}=-\begin{bmatrix}\left(2\Gamma_3^{LW}\right)+\left(4\sqrt{\Gamma_3^{+}\Gamma_3^{-}}\right)- \\ \left(2\sqrt{\Gamma_1^{LW}\Gamma_3^{LW}}\right)-\left(2\sqrt{\Gamma_3^{+}\Gamma_1^{-}}\right)- \\ \left(2\sqrt{\Gamma_1^{+}\Gamma_3^{-}}\right)-\left(2\sqrt{\Gamma_2^{LW}\Gamma_3^{LW}}\right) \\ -\left(2\sqrt{\Gamma_3^{+}\Gamma_2^{-}}\right)-\left(2\sqrt{\Gamma_2^{+}\Gamma_3^{-}}\right)+ \\ \left(2\sqrt{\Gamma_1^{LW}\Gamma_2^{LW}}\right)+\left(2\sqrt{\Gamma_1^{+}\Gamma_2^{-}}\right)+ \\ \left(2\sqrt{\Gamma_2^{+}\Gamma_2^{-}}\right)\end{bmatrix} \quad (6)$$

Where W_{123} is de-bounding energy and 1, 2, and 3 indices show the surface free energy components of asphalt cement, aggregate, and water, respectively.

1.1. Determination of moisture susceptibility of asphalt mixtures

In this study, the mechanical method based on the AASHTO T283 standard, as the most comprehensive method, has been used to investigate the effect of the performance of asphalt mixtures on moisture damage. To clarify the differences in the performance of different asphalt mixtures, ITS tests have been used in 1, 3, and 5 freeze-thaw cycles. To test the moisture susceptibility by the modified Lottman method for each mixture, three samples should be made in wet conditions and three in dry conditions. Samples with a diameter of 100 mm and a height of 63.5 ± 2.5 mm are tested and should be compacted in such a way that their air content to be between 7 ± 0.5%.

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 the 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. In the end, the samples are brought to room temperature (25 ° C); in this way, they are called wet samples.

Loading of the ITS test is carried out at a loading rate of 5.08 cm (2 inches) per minute until the sample is ruptured. The amount of load is recorded at the rupture moment. Then

Table 4. SFE Components of Aggregate (mJ/m2).

Aggregate type	SFE components				
	Total SFE (Γ)	Nonpolar component (Γ^{LW})	Polar component (Γ^{AB})	Acidic component (Γ^{+})	Basic component (Γ^{-})
Granite	365.62	50.77	314.85	57.24	432.95
Limestone	288.14	42.32	245.82	26.73	565.16

Table 5. SFE Components of asphalt cement (mJ/m2).

Asphalt cement (AC) types	pure AC	AC with 3% PE/NC	AC with 6% PE/NC
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

the ITS value of the samples is obtained using Eq. (7).

$$ITS = \frac{2F}{t\pi d} \tag{7}$$

Where ITS is the indirect tensile strength (kPa), F is the peak value of the applied vertical load (kN), t is the mean thickness of the test specimen (m), and d is the specimen diameter (m).

The average ITS value of dry (three samples) and wet (three samples) samples is calculated separately. The moisture susceptibility or the stripping potential for asphalt mixture samples is obtained by the ratio of the average ITS value of the wet to dry samples (in percent).

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

Which, TSR is the indirect tensile strength ratio, ITS_{Wet} is the average ITS value of the wet set samples that are subjected to freeze-thaw cycles, and ITS_{Dry} is the average ITS value of the dry set samples.

The minimum allowable value for the average indirect tensile strength ratio (TSR) is 70%, which is set at 80% in some codes, especially in wet climate conditions. Although it has remained a challenge for researchers to present a practical test procedure to determine moisture damage of asphalt mixture, the ITS test method has been accepted and widely used [24].

4- Results and Discussion

4- 1- Results of SFE experiments

In the event of moisture damages, failure is rarely observed in the aggregates, and this failure is due to the asphalt cement cohesion failure and the adhesion failure at the asphalt cement-aggregate interface. In other words, the failure does not occur in the cohesion of aggregates. Therefore, the total SFE of the aggregates alone cannot significantly affect the moisture damage. Since to increase the adhesion between asphalt cement and aggregates in the presence of water, it is necessary to respectively increase and decrease the basic and acidic component of aggregates, therefore, the effect of aggregates in preventing this failure can be attributed to changing these parameters. The results of measurements of SFE components of aggregates used in this study are presented in Table 4. The base component of both aggregates is larger than their acid component, which is the same for all aggregates, however as clear, the ratio of the acid component to base component is higher in granite aggregates compared to limestone.

The SFE results of control and modified asphalt cement are presented in Table 5. As seen, the acid component of the pure asphalt cement is much larger than its base component. This makes the asphalt cement have more acidic characteristics. The acidic characteristic of asphalt cement causes the formation of stronger bonds with base materials like limestone aggregates. The use of PE/NC causes the decrease and increase of acid and base components of the modified asphalt cement, respectively. The effect of nanocomposite on the base component is higher than the acid component; this is due to the basic nature of PE ($8<pH<10$), leading to the formation of more basic characteristics in modified asphalt cement with this material.

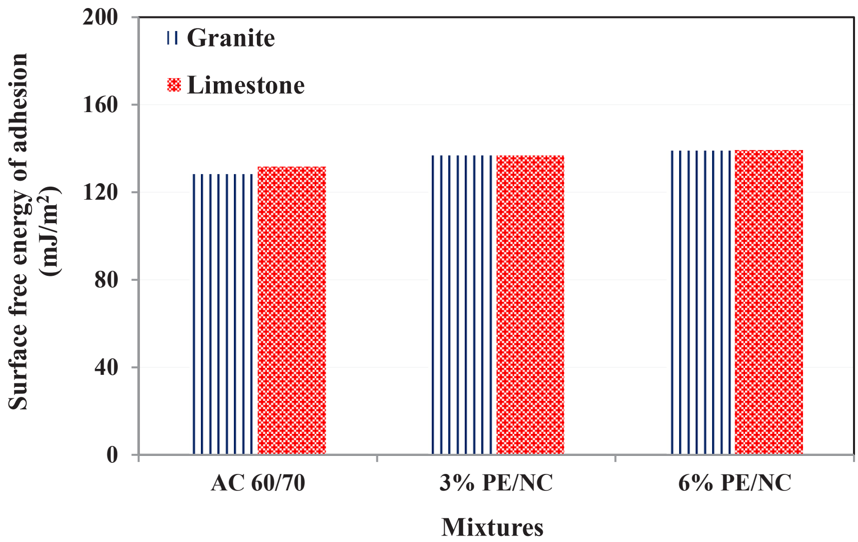

Fig. 3. Adhesion surface free energy of different mixtures at dry condition.

Moreover, based on the results given in Table 5, the nonpolar component of PE/NC-modified asphalt cement is increased in comparison with pure asphalt cement. Since the bond between asphalt cement and aggregates is nonpolar in asphalt mixtures, this leads to the formation of stronger nonpolar bonds. Furthermore, the results of the total SFE indicate that the use of PE/NC has caused an increase in this parameter. The total SFE is directly and linearly related to the cohesion-free energy, hence, the increase in total SFE results in increased cohesion-free energy. Therefore, the potential for cohesion failure in the modified asphalt cement is less than pure asphalt cement.

4- 2- Results of SFE parameters

According to Eq. (4) and the results of asphalt cement SFE components (Table 5), the cohesion-free energy of pure asphalt cement and asphalt cement modified with 3% and 6% PE/NC is 27.24, 36.36, and 39.40 mJ/m^2, respectively. These results indicate that the addition of nanocomposite has increased the cohesion-free energy and hence, the resistance of the modified asphalt cement to the cracking in the asphalt film has increased. Based on the results, it can be seen that the main reason for this increase in strength is due to the increase of the nonpolar component of asphalt cement SFE, whereas the polar component (acid-base) does not significantly contribute to changing the asphalt cement resistance to cohesion failure.

The results for asphalt cement-aggregate adhesion-free energy in dry conditions are shown in Fig. 3. This parameter indicates some of the energy required to create a rupture with a unit area at the asphalt cement-aggregate interface. As can be seen, the use of PE/NC has led to an increase in the value of the adhesion-free energy in samples containing both types of aggregates. This causes an increase in the amount of energy required to separate asphalt cement from the aggregate unit area. An increase in the amount of PE/NC up to 6% increases adhesion-free energy, however, its increasing rate decreases in nanocomposite values of more than 3%. In addition, the value of adhesion-free energy is lower in samples made with pure asphalt cement and granite aggregates. This indicates less energy required for the de-bounding of pure asphalt cement from the unit area of granite aggregates. However, the adhesion-free energy values are not significantly different for mixtures containing modified asphalt cement for both types of aggregates.

The energy released from the system when stripping event or adhesion free energy of asphalt cement-aggregate under wet conditions (de-bonding energy) is the amount of energy released during the stripping process. Given that these values are negative, their absolute values are presented in Fig. 4. According to the principles of thermodynamics, any exothermic process is performed spontaneously. Therefore, it is expected that when the water enters the asphalt cement-aggregate system, the de-bounding of asphalt cement from the surface of the aggregate and the stripping process occur spontaneously. The important thing is that the greater the amount of released energy, the greater the rate of stripping. The results presented in Fig. 4 show that the use of PE/NC in samples made with both types of aggregates used in this study has reduced the de-bounding energy. An increase in the amount of this substance from 3 to 6% has led to a decrease in the amount of this parameter, but at a slower rate compared to the increase of this material to 3%. This makes the tendency to stripping decrease with increasing nanomaterial. Moreover, as it can be seen, a higher amount of energy is released in the mixtures containing granite aggregate, indicating a higher tendency to strip per unit area in granite aggregates.

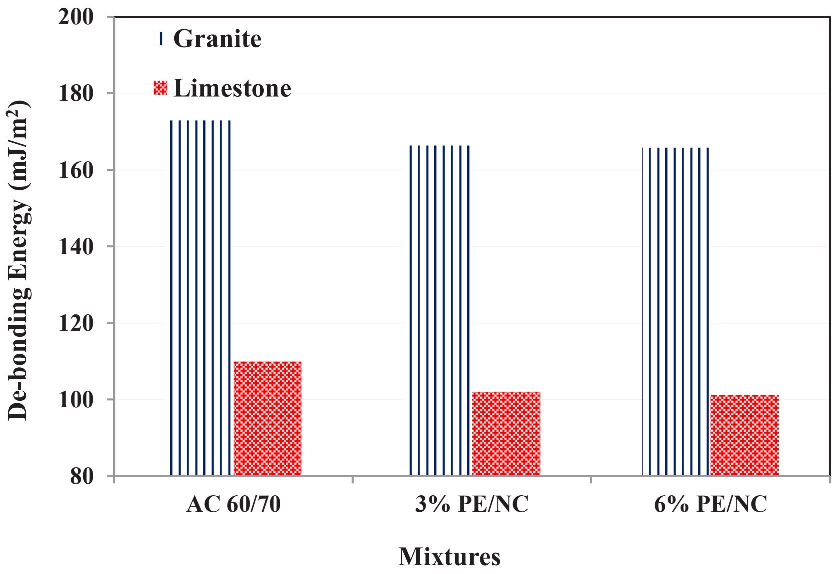

Fig. 4. Adhesion surface free energy of different mixtures at wet condition (De-bonding energy).

4- 3- ITS test results

The results of the ITS test for samples made with granite and limestone aggregates are shown in Figs. 5 and 6, respectively. As can be observed, control samples (without additives) made with limestone aggregates have the same performance against loading in dry conditions in comparison with granite aggregate samples. The close values of ITS are because the granite aggregates have better physical resistance, however, the mixing adhesion (adhesion-free energy multiplied by the specific surface area of the aggregate) is better in limestone aggregates, which caused the behavior of the samples of both groups to be almost identical. However, in wet conditions, the performance of asphalt mix samples containing granite aggregates was much weaker compared to similar samples made with limestone aggregates. This low strength in granite aggregate samples could be attributed to the higher hydrophilicity of minerals of these aggregates. Strong bonds formed in dry conditions are lost under wet conditions, resulting in a larger drop in aggregate resistance in this group.

Moreover, the addition of PE/NC increases the ITS of samples made with both types of granite and limestone aggregates in wet and dry conditions, with better performance of the nanocomposite additive in samples containing granite aggregates. Since the use of nanocomposite as an asphalt cement modifier increases the asphalt cement basic characteristics and thus improves adhesion to acidic granite aggregate. Therefore, a greater amount of energy is required for asphalt cement de-bonding from granite aggregate surface and the occurrence of an adhesion rupture failure.

Furthermore, the resistance of asphalt mixtures in wet conditions has decreased in comparison with similar samples in dry conditions. The decrease in ITS of samples in wet conditions can be attributed to the loss of adhesion of the mixture or the cohesion of asphalt cement in the presence of moisture. The presence of water will cause the system to become more irregular and reduce the amount of Gibbs's free energy. This will cause the asphalt cement de-bonding from the aggregate surface or stripping as a spontaneous reaction.

The index of TSR of asphalt mixtures in wet to dry conditions is the most common indicator in determining the moisture susceptibility of an asphalt mixture before its implementation, which can help predict the performance of the asphalt mix in the design stage. Figs. 7 and 8 show the results of testing the moisture susceptibility index in samples containing both types of aggregates used in this study. As evident from Figs. 7 and 8, tensile strength significantly decreased from the dry samples to the conditioned samples, which was an indication of moisture damage due to the presence of moisture.

To more closely investigate the effect of PE/NC additives used in this study on the moisture susceptibility of asphalt mixtures, 1, 3, and 5 freeze-thaw cycles were applied to the samples according to the AASHTO T283 standard.

The results indicate that samples containing limestone aggregates have more strength against moisture damage. One of the most important factors in the occurrence of moisture damage is the structure of the aggregate minerals used in asphalt mixtures. The two minerals SiO_2 and CaO cause a fundamental change in the hydrophilicity or hydrophobicity characteristics of the asphalt mixtures. As shown in Table 1, a large part of granite aggregates is formed by the silicon dioxide (SiO_2) mineral, which results in strong acidic characteristics and high hydrophilicity. In fact, the hydroxyl groups (OH) are found on the surface of the acidic aggregates. These groups react with carboxylic acid groups, forming hydrogen bonding, which is very effective in asphalt cement- acidic ag-

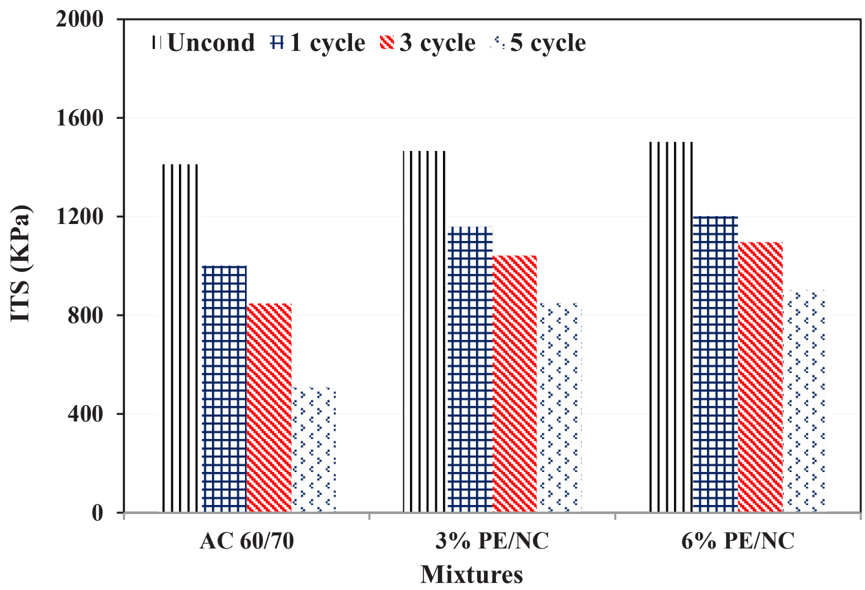

Fig. 5. ITS for mixtures made with granite aggregate with and without PE/NC.

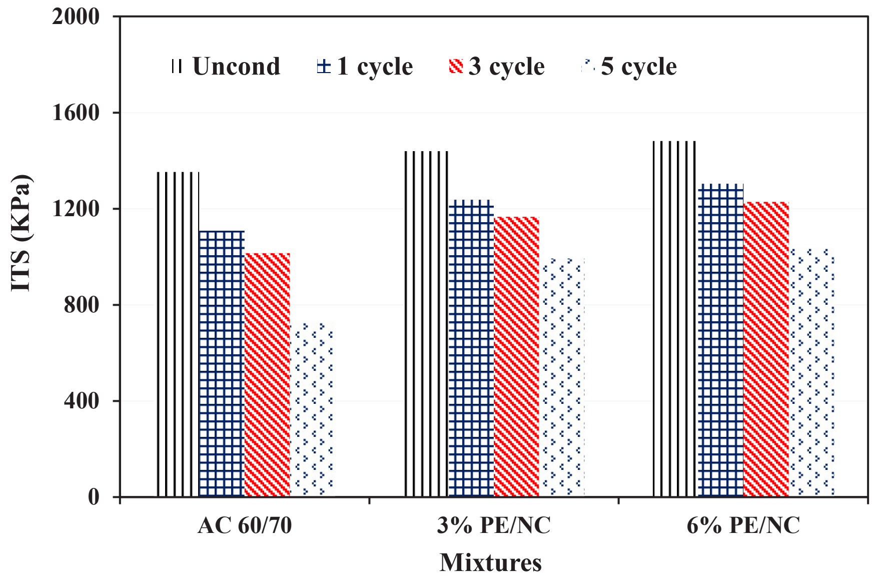

Fig. 6. ITS for mixtures made with limestone aggregate with and without PE/NC.

gregate adhesion. However, this hydrogen bond is easily broken down in the presence of water and these two groups are separated from each other, each producing hydrogen bonding with water molecules, which accelerates the phenomenon of stripping.

The use of PE/NC in the samples of both types of aggregates increased the strength of asphalt mixes against moisture and improved the TSR index. As shown in Figs. 7 and 8, the use of nanocomposite has less effect on the strength of asphalt mixtures made with limestone aggregates. This can be attributed to the good adhesion of limestone aggregate-pure asphalt cement, which is an acidic material. The use of nanocomposite in both dry and wet conditions increases the strength of samples containing the limestone aggregate to a similar extent. This leads to a slight improvement of TSR in samples made with this type of aggregate. However on the other hand, in samples made with acidic granite aggregates, the use of the PE/NC has significantly improved the perfor-

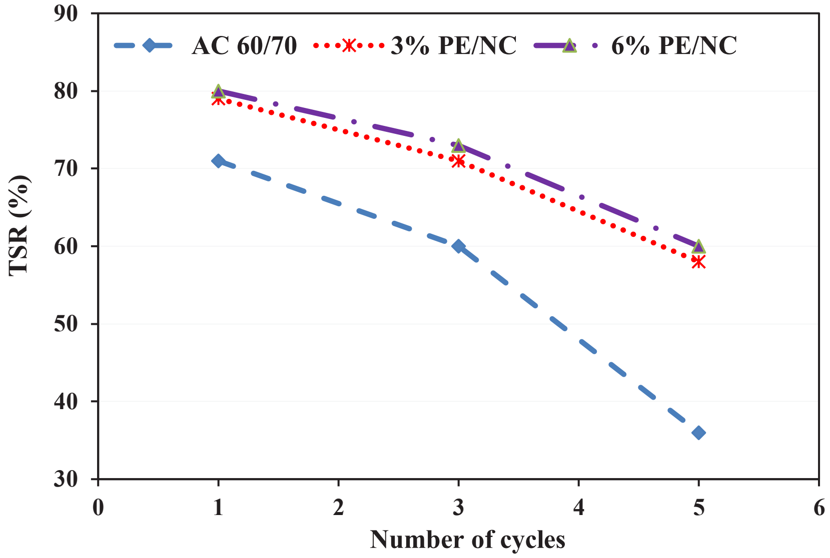

Fig. 7. Effects of PE/NC and freeze-thaw cycles on TSR in mixtures made with granite aggregate.

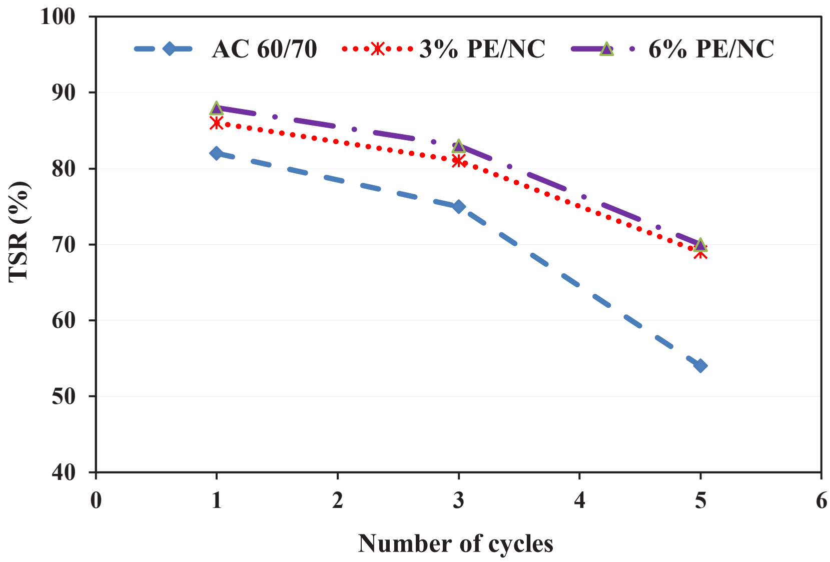

Fig. 8. Effects of PE/NC and freeze-thaw cycles on TSR in mixtures made with limestone aggregate.

mance of the asphalt mix against moisture. Also, it was observed that a decrease in the indirect tensile strength of the mixtures modified by PE/NC was not equal to the one in the control mixtures for different cycles. The decrease in the TSR in cycles 1-3 was less than that in the TSR in cycles 3-5, which could be because increasing the freeze-thaw cycles decreased the anti-stripping on the aggregate surface.

5- Conclusion

The objective of the researchers in the present study was to strengthen asphalt mixtures to moisture damage using PE/NC as an asphalt cement modifier. Therefore, the mechanical and thermodynamic methods have been used to investigate the effect of the additive used in this study. The most important results obtained in this study are as follows:

- The use of PE/NC has led to an increase in the asphalt cement base component. This causes the amount of adhesion of asphalt cement to increase to granite aggregates, which have acidic characteristics.
- PE/NC has greatly increased the nonpolar component of SFE. This results in the formation of better nonpolar water-insoluble bonds.
- The amount of total SFE of the modified asphalt cement is higher than the pure asphalt cement. This leads to a reduction in the potential of moisture damage of the cohesion rupture type.
- Adhesion-free energy increases in modified samples compared to control samples, and in fact, more energy is required to remove asphalt cement from the aggregate unit area, which reduces the potential of stripping.
- The use of PE/NC reduces the amount of de-bonding energy in the modified samples. This makes the asphalt cement-aggregate system thermodynamically more stable and reduces the severity of the stripping phenomenon.
- The use of PE/NC increases the TSR in asphalt mixtures containing both types of aggregates used in this study, and hence, their resistance to moisture damage.

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