



## Evaluation of Moisture Durability of Modified Asphalt Mixture with Nano-Titanium Dioxide Using Surface Free Energy Method

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**ABSTRACT:** Moisture damage is one of the forms of asphalt pavement distress that occurs due to the presence of water and its effect on the mechanical properties of the asphalt mixture. Using nanomaterial as an additive is one of the solutions that delays this event and increases the durability of the mixture. In this study, the effect of nanomaterial (Nano-TiO<sub>2</sub>) on the moisture susceptibility of asphalt mixtures was investigated using the surface free energy method, indirect tensile strength test (ITS) and resilient modulus (Mr). Asphalt samples were fabricated by neat bitumen with a penetration grade of 85/100 and Siliceous aggregate. The bitumen was modified with 3 and 6% (weight of bitumen) of Nano-TiO<sub>2</sub>. The results of the bitumen section indicate that by modifying the bitumen with Nano-TiO<sub>2</sub>, the acidic component of surface free energy decreases and its basic component increases. On the other hand, as the non-polar component increases, the bitumen-free energy would be increased. The addition of Nano-TiO<sub>2</sub> to the asphalt mixture also increased the TSR. TSR reduction through the different freezing-thaw cycles for the modified mixtures was less compared to the control mixtures. The separation energy between bitumen-rock materials is also reduced by modifying the bitumen with this nanomaterial. Therefore, it improves the stripping resistance of the asphalt mixture. In addition, the results of resilient modulus indicate that bitumen modification with Nano-TiO<sub>2</sub> increased the Mr values. Similar to changes in the TSR, the RMR value has been increased for the modified HMA and it increased the hot mix asphalt durability.

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### 1- Introduction

In the last decades, a lot of information has been done to identify the moisture susceptibility [1]. Based on thermodynamic theory, the effective internal factors, i.e., adhesion and cohesion, were considered as the most concepts among the other properties [2]. Surface free energy (SFE) and its relationship with bond energy were accepted as an indicator for measuring the adhesion and cohesion of materials [3]. Therefore, by quantifying the moisture potential using the SFE method, the moisture damage of the asphalt mixture can be easily investigated.

There are many solutions to prevent the moisture damage of asphalt mixture. Using additives as a modifier of the mixture properties is one of the most common solutions [4]. These additives include nanomaterials, which have been recently considered by researchers. Nano-TiO<sub>2</sub> is also one of the nanomaterials that has been applied in asphalt mixtures in the last decade [5]. However, the effect of Nano-TiO<sub>2</sub> on moisture damage of mixture under different freezing-thaw cycles using the SFE method has not been studied. In this

regard, this issue was investigated using different techniques such as the SFE method, indirect tensile test and resilient modulus test. Therefore, the SFE components of stone materials, neat bitumen, and modified bitumen with Nano-TiO<sub>2</sub> were obtained and compared with the corresponding mixture results. As a result, the effect of Nano-TiO<sub>2</sub> on moisture susceptibility and different freezing-thaw cycles was determined.

### 2- Materials

#### 2- 1- Aggregate

A silica aggregate with NMAS of 19 mm was used to fabricate the asphalt mixture.

#### 2- 2- Bitumen

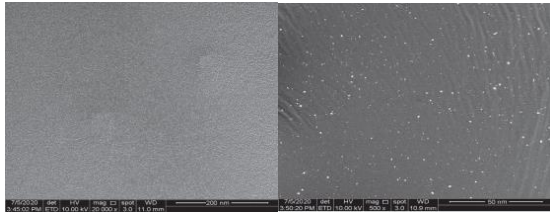
A neat binder with PG64-22 was used in this study

#### 2- 3- Nano-TiO<sub>2</sub>

Nano-TiO<sub>2</sub> with a maximum particle size of 5 nm was used in this research. Nano-TiO<sub>2</sub> with total weight percentages of 0, 1%, 3% and 5% were blended with bitumen and named

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**Fig. 1. FESEM image of bitumen modified with 5% Nano-TiO<sub>2</sub> in different magnifications**

T0, T1, T3 and T5, respectively. The uniformity of dispersion of nanomaterials in the modified bitumen was investigated using field emission scanning electron microscopy (FESEM), as shown in Figure 1.

### 3- Experimental Program

#### 3- 1- Mixing and compact temperature

According to ASTM-D4402, the viscosity of different bitumens was measured at 135 and 160 °C using Brookfield device and the mixing and compaction temperatures were obtained.

#### 3- 2- Optimum bitumen content (OBC)

OBC was determined according to ASTM D1559. It was found to be 5.6% for neat bitumen. It should be noted that the addition of Nano-TiO<sub>2</sub> did not have a significant effect on OBC.

#### 3- 3- SFE measurement

In this research, the acid-base theory was used to measure SFE components including 1-Non-polar component ( $\Gamma^{AB}$ ), 2-acidic component ( $\Gamma^+$ ), and 3- base component ( $\Gamma^-$ ). Therefore the total SFE ( $\Gamma$ ), will be determined as Eq. 1:

$$\tilde{A} = \tilde{A}^{LW} + \tilde{A}^{AB} = \tilde{A}^{LW} + 2\sqrt{\tilde{A}^+ \tilde{A}^-} \quad (1)$$

To aim this, the sessile drop (SD) method was applied with three probe liquids. After finding the contact angle of these liquids with known SFE components, three equations as Eq. 2 can be simultaneously considered to find three unknowns of SFE components of bitumen:

$$\Gamma_L^{Total} (1 + \cos \theta) = 2[(\sqrt{\Gamma_b^{LW} \Gamma_L^{LW}}) + (\sqrt{\Gamma_b^+ \Gamma_L^-} + \sqrt{\Gamma_b^- \Gamma_L^+})] \quad (2)$$

In which,  $\theta$  is contact angle of each liquid. Two indexes of b and L are corresponded to bitumen and probe liquid.

### 3- 4- Moisture susceptibility

#### 3- 4- 1- Indirect tensile strength (ITS) test

ITS test was performed on a cylindrical sample with an air void of 7%, according to AASHTO-T283 with 1, 3, and 5 freezing-thaw cycles. Tensile strength ratio (TSR) was calculated as Eq. 3 that  $ITS_{wet}$  and  $ITS_{Dry}$  are ITS of unconditioned and conditioned mixture samples:

$$TSR = \frac{ITS_{Wet}}{ITS_{Dry}} \times 100 \quad (3)$$

#### 3- 4- 2- Resilient modulus ( $M_r$ ) test

$M_r$  of mixture samples was determined as Eq. 4 using UTM25 at 25°C:

$$M_r = \frac{p(v + 0.27)}{t \times \delta_h} \quad (4)$$

Resilient modulus ratio (RMR) was determined from division of  $M_r$  of wet sample to dry sample.

## 4- Result and summary

### 4- 1- SFE results

Regarding the contact angle of three probe liquids and investigation of their validity using statistical analysis (one way ANOVA), the results of total SFE of different bitumen types were found as Table 1.

According to Table 1, the total free energy value of neat bitumen is increased from 16.34 to 17.68 and 18.07 (mj/m<sup>2</sup>) through adding 3 and 6% Nano-TiO<sub>2</sub>, respectively. Therefore, the cohesion failure potential of modified bitumens is less than that of neat bitumen. Acidic properties reduction of bitumen and increasing its alkaline properties leads to improve the adhesion of bitumen-aggregate in the presence of water. Due to the fact that Nano-TiO<sub>2</sub> has an alkalinity behavior (8<PH<10), the change in acidity and alkalinity parameters of the modified bitumens occurs, which affects the bitumen properties.

**Table 1. SFE values of different bitumens (mj/m<sup>2</sup>)**

Type of bitumen	$\Gamma$	$\Gamma^{LW}$	$\Gamma^{AB}$	$\Gamma^+$	$\Gamma^-$
T0	16.3	14.0	2.4	2.6	0.5
T3	17.7	14.9	2.8	2.4	0.8
T6	18.1	15.1	2.9	2.4	0.9

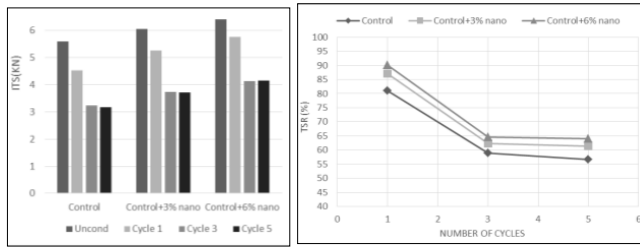


Fig. 2. ITS and TSR results of different mixture

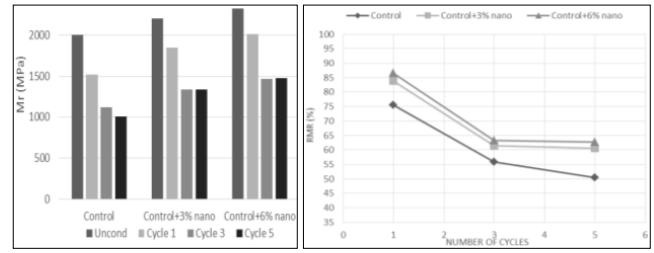


Fig. 3. Mr and RMR results of different mixture

The results presented in Table 1 show that the non-polar component of modified bitumens increases compared to the neat bitumens. Given that the bond of bitumen-aggregate is non-polar; it can be concluded that increasing the non-polar components of SFE improves the strength of this bond.

#### 4- 2- Mixture results

##### 4- 2- 1- ITS and TSR results

ITS value of mixtures and corresponding TSR results were determined, the results of which are presented in Figure 2 for different freezing-thaw cycles. As shown in Figure 2, using Nano-TiO<sub>2</sub> increases the ITS and TSR value of mixtures (in both dry and wet conditions). Three main reasons can be described for this increase: 1- Nano-TiO<sub>2</sub> has increased the adhesion of bitumen-aggregate. 2- The addition of Nano-TiO<sub>2</sub> increases the bitumen viscosity and makes it harder. Therefore, the bitumen can strongly stick to the aggregate. 3- Increasing the SFE of bitumen has reduced the possibility of failure in mastic.

##### 4- 2- 2- M<sub>r</sub> and RMR results

Resilient modulus and their ratio were determined for different mixtures as shown in Fig. 3.

Figure 3 shows that the using Nano-TiO<sub>2</sub> has increased the M<sub>r</sub> of mixtures (in both dry and wet conditions). Also, through increasing freezing-thaw cycles, the decrease in RMR of modified samples is less than that of control samples. It indicates that under multiple freezing-thaw cycles, the modified mixtures have a higher moisture resistance than the

unmodified samples. Also, adding 3% of Nano-TiO<sub>2</sub> has more RMR improvement than 6%. Therefore, it can be said that 3% of nanomaterial can be selected as the optimum percentage.

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#### HOW TO CITE THIS ARTICLE

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