Asphalt mixture performance and testing

**Comparison of the effects of anti-stripping fillers and nanomaterials on moisture resistance of asphalt mixes**

*Amir Kavussi, Seyed-Hamed Razavi*
*Faculty of Civil and Environmental Engineering, Tarbiat Modares University, Tehran, Iran*

Abstract

The role of some active fillers in increasing moisture resistance of asphalt mixes has been proved since few decades back. Nanomaterials have recently been used to modify bitumen binders and enhance properties of asphalt mixes. The aim of this research was to compare the effects of active fillers (such as hydrated lime), and these in their nano size conditions. In order to produce nano-hydrated lime in laboratory, a planetary rotary ball mill was used and nano-hydrated lime was produced from hydrated lime filler. In addition, calcium carbonate filler and a nano-calcium carbonate material were selected too. The particle size distribution of produced nano-hydrated lime was determined using Scanning Electron Microscope (SEM) and Dynamic Light Scattering (DLS) techniques. With applying these methods, it was possible to determine the approximate sizes of the tested nanomaterials, although some differences were observed in the two methods. For the produced nano-hydrated lime, sizes of 125 and 208 nm were recorded, respectively in these methods. In this study, nano-hydrated lime, nano-calcium carbonate, nano-bentonite and nano-silica, and two types of antistripping fillers, namely hydrated lime and calcium carbonate as additives were selected. Each of the above additives was mixed with a 60-70 pen bitumen at different concentrations, using a conventional mixer. With using FE-SEM testing machine, it was assured of the good distribution and homogeneity of all the filler-bitumen and nanomaterial-bitumen blends. A hard and siliceous aggregate type was selected and the above blends were used to prepare compacted bituminous samples. Indirect Tensile Stiffness Modulus (ITSM) testing was performed and a parameter named "Index of Retained Resilient Modulus (IRMr)" was determined for comparison purposes and for ranking the various mixes. The findings of the research indicated that when nanomaterials were used, a lower rate of material (compared with the same material in its filler size) would be needed in the mix so that to produce similar effects in terms of resistance against moisture damage. For hydrated lime, for example, 4% nano-hydrated lime provided similar effects on mixes that 20% hydrated lime filler had.

## 1. INTRODUCTION

Moisture damage is a complicated distress in bituminous pavements that results in reduced stiffness and reduced structural strength [1]. Researchers are looking to find methods for eliminating or reducing this problem [2]. Stiffness and moisture resistance of Hot Mix Asphalt (HMA) is improved by addition of hydrated lime [3].

In order to increase coating of aggregate particles, researchers started to use nano-scale materials as new anti-stripping additives in hot mix asphalt [4]. International System of Units (SI) accounts nano as a prefix to show $10^{-9}$ part of a unit and nanomaterials are conventionally defined as materials having at least a dimension between 1 and 100_nm. Nevertheless, considering 100 nm as an upper limit for a nanomaterial is not always accepted and still a matter of debate [6]. There are two methods of producing nanomaterials, namely, the top-down approach and the bottom-up approach. The top-down approach consists of two methods. In the first, bigger structures are diminished in size until these reach to nano-scale. The second approach consists of deconstruction into their composite parts. The bottom-up approach is used where nanoparticles are made from atomic or molecular fragments [7].

The addition of nano hydrophobic silane silica is a decent method for reducing F-T cycle damage in asphalt pavements [8]. Resilient Modulus ($M_r$) of asphalt mixtures improved as the amount of nano-silica and hydrated lime were increased [9]. Using Zycosoil and lime slurry as additives enhanced resilient modulus ratio and ITS of the mixtures [10]. Nano-clay, that is composed of layered mineral silicates, is considered as an inexpensive and abundant material. Nano-clay, based on its chemical composition and nanoparticle morphology, is classified into different groups, including montmorillonite, bentonite, kaolinite, hectorite, and halloysite [11]. Bentonite was used as nano-additive in bituminous concrete mixture and the result showed that mechanical performance of mixes improved when 20% bentonite (by weight of bitumen) was added [12].

The effects of nano-clay and nano-hydrated lime as additives were evaluated on asphalt mixes. Results showed that 5% nano-hydrated lime and 2% nano-clay increased TSR of asphalt mixes to 52% and 49%, respectively [13]. In another research, different percentages of nano-silica were added to asphalt mixtures and these were tested against moisture susceptibility. They concluded that the addition of 4% nano-silica (by weight of asphalt binder) was the optimum content to reduce susceptibility of mixes to moisture damage [14]. In ITS and ITSM tests, the addition of nano-silica at 6% led to increase ITS and $M_r$ values of 29% and 31%, respectively [15]. In another research, moisture resistance was tested on mixtures containing limestone and siliceous aggregates, and two anti-stripping agents (nano-organosilane and hydrated lime). Their findings showed that using both anti-stripping additives, increased adhesion bond between aggregate particles and bitumen [10]. A study was performed on the impact of nano-$CaCO_3$ on asphalt mixtures. In this study, different amounts of nano-$CaCO_3$ and two sources of aggregates were used. Multiple freeze-thaw cycles were imparted and samples were subjected to Surface Free Energy (SFE) and modified Lottman testing. Their findings showed that this nanomaterial could be used as an additive to reduce water sensitivity of HMA mixes [16].

## 2. RESEARCH OBJECTIVES

The main purpose of this study was to investigate the effects of two different filler types at their conventional sizes and their nano sizes on moisture susceptibility of asphalt mixes. In addition, in this research, by performing a stiffness test (ITSM) as a nondestructive and more sensitive test than the indirect tensile strength moisture susceptibility of bituminous mixes was evaluated.

## 3. EXPERIMENTAL WORKS

### 3.1. Materials

#### 3.1.1. Asphalt binder and aggregates

A 60-70 penetration grade bitumen from Refinery of Tehran, was used to prepare HMA mixes. Properties of the bitumen are reported in Table 1. A siliceous type of aggregate, with nominal maximum size of 12.5 mm, was used. Gradation was based on ASTM Standard for dense aggregate gradation, as shown in Fig. 1 [17].

#### 3.1.2. Additives

In order to investigate and compare the effects of various additives on moisture susceptibility of the HMA mix, the following additives were utilized at different percentages:

a) A calcium carbonate filler (passing 75-micron sieve size) with $CaCO_3$ molecular formula

b) A hydrated lime filler (passing 75-micron sieve size) with $Ca(OH)_2$ molecular formula. Physical and geometrical properties of the fillers used in this research are reported in Table 2.

**Table 1. Characteristics of the asphalt binder 60-70 penetration grade used in this research.**

| Properties | Value | Test Method |
|---|---|---|
| Penetration (100g, 5s, 25°C), 0.1 mm | 62 | ASTM D5 |
| Ductility (25°C, 5 cm/min), cm | 110 | ASTM D113 |
| Ring and ball softening point, °C | 51 | ASTM D36 |
| Specific gravity at 25°C, g/cm$^3$ | 1.016 | ASTM D70 |
| Viscosity at 135°C, cSt | 292 | ASTM D2170 |
| Flash point, °C | 269 | ASTM D92-78 |

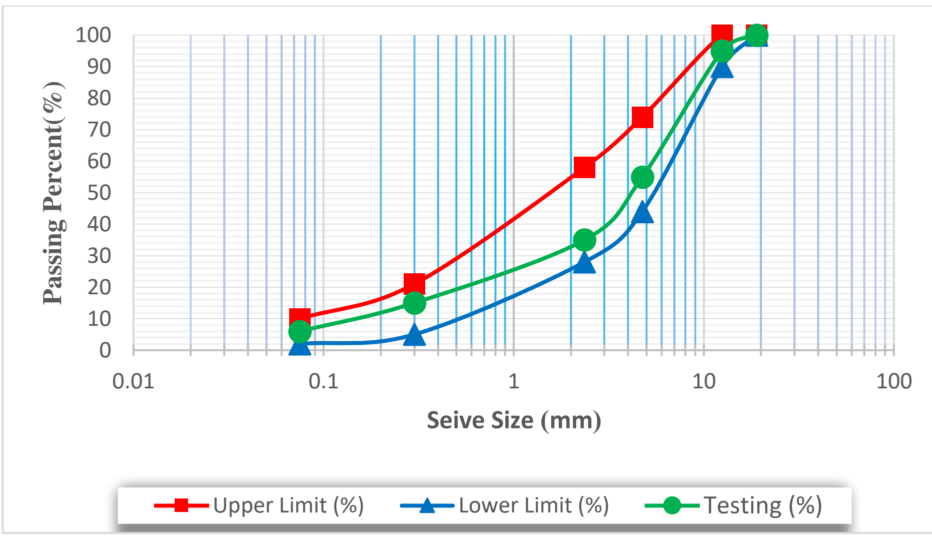



**Figure 1. Gradation of the aggregate used in this research.**

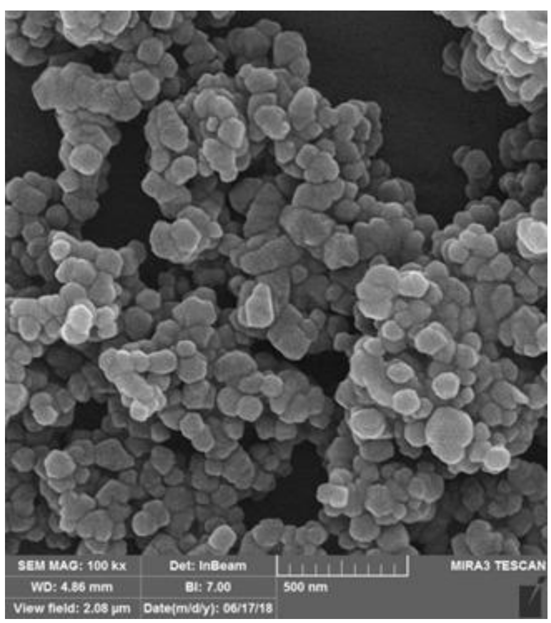



**Fig. 2. SEM image of nano-CaCO$_3$ at 100 000x magnification.**

**Table 2. Physical and geometrical properties of the fillers used in this research.**

| Properties | Filler of the aggregates | Hydrated lime filler | $CaCO_3$ filler |
|---|---|---|---|
| Retained on sieve #200 (%) | 0 | 3.4 | 4.1 |
| Chemical name | Granite | Hydrated lime or calcium hydroxide | calcium carbonate |
| Physical form | Powder | Powder | Powder |
| Color | Gray | White | White |
| Shape of particle | Angular | Hexagonal | Hexagonal |
| Molecular formula | - | $Ca(OH)_2$ | $CaCO_3$ |
| Formula Weight (g/mol) | - | 74.09 | 100.09 |
| Melting/decomposition temperature (℃) | - | 580 | 825 |
| Specific gravity ($g/cm^3$) | 2.66 | 2.34 | 2.71 |
| Specific Surface Area ($m^2/g$) | 1.79 | 4.82 | 3.28 |
| Rigden voids (%) | 38 | 62 | 34 |

c) Nano-hydrated lime of 125 nanometer size, produced using a rotary ball mill.

d) Nano-calcium carbonate with $CaCO_3$ molecular formula that was designated as CAS registry number 471-34-1. This nano-$CaCO_3$ was manufactured by American Elements US Corporate Headquarters. Properties of this nanomaterial are reported in Table 3. Fig. 2 shows its SEM image.

**Table 3. Properties of nano-calcium carbonate.**

| Properties | Nano-$CaCO_3$ |
|---|---|
| Molecular Weight (g/mol) | 100.09 |
| Appearance | Powder |
| Melting Point (℃) | 825 |
| Boiling Point (℃) | Decomposes |
| True Density ($g/cm^3$) | 2.93 |
| Bulk Density (g/ml) | 0.68 |
| Average Particle Size-APS (nm) | 10-80 |
| Morphology | Cubic or Hexagonal |
| Color | White |

e) Nano-silica with $SiO_2$ molecular formula (i.e. silica fume), that was produced by Evonik Industries AG – Germany. Characteristics of this nanomaterial are reported in Table 4. In order to investigate practical size distribution of nanoparticles, Transmission Electron Microscopy (TEM, EM 208 Philips) was performed. Fig. 3, shows a TEM image of the nano-$SiO_2$.

**Table 4. Properties of nano-hydrophilic fumed silica.**

| Properties | Nano-silica |
|---|---|
| Purity | 99+% |
| Average Particle Size – APS (nm) | 11-13 |
| Specific Surface Area – SSA ($m^2/g$) | 200 |
| Color | White |
| Bulk Density ($g/cm^3$) | <0.10 |
| True Density ($g/cm^3$) | 2.4 |

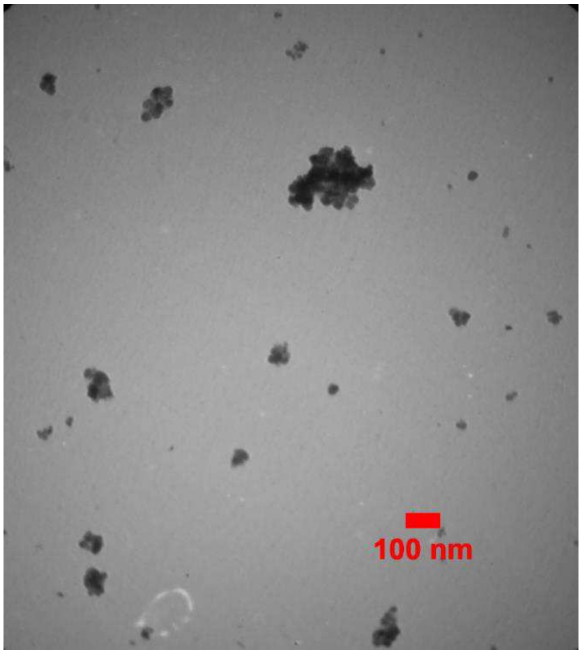



**Fig. 3. TEM image of Nano-$SiO_2$.**

f) A Nano-Clay, namely, bentonite with $H_2Al_2O_6$ Si molecular formula, produced by Sigma-Aldrich, USA, assigned with designation CAS registry number 1302-78-9. The SEM (LEO 440i) image of this nanoparticle is shown in Fig. 4. Table 5 reports properties of nano-clay, bentonite.

**Table 5. Properties of nano-clay, hydrophilic bentonite.**

| Properties | Nano-bentonite |
|---|---|
| Color | Light Tan to Brown |
| Appearance | Powder |
| Loss on Drying (%) | ≤18.0 |
| Bulk Density ($kg/m^3$) | 600 – 1100 |
| Average Particle Size (micron) | ≤25 |
| Thickness of silicate layers (nm) | 1-2 |

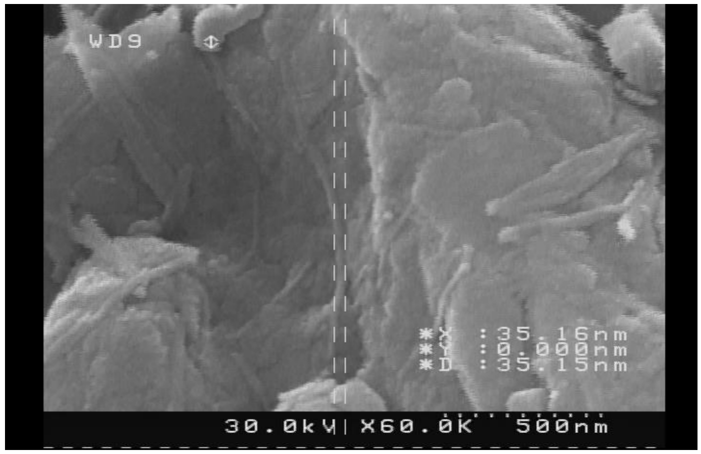



**Fig. 4. SEM image of Nano-clay bentonite at 60 000x magnification.**

According to previous research works, the amounts of nanoparticles which were used in asphalt mixes were between 1% and 8% by weight of binder. These amounts were enough to modify properties of bituminous concrete mixes [16,18]. As the nanomaterials have very high surface area, in this research these were added first to the control asphalt binder at 2% and 4% by weight of bitumen. In contrast to the nanomaterials and nano-fillers, conventional fillers, such as calcium carbonate ($CaCO_3$) and hydrated lime ($Ca(OH_2)$) fillers were used as anti-stripping agents. These were used at the amounts of 5, 10 and 20% (by weight of asphalt binder).

### 3.2. Preparation of modified asphalt binders

In order to prepare modified asphalt binders, the aforementioned percentages of additives were added to the neat asphalt binder. As homogenous distribution of the additives (especially where nanomaterials were used) was of great importance, a high shear rate mixer, at high rotation rate and at high temperatures was utilized. Mixing conditions, including mixing time, rotation speed and mixing temperatures are reported in Table 6. In order to maintain the similar condition, the neat binder was stirred too applying temperature 160°C, time 35 min, and speed 4000 rpm as the average values from Table 6 results.

**Table 6. Mixing conditions for preparing the modified binders.**

| Additive | Mixing | | |
|---|---|---|---|
| | Time (min) | Speed (rpm) | Temperature (°C) |
| $CaCO_3$ Filler | 25 | 3600 | 165 |
| Nano-$CaCO_3$ | 35 | 5200 | 160 |
| Hydrated lime Filler | 25 | 3600 | 165 |
| Nano-hydrated lime | 35 | 5200 | 160 |
| Nano-silica | 50 | 2600 | 160 |
| Nano-clay (bentonite) | 45 | 4000 | 160 |

### 3.3. Mixture Design

Optimum asphalt binder content of the mixture was determined based on Marshall Method with 75 blows on each side of the cylindrical samples for high traffic loading condition [19]. It is necessary to mention that mixture design was performed using the neat asphalt binder (i.e. without using any additives). Therefore, optimum binder contents of mixes were taken equal in all mixtures, eliminating the role of binder contents in analysis of the test data.

### 3.4. Laboratory tests

#### 3.4.1. XRD Test

One of the most important non-destructive tests that is performed to identify crystalline phases of materials is X-ray diffraction spectrometer (XRD). X-rays are directed toward samples by applying the voltage and reflected X-rays are gathered by the detector. Results are usually reported in an XY plot; x-axis showing the angle between the radiated and reflected X-ray and y-axis depicting the counts of reflected X-ray. Compositions of the aggregates used in this study, as determined by XRD analysis (Explorer, G.N.R, Italy) are reported in Fig. 5. XRD pattern was measured using a scintillator detector over the 2θ range of 5°-50°. X-ray source was a conventional X-ray tube with a Cu-Kα target operated at 1.541874 Å, 40 kV and 30 mA.

Regarding the XRD pattern in Fig.5, it can be seen that main mineralogical constituents of the aggregate were Silicon Oxide ($SiO_2$) and magnesium calcium carbonate. In addition, most of the peaks and the maximum peak value at 2theta of 27° were for silicon oxide. Therefore, as can be seen in Fig.5, the aggregates consisted of almost 70% $SiO_2$. The main cause of this selection was that siliceous aggregates are more susceptible to moisture damage due to their mineralogy and surface structure. In this case, the effectiveness of using anti-stripping additives will be more pronounced.

### 3.4.2. FE-SEM Test

FE-SEM is one of the useful tools for high resolution surface imaging that characterizes nanomaterials and nanostructures in asphalt mixes. In this study, in order to show the effects of mixing time and to make sure of homogenous distribution of the additives, FE-SEM (FEI-Nova Nano SEM 450) images were taken at different mixing time and processing.

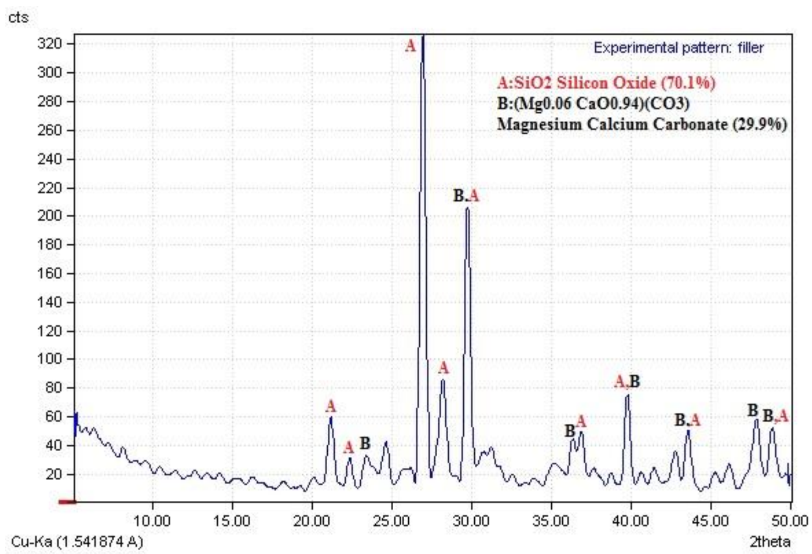



**Fig. 5. Result of XRD test on the aggregates.**

### 3.4.3. Production of Nano-Hydrated Lime

The milling process that was adopted in this research was a top-down approach for producing nano-hydrated lime from hydrated lime filler [20]. This technique has the advantage of using conventional milling units to produce nano-size fillers. In fact, as for definition, planetary rotary ball mills are low-cost laboratory units that can reduce particle sizes into nano-size materials. In these mills, a high centrifugal force is applied, achieving appropriate mixing and homogenization of materials. The planetary rotary ball mill used in this study is shown in Fig. 6. The steel ball mill has two or four ball grinding containers that are mounted eccentrically on a turn plate. Direction of the plate movement is opposite to the grinding containers. When the plate spins, the container axis makes the planetary movement, and the balls and samples inside the containers are impacted strongly in high-speed movement. Samples are then ultimately grounded into powder. Three types of milling methods are available, namely, dry mill, wet mill, and vacuum mill. Two or four grinding tanks can work together. In order to perform the process a small amount of Process Control Agent (PCA) is introduced into the jar of the apparatus together with powders and steel balls. PCAs create notable influence on the particle size, likewise on the structural behavior and thermal stability of the milled powders, when compared with milling synthesized materials without presence of a surfactant [21].

**Fig. 6. Planetary ball mill apparatus.**

In a research work, the effect of applying uniform size balls, compared with different diameters balls, was investigated. The results showed that producing $CaCO_3$ in planetary ball mills will be improved when uniform-size balls are used [22]. In this research, nano-hydrated lime was manufactured, using a vertical laboratory planetary ball mill set (Feritsch, Pulverisette 5 Classic Line-Germany). The main parameters that affected particle size reduction, consisted of rotation speed, milling time, size of balls, medium of milling and Ball to Powder Ratio (BPR). These parameters were optimized, applying trial and error method. Based on previous studies, 2-Propanol material (at 5% by weight of hydrated lime) was used as PCA. In addition, uniform steel balls and a 5:1 ratio as BPR were selected [13,23,24]. Hydrated lime filler was milled for 9 hours at 250 rpm speed. Using Dynamic Light Scattering (DLS, ZSP, Malvern Instruments Ltd., Worcestershire, UK) and SEM (Leo 1450VP, Zeiss, Germany) machines. The average particle size of this nanomaterial was measured at different milling times. The diameter and weight of each of the uniform steel balls were 5 mm and 33 g, respectively.

#### 3.4.4. ITSM Test

One of the major factors in analysis and design of asphalt pavements is stiffness modulus (or resilient modulus) which indicates the ability of asphalt layers to spread traffic loads on the underlying layers. Resilient modulus is defined as the ratio of deviator stress to recoverable strain of a sample under cyclic loading.

The resilient modulus is directly affected by loss of adhesion and cohesion [25]. In order to investigate susceptibility of asphalt mixtures to water damage, resilient modulus is more sensitive than the tensile strength [26]. This non-destructive test was performed according to ASTM D4123 procedure [27]. Using a Universal Testing Machine (UTM-14P), samples were tested at 25℃ by applying a haversine loading waveshape consisting of 0.1-s loading time and 0.9-s rest time and frequency of 1 Hz. Samples were kept at the test temperature for 24 h in the temperature control chamber before testing. The chamber was equipped with a reference specimen containing two thermometers to measure and record the core and skin temperatures. Each sample was tested twice, at a 90-degree rotation, and the mean values of both tests were reported as stiffness modulus. The load was induced along the vertical diametric axis of the cylindrical sample and two Linear Variable Differential Transducers (LVDTs) measured its horizontal deformation. Specimens were preconditioned by initial load cycles; 75 preconditioning pulses were applied to resilient deformations become stable. Then 10 pulses of maximum loading were applied along the diameter. Resilient modulus of samples was calculated by the software connected to the test set up using the following equation:

$$M_r = \frac{P\,(\vartheta + 0.27)}{t \times \Delta H} \qquad (1)$$

Where $M_r$ is resilient modulus (MPa), P is cyclic load (N) that was 2500 N in this study, $\vartheta$ is the Poisson's ratio (assumed 0.35), t is the specimen thickness (mm), and $\Delta H$ is the recoverable horizontal deflection (mm).

### 3.4.5. Index of Retained Resilient Modulus ($IRM_r$) Test

In order to evaluate moisture susceptibility of asphalt mixtures, index of retained resilient modulus ($IRM_r$) was defined as in Eq. (2) below:

$$IRM_r = \frac{\text{Mr of conditioned specimen}}{\text{Mr of dry (control) specimen}} \times 100 \qquad (2)$$

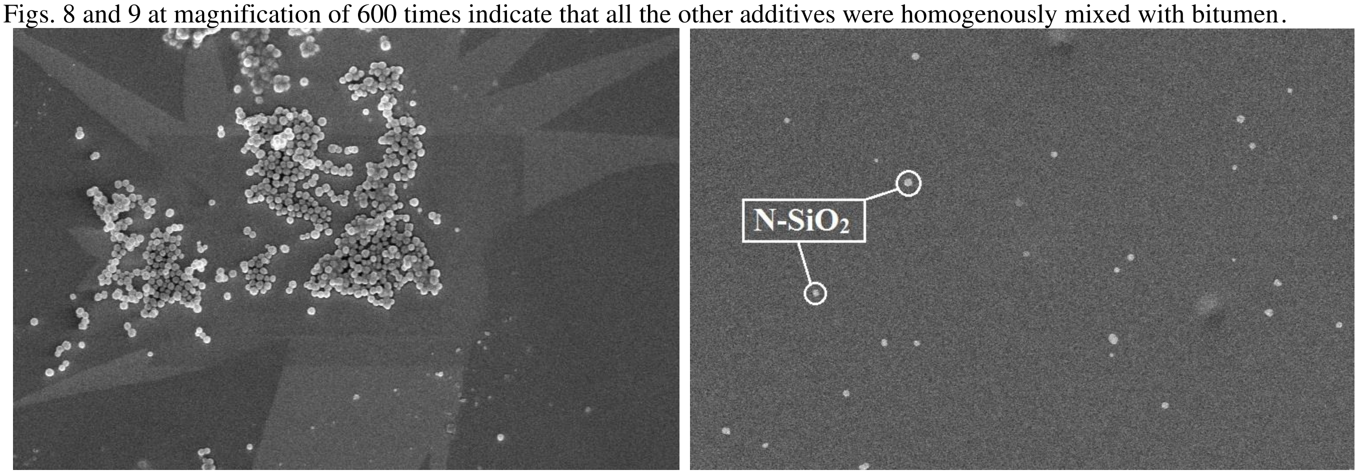
Where $M_r$ is resilient modulus.

$IRM_r$ is an indicative of mix's resistivity to moisture damage. The greater $IRM_r$, the better the mix resistance to damage. $IRM_r$ value of 70% was taken as a minimum acceptable value to ensure good performance against stripping of HMA mixtures [25]. For conditioning test specimens in the determination of the $IRM_r$, Lottman procedure was employed. In this test, asphalt specimens with diameter of 100±2 mm and height of 55±2 mm were utilized.

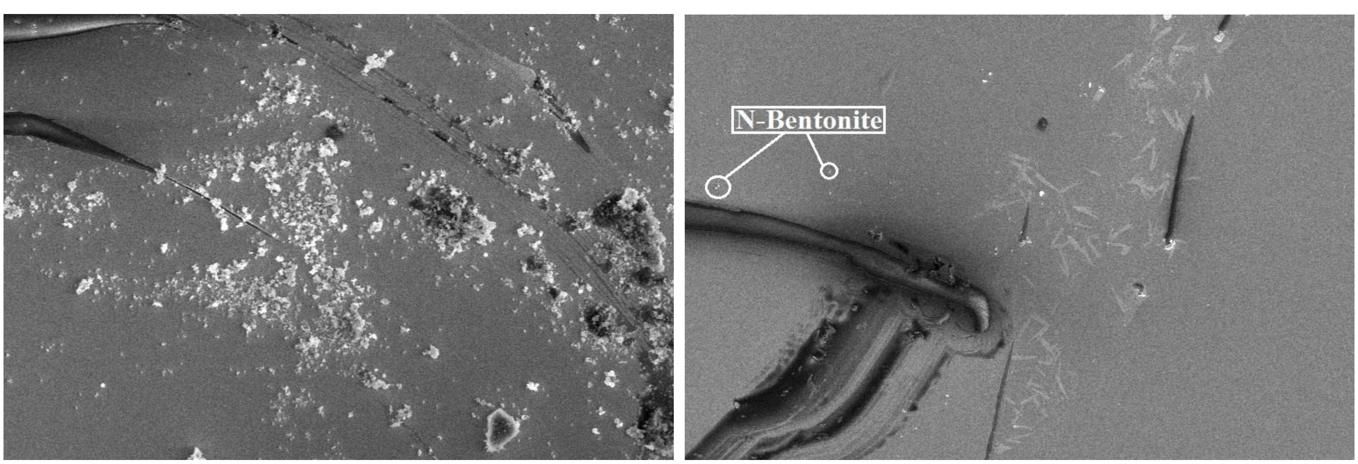
## 4. RESULTS AND DISCUSSION

### 4.1. FE-SEM test results

Fig. 7 shows FE-SEM images of mixes at different mixing times. These at magnification of 4000 times showed that when 2% nano-silica were mixed with the binder, after 10 minutes the accumulated nanomaterials could still be seen quite clearly; while these rarely could be seen after 50 minutes of mixing. The 4% nano-bentonite modified binder when it was mixed for 5 minutes, was not homogenously mixed with the binder. It was well-dispersed after 45 minutes of mixing. With using this technique, it was confirmed that the adopted circumstances were appropriate for mixing these nanomaterials with the bitumen binder. A previous study revealed that by applying a mechanical mixer at 1500 rpm speed and a mixing temperature of 145℃ ± 5℃, the optimum mixing time will be around 45 minutes for nano-silica and 60 minutes for nano-clay [28]. FE-SEM images of Figs. 8 and 9 at magnification of 600 times indicate that all the other additives were homogenously mixed with bitumen.

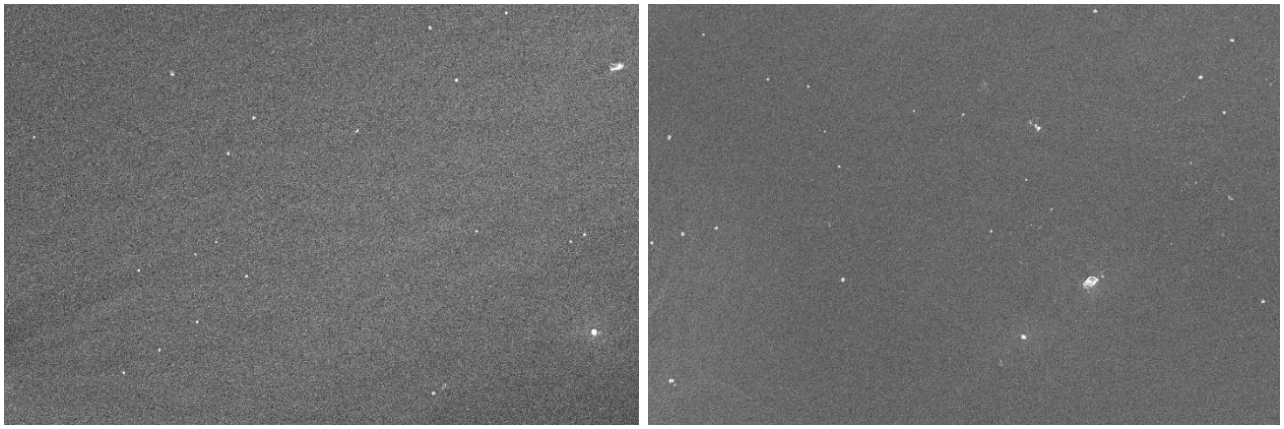



(a) Nano-$SiO_2$ modified asphalt-10 min mixing (b) Nano-$SiO_2$ modified asphalt-50 min mixing



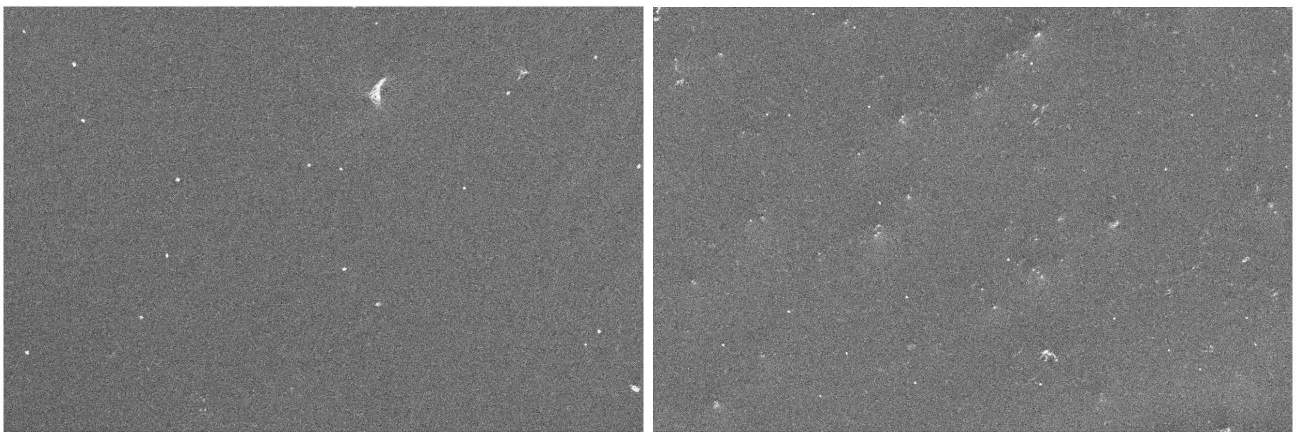

(c) Nano-clay modified asphalt-5 min mixing (d) Nano-clay modified asphalt-45 min mixing

**Fig. 7. FE-SEM images of nano-modified binders mixed at different mixing times.**



a) 2% nano-hydrated lime modified asphalt b) 2% nano-$CaCO_3$ modified asphalt

**Fig.8. FE-SEM images of nano-modified binders at magnification of 600 times.**



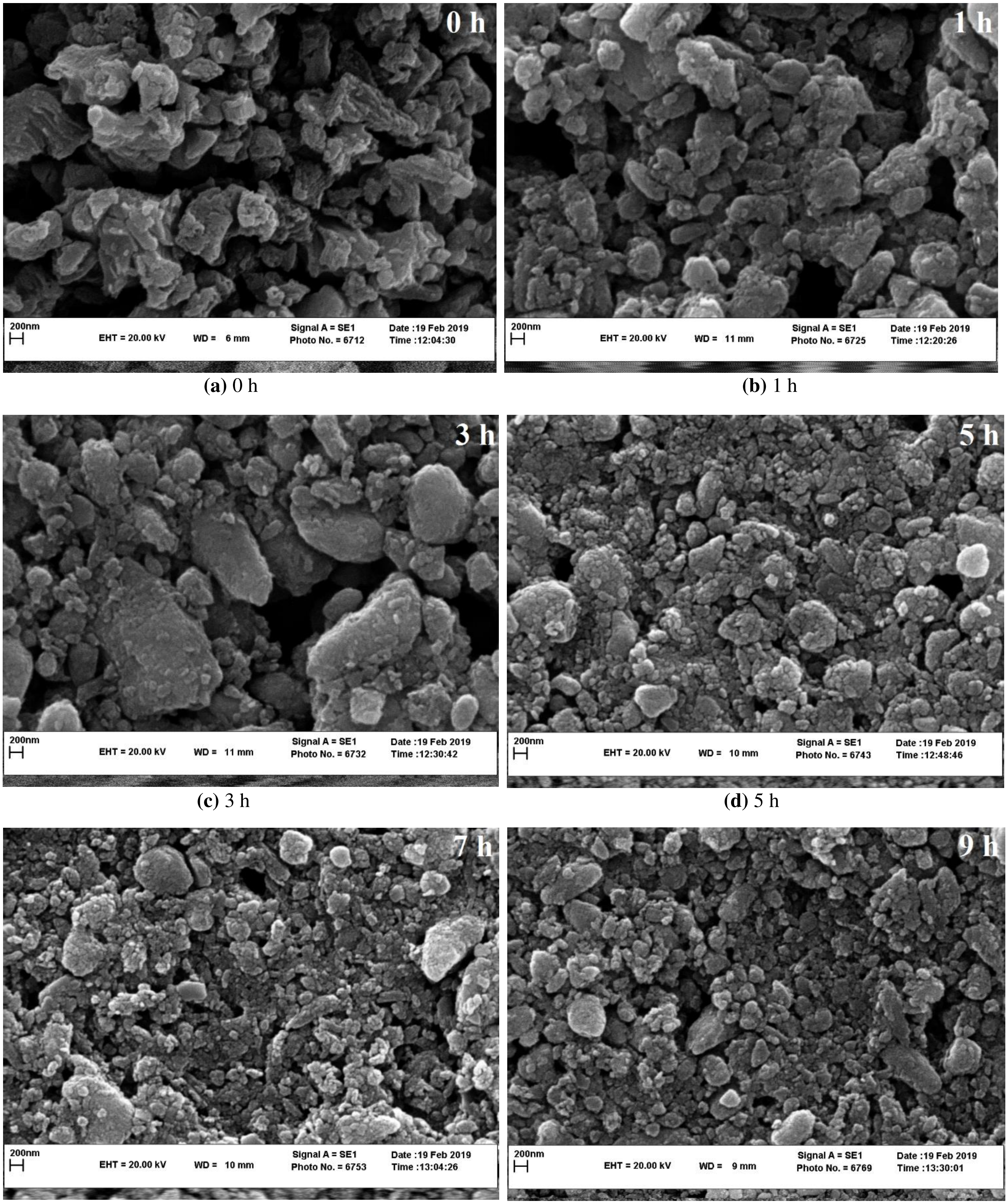
a) 10% hydrated-lime filler modified asphalt b) 10% $CaCO_3$ filler-modified asphalt

**Fig.9. FE-SEM images of fillers modified binders at magnification of 600 times.**

### 4.2. Production of nano-hydrated lime results

Several methods are available to characterize Average Particle Size (APS) of nanomaterials. Each technique has its own advantages and limitations. Therefore, a combination of at least two methods, one of which should be a microscopic method, is highly recommended [29].

During ball mill processing of nano-hydrated lime, the APS of this material was determined at various milling times applying SEM and DLS tests. The results are reported in Table 7. Since hydrodynamic diameters of the particles are measured in DLS test, in this research, SEM test was performed to measure APS values beside DLS test. Results of DLS and SEM tests indicated that APS values of all samples in DLS technique were bigger than their SEM measurements. The finest particle size was observed in sample that was milled for 5 hours in both techniques. According to SEM images (analyzed by Image-J software) and DLS test, the minimum achieved particle sizes were 125 and 208 nm, respectively. As it can be seen from Fig. 10, morphology and size of the powders were severely changed after 5 h ball-milling. With this processing, the produced nanomaterial showed semi-spherical shape and considerably smaller sizes than those that were produced after ball milling for 1 and 3 hours. Particle sizes did not exhibit a significant change for 9 hours of milling, compared with 7 hours. The reason might be that during ball mill processing, the fine materials experienced cold welding (i.e. particle adhesion and sticking). Morphology and microstructure of the milled powders changed with changing the milling time. Considering SEM images of the samples before and after ball mill processing, it was resulted that the flat and smooth plates of hydrated lime particles were changed into semi-spherical shape with high specific area.




**(a)** 0 h **(b)** 1 h

**(c)** 3 h **(d)** 5 h

**(e)** 7 h **(f)** 9 h

**Fig. 10. SEM images of hydrated lime after different ball milling times.**

**Table 7. APS of hydrated lime in ball mill processing as determined with SEM and DLS methods.**

| Ball milling time (h) | APS* – SEM (nm) | APS – DLS (nm) |
|---|---|---|
| 0 | 1942 | 4059 |
| 1 | 770 | 1639 |
| 3 | 521 | 967 |
| 5 | 125 | 208 |
| 7 | 204 | 309 |
| 9 | 216 | 324 |

* APS: Average Particle Size.

### 4.3. Resilient modulus test results

Findings of the resilient modulus test for dry and conditioned HMA mixes at 25℃ are shown in Fig. 11. As can be seen, the stiffness modulus of modified samples is greater than the control mix. Each additive contributes to stiffen the binder which results in increased resilient modulus. In dry samples, the addition of nano-additives up to 4% and anti-stripping fillers up to 10%, the stiffness modulus increased. In contrast with adding 20% hydrated lime or calcium carbonate fillers the resilient modulus decreased. The reason might be that the high amounts of these fillers caused agglomeration, leading to a negative effect on performance of the modified binder [5,30]. The reason for the increased $M_r$ value in the dry samples containing high amounts of nanomaterials could be attributed to very high surface area of nanoparticles. As a result of this, more interaction might exist between bitumen and nanoparticles. In fact, excessive absorption of the oils in asphalt cement, leads to greater stiffness values [31].

Other researchers observed a similar trend of increased $M_r$ in dry condition for hydrated lime filler modified mixes [9]. The reason for increased stiffness of hydrated lime filler might be that hydrated lime has greater porosity than other mineral fillers. This property differentiates hydrated lime from other fillers. Mineral fillers generally have 30-34% air voids in dry compacted state (Rigden voids); while hydrated lime filler has this between 60 and 70% [32]. As reported in Table 2, hydrated lime filler had Rigden voids of 62% which is greater than all the other fillers.

As can be seen in Fig.11, $M_r$ in a dry state increased as a result of increased nano-$SiO_2$ content. This is similar to the results of previous researches [14,31,33]. Among mixes, 4% nano-$SiO_2$ resulted in mixes to have the most resilient modulus in dry conditions; while in wet conditions weak performance was observed. The reason for this fact is related to chemical properties of this material.

Generally, for all mixes resilient modulus values were decreased after F-T conditioning. However, this parameter was profoundly enhanced when anti-stripping additives were used.

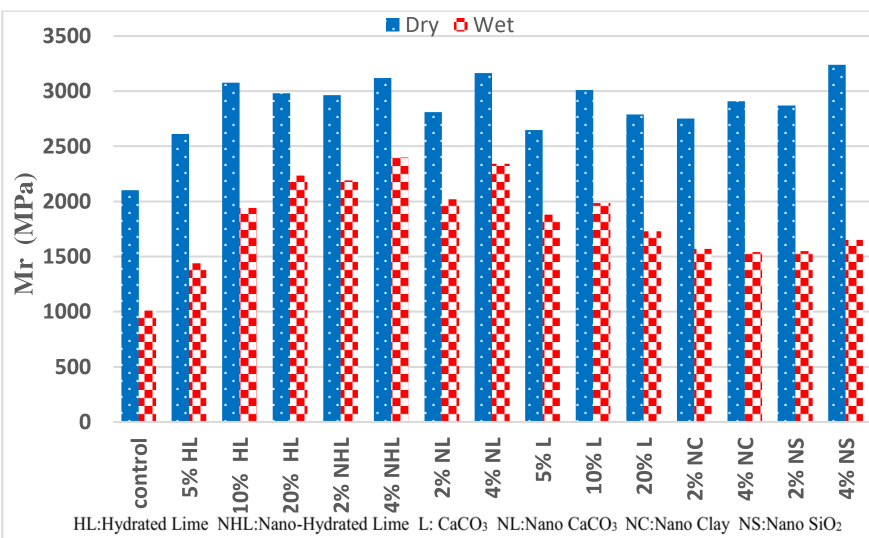



**Fig.11. Resilient modulus of mixes containing various additives at dry and wet conditions.**

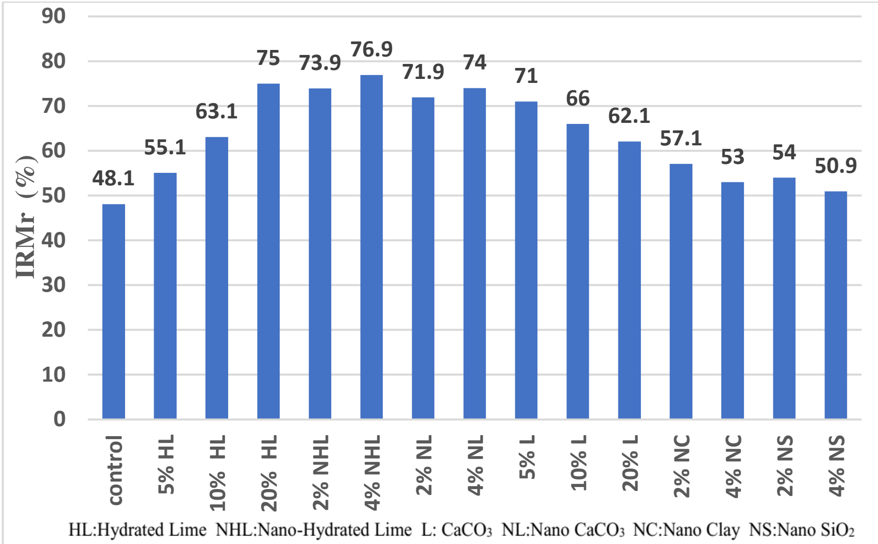



**Fig.12. IRM$_r$ results of mixes.**

To investigate potential of mixtures to stripping, IRM$_r$ was used, similar to what was performed in another research [10]. Resilient modulus ratio (IRM$_r$) results of samples are presented in Fig. 12. Generally, IRM$_r$ values of the modified mixtures are greater than the unmodified mixtures. Among the specimens, those containing 20% hydrated lime filler, 5% calcium carbonate filler, 2 and 4% of nano-hydrated lime and nano-calcium carbonate met the required minimum 70% IRM$_r$.

Among various additives, nano-calcium carbonate and nano-hydrated lime had higher IRM$_r$ values and showed better performance in resistance to moisture damage than nano-bentonite and nano-$SiO_2$ materials. This can be attributed to their chemical properties. Nano-calcium carbonate and nano-hydrated lime consisted of calcium oxide while nano-bentonite and nano-$SiO_2$ were of silica type.

As can be seen in the results of resilient modulus of mixes, nano-hydrated lime and nano-calcium carbonate had greater M$_r$, compared with hydrated lime and calcium carbonate fillers at lower amounts. The reason can be attributed to physical properties and nanostructure of these materials. Specific Surface Area (SSA) property is related to the particle size of the filler. Hence, greater SSA values will be resulted in nanoscale particles. Therefore, it is expected that these materials absorb more the oily components of the bitumen binder, making it stiffer.

Table 8 reports the effects of anti-stripping additives on asphalt mixes. It reports the percentage of changes in M$_r$ and IRM$_r$ values of the modified specimens, compared with the control specimen. As can be seen, by adding 20% hydrated lime filler and 4% nano-hydrated lime to bitumen resulted in improving the IRM$_r$ values of 56% and 60%, respectively. IRM$_r$ values of asphalt mixes increased to 48% and 54% when 5% calcium carbonate filler and 4% nano-calcium carbonate were added, respectively. The mix with 4% nano-hydrated lime had the highest IRM$_r$ value and showed the most resistance to moisture damage.

**Table 8. Percentage of increase in M$_r$ and IRM$_r$ values of the modified mixtures.**

| | Mixture | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Control | 5% HL | 10%HL | 20% HL | 2%NHL | 4%NHL | 2%NL | 4%NL | 5%L | 10%L | 20%L | 2%NC | 4%NC | 2%NS | 4%NS |
| M$_{r\ Dry}$ | 0 | 24.4 | 46.5 | 41.9 | 41.1 | 48.6 | 33.8 | 50.6 | 26.1 | 43.2 | 32.8 | 31 | 38.5 | 36.7 | 54.3 |
| M$_{rWet}$ | 0 | 42.5 | 92.1 | 121.3 | 116.8 | 137.6 | 100.1 | 131.9 | 86.1 | 96.5 | 71.3 | 55.4 | 52.5 | 53.5 | 63.4 |
| IRM$_r$ | 0 | 14.5 | 31.1 | 55.9 | 53.6 | 59.9 | 49.5 | 54 | 47.6 | 37.2 | 29 | 18.7 | 10.1 | 12.3 | 5.9 |

HL:Hydrated Lime NHL:Nano-Hydrated Lime L: $CaCO_3$ NL:Nano $CaCO_3$ NC:Nano Clay NS:Nano $SiO_2$

## 5. CONCLUSIONS

The following conclusions were drawn based upon the experimental findings obtained from this research study:

- Milling process as a top-down approach for producing nanomaterials was recognized as a cost-effective method. At the optimum condition, by performing SEM and DLS tests minimum particle sizes of nano-hydrated lime were determined 125 and 208 nm, respectively.
- The optimum conditions of the main parameters that affected the particle size reduction in reducing nano-hydrated lime were 5 hours of milling, using uniform steel balls, applying 250 rpm rotation and a 5:1 ratio as the BPR.
- The effects of mixing time on homogenous dispersion of nano-silica and nano-bentonite in binder were evaluated by FE-SEM test.
- $IRM_r$ of mixes improved appreciably when anti-stripping additives were used. Mixes containing 20% hydrated lime filler, 5% calcium carbonate filler, 2 and 4% nano-hydrated lime and nano-calcium carbonate met the required minimum 70% $IRM_r$.
- It is recommended to use nanomaterials at lower percentages rather than using high amounts of conventional anti-stripping fillers in reducing moisture susceptibility of asphalt mixes.
- Nano-hydrated lime showed the best resistance of asphalt mixes against moisture damage in comparison with other additives.

## REFERENCES


[1] A. Diab, J.C. Pais, Moisture Susceptibility of Asphalt Mixes: A Literature Review, 2017. https://www.researchgate.net/publication/321904870.

[2] F. Mansour, V. Vahid, Effect of Liquid Nano Material and Hydrated Lime in Improving the Moisture Behaviour of HMA, in: Transp. Res. Procedia, 2016: pp. 506–512. doi:10.1016/j.trpro.2016.11.101.

[3] M. Ameri, M. Vamegh, S.F. Chavoshian Naeni, M. Molayem, Moisture susceptibility evaluation of asphalt mixtures containing Evonik, Zycotherm and hydrated lime, Constr. Build. Mater. 165 (2018) 958–965. doi:10.1016/j.conbuildmat.2017.12.113.

[4] H. Fallahi Abandansari, A. Modarres, Investigating effects of using nanomaterial on moisture susceptibility of hot-mix asphalt using mechanical and thermodynamic methods, Constr. Build. Mater. 131 (2017) 667–675. doi:10.1016/j.conbuildmat.2016.11.052.

[5] R. Li, F. Xiao, S. Amirkhanian, Z. You, J. Huang, Developments of nano materials and technologies on asphalt materials – A review, Constr. Build. Mater. 143 (2017) 633–648. doi:10.1016/j.conbuildmat.2017.03.158.

[6] F. Trotta, A. Mele, Nanosponges : Synthesis and Applications, Publisher John Wiley & Sons, 2019, ISBN 3527340998,9783527340996, https://books.google.com/books?id=gnWFDwAAQBAJ&printsec=frontcover&dq=nanomaterials+definitions+Nanosponges&hl=en&sa=X&ved=0ahUKEwiI1_fGtLzhAhVp_SoKHa2QDzEQ6AEIJzAA#v=onepage&q=nanomaterials definitions Nanosponges&f=false (accessed April 7, 2019).

[7] P. History, P. Rawat, A. Kumar, A review on nanotechnology in civil engineering, 39 (2015) 152–158.

[8] W. Guo, X. Guo, M. Sun, W. Dai, Evaluation of the Durability and the Property of an Asphalt Concrete with Nano Hydrophobic Silane Silica in Spring-Thawing Season, Appl. Sci. 8 (2018) 1475. doi:10.3390/app8091475.

[9] H. Taherkhani, M. Tajdini, Comparing the effects of nano-silica and hydrated lime on the properties of asphalt concrete, Constr. Build. Mater. 218 (2019) 308–315. doi:10.1016/j.conbuildmat.2019.05.116.

[10] M. Ameri, S. Kouchaki, H. Roshani, Laboratory evaluation of the effect of nano-organosilane anti-stripping additive on the moisture susceptibility of HMA mixtures under freeze-thaw cycles, Constr. Build. Mater. 48 (2013) 1009–1016. doi:10.1016/j.conbuildmat.2013.07.030.

[11] M.S.M. Norhasri, M.S. Hamidah, A.M. Fadzil, Applications of using nano material in concrete: A review, Constr. Build. Mater. 133 (2017) 91–97. doi:10.1016/j.conbuildmat.2016.12.005.

[12] Z. Hassan, D. Hassan, B. Rezvan, A. Ali, Influence of Bentonite Additive on Bitumen and Asphalt Mixture Properties, 6 (2012) 1534–1539.

[13] A. Kavussi, P. Barghabani, The Influence of Nano Materials on Moisture Resistance of Asphalt Mixes, Study Civ. Eng. Archit. 3 (2014) 36–40.

[14] N.I.M. Yusoff, A.A.S. Breem, H.N.M. Alattug, A. Hamim, J. Ahmad, The effects of moisture susceptibility and ageing conditions on nano-silica/polymer-modified asphalt mixtures, Constr. Build. Mater. 72 (2014) 139–147. doi:10.1016/j.conbuildmat.2014.09.014.

[15] M. Hasaninia, F. Haddadi, The characteristics of hot mixed asphalt modified by nanosilica, Pet. Sci. Technol. 35 (2017) 351–359. doi:10.1080/10916466.2016.1258412.

[16] G.H. Hamedi, F. Moghadas Nejad, K. Oveisi, Investigating the effects of using nanomaterials on moisture damage of HMA, Road Mater. Pavement Des. 16 (2015) 536–552. doi:10.1080/14680629.2015.1020850.

[17] ASTM D3515-01, Standard Specification for Hot-Mixed, Hot-Laid Bituminous Paving Mixtures (Withdrawn 2009), ASTM International, West Conshohocken, PA, 2001, www.astm.org. doi:10.1520/D3515-01.

[18] J.M.L. Crucho, J.M.C. das Neves, S.D. Capitão, L.G. de Picado-Santos, Mechanical performance of asphalt concrete modified with nanoparticles: Nanosilica, zero-valent iron and nanoclay, Constr. Build. Mater. 181 (2018) 309–318. doi:10.1016/j.conbuildmat.2018.06.052.

[19] ASTM D1559-89, Test Method for Resistance of Plastic Flow of Bituminous Mixtures Using Marshall Apparatus (Withdrawn 1998), 1989. doi:10.1520/D1559-89.

[20] T. Prasad Yadav, R. Manohar Yadav, D. Pratap Singh, Mechanical Milling: a Top Down Approach for the Synthesis of Nanomaterials and Nanocomposites, Nanosci. Nanotechnol. 2 (2012) 22–48. doi:10.5923/j.nn.20120203.01.

[21] M. Pilar, J.J. Suñol, J. Bonastre, L. Escoda, Influence of process control agents in the development of a metastable Fe-Zr based alloy, J. Non. Cryst. Solids. 353 (2007) 848–850. doi:10.1016/j.jnoncrysol.2006.12.054.

[22] A.A.O.A.A.O. Gezerman, B. Dideem, B.C.-I.J.M. Chem, U. 2012, B. Dideem, Use of Uniform-Sized Balls to Improve the Manufacturing of, Researchgate.Net. 1 (2012) 116–124. https://www.researchgate.net/profile/Ahmet_Ozan_Gezerman/publication/235782102_Use_of_Uniform-Sized_Balls_to_Improve_the_Manufacturing_of_CaCO3_in_Ball_Millspdf/links/0c96052d176830ff8d000000/Use-of-Uniform-Sized-Balls-to-Improve-the-Manufacturing-of-CaCO (accessed July 11, 2019).

[23] A. Kavussi, P. Barghabany, Investigating Fatigue Behavior of Nanoclay and Nano Hydrated Lime Modified Bitumen Using LAS Test, J. Mater. Civ. Eng. 28 (2015) 04015136. doi:10.1061/(asce)mt.1943-5533.0001376.

[24] H. Attar, K.G. Prashanth, L.C. Zhang, M. Calin, I. V. Okulov, S. Scudino, C. Yang, J. Eckert, Effect of powder particle shape on the properties of in situ Ti-TiB composite materials produced by selective laser melting, J. Mater. Sci. Technol. 31 (2015) 1001–1005. doi:10.1016/j.jmst.2015.08.007.

[25] J.J. Heinicke, T.S. Vinson, Effect of Test Condition Parameters on IRMr, J. Transp. Eng. 114 (2008) 153–172. doi:10.1061/(asce)0733-947x(1988)114:2(153).

[26] Epps JA, Sebaaly PE, Penaranda J, Mather MR, Mccann MB, Hand Aj. Compatibility of a Test for Moisture-Induced Damage with Superpave Volumetric Mix Design. NCHRP report no.508, Transportation Research Board, National Research Council; 2000.

[27] ASTM D4123-82(1995), Standard Test Method for Indirect Tension Test for Resilient Modulus of Bituminous Mixtures (Withdrawn 2003), ASTM International, West Conshohocken, PA, 1995. www.astm.org. DOI: 10.1520/D4123-82R95.

[28] H. Ezzat, S. El-Badawy, A. Gabr, E. Zaki, T.Breakah, Evaluation of asphalt binders modified with nanoclay and nanosilica, Elsevier. Procedia engineering, Volume 143,2016, 1260–1267, https://doi.org/10.1016/j.proeng.2016.06.119.

[29] M. Gaumet, A. Vargas, R. Gurny, F. Delie, Review article-Nanoparticles for drug delivery: The need for precision in reporting particle size parameters, European Journal of Pharmaceutics and Biopharmaceutics 69 (2008) 1–9. https://doi.org/10.1016/j.ejpb.2007.08.001.

[30] M. Faramarzi, M. Arabani, A.K. Haghi, V. Mottaghitalab, Carbon nanotubes-modified asphalt binder: Preparation and characterization, Int. J. Pavement Res. Technol. 8 (2015) 29–37. doi:10.6135/ijprt.org.tw/2015.8(1).29.

[31] H. Taherkhani, S. Afroozi, S. Javanmard, Comparative Study of the Effects of Nanosilica and Zyco-Soil Nanomaterials on the Properties of Asphalt Concrete, J. Mater. Civ. Eng. 29 (2017) 04017054. doi:10.1061/(asce)mt.1943-5533.0001889.

[32] D. Lesueur, J. Petit, H.J. Ritter, The mechanisms of hydrated lime modification of asphalt mixtures: A state-of-the-art review, Road Mater. Pavement Des. 14 (2013) 1–16. doi:10.1080/14680629.2012.743669.

[33] M. Hasaninia, F. Haddadi, Studying Engineering Characteristics of Asphalt Binder and Mixture Modified by Nanosilica and Estimating Their Correlations, Adv. Mater. Sci. Eng. 2018 (2018). doi:10.1155/2018/4560101.