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# Assessment of Asphalt Binders and Hot Mix Asphalt Modified with Nanomaterials

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**Abstract**

In the recent times, asphalt binder modification has emerged an inevitable alternative in the paving industry to ensure better performing pavements against the distresses caused by common factors such as; moisture susceptibility and high-temperature sensitivity of asphalt binders. Nanomaterials, as asphalt-modifiers, have proved to be the most promising materials in the industry owing to their higher active surface area and small particle size. This study was devoted to assessing the modification influence of three different types of nanomaterials, including nano-Bentonite, nano-$CaCO_3$, and ZycoTherm, on the properties of asphalt binder and HMA. Conventional and rheological tests on asphalt binders, as well as, Marshall mix design and modified Lottman test on laboratory-prepared HMA specimens were conducted in order to signify the influence of nanomodification. The research findings suggested that nanomaterials can potentially enhance the high-temperature susceptibility resistance, storage stability, and rheological properties of asphalt binder samples. Mix design results revealed that the optimum binder contents decreased and Marshall stabilities were slightly improved with nanomodification. Moreover, the modified Lottman test results indicated that 0.1 % of ZycoTherm increased the TSR by 22 % as compared to the control mixture that infers its efficiency in terms of improving the HMA resistance against the moisture-induced damages.

**Keywords**

nanomaterials, nano-Bentonite, nano-$CaCO_3$, Zycotherm, modified Lottman test

## 1 Introduction

The ever-increasing traffic with heavy axle loads and variation in the climatic conditions are known to be the main damaging factors for asphalt pavements accelerating the deterioration process that might end up in the premature failure of pavement structures [1, 2]. Asphalt binder, functioning as the main component of asphalt mixtures, is highly susceptible to the coupled effect of temperature and the applied loading stresses. These factors would eventually arise various forms of defects such as plastic deformation (rutting), fatigue cracking, low temperature cracking, and moisture induced distresses (i.e. stripping) [3]. With the appearance of these defects, pavement structures would no longer tend to perform desirably thus decreasing the serviceability of the structure [4].

Pavements constructed with conventional, unmodified asphalt binders may not sustain the adverse traffic and environmental conditions [5]. This has inspired the researchers and road agencies to look for a reliable and at the same time economical alternative that can potentially reinforce the mechanical and rheological features of neat asphalt binder. The modification of asphalt binder with various additive types has emerged as an ideal choice. Modification generally improves the binder performance from various aspects including adhesion, temperature sensitivity, friction properties, oxidation resistance, durability, and others. So far, numerous types of asphalt binder modifiers are utilized in the paving industry, namely resins, polymers, rubbers, sulfur, metal complexes, fiber, various chemical agents for enhancing the asphalt binder quality [6].

In the last decade or so, the incorporation of nanomaterials into asphalt binder has attracted the interest of a vast number of researchers and engineers [6, 7]. A nanoparticle is defined as a miniaturized particle with at least one dimension less than 100 nm [8]. Materials at nano-level exhibit significantly different behavior both physically and chemically stemmed from their inherent features like

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the high active surface area to volume ratio and also the exhibition of quantum effects arising from their small particle dimensions; i.e. spatial confinement [9, 10]. Besides, the introduction of nanomaterials leads to the reduction in the acid component of surface free energy (SFE) combined with increasing the basic SFE component of the binder that would eventually lead to better performance against the moisture damage by enhancing the adhesion between binder and sensitive aggregates [11].

Nanomaterials, with these novel features, modify the asphalt binder properties at a nano-scale that will enable them to become substantially influential and contribute extensively to the enhancement of pavement performances thus providing sustainable pavements with longer serviceability. In August 2006, the National Science Foundation (NSF) workshop entitled "Nanomodification of Cementitious Materials" was held in the USA, mainly focused on the application of nanotechnology for improvement of asphalt concrete. One of the main conclusions of this workshop was that nanoscience and nanotechnology could potentially lead to improvements in asphalt pavement technology. In this workshop, the field of "Asphalt nanomaterial science" was established [12, 13].

Nanomaterials are generally added at comparatively lower concentrations for asphalt modification considering their huge active surface area to interact with asphalt binder and their costliness. The selection of a certain nanomaterial type is totally dependent on the specific requirements and objective for which the modification is performed.

Such nanomaterials that are applicable in asphalt paving industry include nano-clay, nano-silica, nano-titanium, nano-hydrated lime, nanosized plastic powders, or polymerized powders, nanofibers, nanotubes and many others [13–15]. Nano-size bypass was used in a study to modify asphalt, as a result, the compressive strength, penetration, and softening point got increased, however, the tensile strength got reduced [16].

In a research, Jahromi et al. [17] discovered that a small amount of nano-clay can improve stiffness, tensile strength, tensile modulus, flexural strength and modulus thermal stability of asphalt binders. Furthermore, the addition of nano-clay can decrease the moisture damage of asphalt mixture [13, 18]. A research conducted over nano-$CaCO_3$ concluded that the dynamic and residual stability of asphalt mixture increased at 6 % nano-$CaCO_3$, which infers that both the high-temperature performance and water stability of asphalt mixture gets improved [19].

The utilization of liquid antistripping agents, such as ZycoTherm, has recently emerged as the favorite option in the asphalt industry to tackle the stripping issue of asphalt mixtures resulting from the presence of moisture. ZycoTherm is claimed to be capable of forming a hydrophobic layer over the surface of aggregate thus becoming water-repellent and thereby enhancing the moisture resistance of mixtures. Zycotherm was used in a study to modify the properties of crumb rubber modified bitumen (CRMB-60), in which the optimum dosage of ZycoTherm was suggested to be 0.15 % as a result of conducting the boiling test [20].

Within the context of this laboratory study, it was initially aimed to assess the influence of the three aforementioned nanomaterials on the physical and rheological properties of asphalt binder and subsequently examine the mechanical behavior and moisture resistance performance of asphalt mixtures involving these nanomaterials.

## 2 Experimental procedure

All the experiments performed over asphalt binders and hot mix asphalt during this research work are depicted in a flow chart as illustrated in Fig. 1.

### 2.1 Materials

The binder used in this study was 50/70 penetration grade neat asphalt binder supplied by Aliaga/ Izmir Oil Terminal of the Turkish Petroleum Refinery Corporation (TUPRAS Corp.). The summary for the properties of 50/70 asphalt binder is presented in Table 1.

Hot mix asphalt produced in the laboratory, involved limestone crushed aggregate, procured from Dere Group Inc./ Belkahve Izmir quarry. Turkish Technical Specification for Highways (KTS) was followed for implementing a dense-graded, Type-1 limestone aggregate for wearing course of flexible pavements. The physical and chemical properties as well as the granular distribution chart of limestone aggregate are respectively given in Table 2, Table 3, and Fig. 2.

Asphalt binder tends to adhere to alkaline (basic) aggregate better since the opposite ionic charges attract, e.g., limestone. Whereas, siliceous aggregates, for being acidic in nature, make binder less adhering to its surface [21]. Hence, from the adhesion aspect, limestone is widely preferred and is generally expected to perform relatively better in terms of resistance to moisture [22].

Three different types of nanomaterials, as shown in Fig. 3, were used in this study to modify the properties of binder.

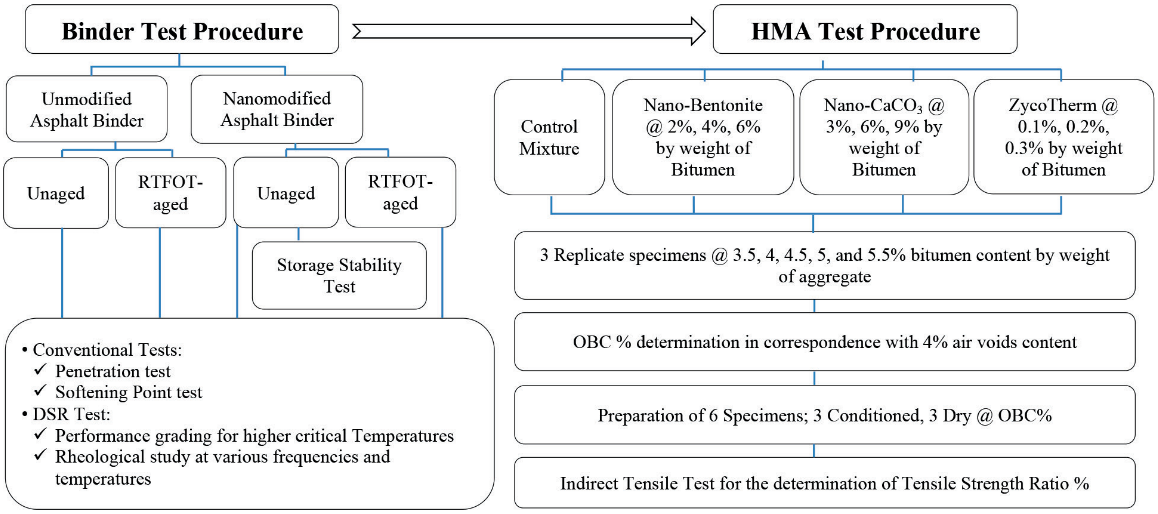


**Fig. 1** Flow chart to illustrate the experimental design procedure for asphalt binders and asphalt mixtures

**Table 1** 50/70 Bitumen binder properties

| Test | Result | Spec. Limits | Standard |
|---|---|---|---|
| Penetration Test (0.1 mm) | 64 | 50–70 | ASTM D5-06/ EN 1426 |
| Softening Point Test (°C) | 51.5 | 46–54 | `ASTM D36-06/ EN 1427 |
| Viscosity (mPa.s) @ 135°C | 0.425 | 3000 mPa.s (max.) | ASTM D4402-06 |
| Viscosity (mPa.s) @ 165°C | 0.138 | - | ASTM D4402-06 |
| Performance after RTFO-Aging | | | ASTM D2872-12 |
| Change of Mass after RTFOT (%) | 0.08 | 0.5 (max.) | |
| Retained Penetration (% of orig.) | 60.9 | 50 (min.) | ASTM D5 EN 1426 |
| Increase in Softening Point | 5.7 | 9 (max.) | TS EN 12607-1 |
| Flash Point | +260 | 230 (min.) | ASTM D92 EN 22592 |
| Specific Gravity | 1.03 | - | ASTM D70 |

**Table 2** Limestone physical properties

| Test | Results | Spec. Limits | Test Method |
|---|---|---|---|
| Specific Gravity (Coarse Agg.) | | | ASTM C127-07 |
| • Bulk | 2.694 | - | |
| • Saturated surface dry (SSD) | 2.701 | - | |
| • Apparent | 2.734 | - | |
| Specific Gravity (Fine Agg.) | | | ASTM C128-07 |
| • Bulk | 2.695 | - | |
| • SSD | 2.703 | - | |
| • Apparent | 2.737 | - | |
| Specific Gravity (Filler) | 2.725 | - | |
| Los Angeles Abrasion (%) | 24.4 | 45 (max.) | ASTM C1252-06 |
| Flat and Elongated particles (%) | 7.5 | 10 (max.) | ASTM D4791-10 |
| Sodium Sulfate Soundness (%) | 1.47 | 10-20 (max.) | ASTM C88-05 |
| Fine Aggregate Angularity (FAA) | 47.85 | 40 (min.) | ASTM C1252-06 |

Nano-Bentonite (a montmorillonite-rich clay) and nano-$CaCO_3$ are basically inorganic mineral fillers, procured from ESAN Eczacibasi Corp. and Guangdong Qiangda New Materials Technology Co., Ltd (China), respectively. ZycoTherm is produced by Zydex Industries (India) which is basically an odorless liquid additive with pale yellow appearance, based on an organo-silane nanotechnology reactive chemistry that is hydrophobic in nature.

Asphalt binder related tests (except the viscosity test) were performed on the short-term aged binder in order to get the idea of their performance against aging. Penetration index (PI) was another index considered in this study for estimating the temperature sensitivity of asphalt binder. The Storage stability test was performed on nano-modified asphalt binder samples in accordance with European Standard (EN 13399) to observe the influence of nanomaterials on storage stability of asphalt binder at high temperatures.

**Table 3** Chemical analysis results for Limestone aggregate procured from Belkahve Izmir quarry

| Oxides | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | MgO | CaO | $Na_2O$ | $K_2O$ | $TiO_2$ | MnO | L.o.I | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|
| (%) | 34.37 | 9.11 | 3.68 | 1.74 | 22.82 | 0.66 | 2.48 | 0.46 | 0.057 | 22.19 | 97.57 |

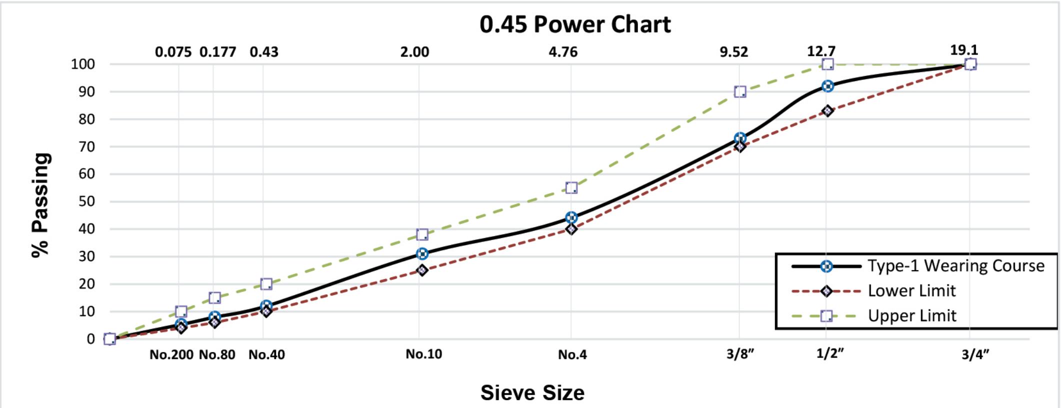


**Fig. 2** Limestone 0.45 power gradation chart for the type-1 wearing course

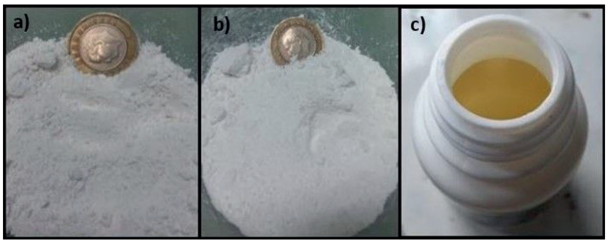


**Fig. 3** Physical appearance of nanomaterials used in this research work, a) Nano-Bentonite, b) Nano-$CaCO_3$ c) ZycoTherm® liquid antistripping nanotechnology

## 2.2 Experimental

### 2.2.1 Production of nanomodified asphalt binders

During the production of modified binders, the selected modifiers were directly incorporated into asphalt binder. The samples were physically mixed with the means of a high-speed shearing laboratory mixer. The modification manner, additive proportions, sample conditioning, production temperature and mixer shearing speed for all the three modifiers were different and were selected by referring to the existing literature on these additives. These are briefly summarized in Table 4. It is obvious that considering these different production conditions, the difference in their performance is also inevitably expected.

### 2.2.2 Conventional asphalt binder tests

Penetration and softening point tests were performed over both neat and nanomodified asphalt binder samples. Brookfield Rotational Viscometer (RV) was used to determine viscosity values to select mixing and compaction temperature ranges for asphalt mixture preparation in conformance with (ASTM D4402). RTFOT was conducted in conformance with (ASTM D2872) to simulate the short-term aging of neat and Nano modified binder sample.

### 2.2.3 Rheological characterization of asphalt binders

Asphalt binders exhibit strongly temperature-dependent viscoelastic behavior influenced by various factors, especially temperature and the loading time (traffic speed) [23].

**Table 4** Production conditions of nanomodified bitumen binders

| Additive | Content (%) | Production Temp. (°C) | Mixer Speed (rpm) | Production Procedure |
|---|---|---|---|---|
| Nano-Bentonite | 2<br>4<br>6 | 170 | 1000–2000 | After completely adding the additive, 1 hour of shearing @2000 rpm constant speed is applied. |
| Nano-$CaCO_3$ | 3<br>6<br>9 | 160 | 2500–3000 | 30 min. shearing + sample kept inside a 100°C oven for 24 hrs. (for maturity purpose) + additional 20 min. shearing prior to the usage of modified sample. |
| ZycoTherm® | 0.1<br>0.2<br>0.3 | 150 | 900–1100 | 10 minutes of continuous shearing after the addition of ZycoTherm. |

Dynamic Shear Rheometer (DSR) was employed to characterize the rheological behavior of asphalt binders, which determines two main parameters; complex shear modulus ($G^*$) and phase angle ($\delta$) $\cdot G^*$ is considered as the sample's total resistance to deformation when repeatedly sheared by the application of shear stress. This parameter is essentially intended for assessing two behaviors of the binder; elastic behavior (recoverable) and viscous (non-recoverable) behavior of binders. Phase angle ($\delta$), on the other hand, is the time lag between the applied shear stress on the sample and its resultant shear strain. $\delta$ is actually an indicator of relative amounts of the elastic and viscous behavior of asphalt binders whose values range between 0 to 90, considering which, a higher $\delta$ value represents a more viscous binder sample.

DSR uses samples having 1mm thickness and 25 mm diameter, sandwiched in between two parallel plates, the lower of which is fixed to the base and the upper plate oscillates back and forth at a frequency of 10 rad/s (1.59 Hz) simulating the traffic speed of approximately 90 km/h by applying the shearing impact on the sample [24]. The obtained values of $G^*$ and $\delta$ are used to predict the performance of asphalt binder against rutting ($G^*/\sin\delta$) and fatigue cracking ($G^* \cdot \sin\delta$) as per PG asphalt binder specifications stated in Superpave binder characterization system (AASHTO T315). DSR test is generally conducted on unaged, short-term aged (RTFO-aged) and long-term aged (PAV-aged) samples, the specifications for which are presented in Table 5.

### 2.2.4 Hot mix asphalt design

Marshall mix design method (ASTM D1559) was adopted to prepare asphalt mixtures. At least three replicate Marshall specimens were cast at 3.5 %, 4 %, 4.5 %, 5 %, and 5.5 % by weight of aggregates. Optimum asphalt binder contents (OBC) were determined individually for each asphalt mixtures containing all the three types of nanomaterials added at their various proportions corresponding to 4 % air voids content. All the other Marshall parameter values were controlled for meeting the specification limits. The Marshall design criterion in Turkish specifications (KTS) for Type-1 wearing course is presented in Table 6.

**Table 5** Performance graded asphalt binder DSR specifications [25]

| Material | Value | Specification | HMA Distress of Concern |
|---|---|---|---|
| Unaged binder | $G^*/\sin\delta$ | ≥ 1.0 kPa (0.145 psi) | Rutting |
| RTFO residue | $G^*/\sin\delta$ | ≥ 2.2 kPa (0.319 psi) | Rutting |
| PAV residue | $G^* \cdot \sin\delta$ | ≤ 5000 kPa (725 psi) | Fatigue cracking |

### 2.2.5 Modified Lottman test (AASHTO T283)

Moisture damage is a consequential phenomenon of moisture interaction with the binder-aggregate interface within an asphalt mixture. As a result of this interaction, a reduction of adhesion between the asphalt binder and aggregate, termed as stripping, is occurred. Stripping can potentially lead to various forms of HMA pavement distress including rutting and fatigue cracking [26].

The conditioning and preparation of modified Lottman testing specimens are executed as per AASHTO T 283 considering the fact that it is practiced widely by most of the laboratories across the world in order to assess the moisture susceptibility of asphalt mixtures.

Both the conditioned and dry specimens are subjected to split tensile test widely termed as the Indirect tensile strength test (*ITS*), which apply the splitting (tensile) force on specimens. The average tensile strength value is calculated for each subset with the formula as in Eq. (1).

$$ITS = \left(2000 \times P_{max}\right) / \pi t D \,. \tag{1}$$

Where *ITS* is the indirect tensile strength of the specimen in kPa, $P_{max}$ is the measured maximum load at failure in Newton, $t$ is the specimen thickness in mm, and $D$ is specimen's diameter in mm.

The expression used for predicting the moisture resistance quantitatively is termed as the Tensile Strength Ratio (TSR, %) which is expressed in Eq. (2).

$$TSR, \% = \left(ITS_{Conditioned} \,/\, ITS_{Dry}\right) \times 100 \,. \tag{2}$$

*ITS* conditioned and *ITS* dry are the average indirect tensile strength values of conditioned and dry subsets, respectively.

**Table 6** Marshall mix design criteria for the type-1 wearing course

| Mix Design Criteria | Standard | Wearing Type-1 |
|---|---|---|
| Compaction; [number of blows on each end of the sample] | TS EN 12697-30 | 75 |
| Stability (kg) | TS EN 12697-34 | 900 |
| Flow (mm) | TS EN 12697-34 | 2–4 |
| Air Voids (%) | TS EN 12697-8 | 3–5 |
| VFA (%) | TS EN 12697-8 | 65–75 |
| VMA (%); [varies with the nominal max. aggregate size] | TS EN 12697-8 | 14–16 |

## 3 Results and discussions

### 3.1 Conventional asphalt binder test results

The influence indication of nanomaterials on basic properties of 50/70 asphalt binder is tabulated in Table 7.

As per the findings in Table 7, nanomaterials did not seem very influential on the penetration and softening point values except for nano-Bentonite which resulted in decreased penetration and increased softening point values. However, the short-term aged binder exhibited exceptionally promising results. The retained penetration and increment in softening point values for short-term aged nanomodified binders were slightly improved as compared to neat binders. This indicates the positive contribution of nanomaterials to the enhancement of asphalt binder performance against the aging phenomena. Penetration index values consistently increased with the increase in nano-Bentonite and nano-$CaCO_3$ contents which proves the enhancement of modified binder in terms of its thermal stability. In the case of ZycoTherm, although the PI value decreased as compared to the neat binder, it was still improved with the increment in ZycoTherm dosage. Overall, ZycoTherm did not have a considerable impact on the physical properties of the binder, however, it might slightly lower the viscosity of asphalt binder.

Storage stability test was performed on unaged asphalt binder samples involving the nano-modifiers regarding the state of phase bonding between the asphalt binder and the modifier when stored at high temperatures. Conventional softening point test was performed on the top and the bottom portion of the sample in cylindrical containers (split into roughly three equal portions) and looked for the difference. Based on Table 7, the softening point temperature difference of top and bottom portions of the tested cylindrical samples remain below 2.5 °C (as per EN 13399 standard).

Brookfield rotational viscometer was employed to get the viscosity values of neat and nanomodified asphalt binders at 135 °C and 165 °C. As presented in Table 7, all the asphalt binder samples resulted in lower viscosities at the higher temperature of 165 °C as compared to the viscosities obtained at 135 °C. Generally, by increasing the temperature, the viscosity values get decreased. Nano-$CaCO_3$ somewhat lowers the viscosity which is considered as a favorable feature of an additive when evaluating its efficiency since it reduces the operating temperatures and thus helping in the preparation of potentially economical and eco-friendly pavements. ZycoTherm seemed very influential in terms of lowering the viscosity and the best results were obtained for 0.1 % ZycoTherm dosage at which the viscosity got reduced to 100 mPa · s. ZycoTherm being in liquid state is considered as one of the factors contributing to the viscosity reduction of asphalt binders.

### 3.2 Rheological test results

The rheological charazterization for the current study primarily covered; the classification according to Performance Grade (PG) for the upper critical temperature as well as the

**Table 7** Neat and nanomaterial-modified asphalt binder test results

| Test | Specification | Neat Binder | Nano-Bentonite | | | Nano-$CaCO_3$ | | | ZycoTherm® | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 0% | 2% | 4% | 6% | 3% | 6% | 9% | 0.1% | 0.2% | 0.3% |
| Penetration (0.1 mm) | ASTM D 5-06 | 64 | 61.0 | 60.0 | 57.7 | 66.3 | 70.7 | 69.7 | 61.7 | 61.0 | 60.5 |
| Softening Point (°C) | ASTM D 36-06 | 51.5 | 52.9 | 53.2 | 54.7 | 52.8 | 53.2 | 54.7 | 51.7 | 52.1 | 53.5 |
| Penetration Index (PI) | - | -0.23 | -0.02 | 0.01 | 0.26 | 0.18 | 0.45 | 0.77 | -0.28 | -0.21 | 0.11 |
| Viscosity @ 135 °C, mPa.s | ASTM D 4402-06 | 425 | 475 | 600 | 775 | 425 | 463 | 575 | 100 | 125 | 113 |
| Viscosity @ 165 °C, mPa.s | ASTM D 4402-06 | 138 | 138 | 200 | 288 | 125 | 125 | 175 | 425 | 450 | 425 |
| After Rolling Thin Film Oven Test (ASTM D 2872-12) | | | | | | | | | | | |
| Change in Mass (%) | - | 0.08 | 0.02 | 0.02 | -0.01 | -0.01 | 0.03 | 0.04 | -0.07 | -0.10 | -0.10 |
| Retained Penetration (%) | - | 60.9 | 64.5 | 68.3 | 71.8 | 68.1 | 64.5 | 64.8 | 67.6 | 64.5 | 66.5 |
| Increase in Softening Point | - | 5.7 | 4 | 4.5 | 4.7 | 4 | 4.7 | 4.4 | 4.4 | 4.9 | 3.05 |
| Storage Stability Test (EN 13399) | | | | | | | | | | | |
| Softening Point (°C) of top segment | ASTM D 36-06 | - | 52.0 | 52.4 | 52.9 | 54.5 | 57.2 | 56.2 | 55.1 | 53.8 | 54.5 |
| Softening Point (°C) of bottom segment | ASTM D 36-06 | - | 52.4 | 52.8 | 52.0 | 53.7 | 55.9 | 55 | 56.8 | 54.7 | 55.8 |
| Difference (°C) | - | - | 0.4 | 0.4 | 0.9 | 0.8 | 1.3 | 1.2 | 1.7 | 0.9 | 1.3 |

evaluation of rheological properties and variations over the range of two different frequencies and four different temperature cycles.

The unaged and RTFOT-aged samples of the neat and nano-modified asphalt binder were subjected to DSR oscillating shear maintaining a frequency of 10 rad/s (1.59 Hz) which represents the field traffic moving at approximately 90 km/h. The initial temperature values were set to 52 °C for unaged and 64 °C for RTFOT-aged samples with a run-up in 6 °C increments. The upper critical temperatures used in the PG system were determined for each sample by obtaining the $G^*/\sin\delta$ values.

With reference to the specifications given in Table 5, the results for upper critical temperatures of the neat and nanomodified asphalt binder samples are determined and tabulated in Table 8.

It can be observed from the results in Table 8 that with a rise in temperature, the rutting parameter ($G^*/\sin\delta$) value decreases uniformly which implies that the binder performance gets negatively affected in terms of rutting resistance thus becoming vulnerable to permanent deformation.

The nanomaterials used in this study were not considerably effective in terms of enhancing binder performance grading (growth in $T_{crit}$ values). However, only 6 % nano-Bentonite and 9 % nano-$CaCO_3$ modified asphalt binder samples improved $T_{crit}$ from 64 °C to 70 °C.

All the unaged and RTFOT-aged neat and modified asphalt binder samples were subjected to oscillating shear conducted at 0.01 and 10 Hz frequencies and four different temperatures ranging from 50 to 80 °C with 10 °C increment. The objective of presenting the unaged asphalt binder samples and RTFO-aged sample results together was to understand the impact of aging on the behavior of binders. Figs. 4–7 illustrate the correlation between $G^*/\sin\delta$ and selected temperatures for all types of binder samples in order to observe the variation at low and high frequencies.

As can be seen in Fig. 4 through Fig. 7 that all the binder samples exhibited almost the same trend for rutting ($G^*/\sin\delta$). The $G^*/\sin\delta$ increased with the reduction in temperature at both frequencies. An increment in $G^*/\sin\delta$ value infers a better performance against rutting. At lower temperatures, all the samples showed higher rutting resistance.

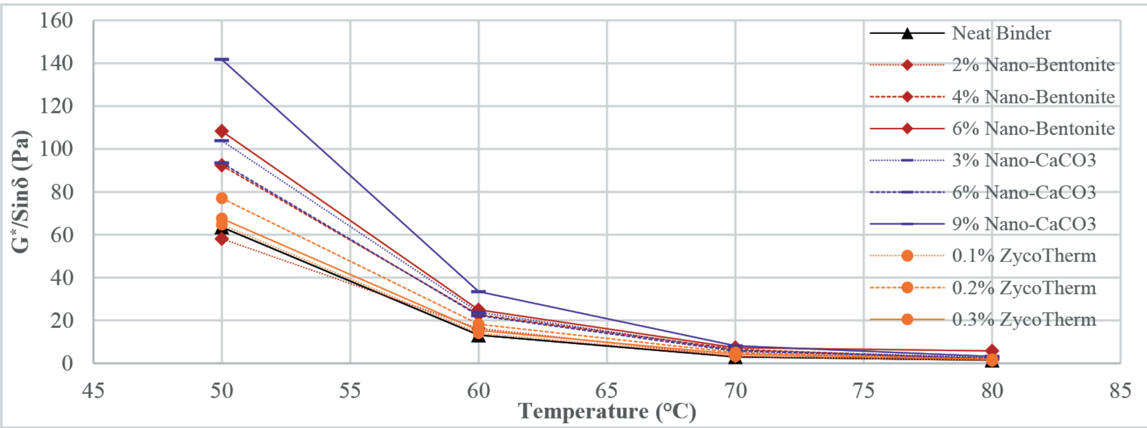


**Fig. 4** $G^*/\sin\delta$ values for unaged samples at 0.01 Hz

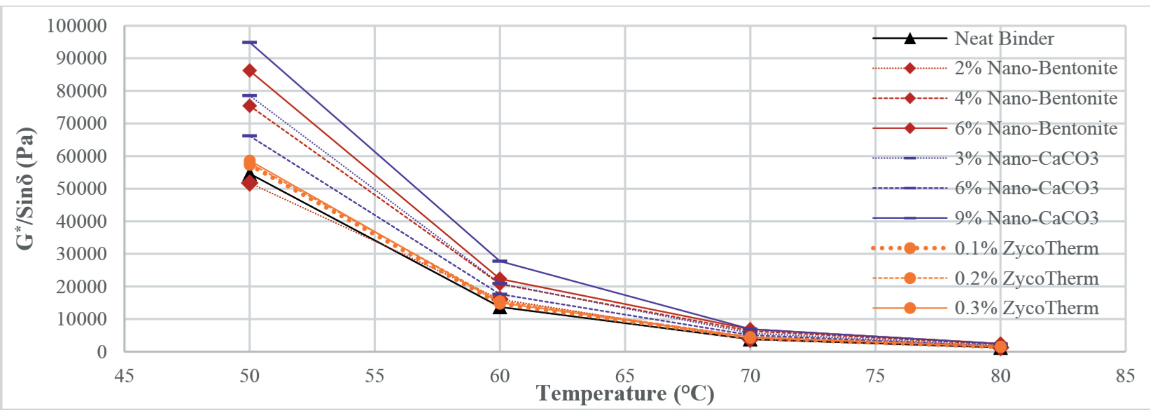


**Fig. 5** $G^*/\sin\delta$ values for RTFOT-aged samples at 0.01 Hz

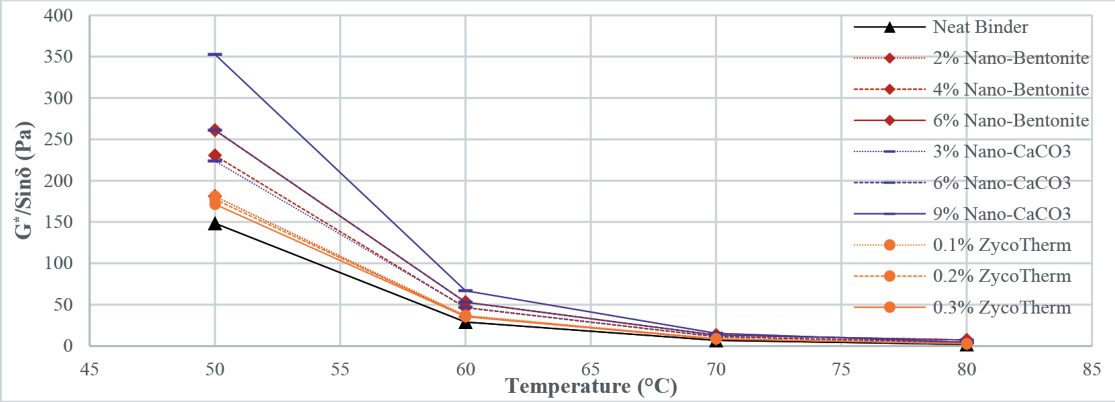


**Fig. 6** $G^*/\sin\delta$ values for unaged samples at 10 Hz

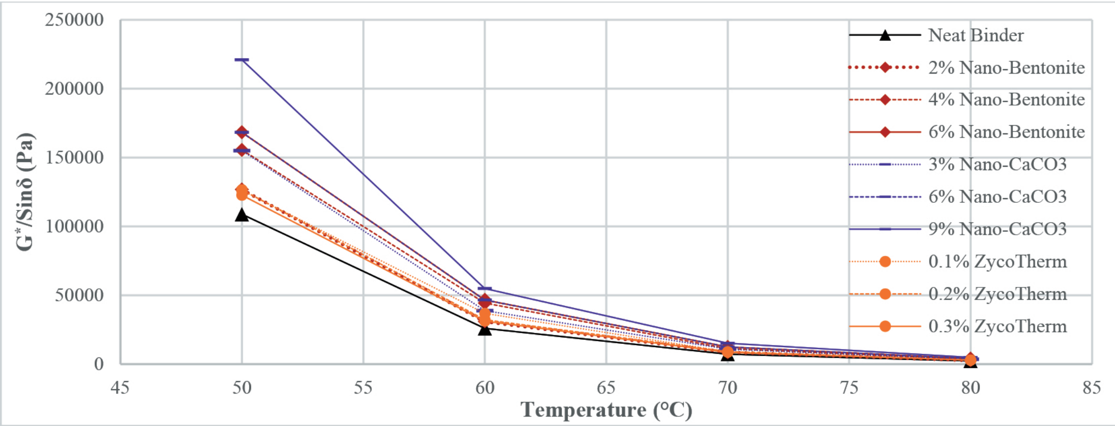


**Fig. 7** $G^*/\sin\delta$ values for RTFOT-aged samples at 10 Hz

Moreover, as expected, $G^*/\sin\delta$ values rose at a higher frequency (10 Hz) for all the asphalt binder samples. This is stemmed from the rheological behavior of the binder under shorter loading times (high-frequency level) exhibiting elastic behavior [27, 28].

By referring to Fig. 5 and Fig. 7, the results appear pretty similar to the ones obtained for unaged samples. As expected, due to the impact of aging (binder gets oxidized and thereby hardens), the $G^*/\sin\delta$ values gets substantially higher that reaches to approximately 100 kPa and over 200 kPa at 0.01 and 10 Hz frequencies, rescpectively. The after short-term aging performance of ZycoTherm modified binder seems to get improved from rutting aspect and resulted in higher $G^*/\sin\delta$ values as compared to the neat binder at low and high frequencies for the entire temperature cycle.

Overall, the results concluded that the improvement of asphalt binder in terms of its performance against rutting is achievable by nanomodification. The effectiveness of nanomodification in rutting resistance can be further examined and explored by conducting wheel-tracking, Asphalt Pavement Analyzer and other customary performance tests.

### 3.3 Hot mix asphalt design results

The results for other Marshall parameters corresponding to optimum asphalt binder contents (OBC) are presented in Table 9. After the determination of OBC, the values were re-checked for other Marshall parameters (given in Table 6). Based on the results, The OBC for all types of mixtures met the criterions and were within the limits set by the Turkish specifications (KTS).

As depicted in Table 9, all the mixtures prepared with nanomodified asphalt binder resulted in lower optimum binder contents as compared to the control mixture. Nano-Bentonite, for being filler in nature, may cause the reduction in total air voids and thus required lower asphalt binder contents to prepare asphalt mixtures with desired qualities. The same was true for nano-$CaCO_3$ since it is also a nano-filler thus by increasing the filler content, the reduction in VMA % and VFA % is also clearly observed.

ZycoTherm also reduced the optimum content of asphalt binder which could be attributed to the ZycoTherm being in liquid physical form and reduces the viscosity of asphalt binder thus resulting in reduction of the mixing and compaction temperatures. Owing to the fact that Zycotherm

**Table 8** PG upper critical temperature (Tcrit) for the neat and nanomodified asphalt binders

| Binder Type | Additive (%) by weight of Binder | Temperature (°C) | DSR, $G^*/\mathrm{Sin}\delta$ (Pa) | | PG Upper Critical Temperature (°C) |
|---|---|---|---|---|---|
| | | | Unaged | RTFO-Aged | |
| Neat Binder | **0** | 52 | 7652 | | **64** |
| | | 58 | 3074 | | |
| | | 64 | **1385** | **2857** | |
| | | 70 | 644.5 | 1328 | |
| Nano-Bentonite | **2** | 52 | 7723 | | **64** |
| | | 58 | 3370 | | |
| | | 64 | **1549** | **3291** | |
| | | 70 | 739.6 | 1532 | |
| | **4** | 52 | 9576 | | **64** |
| | | 58 | 4183 | | |
| | | 64 | **1931** | **4518** | |
| | | 70 | 924.6 | 2119 | |
| | **6** | 52 | 10970 | | **70** |
| | | 58 | 4839 | | |
| | | 64 | 2248 | 5523 | |
| | | 70 | **1072** | **2500** | |
| | | 76 | 577.8 | 1242 | |
| Nano-$CaCO_3$ | **3** | 52 | 9895 | | **64** |
| | | 58 | 4300 | | |
| | | 64 | **1830** | **4285** | |
| | | 70 | 843.7 | 2020 | |
| | **6** | 52 | 8245 | | **64** |
| | | 58 | 3567 | | |
| | | 64 | **1578** | **4011** | |
| | | 70 | 787.4 | 1837 | |
| | **9** | 52 | 12950 | | **70** |
| | | 58 | 5509 | | |
| | | 64 | 2459 | 5753 | |
| | | 70 | **1132** | **2710** | |
| | | 76 | 574 | 1304 | |
| ZycoTherm® | **0.1** | 52 | 6910 | | **64** |
| | | 58 | 3105 | | |
| | | 64 | **1382** | **3445** | |
| | | 70 | 661.1 | 1529 | |
| | **0.2** | 52 | 7494 | | **64** |
| | | 58 | 3310 | | |
| | | 64 | **1634** | **3301** | |
| | | 70 | 721.6 | 1470 | |
| | **0.3** | 52 | 7332 | | **64** |
| | | 58 | 3213 | | |
| | | 64 | **1443** | **3299** | |
| | | 70 | 683.1 | 1502 | |

**Table 9** Marshall mechanical and volumetric properties corresponding to optimum binder content

| Mix Type | Additive (%) | Opt. Binder Content (%) | Stability (kgf) | Flow (mm) | VMA (%) | VFA (%) | Density (gr/cm³) |
|---|---|---|---|---|---|---|---|
| Control Mixture | 0 | 4.59 | 1182 | 2.53 | 14.3 | 72.0 | 2.41 |
| | 2 | 4.26 | 1309 | 2.41 | 14.3 | 71.9 | 2.41 |
| Nano-Bentonite Modified | 4 | 4.40 | 1250 | 2.44 | 14.3 | 73.2 | 2.39 |
| | 6 | 4.38 | 1332 | 2.35 | 14.1 | 71.5 | 2.41 |
| | 3 | 4.07 | 1213 | 2.13 | 14.5 | 66.3 | 2.40 |
| Nano-$CaCO_3$ Modified | 6 | 4.17 | 1207 | 2.17 | 14.4 | 68.1 | 2.40 |
| | 9 | 4.15 | 1246 | 2.00 | 14.2 | 71.3 | 2.46 |
| | 0.1 | 4.38 | 1193 | 2.38 | 14.2 | 71.6 | 2.41 |
| ZycoTherm® Modified | 0.2 | 4.29 | 1180 | 2.12 | 14.1 | 71.6 | 2.41 |
| | 0.3 | 4.35 | 1210 | 2.13 | 14.1 | 71.6 | 2.41 |

potentially coats the aggregate surface completely even at relatively lower temperatures, it may require lower asphalt binder content to obtain optimal results.

VMA % of neat and all nanomodified mixture types met the minimum specification limit of 14 % for nominal maximum aggregate size (NMAS) of 12.5 mm gradation recommended by the Turkish technical specifications of general directorate of highways (KTS) for wearing course.

All the stability values were well above the minimum limit of 900 kgf and met the Turkish standards. The stability values raised significantly higher when modified with 6 % nano-Bentonite. In this proportion, the stability was observed to raise more than 11 % higher as compared to the control mixture. This improvement can be sourced from nano-Bentonite being added in the form of a filler. Nano-$CaCO_3$ was also efficient in terms of enhancing the mixture stability. Although ZycoTherm modification caused the increment in the mix stability, it was still insignificant.

### 3.4 Modified Lottman (AASHTO T283) test results

In order to clearly distinguish the influence of nanomodification on the performance against moisture susceptibility, the prepared mixtures with and without modifiers are plotted against their ITS results achieved for both dry and conditioned specimens as illustrated in Fig. 8.

The resultant TSR values are also shown on the plot with a linear curve.

Based on Fig. 8, it is observed that the ITS values for the conditioned specimens are lower than those for dry specimens. This is the behavior expected, because in the conditioning process the presence of water weakens the bond between aggregate and asphalt binder, consequently getting lower ITS values. After conditioning, mixtures involving nanomaterials generally exhibited less decrease than control mixtures.

The specimens prepared with neat asphalt binder exhibited the lowest TSR % compared to specimens with nano-modified binders. This infers that the performance against moisture improves significantly when modified with nanomaterials. Higher values of TSR ensure better resistance to moisture damage in mixtures.

TSR % values obtained for nano-Bentonite were also significantly improved and reached the highest TSR for the specimens involving 4 % of the modifier. In comparison with control mixture, nano-Bentonite increased TSR values by 12 %, 14 %, and 8 % with the incorporation of 2 %, 4 %, and 6 %, respectively. These results infer that Bentonite in nano-size can potentially help in enhancing the adhesion and cohesion capability of asphalt binder. This result could be attributed to the increasing viscosity and thus cause the stiffening of the binder with modification. Stiffer binder would generally resist the peeling of its coating from the aggregate particle surface, consequently become moisture resistant.

The results obtained for dry specimens exhibit almost the same ITS value as for the control mix except for the 6 % of nano-$CaCO_3$ content, at which the ITS value was slightly improved. Whereas, the values of ITS for the conditioned specimens were improved substantially.

For nano-$CaCO_3$, the highest ITS for the conditioned specimens was achieved at 6 %, which increased the ITS values up to 12 % and the highest TSR was also achieved at same content. At this dose, the growth in TSR was 11 %.

By scrutinizing the results for the TSR values of the mixtures involving ZycoTherm, it is clearly evident that the modification of asphalt binder with ZycoTherm, despite its significantly lower dosages, increases the TSR values considerably higher.

Compared to the control mixture, the TSR increased up to 22 % with 0.1 % ZycoTherm, which is considered to be the optimum dosage. This positive influence perhaps

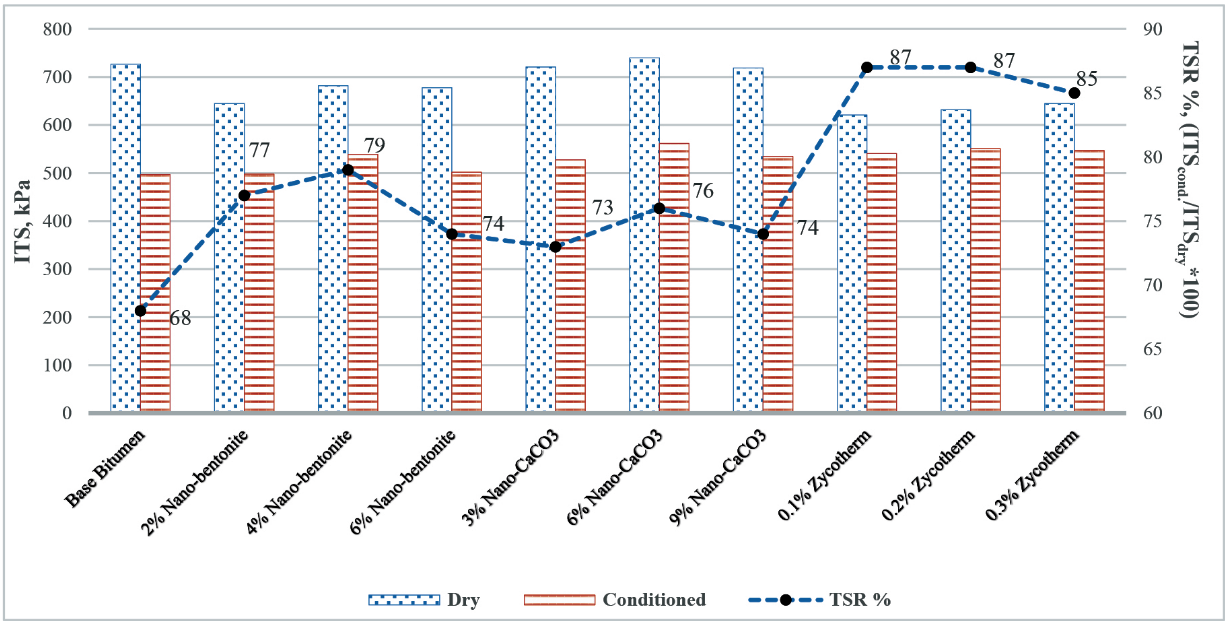


**Fig. 8** ITS and TSR results for mixtures prepared with neat and nanomodified binders

originates from the ZycoTherm basically being a silane antistripping additive. In fact, ZycoTherm assures chemical bonding between the binder and the aggregate in a way that it reduces the stripping potential at the aggregate-binder interface by eradicating the air interface that exists on the aggregate surface.

The variance values calculated for the dry and conditioned ITS specimens prepared at various dosages of the mentioned nanomaterial additives were 1724 and 488, respectively, that corresponds to a coefficient of variation value of 0.06 and 0.04. These coefficient values reflect an average variability of the obtained ITS values from the mean. Moreover, the data for TSR values exhibited a variance of 37 that would correspond to an average of 7.8 % variability of TSR values from the mean. These analytical results confirm that the deviation of ITS and TSR values from the mean is insignificant and thus are declared as satisfactory.

## 4 Conclusions

The conclusions drawn from this study are summarized as below:

- Nanomaterials do not significantly alter the conventional properties of the neat bitumen. Thus, the conventional test results are not solely adequate for the evaluation of the nanomodified asphalt binders.
- Nanomaterials are highly influential in terms of reducing the high-temperature susceptibility and enhancing the storage stability of modified binders at high temperatures.
- Nanomaterials can improve the rheological characteristics of asphalt binder.
- Moisture resistance of nanomodified asphalt mixtures gets considerably improved especially with ZyocTherm.

The future potential research areas and problems that could be addressed are the followings:

- Advanced nanoscopic characterization of nanomaterials and nanomodified binders are required to further understand the nanostructural architecture and relate its impact to the macroscale performance of the binder.
- Further performance tests (e.g. assess the performance against rutting and the fatigue life) are required to be carried out in order to get a thorough understanding of nanomaterials influence on asphalt mixtures.
- A similar study is recommended over the nanomodified asphalt mixtures involving granite and basalt.

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