Characterization of Nano-Alumina Modified Asphalt Binders and Mixtures

Pubali Nazir, Rajan Choudhary, Abhinay Kumar, and Ankush Kumar

1 Introduction

Asphalt binder modification is a popular technique to enhance the structural capacity and functional life of asphalt pavements. Several types of modifiers have been introduced in the realm of bituminous pavements aiming to combat premature deterioration and distress that occur on account of heavier traffic loads, high tire pressures, and severe climatic conditions. The materials that are used as asphalt modifiers include polymers, fibers, chemical agents, natural asphalt, tire rubber, and a more recently introduced class of modifiers, the nano-materials.

Nanotechnology is an emerging technology with the size of the material (at least one dimension) in the nano-size range (10^{-9} m). Although major nano-technological developments have taken place in the field of electronics, physics, and chemistry, the field has taken a recent stride toward construction engineering [1]. The behavior of nano-materials at the nano-range facilitates the improvement in the properties of construction materials, including pavement materials. Although asphalt binders and asphalt mixtures are used in bulk quantities for the construction and maintenance of pavements, their behavior on a macro-scale is influenced by their properties at micro- and nano-scales [2]. In recent times, various research efforts have been put into the application of nanotechnology to pavement engineering [3–5]. Several nano-materials that have been employed for this purpose are carbon nano-tubes (CNTs) [6, 7], nano-silica [8, 9], nano-clays [10], etc.

P. Nazir · R. Choudhary (✉) · A. Kumar · A. Kumar
Department of Civil Engineering, Indian Institute of Technology Guwahati, Assam, India
e-mail: rajandce@iitg.ac.in

A. Kumar
e-mail: abhinay.kumar@iitg.ac.in

A. Kumar
e-mail: ankus174104035@iitg.ac.in

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Table 1 Properties of nano-alumina (nano-Al_2O_3)

Property	Unit	Value
Specific gravity	–	3.340
Specific surface area	m^2/g	100 + 15
Average primary particle size	nm	13
Tamped density	g/l	Approx. 50
Moisture	wt. %	<5.0
Ignition loss	wt. %	<3.0
pH (in 4% dispersion state)	–	4.5–5.5
Al_2O_3 content	wt. %	>99.8
Sieve residue	wt. %	<0.050

This study seeks to assess the influence of alumina nano-particles as a modifier to asphalt binders by analyzing the physical and rheological characteristics of the modified as well as neat (control) asphalt binders. Physical tests included in the study are specific gravity, softening point, and viscosity. Rheological tests conducted on binders include multiple stress creep and recovery (MSCR), temperature sweep, and frequency sweep. Further, the study included the performance characteristics of asphalt mixtures fabricated with nano-alumina modified binders.

2 Experimental Methods

2.1 Materials

The base binder used was a viscosity grade 30 (VG-30) binder meeting the requirements of IS 73 [11]. Nano-alumina (nano-Al_2O_3) was obtained from NU Patel & Company, Ahmedabad (India). Table 1 presents the properties of nano-Al_2O_3 particles. Figure 1 shows a naked eye view of nano-Al_2O_3. Energy-dispersive X-ray (EDX) results shown in Fig. 2 indicate that aluminum (36.5%) and oxygen (63.5%) are the two elements present in nano-Al_2O_3.

2.2 Preparation of Modified Asphalt Binders

The modified asphalt binder blends were prepared using dosages of nano-Al_2O_3 varying between 0 and 8% (by weight of base binder) at an increment of 2%. The neat binder was heated on a temperature-controlled hotplate to 160 °C. Then, the desired quantity of nano-Al_2O_3 was introduced and a high shear mixer was employed for blending under a speed of 14,000 rpm for 30 min. For uniform dispersion and homogeneity, the blends were then stored at –15 °C in metallic containers for further use.

Fig. 1 Naked eye view of nano-Al_2O_3

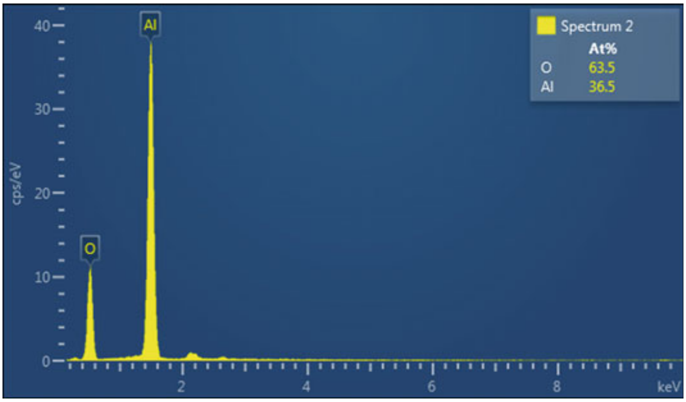

Fig. 2 EDX results of nano-Al_2O_3

2.3 Conventional Properties

The conventional properties including specific gravity, viscosity, and softening point were measured. The specific gravity of the binders was measured as per IS 1202 [12]. The softening point test was completed in line with IS 1205 with the ring and ball apparatus [13]. The viscosity of binders was computed at 135 °C through a Brookfield rotational viscometer with spindle #21, according to ASTM D4402 [14].

Fig. 3 Aluminum tubes used in the storage stability test

2.4 Storage Stability Test

The control binder and nano-Al_2O_3 modified binders were submitted to thermal storage stability test according to ASTM D7173 [15]. For this test, a 50-g bitumen sample was heated and poured in an aluminum tube of 14 cm height and 2.5 cm diameter. The sealed tube was kept at 163 °C in an oven for 48 h before being transferred to a freezer at –10 °C for 4 h. Thereafter, the difference in softening point of binder residues from the top and bottom third sections was checked for a limit of 3 °C, as per the requirements of IS 15462 [16]. Figure 3 shows the tubes used in the test along with a cut tube.

2.5 Rheological Tests and Modeling

Rheological characterization was conducted on short-term aged binders using a dynamic shear rheometer (DSR). As per ASTM D2872, the binders were aged in a rolling thin film oven (RTFO) for 85 min at 163 °C [17]. Rheological tests were conducted with a parallel plate geometry using a 1-mm-gap with a 25-mm-diameter plate. The two main rheological parameters, such as complex shear modulus (G*) and phase angle (δ), were determined using a temperature sweep test. The range of temperatures considered was 25–80 °C at 10 rad/s (1.59 Hz) frequency. A frequency sweep test was conducted to assess the elastic modulus (G′) and viscous modulus (G″) at frequencies varying between 0.1 and 100 rad/s. The MSCR test was also conducted on short-term aged control and nano-Al_2O_3 modified binders at 60 °C, a temperature representing the typical high-service pavement temperature. The MSCR test was performed in line with ASTM D7405 [18], with ten creep-recovery cycles (1 s creep and 9 s recovery for each cycle) at each 0.1 and 3.2 kPa stress level. The strain undergone by the binder was recorded as a function of time and was employed to calculate percent recovery (R) and non-recoverable creep compliance (J_{nr}) corresponding to each creep-recovery cycle and stress level. Equations 1 and 2 present the expressions to determine R and J_{nr}, respectively.

$$R = \frac{\varepsilon_t - \varepsilon_r}{\varepsilon_t} \times 100 \tag{1}$$

$$J_{nr} = \frac{\varepsilon_r}{\sigma} \tag{2}$$

Here, ε_t = total strain, ε_r = residual strain, and σ = applied stress.

2.6 Design and Evaluation of Bituminous Concrete Mixtures

Bituminous mixtures were prepared using a bituminous concrete (BC) grading II (aggregate gradation shown in Fig. 4) with 13.2-mm nominal maximum aggregate size (NMAS). BC-II gradation is commonly used for the design of dense-graded bituminous mixtures for wearing courses of highways in India. Three mix specimens were produced at binder content between 4.5 and 6.5% at an increment of 0.5% by weight of mix during the design of the BC mix. The optimum binder content (OBC) in bituminous mix design was determined using the Marshall method, which is presently used in India. The OBC was found to be 5.5%, and the mix design parameters acquired at the OBC fulfilled the criteria outlined in MoRTH [19] guidelines. The OBC obtained with a neat binder was also used for the preparation of mixes with nano-Al_2O_3 modified binders. This technique enabled for an assessment of all mixes' efficacy without including the binder content as a separate variable.

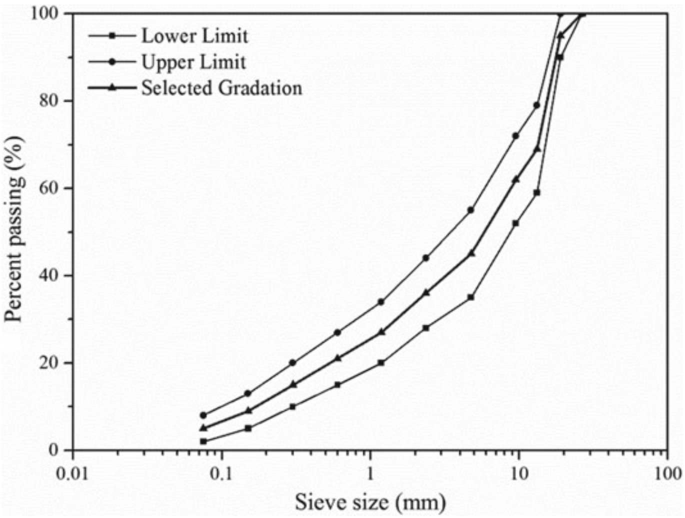

Fig. 4 Bituminous concrete (BC-II) gradation with specification limits

The performance of BC mixes containing control and nano-Al_2O_3 modified binders was assessed using the indirect tensile stiffness modulus (ITSM) test at two temperatures of 25 and 40 °C. The specimens were produced at 4 ± 0.5% air voids. The ITSM test evaluates the stiffness properties of asphalt mixtures and was analyzed in accordance with EN 12697-26 [20] protocol. A 14-kN universal testing machine was used for the test (Fig. 5). The test consisted of applying a haversine waveform load to reach a rise time of 124 ms (the time it takes for the load pulse to reach its maximum value). The specimen deformation was recorded in a horizontal plane. In the first ten load pulses, the stress magnitude was automatically adjusted for a transitory deformation of 0.005% of the diameter. The stiffness modulus was then calculated using the next five load pulses. After turning the specimen by 90 degrees, the test was repeated. Equation 3 was used for the modulus:

$$S_m = \frac{F \times (\mu + 0.27)}{z \times h} \tag{3}$$

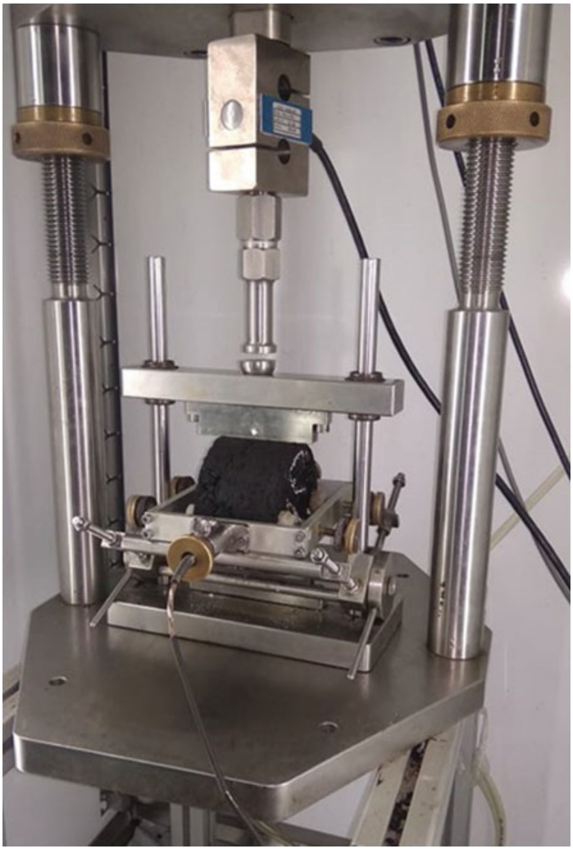

Fig. 5 ITSM test assembly

Here, F = peak vertical load, N; h = sample height, mm; z = amplitude of the horizontal deformation, mm; μ = Poisson's ratio (assumed 0.35); S_m = stiffness modulus, MPa.

3 Results and Discussion

3.1 Results on Nano-modified Asphalt Binders

Conventional Properties. The outcomes of conventional parameters (softening point, viscosity, and specific gravity) of control and nano-Al_2O_3 modified asphalt binders are shown in Fig. 6. As nano-Al_2O_3 particles had a high specific gravity of 3.340, their addition caused an increase in the specific gravity of the asphalt binder. The increase in binder stiffness with the addition of nano-Al_2O_3 is seen from an increase in softening point and viscosity measured at 135 °C. Further at 135 °C, both control and nano-Al_2O_3 modified binders fulfilled the viscosity threshold of 3.0 Pa s, which indicates that these binders would not pose a hindrance in pumping and mixing.

Storage Stability. The storage stability is computed as the difference in softening point between the top and bottom sections of the aluminum tube containing nano-Al_2O_3 modified binders. Figure 7 depicts a difference of less than 3 °C in softening point of the top and bottom sections for all nano-Al_2O_3 modified binders, indicating adequate storage stability. The results show that nano-Al_2O_3 modified binders had good compatibility and homogeneity at elevated temperatures. The very small particle volume of nano-Al_2O_3 is likely the reason for the good dispersion and compatibility of the modified binders.

Temperature Sweep. The temperature sweep test results for the control and nano-Al_2O_3 modified binders are shown in Fig. 8. After adding nano-Al_2O_3 to

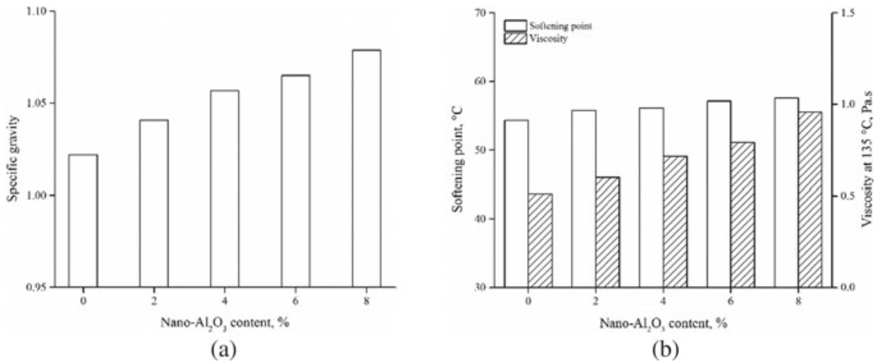

Fig. 6 **a** Specific gravity results. **b** Softening point and viscosity results

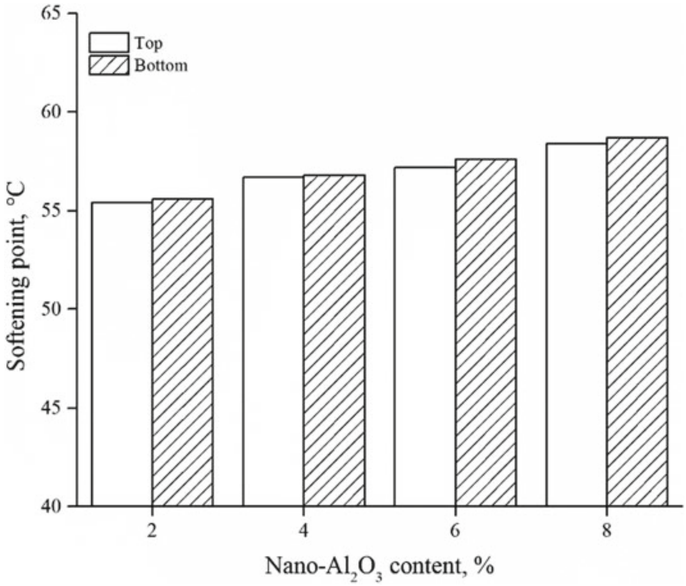

Fig. 7 Storage stability results

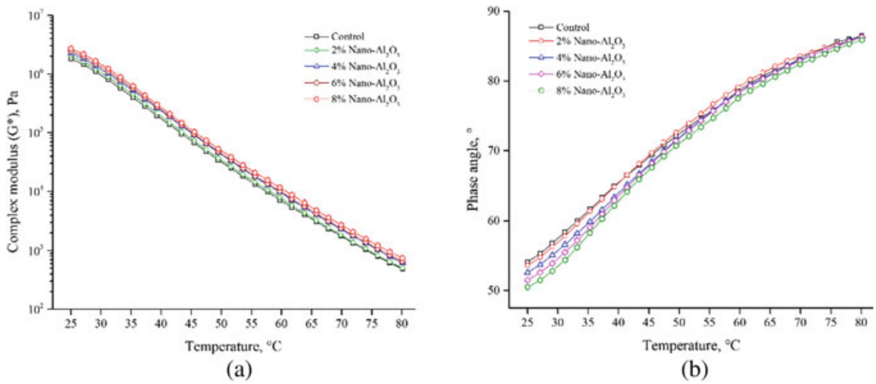

Fig. 8 Temperature sweep results: **a** G*, **b** δ

the base binder, G* increased and δ decreased at all temperatures, indicating that the binder's stiffness and elasticity improved. Additionally, when the nano-Al_2O_3 dosage increased, the G* increased and the δ lowered across the temperature domain considered in the test. Percent increase of 8%, 31%, 39%, and 55% was found for G* with 2, 4, 6, and 8% nano-Al_2O_3 contents, respectively, as compared to the control binder. For a greater ability of asphalt binder against deformation, a larger G* and a reduced δ are preferable [21, 22]; hence, the effects of nano-Al_2O_3 are beneficial toward a better deformation resistance.

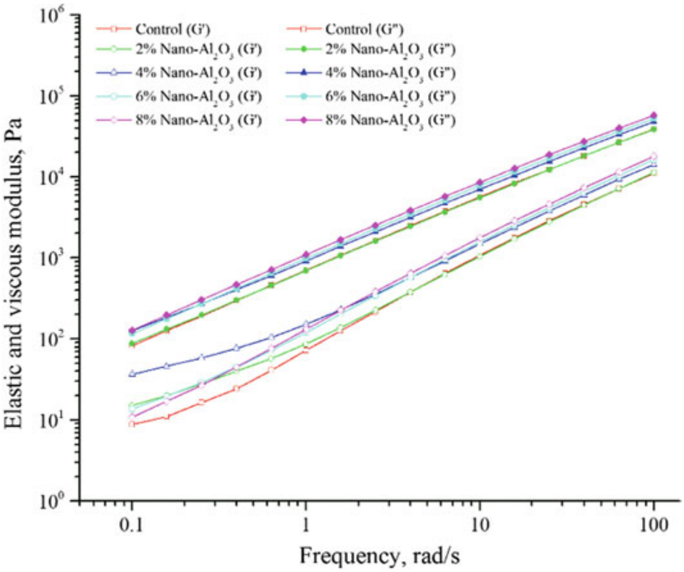

Fig. 9 Frequency sweep results at 60 °C

Frequency Sweep. The frequency sweep test was evaluated to assess the influence of nano-Al_2O_3 on rheological variables under varying frequencies at 60 °C temperature. The results over frequencies ranging from 0.1 to 100 rad/s are expressed as storage modulus (G′) and loss modulus (G″). Figure 9 shows the trends of the frequency sweep test for different dosages of nano-Al_2O_3. The addition of nano-Al_2O_3 enhanced the G′ and G″ of the binders at all frequencies, which shows that the viscoelastic characteristics of the binder improved. The highest moduli are observed for the binder with 8% nano-Al_2O_3.

MSCR. The MSCR test was performed to assess the creep and recovery response of binders at 60 °C to study the resistance of binder against rutting. The plot of accumulated strain against time in the MSCR test at both 0.1 and 3.2 kPa stress levels is shown in Fig. 10. Results from 0 to 100 s (Fig. 10a) and those from 100 to 200 s (Fig. 10b), respectively, represent the stress levels of 0.1 kPa and 3.2 kPa. When compared to the control binder at 0.1 kPa stress levels, the inclusion of nano-Al_2O_3 decreased the total strain by 13, 26, 34, and 45%. Corresponding reductions were 12, 23, 32, and 43% at 3.2 kPa stress level.

Figure 11a shows the variation of MSCR creep compliance (J_{nr}) for different binders measured at both stress levels. A binder with lower J_{nr} is preferable for an improved potential against rutting. J_{nr} for the control binder was as 1.2 and 1.4 kPa^{-1} at 0.1 kPa and 3.2 kPa stress levels, respectively. Further addition of nano-Al_2O_3 resulted in a significant reduction in J_{nr} at both stress levels, which is highly favorable for a better rutting performance. The results of MSCR recovery are presented in Fig. 11b. Recovery results corroborate the results of J_{nr}. Since J_{nr} is related to the

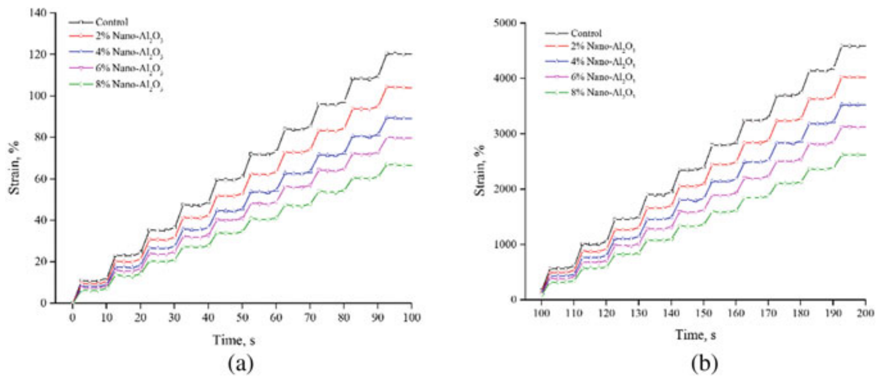

Fig. 10 MSCR accumulated strain versus time curves at stress levels of: **a** 0.1 kPa; **b** 3.2 kPa

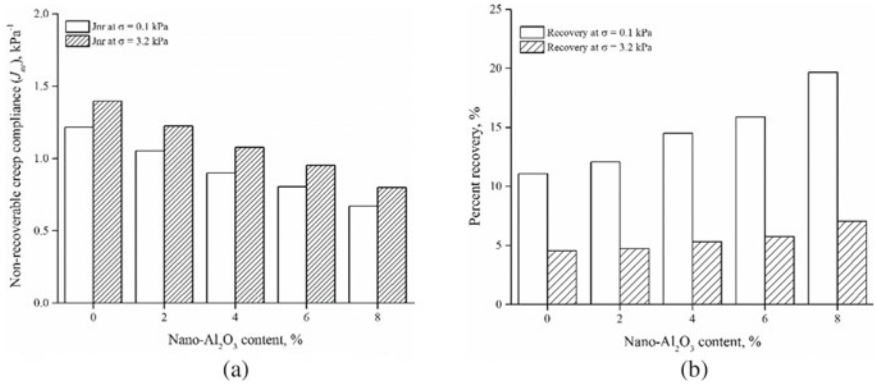

Fig. 11 MSCR results of **a** J_{nr}; **b** recovery

amount of non-recovered strain in the creep-recovery cycle, a binder with a lower J_{nr} is expected to demonstrate a relatively higher recovery. Nano-Al_2O_3 particles enhance the rutting performance of the binder and thus can be highly beneficial to countries/regions with hot/tropical climatic conditions, e.g., India.

3.2 Characteristics of Asphalt Mixtures with Nano-modified Asphalt Binders

The ITSM test compares the stiffness of bituminous mixes with and without nano-Al_2O_3. Results of the ITSM tests performed at 25 and 40 °C temperatures are presented in Fig. 12. As expected, the ITSM at 40 °C was lower than that at 25 °C as the binder's stiffness reduces at higher temperatures. At 25 °C, the ITSM of mixtures

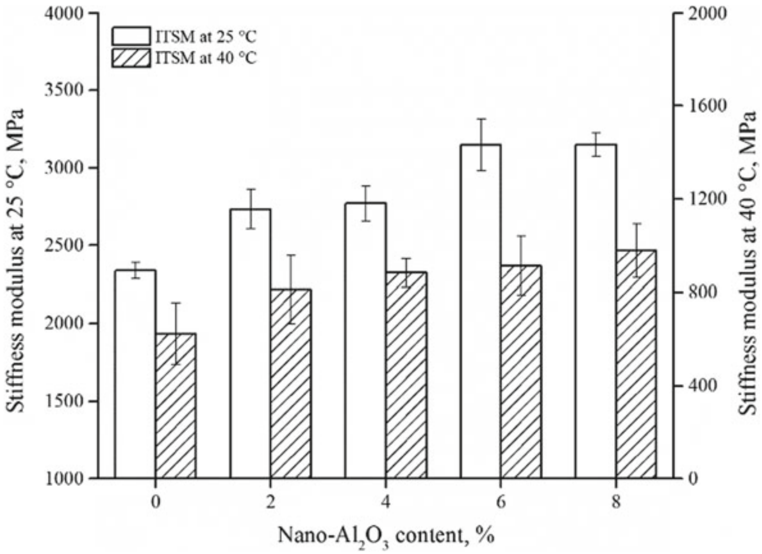

Fig. 12 ITSM results at 25 and 40 °C

with 2, 4, 6, and 8% nano-Al_2O_3 were 17, 19, 35, and 36% higher than the ITSM of the control mix. Corresponding improvements at 40 °C were 30, 42, 47, and 57%. The improvements at the high-service pavement temperature of 40 °C were more prominent than those at 25 °C. This finding indicated that the nano-Al_2O_3 modified mixtures demonstrated better stiffness properties than the control mixture, and the improvements increased with an increase in nano-Al_2O_3 content. The results of temperature sweep and MSCR testing also revealed that the nano-Al_2O_3 modified binder had a higher stiffness than the control binder.

4 Conclusions

In this study, the characteristics of asphalt binders and mixes modified with various dosages of nano-Al_2O_3 particles were examined. The following conclusions are formed based on the outcomes:

- Blends prepared with nano-Al_2O_3 were found to be storage stable. In comparison with the control binder, adding nano-Al_2O_3 enhanced the viscosity and softening point.
- The results of temperature and frequency sweep tests revealed that nano-Al_2O_3 improved the stiffness and elastic characteristics of the binders, resulting in improved rutting resistance.

- The MSCR J_{nr} values decreased when the nano-Al_2O_3 dosage was increased, indicating that the binders were more resistant to permanent deformation.
- The addition of nano-Al_2O_3 to the asphalt mixtures enhanced the indirect tensile stiffness modulus, showing that the asphalt mixes with nano-Al_2O_3 modified asphalt binders had improved stiffness characteristics.

Findings of the study indicate that nano-Al_2O_3 fares favorably as an asphalt binder modifier. Further, characterization of asphalt mixes incorporating the nano-Al_2O_3 modified binder needs to be done to arrive at understanding of fatigue and moisture damage resistance benefits of using the nano-Al_2O_3 in asphalt binder and mixes.

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