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Evaluation of Selected Performance Properties of Nanoclay-Modified Asphalt Binders

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Abstract. Asphalt binders are often modified with additives such as acid, polymer, or a combination of multiple additives to achieve improved performance to sustain heavy loads and adverse weather conditions. According to some previous researches, nanoclay can be a good alternative of currently practiced Styrene-Butadiene-Styrene (SBS) modification, and the former is expected to reduce the overall cost of the asphalt binder. Three types of nanoclay (Cloisite 10A, 11B, and 15A) were blended with asphalt binders prepared from two different sources (Arabian Crude and Canadian Crude). A blending protocol has been developed to blend nanoclay with the base binders. Mechanical properties including viscosity, rutting parameter have undergone significant changes after the nanoclay modification. It was also observed that nanoclay modified binders offer different moisture susceptibility while bonding with different aggregates; the nanoclay modified asphalt binder exhibits better bonding with gravel than sandstone. Mechanistic properties such as viscosity and rutting parameter are found to be highly correlated with the chemical compositions. Binders from the Canadian crude showed more colloidal stability than binders from the Arabian crude after nanoclay modification.

1 Introduction

As a viscoelastic material, the general tendency of asphalt binder is to flow at a higher temperature and becomes hard at a lower temperature. Surface chemical properties and temperature susceptibility of asphalt largely control the pavement stiffness both at high temperature (rutting) and low temperature (cracking). The extent of temperature susceptibility largely depends on the petroleum source from where the asphalt binder has been prepared. As the temperatures in the United States vary significantly from one place to another, a base binder prepared from the same source may require a physical, mechanical, or chemical modification, a combination of two or more types of modification before it can be used in the designated temperature regions. Though asphalt binder is a complicated combination of hydrocarbons, it can be divided into four major fractions: Saturates, Aromatics, Resins, and Asphaltenes (SARA). Chemical modification may also cause changes in both chemical composition and mechanistic properties of asphalt binder. So far, polymers such as rubber, SBR (Styrene Butadiene Rubber), SBS (Styrene Butadiene Styrene), Elvaloy® have been used as modifiers to improve the binder performance. Among these polymers, SBS is widely being used to modify performance grade (PG) binders so that asphalt can sustain higher load and extreme temperature events. But, it increases the binder cost significantly. Therefore, researchers have looked for an alternative modifier, which will improve the mechanical properties of binders at a lower cost. Nanoclay is economical and naturally abundant, and many researchers have proposed nanoclays as a suitable alternative. This is because nanoclays possess nanoscale phenomena such as the quantum effects, high surface energy, spatial confinement, and a large fraction of surface atoms.

2 Literature review

Several publications were reviewed for accumulating the existing research on the nanoclay modified asphalt binders. Publications from different reputed research entity including Transportation Research Records, Federal Highway Administration (FHWA) records, and projects of Departments of Transportation (DOTs) were considered for the literature review. Previous studies have claimed that when HMA mix is dispersed at a nanoscopic level, nanoclays improve properties of asphalt binders including quantum effects, structural features, high surface energy, spatial confinement, and a large fraction of surface atoms. You et al. [1] recommended a blending protocol of a rotation of 2500 rpm, a temperature of 160°C, and a mixing duration of 3 hours. Another group of researchers [2] used blending protocol consists of a rotation of 4000 rpm, a temperature of 130°C, and a mixing duration of 2 hours. Zhang et al. [3] used two steps: mixing nanoclay with the binder at 160°C for 20 minutes at the rotation speed of 2000 rpm and followed by an increased temperature of 170°C for 40 minutes with a rotational speed of 4500

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rpm. Other researchers [e.g., 4, 5] used different blending protocol for different types of nanoclay.

You et al. [6] also studied the effect of nanoclay on PG 58-34 asphalt binder. The complex shear modulus (G*) was found to increase by 66% and 125% for 2% and 4% nanoclay modifications, respectively. Jahromi and Ahmadi [7] tried Cloisite 15A and Nanofill15 and observed increased stiffness, rutting resistance, indirect tensile strength, and a resilient modulus but a decreased fatigue performance. Ghile [8] reported that nanoclay modification enhanced mechanical properties such as creep and fatigue resistance. You et al. [1] studied two types of nanoclays (A and B) as modifiers of a performance grade binder PG 58-22 and found a significant increase in the rutting parameter of nanoclay-modified binders.

Molecular level mechanistic properties can be used to predict the field performance of asphalt pavements which can be evaluated by using an Atomic Force Microscope (AFM). The AFM collects nanoscopic level data that provides the morphology of the surface and nanomechanical properties such as elastic modulus, hardness, adhesion, and energy dissipation. There are multiple studies that evaluated the mechanical properties of asphalt binders using different AFM systems. Masson et al. [9] studied 13 asphalt binder samples to characterize the surface morphology and observed distinct morphological clusters. Dourado et al. [10] used the AFM-based nano-indentation technique for evaluating selective mechanical properties (e.g., elastic modulus) at different places on the surfaces of samples. You et al. [6] developed a systematic AFM-based test procedure to evaluate the adhesive properties of asphalt binders.

Researchers at Texas Transportation Institute introduced a parameter “compatibility ratio” (CR) using the surface free energy (SFE) theory. The CR is the ratio of work of adhesion of an aggregate and binder system in dry condition to that of the same system in the presence of water. For evaluating the SFE of asphalt binders, these researchers used the Good-van Oss-Chaudhury theory to estimate the SFE. In this procedure, three reference solvents have been used to measure the contact angles to quantify three major SFE components: monopolar acidic (Γ^{+}), monopolar basic, (Γ^{-}) and polar Lifshitz-van der Waals (Γ^{LW}) components.

Weigel and Stephen [11] studied the interrelationship between the chemical fractions of the asphalt binder with mechanical properties. They studied 11 binder samples with four different types of aggregates. They found a strong influence of chemical fractions on mechanistic properties (stiffness, viscosity, deformation behavior, and temperature sensitivity) of asphalt binders. They also claimed that the binder-aggregate interaction depends mostly on the adhesion properties. Their research showed a significant influence of the chemical fractions on the physical, rheological, aging and adhesion behavior of the properties of asphalt binders. Alam and Hossain [12, 13] studied asphalt binders modified with PPA (Polyphosphoric acid) and SBS. They found that modification increase the Asphaltene contents as well as the viscosity of asphalt binder. Moreover, a rearrangement in the chemical fractions was observed due to the SBS modification. A different group of researchers [14] claimed that SBS performs far better than the combination of PPA and SBS or PPA alone.

Paliukaite et al. [15] introduced a model for evaluating the colloidal stability of the asphalt binder. Among the four chemical fractions of asphalt binder, Asphaltenes are highly polarized and dispersed in a system of Aromatics and Resins. The solubility of asphaltene determines the colloidal stability of an asphalt binder and can be determined by Gaestel Index (I_c), as shown in Equation 1. A very high I_c indicates an unstable colloidal structure, whereas a very lower I_c means the binder is soft and also colloidally unstable. This is why neither too high or too low I_c is desirable.

$$\text{Gaestel Index } (I_c) = \frac{\%\text{ Saturates } + \%\text{Asphaltnes}}{\%\text{ Aromatics } + \%\text{ Resins}} \quad (1)$$

The primary objective of this study is to observe the performance of nanoclay modified asphalt binders. Specific objectives of the proposed study are: (i) develop a suitable blending protocol to modify base asphalt binders with nanoclay; and (ii) examine performance properties (rutting, fatigue, and moisture resistance) of nanoclay-modified asphalt binders.

3 Materials and methodology

PG 64-22 binder samples from two different sources (S1 is an Arabian crude and S2 is a Canadian crude) were collected from a local refinery. Three types of organically treated nanoclay (Cloisite 10A, Cloisite 11B, and Cloisite 15A; each at 1%, 2%, and 3%) were used to modify the virgin binders. The percentages of nanoclay were selected based on existing literature and manufacturer’s recommendations.

A high shear mixer was used to blend the nanoclay with asphalt binder which can be operated at different durations, rotational speeds, and temperatures. Nine different trials were conducted using different combinations of time (2, 3, and 4h), rotation (1500 and 2000 rpm) and temperature (150 and 160℃). Rotational Viscosity (RV) test (AASHTO T 316), Dynamic Shear Rheometer (DSR) test (AASHTO T 315), and Atomic Force Microscope (AFM) tests were completed for each trial to find the suitable blending combination. Besides routine Superpave tests, the following tests were conducted to estimate performance properties:

An optical Contact Analyzer (OCA) was used to evaluate the moisture susceptibility of the nanoclay-modified binders. The Sessile Drop analysis uses the SFE theory to estimate CR of the modified binder samples. In this method, a droplet of a liquid with known surface energy was placed on a solid surface. Properties like the shape of the drop, contact angle, and surface energy of the liquid are used to determine the SFE of the solid. Moisture susceptibility is then estimated from this approach by observation of the CR values of the selected binder-aggregate system. Also, the AFM technology was used for evaluating moisture susceptibility. The PFQNM mode of a Bruker AFM was to estimate molecular level morphological and nanomechanical properties of the nanoclay-modified asphalt binders. Furthermore, all the nanoclay-modified asphalt binders were characterized in terms of the changes in their chemical compositions: Saturate, Aromatic, Resin, and Asphaltene. The test was executed in accordance with ASTM D 4124-09.

3 Results and discussions

3.1 Blending protocol

Among others, the dynamic viscosity at two different rotations (1500 and 200 rpm), two selected temperatures (150 and 160°C), and two different durations (2 and 3 hrs) were recorded to establish the blending protocol. As seen in Figure 1, for a rotation of 2000 rpm, a temperature of 150°C, and a blending time of 2 hours, shown as 2000-150-2 in the legend in the chart, the viscosity values remained in an acceptable range and had a very little variation with respect to time. At the same test condition, the morphology, adhesion, DMT (Derjaguin–Muller–Toporov) modulus and deformation values of the samples obtained from the AFM test were investigated and they were found to be uniformly distributed within the scan area (Table 1). Thus, a blending protocol (2h, 2000 rpm, and 150°C) was established.

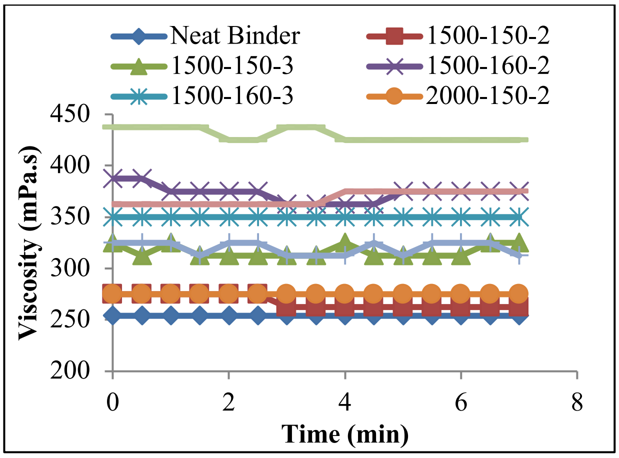


Fig. 1. Viscosity at different rotations, temperatures, and durations for modified binders.

3.2 Viscosity and stiffness

Irrespective to the source, the viscosity values were observed to increase after modification (Figure 2). For binders with 1%Cloisite 10A, the viscosity values at 135°C increased by 187% which is higher than any other nanoclay modified Source 2 binders considered during this study.

Black diagrams for modified binders are observed to shift to left from the black diagram of neat binders (Figure 3). The G* values for nanoclay-modified asphalt binders increased but δ values decreased with respect to unmodified asphalt binder. At 64°C, asphalt binder from Source 1 with the 1% Cloisite 11B showed the maximum G* and the δ. Both "A" (intercept) and VTS (viscosity temperature susceptibility) parameters for nanoclay-modified asphalt binder decreased from that of the neat binder. Thus, the nanoclay-modified asphalt binder is found to be less temperature susceptible compared to the neat binder. The G*/sinδ values also increased for modified binders, and binder with the 1% Cloisite 11B showed the maximum G*/sin d value. For Source 2 binder modified with nanoclay, the G* values also increased and δ values decreased. The maximum G* value was found for the Source 2 asphalt binder with 1% Cloisite 10A.

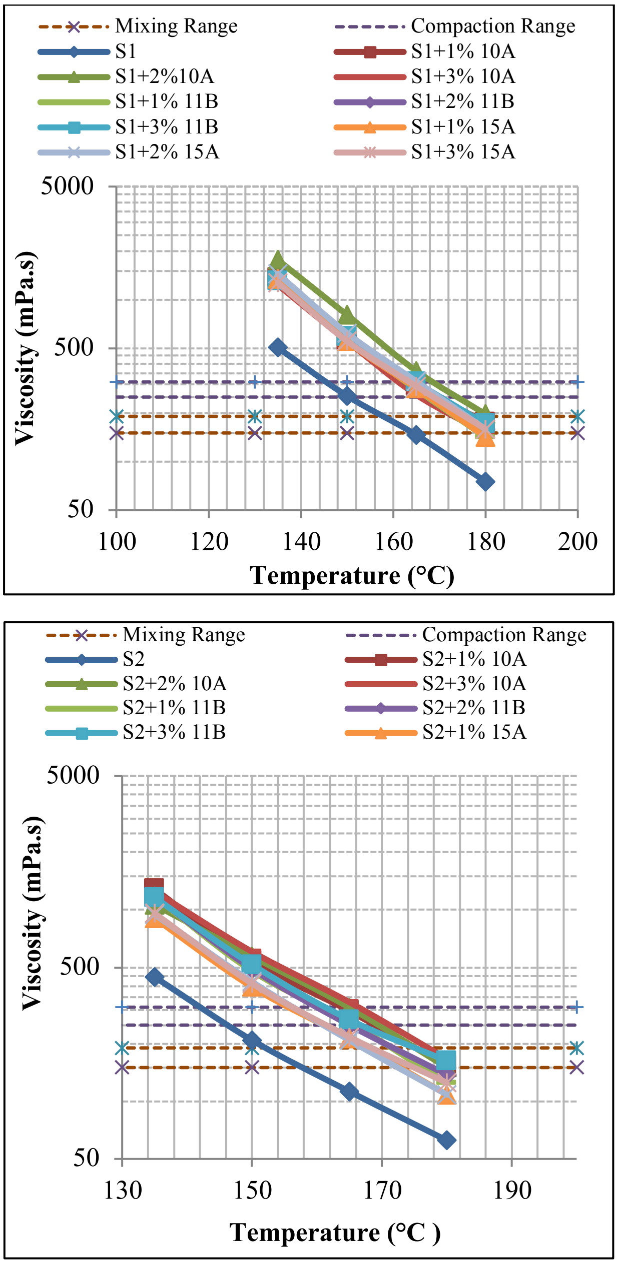


Fig. 2. Viscosity vs. temperature for modified binders (top Source 1 and bottom Source 2).

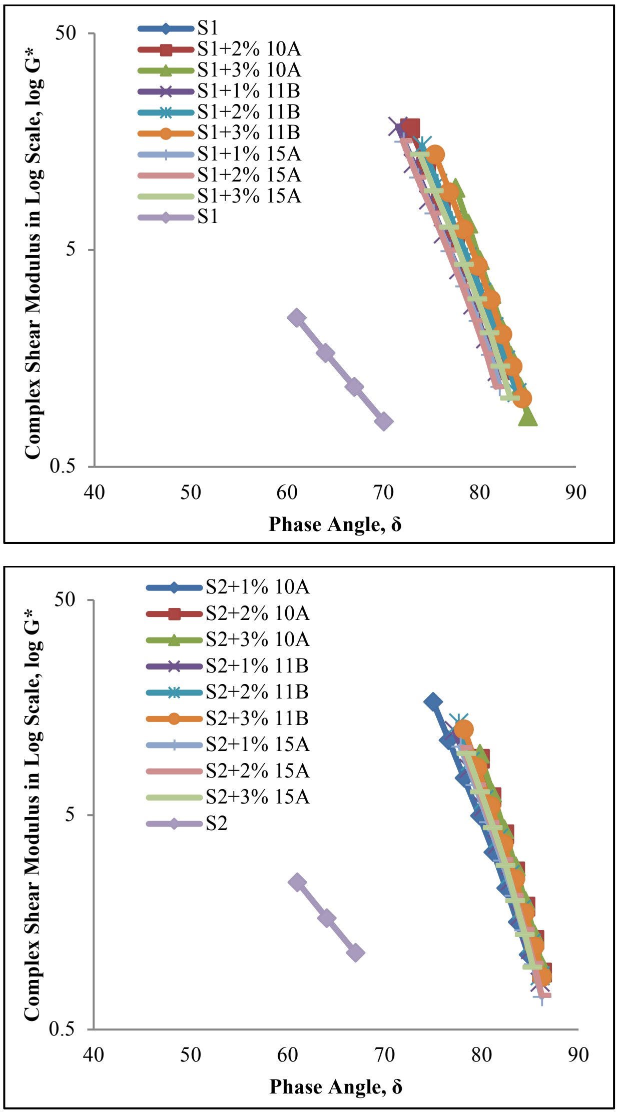


Fig. 3. Complex shear modulus (G*) vs. phase angle (δ) curve for nanoclay modified binder.

3.3 Sessile drop test

For evaluating stripping resistance of aggregate-binder systems, two types of local aggregates (sandstone and limestone gravel) were considered. The CR values for S1 binders with sandstone remained below 1.0 (Figure 4). But, for gravel, the CR is higher for the gravel (2 to 5), which indicates compatibility between the modified binder and gravel. It is noted that a CR > 1.5 indicates very good bonding, CR from 0.75 to 1.5 is good, CR from 0.5 to 0.75 is poor, and CR < 0.5 is very poor. For Source 2 binders, the CR found to be higher than Source 1 binders. Moreover, the CR for gravel was also higher than sandstone. So, it is conclusive that the nanoclay-modified binders would always provide good bonding with limestone gravel.

3.4 Atomic force microscope (AFM)

Morphological and nanomechanical properties of tested asphalt binders as shown in Table 1. The maximum height sensor value was observed for the asphalt binder modified by 3% Cloisite 15A and the minimum for asphalt binder modified by 1% Cloisite 15A. The DMT modulus, adhesion and deformation decreased for nanoclay-modified asphalt binders. Asphalt binders from Source 1 with 1% Cloisite 10A showed the minimum adhesion and deformation values.

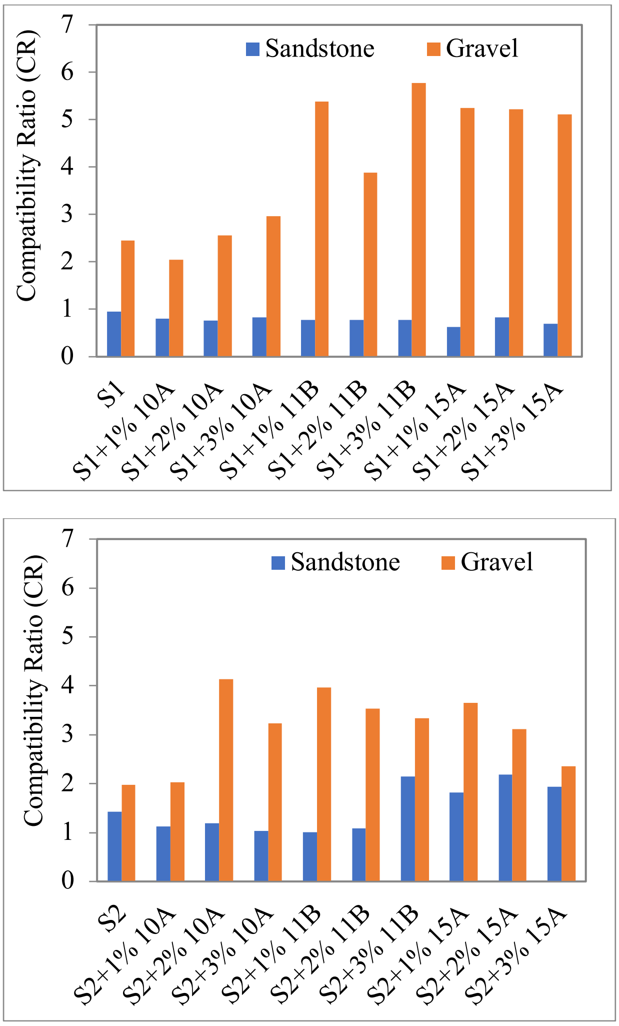


Fig. 4. Compatibility of nanoclay modified asphalt binders (top Source 1, bottom Source 2).

3.5 SARA analysis

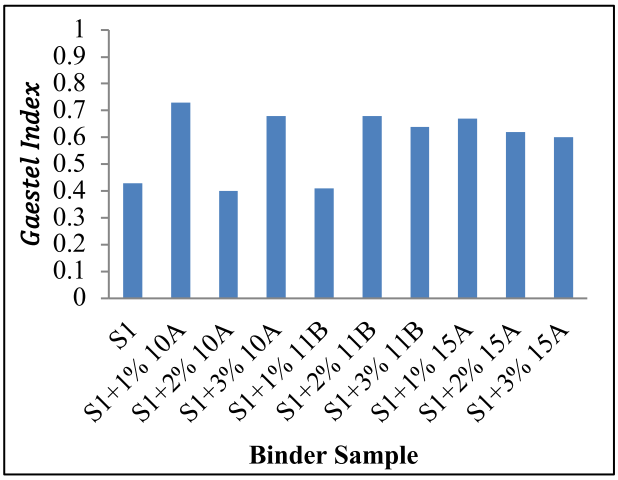
After the chromatographic separation, chemical fractions were determined to estimate the I_c. A majority of the nanoclay-modified Source 2 binders have lower I_c than the corresponding Source 1 binders, as shown in Figure 5. Such observations indicate that most of the Source 2 binders are colloidally more stable than the corresponding Source 1 binders. Asphaltene contents were found to be highly correlated with the G*/sinδ. An inversely linear relationship was observed between the Asphaltene content and rutting parameter (Figure 6). Moreover, the Asphaltene content also had a significant impact on the viscosity of the binders. With the increase in the Asphaltene content, the viscosity at 150°C was observed to increase gradually in a linear fashion (Figure 7).

Table 1. Value of the morphological and nanomechanical properties.

Sample ID	Average Height Sensor (nm)	Average DMT Modulus (MPa)	Average Adhesion (nN)	Average Deformation (nm)
S1 (Neat Binder)	7.79	3221	362	5.41
S1+1% 10A	7.32	755	73.7	1.94
S1+2% 10A	13.5	1768	222	2.8
S1+3% 10A	6.52	2937	305	5.37
S1+1% 11B	13.7	625	136	4.2
S1+2% 11B	8.36	682	102	3.19
S1+3% 11B	9.32	2081	196	4.41
S1+1% 15A	6.5	694	176	4.21
S1+2% 15A	9.46	1522	163	4.05
S1+3% 15A	15.8	1234	261	3.55

3 Conclusions

Modification of asphalt binders with nanoclays appears to be a promising technology to improve mechanical and chemical properties of asphalt binder. In this study, nanoclay was blended with asphalt binders using a high shear mixer to make a fully dispersed and exfoliated binder. Viscosity increased significantly (up to 187%) due to different dosages of nanoclay compared to the neat binder. The G*/sinδ values also increased significantly due to the addition of nanoclay. Morphological and nanomechanical obtained through an atomic force microscope (AFM) revealed that the surface roughness did not vary significantly, but the adhesion and deformation values were found to decrease. While evaluating the aggregate-binder compatibility, the work of cohesion values was found to be higher than the base binder. It was also observed that the nanoclay modified binder offered better bonding with gravel than sandstone. From the chemical analysis of the unaged nanoclay-modified asphalt binders, correlations were found between the SARA fractions and the mechanistic properties of the binder. Using regression analysis, it was observed that mechanical properties like viscosity, rutting parameter etc. are highly correlated with the Asphaltene fraction of the modified asphalt binders. Based on the findings of this limited study, it could be said that Cloisite 10A and Cloisite 11B have high potential to become alternatives of polymers. But, further laboratory and field performance data are required to establish this idea.



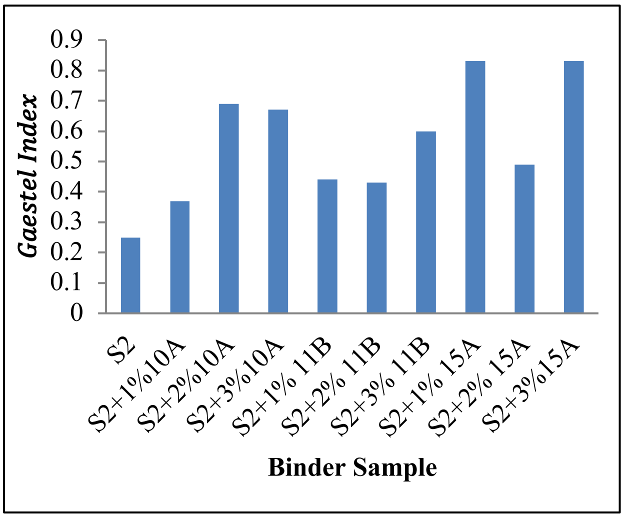


Fig. 5. Colloidal stability for nanoclay-modified binders (top source 1, bottom source 2).

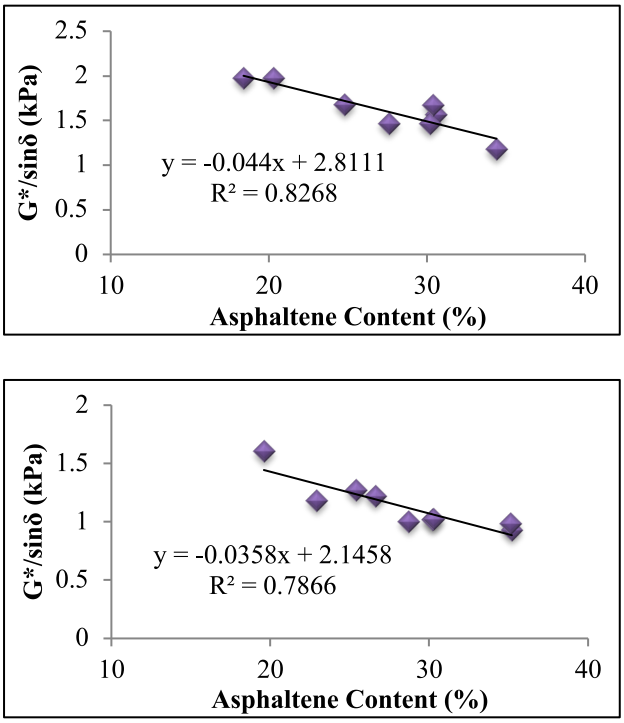


Fig. 6. Correlation between asphaltene and rutting parameters for nanoclay modified asphalt binders (top source 1, bottom for source 2).

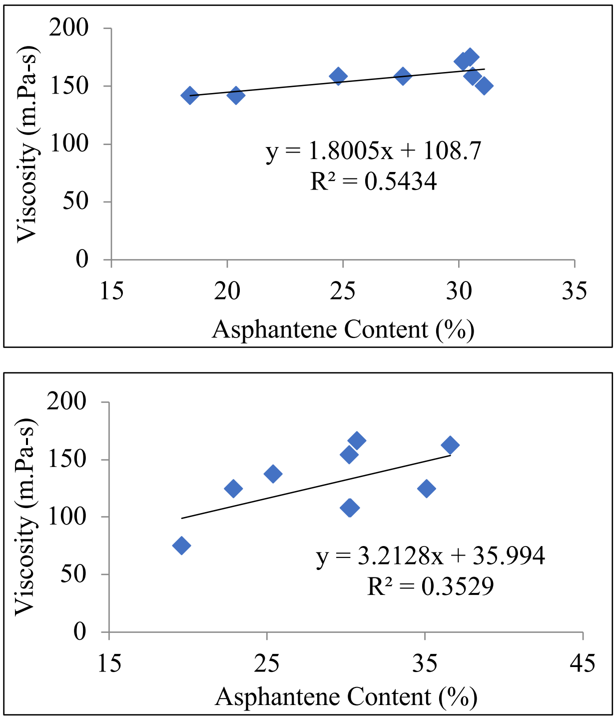


Fig. 7. Correlation Between Asphaltene and Viscosity for Nanoclay Modified Asphalt Binders (top Source 1, bottom Source 2).

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