Effects of nanoclay modification on the rheological properties of bituminous binders

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Digital Object Identifier (DOI): dx.doi.org/10.14311/EE.2016.235

ABSTRACT

The rheological behavior of bitumen is very complex phenomenon varying from purely viscous to elastic depending on loading time and temperature. As a visco-elastic material, bitumen plays a prominent role in determining many aspects of road performance. Numerous investigations have been carried out on incorporating modified bitumens to improve the performance of bituminous composites. This paper presents a laboratory-scale evaluation of the conventional and the fundamental rheological characteristics of modified binders including nanoclay contains 35-45 wt. % dimethyl dialkyl (C14-C18) amine (DANC) and montmorillonite. Modified bitumen samples were produced by mixing base bitumen with DANC and montmorillonite at three different additive contents. The conventional properties of the modified binders were evaluated in terms of their properties using penetration, softening point and dynamic viscosity tests. The fundamental viscoelastic properties of the modified binders were determined using dynamic (oscillatory) mechanical analysis and were presented in the form of temperature- and frequency-dependent rheological parameters. It was determined by the results obtained from the conventional tests that the softening point and the viscosity increased and the penetration and the thermal sensitivity decreased with increased DANC. Dynamic shear rheometer test results indicated that the temperature and the frequency had a significant effect on the complex modulus of DANC and montmorillonite modified binders. The research results are an indication that the DANC has promising potential to reduce the permanent deformation or rutting of asphalt pavements. Investigation of the types of different additives yielded that the most effective additive was DANC in all experiments.

Keywords: Additives, Modified Binders, Rheology, Viscosity

1. INTRODUCTION

Bitumen is basically defined as a viscous non-volatile liquid or solid matter that contains hydrocarbons and derivatives, soluble in trichloroethylene, and softens with heat [1]. Bitumen could be obtained during refining of petroleum, could be found as a natural deposit (Lake Trinidad), or as a compound in asphalt formed naturally with mineral content [1]. Bitumen is a bright black material conventionally used to create a water impermeable layer and to bind aggregates in asphalt mixtures with its adhesive properties, with high molecular weight and containing various hydrocarbons in its structure. Bituminous materials are usually obtained by refining petroleum and their costs continuously increase due to the reduction of petroleum reserves. Thus, it is important to improve the properties of bituminous material and prolong their economic lives [1].

Impairments such as wheel tracking, moisture-induced damage, low temperature and fatigue cracks occur due to traffic loads and environmental conditions on hot mix asphalts [2]. To increase the resistance and performance of bitumen and hot mix asphalts against temperatures and traffic loads and hence to prolong the service life of the pavement, mineral, organic, natural and industrial additives are used [3]. These additives could be directly added to the mixture, or could be added to bituminous binder as well. When they are added to bitumen, modified bitumen; when they are added to the mixture, modified mixture is obtained. Usually polymer-type material is used in bitumen modifications. The most commonly used polymer for bitumen modification is styrene–butadiene–styrene (SBS) followed by other polymers such as styrene–butadiene–rubber (SBR), ethylene–vinyl-acetate (EVA), and polyethylene [4,5]. Another additive is natural asphalt to modify the base bitumen. Trinidad Lake Asphalt (TLA) and gilsonite are most widely used natural binder modifiers. Various studies showed that use of TLA and gilsonite in hot mix asphalts enhances their properties [6-9]. In addition, various studies are being conducted to improve the properties of bituminous binders and mixtures using different material.

Recently studies that scrutinize the use of nanomaterials to improve the endurance of construction material as a result of developing technology gathered momentum. Nanomaterials are defined as materials with at least one dimension that falls in the length scale of 1– 100 nm. Due to the small size and high surface area, the property of nanomaterial is much different from normal size materials. Thus, research engineers attempted to apply the nanomaterial into pavement engineering. Studies are concentrated on especially the use of Nano clay as an additive in bituminous binders [10].

A study by Yao et al. scrutinized the effects of the use of only Nanoclay and the use of Nanoclay with polymers in bitumen modifications on the rheological properties of the binders. It was determined as a result of binder experiments that the use of only Nanoclay in bitumen modification significantly increased viscosity and complex shear modulus values. It was also indicated that polymer modified Nanoclay use decreased these values slightly. Furthermore polymer modified Nanoclay use gave better results for fatigue crack and rutting when compared to Nanoclay use [11].

Yao et al. attempted to increase fatigue crack and rutting resistance of bituminous binders by utilizing 4 different Nano or micro-sized material in bitumen modification in a study they conducted. Experiments conducted on modified bitumen determined that use of Nanomer, carbon microfibers and Nanoclay increased resistance to permanent deformation. In addition, polymer modified Nanoclay use decreased complex shear modulus, however increased resistance to fatigue crack [12].

Jasso et al. examined the effects of montmorillonite clay addition to styrene-butadiene-styrene modified bituminous binders in the study they conducted. Results of dynamic shear rheometer and bending beam rheometer tests demonstrated that montmorillonite addition to polymer modified bitumen provided rheological benefits [13].

Bonati et al. analyzed the effects of conventional and Nanoclay additives on fire reaction in their study. Nano calorimeter test results showed that aluminum hydroxide use provided the best results and Nano composite use provided benefits [14]. A similar study by Pei et al. determined that use of 1% organo-montmorillonite and 3% alumina-trihydrate provided the best results for fire reaction. It was identified that use of both additives together provided less gas emissions during fire and sustained better thermal stability results when compared to pure bitumen [15].

Yu et al. used montmorillonite and organomodified montmorillonite in bitumen modification in the study they conducted. X-Ray diffraction analyses demonstrated that montmorillonite modified bitumen had an intercalated structure, while organomodified montmorillonite had exfoliated structure. It was indicated that both additives increased viscosity, softening point, and complex shear modulus values, and reduced phase angle values. Using these values, it was determined that both additives improved the rheological properties of the bituminous binder and increased their high temperature resistance. It was also indicated that montmorillonite provided better results when compared to organomodified montmorillonite, and when less than 3% is used from both additives, stable results were obtained for storage stability [16].

Yusoff et al. analyzed the effects of Nano-silica addition to polymer modified bitumen on hot mix moisture sensitivity in their study. They added 2% and 4% Nano-silica to PG 76 polymer modified bitumen and conducted moisture susceptibility, resilient modulus and dynamic creep tests on HMAs using the modified bitumen prepared. Scanning electron microscopy tests indicated that Nano-silica was distributed well in modified bitumen. Nano-silica use in addition to polymer modified bitumen increased the resistance of bituminous hot mixes to moisture damage, fatigue crack and tracking. Furthermore, as the Nano-silica content increased, ageing index increased as well, thus it was determined that Nano-silica use decreased the ageing effect [17].

Yu et al. examined the effects of organo-montmorillonite on ageing of the bituminous binders in the study they conducted. Viscosity and softening point test results indicated that organo-montmorillonite use decreased the effects of ageing and

after short and long term ageing ductility retention rate increased. In addition, it was determined that after UV ageing, organo-montmorillonite use decreased the ageing effect considerably when compared to pure bitumen [18].
In this study, two different types of Nano material (Nanoclay containing 35-45 wt. % dimethyl dialkyl (C14-C18) amine (DANC) and montmorillonite) in three different ratios (2%, 3%, and 4%) were added to pure bitumen to obtain modified bitumen. Penetration, softening point, rotational viscosimeter (RV) anddynamic shear rheometer (DSR) tests were conducted on pure and modified binders to determine the effects of additives on the rheological structure of bitumen.

2. MATERIALS and METHODOLOGY

The binder used in the study was B 160/220 class asphalt cement procured from TÜPRAŞ refinery in Turkey. Nanoclay containing 35-45 wt. % dimethyl dialkyl (C14-C18) amine (DANC) and montmorillonite were used in bitumen modifications. During the modification process of the binder, the additives were added 2%, 3%, and 4% per weight to the binder and mixed. The mixing process was conducted by a mixer with 1000 rpm speed at 180oC temperature and the original bitumen and the additive were mixed for 60 minutes. A precise mixer with a capability of 0-2000 rpm speeds (Figure 2.1) was used in the study. Softening point (EN 1427), penetration (EN 1426), rotational viscosity (ASTM D4402), and dynamic shear rheometer (AASHTO TP5) tests were conducted on the binders obtained in 3 different combinations using the mixer mentioned above. Test equipment are presented in Figure 2.2.

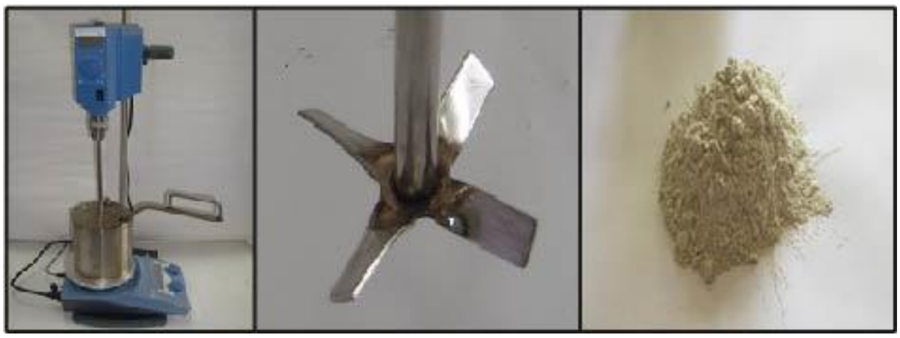

Figure 2.1: Modified bitumen mixture equipment and the montmorillonite used.

Figure 2.2: Penetration, softening point, viscosity and DSR experiment equipment.

3. EXPERIMENTAL STUDY

3.1. Penetration Test Results

The results of the penetration test conducted in compliance with the EN 1426 standard are presented in Figure 3.1. Penetration test results indicated that penetration values decreased with additive use with the exception of 2% montmorillonite in bitumen modifications, and penetration values decreased as the additive content increased. Furthermore, it was determined that DANC use in bitumen modifications was more effective than the use of montmorrilonite (Figure 3.1). 2%, 3%, and 4% DANC use decreased the penetration values by 5.0%, 13.0%, and 16.2% respectively when compared to pure binder. With the use of 2% montmorrilonite, the penetration value increased by 5.5%, thus decreasing the consistency of the binder. With the use of 3% and 4% montmorrilonite, the penetration values were reduced by 3.4% and 3.7%, respectively. It was determined that the penetration value for the modified bitumen containing 4% montmorillonite was higher than all DANC modified bitumen, thus having lower stiffness.

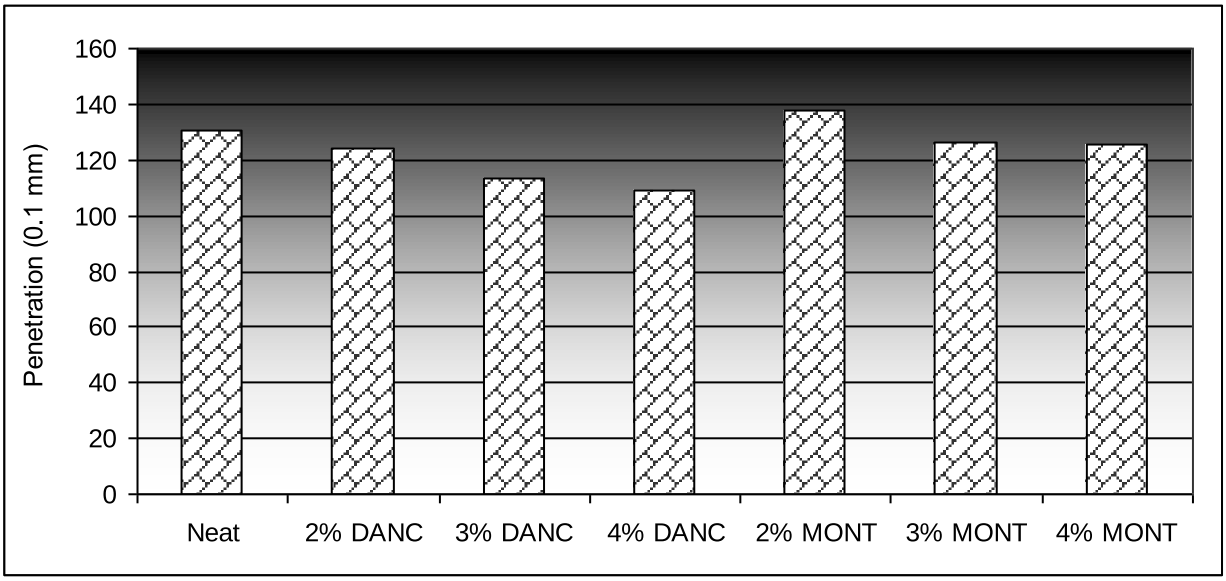

Figure 3.1: The penetration values for pure, DANC and montmorillonite added modified bitumen.

3.2. Softening Point Test Results

Examination of the Figure 3.2, where the softening point values applied to pure and modified bitumen are given would indicate that use of the additives with the exception of 2% montmorillonite increased the softening point values and as the additive content increased, the rise in these values continued. When compared to use of pure bitumen, 2% DANC use in bitumen modification resulted a 0.6% increase, 3% DANC use resulted in a 2.4% increase, and 4% DANC use resulted in a 5.4% increase in softening point values. With the use of 2% montmorillonite, softening point value decreased 2.2% when compared to pure bitumen. Softening point values, parallel to the penetration values, demonstrated that 2% montmorillonite use decreased the stiffness of bituminous binders for all bitumen modifications. While 3% montmorillonite use increased the softening point value by 0.9% relative to pure bitumen, 4% montmorillonite use increased the same value by 1.4%. Softening point values, parallel to the penetration values, showed that DANC use was more efficient in all bitumen modifications when compared to montmorillonite use, and it was determined that even 3% DANC use was more efficient than 4% montmorillonite use.

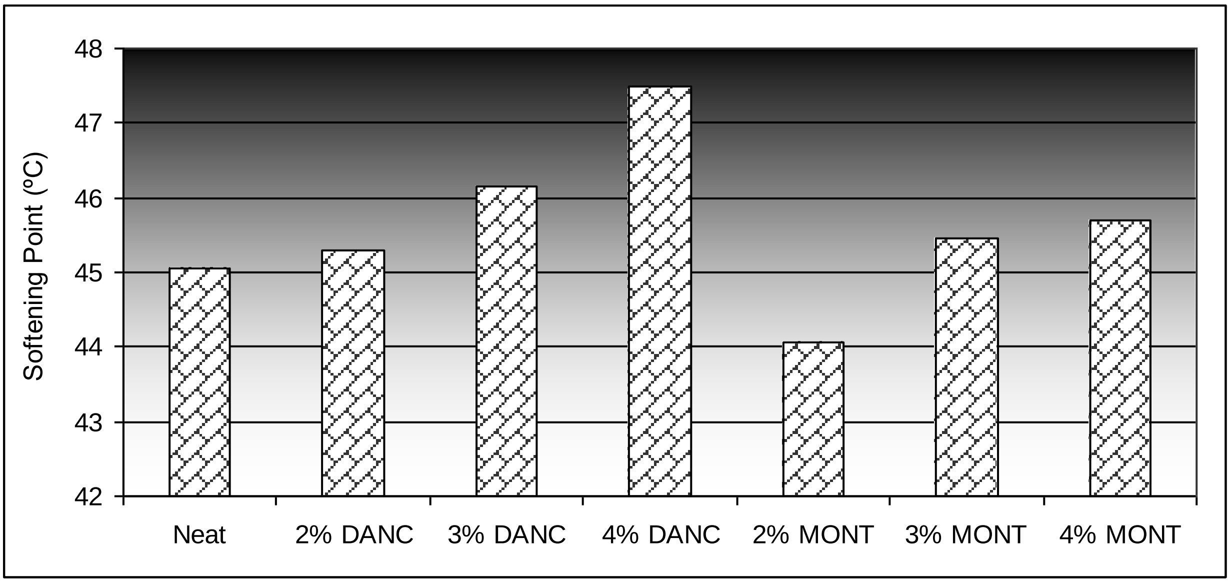

Figure 3.2: Change in binder softening point values with additive type and content

3.4. Thermal Sensitivities of Binders

Penetration index (PI) values that are an indicator of thermal sensitivities of bituminous binders, which are calculated by using penetration and softening point values, were calculated using Formula 1 [1].

$$\frac{20-PI}{10+PI}=50\frac{\log 800-pen}{T_{RB}-25} \tag{1}$$

In the formula, pen. depicts the standard penetration value at 25°C; and TRB denominates the softening point (ring and ball method) value. There is an inverse proportion between PI value and thermal sensitivity. As PI value increases, thermal sensitivity decreases. Figure 3 demonstrates the penetration index values for pure and modified binders. It was identified that use of additives did not caused a consistent change in PI values and the increase in additive content resulted in inconsistent changes (Figure 3.3). It was found that modified bitumen with 4% DANC, 3% and 4% montmorillonite content had higher PI values when compared to pure binder, thus had lower thermal sensitivities. It was determined that thermal sensitivities of other modified bitumen (2% and 3% DANC, and 2% montmorillonite modified bitumen) were higher than the pure binder. Assessment of all binders identified that the binder with the highest thermal sensitivity was 2% montmorillonite modified binder, and the binder with the lowest thermal sensitivity was 4% DANC modified bitumen.

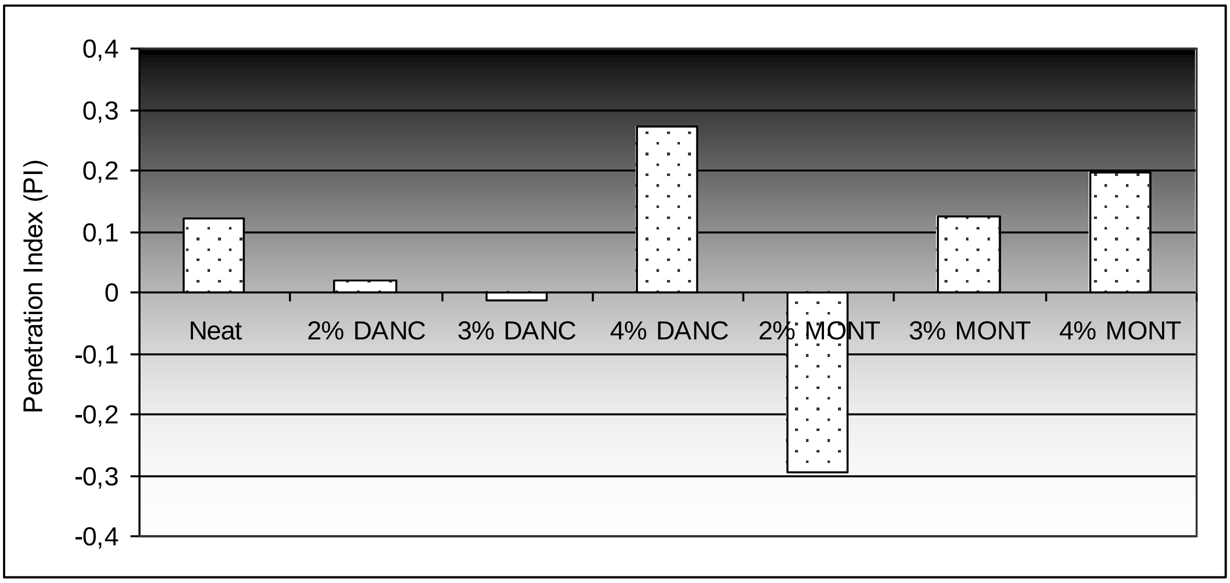

Figure 3.3: Penetration index values for the binders

3.4. Rotational Viscometer Test Results

Rotational viscosity tests were conducted on pure and modified binders at 135 and 165°C temperatures. Spindle nr. 27 and 20 rpm speed were used in the test. Figure 3.4, where the results of rotational viscosity tests that were applied to the binders are displayed, demonstrated that although the viscosity values increased with DANC use, use of montmorillonite in bitumen modifications did not have a significant effect on viscosity. It was identified that as DANC content increased, viscosity values increased consistently under both temperatures.

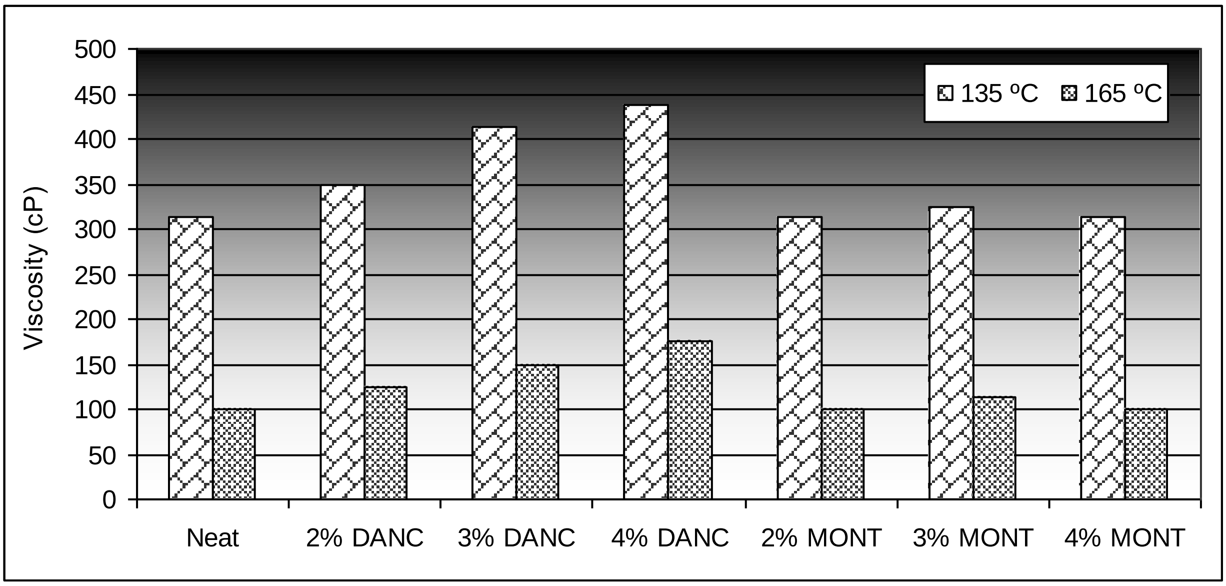

Figure 3.4: The change of viscosity values of binders due to temperature and the use of additive.

Modification index values were determined to assess the effect of additive type on viscosity values by comparing the viscosity values of the modified bitumen with the viscosity values of the pure bitumen at the same temperature. These values are presented in Table 3.1. It was determined from the modification index values that the additive that increased the viscosity value the most was the one with 4% DANC content (40% at 135ºC, 75% at 165ºC). Although the viscosity values for the modified bitumen containing 3% montmorillonite was slightly higher when compared to pure binder, viscosity values of modified bitumen with 2% and 4% montmorillonite were the same as the pure bitumen under both 135 and 165ºC temperatures.

Table 3.1: Mixing and compaction temperatures of mixtures and viscosity ratios of binders

Binder type	Viscosity at 135ºC (cP)	Viscosity at 165ºC (cP)	$\eta_{modified} / \eta_{neat}$ at 135ºC	$\eta_{modified} / \eta_{neat}$ at 165ºC	Mixing Range, ºC	Compaction Range, ºC
PG 52-28	312.5	100.0	1.00	1.00	148.0 - 154.2	135.1 - 140.8
%2 DANC	350.0	125.0	1.12	1.25	154.2 - 161.1	139.8 - 146.1
%3 DANC	412.5	150.0	1.32	1.50	156.7 - 163.6	142.3 - 148.6
%4 DANC	437.5	175.0	1.40	1.75	159.9 - 167.5	144.1 - 151.1
2% montmorillonite	312.5	100.0	1.00	1.00	148.0 - 154.2	135.1 - 140.8
3% montmorillonite	325.0	112.5	1.04	1.13	151.8 - 158.5	137.7 - 143.9
4% montmorillonite	312.5	100.0	1.00	1.00	148.0 - 154.2	135.1 - 140.8

Viscosity – temperature graph was plotted using the viscosity values obtained and aggregate mixing and compaction temperatures for the bituminous binders were determined. Temperature values corresponding to 170 ± 20 cP (150 and 190 cP) for mixing, and 280 ± 30 cP (250 and 310 cP) viscosity values for compaction were determined for this purpose [19,20]. The results are presented in Table 1. It was found that DANC use would require higher temperatures for mixing and compaction, thus more energy would be required to heat the bitumen. It was identified that if 4% DANC modified bitumen is used, 12.6ºC more heat during mixing and 9.4ºC more heat during compression would be required.

3.5. Dynamic Shear Rheometer Test Results

Binder properties were assessed in two different ways using dynamic shear rheometer (DSR) test equipment in the study. Initially, rutting parameter G*/sin δ values were determined by applying loading at 10 rad/sec velocity on the binders in compliance with the Superpave method. To assess the effects of the additives more clearly, the variation of G*/sin δ values for binders that contain 3% DANC and 3% montmorillonite with the temperature was plotted (Figure 3.5).

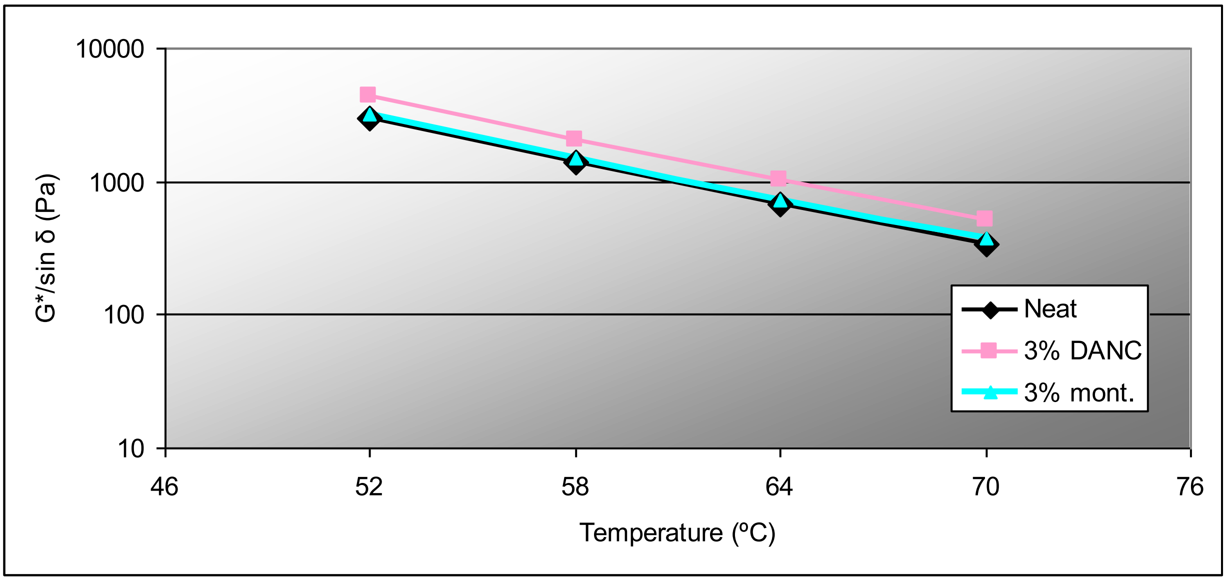

Figure 3.5: The change of G*/sin δ values of the binders due to temperature.

Figure 3.5 demonstrates that modified bitumen with 3% DANC content displayed the highest values and pure binder had the lowest values. It was determined that pure and modified bitumen with 3% montmorillonite content conformed to Superpave specifications criterion of 1000 Pa at 64ºC temperature the latest. Based on these values it was determined that performance level high temperature value for pure and modified bitumen containing 3% montmorillonite was PG 58 and performance level high temperature value for modified bitumen containing 3% DANC was PG 64. It was determined based on G*/sin δ values that failure temperature for the pure binder (the temperature where G*/sin δ value is 1000 Pa) was 60.6ºC, failure temperature for the binder with 3% montmorillonite was 60.8ºC, and failure temperature for the binder with 3% DANC was 64.1ºC. Results demonstrated that montmorillonite use did not have any positive or negative effects on rutting parameter, while DANC use provided significant benefits under all test temperatures.

DSR tests were conducted further in the study on binders in 10 different frequencies that changed between 0.1 and 4 Hz and under 4 different temperatures (40, 50, 60, and 70ºC). Master curves for the results were plotted using Arrhenius equation. Figure 3.6 shows the variations of the master curves for pure and modified bitumen containing 3% montmorillonite and 3% DANC with frequency.

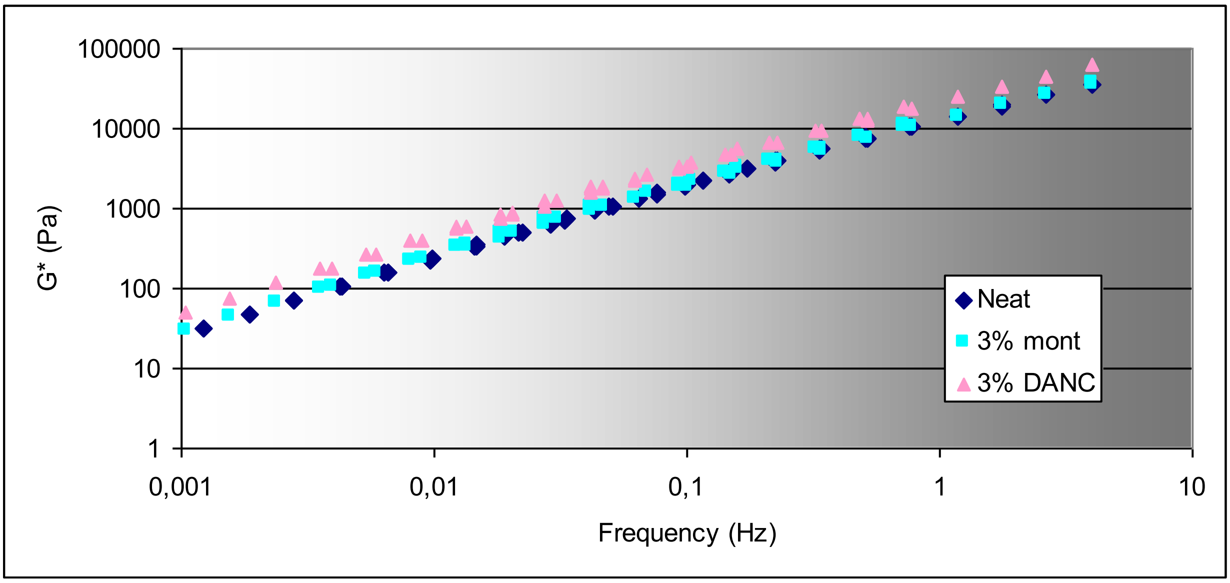

Figure 3.6: The master curves of modified bitumen that contain pure and 3% montmorillonite and DANC.

It was determined as displayed in Figure 6 that master curves for pure and modified binders with 3% montmorillonite content were close to each other and the master curve for the modified bitumen containing 3% DANC had higher G* values when compared to other binders. It was identified that master curves of modified bitumen containing montmorillonite were similar to each other. Results showed that DANC use was more efficient than the use of montmorillonite.

4. RESULTS

Two different Nanomaterial (Nanoclay containing 35-45 wt. % dimethyl dialkyl (C14-C18) amine (DANC) and montmorillonite) were tested in bitumen modification and penetration, softening point, rotational viscometer, and dynamic shear rheometer tests were conducted on modified bitumen. Penetration index values, the indicator for thermal sensitivity, were determined based on penetration and softening point values. Both rutting parameters for the binders based on the Superpave method were scrutinized using DSR tests, and master curves were plotted to assess the effects of temperature and frequency on the complex shear modulus.

According to the results of the experiments conducted; penetration, softening point, viscosity and DSR experiment results, it has been determined that use of montmorillonite has no effect on the rheological characteristics of the pure binder, yet the use of DANC has positive effects on the rheological characteristics of the bituminous binder. According to the penetration index values, it was determined that 4% of DANC use is the additive type and content that decreases the thermal sensitivity most. In the literature review it was emphasized that the use of montmorillonite improves the rheological characteristics of the bituminous binder [16]. The reason not to obtain similar results in this study is considered due to the characteristics of both montmorillonite and bitumen. In order to consider this study valid, it is necessary to conduct similar studies with different bitumen and in addition it would be useful to conduct mixture experiments along with the binder experiments.

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