PERFORMANCE EVALUATION OF NANO-MATERIALS IN ASPHALT CONCRETE MIXTURES

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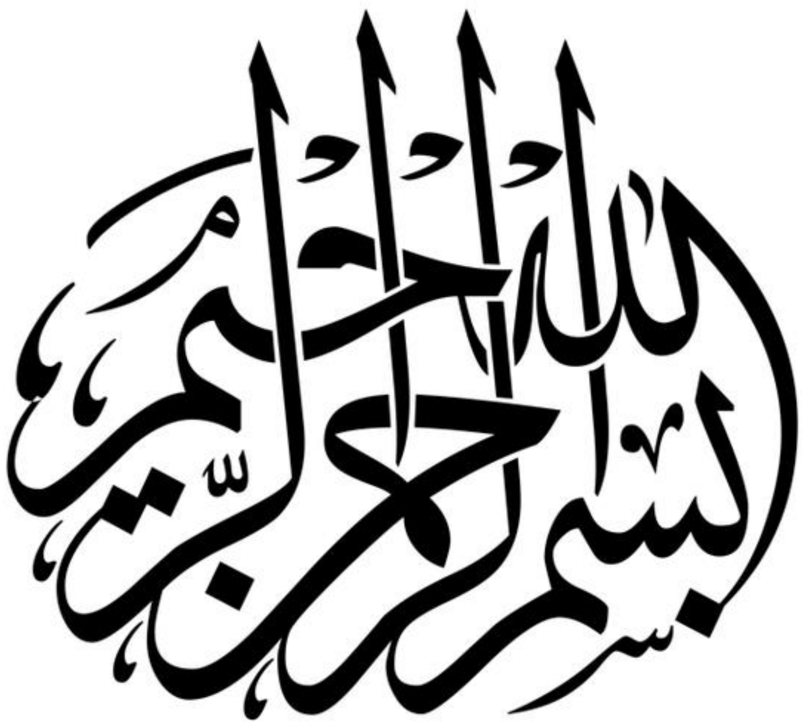

IN THE NAME OF ALLAH THE BENEFICENT THE MERCIFUL

This is to certify that the thesis titled

PERFORMANCE EVALUATION OF NANO-MATERIALS IN ASPHALT CONCRETE BINDERS (A SYNTHESIS OF EXISTING BODY OF KNOWLEDGE)

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The Syndicate

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Abstract

Nanoparticles are utilized to modify the asphalt binders and improve the pavement mechanical performance against the common distresses of permanent deformation (rutting propensity) and fatigue, manifested on asphalt pavements. This study reviews the existing body of knowledge on Nano-modification of asphalt binder using four different Nano-materials: Carbon Nanotubes (CNTs), Carbon Black, Graphene Nano Platelets (GNPs) and Nano Clay. The motivation behind this in-depth review of Nano-modification of asphalt binder was to synthesize the implications of various Nano-materials on the mechanical properties of asphalt binder. The study concludes by proposing the suitability of each of the Nano-material – its extent/ proportion by weight of asphalt binder, economic suitability, environmental compatibility and availability in Pakistan. CNTs (with optimum percentage of 1%) yielded best results – increases stiffness, rutting performance and resistance against fatigue cracking. Carbon Black improved high-temperature performance, such as rutting resistance, fatigue performance, and stiffness, but had no considerable effect on low-temperature cracking. Subjected to the type of binder and polymers employed, carbon black up to 6% (by weight of binder) revealed to be a potential modifier of asphalt binder. Graphene Nano-platelets (GNPs) produced PG-70 when 4% of GNPs are added to the binder. The wheel-tracking slope (WTS) decreased from 0.58 to 0.35 and this reduction is also suggestive/ attributed to high resistance to permanent deformation. Nano Clay added asphalt binder's Complex Shear Modulus (G*) increased while the Phase Angle (δ) dropped, indicating enhanced stiffness and elasticity. Enhanced rigidity improved rutting resistance, while increased elasticity provided maximum deformation recovery. 2-4% (by weight of binder) of Nano-clay in asphalt binder yielded optimum results. The results indicate that the addition of Nanoparticles enhanced the rutting performance and strength of asphalt mixtures. Nano-modified asphalt (given the reasonable selection of Nanomaterials for the base binder) can offer many benefits (i.e. improve the durability of asphalt pavements, save energy and cost, decrease maintenance and rehabilitation) requirements in road construction industry of Pakistan.

CHAPTER 1

INTRODUCTION

1.1.General

The mainstay of a country's economy and transportation is efficient road infrastructure. Worldwide evolution has erupted because of massive purchasing power, domestic growth, commercial arcades and corporate governance laws. As the demand for user satisfaction with road loading capacity is increasing. Researchers in this area are very focused on the needs of the users and strive to meet these requirements. A common use of bitumen globally is for constructing pavements. Ancient civilizations used Bitumen as a bonding material and a water proofing agent. It is made up of highly concentrated organic liquids with a high viscosity that is easily soluble in carbon disulfide. This composition, which has a dark and sticky appearance, is generally composed of polycyclic aroma of highly condensed hydrocarbon.

Bitumen is still used in the construction of pavements around the world today. Crude oil distillation in refineries is used to produce this bonding agent. It increases the elasticity and viscosity of asphalt in pavements, making them more flexible. The composition of asphalt-based concrete is complex because it is primarily determined by the degree of aggregation of binding interfaces, conveyance based on void size, and void interconnectivity. In the case of heavy traffic, one-of-a-kind applications are required, which are obtained through stiffening mixtures. Taking into account all of these important facts and figures, observations were made that led to efforts such as the addition of certain chemical additives and the understanding of various bituminous parameters. Because of its complexity, understanding the nature of asphalt is tiresome. It is necessary to understand asphalt pavements whether they can bear fractures or not during the designation of highly demanded and respected HMA pavements. Researchers in the past studied and observed the presence of fatigue and its likelihood of failure under heavy traffic. The researchers' current challenge is to understand how fatigue behaves in pavements while taking into account newer, more complex materials.

1.2.Problem Statement

The road traffic has increased to a high level during the last two decades, whereas the retention of these roads was almost impossible, probably due to the budget. This resulted in a rapid deterioration of roads in Pakistan. There are two possible solutions for avoiding the disasters.

- Increased budget for road maintenance
- Improved road structures, innovative road designs, and new effective and high-quality construction materials.

This study focuses on the effects of Nanomaterials and variations in bitumen gradation. Following the research's main concept of determining bitumen characteristics by adding Nanomaterials. Carbon nanotubes, Graphene Nanoplatelets, Nano silica, Carbon black, and Nano clay are among the Nanomaterials used here. These materials are used in road construction as binding agents, protective coatings, and waterproofing.

Various failures occur during the life of asphalt binders. Thermal and fatigue cracking, as well as rutting, are examples of these. These gradations or failures reduce pavement quality and performance. Considering modified bitumen, which is primarily polymers that are bitumen mixtures with percentages ranging from 3% to 6%. Large amounts of polymers are added to produce modified bitumen, but the end result is unsatisfactory in terms of performance and cost. The term Nano-composite was coined later; previously, it was referred to as sub-atomic compositions or half breeds. The essentials of these nanoparticles were a combination of at least one nanoparticle layered with binders.

When regular inorganic fillers are added, the rates fluctuate between a minimum of 20% and a maximum of 40% by weight. In the case of Nano-composites, the mill amount would be between 1% and 6%. This pattern leads to contented circumstances that include less weight, which is financially beneficial. Other focal points include improvements in mechanical conductivity, thermal properties, and gas obstruction properties.

1.3. Research objectives

To determine the properties of bitumen by adding nanoparticles. Nanoparticles are the handheld dirt of the new Era, resulting in a wide range of complex composites. Because of their energized nature, Nano-composite polymers have been identified as one of the most promising classes discovered to date.

Different methods were used to add different nanoparticles to the bitumen, changing the quantity of nanoparticles different physical properties of bitumen can be upgraded efficiently. Different binder tests were conducted including softening point, penetration, ductility rotational viscosity (RV), and dynamic shear rheometer (DSR) tests, and the results were compared to the results of tests performed on unmodified asphalt binder. Tests results visualize change in rheological properties of bitumen such as solidness, edge diminishing and protection at mature level. There are other objectives that are going to be covered:

1. To thoroughly examine the existing literature and discusses Nano-modification of bitumen and approaches to applying Nanomaterials to bitumen to improve performance.
2. To inspect Asphalt's thermal and physical properties bind at maximum and minimum temperatures, causing variations in mixture cost and end performance.
3. To propose the extent of suitability of each of the Nano-material and come up with best percentile by weight of bitumen binder, economic suitability, environmental compatibility and availability in Pakistan.

1.4. Scope

The main purpose of this synthesis is to determine the bitumen characteristics by its Nano-Modification. The research focus on comparative performance analysis of asphalt binder by modification with each Nanoparticle and to assess the improvements in various binding agent essential properties, resistance to rutting, fatigue resistance, value of stability, resistance to flow penetration and temperature susceptibility. Also the best percentile by weight of bitumen binder, economic suitability, environmental compatibility and availability in Pakistan.

CHAPTER 2

LITERATURE REVIEW

2.1.Bitumen

It is a unique mixture of both synthetic and natural components obtained via ocean deposits, crude oil, vegetable matters, remnant of plants and fossils. Considering the layers of the earth, the top most matter travelled from top layer to the last layer and ultimately to the earth crust where it got compressed, decayed, burnt and got converted into recognizable raw form. This process goes millions of years, resulting in formation of massive reservoirs in layer of pervious rocks. Today, crude oil is obtained via drilling in oil and gas sectors, and dynamiting mines. Bitumen id extracted from all these resources and still comes in very less amount.

Certain standards identifies Bitumen in various ways, but in accordance with the British standards, it defines bitumen as " It can be in any composition of matter i.e. Solid, Liquid, Gas Hydrocarbons and their derivatives".

2.2.Bitumen Composition

This section foreshadows both chemical and physical composition of bitumen. The structure of bitumen is composed of different molecules having different chemical and structural properties all in a manner of complex structure. As it does not have any fixed composition, it contains functional groups, which include functional groups of Hydrogen, Sulfur, Carbon dioxide and Oxygen. Though there is no fixed composition, there are few rough percentages which are as follows:

- Oxygen 0% to 1.5%
- Hydrogen 8% to 11%
- Nitrogen 0% to 1%
- Sulfur 0% to 6%
- Carbon 82% to 88%

2.3.Physical Properties

An important part of discipline of Engineering, testing the samples to check whether they measure up to the standards of ASTM and ASME. This shows that there exist some physical properties in bitumen which undergo testing and observations.

2.4. Penetration

A standard procedure for checking products consistency, a needle of 0.1kg is sustained on bitumen surface for 5 seconds for testing penetration as bitumen is a blend of various ingredients, importance of temperature measurement comes in testing at a standard temperature of 287K.

2.4.1. Softening Point

Softening is an alternative methodology to penetration. To further check the penetration in various styles, it plays its role. This test is performed with two steel balls that are occupied with metallic rings and are carved with bitumen sheets and then temperature is raised, heat exchanger efficiency is reduced. The vibrations cause shortening in life expectancy of the boilers. As there is danger to boilers life expectancy, investigation of the vibrations becomes an important part. As the area of caution is to minimize the vibrations, this method helps in understanding the change of phase of bitumen in crucial or areas with construction work or extreme temperature.

2.4.2. Viscosity

Viscosity is the type of physical property and the main definition is “resistance to flow”, that can be studied at different temperatures. A ratio between stress and strain. A material also contains shear due to viscosity, but if that material became independent of shear, the material shift towards Newtonian behavior. For successful operations, engineers estimate time changing stress damage and fatigue damage associated with them. Furthermore, VIV leads to enhance drag force which results in massive elastic displacements and forces of tensile, and are categorized in two types of viscosity that is dynamic and kinematic viscosity. As mentioned before, the relation of temperature is of core importance in kinematic and absolute viscosity which ranges from 65^{o}C to 135^{o}C. A capillary tube viscometer is used for testing that can measure viscosity of an asphalt in specific ranges that are 30^{o}C to 260^{o}C.

2.4.3. Bitumen Rheology

Bitumen rheology is a core component because its application related with dynamic classics which further relates with the study of mechanical vibrations terms an Fourier series. For experimentation, a rigid cylinder having certain degree of freedom and transverse direction for flowing. Simulation doesn't have preferred arrangements, so we can have both one and two degrees of motion freedom inside rigid and flexible cylinders. Short note long, mechanical and thermal behaviors of bitumen can be accessed by graph of stress and strain along with time and temperature response.

2.5.Mechanical Properties

2.5.1.Stiffness

An important mechanical property related with base layer and binder layer. This shows the scale of actual performance. Stiffness is in short, defines how flexible a material is. It distributes the load of traffic on the whole area through the materials flexibility. This property depends upon load frequency and temperature. A ratio of elasticity of stress over strain.

$$E=\alpha/\varepsilon$$

E = Elastic Stiffness

α = Applied Stress

ε = Resultant Strain

For the purpose of design, stiffness requirement is important for observing products behavior that is more or less viscoelastic. There are different methods to observe stiffness of mixture of asphalt that includes multiple bending curves, shear and compression tests etc. There are iterations as well as unreplaced vibration cases that can be handled under the study of poisons ratio and structural properties of fatigue. Although constituents of binder greatly impacts stiffness.

2.5.2.Fatigue

Fatigue is observed in phases of iterations or fluctuations of stresses as both impact and creep loads having negligible tensile strength value. It occurs in two transformations

- Crack Formation
- Crack Propagation

Not only traffic load has impact on it, but environment factors also play along in having a great influence to it. In case of massive vibrations, heat exchangers can get damaged. In order to prevent damage to heat exchangers, vibrations based on vortex induction must be minimized. The property of fatigue in asphalt mixtures gets tackled by stress or strain initially and just by the amount of load, including fatigue or static.

2.6. What is Nano-Technology?

Nano-Technology is the implementation of engineering and science at Nano-scale (i.e. at nanometers). Nano Science and Nano Technology is the application of very small material that cannot be seen with a naked eye into different fields of science. On December 29, 1959 Physicist Richard Feynman, the father of nanotechnology started the first talk on Nanotechnology by saying "There's Plenty of Room at the Bottom" in an American Physical Society meeting at the California Institute of Technology (CalTech). Furthermore he explained scientist would be able to control the particles at atomic and molecular level in future. Ten years later Professor Norio Taniguchi used the term "Nanotechnology" after his explorations of ultra-precision machining.

Nano Technology is approached by two ways which are as follows:

1. Growing from the bottom up.
2. Shrinking from to bottom.

Materials and devices are constructed from molecular components that assemble chemically using molecular recognition principles in the "bottom-up" method. Nano-objects are built from bigger things in the "top-down" manner, which lacks atomic-level control.

2.7. Application of Nano-Technology in Transportation Engineering

2.7.1. Carbon Nanotubes

Carbon Nanotubes are the tubes of graphite carbon at molecular scale and are among one of the most widely used Nano-materials due to their strength, weight, considerable surface area, and compact scale. As compared to other modifiers, CNT incorporation improves substrate properties as well.

Three main types of CNTs are:

- SWCNT (Single-Walled Carbon Nanotube)
- DWCNT (Double-Walled Carbon Nanotube)
- MWCNT (Multi-Walled Carbon Nanotube)

Main properties on CNTs are

- They have low diameter to length ratio.
- Have very stiff and strong fibers.
- Carbon Nanotubes are the strongest Nanoparticle.
- Massive flexibility is found in CNTs.

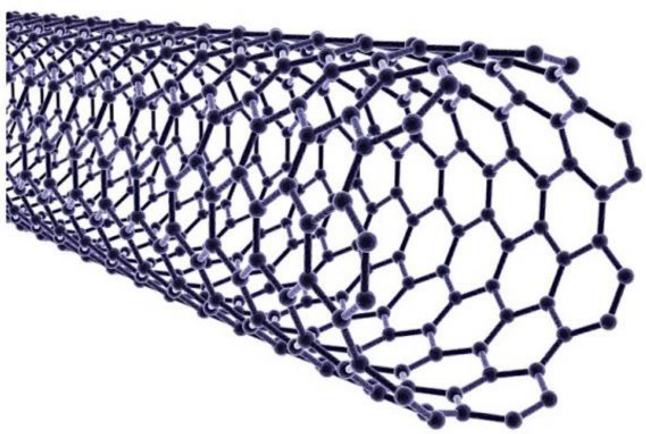

Figure 2.1 Structure of Carbon Nanotube

2.7.2. Carbon Black

Carbon black is obtained by the incomplete combustion of heavy petroleum products and its production occurs under controlled conditions via two processes:

1. Thermal Decomposition of Liquid or Gaseous Hydrocarbons.
2. Incomplete Combustion.

Carbon Black is finding its foot steadily in road engineering as an additive in asphalt binder for enhanced pavement performance. Carbon black filler as bitumen modifier has positive implications on high temperature performance, fatigue resistance, rutting depth and other important engineering properties of the asphalt pavement.

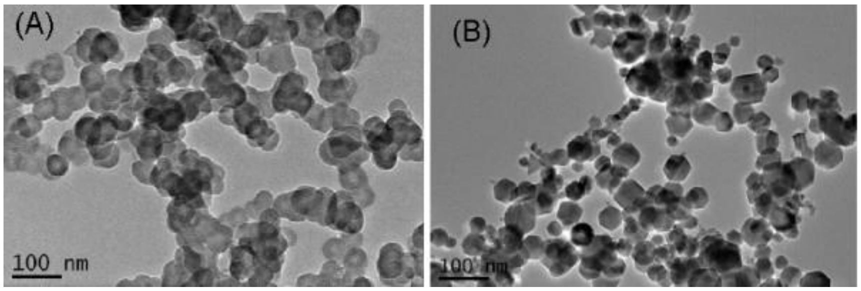

Figure 2.2 Structure development of Carbon Black

2.7.3. Graphene Nano Platelets

Graphene Nano-Platelets are graphene sheets that have been stacked together. A monolayer of carbon atoms makes up a single graphene sheet. The carbon atoms in this structure are arranged in a hexagonal pattern. Graphene is stacked, rolled, and wrapped to make graphite, carbon nanotubes, and fullerenes, respectively. Graphene may be thought of as a building block for the synthesis of carbon allotropes.

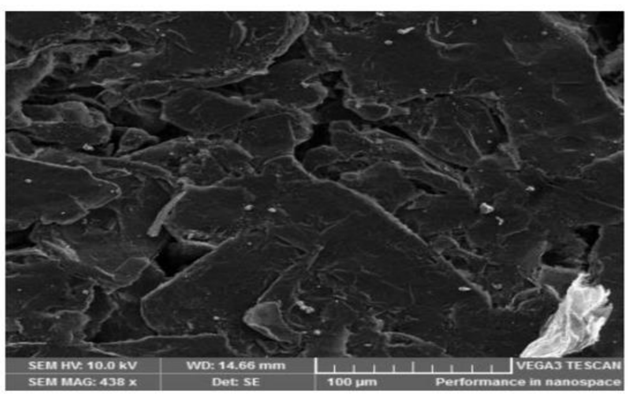

Figure 2.3 A Scanning Electron Microscope (SEM) image of the Graphene Nano-Platelets (GNPs) (100 µm).

GNPs to asphalt mixture pavements can improve a variety of compaction and mechanical properties, hence improving the pavement's durability and performance. The GNPs reinforced asphalt pavements have the potential for long-term applications in the road industry, including both new pavement and road construction and pavement repair, due to their cheap material cost relatively.

2.7.4. Nano Clay

Nanoclay, which is made up of stacked layers of silicates, has been proposed as a cost-effective way to improve the mechanical, thermal, and barrier characteristics of polymer systems. Dispersion of Nanoclay in hydrogel in homogenous manner results in enhancement to its properties. But there is difficulty when dispersion is done with organic polymer when they are in their extreme hydrophilic phase. There are comprehensive revisions on the application, penetration and processing of Nano-Clays. Some common techniques of dispersion are

- Exfoliation
- Flocculation
- Intercalation

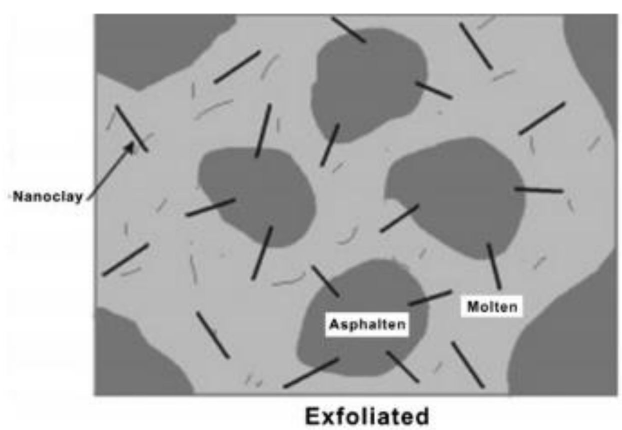

Figure 2.4 Nano-Clay Modified Asphalt

Nano-clay can be effectively used as modifier in asphalt pavements in the regions exposed to higher temperature but Nano-clay modification is least desired for pavements in areas where temperature drops quite low, it is because Nano-silica don't add to the low temperature thermal cracking performance of asphalt binder.

CARBON NANO TUBES

3.1. Carbon Nanotubes

Carbon Nanotubes are the tubes of graphite carbon at molecular scale and are among one of the most widely used Nano-materials due to their strength, weight, considerable surface area, and compact scale. As compared to other modifiers, CNT incorporation improves substrate properties as well.

3.2. Carbon Nanotubes (CNTs) in Asphalt binder: uniform dispersion and improved performance

Due to increased traffic levels and loads, conventional binders are unable to fulfill the new efficiency standards of asphaltic pavements. Because of their outstanding automated attributes, Nanomaterials have gained prominence in modifying bitumen to increase efficiency characteristics of asphaltic concrete. (CNTs) Carbon Nanotubes are among one of the most widely used Nanomaterials due to their strength, weight, considerable surface area, and compact scale. As compared to other modifiers, CNT incorporation improves substrate properties. CNT dispersion of bitumen is a dynamic phenomenon because of the lower diameter to length ratio. In this analysis, Carbon Nanotubes were spread using two different methods into the bitumen i.e., dry, and wet mixing, and the wet mixing process was chosen due to the homogeneity of resulting mixture. To examine the diffusion of Carbon Nanotubes in the asphalt binder, (SEM) Scanning Electron Microscopy was used, while (FTIR) Fourier Transform Infrared Spectroscopy was used to make sure that the solvent in the mixture was fully removed during the wet mixing process. CNTs increased resistance to higher temperatures and permanent deformation tolerance in both mixtures and binders, according to the results. There was also an improvement in moisture tolerance and adhesion properties of bitumen-aggregate (Ahmad et al., 2018).

The materials and methods used here include a 60/70 grade Bitumen as base binder; Multi-walled CNTs were imported from US-Nano, USA. Aggregate was procured from Margalla quarries and NHA class B grade was selected for the asphaltic concrete course, Midpoint gradation was used for this. For mixing of materials two different types of mixers were used i.e., mechanical stirrer and high shear mixer.

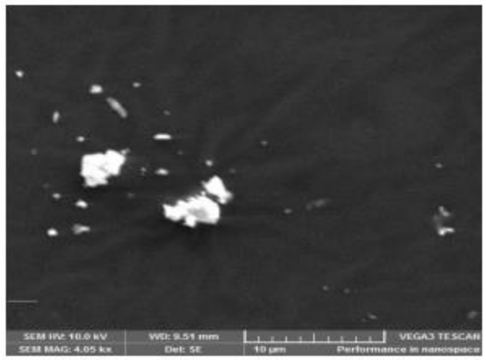

Figure 3.1 CNTs dispersion in bitumen using mechanical stirrer.

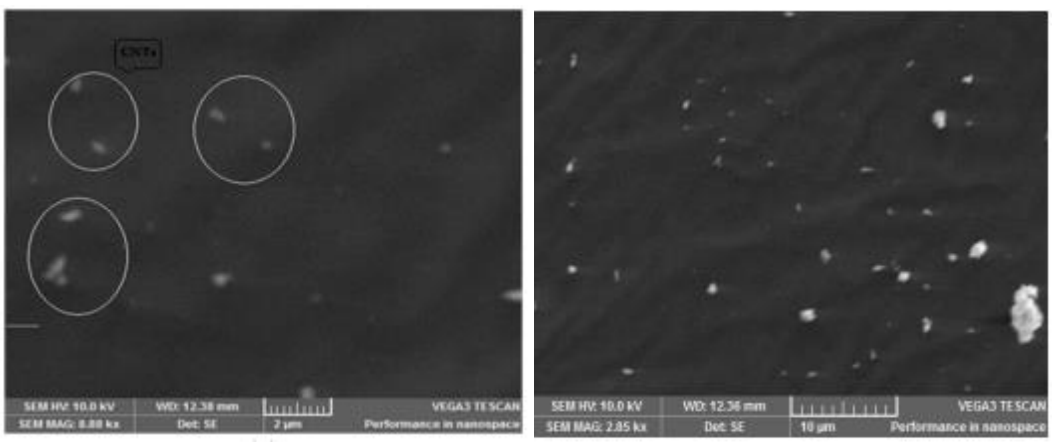

Figure 3.2 CNTs dispersion in bitumen using high shear mixer at different magnifications.

Two different methods of mixing were also used that include the dry mixing and wet mixing. Wet mixing is giving us better results because wet mixing allows CNTs to uniformly disperse into the asphalt binder. Solvent selection for wet mixing was done by testing for time taken for evaporation of different solvents. For this purpose, methanol was selected because of its high evaporation rate. After the preparation of sample, the tests which were run on the sample include SEM analysis, FTIR analysis, Conventional binder tests (softening point, penetration, ductility), Storage stability test, Dynamic Mechanical Analysis (DMA), Bitumen bond strength test, Permanent deformation analysis and Moisture susceptibility analysis (Ahmad et al., 2018).

In comparison to dry mixing, wet mixing methods aid in the uniform diffusion of CNTs in bitumen. For improving the stability of Carbon Nanotubes in solvent, sonication and magnetic stirring are needed. The inclusion of CNTs decreased the penetration and ductility values while increasing the softening point value, implying that inclusion of carbon nanotubes to the bitumen increased its stiffness values.

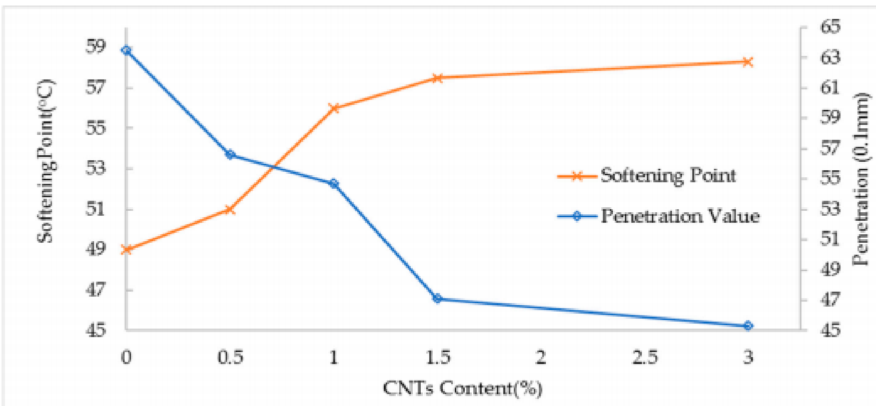

Figure 3.3 Effect on penetration value and softening point value with addition of CNTs.

Adding carbon nanotubes increased the Penetration Index (PI) values of bitumen which decreased the thermal sensitivity and susceptibility.

$$PI = \frac{20 - 500A}{1 + 50A} \ where\ A = \frac{\log(800) - \log(Pen\ at\ T)}{SP - 25}$$

Where T is the temperature at which penetration test is performed (25°C)

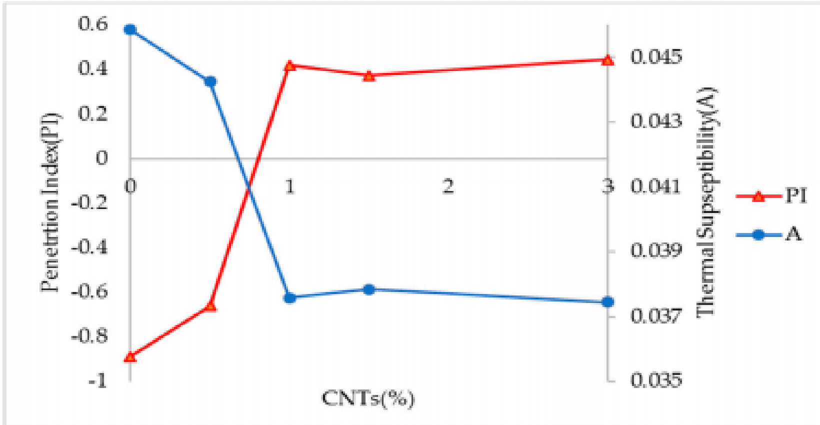

Figure 3.4 Effect on Penetration Index and Thermal Susceptibility with addition of CNTs.

Adding CNTs to the binder, the value of complex shear modulus (G*) increased, and the phase angle appeared to decrease, indicating that the stiffness and elastic behavior of bitumen improved. Rut factor value also increased, which increased the resistance to permanent deformation.

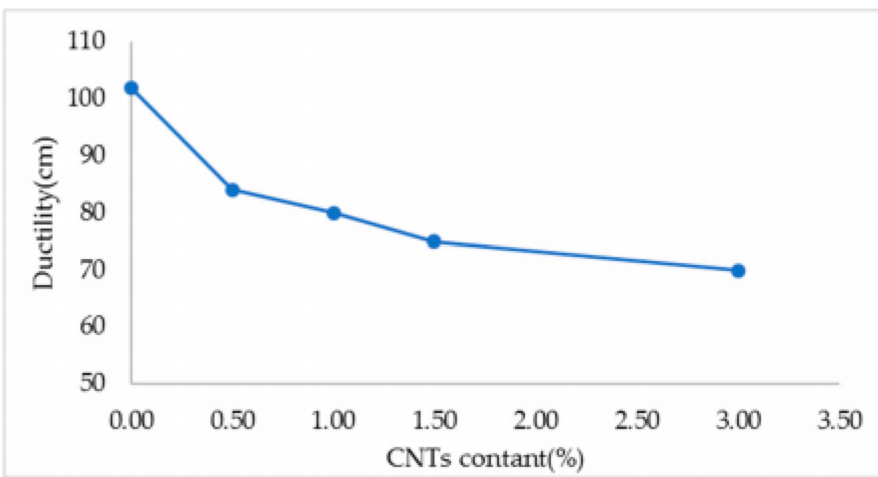

Figure 3.5 Ductility of bitumen with different contents of CNTs.

High Efficiency Rating (PG) of bitumen improved as the CNTs dose increased. PG 76 was accomplished with a 3% addition of CNTs to bitumen, while PG 70 is prescribed for most Pakistan's regions. The addition of CNTs to bitumen increased its bond strength value in both 24 hours dry and 24 hours wet conditions, while the addition of CNTs reduced bitumen's moisture susceptibility. Based on wheel tracker data, according to the results addition of 1% and 3% CNTs lowered the rut depth by 25% and 37%, respectively, measured at 40 °C.

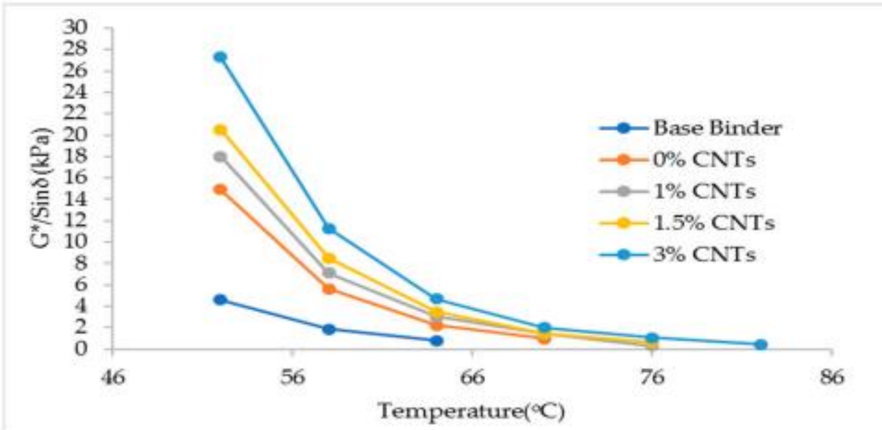

Figure 3.6 Rutting parameter (G/Sinδ) versus temperature for unaged asphalt binder at 10 rad/s.*

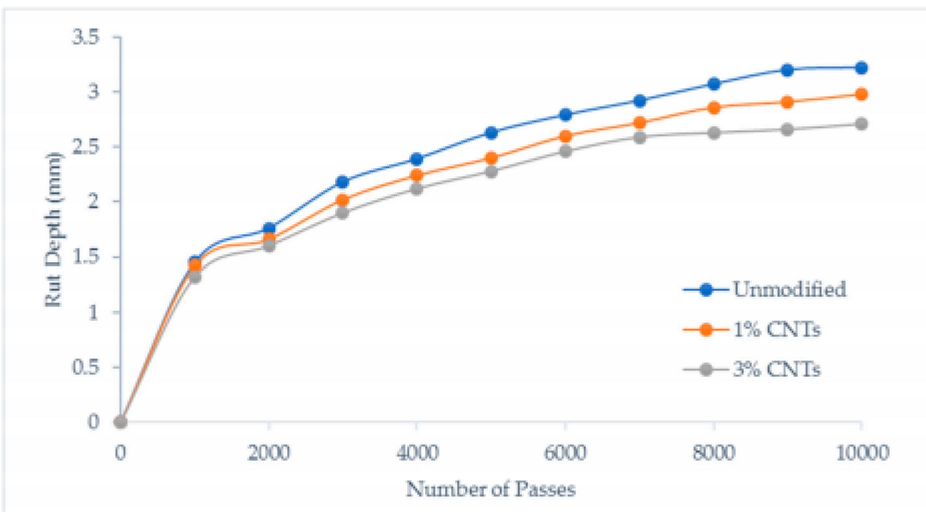

Figure 3.7 Rut depth for unmodified and CNT-modified bitumen mix at 40 ◦C

As wet mixing is a time-consuming procedure, it is still favoured over dry mixing due to its uniform dispersion of CNTs (Ahmad et al., 2018).

3.3. Preparation and Characterization of a Carbon Nanotube-Modified Asphalt Binder

Nanomaterials have been used in a variety of science and technical areas in recent years. Nano-modifiers, compared to macro and micro modifiers, result in better substrate properties due to their compact scale and high surface area. Nanomaterials have remarkable properties that make them ideal for use as asphalt additives. The role of Nanomaterials is discussed in this article, with a focus on using (CNTs) as a modifier for asphalt binders. Different CNT synthesis processes, such as laser ablation, chemical vapor deposition and arc discharge, are discussed, as well as different forms of CNT dispersion techniques in bitumen. The findings of traditional research techniques to define the mechanical capability of CNT-modified asphalt binders, such as penetration grade, softening point, ductility, and viscosity measurements, are also outlined in this work. A thorough review of laboratory experiments on CNT-modified asphalt binder was conducted. Addition of carbon nanotubes to an asphalt binder increases the toughness of material, making it more resistant to rutting. Mixing process, CNT properties, binder type, mixer type, and mixing time all these factors play an important role in modifying the bitumen with carbon nanotubes, influencing the efficiency of the resulting asphalt binder (Faizan et al., 2020).

The impact of carbon nanotubes on asphalt binder strongly depends on the attributes of bitumen used as base and carbon nanotubes used. The homogeneous diffusion of Carbon Nanotubes is the most complicated method in bitumen modification with CNTs. The homogeneous dispersion of CNTs is the most complicated method in bitumen modification with CNTs. Procedure used for mixing i.e., wet, or dry, mixing conditions, and the type of mixer used, which include mixing temperature, mixing frequency, and mixing time, all affect the uniform dispersion of CNTs. The addition of carbon nanotubes to bitumen improves its resilience and elasticity, as shown by lower penetration and higher G* values and softening point. The rutting resistance of a stiffer binder is higher. The impact of carbon nanotubes on molecular structure and chemical composition is yet to be extensively studied. The addition of carbon nanotubes increases binder stiffness, which leads to fatigue cracking. In this case, a thorough examination of modified mixtures and binders is needed (Faizan et al., 2020).

Dry mixing of CNTs in bitumen has gotten a lot of attention, but wet mixing has gotten a lot less. Wet mixing involves dissolving CNTs in a solvent before adding them to the bitumen and mixing them together. The evaporation of the solvent used is a problem with wet mixing. It can alter the properties of the base binder if it is not evaporated. Kerosene, acetone, methanol, and toluene are some of the more commonly used solvents. As a result, more research is needed differentiate the solvents for CNT mixing. Wet mixing is preferred over dry mixing because it gives a more uniform mixture of binder and CNTs. Trials for the best results should be conducted rather than choosing an approach at random (Faizan et al., 2020).

3.4. Examining the impact of wet and simple processes for incorporating Carbon Nanotube modifier into hot mix asphalt

A study conducted by Faramarzi et al., on the subject of incorporation of Nano science in asphalt mixtures was studied. This study aims to conduct an exploratory review of the techniques used for mixing of CNTs with asphalt cement and to examine the viscoelastic properties of normal binders and the AC binders modified with Carbon Nanotubes. Two different mixing techniques, wet and dry, were investigated. The properties of asphalt binder containing different percentages of CNT were tested, with tests including bitumen penetration, softening point, ductility, rotational viscosity (RV), and dynamic shear rheometer (DSR) tests, and the results were compared to the results of tests performed on unmodified asphalt binder. It was concluded that the wet mixing technique produces a more uniform CNT-asphalt binder mixture while dry mixing technique does not make a homogenous mixture but is simpler and more practical than wet mixing technique. Furthermore, the addition of carbon Nano tubes (CNTs) improves rutting resistance ability as well as resistance to thermal cracking (Faramarzi et al., 2015).

There were numerous tests conducted during the study which include SEM analysis, penetration degree test, softening point, ductility, viscosity, and dynamic shear rheometery tests.

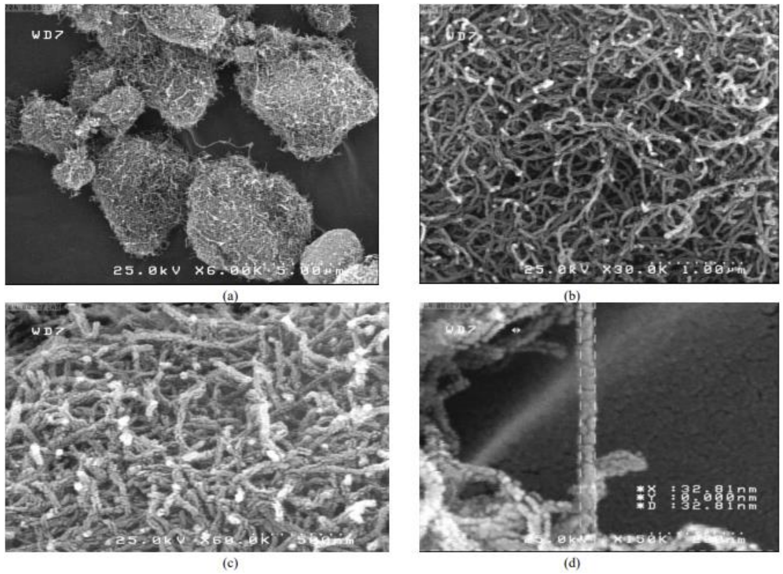

Figure 3.8 SEM Images of Carbon Nanotubes, (a) 5 µm; (b) 1 µm; (c) 500 nm; (d) 200 nm

The results of this study concluded the wet process is more effective way of mixing and it creates a more consistent mixture. Wet processed transformed asphalt binder performed better in the ductility and penetration degree tests, while plain processed asphalt binder performed better in dynamic shear rheometer, viscosity, and softening point tests.

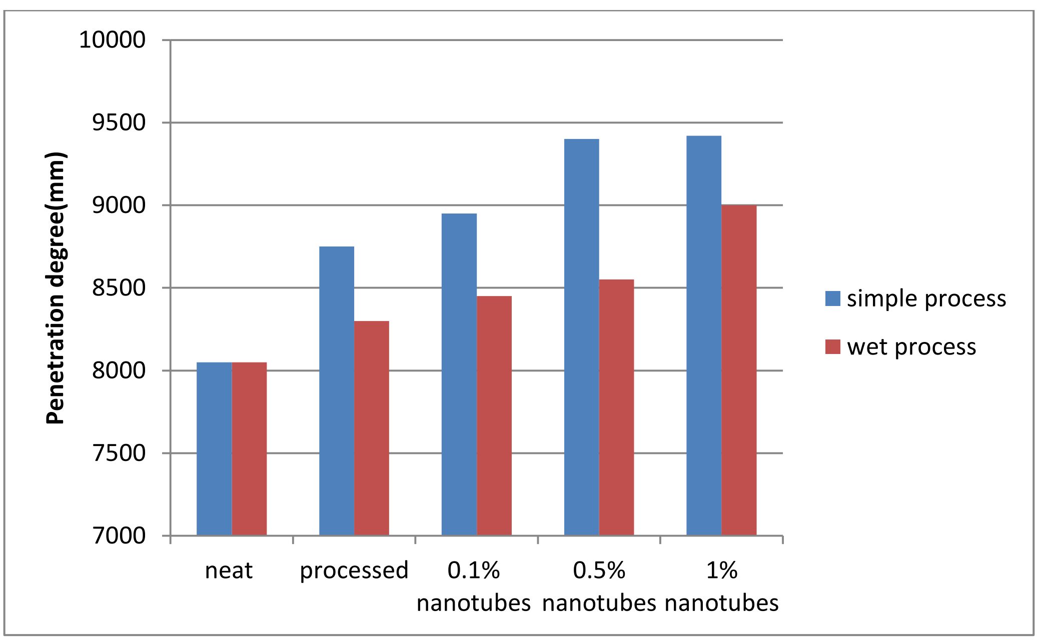

Figure 3.9 Penetration at 25°C as Function of CNT Dosage.

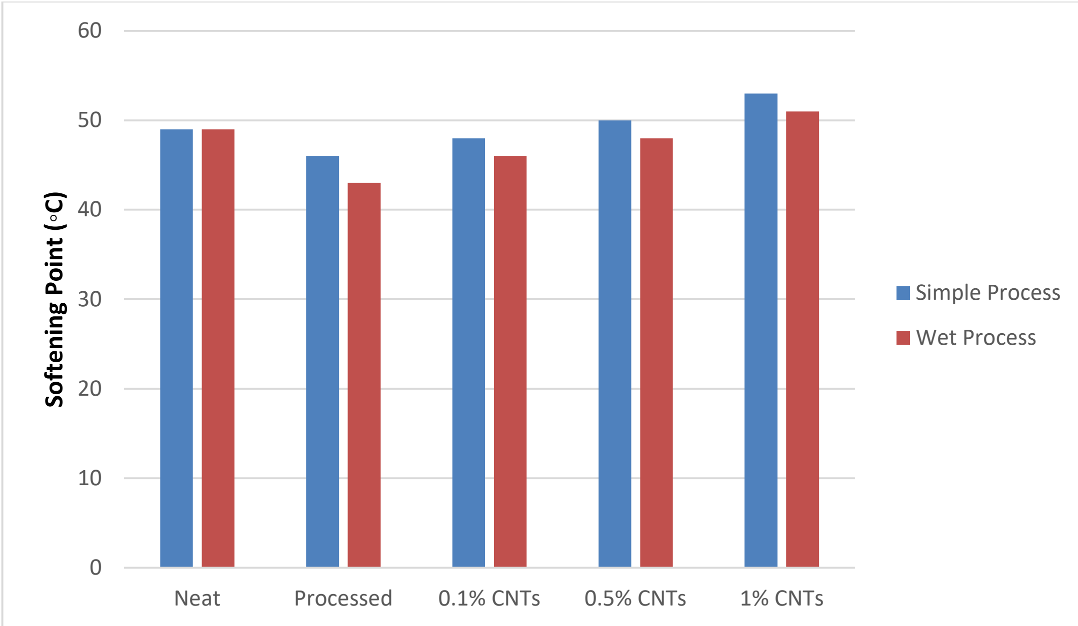

Figure 3.10 Comparison of Softening Point Test Results for Different Samples

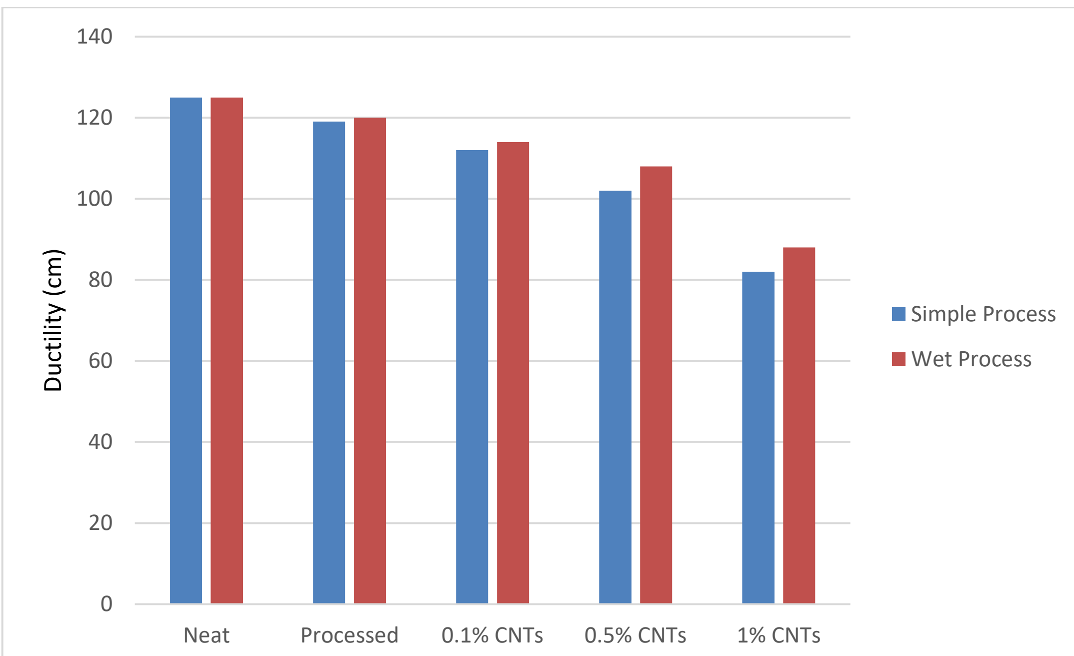

Figure 3.11 Ductility at 25°C as Function of CNT Dosage

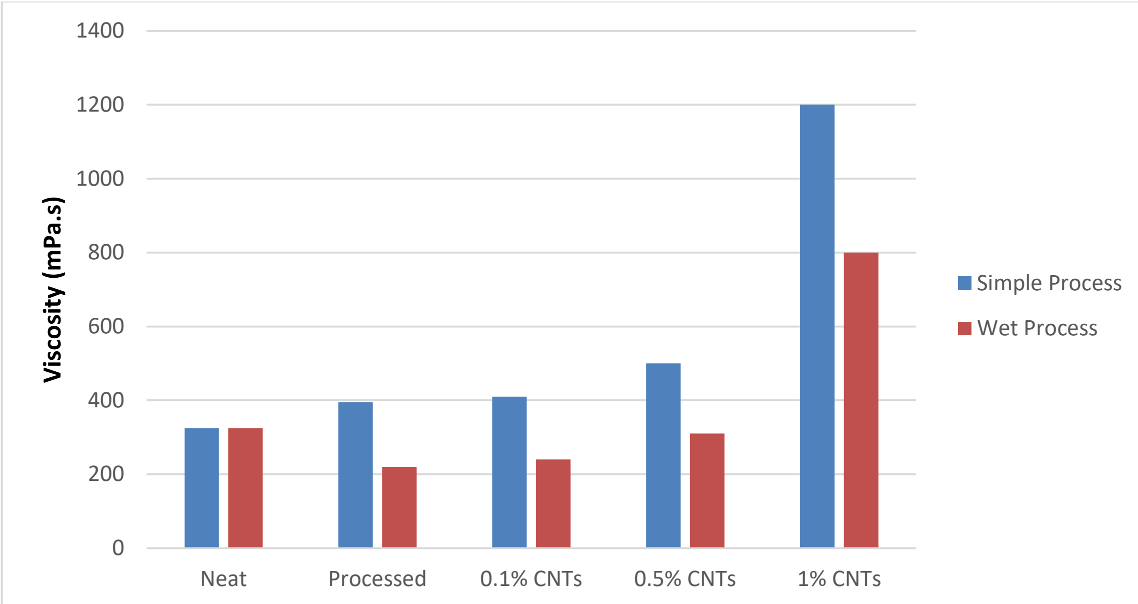

Figure 3.12 Viscosity at 135°C as Function of CNT Content

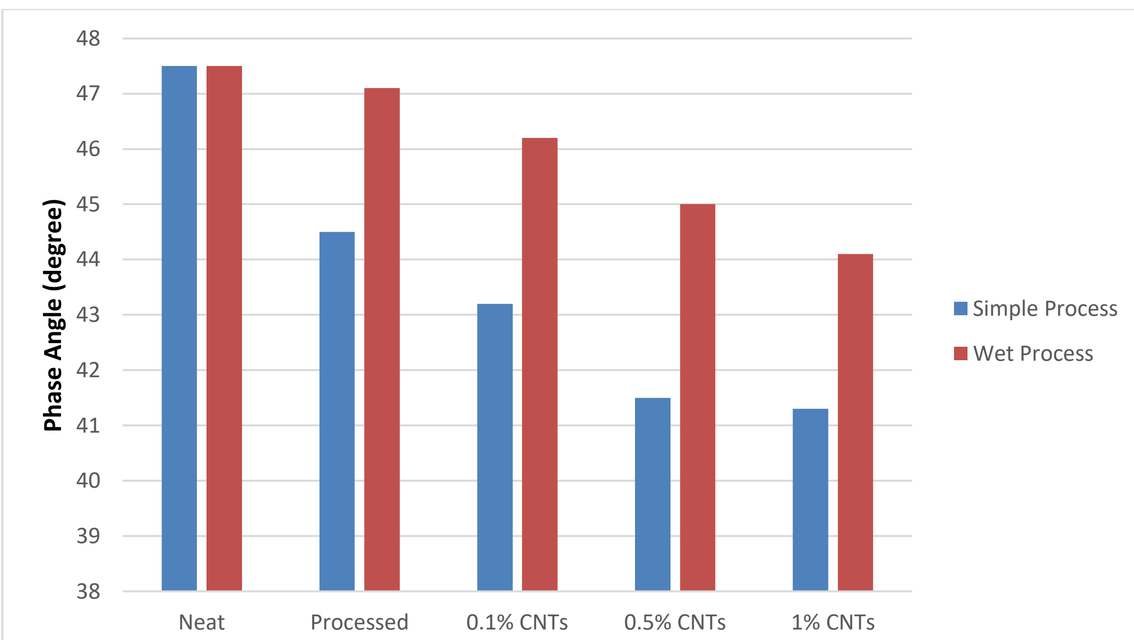

Figure 3.13 δ Values at 60°C as Function of CNT Dosage

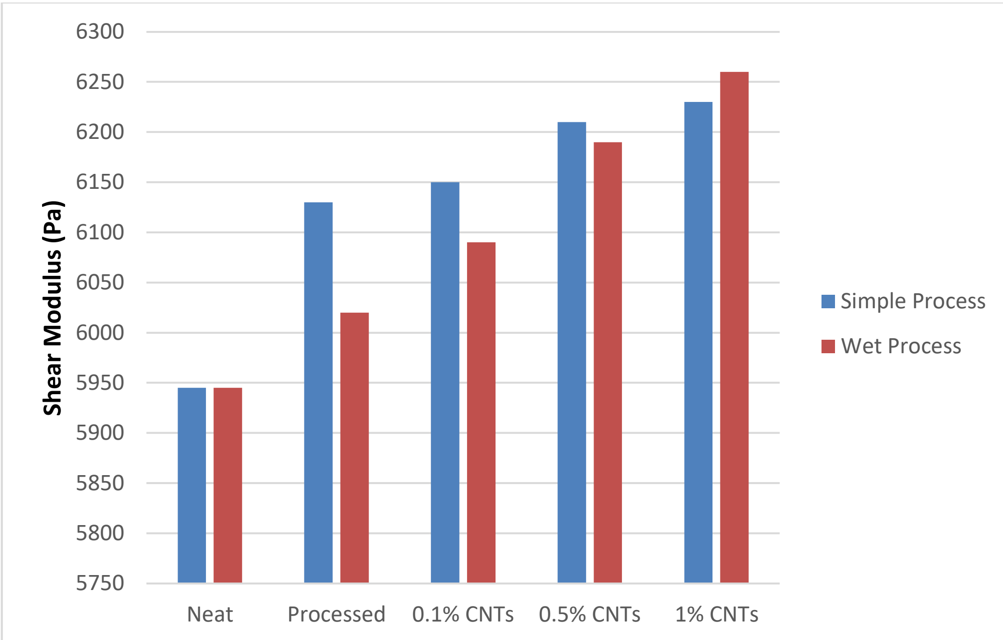

Figure 3.14 G Values at 60°C as Function of CNT Dosage.*

Despite stronger diffusion of carbon nanotubes in the wet mixing system, the G*/sin parameter was found to be improved more by the simple process adjusted binder. The shortage of solvent in the basic mixing process was the cause of this.

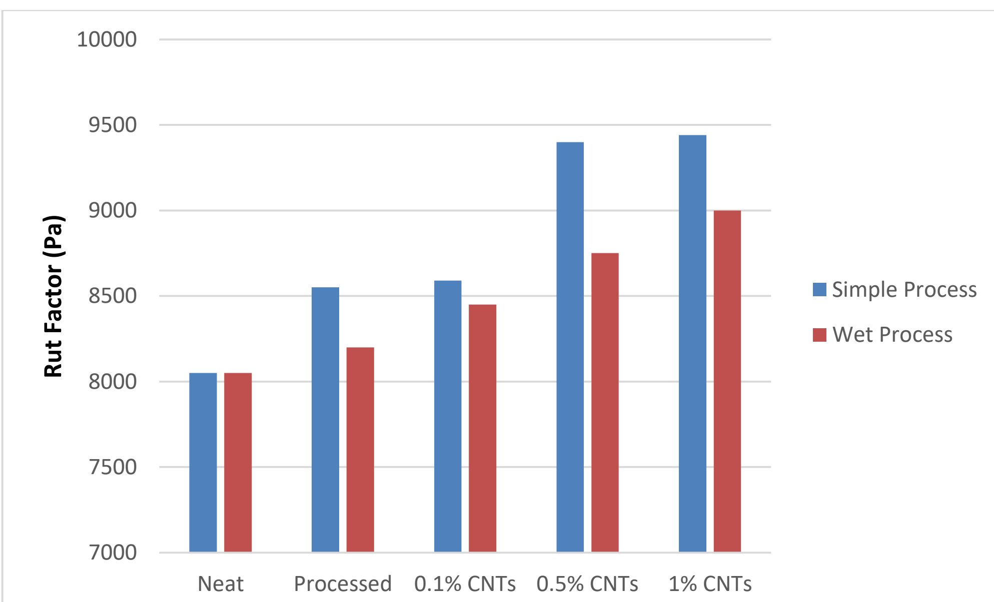

Figure 3.15 G/sinδ Values at 60°C as Function of CNT Dosage.*

According to laboratory experiments, samples containing 1% and 0.5 percent CNTs by weight of binder improved the G*/sin parameter for all mixing processes, resulting in increased resistance to permanent deformation resistance for higher CNTs contents. While wet procedure increases diffusion of CNTs, for large-scale construction the simple approach is more acceptable because wet processes are costlier and more complex than simple process (Faramarzi et al., 2015).

3.5. Simultaneous treatment of asphalt binder and particles using Carbon Nanofiber and Carbon Nanotubes to improve moisture sensitivity of asphalt mixtures

Another research conducted in Iran by Nikookar et al., was studied for this report. This study looked at the effects of aggregates modified with CNTs and asphalt binder modified with carbon Nanofiber (CNF) on the moisture sensitivity of asphalt mixtures at the same time. Moisture sensitivity was investigated using the surface free energy principle and indirect tensile strength test. This test showed that adding CNF and CNT to the asphalt binder and aggregates, respectively, improved values of ratio of tensile strength and indirect tensile strength. Using CNF and CNT also increased the adhesion free energy of the system, according to surface free energy findings. Furthermore, modifying asphalt binder with carbon Nanofiber improved the cohesion free energy values in the asphalt binder membrane. In addition, CNF and CNT reduced the system's detachment energy, suggesting a reduced desire to strip the mixtures. In general, the two approaches revealed that coating aggregates with carbon nanotubes and using CNF as modifier for asphalt binder had a beneficial effect on reducing asphalt mixture's moisture sensitivity (Nikookar et al., 2021).

The findings of this study states that adjusted asphalt binder's penetration degree was decreased and its softening point was improved by using carbon nanotubes for modifying aggregate. These parameters also improved Penetration Index values, which improved response of the adjusted asphalt binder to temperature variations.

$$PI = \frac{20 - 500X}{1 + 50X} \rightarrow X = \frac{\log 800 - \log P}{T_{RB} - T},$$

T_{RB} = softening point

P = penetration degree at *t* degree

ITS and TSR values of mixtures were improved by modifying the asphalt binder and aggregates with CNF and CNT, respectively, according to the results of ITS test.

$$ITS = \frac{2\pi}{t\pi d},$$

d =mixture diameter (m)

P = rupture force (KN)

t = mixture thickness (m)

The use of 2.4 percent CNT and 2 percent CNF at the same time had the greatest impact on the TSR and ITS values.

$$TSR = \frac{ITS_{wet}}{ITS_{dry}} \times 100,$$

The results of SFE test concluded that modifying aggregate using CNT and binder using CNF improved the AFE values of asphalt binder, which tells us that for a rupture to occur at the contact surface of asphalt binder and aggregate in dry conditions more energy is required (Nikookar et al., 2021).

Using 2.4 % of CNT with 2 % of CNF at the same time has the greatest impact on AFE enhancement. The SFE findings also showed that asphalt binder containing CNF has an increased amount of CFE in the membrane. In the presence of water, the DE findings between asphalt binder and aggregates revealed that using carbon Nanofiber and carbon nanotube reduced the DE of the method to zero, indicating that the mixtures had less desire to be stripped. The energy of the system was increased by using mixtures containing 2.4 percent CNT + 2 percent CNF, and stripping would take place later. In general, combining CNT and CNF has the largest impact on increasing mixture ITS and TSR, as well as the SFE of the asphalt binder-aggregate system (Nikookar et al., 2021).

3.6. An overview of Carbon Nanotubes and their use in asphalt binder modification

A research being conducted by Hassan Latifi and Parham Hayati was studied. The main aim of this research is to compare traditional hot mix asphalt with the asphalt modified with carbon nanotubes in order to determine the optimal carbon nanotube percentage needed. To begin, two separate mixing methods were studied in order to determine which was the best for mixing CNTs in asphalt binder as uniformly as possible. Secondly, a scanning electron microscope was used to examine the morphology of raw CNTs and CNTs scattered in asphalt binder (SEM).

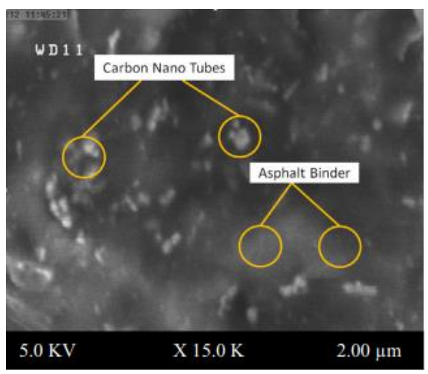

Figure 3.16 SEM image of wet processed CNT-modified asphalt binder

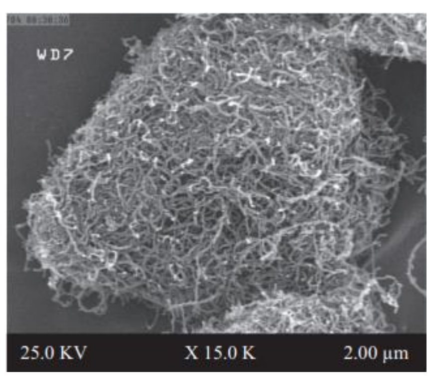

Figure 3.17 SEM image of aggregated-carbon nanotubes.

At last, several tests were performed in order to determine the properties of modified and unmodified asphalt binders and asphalt mixtures, including the (ITS) test, (RV) test, resilient modulus test, and indirect tensile fatigue (ITF) test. The results of SEM analysis concluded that, the wet-mix process produced more uniform mixtures. The viscosity of asphalt binder containing CNTs developed using wet-mix method is less than the maximum range, according to RV test results. It was discovered that using CNTs increased stiffness and, as a result, improved rutting resistance, particularly when 0.5 percent to 1 percent CNT was used. The addition of CNTs improved the resistance of HMA specimens to fatigue, especially at low temperature levels (Latifi et al., 2018).

Several tests run on the mixture gave us some results which include the images from the microscope which tells us that the wet mixing technique that was used for mixing gave us a more homogenous mixture as compared to the mixture made using the dry technique. Wet mixing also prevented the formation of lumps of CNTs at single point, but this technique is considered more expansive and complicated. This method increased the values of viscosity, but they were still below the maximum limit. Addition of 1% CNT increased the viscosity of the mixture by 1.5 times which increased the stiffness which resulted in higher rutting resistance at higher temperatures. CNT modification also increased the tensile strength of mixture which provides a higher resistance against thermal cracking.

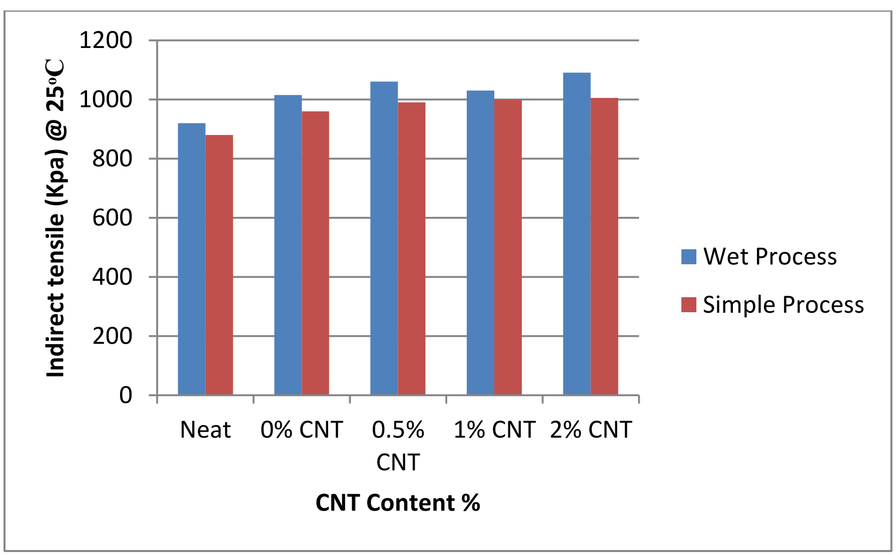

Figure 3.18 Indirect tensile strength values at 25°C

Wet mixing process gave us higher values of resilient modulus but adding a percentage of more than 1 % CNT decreased the resilient modulus values considerably. So, the optimum percentage of CNTs to be added to the binder for modifying was found to be 1 % (Latifi et al., 2018).

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CHAPTER 4

CARBON BLACK

4.1. Carbon Black

Carbon black is obtained by the incomplete combustion of heavy petroleum products and its production occurs under controlled conditions via two processes:

1. Thermal Decomposition of Liquid or Gaseous Hydrocarbons.
2. Incomplete Combustion.

Carbon Black is finding its foot steadily in road engineering as an additive in asphalt binder for enhanced pavement performance. Carbon black filler as bitumen modifier has positive implications on high temperature performance, fatigue resistance, rutting depth and other important engineering properties of the asphalt pavement.

4.2. Study on use of Carbon Black powder in Bituminous Road Construction

Carbon black obtained by the incomplete combustion of heavy petroleum products, is finding its foot steadily in road engineering as an additive in asphalt binder for enhanced pavement performance. Carbon black filler as bitumen modifier has positive implications on high temperature performance, fatigue resistance, rutting depth and other important engineering properties of the asphalt pavement. Here we shall briefly discuss various studies undertaken to analyze various pavement performance indicators after the adding carbon black as reinforcing filler to asphalt binder.

For this study, different percentages 0.25%, 0.5%, 0.75%, 1%, 1.25%, 1.5%, 1.75% and 2% of carbon black were added to the bitumen grade VG-10 and various tests were performed to identify effects of different carbon black percentages on important pavement performance indicators. Then optimum carbon black percentage was determined for Marshal Mix design to calculate OBC. (Saritha N et al, 2015)

Aggregates were procured and their basic properties like flashing point, softening point, penetration, ductility and specific gravity were determined. Bitumen binder and its crushing, impact, abrasion, water absorption, combined index and specific gravity were found. Then carbon black was obtained from a plastic waste source in Bengaluru. In laboratory the physical and engineering properties of carbon black and virgin bitumen were investigated. Marshal Method was adopted to find the optimum binder content (OBC). Right marshal specimens were prepared using different trial percentages of bitumen and tested to find the optimum binder content. The properties like air voids, voids filled with bitumen (VFB), flow, stability and density of these marshal specimens are evaluated to reach optimum binder content. MORTH-IV revision BC grade two values were consulted to arrive at appropriate job mix formula (JMF), as better gradation results in better pavement performance. Then compacted bituminous specimens of 63.5mm thickness were prepared using the right proportion and gradation of aggregates and fillers and tested as per ASTM-D1559-96 recommendations. Different specimens were prepared of varying percentages 4.75, 5.0, 5.25, 5.5, 5.75, 6.0 and 6.25 of the bitumen binder. OBC was found to be 5.75 with maximum stability of 1913.6 and flow value, air voids and VFB 1.98, 3.57 and 78.76 respectively at OBC. On adding carbon black additives in varying percentages in virgin bitumen, properties like softening point, penetration and specific gravity improved. The percentage of carbon black was restricted to 5% because with rising percentage of CB, viscosity of asphalt mixture was decreasing consequently increasing brittleness and reducing workability. (Saritha N et al, 2015)

SL NO	Tests	VG-10
1	Penetration at 25°C, 5 sec	100
2	Softening point, °C	44.5
3	Flash point, °C	250
4	Ductility at 25°C,	77
5	Specific gravity	0.962

Table 4-1 Physical properties results

SL NO	Tests	Aggregates
1	Crushing Value (%)	21.5
2	Impact Value (%)	20.01
3	Abrasion Value (%)	14.15
4	Combined Index (%)	26.19
5	Specific gravity	2.52
6	Water Absorption (%)	1.2

Table 4-2 Basic properties of bitumen binder

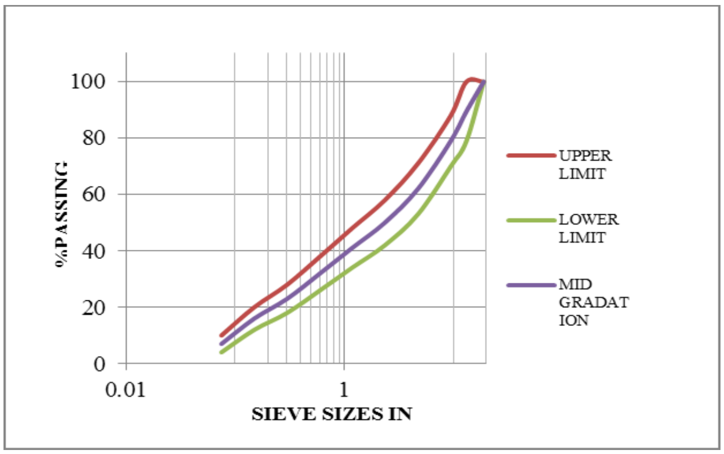


Figure 4.1 Showing gradation curves for BC grade-II

Asphalt being thermoplastic softens in higher temperature and hardens in lower temperature consequently causes pavement rutting in summers and cracking in winter. Though harder asphalt with thermo-elastomers and resins help improve pavement rutting performance but longitudinal cracking overreaches specified limits. Previously studies focused on penetration and viscosity after carbon black addition to asphalt in higher temperature but no study was made to assess viscoelasticity in cold temperatures. The purpose of this study was to use reinforcing carbon black with the asphalt to improve pavement rutting and deformation performance in hot and cracking performance in cold weathers using strategic highway research program (SHRP). (Dr. Kiran Kumar B V et al, 2015)

Specific gravity	Softening point in °C	Viscosity in sec	penetration in mm	Ductility in cm
0.962	44.5	101.66	100	77
0.964	45	101	98	74
0.972	45.3	100	95	70
0.978	46	99	93	66
0.98	46.5	98	94	64
0.982	46.83	97	93	60
0.997	47.15	96	90	58
0.999	48	94	85	50
1.12	51	85	84	45

Table 4-3 Basic test results after addition of CB

Straight asphalt and carbon black satisfying specified properties were obtained. CB10 and CB20 samples meant 10 pha and 20 pha of carbon black in stAs respectively. Unaged (ORG) sample was prepared by predrying carbon black at 150 C for 24 hours and then it was kneaded with straight asphalt for 45 min at 60 C. This ORG sample then undergone thin film oven test (TFO) and pressure aging vessel (PAV) test to check for short term and long term aging effects of the prepared sample. Dynamic Shear Rheometer (DSR) test measured the dynamic viscoelastic properties like fatigue resistance and permanent deformation of the sample. PAV aged sample was molded to beam specimens and Bending Beam Rheometer test measured static viscoelastic properties like the creep and stiffness of the specimens. It was followed up by Destructive Bending Test of the PAV aged sample at -5 C to find the failure properties of sample in lower temperatures. Then coefficient of thermal expansion and density of the sample were found. (Dr. Kiran Kumar B V et al, 2015)

Results obtained by plotting graphs of permanent deformation and fatigue cracking against increasing temperature revealed that permanent deformation increased while fatigue cracking decreased with rising percentage of carbon black CB. Stiffness against test temperature increased with increased CB percentage while m-value (slope of stiffness vs. time curve) was same of stAs and CB10 while slightly lower for CB20. The strain properties increased with rising CB content and failure strain of CB20 was found double than stAs. Coefficient of thermal expansion CTE decreased with increase in CB percentage. Overall both the deformation and crack resistance improved by modifying asphalt binder with reinforcing Carbon black. (Dr. Kiran Kumar B V et al, 2015)

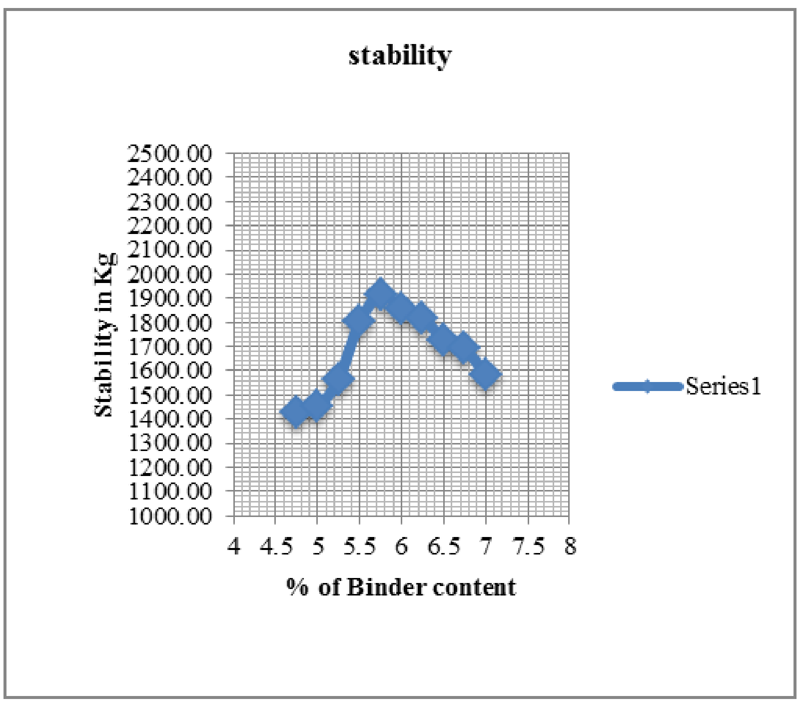


Figure 4.2 Graph Showing Stability values and OBC

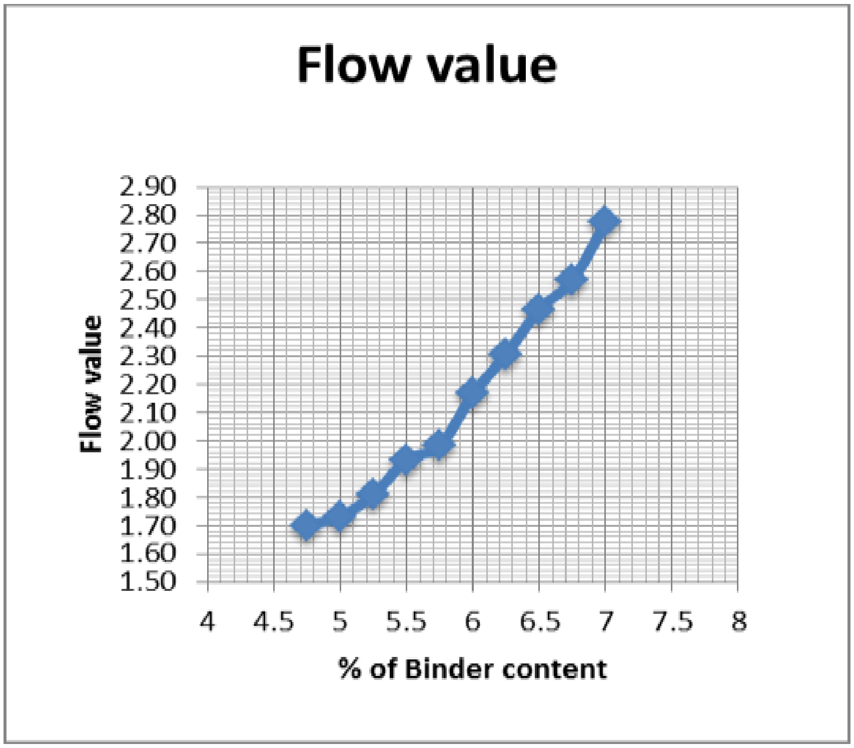


Figure 4.3 Graph Showing Flow Values

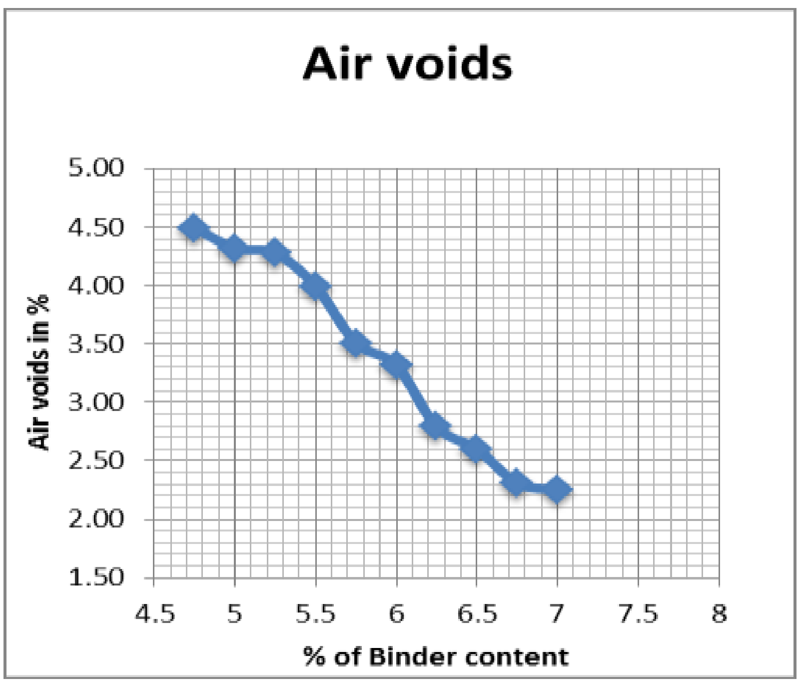


Figure 4.4 Graph Showing Air Voids

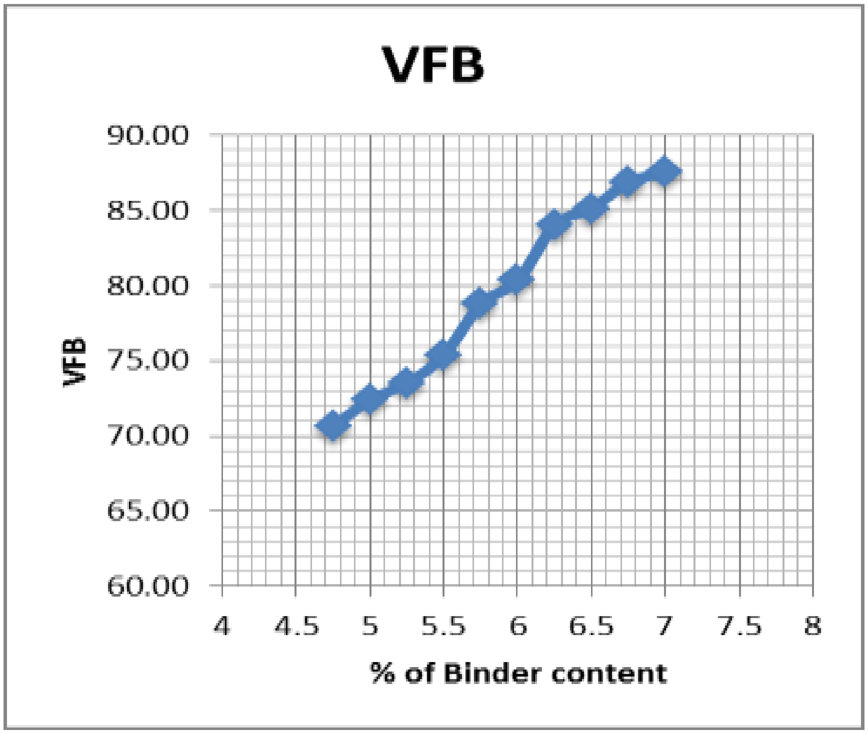


Figure 4.5 Graph Showing Voids filled with Bitumen

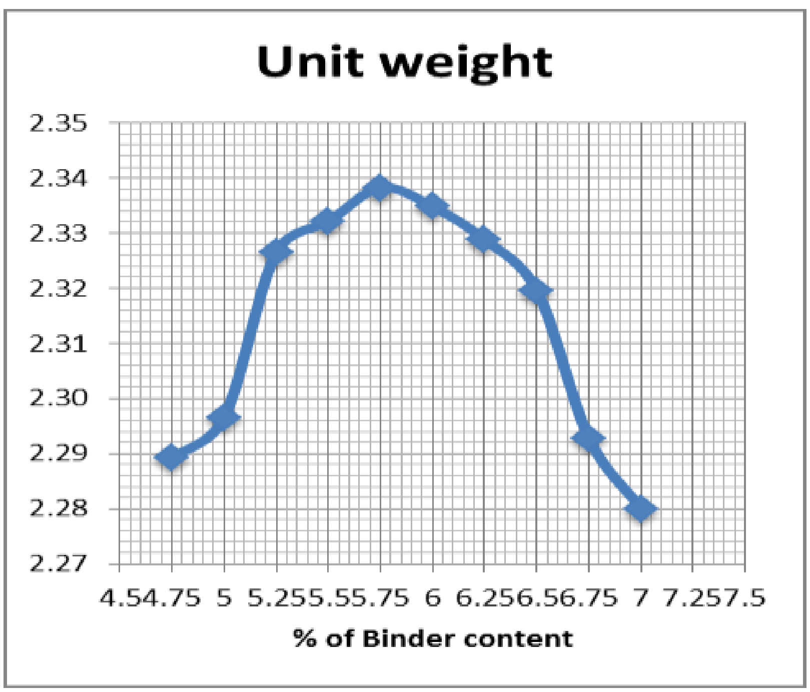


Figure 4.6 Graph Showing Unit Weight

4.3.Effect of Carbon Black on Fatigue performance and Rutting of Asphalt

This research involved effect of various particle sizes and varying content of carbon black CB on asphalt rutting and fatigue performance. #70 asphalt binder and CB1, CB2 and CB3 of particle size 270 um, 25 um and 2.6 um respectively obtained.

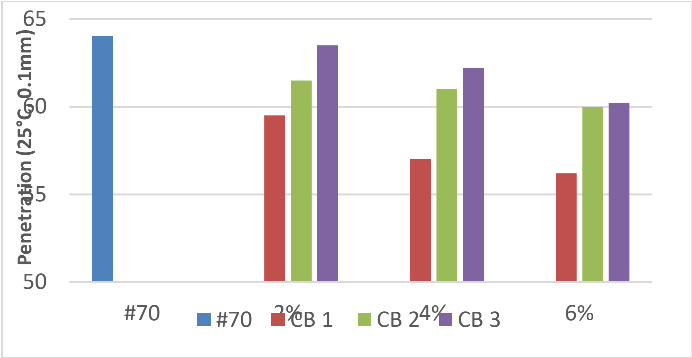
Indicators	Unit	Values
Softening Point	C	47.5
Ductility	cm	150
Penetration	0.1 mm	64
Flash Point	C	> 260
Density	g/cm3	1.034

Table 4-4 Properties of 70# asphalt binder

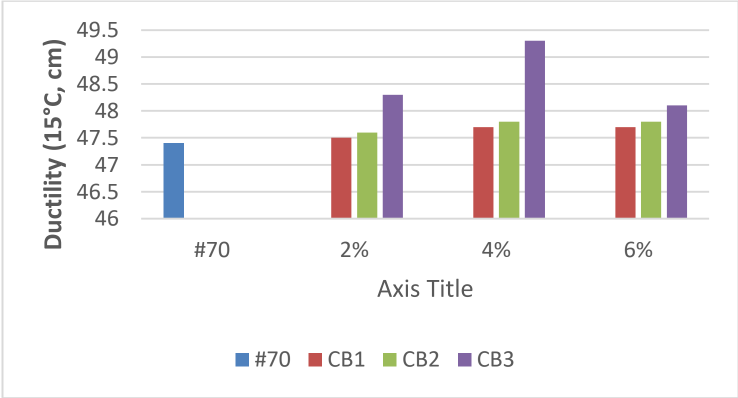
(a) (b) (c)

Figure 4.7 Carbon blacks: (a) CB-1, 270 μm, (b) CB-2, 25 μm, (c) CB-3, 2.6 μm.

CB modified asphalt binder was made via melt blending by first heating neat asphalt binder and then adding three different particle sizes of CB in varying proportions of 2%, 4% and 6%. Then these prepared sample underwent softening, penetration and ductility tests. Then DSR testing for estimating rheological properties of sample. The anti-rutting performance was known by Multiple Stress Creep Recovery (MSCR) test. Similarly Linear Amplitude Sweep (LAS) test was performed to find fatigue resistance. Short and long term thermal oxidative aging effects of CB modified binder were studied by TFO and PAV tests. Softening point increased while ductility and penetration decreased thus enhancing pavement performance.



(a)



(b)

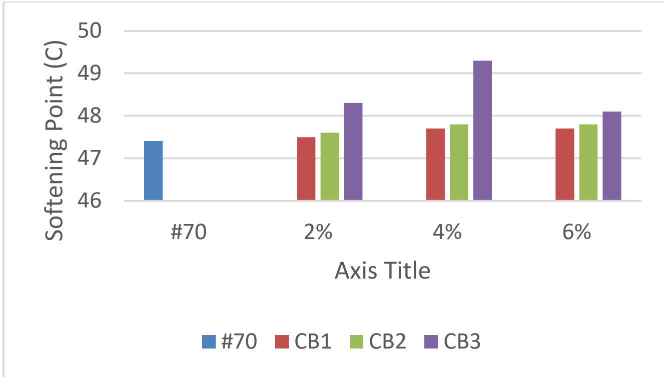
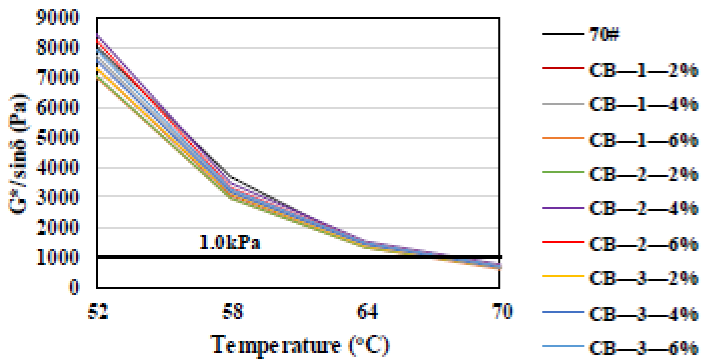


Figure 4.8 Physical properties of asphalt: (a) penetration; (b) ductility; (c) softening point

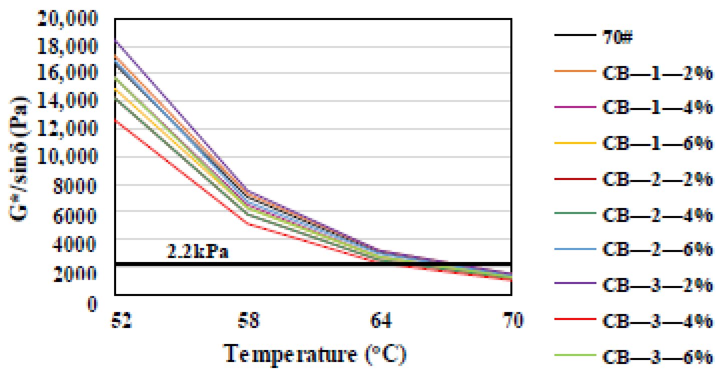
(c)

Modification effect with the smaller CB particles decreased for penetration and ductility while increased for softening. 25 um CB gave the optimum results.

Rutting factor (resistance) increased of CB modified asphalt, where CB-1 (270 um) and CB-2 (25 um) modified asphalt with 4% CB content showed optimum rutting performance while CB-3 (2.6 um) with 6% CB content indicated better rutting resistance.



(a)



(b)

Figure 4.9 Results of temperature scanning tests: (a) virgin asphalt; (b) asphalt after TFOT aging.

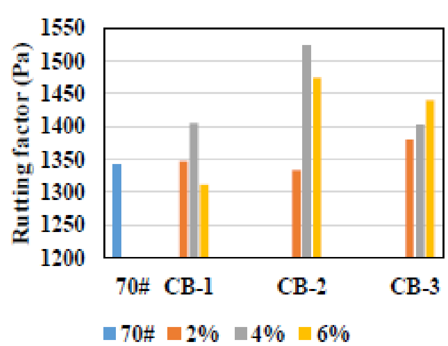


Figure 4.10 Rutting Factor Of Unaged Asphalt Specimens

MSCR test results shown that in CB modified asphalt non-recoverable creep was comparatively lower, where CB-2 and CB-3 had least non recoverable creep for 6% CB content while 4% CB content in CB-1 had least creep.

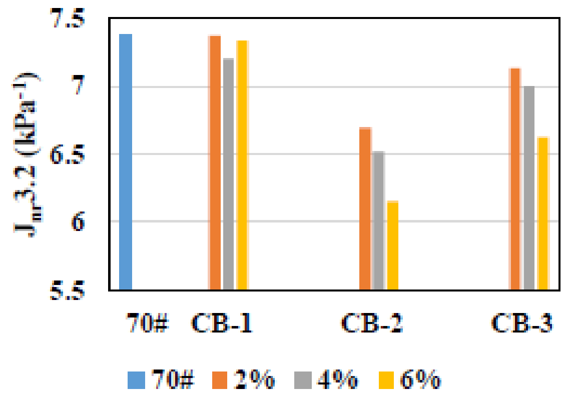


Figure 4.11 Vvalues of unaged asphalt specimens.

Fatigue factor increased with CB modifying and all CB particle sizes shown increasing trend in fatigue factor with increasing percentile of CB content with slight variation in CB-3.

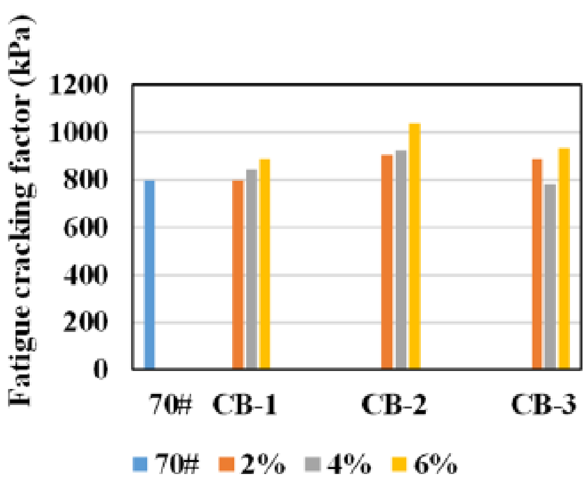


Figure 4.12 Fatigue cracking factors of unaged asphalt specimens.

Before aging, CB-2(25 um) overall shown the best rutting, creep and fatigue performance amongst all other particle sizes. After TFO test, on contrary CB modified asphalt shown worse rutting than the neat asphalt, owing to lower complex modulus after aging. CB modified asphalt binder resulted in better resilience after TFO aging because CB absorbed light components and it led to least volatilization of lighter particles and better resilience overall.

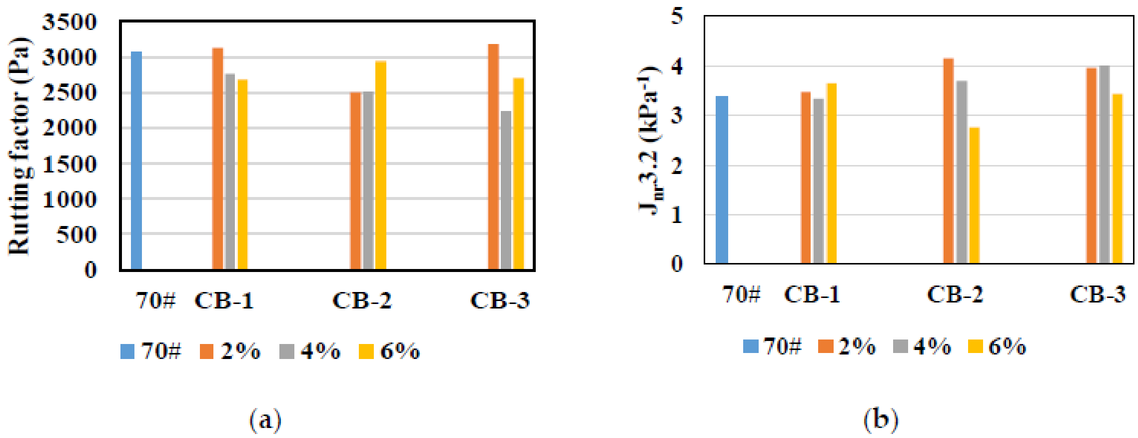


Figure 4.13 Rutting factors and Jnr3.2 values of asphalt specimens after TFOT aging: (a) rutting factor; (b) Jnr3

CB increases PAV ageing asphalt's fatigue resistance in general. Although the effect of 270 um CB on asphalt fatigue resistance is the highest, the anti-fatigue efficiency of the asphalt binder decreases as the CB dosage is increased for 25 um and 2.6 um CB, So with different particle sizes, it is important to monitor the content of CB. Based on the results of all of the tests, the recommended CB content and particle size are 2% and 2.6 um, respectively. (Kunzhi Zhong 1, Zhi Li 2, Jianwei Fan 1, Guangji Xu 1 and Xiaoming Huang 1, et al, 2021).

4.4. Comparison of Carbon Black from pyrolized tyres to other fillers as asphalt rheology modifiers

It was a comparative study between carbon black CB, ball clay and other mineral fillers filler in asphalt binder. . The high temperature and low temperature performance was assessed after modifying asphalt binder with either of these fillers.

Filler	Supplier	Specific Gravity (g/cm3)	Fineness Modulus	Ridgen Air Voids (%)	m value from equation (2) @ 55°C	@ 65°C	@ 135°C
Ralston Quarry	Colorado	2.822	2.90	48.4	0.35	0.27	0.20
Sievers Pit	Colorado	2.717	2.83	45.9	0.36	0.19	0.20
Carbon Black	Jarrel Group	1.690	3.66	39.9	0.37	0.30	0.95
Ball Clay	KY-TN Clay Co.	2.960	5.59		0.49	0.34	0.67

Table 4-5 Filler Properties

Two binders AC-10, MAC-10, CB filler, two mineral fillers from Ralston quarries, silver pits crushed and ball clay procured. Each binder was heated at 185 C and then 17 mastic samples. Each sample was made by adding 20-30% (by mass in binder) of filler in a binder. To stimulate Indian condition, Michigan specifications were met for different aggregate mixes. (DIDIER LESUEUR et al, 1995)

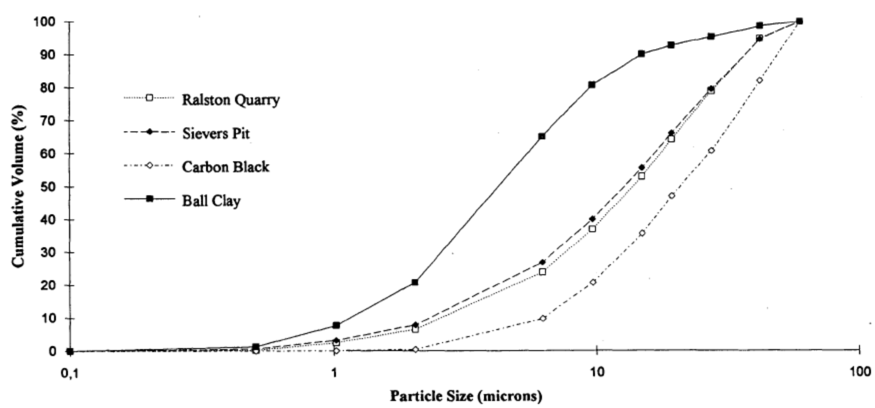


Figure 4.14 Particle size distribution of the fillers.

Particle size analysis was done using sieve analysis particle size analyzer. SHRP procedures, DMA analysis of unaged and RTFOT of aged materials at 60 C, Brookfield's viscosity test at 135 C, DMA analysis at 20 C of PAV-RTFOT residues, BBR and DTT tests of PAV-RTFOT aged materials at -15 C and Hamburg Wheel tracking test to analyze rutting performance and other properties of four mixes. (DON L. DEKKER et al, 1995)

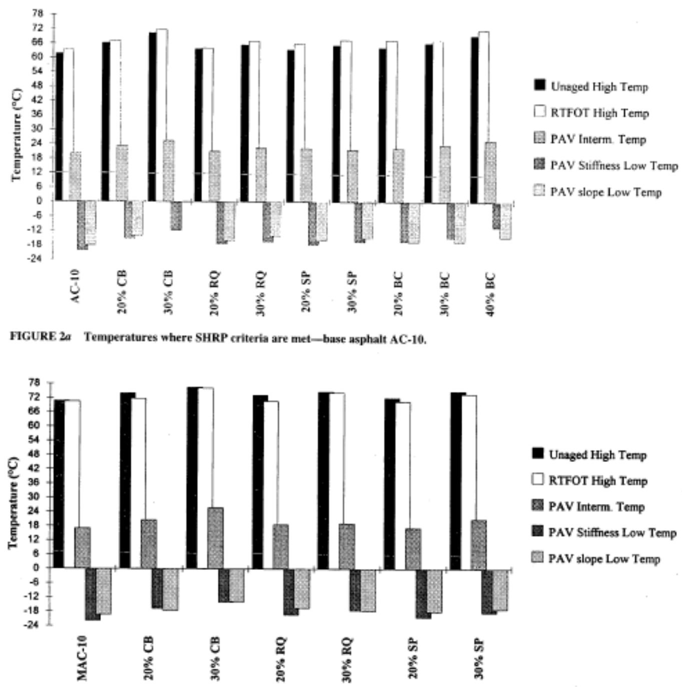


Figure 4.15 Temperatures where SHRP criteria are met-base asphalt MAC-10.

The amount of fines and their characteristics had very sound impact on the performance of asphalt mixes. Carbon black and other mineral fillers proved vital to enhance the rutting resistance and high temperature performance of asphalt mixes.

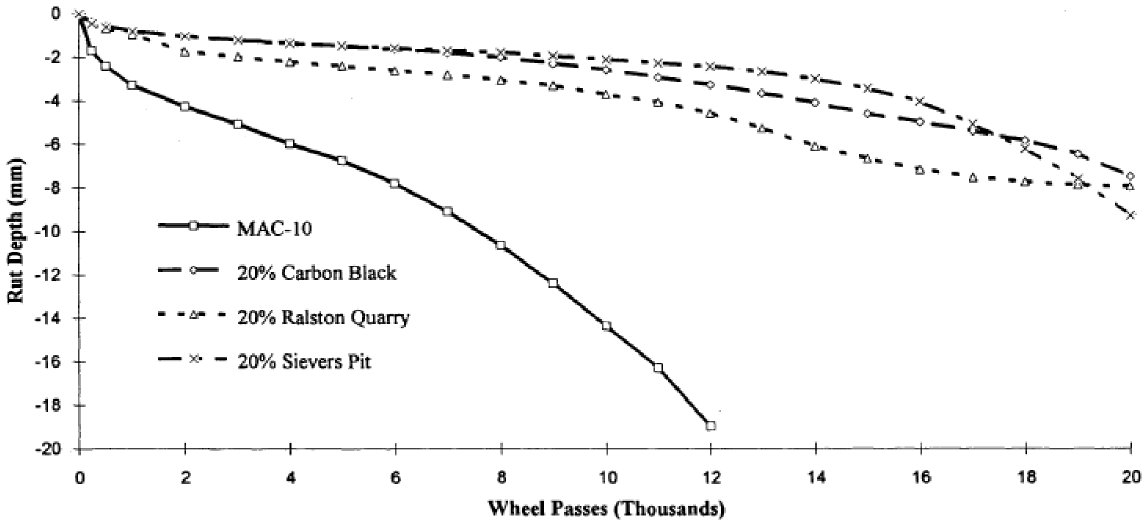


Figure 4.16 Rutting Resistance of Mastics used as binders

Aging	Temperature (°C)	Measurements	Units	Base Asphalt : AC-10							Base Asphalt : MAC-10			
				0% Filler	20% CB	30% CB	20% RQ	30% RQ	20% SP	30% SP	0% Filler	20% CB	30% CB	20% RQ
PAV	-6	Load at Failure	N	>50.0	71.3	83.1	71.3	102.0		92.8				
PAV	-6	Strain at Failure	%	>2.00	1.06	0.56	3.16	4.26		1.93				
PAV	-12	Load at Failure	N	49.8	74.6		72.7	81.1	94.1	88.5	83.7	79.7	76.8	121.2
PAV	-12	Strain at Failure	%	0.33	0.34		0.45	0.27	0.42	0.41	1.91	1.10	0.38	2.06
No	-15	BBR Stiffness	MPa	80			103	126	105	137				
No	-15	BBR Slope		0.49			0.48	0.47	0.48	0.48				
No	-18	Load at Failure	N	43.9			70.3	93.6	54.8	107.3				
No	-18	Strain at Failure	%	0.19			0.22	0.40	0.12	0.25				

Figure 4.17 Direct Tension Test Resufts on PAV Aged and unaged Specimens and Corresponding Creep Stiffness at 60 S Loading Time

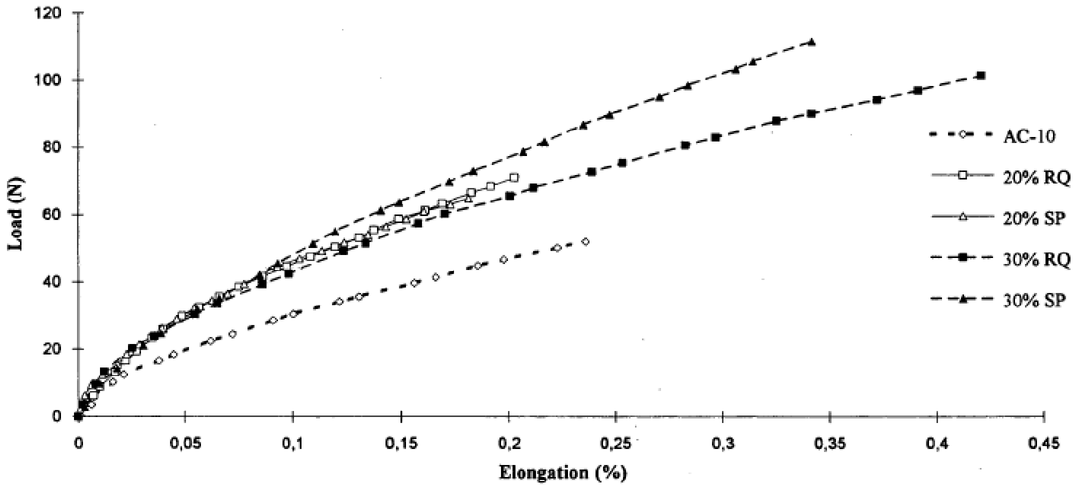


Figure 4.18 DTT results on the unaged samples at -18°C.

The toughening effect and low temperature performance of mixes of mineral fillers was fine but this toughening effect with carbon black and ball clay filler was not satisfying. Carbon black proved to an efficient rheology modifier when mixed with asphalt binder such as polymer-modified asphalts, having good low temperature properties. (JEAN-PASCAL fLANCHE et al, 1995)

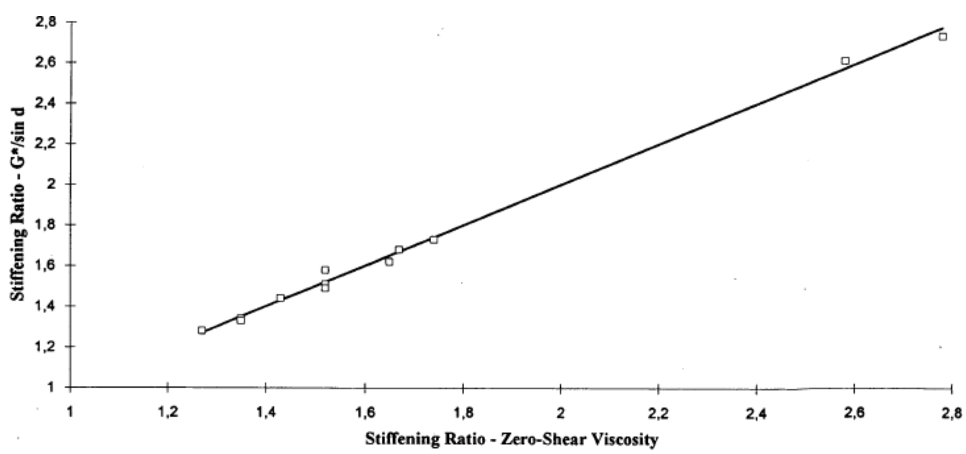


Figure 4.19 Stiffening ratios from G/sin8 versus stiffening ratios from zero-shear viscosities.*

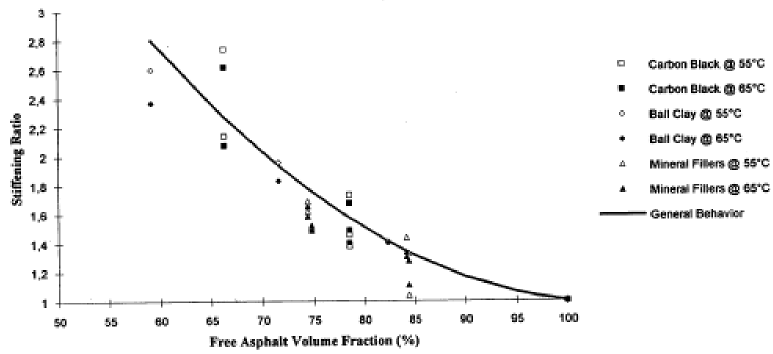


FIGURE 6a Stiffening ratio versus free asphalt volume at 55°C and 65°C.

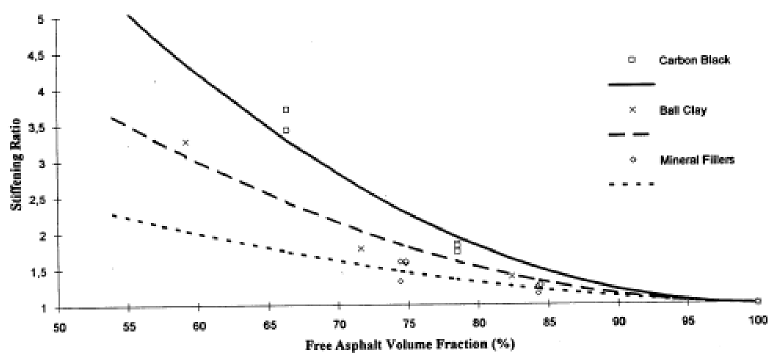


Figure 4.20 Stiffening ratio versus free asphalt volume fraction at 135°C.

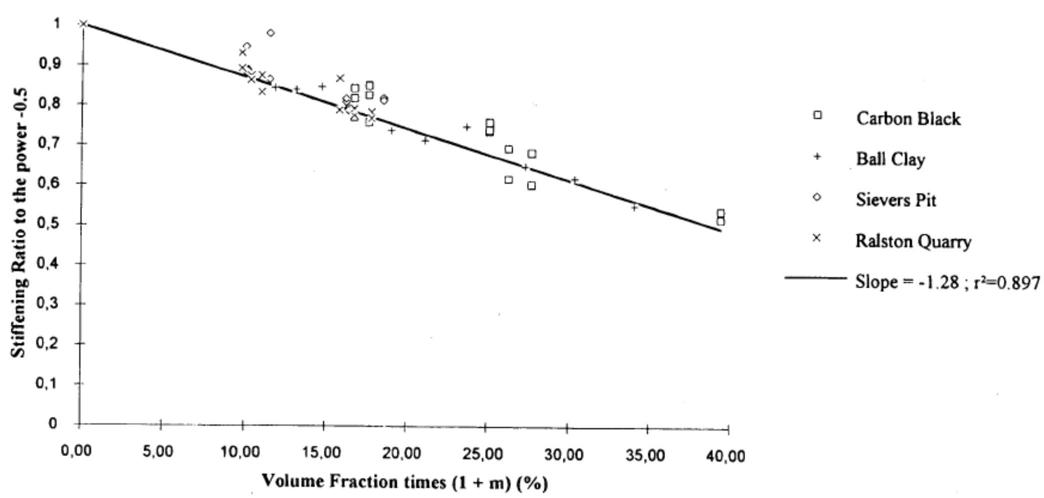


Figure 4.21 Experimental verification of Heukelom's equation

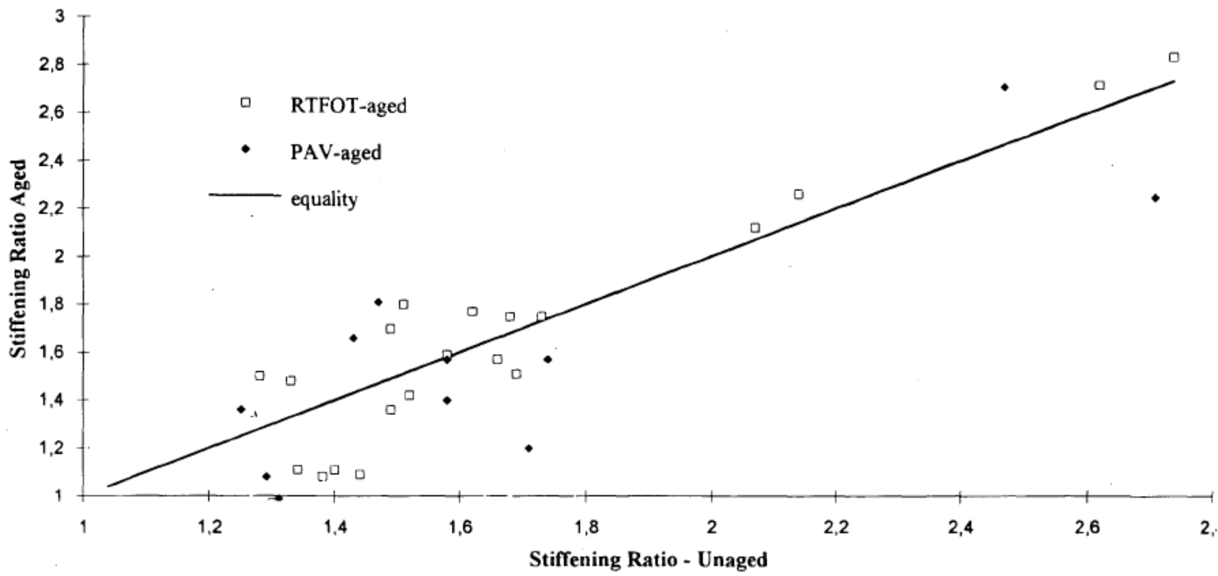


Figure 4.22 Stiffening ratios of the aged mastics versus stiffening ratios of the unaged mastics.

In this research, the effect of three kinds of CB on physical properties, rheological properties, thermal conductivity, electrical resistivity and aging of asphalt binders with styrene-butadiene-stryene-copolymer (SBS) triblock copolymer was studied.

4.5.Effects of Hydroxyl-methyl Carbon Black (HCB) on Bitumen

This research was about physical, rheological, dynamic shear, thermal conductivity, electrical resistivity and anti-aging outcomes of modifying asphalt binder with hydroxyl-methyl carbon black (HCB). The structure of HCB was studied.

Test Indicators	Base Asphalt	Test Methods
Penetration (25 °C, 5 s, 100 g)/(1/10 mm)	83	ASTM D5
Softening point (R&B)/°C	44.5	ASTM D36
Ductility (5 °C, 5 cm/min)/cm	7.4	ASTM D113
Viscosity (135 °C)/pa.s	0.370	ASTM D 4402

Table 4.6 Properties of Asphalt Binder

Base asphalt SK90# procured. CB was oxygenated by nitric acid reaction and then from oxygenated CB reaction with formaldehyde and NAOH, HCB was prepared. HCB modified asphalt was obtained by heating base asphalt for 85 C and pouring 5% HCB or CB of asphalt mass. Then HCB modified asphalt mixture; AC-13 was prepared by adding in proportions, amphibolite rock's coarse and fine aggregates, base asphalt mixture (BAM) and HCB modified asphalt mixture (HAM). Optimal asphalt content as determined by marshal mix design was 4.5%. (Peilong Li et al, 2020).

Mixture	16 mm	13.2 mm	9.5 mm	4.75 mm	2.36 mm	1.18 mm	0.6 mm	0.3 mm	0.15 mm	0.075 mm
AC-13	100	95.6	72.7	40.4	30	19.4	14.5	10.3	8.1	5.1

Table 4-6 Mixture gradation table

Asphalt Mixture	Optimal Asphalt Content (%)	Volume of Air Voids (%)	Voids in Mineral Aggregate (%)	Voids Filled with Asphalt (%)	Marshall Stability (kN)	Flow Value (mm)
BAM	4.5	3.95	14.5	72.8	12.5	3.1
HAM	4.5	4.18	14.4	72.3	13.4	2.5

Table 4-7 Parameters of asphalt mixture for the Marshall design method.

Morphology, structure and elemental composition of CB and HCB were determined by scanning electron microscopy (SEM), energy dispersive X-ray system (EDS) and Fourier transform microscopy (FTIR) tests. Physical properties softening point, Brookfield's viscosity and ductility of HCB modified asphalt were determined in accordance with (JTG E20–2011) specifications. Dynamic shear rheometer (DSR) test evaluated rheological properties, complex modulus (G*), phase angle (δ), and rutting factor (G*/sin δ) of the modified sample. Then simple performance test (SPT) measured dynamic moduli and phase angle.(Hui Bing et al, 2020).

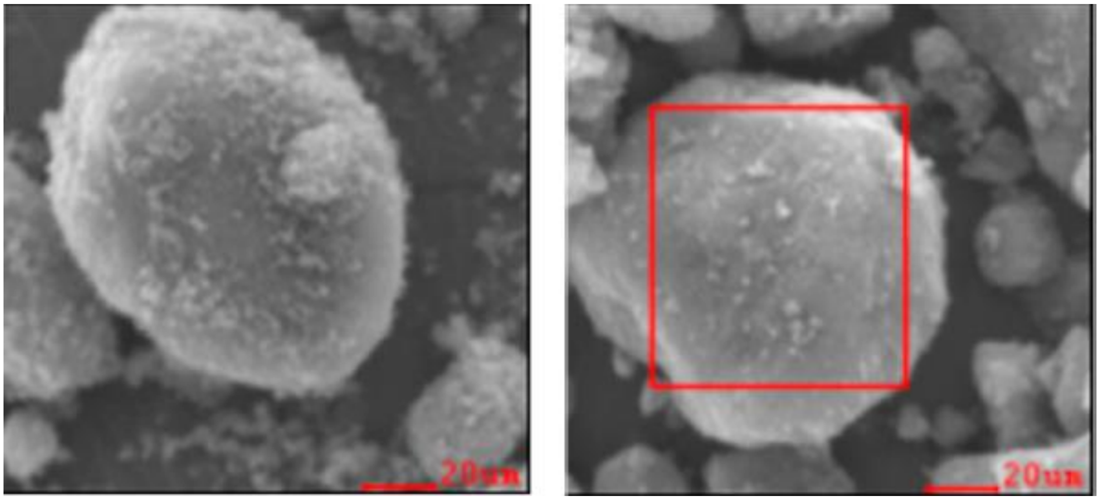


*Fig 4.22 The microstructures of (**a**) CB and (**b**) HCB.*

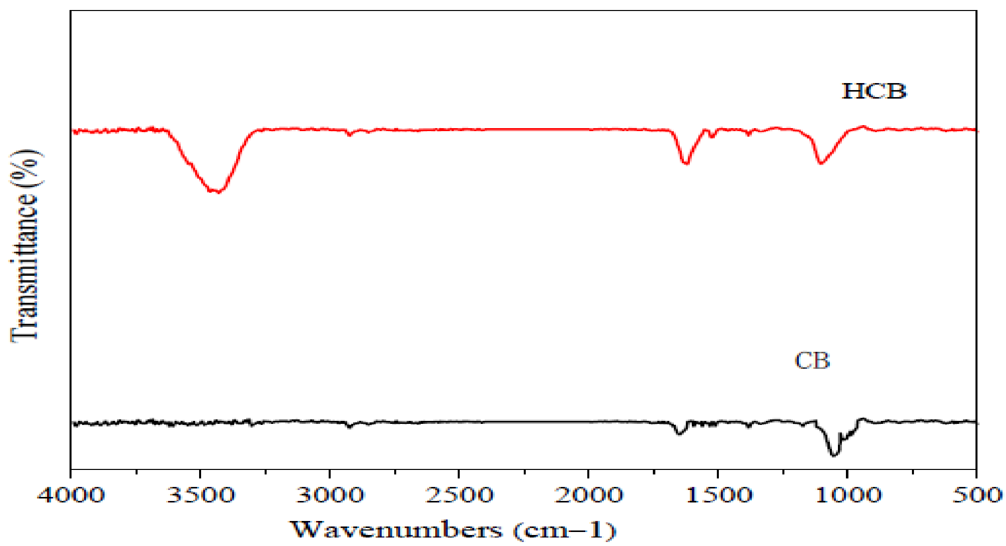
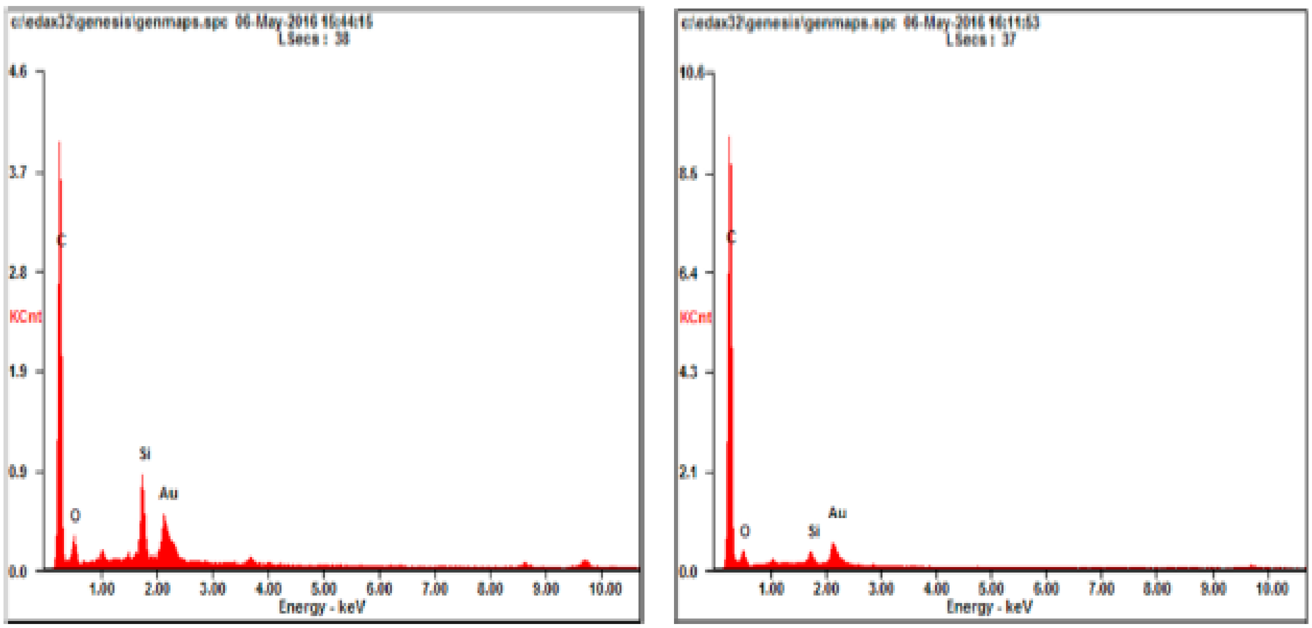


Figure 4.23 The infrared spectra of CB and HCB.

Different degree of polymerization, varying particle sizes and irregular surface of HCB compared with CB had potency of strong molecular forces, higher surface energy that resulted in comparatively strong interaction of HCB with asphalt. The infrared spectra of HCB and CB shown that hydrogen bonds formed by the reaction of hydroxyl group on surface of HCB and phenyl of asphalt have impact on asphalt properties. From X-ray diffraction spectra of CB and

HCB results, CB had 13.62% and HCB had 24.78% of active oxygen content, it meant HCB as compared with CB has the strong bondage with asphalt due to higher active oxygen.



(a) (b)

Figure 4.24 The X-ray diffraction spectra of (a) CB and (b) HCB.

Higher the oxygen content in CB more its surface chemical properties. Penetration reduced by 10 mm, softening point increased by 3 °C, ductility increased by 0.7 cm, and the viscosity increased by 0.05 pa.s of the HCB modified asphalt. G* values (indicative of hardness of asphalt) of CB and HCB modified asphalt were more than neat asphalt but this improvement in CB or HCB modified asphalt slimmed when temperature increased beyond 40 C.

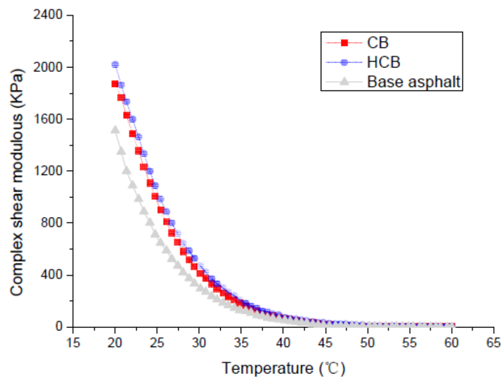


Figure 4.25 Effect of CB and HCB on complex shear modulus of asphalt

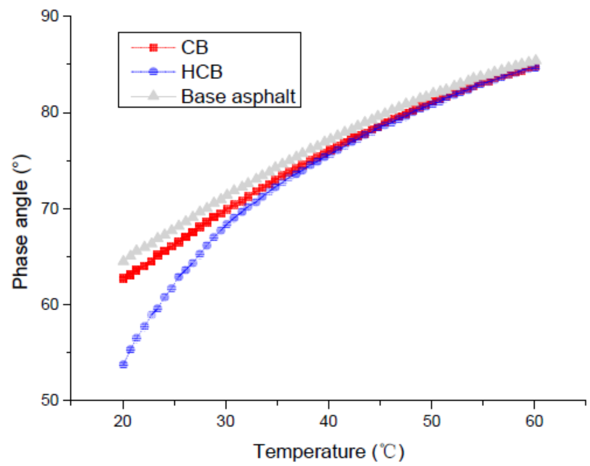


Figure 4.26 Effect of CB and HCB on phase angle of asphalt.

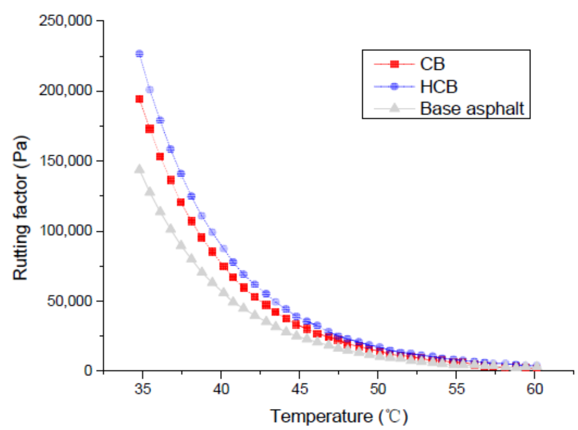


Figure 4.27 Effect of CB and HCB on asphalt rutting factor.

The phase angle of HCB or CB modified asphalt improved thus enhancing the anti-deformation performance of asphalt and like G values, phase angles improvement also slimmed after 40 C. The strength (G values) and anti-deformation performance of HCB> CB> Neat asphalt. Similarly rutting performance ($G^*/\sin\delta$) of HCB>CB>Neat asphalt and this difference became minimal with increasing temperature. –OH formed on the surface of HCB increased the polarity that reduced adsorption and increased dispersion of HCB particles within asphalt mixtures. It resulted in stronger interaction between asphalt and HCB thus enhancing the resistance to cracking and shear–slip deformation of HCB-modified asphalt at low temperatures. Penetration, ductility and softening tests performed deduced that HCB modified asphalt had better anti-aging performance than CB modified asphalt then followed by base asphalt (BA). (Zhan Ding , Jinfei Su et al 2020).

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GRAPHENE NANO PLATELETS

5.1.Graphene Nano Platelets

Graphene Nano-Platelets are graphene sheets that have been stacked together. A monolayer of carbon atoms makes up a single graphene sheet. The carbon atoms in this structure are arranged in a hexagonal pattern. Graphene is stacked, rolled, and wrapped to make graphite, carbon nanotubes, and fullerenes, respectively. Graphene may be thought of as a building block for the synthesis of carbon allotropes.

5.2.The structural and functional properties of Graphene Nano Platelet (GNP)-doped asphalt investigated in an experimental setting.

With the rising costs for bituminous, it is more critical than ever for Civil Engineers to certify the maintenance of long-lasting pavements. It is evident after a thorough investigation, functional as well as the constructional characteristics of the pavement is taken into consideration. The current investigation investigates Graphene Nano-Platelets (GNPs) indicates it’s a novel material utilized to increase the performance of both rigid and flexible pavements. For asphalt binder improvement, GNPs is utilized 2% and 4% in terms of weight to produce the correct Performance Grade (Hafeez et al., 2019).

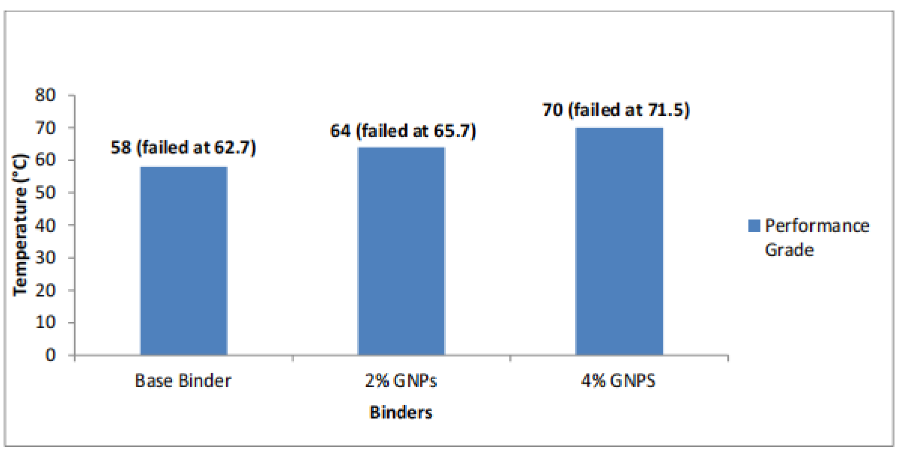


Figure 5.1 The performance grades (PGs) of the asphalt binders.

Scanning Electron Microscope (SEM) photos demonstrate the asphalt binder contained GNPs with a uniformly distributed asphalt. Hot Storage Stability Test is also utilized with SEM for current exploration. Researchers looked at its rheology of GNPs-doped asphalt to investigate the structural excellence of GNPs-doped asphalt. It checks the bitumen-aggregate binding strength properties, moisture impact resistance and permanent deformation resistance as necessary factors for consideration (Hafeez et al., 2019).

Softening Point (°C)	Base Binder	2% Graphene Nano-Platelets (GNPs)	4% Graphene Nano-Platelets (GNPs)
Top Section	48.5	49.8	57.4
Bottom Section	49	50.5	57.8
Difference	0.5	0.7	0.4

Table 5-1 The softening point test results for storage stability.

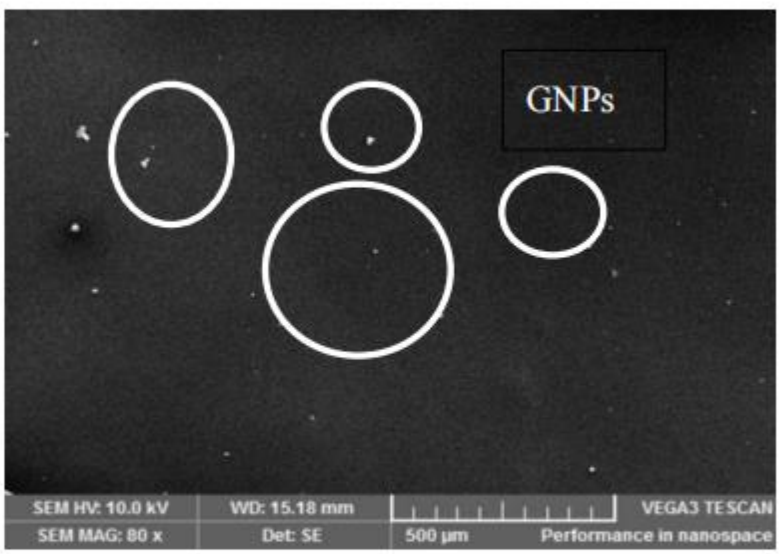


Figure 5.2 A Scanning Electron Microscope (SEM) image of the Graphene Nano-Platelets (GNPs) in the asphalt binder (500μm).

A British Pendulum Skid Resistance Tester has been used to measure the polishing effect and skid resistance for the realistic performance study. GNPs improved the pavement's rutting resistance as well as its durability, according to the findings. GNPs have a large surface area, which increases the concrete's attachment capacity and stiffens the binding of asphalt. To improve the skid resistance GNPs can add Micro-textures to the surface of the pavements (Hafeez et al., 2019).

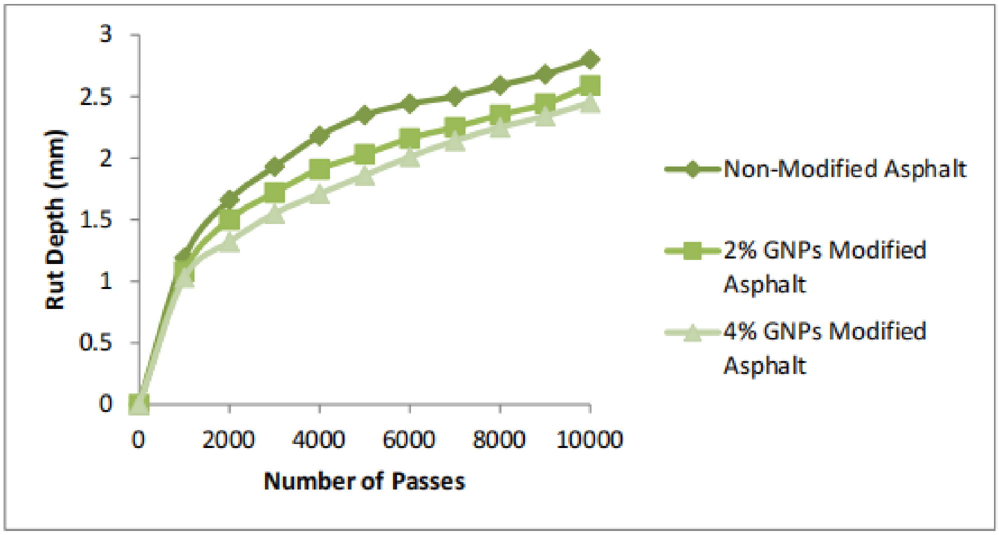


Figure 5.3 The Wheel Tracking Test results at 40°C GNPs

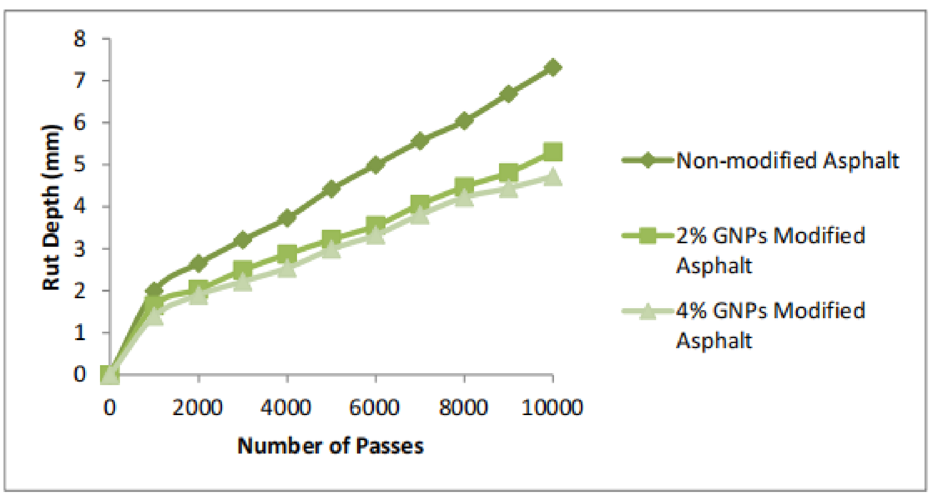


Figure 5.4 The Wheel Tracking Test results at 55°C GNPs.

Graphene Nano-Platelets are easy to diffuse as compared to other nanoparticles. The penetration value of the asphalt mixture will be reduced by up to 48%, while the elastic modulus will be increased by up to 19% by the use of GNP, according to conventional research findings. The softening point rises to 57 C with the addition of 4% of GNPs, which is suitable considering Pakistan's high temperatures(Hafeez et al., 2019).

Test	Base Binder	2% Graphene Nano-Platelets (GNPs)	4% Graphene Nano-Platelets (GNPs)
Penetration (0.1 mm)	61	40	32
Softening Point (°C)	48	49.5	57
Ductility (cm)	100	14	13

Table 5-2 The physical properties of the base and modified binders.

The Dynamic Modulus Test is performed at 40 and 55 deg. Cel. using NU-14.Dynamic Modulus is a direct measure of the rut resistance. The Dynamic Modulus is a measurement of rut resistance. The value of the Dynamic Modulus is higher for GNP-modified asphalt, as shown by the data. Regardless of temperature or stress circumstances, asphalt amended with 4% GNPs had the greatest Dynamic Modulus values. In the Wheel Tracking Test, the similar pattern was seen. In general, the Dynamic Modulus values at 55°C are lower than those at 40°C, indicating that rut susceptibility is greater at higher temperatures. When the loading frequency is increased, the load response lag phenomenon becomes more apparent. This means that as the loading frequency is increased, the asphalt mixture's Dynamic Modulus or strength increases. GNPs with a good dispersion can help asphalt by improving the interaction and adhesion strengths inside it. These effects could raise the Dynamic Modulus of GNP-doped asphalt and make it more resistant to rutting (Hafeez et al., 2019).

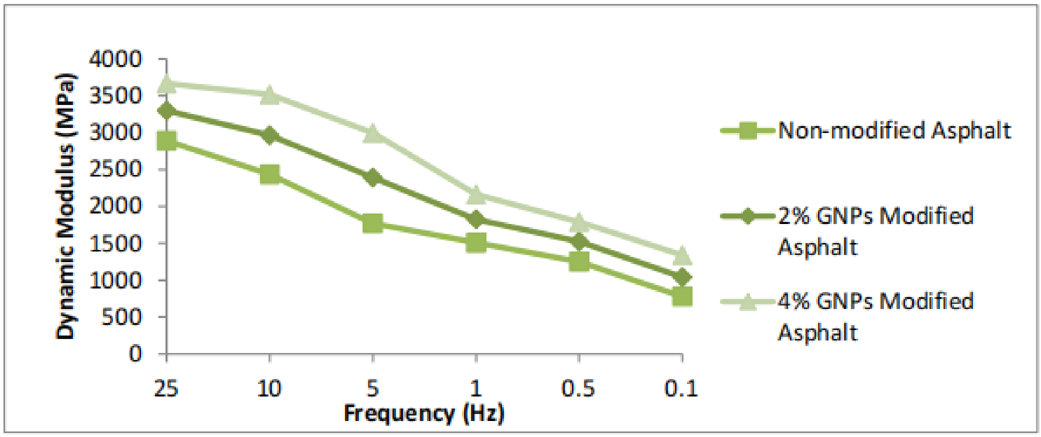


Figure 5.5 Dynamic Modulus at 40 ◦C. GNPs = Graphene Nano-Platelets.

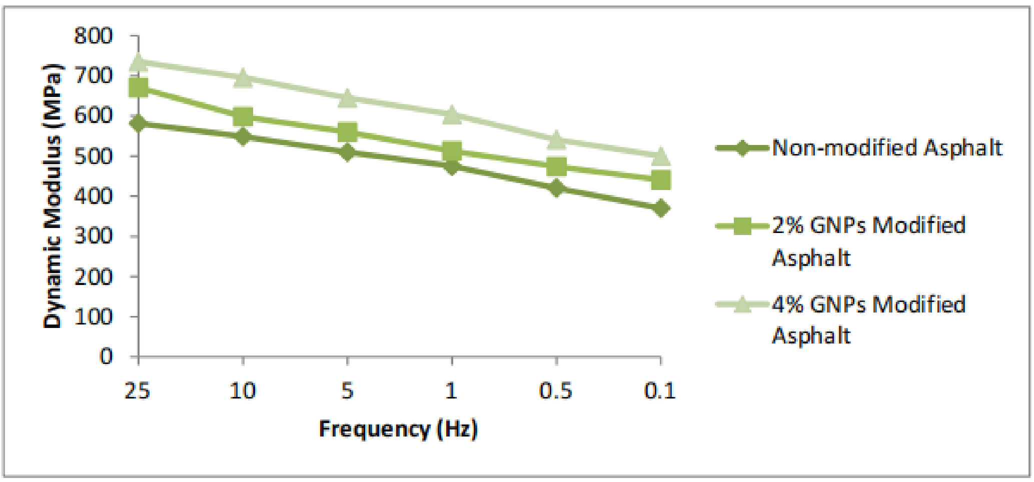


Figure 5.6 Dynamic Modulus at 55 ◦C. GNPs = Graphene Nano-Platelets.

The asphalt binder improved with GNP is durable and could be kept for extended periods of time before making the settlement of nanoparticles, according to the storage stability test results. PG 70 can be made by composing 4% of GNPs, which is appropriate for Pakistan's environmental conditions. The rheology of the binder is investigated, and the GNP-modified binder's stiffness properties are greatly improved. As the amount of GNPs increases, the optimal binder content (OBC) rises(Hafeez et al., 2019).

Type of Mix	Optimum Binder Content
Base Binder	4.38
2% GNPs	4.49
4% GNPs	4.67

Table 5-3 The Optimum Binder Content (OBC) of the asphalt mixtures.

This trend indicates that GNP-modified asphalt would have a slightly higher initial cost than normal asphalt. GNPs reduce temperature sensitivity while also increasing permanent deformation resistance. Asphalt uses GNPs as a reinforcing material, giving it strength and increasing the complex modulus of the material. GNPs significantly reduce asphalt's moisture tolerance. GNPs appear to enhance the cohesive and adhesive bonding of the bitumen binder, according to a PATTI bitumen bond strength test (Hafeez et al., 2019).

5.3. Introduction of Graphene Nanoplatelets (GNPs) doped asphalt to improve roadway functional performance

For road safety, skid resistance is a key component to consider. The surface texture of the pavement and its resistance to the polishing action of traffic plays a big influence in skid resistance. The use of nanotechnology in pavement engineering has recently advanced, resulting in amazing improvements in asphalt qualities. Graphene Nano-platelets (GNPs) are a low-cost material that considerably enhances the pavement's structural performance by boosting rutting resistance and boosting adhesion qualities. For the manufacture of the asphalt mixture in this investigation, a gradation of 19.5 mm NMAS was used. The asphalt mixture slabs were made with a 60/70 penetration grade asphalt binder that had been amended with 2% and 4% GNPs (by weight of the binder). To evaluate the skid resistance of their surfaces, they used a British Pendulum Skid Resistance Tester. A Wheel Tracker Machine was used to apply 10,000 passes of a 700N loaded wheel on the slabs to examine the polishing effect. The skid resistance of the tracks generated in the slabs as a result of wheel passage was measured. SEM pictures were also used to investigate the micro-texture. In comparison to the combination created with a base binder, the GNPs treated asphalt had a rough texture. The results show that the surface of slabs constructed from GNPs doped asphalt exhibited good skid resistance both before and after the wheel passes were applied (Hafeez et al., 2018).

5.4. Graphene Nano-platelet (GNP) bituminous binders characterized tribologically.

Recent researches show that if bitumen is mixed with a fine quantity of graphene Nano-platelets (GNP), it could considerably enhance the compactness and workability of the HMA mixtures. On the other hand, it does not have a reduction effect on the binder in terms of its viscosity. The synthetic graphite GNPs are composed of carbon and ash in proportion by percentages 99.66 and 0.34 respectively. The base binder which is plain PG58-28 bitumen is mixed with the composition of GNPs. The GNPs were used with the amount of 3% and 6% by weight of the binder (Ingrassia et al., 2019).

Base bitumen was tested along with GNP binders with the help of tribological tests. A Dynamic Shear Rheometer (DSR) was placed on ball-on-three-plates fixtures for this test. It is used to calculate the friction coefficient (μ) as per the principle of measurement. It is calculated by the following equation:

The total frictional force is represented in the equation by FF-TOT. Total normal force in the equation is represented as FN, tribo-TOT. Both these forces experienced by the specimen are calculated with the help of equations mentioned below:

FN = DSR's axial force T =Moment (torque) rball = ball radius

α = the angle of the horizontal plane and the plates, it is 45 degree for a ball on three plates apparatus (Ingrassia et al., 2019).

The purpose of the current research is to characterize tribological properties of the graphene Nano-platelets GNPs in bituminous binders to connect their lubricating properties to the increased compactness of GNP bituminous mixes. The viscosity tests were carried out to determine the relationship between viscosity and friction. The GNP has a higher viscosity than the base bitumen, so the improved workability of the GNP asphalt binder is not due to the reduction of viscosity caused by adding the Graphene Nanoplatelets.

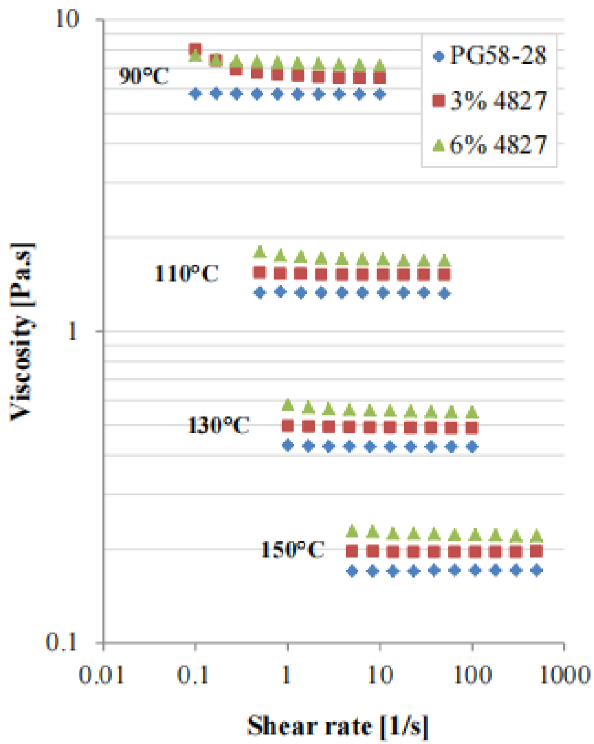


Figure 5.7 Viscosity of the binders tested as a function of shear rate.

Temperature [°C]	PG58-28	3% 4827	6% 4827
110	1.32	1.52	1.69
130	0.43	0.49	0.55
150	0.17	0.20	0.22

Table 5-4 Viscosity of the binders tested [Pa.s].

The tribological results, on the other hand, revealed that there was no improvement in lubrication after the addition of GNP under the testing conditions. This improvement is significant and, in any case, not predicted in the elastohydrodynamic regime due to a good link between the minimum coefficient of friction and viscosity. Rather, a boundary or mixed lubrication regime is likely to occur during the manufacturing and compaction of the mixture, and a friction reduction should be observed in these regimes. The rough surfaces, such as aggregates, may reduce the irregularity between the asperities by occupying the spaces, but this is not observed in this case because of even and the smooth substrate being used in the experiment, the roughness of which was possibly increased further due to adding GNPs (Ingrassia et al., 2019).

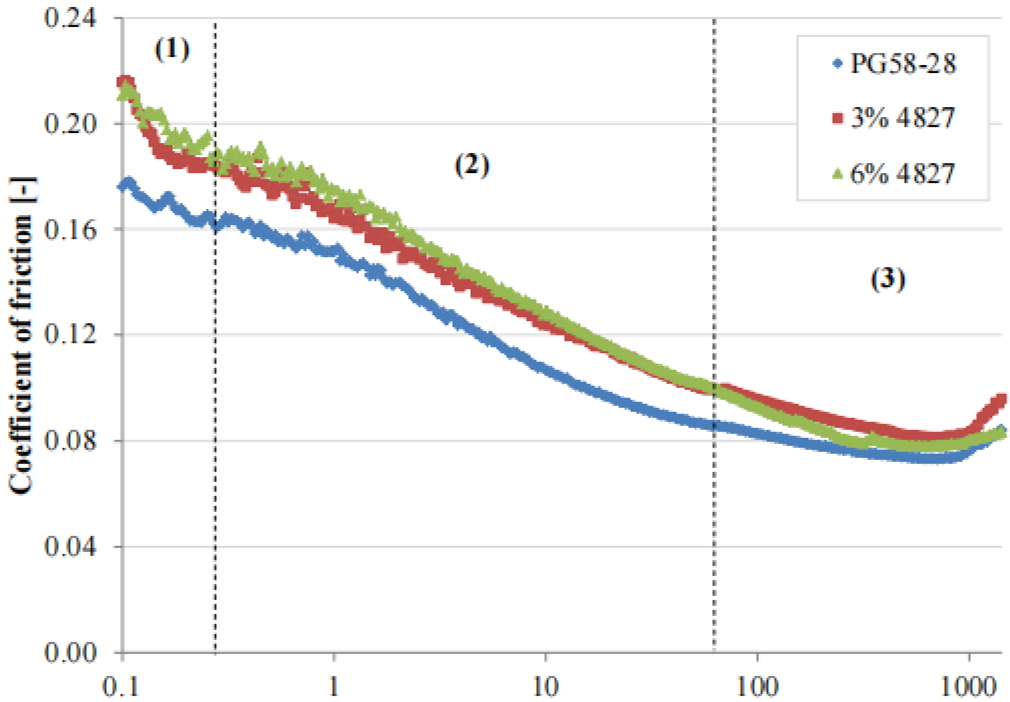


Figure 5.8 Tribological results at 110°C.

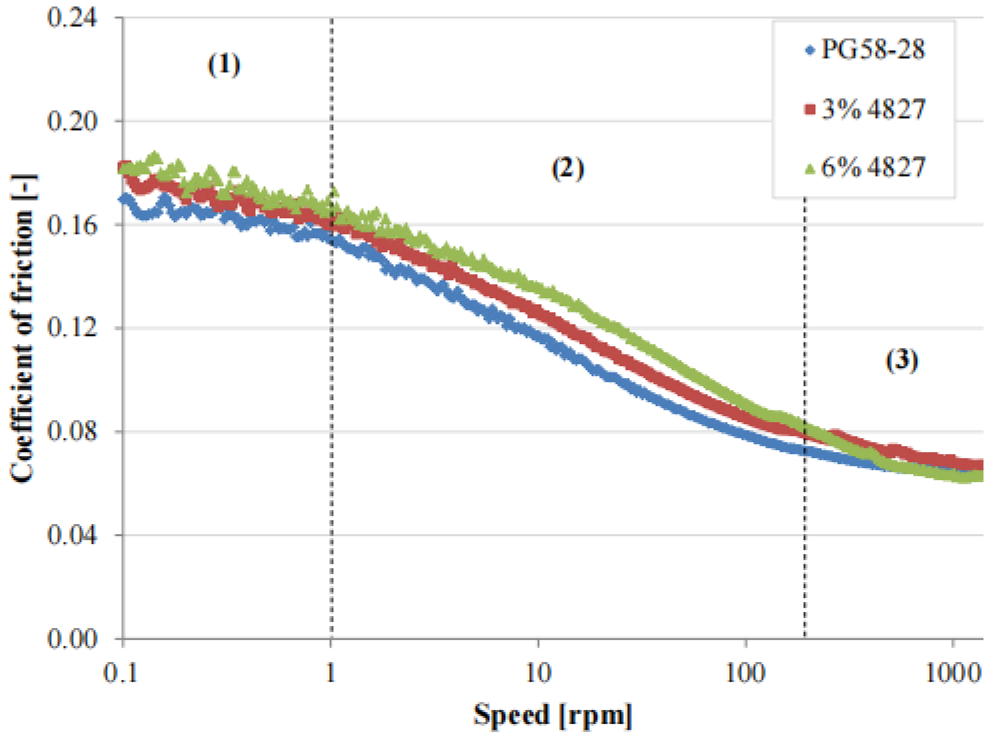


Figure 5.9 Tribological results at 130°C.

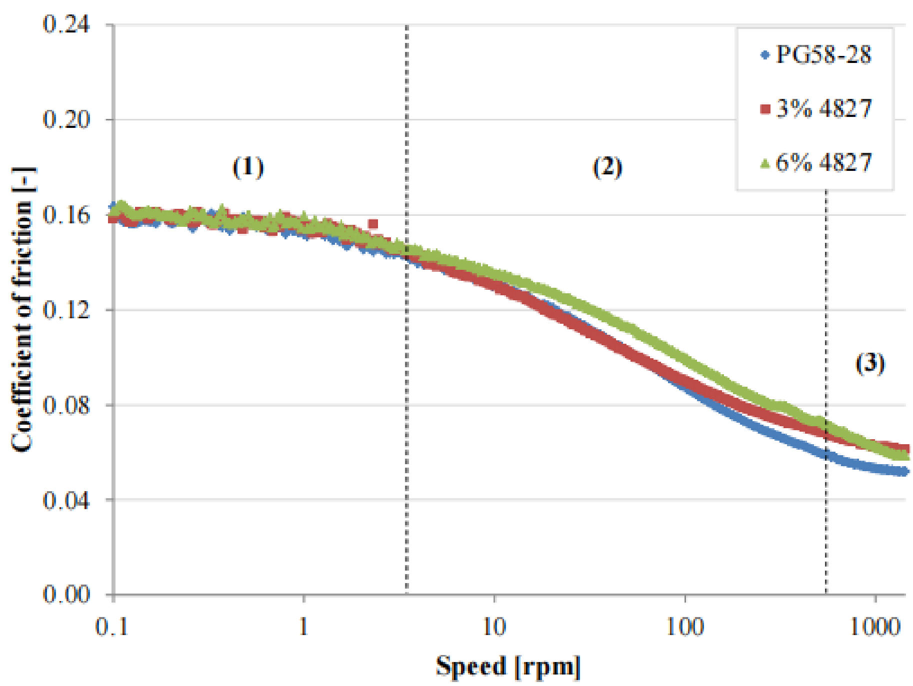


Figure 5.10 Tribological results at 150°C.

As a result, more research should be conducted on rock surfaces with regulated roughness to effectively mimic the occurrence of friction comprising aggregates along with the bitumen for making the composition mixture. A good understanding of whole processes which would determine the compaction response of HMA due to this approach could contribute to the development of more reliable, efficient and sustainable pavement mixtures that use less power in the compaction process as well as mixing process (Ingrassia et al., 2019).

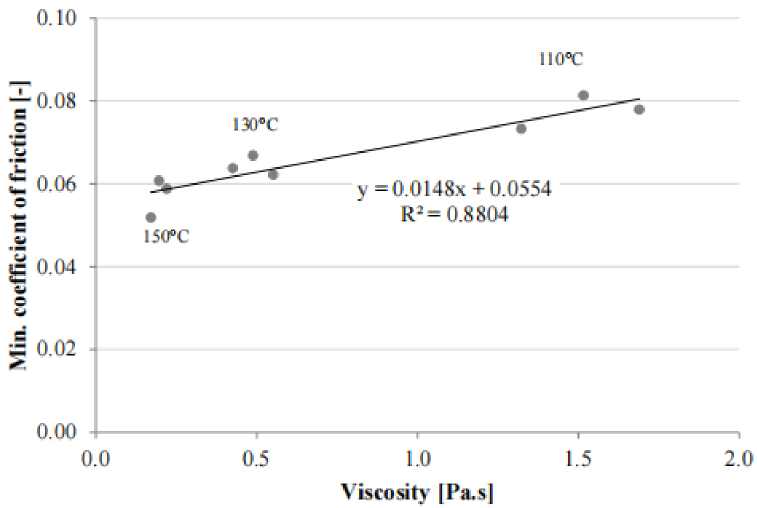


Figure 5.11Correlation between minimum coefficient of friction and viscosity.

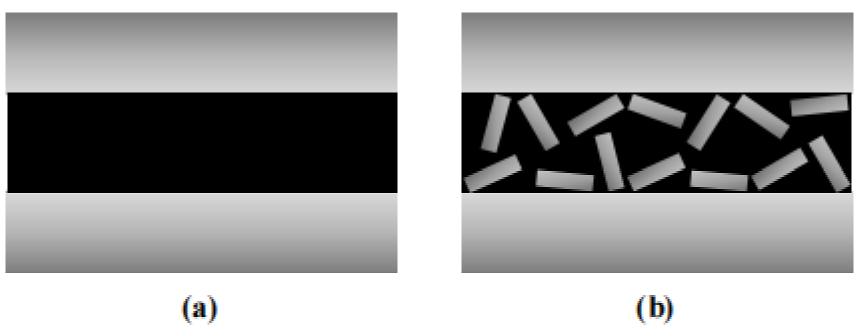


Figure 5.12 Scheme of the lubricating film between smooth surfaces: (a) without GNPs and (b) with GNPs.

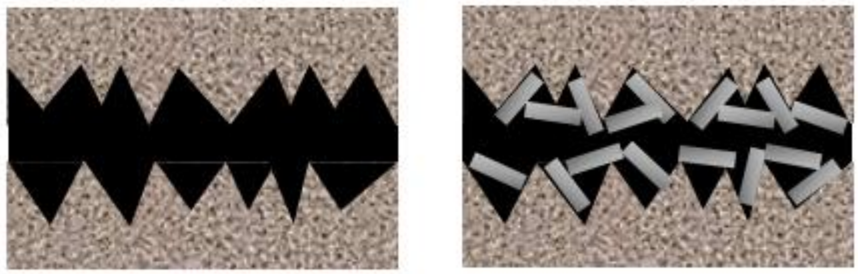


Figure 5.13 Scheme of the lubricating film between rough surfaces: (a) without GNPs and (b) with GNPs.

5.5. Asphalt binders and mixes using Graphene Nanoplatelets (GNP) reinforcement.

Approximately 90% of the USA roads are constructed using asphaltic mixtures. To increase the performance of the pavement consistent efforts have been performed. The main part of these efforts was to make a new asphalt-based HMA mixture to gain good mechanical properties of the pavement, and for this purpose, nanotechnology has been used in recent times (Marasteanu et al., 2016).

In this research, we will study the effect of adding graphene Nano-platelet to the asphalt binder and check its compaction and mechanical properties. Meanwhile, it provides an overview of some basic characteristics of GNP materials and their applications to transportation engineering, which motivates further research into their great potential application in asphalt pavements (Marasteanu et al., 2016).

The report continues with a series of experiments evaluating the mechanical properties of GNP reinforced pavement mixture and asphalt binders, including one with a detailed phenomenon for pavement material preparation and the quantitative analysis of the impact of GNP on mechanical properties of the asphalt binders (mixtures). It has been discovered that GNP can also be mixed to asphalt mixtures and binders without causing significant dispersion issues. Binder and mixture samples prepared with various numbers and types of GNP are used in the study. Three different types of mechanical tests are performed for every type of design mix: First, at room temperature, the complex modulus of the GNP-reinforced asphalt binders was tested. Second, indirect tension creep test and the strength tests of the GNP-reinforced asphalt binders, mixtures measuring creep property, relaxation and strength properties. Third, the low-temperature fracture test of GNP reinforced binder calculating fracture energy. The tests show the adding of GNPs to asphalt binders can significantly improve flexural strength at low temperatures and moderately increase creep stiffness while having no negative effect on the relaxation properties. It also discovered that, when compared to standard asphalt mixtures, GNPs reinforced asphalt mix specimens have higher strength and, under certain cases, higher fracture energy. GNPs addition, however, doesn't really improve the electrical conductivity of asphalt mixtures using the current mixing method and process (Marasteanu et al., 2016).

The compaction process of GNPs reinforced asphalt binders is studied, which includes the following areas: (i) the air void content that can be accomplished for a given compaction effort based on several gyrations; (ii) the air voids content which can be obtained for the given compaction test; (iii) For the given compaction effort and the target air void value, the compaction temperature is calculated (Marasteanu et al., 2016).

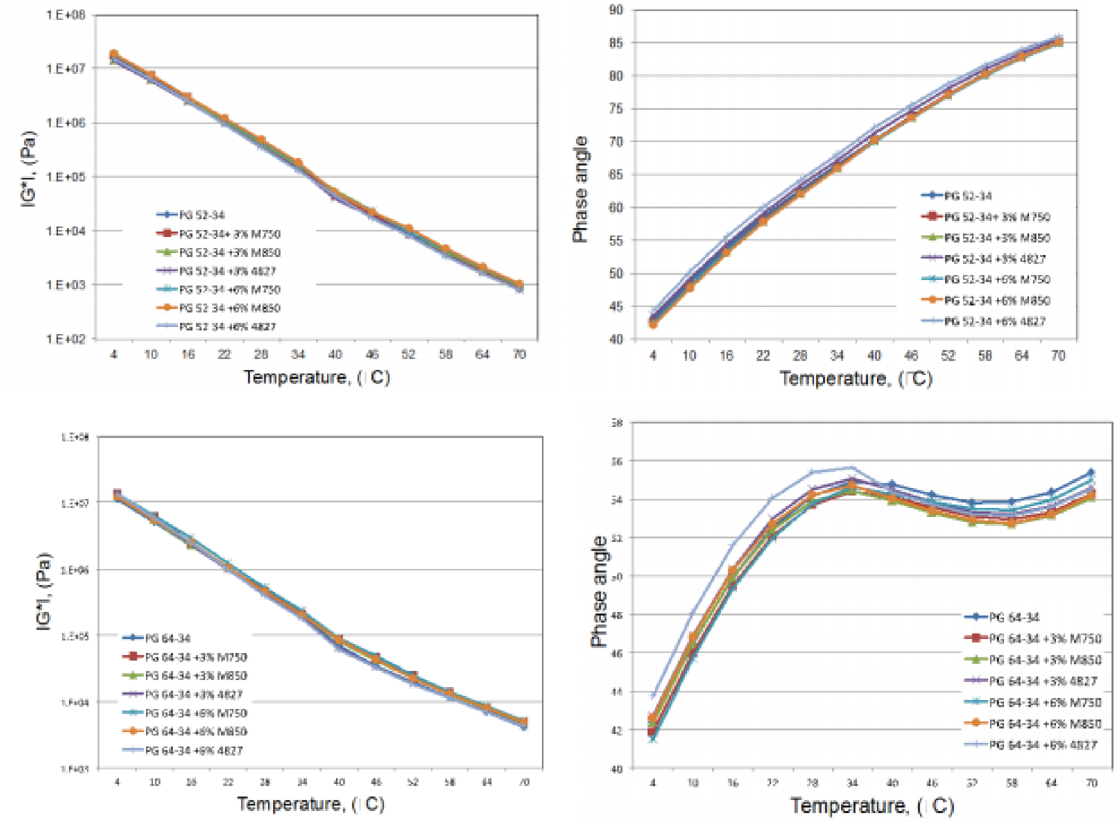


Figure 5.14 Measured complex shear modulus and phase angle of GNP-reinforced asphalt binders.

The mechanical properties experiments of GNPs reinforced asphalt binders were studied, and it was discovered that, depending upon this mix design composition and compaction temperature, GNP might increase or decrease creep stiffness. The introduction of GNPs would result in a slight rise in the IDT strength. This increase is substantially less than the rise in the flexural strength of GNPs reinforced asphalt pavement mixture. This could be due to the significant level of damage that might occur at the interface between the aggregates and binder, which the GNPs materials may not be able to adequately reinforce. The GNP, on the other hand, does not always increase fracture energy. The current research shows that GNP increases the fracture energy of combinations with modified binders, and the same tendency is seen for mixture having unmodified binders compact at a lower temperature. The GNP, on the other hand, has a bad effect on fracture energy in mixes with the unmodified binders that are compacted at a warmer temperature (Marasteanu et al., 2016).

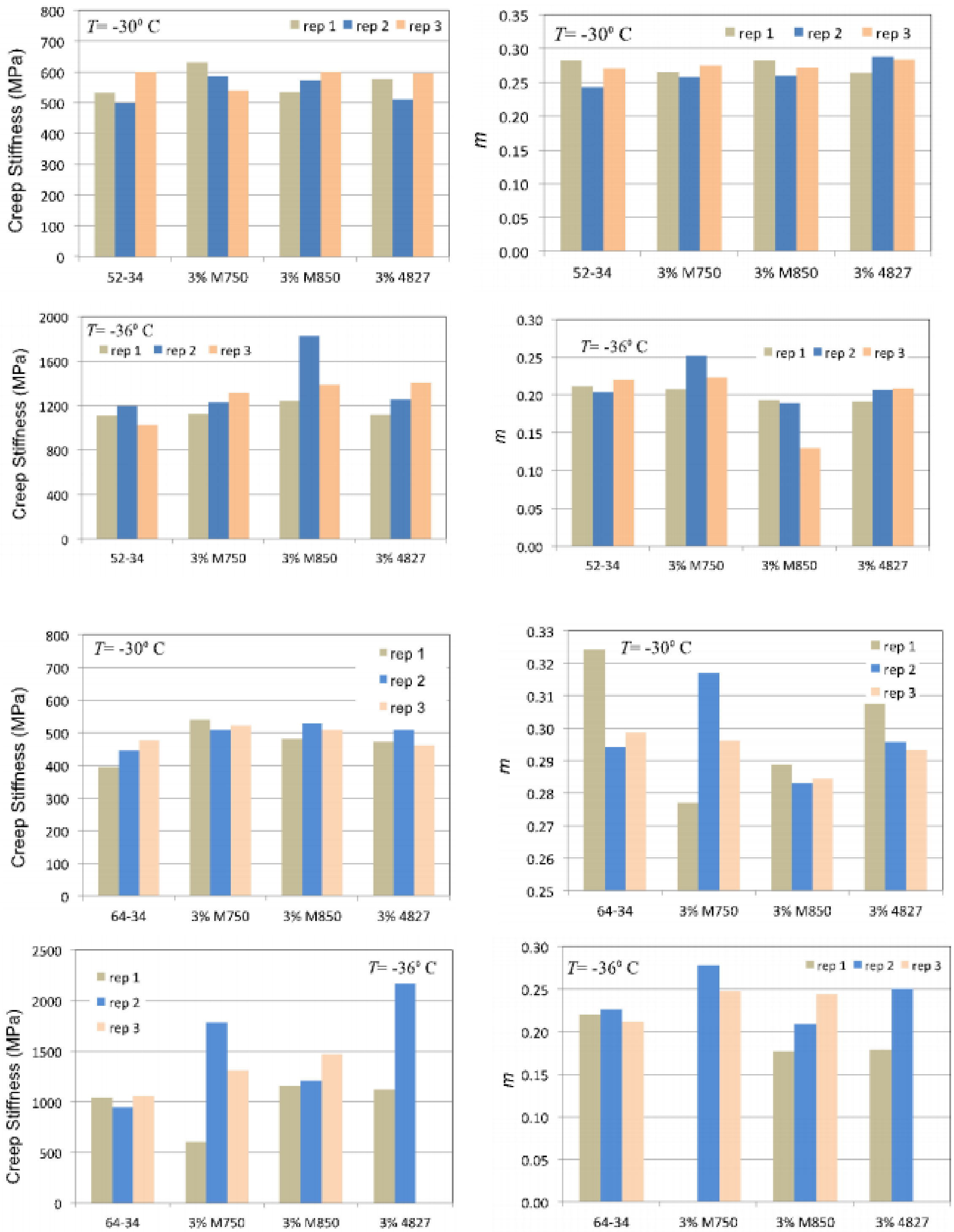


Figure 5.15 Measured creep stiffness and m-value of GNP-reinforced asphalt binders with 3% GNP addition.

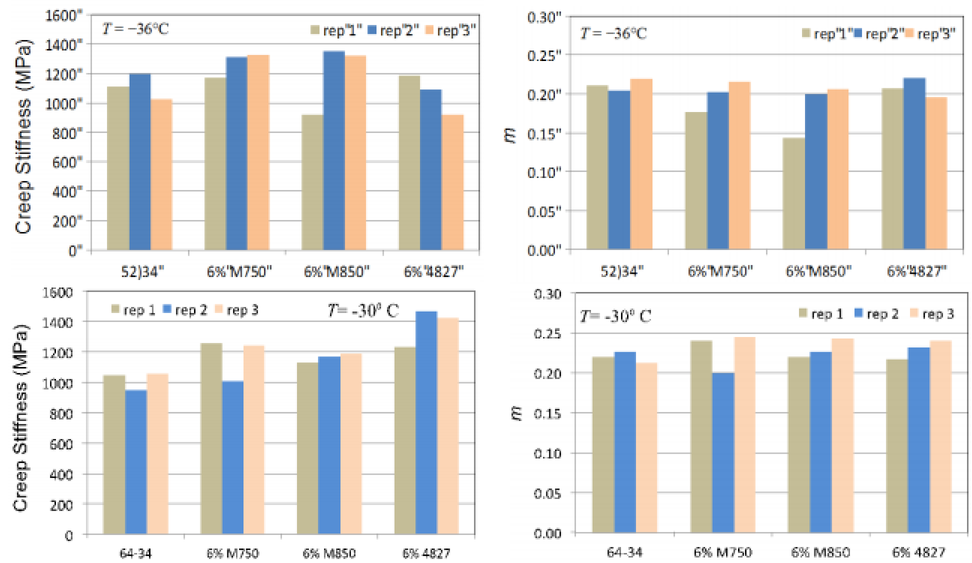


Figure 5.16 Measured creep stiffness and m-value of GNP-reinforced asphalt binders with 6% GNP addition.

Compaction tests on GNPs reinforced bitumen show that the reinforced binders with GNPs can increase the mixtures' compaction ability significantly. The GNPs could reduce the number of compaction gyrations required to attain a set air void content by 20%–40%. It was also discovered that GNPs could lessen the temperature dependence of compaction gyration in specific mix designs. Engineers would be able to create warm asphalt binder as a result of this. The test findings show that adding GNPs to asphalt mixtures can effectively lower the air void content for a given amount of compaction gyrations, improving the long-term performance and durability of the HMA pavements. Parallel to the compaction testing, a series of rut studies are conducted, demonstrating that adding GNP to the pavements can improve rut performance at medium temperatures. However, if the mixes are compacted at a temperature lower, the addition of GNPs could have a negative impact on rut performance (Marasteanu et al., 2016).

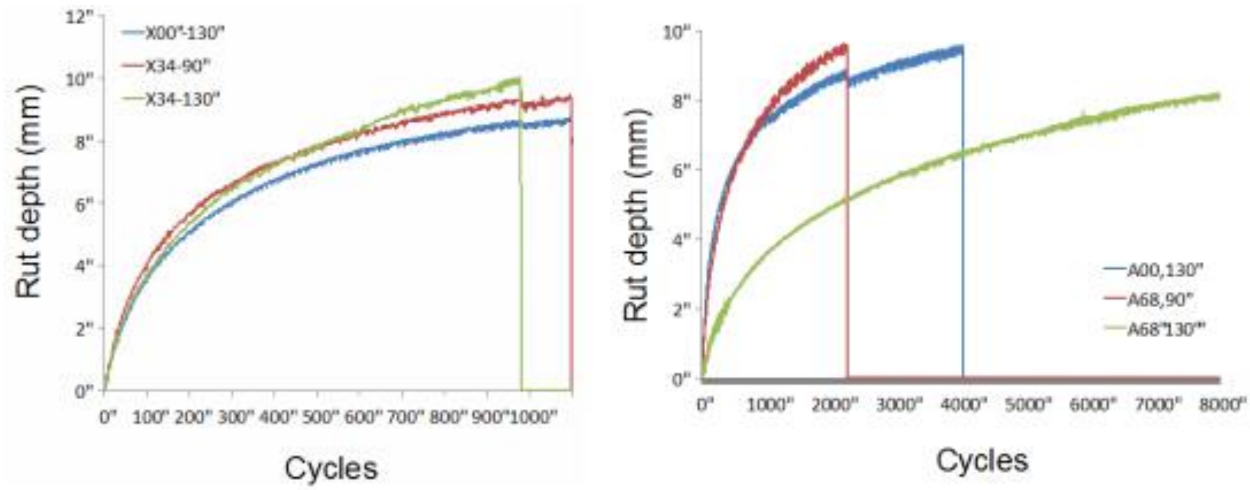
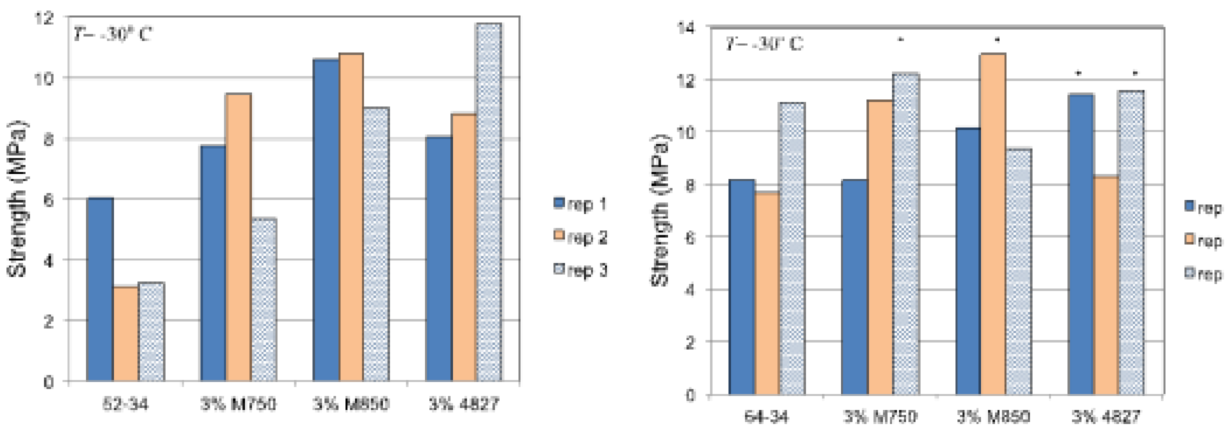


Figure 5.17 Measured rut performances of GNP-reinforced asphalt mixtures.



(a) (b)

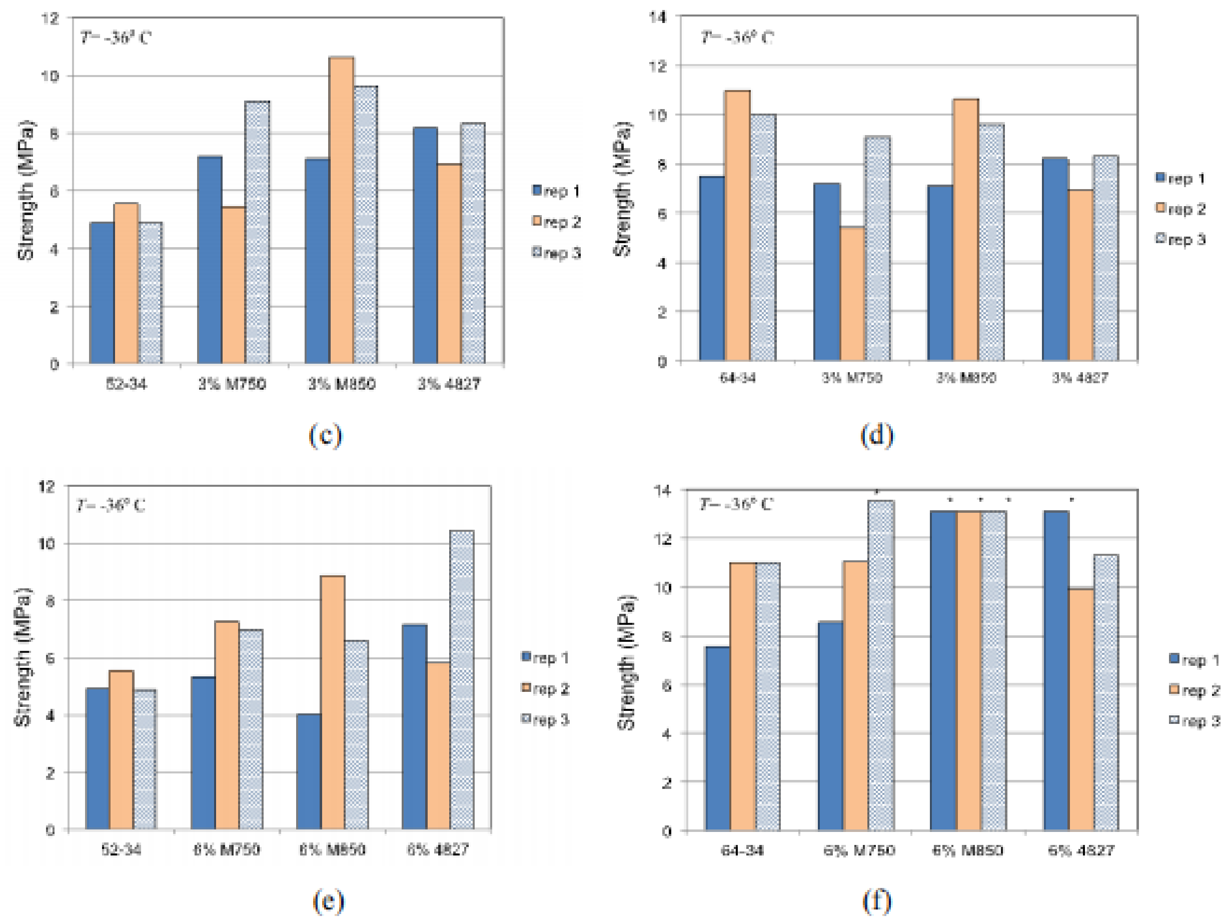


Figure 5.18 Measured flexural strength of GNP-Reinforced asphalt binders.

The application of GNPs to GNP-reinforced bitumen binder had no noticeable impact on the complex modulus of the binder both for traditional polymer modified and unmodified bitumen binder, according to this research. Tests also reveal that adding GNPs to the binding material has no effect on the binder's relaxing property. The integration of GNPs into binders, on the other hand, results in a significant increase in flexural strength under lower temperatures. A modest inclusion of GNPs within polymer modified and unmodified bitumen binder may produce a 130 percent growth in flexural strength, if it is added in the mixture by proportion between 3- 6 percent by weight. It must be noticed that this rise in polymer-modified asphalt binders has never been seen. The strength improvement, on the other hand, is found to be less pronounced when a large amount of GNP is added. This may be due to the possibility of GNPs clumping at high doses (Marasteanu et al., 2016).

The electrical resistance result shows that the GNPs would not make the binders electrically conductive with this current mixing. This may be because the GNPs in the bitumen binder did not reach the homogenous state for producing a network for the electron hopping although the additional amount of the GNPs was way more than the theoretical percolations threshold. Meanwhile, it has been discovered that if the binders contain any water, adding GNPs can make the materials electrically conductive and with high electrical resistance (Marasteanu et al., 2016).

In conclusion, the findings of this study show that adding GNPs to asphalt mixture pavements can improve a variety of compaction and mechanical properties, hence improving the pavement's durability and performance. The GNPs reinforced asphalt pavements have the potential for long-term applications in the road industry, including both new pavement and road construction and pavement repair, due to their cheap material cost relatively (Marasteanu et al., 2016).

NANO CLAY

6.1. Nano Clay

Nanoclay, which is made up of stacked layers of silicates, has been proposed as a cost-effective way to improve the mechanical, thermal, and barrier characteristics of polymer systems. Dispersion of Nanoclay in hydrogel in homogenous manner results in enhancement to its properties.

Nano-clay can be effectively used as modifier in asphalt pavements in the regions exposed to higher temperature but Nano-clay modification is least desired for pavements in areas where temperature drops quite low, it is because Nano-silica don't add to the low temperature thermal cracking performance of asphalt binder

6.2. The physical and rheological characteristics of asphalt binder influenced by the concentration of organic Montmorillonite Nano Clay.

In this research conducted by Muniandy et al. (2013), the physical and rheological properties of asphalt mix were studied after adding (0%, 3%, 5%, 9%) by weight of bitumen of two types N-3 and N-4 of organic Montmorillonite Nanoclay (OMMT) in 80/100 penetration grade asphalt.

Bitumen of grade 80/100 and Nano-clay particles procured. OMMT modified asphalt was prepared at established temperature and r. p.m. Physical properties: penetration, softening point and viscosity of base and OMMT asphalt determined according to ASTM D 5, ASTM D 36, and Viscosity using Brookfield viscometer, respectively. In the next step, a modulus named DSR, or dynamic shear modulus, was utilized to examine the rheological properties of both OMMT modified asphalt and the base. ANOVA statistical analysis done to analyze the type and content of OMMT on asphalt mix performance.

Physical Properties	Result	Specification
Penetration@ 25°C, 0.1mm	80	ASTM D 5
Softening Point ,°C	46.5	ASTM D 36
Viscosity@ 135°C, Pa.s	0.379	ASTM D 4402
G*/ sin δ @ 64 °C , kPa	1.21	AASHTO TP5
Ductility @ 25 °C, cm	>100	ASTM D 113
Specific Gravity, g/cm^3	1.03	ASTM D 70

Table 6-1 Physical Properties of Base Asphalt 80/100 Penetration Grade.

Physical Properties	Nanoclay Type	
	N3	N4
Organic Montmorillonite Treatment	Dimethyl benzyl (hydrogenated tallow alkyl) ammonium cations	Dimethyl di (hydrogenated tallow alkyl) ammonium cations
CEC	90-120 mmol/100g	90-120 mmol/100g
Color	White	White
Appearance	Fine	Fine
X Ray Diffraction Properties d_{001}nm	d = 2.8	d = 3.8
Moisture	<3%	<3%

Table 6-2 Nanoclay Physical Properties.

Blend Type	Penetration@ 25°C	Viscosity@ 135°C, Pa.s	Viscosity@ 165°C, Pa.s	Softening Point, °C
Base AC	80	0.379	0.113	46.5
AC-N3-3%	70	0.508	0.138	47.8
AC-N3-5%	64	0.608	0.201	48.1
AC-N3-9%	57	0.867	0.375	49.1
AC-N4-3%	72	0.463	0.125	47.5
AC-N4-5%	68	0.500	0.150	47.8
AC-N4-9%	62	0.608	0.238	48.9

Table 6-3 The Physical Properties of Organic Montmorillonite Nanoclay Modified Binder.

As a result of this experiment, two major outcomes were noticed. Firstly, a increase was noticed in the softening point and viscosity and secondly, penetration decreased of OMMT modified asphalt thus improving the physical properties. Results indicated that N-3 type OMMT showed better results compared with N-4.

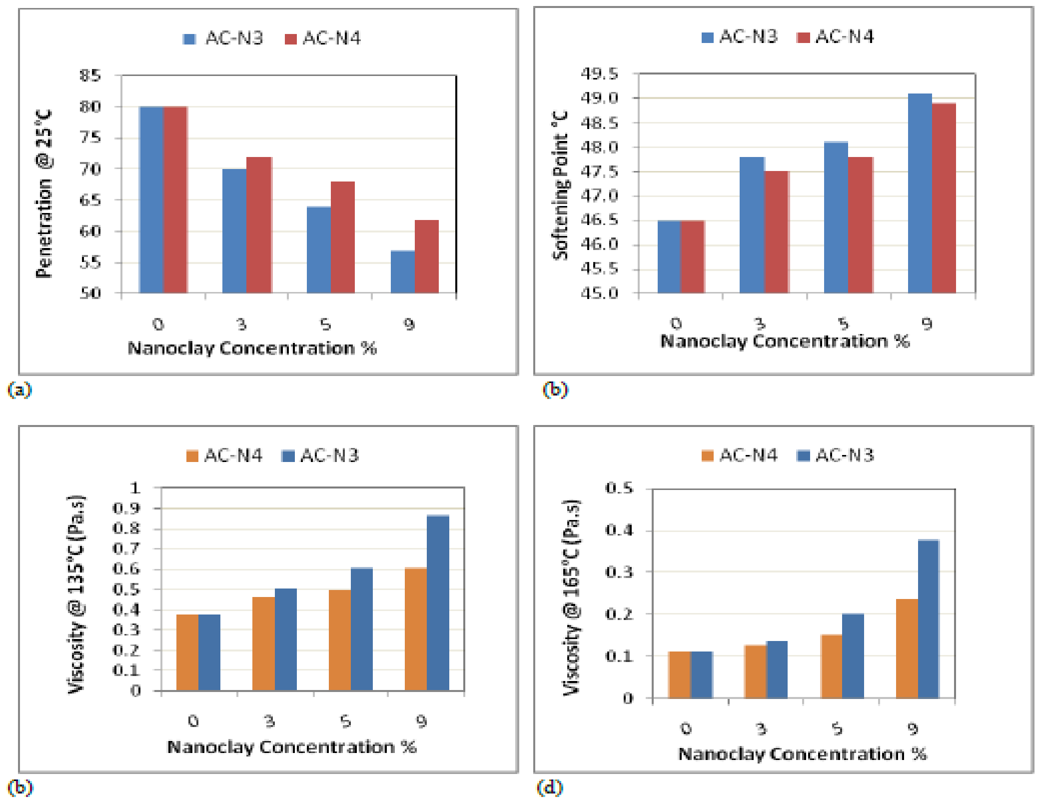


Figure 6.1 (a) Penetration (b) Softening point(c) Viscosity @ 135°C (d) Viscosity @ 165°C of the Modified Asphalt Binder with Various Concentration of OMMT.

Likewise, DSR results showed that there was a reduction reported in the Phase Angle while an increment was reported in the Complex Shear Modulus, thus increasing its stiffness and elasticity. Increased stiffness improved rutting resistance while increased elasticity ensured maximum recovery after deformation by low energy dissipation per load cycle. The increased complex shear modulus (G*) of OMMT modified asphalt is very significant for high temperature performance of asphalt pavements.

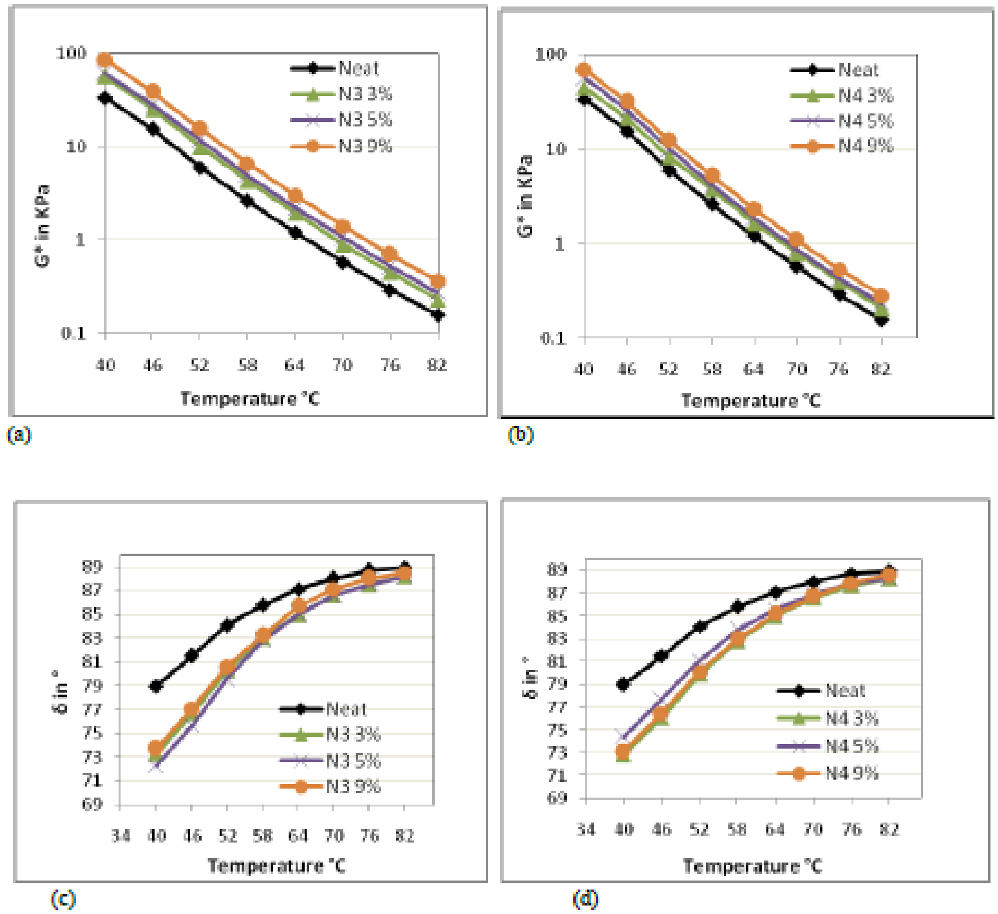


Figure 6.2 (a, b) Complex Shear Modulus (G) and (c, d) Phase Angles (δ) against Temperature for both Type of Nanoclay Modified Asphalt.*

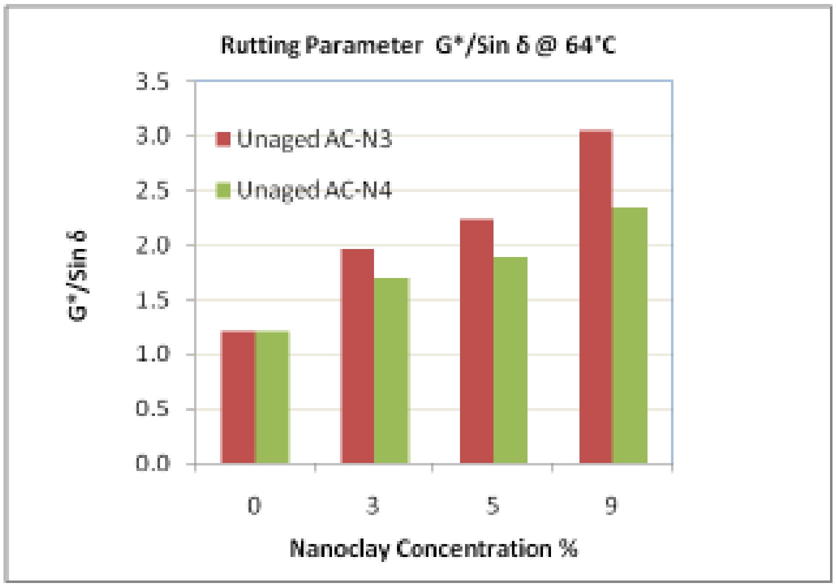


Figure 6.3 Rutting Parameter Variation of OMMT Unaged Modified Asphalt with Three Different Concentrations at 64°C for both Nanoclay Types.

ANOVA statistical analysis results concluded that the content of OMMT Nano-clay have more implications on softening point, viscosity, phase angle and rutting performance while type of OMMT is more of importance for penetration of asphalt mix. (Muniandy et al, 2013)

6.3. Evaluation of Moisture Susceptibility of Nano Clay-Modified Asphalt Binders

In a study conducted by Hosseini et al. (2014), as stiffness of Nano-clay modified asphalt binder is known to be increased, the purpose of this study was to find its moisture susceptibility or moisture resistance. PG 64-22OK asphalt binder and Nanoclay (cloisite-15A) in different percentile 1%, 2% and 4% were procured. To ensure thorough distribution of Nanoclay, Nanoclay and asphalt binder were blended at specified temperature and r.p.m. Two techniques, namely SEM and SAXD were used to determine the dispersion and efficiency of Nanoclay asphalt binder. These terms stand for scanning on electron microscope and small-angle X-ray diffraction, respectively.

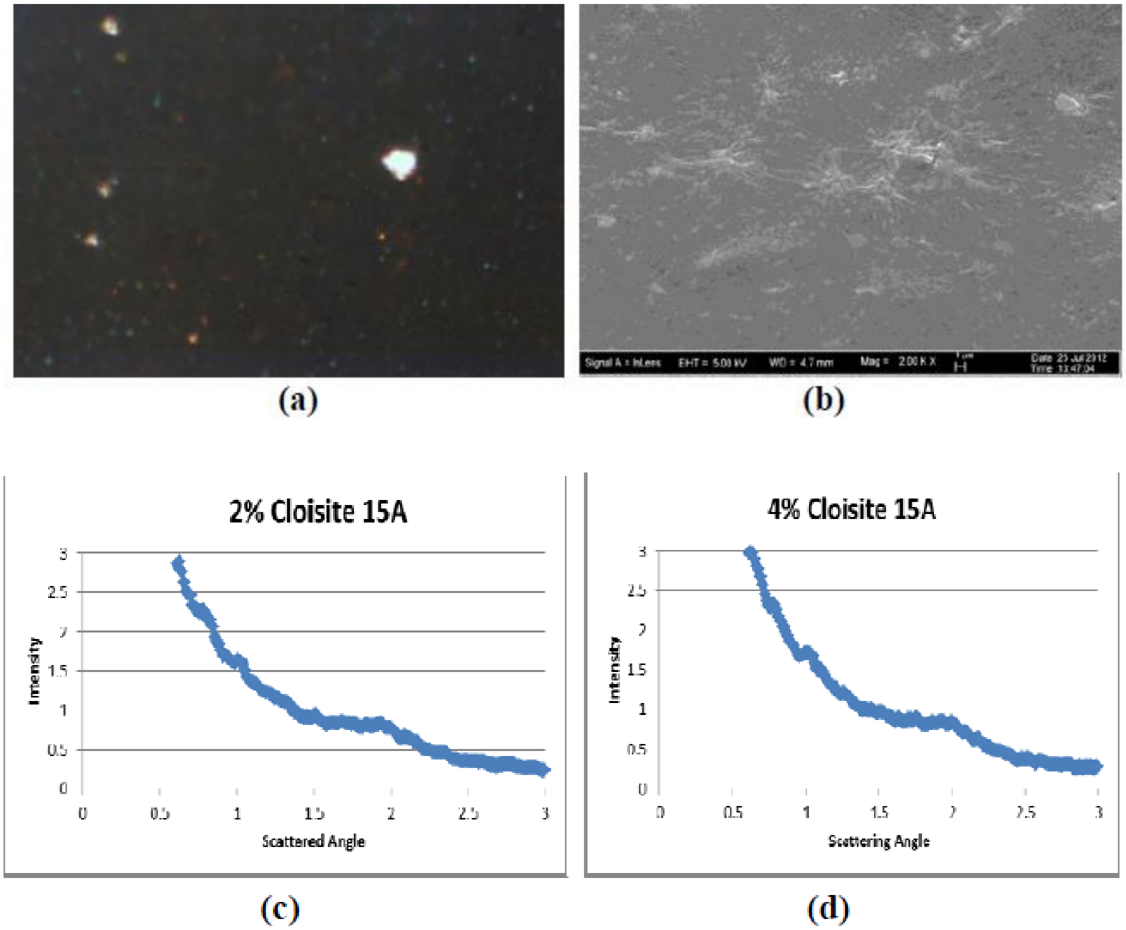
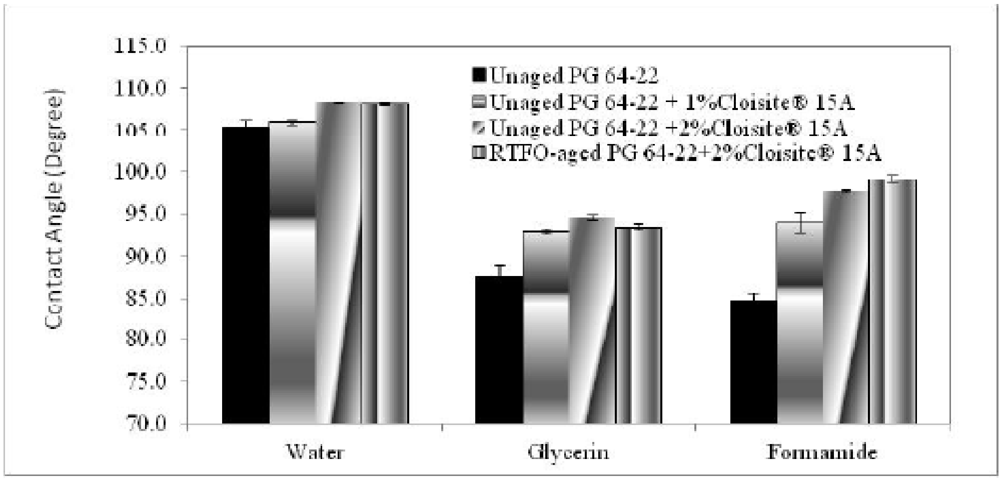
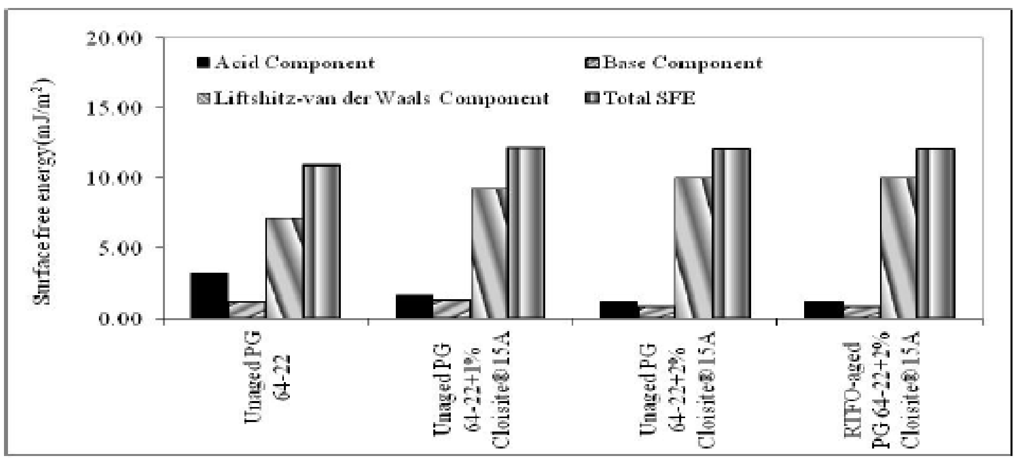


Figure 6.4 Nanoclay dispersion analysis: (a) optical microscope, (b) SEM analysis

SEF components using the Good van Oss-Chaudhury theory (van Oss et al., 1988) was applied to study the impact of water content on adhesion and internal cohesive forces of the binder under study. The contact angles of solvents selected for this experiment, namely formamide, H_2O, and $C_3H_8O_3$, were measured by using a dynamic contact angle, with the asphalt binder.



(a)



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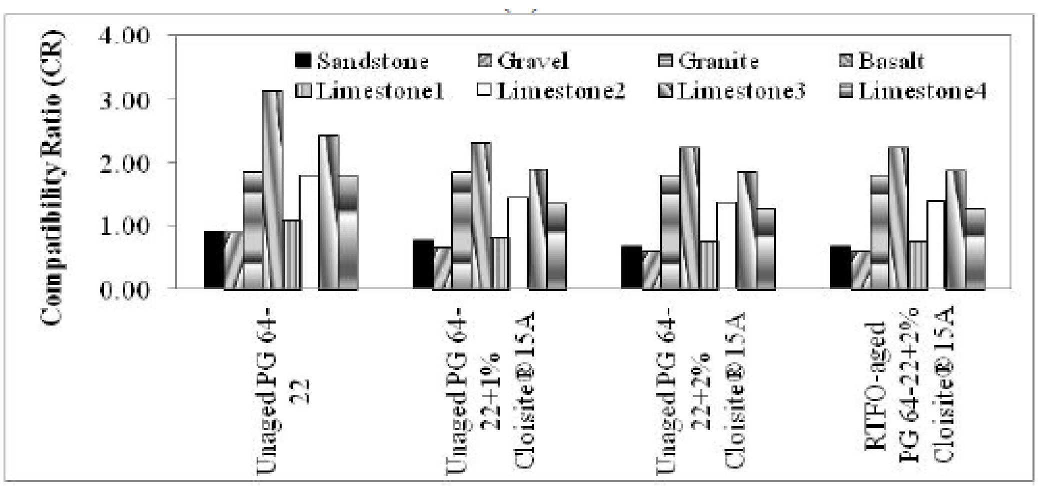

(c)

Figure 6.5 Variation of: (a) contact angle, (b) SFE components, and (c) CR values.

The experiment established the superiority of cohesive energy of the Nano-clay binder over that of base binder. Similarly, dry conditions were found to further decrease the adhesive energy of eight different aggregates, with results showing that the energy decreased by 22%, along with 2% Nanoclay-modified binder. The same held for the adhesion energy in wet conditions, with study showing 24% decrease in the adhesion energy in wet conditions. In all of the above aggregates except granite, a substantial decrease in bond strength has been indicated by the compatibility ratio (CR) values of different aggregates with Nanoclay-modified binders. (Hosseini et al, 2014)

6.4. Evaluation of Selected Performance Properties of Nano Clay-Modified Asphalt Binders

The purpose behind this research was to find a modifier that not only improves the pavement performance parameters but is economic, environmental friendly and readily available. To meet the mentioned objectives three kinds of Nano-clay were procured and their mixes were prepared with asphalt binders obtained from two sources (Arabian Crude and Canadian Crude).Different mixes of three kinds of Nano-clay at 1%, 2%, 3% with source one S1 and source two S2 asphalt binders were prepared in high shear mixer at specified rotational speed and temperature. The kinds of Nano-clay used include Cloisite 15A, Cloisite 11B, and Cloisite 10A. Then Optimum Contact Analyzer OCA measured the moisture susceptibility while The Sessile Drop analysis used surface free energy (SFE) theory to measure the compatibility ratio (CR) of the modified samples. The mechanical and physical formative properties of these binders at molecular level were estimated using the PFQNM mode of a Bruker AFM. Saturate, Aromatic, Resin, and Asphaltene were also used to describe all of the Nanoclay-modified asphalt binders in terms of chemical composition changes. According to ASTM D 4124-09, the test was carried out.

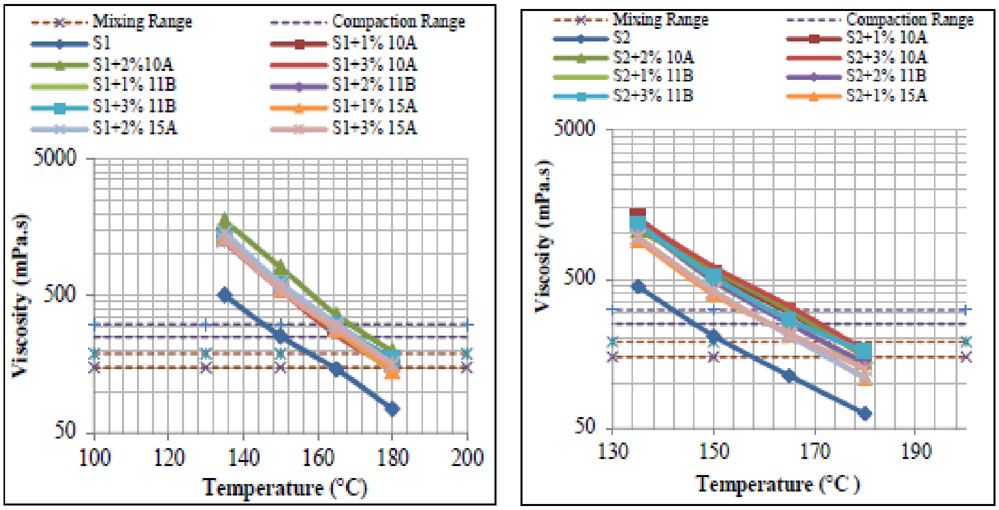

Figure 6.6 Viscosity vs. temperature for modified binders

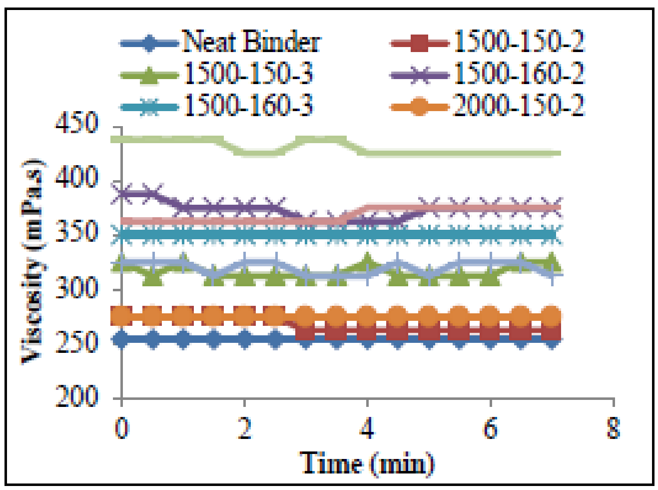

Figure 6.7 Viscosity at different rotations, temperatures, and durations for modified binders.

The viscosity of modified asphalt binders increased up-to 187% with different kinds and percentiles of Nano-clay. The super pave rutting factor (G*/sinδ) of the modified samples increased. Improvement in temperature susceptibility of modified sample was found. The compatibility of Nano-clay with gravel was found more than sand stone for both source binders S1 and S2 and the compatibility of Nano-clay modified binder S2 binder was more than that of modified S1 binder.

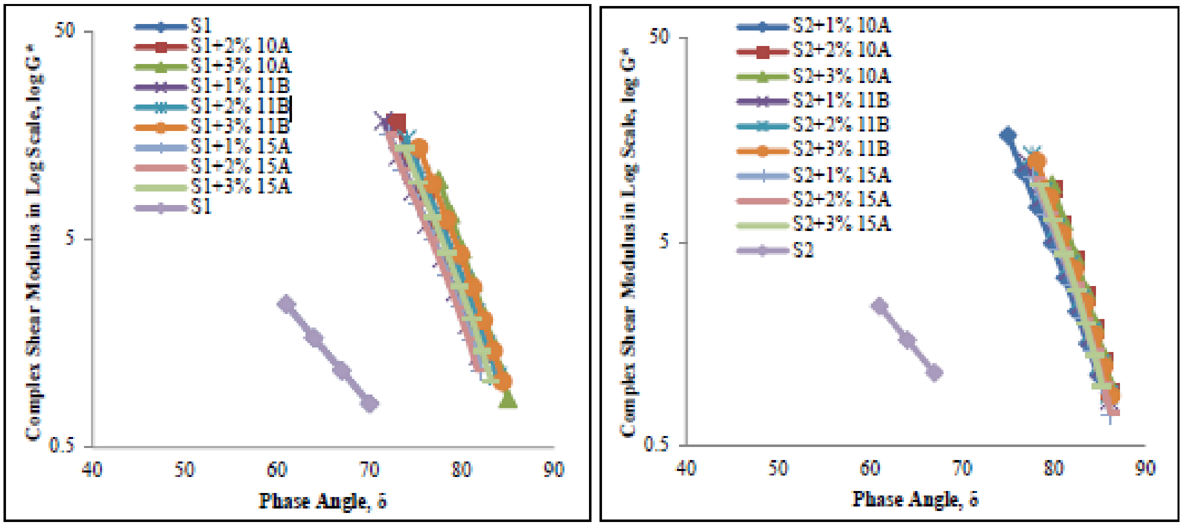

Figure 6.8 Complex shear modulus (G) vs. phase angle (δ) curve for Nanoclay modified binder.*

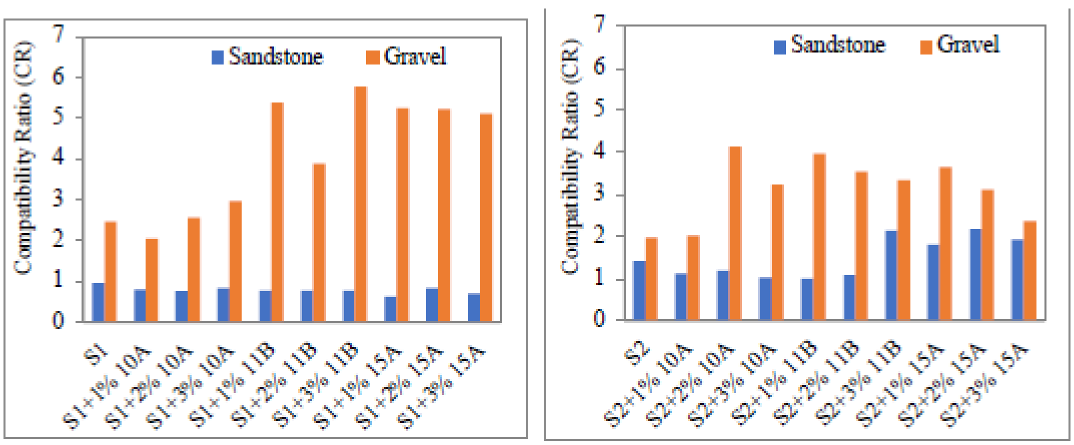

Figure 6.9 Compatibility of Nanoclay modified asphalt binders

Results from atomic force microscope concluded that though the surface roughness of modified binder did not alter much but the deformation and adhesion values decreased. The chemical compositions are found to be strongly associated with mechanistic properties like viscosity and rutting parameter. After Nanoclay alteration, binders from Canadian crude displayed more colloidal stability than binders from Arabian crude.(Mohammad N. Hassan et al, 2019)

6.5. The impact of Nano Clay as a bitumen modifier on the rutting performance of asphalt mixes with a high percentage of rejuvenated reclaimed asphalt pavement.

This research was carried out to improve the rutting performance of reclaimed asphalt pavement RAP. The rationale for this study is that often, in order to rejuvenate some of the qualities of old asphalt binder, it gets compromised owing to the use of different kinds of chemicals aimed at rejuvenating it.

The recouped asphalt road was studied in Hemmat Highway in Tehran and it contained 6% of bitumen content. Two important procurements were made in this regard, virgin bitumen of standard 60/70 penetration and aggregates of virgin crushed limestone (obtained from quarries) was also procured. The gradation of mixtures with or without RAP was achieved as per ASTM D5404 specifications.

Sieve no	Extracted aggregates	RAP
1/2″	100	100
3/8″	94.78	89.7
No.4	62.88	50.54
No.8	42.11	30.84
No.50	11.11	3.94
No.200	2.14	1.7

Table 6-4 Sieve analysis results for RAP and extracted aggregate

Following ASTM D4552, oil was selected as rejuvenator. Optimum concentration of rejuvenator was found to be 0.12% of the RAP material after different contents of rejuvenators were added to improve aged binder and properties of these rejuvenated mixes were studied.

Test	Standard test	Result	With 12% rejuvenator
Viscosity Test at 135°C (cSt)	ASTM D2170	876	358
Penetration Test (dm)	ASTM D5	31	61
Ductility Test (cm)	ASTM D113	37	74
Softening point (°C)	ASTM D36	64.6	49

Table 6-5 The RAP recovered binder properties with and without rejuvenator

The RAP material was first heated at 163 C for 2 hours then the selected Nano-clay for this study. In the next step, Cloisite 30B was mixed with the RPM at specified temperature and rpm in high shear mixer for half an hour, it was followed up with the mixing of virgin aggregates and mixtures into it. The mixture was obtained as per the provisions of Marshal mix design. The air voids of mixture were maintained at 7%. Different asphalt mixtures prepared for this study were of 25%, 50% and 75% of rejuvenated RAP and 0%, 2%, 4% and 6% NC modified virgin bitumen and virgin aggregates. Dynamic creep test as per the specifications of NCHRP 9–19 was performed to measure the accumulated perpetual contortion and rutting resistance of the NC altered RAP mixtures.

The results obtained concluded that with the addition of rejuvenator in RAP mixture, the flow number; that is indicative of rutting resistance, decreases. The increasing percentages of RAP materials makes mixture stiffer increasing flow number. The addition of NC proved significant in increasing flow number thus improving rutting performance of the RAP mixtures. The 80% of improvement in rutting came till 4% NC content in RAP mixtures, after 4% NC content though flow number increased but the improvement in rutting did not follow the steep curve. (Hassan Ziari et al, 2019).

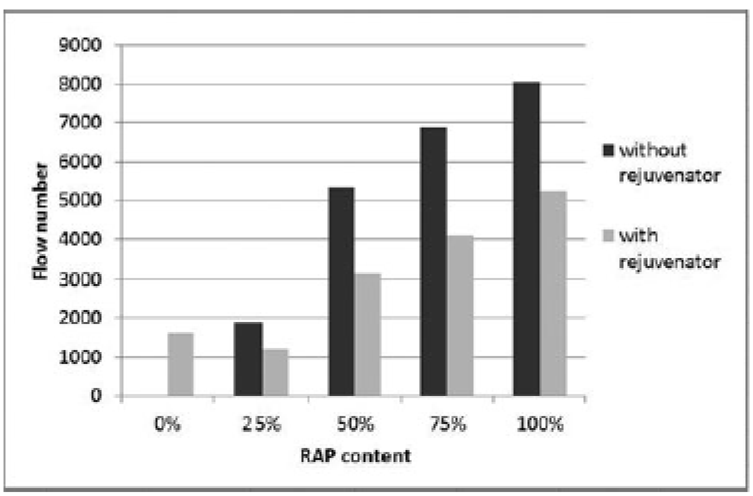

Figure 6.10 Dynamic creep test results of RAP mixtures with and without rejuvenator.

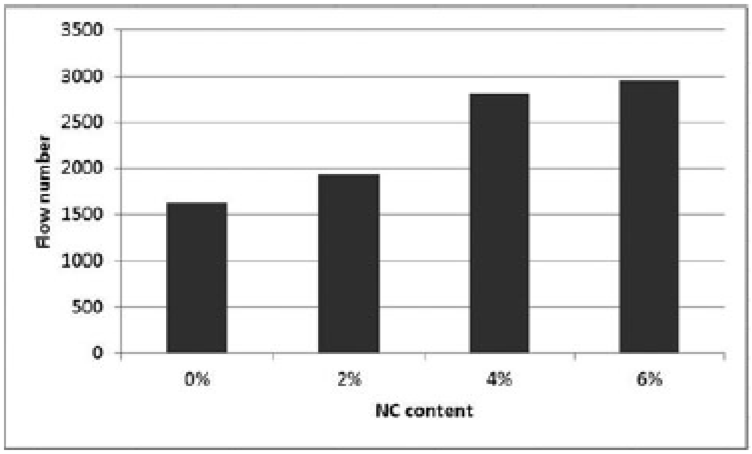

Figure 6.11 Dynamic creep test results of control mixtures modified with NC.

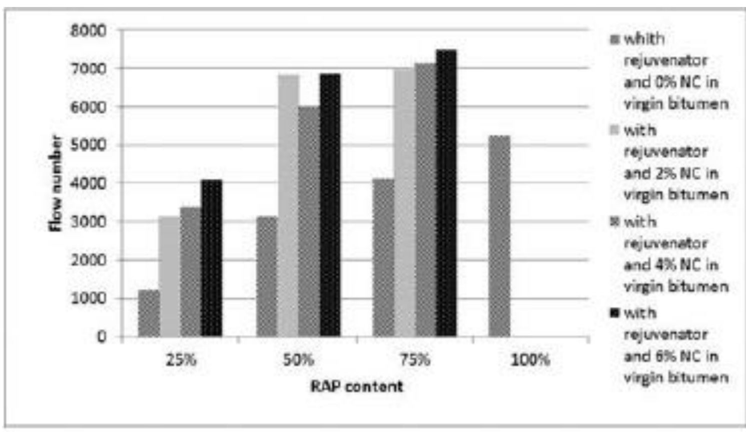

Figure 6.12 Dynamic creep test results of RAP mixtures in combination with NC modified virgin bitumen.

CHAPTER 7

CONCLUSION AND RECOMMENDATIONS

7.1. Carbon Nanotubes

By studying all these articles from different regions, We can conclude what would be best for our country. These studies are done using different techniques, percentages, conditions, and the tests that were conducted in each of them also vary. After a synthesis of these papers, we came to know that there are two techniques that can be used to add CNTs into the binder (wet mixing and dry mixing). Different test results conclude that the best method is the wet mixing technique as it produces a more homogenous mixture but is considered costlier and technical. So, this is the technique we will use for mixing as it gives us the best results.

Secondly, coming on to the optimum percentage of CNT to be added to the binder. As we know from the studies that adding CNTs to the binder can increase stiffness, rutting depth, resistance against thermal cracking. It also increases the values of resilient modulus, $G^*/\sin \delta$ parameter, elasticity, Plasticity index (PI), Efficiency rating (PG). PG 76 was achieved by adding 3% CNT by weight of binder and it increased the rut depth by 37% but adding more than 1% CNT starts decreasing the resilient modulus significantly. So, the best percentage that we can use in Pakistan keeping in mind the weather conditions and other conditions of the country is 1% CNT by weight of the binder.

Carbon Nanotubes are not widely available in the country and are not even manufactured here in Pakistan. All the amounts being used here is mostly imported from different countries of the world including France, China, and USA. Carbon Nanotubes can be easily manufactured in Pakistan if we can get that technology used for manufacturing which can be done in near future. Pakistan has potential to produce all three types of CNTs mentioned below

- SWCNT (Single-Walled Carbon Nanotube)
- DWCNT (Double-Walled Carbon Nanotube)
- MWCNT (Multi-Walled Carbon Nanotube)

This can be done using three different processes known as

- Arc discharge
- Laser ablation
- Chemical vapor deposition (CVD)

The best method among these is the CVD process which can give us a good yield of both SWCNTs and MWCNTs. Pakistan should try to bring this technology into the country in order to have a bright future in nanoparticle research especially Carbon Nanotubes

7.2.Carbon Black

Above we discussed briefly the various implications of using different percentages and contents of carbon black as asphalt binder modifier. The results of experiments under different conditions concluded that carbon black as asphalt binder modifier improves significantly the high temperature performance e.g. rutting resistance; penetration and ductility while carbon black as rheological modifier had no satisfactory outcomes on the low temperature cracking. Asphalt mixture with prior good low temperature resistance blended with optimum carbon black percentage and size improves the engineering properties and life cycle of asphalt pavement. Results showed when 7% carbon black by weight of binder in size ranges of 2.6 um, 25 um and 270 um when blended with asphalt improves rutting resistance, cracking and stability of asphalt pavement. The exact percentile and particle size of carbon black depends on the prevailing conditions of the place and desired outcomes.

Carbon black in Pakistan is manufactured by National Petro-carbon Ltd (NPC) according to ASTM specifications. This is a private company that not only meets up the carbon black demand in Pakistan but also exports it to other neighboring countries. The Carbon black use in pavement engineering despite being a cost effective technique is equally beneficial for environment because instead of disposing off tires waste we use tires pyrolysis carbon black (TPCB) nanoparticles as modifier for asphalt binders

7.3. Graphene Nano Platelets

From the above studies percentage of the graphene Nano-platelets (GNPs) in the binder is 2 to 6 percent by weight of the binder, which is used for the experiments.

PG-70 is achieved when 4 percent of GNPs is added to the binder, which caters to the environmental conditions of Pakistan.. A maximum increase in the complex shear modulus and a decrease in the phase angle is recorded when 4% of GNPs are added to the binder.. At 55 ◦C, the wheel-tracking slope (WTS) decreased from 0.58 to 0.35 when 4% of GNPs were added to the asphalt binder. This reduction in the WTS is also suggestive of high resistance to permanent deformation. The addition of 4% of GNPs to the binder increases the percentage of bitumen coverage from 15% to 70%.

So from all these results the best percentage of graphene Nano-platelets (GNPs) is 4 percent by weight of the binder.

7.4. Nano Clay

Nano-clay is found in abundant in Pakistan and is economical enough to be used as asphalt binder modifier to increase the engineering properties of asphalt. Nano-silica with its layered structure and larger effective area bonds up strongly with bitumen. There are various types of Nano-silica with their particular implications and we decide accordingly which type to use depending upon our desired requirements and asphalt binder properties.

Various experimentations revealed that the Nano-clay treated asphalt's Complex Shear Modulus (G*) increased while the Phase Angle (δ)) dropped, indicating enhanced stiffness and elasticity. Enhanced rigidity improved rutting resistance, while increased elasticity provided maximum deformation recovery with minimal energy dissipation each load cycle. The enhanced complex shear modulus (G*) of Nano-clay treated asphalt is proved to be very significant in improving high temperature performance grade (PG) of asphalt. Nano-clay modification had positive impact on temperature susceptibility of asphalt binder. The Nano-clay layered silicates diffusion in bitumen molecules, their limited oxygen penetration in the bitumen mixture, delays and thus enhances the ageing resistance of modified asphalt binder. Nano-clay can be effectively used as modifier in asphalt pavements in the regions exposed to higher temperature but Nano-clay modification is least desired for pavements in areas where temperature drops quite low, it is because Nano-silica don’t add to the low temperature thermal cracking performance of asphalt binder. 2-4%(by weight of bitumen) of Nano-clay in asphalt binder gave optimum outcomes.

7.5. Best Percentage by weight and Cost Analysis of Nano-materials in Binder for Pakistan

Nanomaterial	Best Percentage
Carbon Nanotubes	1%
Carbon Black	7%
Graphene Nano Platelets	4%
Nano Clay	2-4%

Table 7-1 Best Percentages of Nanomaterials by weight in Binder for Pakistan

Nanomaterial	Cost in Pakistan/gram
Carbon Nanotubes	$ 25
Carbon Black	$ 0.29
Graphene Nano Platelets	$ 2.3
Nano Clay	$ 0.439

Table 7-2 Best Percentages of Nanomaterials by weight in Binder for Pakistan

7.6.Recommendations

While considering the use of Nanoparticles in Pakistan where have a scarce resources and very less state-of-art equipment, also there is a constraint of budget and less skilled individuals. It will be difficult to implement the use of such nanoparticles in large scale construction. As we have a previous example of rubber in the construction of M2 Motorway from Lahore to Islamabad, which used the modifier on a specific level and not in the whole construction or rehabilitation. By following the model we can use these Nanoparticles only in specific areas where we can get benefit from its useful enhanced properties.

- Nanoparticles can be used in the areas where there are temperatures higher than normal due to increased bitumen's softening point by its addition.
- The improved fatigue and rutting resistance due to the use of Nanoparticles also helps in areas where there is a large movement of heavy vehicles like trucks. It will also increase its lifespan and lower the cost and time between period maintenance.
- Reduction in crack formation due to the use of Nanoparticles will help in areas where there is high precipitation. As the resistance is increases, water doesn't move into the cracks and cause damage which increase lifespan.

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