EVALUATION RHEOLOGICAL PROPERTIES OF NANO CLAY MODIFIED BITUMEN

Shantha Y.G.P.B.

(168340K)

Degree of Master of Engineering in Highway & Traffic Engineering

Transport Division, Department of Civil Engineering

University of Moratuwa

Sri Lanka

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DECLARATION OF THE CANDIDATE AND THE SUPERVISOR

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ABSTRACT

Bitumen is a complex hydrocarbon, and its rheological behavior is also very complex. The rheological behavior of bitumen changes from purely viscous to elastic as per the duration of load applied and its temperature. When considering the road pavement, bitumen is the main material, and it plays a major role in many aspects of road performance. Many investigations have been done related to the modified bitumen to enhance the fulfillment of the bituminous mixture. Most of the Roads are not performed well during their whole design period and experienced rutting and cracking in the bituminous layer due to t poor performance of bituminous binders. So, bitumen modification has been the significant approach today, and modified bitumen is effectively used in many countries during the last three decades to construct pavements. This research considers a laboratory-scale assessment of the conventional and the essential rheological characteristics of modified binders using Nano clay.

Montmorillonite (MMT) nano clay is widely using in many engineering applications. In Sri Lanka, few types of research were done about the usability and characterization of MMT clay, which is available at the Mannar area near the Giant tank. The clay powder prepared from the original bulk clay sample was taken from the above area. It was added to the original bitumen of 60/70 penetration grade binder to prepare the modified binder.

Modified bitumen samples were prepared by adding nano clay and mixed at 160^0C with a mixing time of 25minutes. The prepared modified binder with nano clay was then checked with the penetration, softening temperature, ductility, and dynamic viscosity tests to compare the properties with the original binder. Finally, modified bitumen of each sample was evaluated for the rutting and fatigue resistance for fresh and aged samples with the Dynamic Shear Rheometer (DSR) test, Rolling Thin Film Oven (RTFO) test, and Pressure Aging Vessel (PAV) test.

As per the results obtained from the tests, the viscosity and softening point increase with clay percentage. Penetration and ductility have decreased with increasing clay percentage. Rutting resistance has improved compared to conventional bitumen, and it was shown that modified bitumen with 8% clay improved to PG 76 grade from PG 70 grade of the original sample. All other samples except for 8% clay showed PG 70 grade with 2%, 4%, 6%, and original bitumen sample. There was no much effect on the fatigue resistance when the samples were subjected to the DSR test after the PAV test. At the end, Fourier Transform Infrared (FTIR), Differential Scanning Calorimetry and Thermo Gravimetric Analyzer (DSC and TGA) tests have been done for original bitumen samples as well as modified bitumen samples with 4% MMT based nano clay to verify any chemical bonds between the bitumen and nano clay. The result of FTIR and DSC/TGA has shown, no chemical interaction between the bitumen and nano clay.

The conclusion from these results is that the montmorillonite clay modification supported improving the softening point from 51^0C of original bitumen to 53^0C with 4% MMT modified clay. The penetration has been reduced to 45 (0.1mm) from 60 which was in original bitumen sample with 4% MMT modified clay. The ductility value has been reduced from 151cm of original bitumen sample to 90cm with 8% of MMT modified clay. The viscosity increased from 0.38PaS of original bitumen to 0.41PaS with 2% MMT modified clay. Again, it has reduced to 0.40PaS with 4% of clay sample, and then viscosity value remains unchanged up to 8% of MMT modified clay sample. Furthermore, the rutting resistance has been increased compared to the original bitumen sample. The rutting parameter ($G^*/\sin\delta$) has increased up to 2.18 with6% of MMT modified clay sample and it was 1.42 in the original bitumen sample.

Key Words: Nano clay, Montmorillonite, Viscosity, Penetration, Softening point,

Dynamic Shear Rheometer

DEDICATION

To all who guide me to success.

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LIST OF ABBREVIATIONS

Abbreviation	Description
AASTHO	American Association of State Highway Officials
ASTM	American Society of Testing and Materials
BBR	Bending Beam Rheometer
DSC	Differential Scanning Calorimetry
DSR	Dynamic Shear Rheometer
DTT	Direct Tensile Tester
FTIR	Fourier Transform Infrared Spectroscopy
MMT	Montmorillonite
PAV	Pressure Aging Vessel
PG	Performance Grade
RTFO	Rolling Thin Film Oven
RV	Rotational Viscometer
SHRP	Strategic Highway Research Programme
TGA	Thermo Gravimetric Analysis
XRD	X-ray Diffraction

1 INTRODUCTION

1.1 Background

Bitumen is the primary material of pavement, and it has a prominent role when considering the pavement's performance. Earlier the conventional bitumen was performed satisfactorily in many years, but it posed many problems due to increased traffic, reduced maintenance and degradation of the quality of bitumen. Therefore, it is necessary to improve bitumen's performance to meet the increasing demand for traffic and give a longer service life with less maintenance. Many problems have arisen on Sri Lankan roads concerning the performance of short-lived roads and high maintenance costs. The possible cause of these problems,

- Inferior quality of materials
- Poor Design
- Poor Construction and quality control methods
- Poor Workmanship
- Enhancement of wheel load magnitude and repetition of load due to traffic volume growth

A considerable amount of issues has been arisen in Sri Lankan roads due to the inferior qualities of bitumen binder. The problems related to the low-quality bitumen can be addressed by improving the bitumen binder properties using necessary modifiers such as polymers. The modification of bitumen with polymer have become popular in recent years. This has led to the manufacture of Polymer Modified Bitumen (PMB), and it has been already proved the use of PMB for decades (Hunter, Self, & Read, 2015). Modifiers (polymer, additives) to use effectively should be practicable and economical (Hunter, Self, & Read, 2015).

Polymer nanocomposite is one of the latest substances detected and enhanced its physical properties successfully when modified the polymer with a small amount of clay nanoparticles (Ven, Molenaar, & Besamusca, 2009) (Ghaffarpour Jahromi & Khodaii, 2009). Nano clay is one of the most appropriate materials that worked well on polymer bitumen. Nano clays are fine-grained crystalline materials that would make polymers useful enhancers; research has shown that modifying nano-clay can improve the rheological properties and mechanical properties (Ven, Molenaar, & Besamusca, 2009).

1.2 Problem Statement

Since Sri Lanka is a tropical country, the maximum pavement temperatures increase by about 65 ° C in some areas of the country. Therefore, high-temperature deformations are typical, such as rutting, bleeding, shoving, etc. Also, fatigue cracking is another critical problem on Sri Lankan roads. Another significant issue is moisture damage. Therefore, it should mitigate deformation at high temperatures, fatigue cracking, and moisture damage in Sri Lankan asphalt pavements. It is vital to investigate the influence of bitumen properties in pavement distresses and whether modified bitumen will mitigate the above-mentioned pavement distresses.

A penetration grading system is the currently used grading system in Sri Lanka, developed about a century back and consisting of empirical test methods. It is important to study the MMT base nano clay modifier's rheological properties with the most common conventional penetration grade bitumen.

It can be improved bitumen properties with many different additives such as polymer additives, crumb rubber, bio binders, antioxidants, anti-stripping agents, and nano clays.

1.3 The objective of the study

This research was initiated to study the rheological properties and its effect on performance of asphalt binders with addition of nano clays.

In this research, I have studied the following things.

1. Study the nano clay modifiers at the nanoscale level.
2. Analysis of nano clay modification on critical properties of bitumen.

1.4 Research Scope

This research aims to study the variation of rheological properties of bitumen binder with addition of nano clay modifier. Therefore, it is needed to measure modified bitumen's functional properties with original bitumen such as penetration, ductility, softening point, viscosity, etc. The study comprises of Montmorillonite Nano clay modifier On 60/70 penetration grade bitumen binder. In this study, the amount of the nano clay modifiers have been taken 2%, 4%, 6%, and 8% from the binder's weight. Penetration grade and Superpave bitumen testings were then carried out for modified bitumen. FTIR and TGA analysis were performed to investigate the chemical and physical properties of Nano Clay modified bitumen.

2 LITERATURE REVIEW

This chapter covers some theoretical knowledge about nano clay, its application, and the outcome of modification on thermoplastic materials and bitumen. Further, this describes conceptual knowledge about bitumen binders and their effect on improvement and characteristics.

2.1 Introduction to Bitumen and Nano clay

Bitumen is a non-volatile liquid or viscous solid that contains hydrocarbons and derivatives. It is soluble in trichloroethylene and gets softens with heat (Hunter, Self, & Read, 2015). The bitumen's properties decide the interaction between the molecules of bitumen and other molecules' dilution effect in the structure. The main bitumen component includes saturated naphthalene, polar aromatics, and asphaltenes (Hunter, Self, & Read, 2015).

The essential standard method for characterizing the bitumen is based on its rheology. Rheology is the science that gives out matter's flow and its deformation. These rheological properties at a certain temperature can be evaluated by the composition (chemical composition) and structure (physical arrangement) of the molecules in the material (Hunter, Self, & Read, 2015).

2.1.1 Clay and Nano clay

From the beginning of the human life, clay minerals were very useful and benefitted and the history of it is longer than the creation of man.

Common clays are naturally occurring minerals hydrous aluminum phyllosilicates contains variable amounts of iron, magnesium, alkali metals, alkaline earth, and other cations (Clay, n.d.). Generally, clay minerals are crystalline, and the structure of these crystals affects their properties. The purity of the clay can be affected by final nanocomposite properties. The clay particles' diameter is smaller than 0.004mm, and it is varying from 0.002 to 0.001mm for quartz, mica, feldspar, iron, and aluminum oxides. Finest clay particles having less than 0.001mm in diameter are colloidal, and it can be found in layered silicate (Sherman, 2007).

Clay minerals categorize into four types of groups, and the group members varied as per their layered structure. These are the kaolinite group, the smectite group (montmorillonite group), the illite group, and the chlorite group (Uddin, 2008).

The majority of the clays are alumino silicates, which are having a leaf structure (layered). It consists of SiO_4 tetrahedral silica bonded to AlO_6 octahedral alumina in different ways

(Ghaffarpour Jahromi & Khodaii, 2009). The difference of these clay minerals depends on the order of its structure if the clay mineral has tetrahedral or octahedral sheets.

For example, in "1:1 clay mineral, consists of one tetrahedral and one octahedral sheet per clay layer. The meaning of 2:1 clay mineral is, it would contain two tetrahedral sheets and one octahedral sheet sandwiched between the two tetrahedral sheets". A common example for 2:1 sheet structure clay mineral is the montmorillonite of the smectite group, shown in figure 2.1 (Eberl, 2019).

In layered type clay structures, the upper oxygen atoms in the tetrahedral sheet are allocated with octahedral sheets. Further, it has extra metals like Zinc or iron, and, magnesium and it can restore by aluminum in the clay structure. The layer thickness (platelets) consists of 1nm and has higher aspect ratios, typically 100 -1500 (Ghaffarpour Jahromi & Khodaii, 2009).

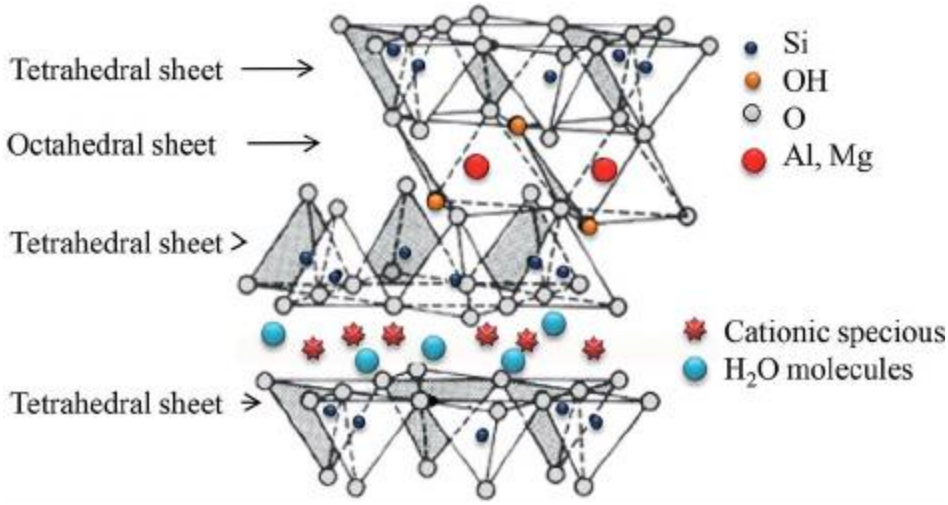


Figure 2.1: Smectite structure of a 2: 1 clay mineral

Nano clays define as nanoparticles of layered mineral silicates (Ven, Molenaar, & Besamusca, 2009). Very few published information regarding nano clay modified bitumen is available. However, some studies have been done and still underway on nano clay modified polymers. This research relates to nano clay modified bitumen, but it is essential to understand the nano clay modified polymers as both modifications based on similar principles. When a polymer does change with a little amount of nano clay, it has improved some specific physical properties of polymers nanoscopic distribution level of the clay (Ven, Molenaar, & Besamusca, 2009). The improvement of these physical properties depends on the type of the final nanocomposite and its properties. This includes the clay pre-treatment method, the nature of clay, the type of polymer component, and how the nanocomposite into the polymer. Nano clay can enhance properties such as strength, stiffness, fatigue resistance, and resistance to aging and, thermal stability (Ven, Molenaar, & Besamusca, 2009).

The most important thing is that the nano clay will create a wide range of effective surface areas ranging from 700 to 800m^2 per gram, hence separating clay discs from each other. This creates an interconnection between the nano clay and its environment.

The clay disc separation mechanism depends on the mixing material; further, it explained as follows.

Generally, the clay disc is a negative charge, and further, it has positive ions between the edges. So, if we take a whole clay particle together, it is neutral. Furthermore, Montmorillonite clay is very hydrophilic. Hence it is incompatible with many polymer types. So, to be compatible with polymer and clay, it is required to change the clay's polarity to make the clay "organophilic." Some researchers have developed Montmorillonite and bentonite nanosheets that mix effectively in polymer and bitumen (Ven, Molenaar, & Besamusca, 2009). Once the clay's polarity is changed, and prepared organoclays can adapt to the binder. It can provide comparable nano clay distribution in the binder when it is entirely compatible with the binder.

The synthetic way to prepare a nanocomposite depends on whether the material needs in the form of an intercalated or exfoliated hybrid (Figure 2.2). Suppose the organic component inserted between the clay layers is intercalated to increase the distance between the layers. In contrast, these layers always have a clearly defined spatial relationship together. The clay layers separated, and all layers were distributed into the organic matrix in exfoliated structure (Ghaffarpour Jahromi & Khodaii, 2009).

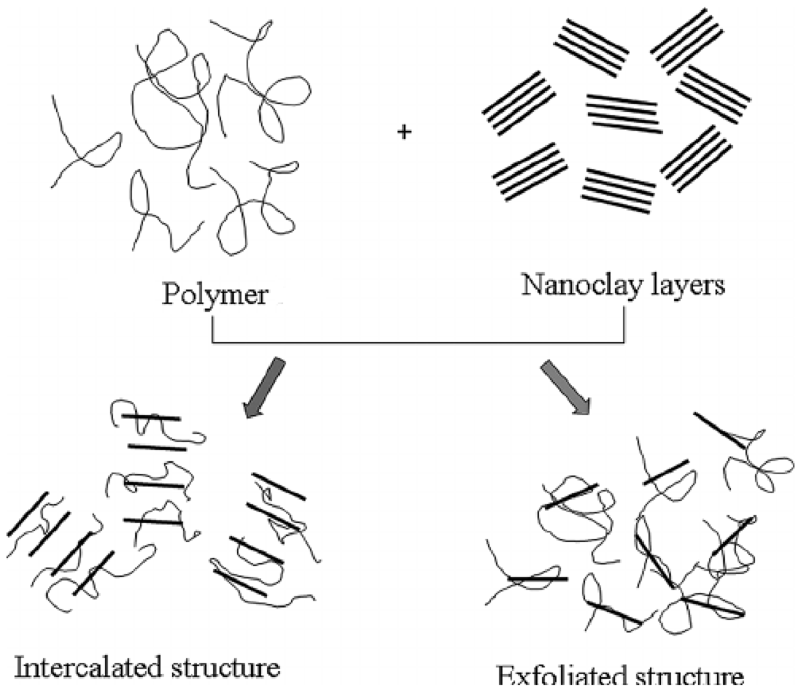


Figure 2.2: Structure of nanocomposites from layered nano clay and polymers

The bitumen is complex hydrocarbon, and the structure of the polymer is well defined. So, it has a structural difference between bitumen and polymers. This could be an unfavorable circumstance for the success of the modification of bitumen with clay due to this complex molecular composition (Ven, Molenaar, & Besamusca, 2009).

The purpose of this research was to evaluate the rheological properties of bitumen binder with Montmorillonite nano clay. Little research has been done about modified bitumen blending with the Montmorillonite nano clay.

In Sri Lanka, clay exists naturally in many areas, and there is a Montmorillonite clay-rich source in Sri Lanka, available at Murunkan area in Mannar District (Adikary, Ashokcline, & Nirojan, 2015). Montmorillonite is a very soft fine silicate group of minerals, and it swells in water and has high cation-exchange capacities. The theoretical chemical formula of montmorillonite is $(OH)_4Si_8Al_4O_{20}.nH_2O$. Montmorillonite typically contains microscopic crystal-forming clay. Montmorillonite is dioctahedral nano clay (Fig.2.3) that consists of a 2:1-layer linkage (Paul & Robeson, 2008). In this research, Montmorillonite nano clay was added to modify the 60-70 penetration grade bitumen.

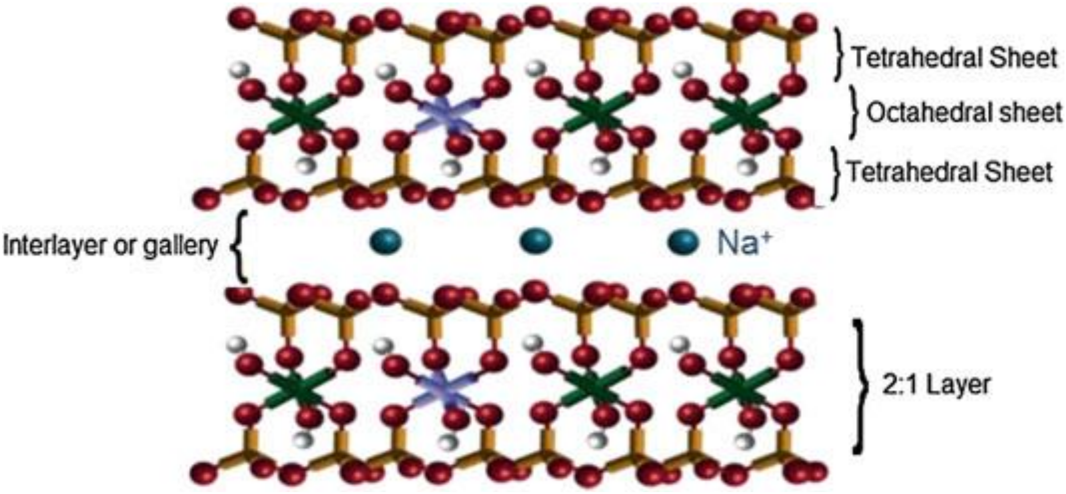


Figure 2.3: Structure of sodium montmorillonite (Paul & Robeson, 2008)

Oxygen atoms are inhabited in all positions above and below in the montmorillonite lattice layers, and these layers are combined with a relatively weak intermolecular force. Due to these weak intermolecular forces, water molecules can smoothly go into the interlayer region, and the result is the expansion of the network. It is increased the interlayer distance by the hydrated cations. As a result, montmorillonite is an expandable clay mineral (Ghaffarpour Jahromi & Khodaii, 2009).

This sound source (Murunkan clay source) was high purity, a rich montmorillonite source, and few research types done about this clay's applicability (Adikary, Ashokcline, & Nirojan, 2015). So, it is the reason to make nano clay from the bulk clay of the Murunkan area.

2.1.2 Application of nano clay

Nano clay is the latest additive used in the pavement industry to extend its service life. There are several applications of nano clay such as,

- Paint industry
- Medicine and Pharmacy
- Cosmetics
- Catalysis
- Food packaging
- Textile industry
- Wastewater treatment – The use of nano clays in wastewater treatment has become common in the industry today.

2.1.3 Rheology of Bitumen

Bitumen is a thermoplastic viscoelastic material, as it behaves liquid as well as solid. It has both deformation and flow properties.

Under low temperatures and short loading period, bitumen binders act as an elastic solid. The deformation due to this rapid loading is recoverable. So, it can come back to its original shape once a load is removed. At the high temperatures and slow loading, the behavior of bitumen is a viscous liquid. The deformation under this condition is not recoverable and cannot be returned to its original position once the load is removed. The bitumen binder behavior is very complicated at median temperatures and loading times (Hunter, Self, & Read, 2015).

Hence, the bitumen binder to stress is varying according to the temperature and the loading time. Therefore, the bitumen's rheology is described by its response to stress, strain, time, and temperature.

2.1.4 Chemical Components of Bitumen

The bitumen is a black, cementing material consisting of high molecular weight hydrocarbons and traces of Sulphur, oxygen, nitrogen, and other elements. These cementing materials are collected from the bottom of the vacuum distillation columns in the crude oil refineries (Institute, 1983).

The chemical composition of the bitumen has an enormous impact on the effect of bitumen. It has two chemical groups called asphaltenes and maltenes. Asphaltenes are complex aromatic materials with high polarity and high molecular weights than maltenes, and it gives to bitumen its color and hardness. The content of asphaltene is varied from 5% to 25%. It has a large impact on the properties of the bitumen. It increases the bitumen's softening point and viscosity with the increasing asphaltene content, decreasing the penetration value.

The maltenes are categorized into three groups called saturates, aromatics, and resins (Hamed & Farag, 2010). In some books, maltenes are subdivided into resin and oil (Institute, 1983). The resins provide the adhesive properties (adhesive strength) in bitumen, and the oils act as a medium in which the asphaltenes and resins are carried (Institute, 1983).

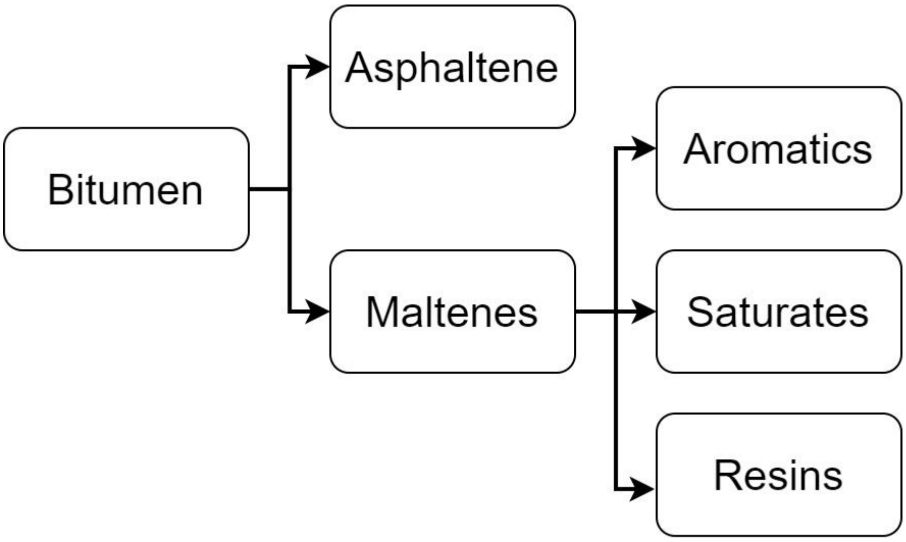


Figure 2.4: The Chemical Group of Bitumen

2.1.5 Performance Grading System for Polymer Modified Bitumen

when the transportation industry is developed, the use of HMA in asphalt pavement applications also increased. Since the materials are the same used in the paved industry with increasing the traffic load, it has given unfavorable pavement results. Hence it was essential to study the new requirement of asphalt material and pavement performance (Anderson & McGennis, 1995) (Hossain, Fager, & Maag, 2016).

In the early 1990s, the SHRP (Strategic Highway Research Program) project in the USA introduced specifications for Super paving binders. As a result, two developments have radically changed the world of bitumen specifications:

(1) the introduction of new rheological testing methods (for the bitumen industry).

(2) Performance Grading (PG) concept to relate pavement, temperature, and traffic conditions to fundamental properties (Federal Highway Administration).

This has led to the development of binder – blind specifications (regardless of whether modified or not). The developments have been successfully implemented in the USA. But in the other part of the world, it has developed slowly due to the new testing devices cost and complexity (Federal Highway Administration). Therefore, the other countries began to develop their specifications for polymer-modified bitumen using simple empirical tests.

2.1.6 Super pave binder tests and their purpose

The super pave system describes Performance Grade (PG) asphalt binder defining with their specific tests. The binders are determined based on the climate and pavement temperature the binders are expected to serve.

Table 2.1 Superpave tests and their purpose

Test of Superpave Binder	**Purpose**
Dynamic Shear Rheometer (DSR)	Evaluate rheological properties at high and intermediate temperatures – and both unaged and aged conditions
Rotational Viscometer (RV)	Evaluate the behavior at high temperatures and monitor the properties at the stage of construction
Bending Beam Rheometer (BBR) Direct Tension Tester (DTT)	Measure Properties at low temperatures in both aged and unaged conditions
Rolling Thin Film Oven (RTFO) Pressure Aging Vessel (PAV)	Simulate hardening (durability) characteristics in the short term and long term

Usually, the Superpave binder system classifies as PG 64-22. The first number, 64, is the "high-temperature grade," which means the binder can bear its physical properties up to 64°C. This should be the highest pavement temperature that binder can survive, corresponding to the climate. Further, the second number, (-22), is mentioned as the "low- temperature grade" that the binder can bear its physical properties down to at least -22°C.

A key subject of the Superpave binder system is to evaluate the asphalt binders under conditions of the binder's critical phases of life. The most critical stages of the binder are:

- throughout the transport, storage, and handling,
- during mix production and construction, and
- after long periods in a pavement

Testing on unaged asphalt is the first step in transportation, storage, and handling. The second step has described the binder's aging in a rolling thin film oven (RTFO) throughout the mixing stage and construction. After a long period in the pavement, which represents the third stage of binder aging. This phase represents a pressure aging vessel (PAV) (Federal Highway Administration).

Three pavement distresses described in the Superpave system. They are,

1. Permanent deformation due to insufficient shear strength in the asphalt mixture at the high temperature of the pavements.
2. Fatigue cracks mainly due to the repeated traffic load at intermediate pavement temperatures.
3. Low- temperature cracking is generated when an asphalt pavement shrinks and the tensile stress exceeds the tensile strength at low pavement temperatures.

2.2 Empirical Tests for the Bitumen

2.2.1 Penetration Test, ASTM D5

The penetration test quantifies the consistency or hardness of the bitumen. The equipment consists of a prescribed dimension of a needle. This needle is permitted to penetrate a sample, under the load of 100g, at a temperature of 25^0C for exactly five seconds (Figure 2.5). The distance that the needle penetrates the bitumen sample is recorded in units of 0.1mm and called the “penetration” of the sample. If the penetration value is low, the bitumen is hard, and the higher penetration value is softer the bitumen.

Figure 2.5: Penetration Test

2.2.2 Ring and Ball Test

This test is performed to measure the softening point of the bitumen sample. It decides the temperature at which a certain viscosity of the bitumen comes into a certain point during the transformation from solid to liquid. A ball of 3.5g is kept in a brass ring on the bitumen sample socket and suspended in a water bath. The bath temperature increases at 5^0C per minute, then the bitumen is softening and is deformed gradually. When the bitumen is softening, the ball is passing through the ring. When the steel ball with bitumen touch a base plate 25mm below the ring, the temperature is recorded. This temperature is called the softening point of the bitumen.

Figure 2.6: Ring and Ball Test

2.2.3 Ductility Test

Ductility is a measure of the extent to which a bitumen sample is stretched before it breaks. It measures by an “extension” test in which the briquette specimen of bitumen is extended or stretched at a specific rate (5cm/min ± 5%) and a temperature (25^0C ±0.5^0C). The sample's extension is continued until the thread of bitumen joining the two halves of the sample breaks. The moment it breaks is measured in centimeters, and the value is called the sample’s ductility (Figure 2.7).

Figure 2.7: Ductility Bath

2.2.4 Rotational Viscosity Test ASTM D 4402

A rotating viscometer uses to measure the apparent viscosity of bitumen at high temperatures. The torque on the device, which rotates in a temperature-controlled sample holder with the asphalt sample, is used to measure the rotational resistance. It requires torque and speed to determine the bitumen's viscosity in pascal seconds, milipascal seconds, or centipoises.

A sample chamber places into the sample chamber holder, and then it is placed in an oven at 135^0C. The same oven is placed “3-ounce” container with the asphalt sample and the appropriate spindle. The spindle is used to determine the anticipated viscosity of the fluid being tested. When the digital display on the equipment's thermosel indicates the desired temperature has been reached, it is removed the sample chamber from the oven and place both on a scale accurate to the nearest 0.1g. Then, it is poured the required amount of asphalt binder into the sample chamber. The sample chamber then places it in the thermo container of the equipment, which aligns with the viscometer. The spindle is removed from the oven and attached to the spindle extension, and gently it lowers the spindle into the sample chamber with the warmed sample. Once the required temperature is stabilized, the viscosity measurement is taken (Anderson & McGennis, 1995).

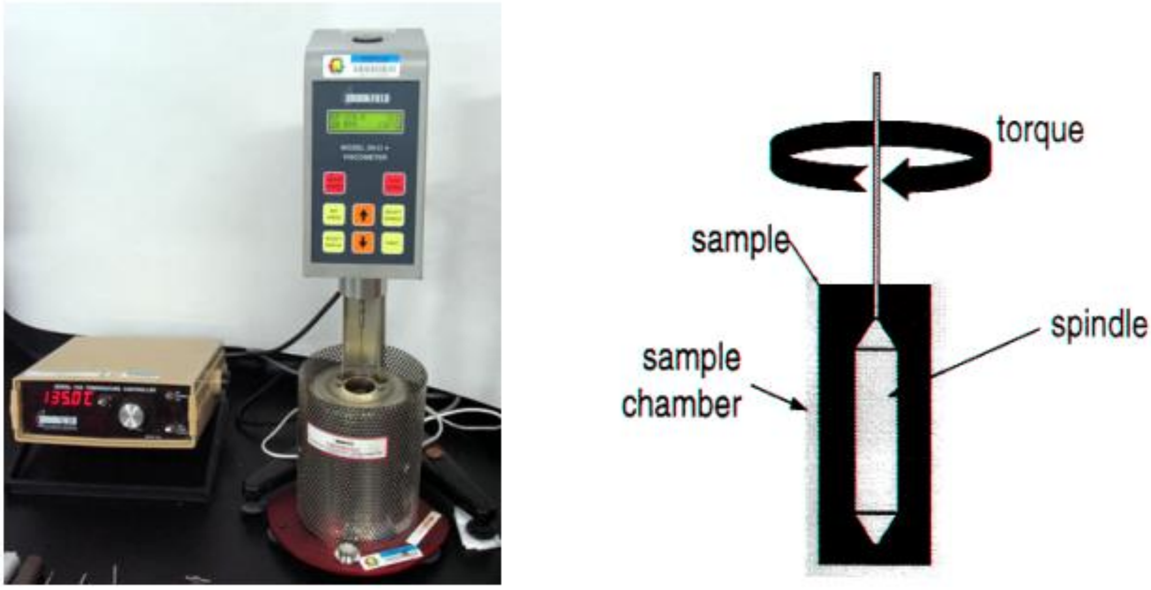
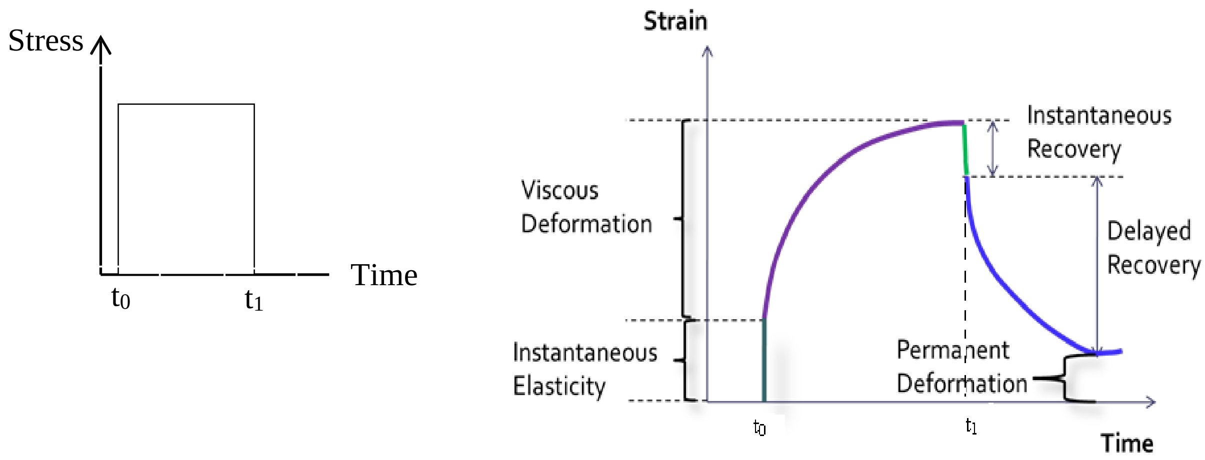


Figure 2.8: Rotational Viscometer (Hossain, Fager, & Maag, 2016)

2.3 Basic Rheological Test of Dynamic Shear Rheometer (DSR)

The visco-elasticity is directly related to the mechanical characteristics of the material. The meaning of that the material can behave as an elastic solid or viscous fluid and a combination of both. It bases on the temperature of the material and its loading time. Since the bitumen binders are shown elastic properties and viscous properties, it is called viscoelastic material (Hunter, Self, & Read, 2015).

It is represented in figure 6.9 feedback of visco-elastic material if the constant load is applied at t_0 and removed at t_1. When the constant stress is applied over time for viscoelastic material, it increases strain over the applied load of time. After removing the load, the material cannot come to its original place resulting in permanent deformation.



a. Stress b. strain

Figure 2.9: Stress-strain behavior of a visco-elastic material

It is applied sinusoidal shear forces to test the bitumen binder, and the Dynamic Shear Rheometer (DSR) use to characterize the viscoelastic behavior of the bitumen binder.

2.4 Dynamic Shear Rheometer (DSR)

DSR test is used to characterize bitumen's viscous and elastic behavior, fatigue resistance, and rutting resistance at high and middle temperature. Further, it defines the characterization procedure of the binder and decides the fail temperatures of bitumen binders. The test standard is AASTHO TP 5.

For the basic DSR test, a sample of thin bitumen is used, which is exchanged between the two circular plates. Oscillatory shear force is applied on a thin bitumen sample between two parallel plates, and the lower plate is fixed. In contrast, the upper plate is oscillated back and forth across the sample to create a shearing action (Figure: 6.10).

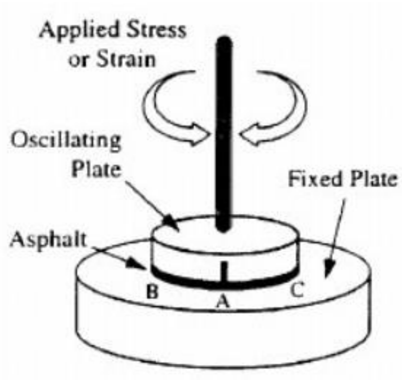


Figure 2.10: Dynamic Shear Rheometer (Hossain, Fager, & Maag, 2016)

The upper plate path, as shown in figure 6.11, starts from point B and goes to point A, and then goes through the initial point (B) to point C and returns to point C, then completes a cycle. The above movement continuously repeats the test (Hossain, Fager, & Maag, 2016).

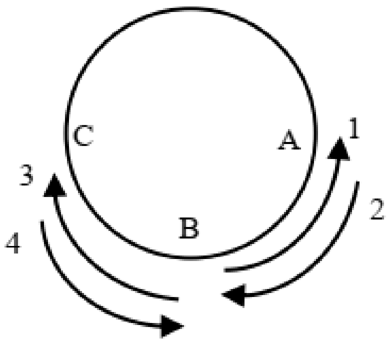


Figure 2.11: Upper plate movement of DSR (Hossain, Fager, & Maag, 2016)

The DSR tests are conducted on unaged, Rolling Thin Film Oven aged (RTFO aged) and Pressure Aging Vessel aged (PAV aged) bitumen binder samples. 1mm thick and 25mm diameter bitumen sample is used for Unaged and RTFO aged samples at which temperature greater than 46^0C and 2mm thick and 8mm diameter bitumen sample is used for PAV-aged samples at temperatures between 4^0C and 46^0C.

The test results will give a complex shear modulus (G*) of the sample and the angle of phase (δ). The complex shear modulus (G*) is defined as the sample's total resistance under deformation when subjected to repeated shearing. The phase angle is defined as delay between the applied shear stress and resulting shear strain and it represents the immediate elastic and the binder's delayed viscous responses, as shown in Figure 6.12. It is not showing any phase angle difference is a purely elastic material. A purely viscous material shows a phase angle of $90^{0,}$ and it has a phase angle of 0^0 for the purely elastic material. Usually, a viscoelastic material will show a phase angle between 0^0 to 90^0, such as bitumen. The angle of phase depends on the type of bitumen, frequency, and temperature.

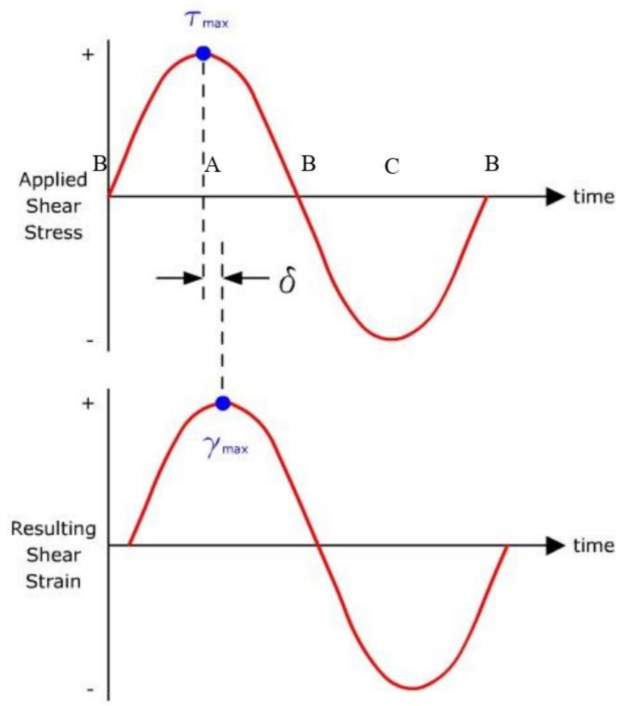


Figure 2.12: Phase angle determination (Dynamic Shear Rheometer, n.d.)

2.4.1 Fatigue and rutting parameter analysis by DSR

2.4.1.1 Effect of Rutting and Rutting parameter

Rutting is a cyclic loading phenomenon and typical damage to asphalt pavement. Each traffic cycle tends to deform the surface of pavement from where it is worked to deform. The percentage of this work is taken back by the elastic rebound of the pavement's surface. The remaining percentage of works dissipates as permanent deformation such as cracking, heat, and propagation of cracks. So, the loading cycle's dissipation should be minimized to reduce the rutting (Ven, Molenaar, & Besamusca, 2009).

Many reasons could cause rutting and heavy-duty vehicles; improper pavement structural designs are the main two factors. The traffic compaction due to heavy-duty vehicles leads to the plastic flow type rutting, and it is directly related to the asphalt binder stiffness. Further, it can be related to the displacement rutting due to excessive asphalt binder, excessive sand or mineral filler, low design air voids, rounded aggregate particles, and low voids filled in mineral aggregate. But it should be noted that the poor mix design is a significant reason for rutting, and it cannot compensate using better quality binders.

When the asphalt binder is aged, the rheological properties and the asphalt mixture performance are changed. Volatilization and oxidation are two main mechanisms causing aging. Asphalt binder viscosity is increased with aging, which results in binder stiff, and it leads to the formation of several pavement distress types, such as rutting, fatigue, and thermal cracking.

Rutting can address by studying the mineral aggregate and asphalt cement. It can clarify the Mohr-Coulomb equation, how the above martial properties can affect the rutting (Federal Highway Administration).

$$\tau = c + \sigma(\tan \emptyset)$$

τ = Shear strength provided by asphalt cement

C = The cohesion of the overall mixture

σ = Normal stress

$\emptyset =$ Angle of friction of aggregate

Asphalt cement gives its shear strength to operate it that is stiffer and behaves like an elastic solid at high pavement temperatures. When the load is put in to mixture, it tries to behave like a rubber band and come back to its initial state rather than stay deformed.

The shear strength of the mixture can enhance by increasing the aggregate angle of friction. The friction angle of aggregate can be increased using cubical aggregate with a rough surface and develop the particle to particle contact of aggregate. Hence it increases the rutting resistance. If the mixture behaves like an unbound mass, it has low shear characteristics (Federal Highway Administration).

A severely rutted road is shown in Figure 6.13. The wheel paths are visible here, and the pavement surface is uplifted due to deformation.

Figure 2.13: Severely rutted road (Dynamic Shear Rheometer, n.d.)

In order to resist the rutting, the bitumen binder should be stiff as well as elastic. Hence, the elastic portion of the complex shear modulus, G*/sin δ, should be large (figure 2.14). When the G* is higher, the bitumen binder is stiff. When the δ value is lower, the elastic portion of the G* is higher (Ven, Molenaar, & Besamusca, 2009).

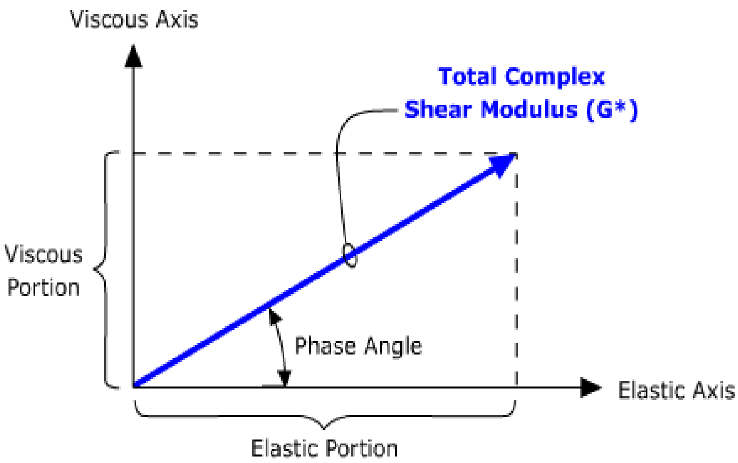


Figure 2.14: Viscous & Elastic components of bitumen (Ghaffarpour Jahromi & Khodaii, 2009)

As per the AASTHO T 190 standard, DSR test results should be as below.

- For new asphalt, G*/sin δ> 1.0KPa
- For RTFO Residue, G*/sin δ> 2.2KPa

2.4.1.2 Effect of Fatigue and Fatigue parameter

One of the most common modes of failure of asphalt pavement is fatigue cracking from the continual traffic load. Mostly fatigue distress is associated with the rheological properties of asphalt binder (Hamed & Farag, 2010). Typically fatigue cracking consists of two main stages, which are crack initiation and crack propagation. It is caused by tensile strain generated in the pavement, traffic loading, and temperature and construction practices (Hunter, Self, & Read, 2015).

If the bitumen binder is elastic and not too stiff, it has a more excellent fatigue cracking resistance. (figure 6.14). Therefore, the viscous portion of the complex shear modulus, G*sin δ, should be minimal.

If the fatigue cracking is of most significant concern, a maximum value for the viscous component of the complex shear modulus is specified, and it happens in a late stage of HMA pavement life (Ven, Molenaar, & Besamusca, 2009). Cracking due to fatigue can be reviewed a fact controlled by the stress in thick pavements of HMA and a fact controlled by the strain in thin pavements of HMA. It is more common fatigue cracking in thin asphalt pavements. If the amount of energy dissipated per load cycle is lowered, it can reduce fatigue cracking. Therefore, the energy dissipated per load cycle should be minimized to reduce fatigue cracking (Ven, Molenaar, & Besamusca, 2009).

As per the AASTHO T 190 standard, the fatigue parameter of the DSR test should be G*sin δ ≤ 5000KPa to reduce the fatigue cracking.

2.5 Rolling Thin Film Oven (RTFO) Test

RTFO test conducts to measure the effect of heat and air on the bitumen binder. It can also provide residue for additional testing (Fig.6.17). The bitumen binder's properties from the impact of this test are evaluated before and after the test.

The oven consists of a vertical circular carriage. There are holes in this vertical carriage to keep the sample bottles. During the test, the carriage is rotated around its center mechanically. The oven consists of an Air jet for blowing air into each sample bottle at its lowest position while it circulates on the carriage (Hossain, Fager, & Maag, 2016). A thin bitumen binder sample is heated in the oven for 85 minutes at 163^{0}C while it is moving. The process of aging is continued during the test period of 35g of sample film. The residue of this test can be taken for some additional tests such as DSR and penetration. It measures the mass change, which calculates bitumen binder volatility and mass changes resulting from oxidation.

$$\text{Weight Loss \%} = \frac{(\text{Original weight} - \text{Aged weight}) \times 100\%}{(\text{Original weight})}$$

This test has simulated the variation of bitumen binder properties during the batching plant mixing at about 150^0C.

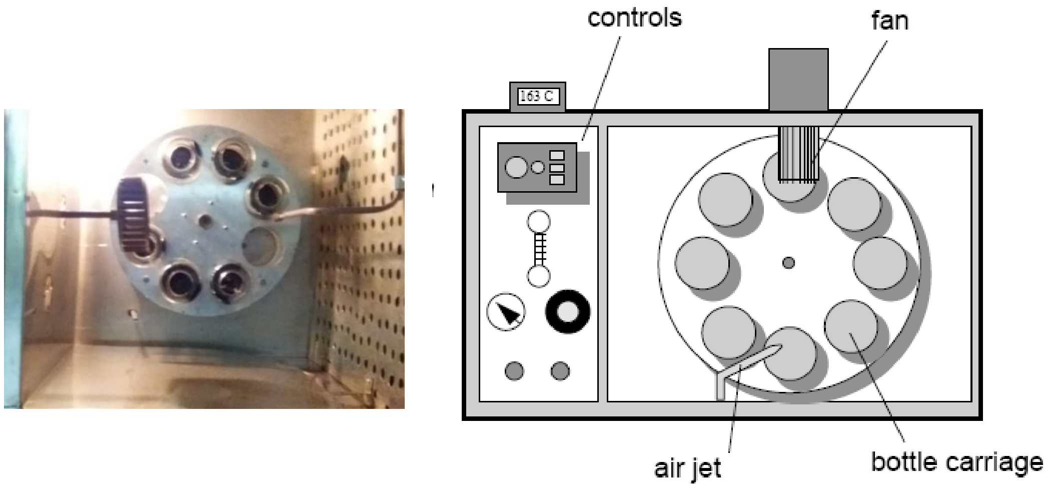


Figure 2.15:Rolling Thin Film Apparatus

2.6 Pressure Aging Vessel (PAV) Test

The test standard is AASTHO PP1, and Pressure Aging Vessel design to simulate in-service aging of bitumen binder after 7 to 10 years**.** During the test, the binder is exposed to high pressure (2.1±0.1MPa) and temperature (between 90^0C and 110^0C) for 20 hours to simulate the effect of long-term oxidative aging.

The PAV apparatus consists of a stainless-steel pressure vessel with encased band heaters and internal pressure and temperature controls. Samples loads in a rack can accommodate at least 10 sample pans and stored inside the vessel to start the test (Hossain, Fager, & Maag, 2016). Temperature and pressure details can save on USB, and the data can be transferred to the computer at the end of the test.

After the PAV test, samples are subjected to the DSR test to determine the binder's stiffness modulus.

2.7 Fourier Transform Infrared (FTIR)

There are several methods to analyze the chemistry of bituminous binders. Some of these techniques are Corbett chromatography, Fourier Transform Infrared Spectroscopy (FTIR), and Gas or Gel Permeation Chromatography. From these all techniques, FTIR is the most popular method to identify the chemical composition of bitumen and investigate its effect on chemical properties. It is vital to analyze the functional group change of bitumen with aging since bitumen binders are sensitive to environment non- load-related actions, mostly oxidative aging.

FTIR is a useful analytical instrument to detect the functional groups as well as characterizing covalent bonding information.

Bitumen is aged by irreversible oxidation due to the existence of oxygen in the air. This produces carbonyl groups (C=O) and sulfoxide groups (S-O), and eventually, it will modify the bitumen composition. As a result, the bitumen's molecular size, polarity, and aromaticity are increased, allowing the more brittle bituminous binder to harden (Dony, et al., 2016). Carbonyl and sulfoxide groups indicate that the bitumen has been aged when it is monitored by FTIR spectroscopy. Sometimes, groups of sulfoxides may be present before aging, as per the origin of crude oil. Table 2.2 describes the reference peak values for a bitumen sample analyzed through the FTIR machine (Dony, et al., 2016).

Few samples from bitumen modified with nano clay and thermally oxidized were subjected to the Fourier Transform Infrared (FTIR) analysis to study any bitumen mixture's chemical composition.

Figure 2.16: FTIR Spectrometer

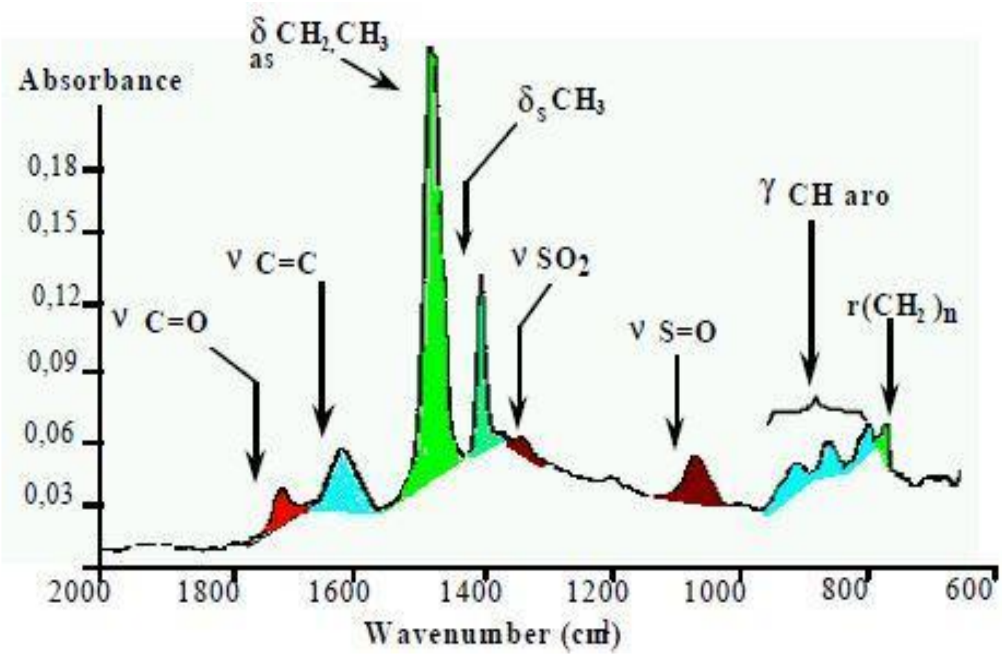


Figure 2.17: FTIR bitumen spectrum – presentation of carbonyl, sulfoxide, and reference peaks (circled in red) - (Dony, et al., 2016)

Table 2.2 Reference functional group Peak values for pure asphalt binder (Dony, et al., 2016)

Wave Number (cm^{-1})	**Assignment**
3400	Hydroxyl, OH^- stretching
3080-3000	Aromatic C-H bonds
2956	asymmetric CH_3 stretching
2925	asymmetric C-H stretching of a methylene group
2872	symmetric CH_3 stretching
2850	symmetric C-H stretching of a methylene group
1745-1680	symmetric C-H stretching of a methylene group Carbonyl C=O stretching
1650-1580	C=C bonds, H2O deformation, aromatic ring stretching
1520-1500	aromatic rings
1450	Asymmetric CH_2 and CH_3 bending
1380-1370	CH_3 and cyclic CH_2 vibrations
1250	Phenolic C-O bond
1050	C-O bonds of alcohols
980-890	C=C bonds
900-700	Aromatic out of plane deformation
725-720	Aliphatic chains longer than C4

2.8 Differential Scanning Calorimetry and Thermo Gravimetric Analyzer (DSC and TGA)

Differential Scanning Calorimetry (DSC) use to study the thermal changes of the material, such as physical changes,

- The glass transitions
- Melting & crystallization
- Vaporization of volatile compounds

Further, any chemical reaction of the sample can be investigated during the thermal events of the DSC. Sample can be characterized concerning its thermal behavior and composition, information obtained from the DSC.

Simultaneous DSC-TGA can measure both the heat flow and weight change in a controlled atmosphere related to temperature or time. So, it is very easy to analyze the results since it shows two material properties. Further, it can differentiate between endothermic and exothermic events with no corresponding weight loss (e.g., melting and crystallization) and those that bring a weight.

2.9 Previous Studies

Few major studies were reviewed to provide insight into nano clay's performance with conventional bitumen in the pavement industry. These studies are,

- ❖ Asphalt binder modification with Nano clay "(M.F.C. van de van & A.A.A. Molennar, Delft University of Technology, Delft, The Netherlands)"

The improvement was observed with the nano clay modification in stiffness, indirect tensile strength & rutting resistance. It assumed that enhancing the above properties due to the additive that was added to the mixture and unlocked the clay structure. Then there was better exchange between clay and the bitumen.

- ❖ Nano clay modified asphalt materials: preparation & characterization (Department of Civil and Environment Engineering, Mitchigan Technological University)

Two different nano clay materials have been used in this research. This research has mostly demonstrated that nano clays can be improved the mechanical properties of asphalt binders as a modifier. The two nano clays were enhanced the G* and viscosity and resistance to low-temperature cracking. But the mixing procedure is crucial to getting a well-distributed nano clay asphalt.

- ❖ The effects of macro and nano clay on the performance of asphalt binder (Egyptian Petroleum Research Institute)

The studies had different percentages of macro clays and modified nano clays 2%, 4%, 6%, and 8%. Macro clay was changed to organically modified nano clay and verified with the XRD technique. Adding nano clay considerably improved the physical and mechanical properties of binders such as penetration, softening point, Kinematic viscosity, and tensile strength. Organically modified nanoclay has been shown more improvement than normal nanoclay.

- ❖ Effect of Nano Clay Modification on Rheology of Bitumen and Performance of Asphalt Mixtures, By Daniel Beyene Ghile Daniel, “DELFT UNIVERSITY OF TECHNOLOGY, DELFT, NETHERLANDS”.

This research has discovered the used nanoclay (cloisite) was a help to improve the rutting resistance and stiffness. The best result was given with 6% of cloisite. In this research, the conclusion said that the indirect tensile strength, fatigue resistance is enhanced due to cloisite clay modification.

3 METHODOLOGY OF THE STUDY

3.1 Introduction

It is proposed to study the variation of rheological properties of bitumen binder with different percentage of nano clay concerning the Dynamic Shear Rheometer (DSR) test for un-aged, Rolling Thin Film Oven (RTFO) test for short term aged and Pressure Aging Vessel (PAV) test for long term aged bitumen samples. Therefore, the selected original bitumen sample (60/70 penetration grade) was modified with prepared nano clays as below. Methodology followed in the study is presented under following steps;

1. Clay sample preparation

   Nano clay was prepared from an original bulk clay sample extracted from the Murunkan area near the Giant Tank, and extracted pit depth was around 3-4ft. Clay powder preparation process is discussed under chapter 3.2.

2. Mixing of Clay modifier with Bitumen

   Prepared clay powder was then mixed with the original binder with 2%, 4%, 6%, and 8% by its weight, respectively. The mixing process is described under chapter 3.3.

3. Experimental Plan

   First, the prepared nano clay was subjected to the X-ray diffraction test to identify the clay type. Softening Point (EN 1427), Penetration (EN 1426), rotational Viscosity (ASTMD4402), and Dynamic Shear Rheometer (AASHTO TP5) tests were carried out on the binders obtained in 4 different combinations using the mixer mentioned above. Rolling Thin Film Oven test and Pressure Aging Vessel Test conducted for the same samples and residue of RTFO and PAV test assesses the DSR test again to analyze the rutting and fatigue resistance. Fourier Transform Infrared (FTIR) test was conducted for original binder, 4% nano clay sample, and residue of RTFO and PAV of 4% nano clay, respectively, to analyze the chemical changes of the mixture during the aging process. Finally, Differential Scanning Calorimetry (DSC) and Thermo Gravimetric Analyzer (TGA) tests were also done for the same samples, which are done for FTIR to identify and confirmed whether it had happened any chemical reaction between clay and bitumen. The summary of experimental procedure is described in Figure 3.1.

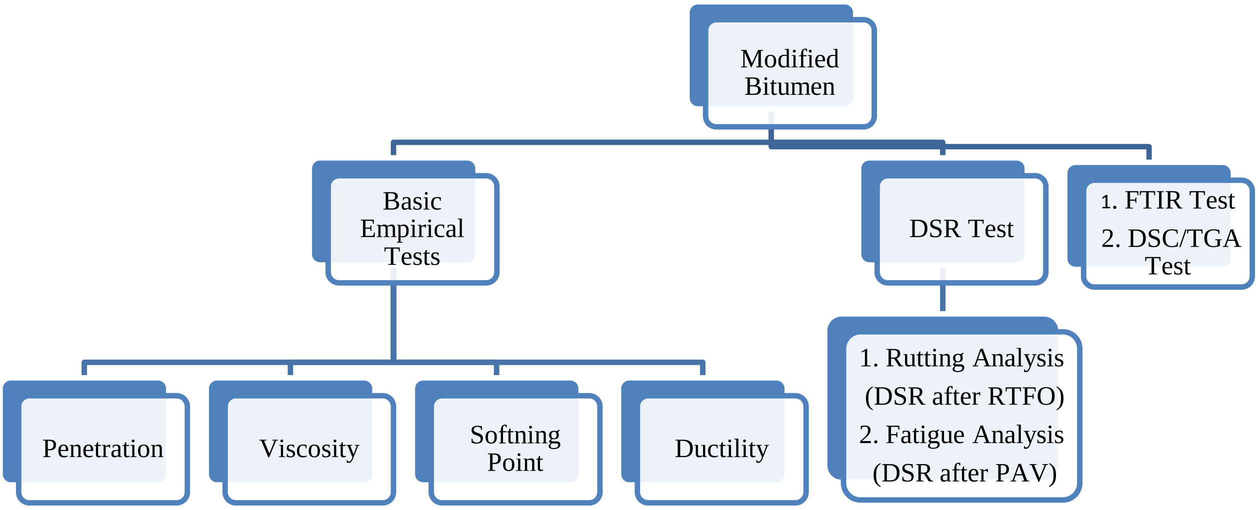


Figure 3.1 Test Procedure for Nano clay Modified Bitumen Samples

3.2 Preparation of Nano clay

Bulk clay sample was taken at a depth of 3 to 4 feet (Fig.3.3) in Giant Tank's vicinity in the Mannar area. After that, bulk clay was crushed and mixed with water and allowed to settle around 24 hours. Once the sedimentation is completed, an excess of pure water is removed from the bucket's top. The remaining clay slurry was wet screened with a 56µm sieve to extract the fine clay fraction. The wet sieve clay fraction was subjected to the oven-dry at 120^{0}C to take dried clay. Then, the dried clay sample was milled with mortar and pestle. Finally, the milled clay sample was sieved again through the same sieve (56µm dry sieve) to obtain a fine clay powder. So, the particle size of the clay powder is less than 56µm.

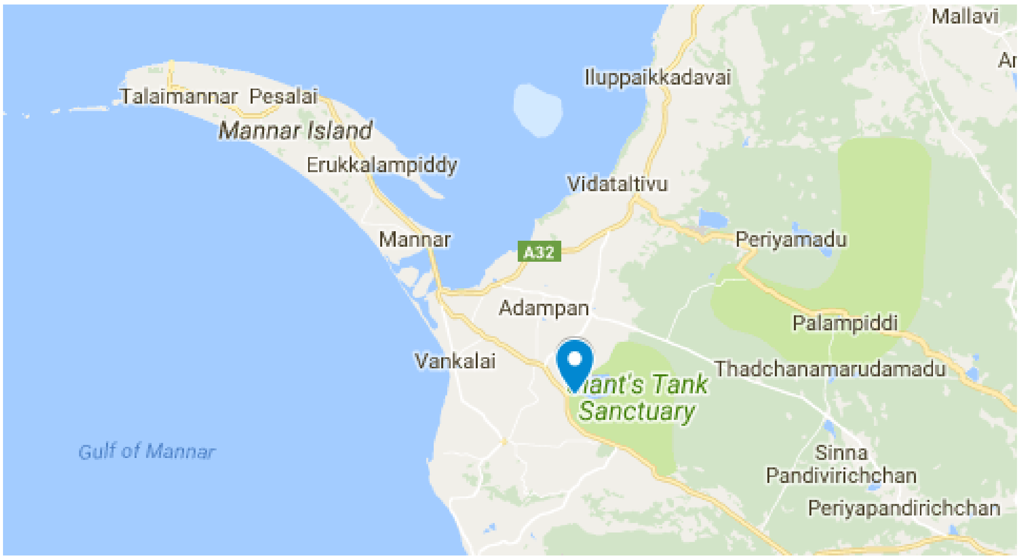


Figure 3.2 Location of the clay deposit

Figure 3.3 Process of clay powder preparation

3.3 Mixing

The mixing process was conducted by a laboratory scale Hobart mixer (Fig. 3.4) with 800-1000 rpm speed at 160°C temperature with original bitumen and the prepared nano clay for 25 minutes of mixing time (Ven, Molenaar, & Besamusca, 2009). The parameter for mixing (mixing time, temperature & rpm) was selected as per the previous research done by Ven, Molenar, & Besamusca, 2009, nano clay for binder modification for asphalt mixture.

Figure 3.4 Laboratory Scale Mixer

4 RESULTS

4.1 Introduction

Empirical basic test data for the original binder and the samples with different proportions of nano-clay 2%, 4%, 6% & 8% of the corresponding values are tabulated in table 8.1. The results of the tests of DSR for unaged bitumen are given in table 8.2. The bitumen samples for the short term (after RTFO) and the long-term aged (after PAV) DSR test results are also shown in table 8.3 and 8.4, respectively. Instead, the FTIR spectrum and DSC/TGA tests for several samples are given to identify the chemical changes during the mixing and the aging process.

4.2 Basic Empirical Test Results

The table 4.1 to 4.4 show the variation of penetration, ductility, softening point, viscosity and Dynamic Shear Rheometer test for the original bitumen sample and mixed samples with nano clays.

Table 4.1: Basic Empirical Test Results

Sample with Clay content (%)	Penetration (0.1mm) ASTM D5	Softening point (^{0}C) ASTM D36	Viscosity at 135^{0}C (PaS) ASTM D4402	Ductility (mm) ASTM D113
0(Original)	60	51	0.38	151
2	55	52	0.41	137
4	45	53	0.40	122
6	50	53	0.40	95
8	50	53	0.40	90

Table 4.2: Test Results of DSR for un-aged Samples

Sample with Clay content (%)	Grade Result		True Grade Temperature(^{0}C)	G*/sinδ (KPa) at PG 76 stage
	PG Grade	G*/sinδ (KPa)		
0(Original)	PG 70	1.10	70.75	0.465
2	PG 70	1.15	71.10	0.598
4	PG 70	1.24	71.82	0.609
6	PG 70	1.75	74.02	0.79
8	PG 70	2.10	75.2	0.906

Table 4.3: Test Results of DSR for Aged (After RTFO) Samples

Sample with Clay content (%)	Grade Result		True Grade Temperature(^{0}C)	G*/sinδ (KPa) at PG 76 stage
	PG Grade	G*/sinδ (KPa)		
0(Original)	PG 70	2.87	72.28	1.42
2	PG 70	3.94	74.7	1.87
4	PG 70	4.12	75.16	1.96
6	PG 70	4.97	75.88	2.18
8	PG 76	21.4	The test could not continue	

Table 4.4: Test Results of DSR for Aged (After PAV) Samples

Sample with Clay content (%)	G*sinδ at 45^0C (KPa)	True Grade Temperature (^{0}C)	G*sinδ at 42^0C (KPa)
0(Original)	3.12E3	42.73	5.96E3
2	3.86E3	43.83	7.48E3
4		Not Done	
6	3.69E3	43.5	7.01E3
Original -RTFO	3.24E3	43.07	6.32E3
2% -RTFO	3.71E3	43.67	7.08E3
4% -RTFO		Not Done	
6% -RTFO	3.30E3	43.13	6.43E3

DSR test has done for aged samples of PAV test of both after the RTFO test and without RTFT test to analyze the effect of fatigue. As per the results from the table 4.4, all the samples were failed from the fatigue in the range of temperature 42^0C – 45^0C.

Table 4.5: Weight change after Pressure Aging Vessel (PAV) test

Sample	Weight of dish (g)	Weight of (dish+sample)	Weight of (dish+sample) After PAV	Weight Increasing (%)
Original	93.77	144.45	144.71	0.18
2% clay	93.86	144.90	145.12	0.15
4% clay	93.87	143.99	144.21	0.15
6% clay	94.65	144.84	145.06	0.15
RTFO- Original	93.51	144.34	144.54	0.14
RTFO– 2% clay	94.04	144.88	145.06	0.12
RTFO– 4% clay	94.94	144.36	144.53	0.12
RTFO– 6% clay	94.71	144.89	145.07	0.12

4.3 XRD Analysis of clay powder

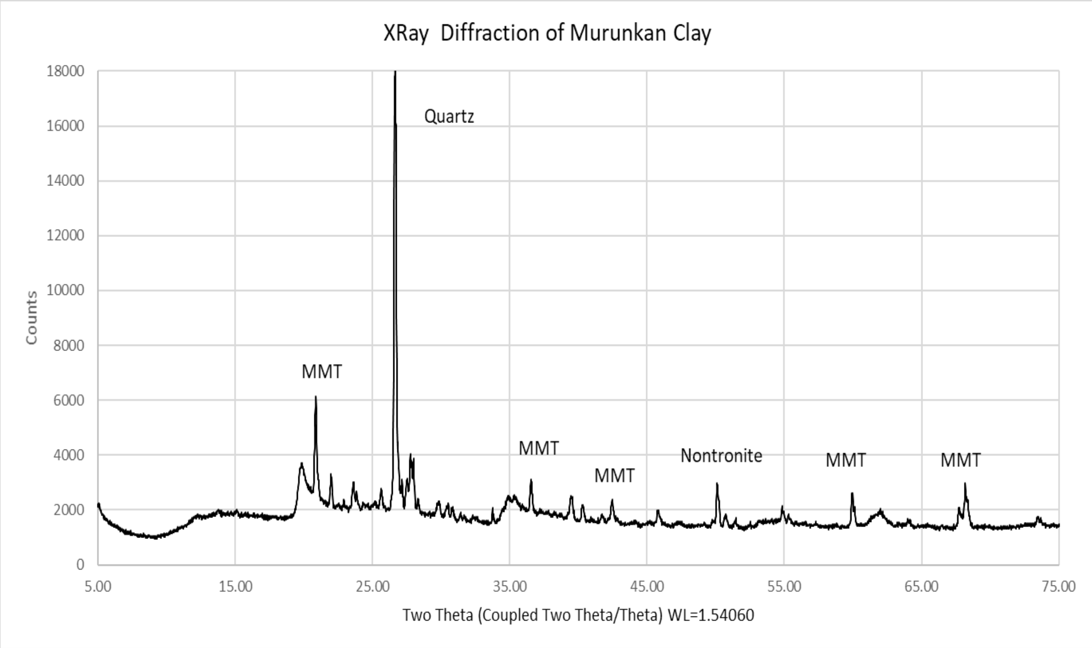


Figure 4.1: XRD spectrums for (Murukkan) clay samples of Giant's tank

Nontronite is an iron-rich clay, a member of the smectite group with a 2:1 structure (Clay, n.d.).

4.4 Soil Properties of Clay Sample

A plastic limit test was performed on the material to get an idea about nano clay material consistency.

Table 4.6: Plastic Limit test result for MMT clay

Original Bulk Clay Sample		**Sample After Wet Sieved (56µm) & Dried (Prepared clay powder mixed with bitumen)**	
Liquid Limit (LL)	44	Liquid Limit (LL)	87
Plastic Limit (PL)	20	Plastic Limit (PL)	36
Plasticity Index (PI)	24	Plasticity Index (PI)	51

Due to the higher plastic limit of the clay, it can say that clay belongs to a family of montmorillonite. Furthermore, it has been confirmed with the X-ray diffraction test.

4.5 FTIR Test Results

Fourier Transform Infrared Spectroscopy (FTIR) has been done for some samples (for un-aged and aged) to identify chemical bonds in a molecule any changes of the bonds after aging by producing an infrared absorption spectrum.

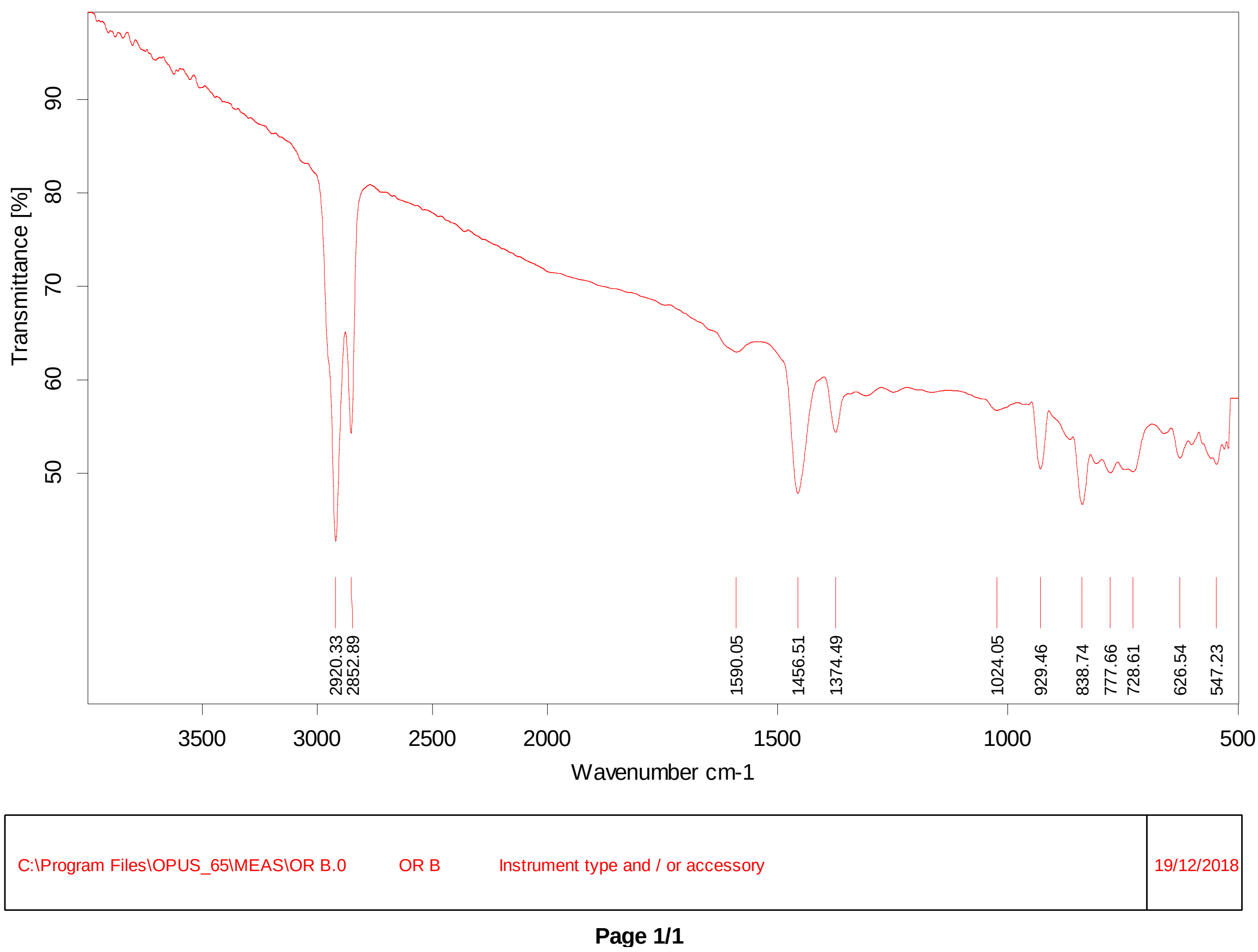
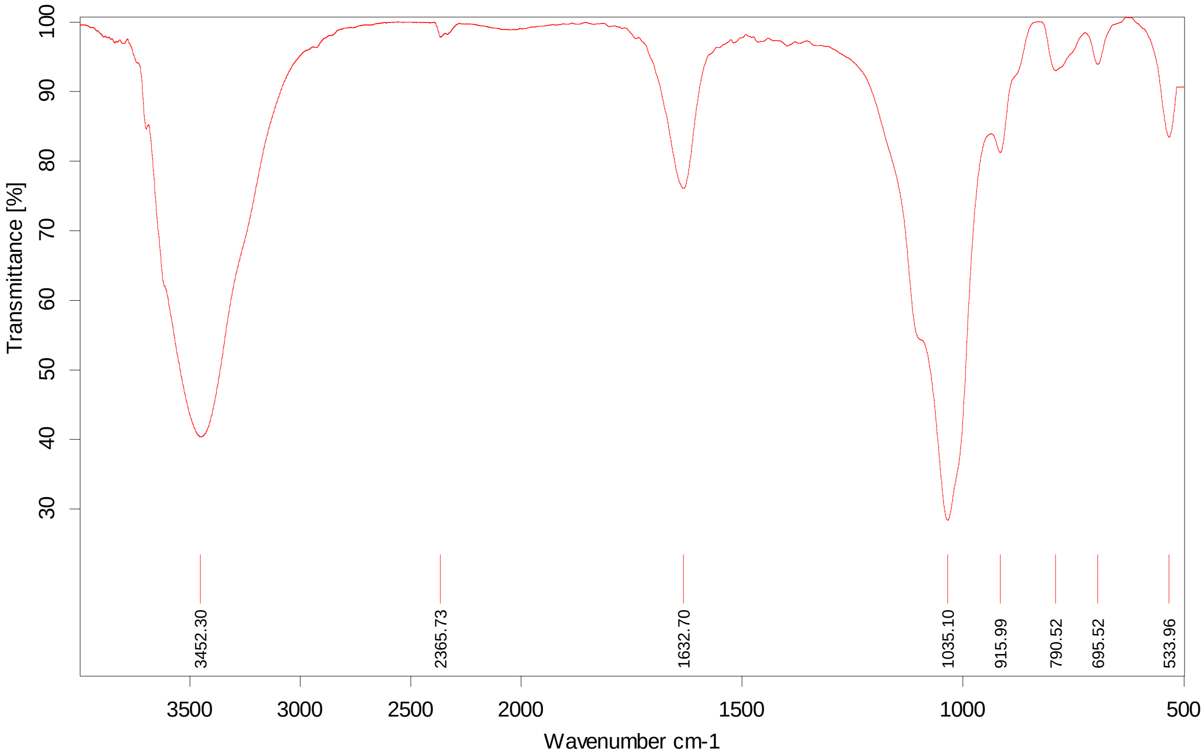


Figure 4.2: FTIR Spectroscopy for Original Bitumen

As mention in the literature review, the type of bond in the bitumen binder is given in table 8.7.

Table 4.7: Reference peak values and type of bonds for Original Bitumen sample (Base Material)

Wave Number (cm^{-1})	Type of Bond
2920	asymmetric C-H stretching of a group of methylene
2852	symmetric C-H bond of a group of methylene
1590	C=C bonds, H2O deformation, aromatic ring stretching
1456	Asymmetric CH_2 and CH_3 bending
1374	CH_3 and cyclic CH_2 vibrations
1024	C-O bonds
929	C=C bonds
833	C=C bonds, H2O deformation, aromatic ring stretching
900-700	Out of plane deformation for aromatic groups
725-720	Aliphatic chains greater than C4



C:\Program Files\OPUS_65\MEAS\CLAY.1	CLAY	Instrument type and / or accessory	01/08/2019

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Figure 4.3: FTIR Spectroscopy for MMT Nano clay

Table 4.8: Reference peak values and type of bonds for MMT clay

Wave Number (cm^{-1})	Bond Type
3452	Quartz
1632	OH bending
1035	Si-O stretching
915	Al-Al-OH
790	Tridymite
695	Quartz
533	Si-O bending

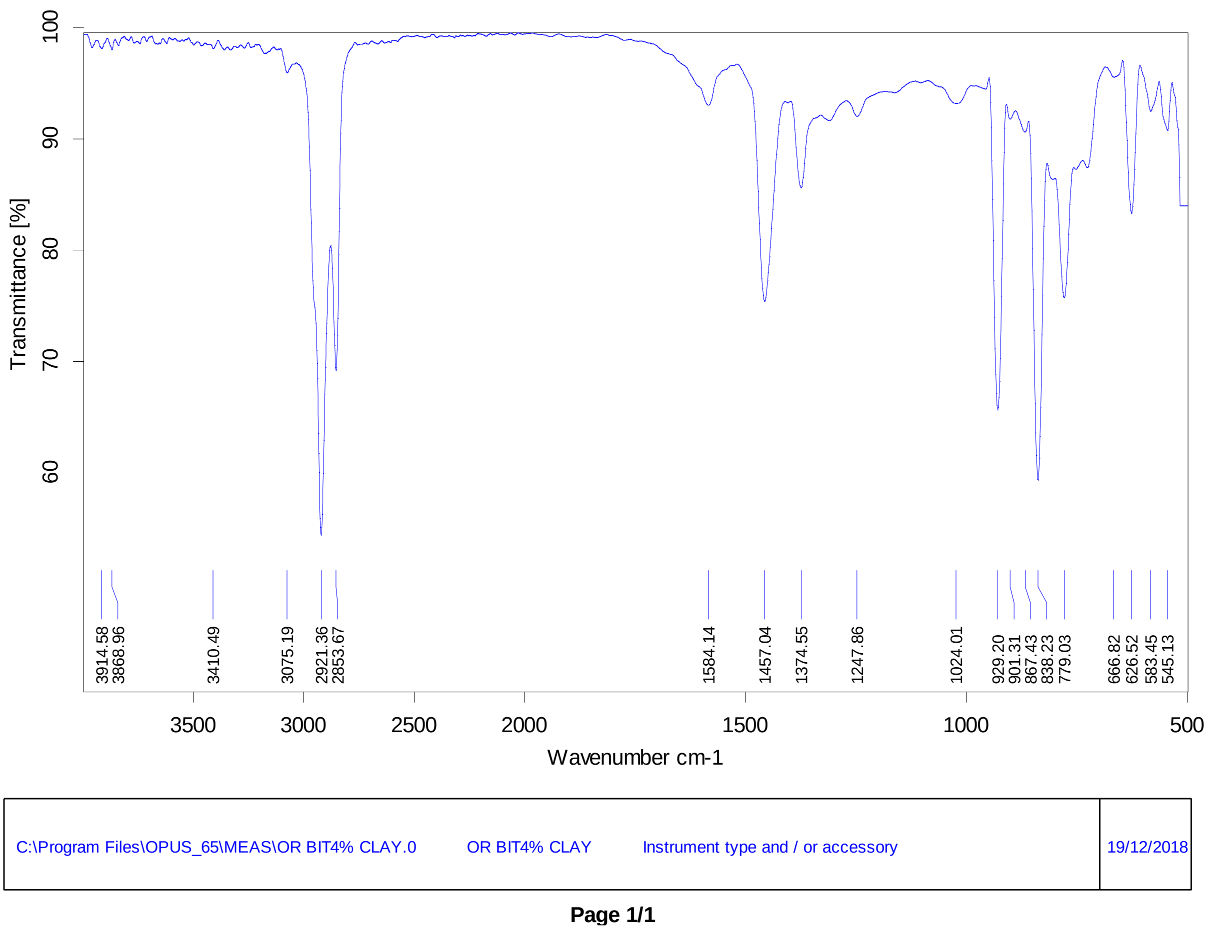

Figure 4.4: FTIR Spectroscopy for Original Bitumen+ 4% clay

Table 4.9: Reference peak values and type of bonds for Original Bitumen + 4% clay (modified bitumen)

Wave Number (cm^{-1})	Type of Bond
3410	Quartz from the clay
2920	asymmetric C-H stretching of a group of methylene
2852	symmetric C-H bond of a group of methylene
1584	C=C bonds, H2O deformation, aromatic ring stretching
1457	Asymmetric CH_2 and CH_3 bending
1374	CH_3 and cyclic CH_2 vibrations
1247	C-O bonds (phenolic)
1024	C-O bonds
929	C=C bonds
833	C=C bonds, H2O deformation, aromatic ring stretching
900-700	Out of plane deformation for aromatic groups
725-720	Aliphatic chains greater than C4
500-700	Si-O bending, Quartz from the clay

As per the FTIR spectroscopy of original bitumen+ 4% clay, it can say that there is no chemical interaction between the bitumen and nano clay since it has no new peak values corresponding to the new functional group of the mixture.

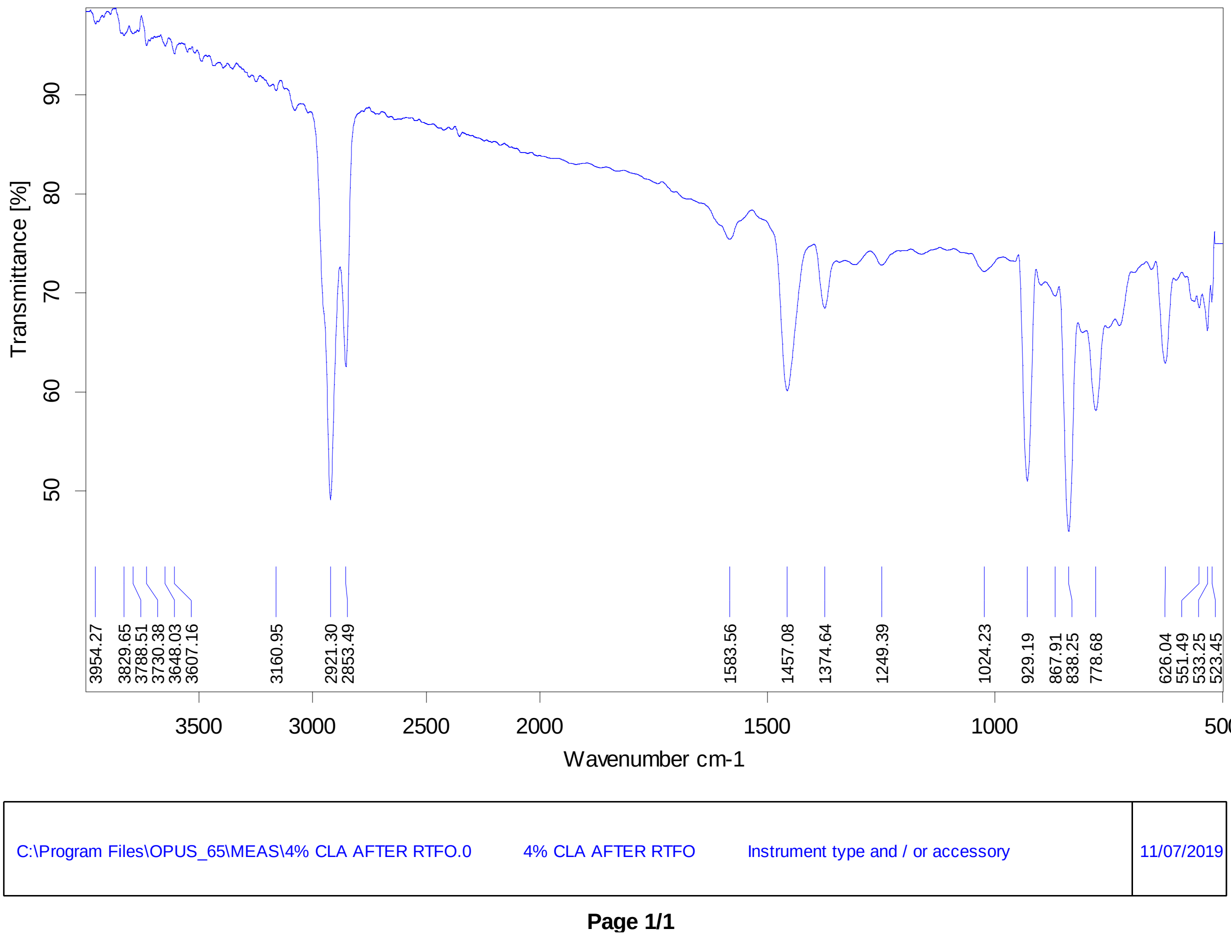

Figure 4.5: FTIR Spectroscopy for Original Bitumen+ 4% clay – After RTFO Test

Reference peak values has not much changed with Original bitumen+ 4% clay sample.

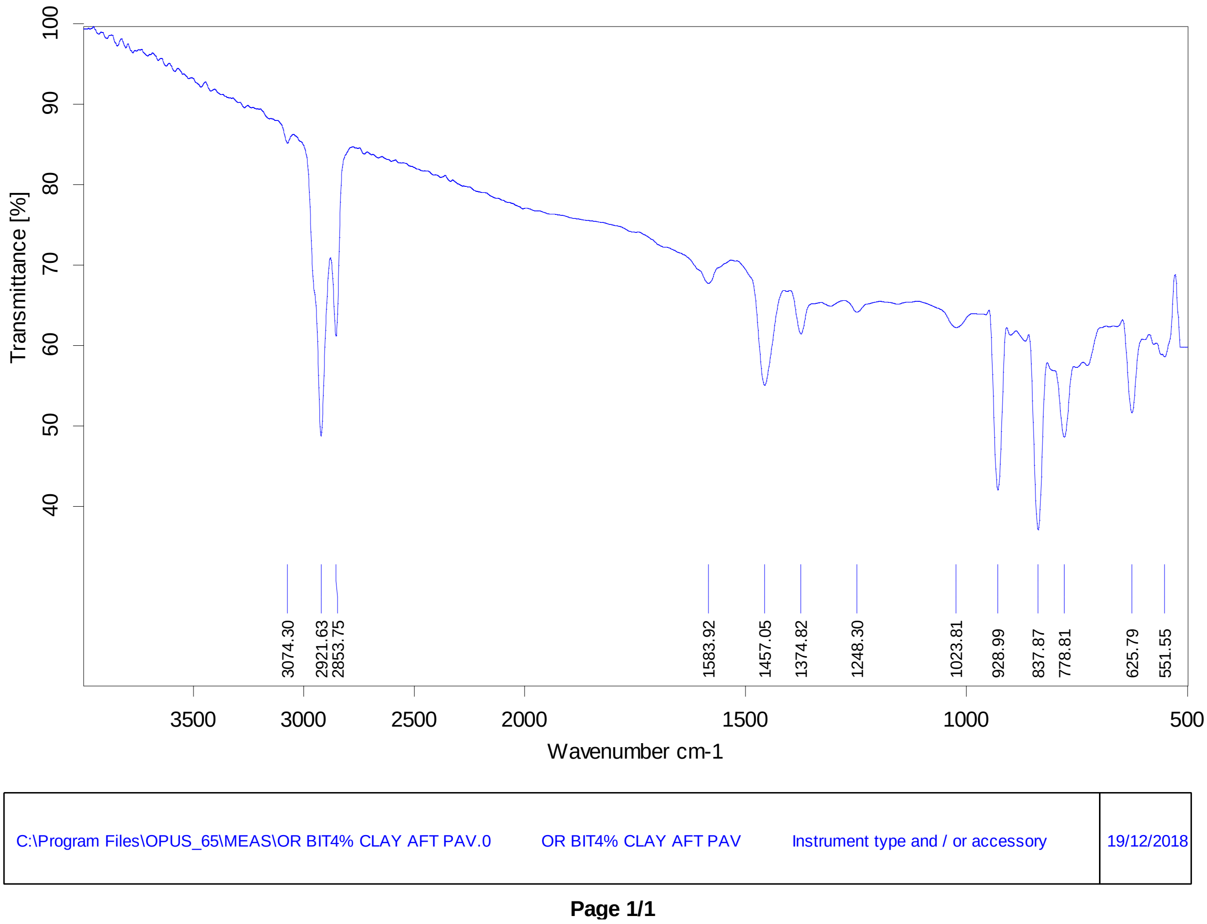

Figure 4.6: FTIR Spectroscopy for Original Bitumen+ 4% clay – After PAV Test

Reference peak values has not much changed with Original bitumen+ 4% clay sample.

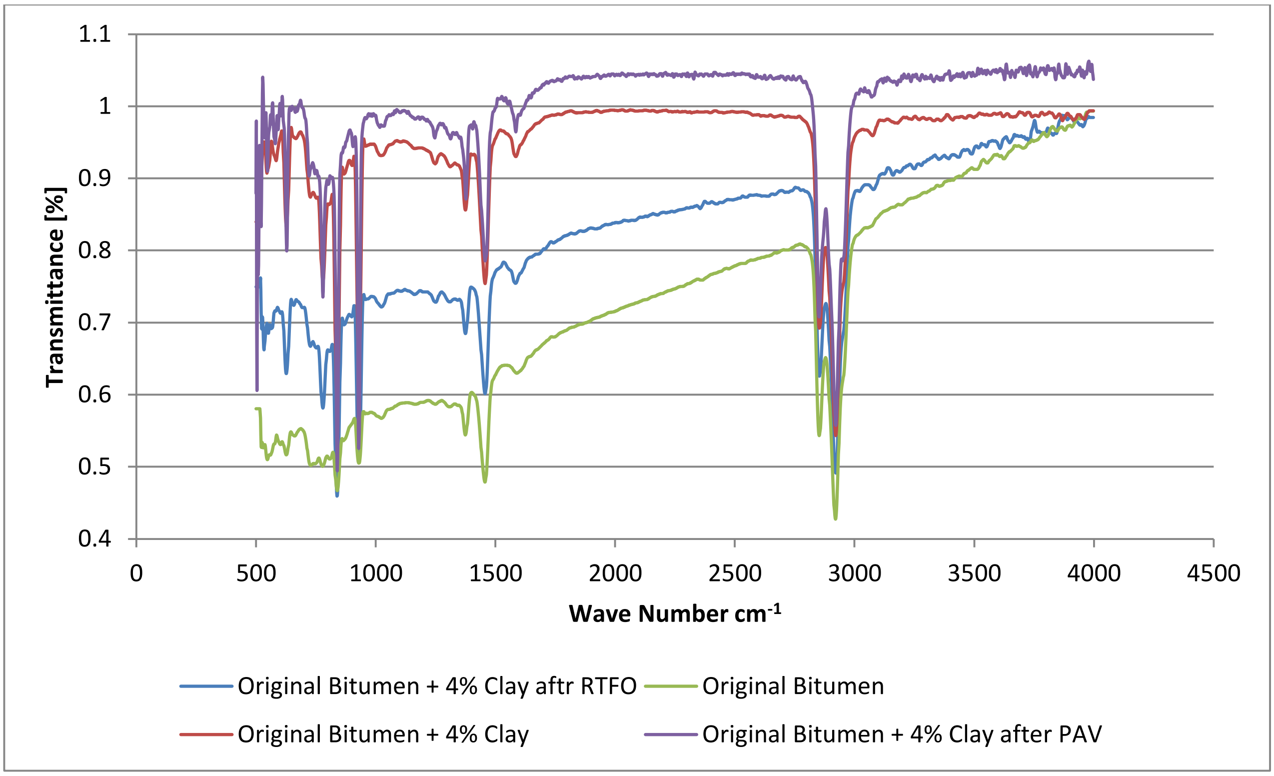

Figure 4.7 FTIR Spectroscopy for all samples in the same graph

As per the figure 4.7, all the peak values of the reference functional groups have not changed in both base material and nano clay modified sample even after RTFO test and PAV test. So, it has not occurred any chemical interaction between the bitumen and nano clay.

8.6 DSC and TGA Test Results

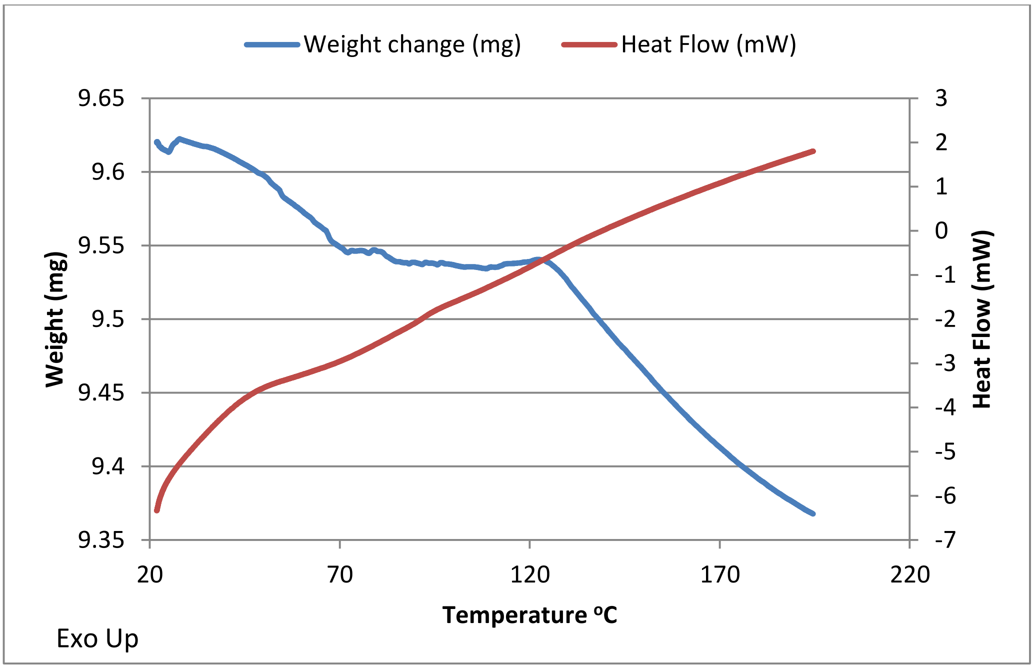

Figure 4.8: DSC – TGA Graph for Original Bitumen

Sample heating rate - 10^0C/min

As per the graph, the bitumen sample's weight has decreased due to the volatile compound of the bitumen binder.

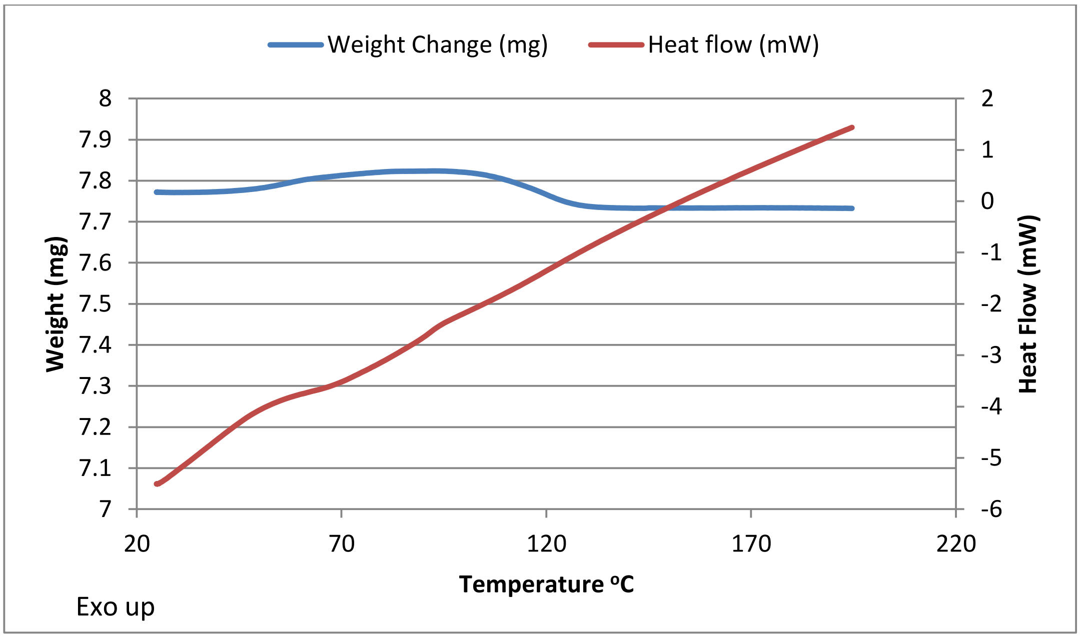

Figure 4.9: DSC – TGA Graph for Original Bitumen + 4% clay

Sample heating rate - 10^0C/min

There is an increase in weight in the modified bitumen sample with 4% clay due to oxidization of both bitumen and the clay. After the range of 100^0C, the sample's weight has been reduced, which may be due to the clay's volatilization of organic compounds. But there is no sudden peak value of the heat flow curve (there is no exothermic or endothermic reaction). Hence it cannot confirm any chemical reaction between bitumen and the clay.

5 ANALYSIS AND DISCUSSION

Some studies have clarified the modification effect of nano clay with polymer and bitumen in the literature review. Furthermore, to get a better result from the modification of bitumen with nano clay, following factors to be considered in preparation of modified bitumen.

- It should be compatible with bitumen
- Purity of clay
- Method of nano clay preparation

5.1 Summary of Basic Empirical Test Results

A summary of basic empirical test results is shown in Figure 5.1 to 5.4.

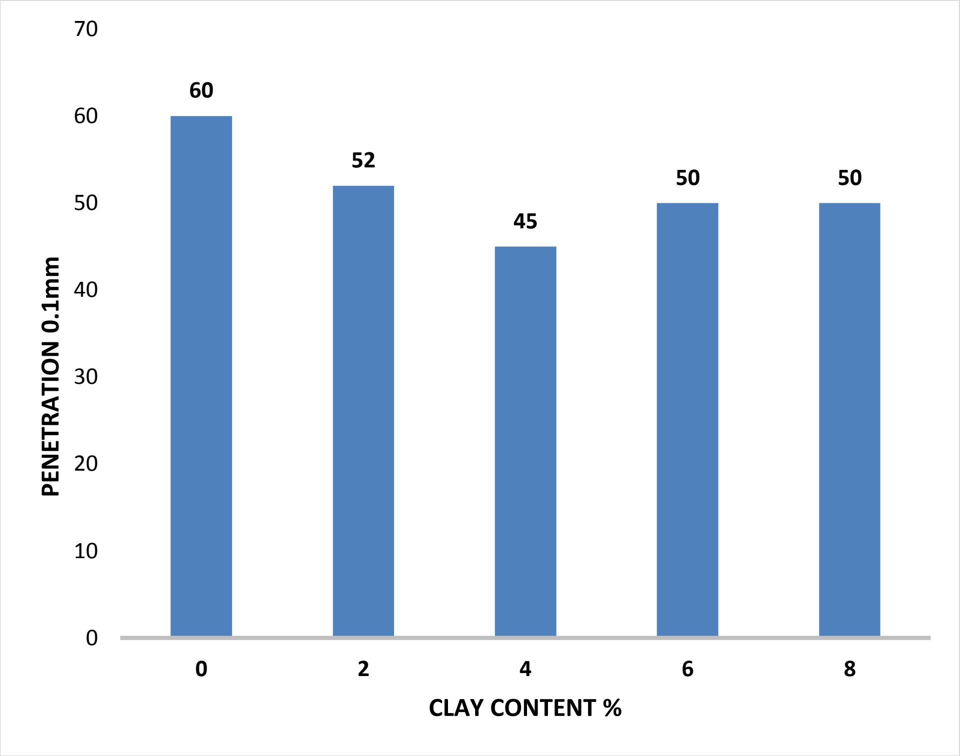

Figure 5.1: Variation of penetration with clay content

The penetration test was carried out in compliance with ASTM D5, and as per the above chart, samples' penetration values have been decreased from 60 to 45 when increasing the MMT clay content up to 4%. Then again, penetration values were increased up to 50 with 6% of clay, and it has remained the same penetration value (50) with 8% clay content.

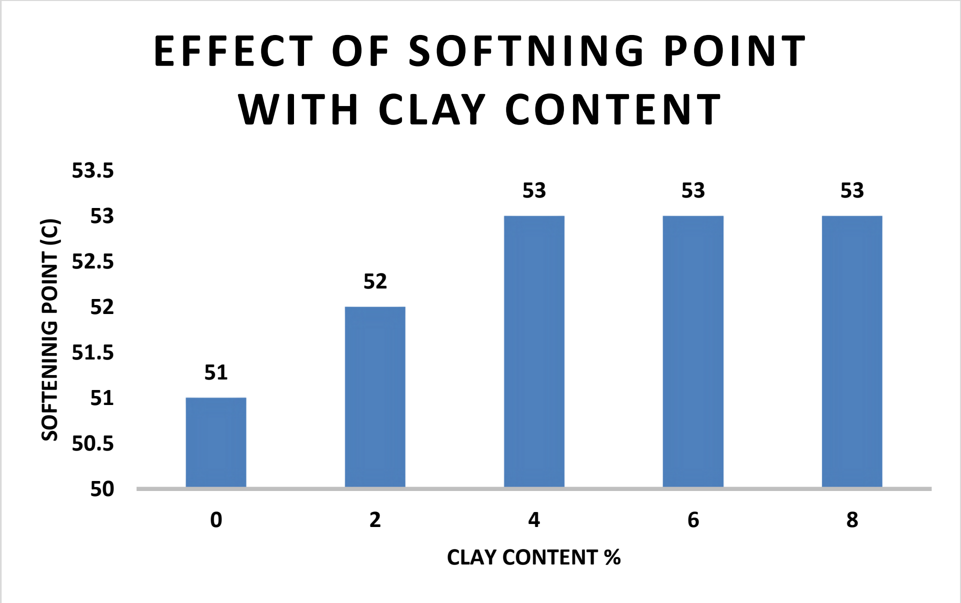

Figure 5.2: Variation of softening point with clay content

Softening point test was carried out in compliance with ASTM D36. Figure 5.2 demonstrates the softening point with clay content, which shows the softening point had increased up to 53^{0}C from 51^{0}C when increasing the clay content up to 4%. It remained 53^{0}C with further increased to clay content to 8%.

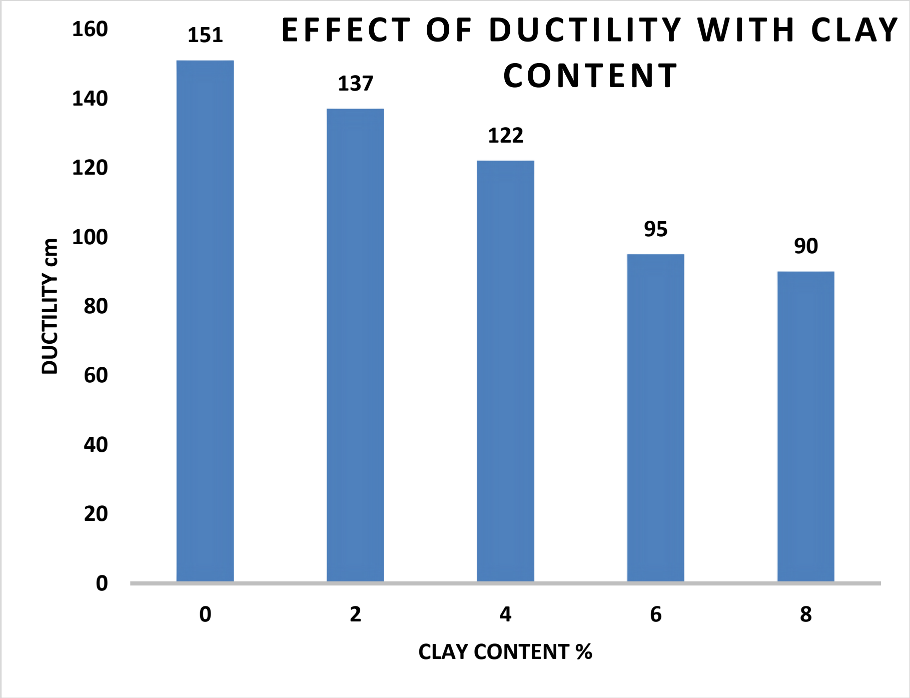

Figure 5.3: Variation in ductility with clay content

The ductility test was conducted in compliance with ASTM D 113. The ductility value of the original sample (0% clay) was 151Cm, and it was further reduced with the increase of clay content. When it increased with clay content, ductility values further reduced to 90cm with 8% clay content in modified sample. When the clay content is increased, the specific gravity of the bitumen is also increased. Hence ductility values are decreasing with the percentage of clay is rising.

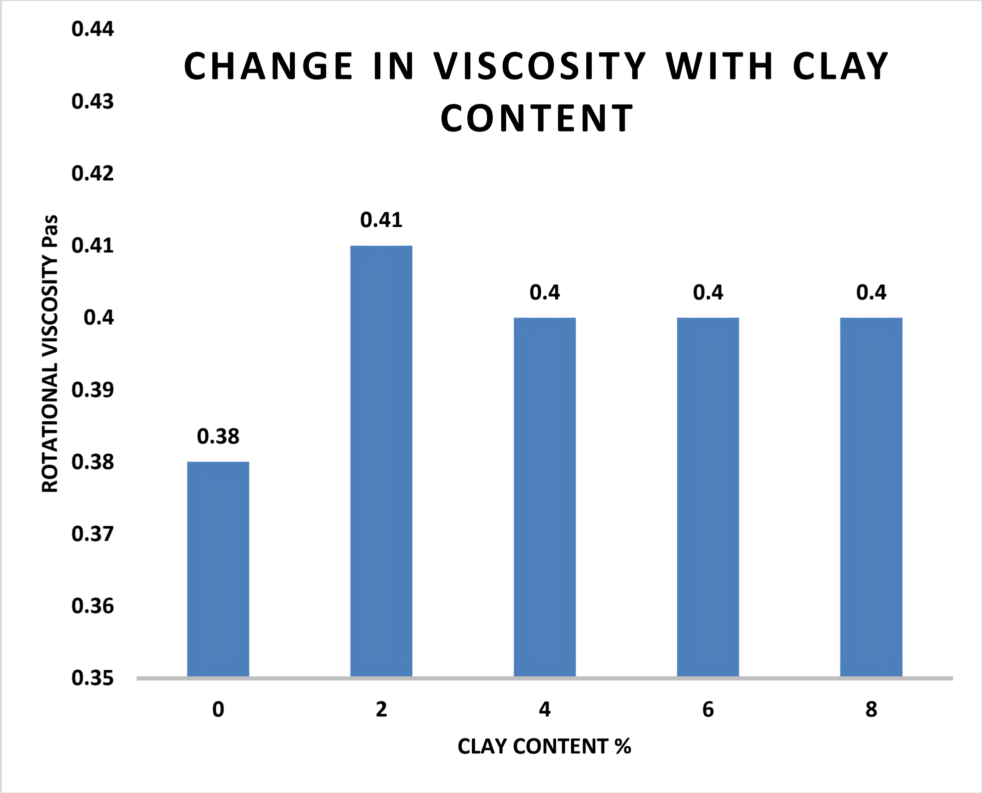

Figure 5.4: Variation in viscosity with clay content

The Rotational Viscosity test was conducted on base (unmodified) and modified binder at 135^{0}C in compliance with ASTM D 4402. Figure 5.4 shows that viscosity value increased from 0.38 Pas to 0.41Pas with 2% of clay. When clay content is further increased up to 8%, the viscosity value remains unchanged at 0.4Pas, which is still higher than the viscosity of unmodified bitumen.

5.2 Analysis of Rutting and Fatigue Parameters

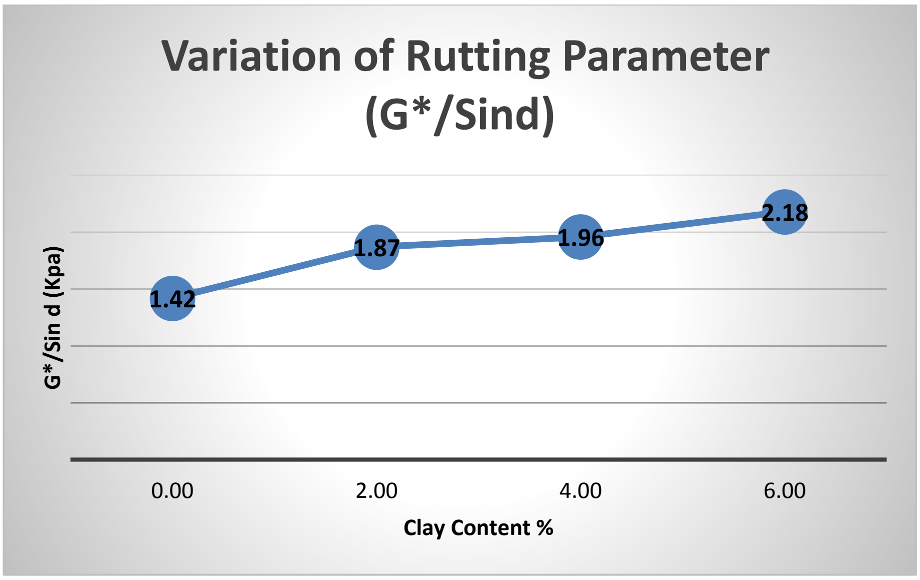

Figure 5.5: Variation of rutting parameter with clay content

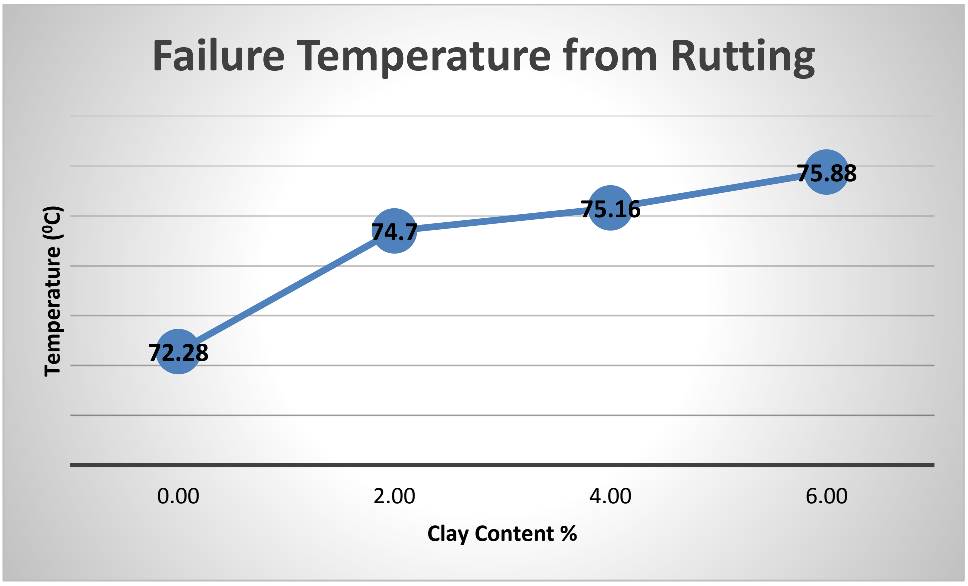

Figure 5.6: Failure temperature from rutting with clay content

The modified bitumen mixture showed higher rutting resistance related to unmodified mixtures at higher temperatures. Further, it has increased with the amount of nano clay.

8% of clay sample was shown PG 76 after the RTFO test with the DSR machine, but the test could not continue due to over modification of the clay. The DSR test for the 8 % clay RTFO sample was stucked after it shows PG 76 grade. So, It can say that the 8 % clay sample is over modified even it has shown PG 76 grade after the RTFO test.

After the samples' PAV test, the weight increased from 0.1 to 0.15g due to the oxidization. Samples after the PAV test were subjected to the DSR test, and it has failed between 42^0C-45^0C of temperature range, giving the $G^*\sin\delta$ more than 5000Kpa. So, the samples, including the original bitumen, failed due to fatigue at the range of temperature between 42^0C-45^0C.

5.3 Analysis of FTIR & DSC/TGA Tests

The FTIR spectra of bitumen and nano clay containing four wt% for un-aged and RTFO aged and PAV aged are shown in figures 8.5, 8.6 & 8.7, respectively. The bitumen spectra show peaks at 2920 and 2852 cm^{-1} due to the asymmetric and symmetric C-H stretching vibrations. The C-O bond shows a peak at 1024cm^{-1}. Also, peaks at 1457 and 1374 cm^{-1} are because of asymmetric CH_2 and CH_3 bending and CH_3 and cyclic CH_2 vibration in bitumen. The C=C bonds show a peak at 929$cm^{-1,}$ and 838cm^{-1} shows the aromatic out of plane deformation in the above FTIR spectra.

In both modified and unmodified (base material), major functional groups' peak values have not changed, and it has changed only the peak intensity of a few functional groups. So, it can be seen the presence of clay in the matrix does not affect the intensity of absorption of the characteristic FTIR peaks, and no new peaks are observed. It can be concluded that the clay is dispersed in the matrix, and there are no significant chemical structural changes in bitumen, owing to the presence of clay.

As per the FTIR & DSC/TGA test results, it has not happened any chemical reaction between the bitumen and MMT nano clay; hence, there is no new peak in the FTIR chart. When considering the DSC/TGA graph, it does not indicate any exothermic or endothermic reaction rather than oxidization weight increasing for the modified bitumen samples. Finally, it can be concluded that any chemical interaction has not happened between the 60-70 penetration grade bitumen and MMT nano clay.

So, it can be said that the improvements regarding the modified bitumen due to the physical interaction between the bitumen and MMT nano clay, and as per the literature review, these enhancements of the rheological properties of modified bitumen due to the exfoliation of the clay plate in the bitumen matrix. At the time of the mixing, the condition applied a high mixing rate (rpm) with laboratory-scale Hobard Mixer and the temperature at160^0C the exfoliation happened.

6 CONCLUSION AND RECOMMENDATION

Nano clay-based modified bitumen has extended the temperature range in the plasticity interval since the softening point has been increased up to 53^0C from 51^0C. The temperature range of bitumen behaves as an elastic solid, and viscous fluid is express the plasticity range. The penetration has been reduced to 45 (0.1mm) of 4% MMT modified clay from 60 (0.1mm) of the original bitumen sample. The ductility value has been reduced from 151mm of original bitumen sample to 90mm of 8% of MMT modified clay. The viscosity increased from 0.38PaS of original bitumen to 0.41PaS of 2% MMT modified clay. Again, it has reduced to 0.40PaS of 4% of clay sample, and then viscosity value remains unchanged up to 8% of MMT modified clay sample.

Penetration and ductility have decreased with an increasing clay content of the modified binder due to an increase in the mixture's specific gravity.

Rutting resistance of modified bitumen has improved compared to conventional bitumen, and the improvement has been proven by the DSR test. The rutting parameter (G*/sin d) has increased up to 2.18 with 6% of the MMT modified clay sample and the rutting parameter (G*/sin d) was 1.42 in the original bitumen sample. However, this improvement is not sufficient to shift the PG 76 grade, and it was closed to the PG 76 level with 6% clay content.

In both modified and unmodified (base material), major functional groups' peak values have not changed, and it has changed only the peak intensity of a few functional groups. So, it can be seen the presence of clay in the matrix does not affect the intensity of absorption of the characteristic FTIR peaks, and no new peaks are observed. It can be concluded that the clay is dispersed in the matrix, and there are no significant chemical structural changes in bitumen, owing to the presence of clay.

Finally, to clarify and conclude, it is recommended further studies to verify the application on a large scale.

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