Bitumen- Organo- Clay Composites

A Thesis submitted to

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BS-MS Dual Degree Programme

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Certificate

This is to certify that this thesis entitled "Bitumen- Organo- Clay Composites" submitted towards the partial fulfillment of the BS-MS dual degree programme at the Indian Institute of Science Education and Research Pune represents original research carried out by Prashant Agrawal at Shell India Markets Private Limited under the supervision of Dr. Sunil Ashtekar, Researcher Experimentation, Shell India Markets Private Limited, Bangalore during the academic year 2011-2012.

Signature of Student

Date:

Signature of Supervisor

Date: 30/03/2012

Declaration

I hereby declare that the matter embodied in the report entitled “Bitumen- Organo- Clay Composites” are the results of the investigations carried out by me at the Department of Innovative Research and Development, Shell India Markets Private Limited, under the supervision of Dr. Sunil Ashtekar and the same has not been submitted elsewhere for any other degree.

Acknowledgement

I would like to express my deep appreciation to my supervisor Dr. Sunil Ashtekar for his guidance, advice, technical and moral support throughout the project work.

I want to express my gratitude for the guidance given to me by Dr. A. A. Natu through visits to Shell India Markets Private Limited in Bangalore.

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Finally, I would like to thank all my friends and my family members for giving me mental support and happiness at times.

Abstract

The physical properties and temperature susceptibility characteristics of bitumen influence pavement performance at low and high field operating temperatures. It was proven that addition of additives like polymers can influence the temperature susceptibility of asphalt cements and as a result an improvement in the performance of asphalt mixtures can be obtained in a wide temperature range. Similar to polymer nanocomposites, a number of physical properties of bitumen can successfully be enhanced when the bitumen is modified with small amount of clay on condition that the clay is dispersed at nanoscopic level. Based on the same principle as used with polymer modifications, we have carried out the modification of bitumen using organically modified and polymer compatibilized clays. Three different types of clays on the basis of polarity and one type of polymer as compatibilizer were selected for bitumen modification. The expectation with the nanoclay modified bitumen is to influence properties like rutting resistance, fatigue resistance and resistance to ageing. The main objectives of the project are to find out if the nanoclay alters the critical properties of bitumen and influences the ageing and rheology of the binder.

To meet the objectives, the first task was performed to study the clay modified bitumen at nanoscopic level and therefore microscopic and x-ray analyses were performed to study the nanoclay dispersion in bitumen. The second task was to study the influence of nanoclay modifiers on bitumen characteristics and therefore the rheological studies of fresh (un-aged) and aged bitumen samples by dynamic shear rheometer (DSR); including the empirical tests such as penetration and softening point measurements were performed.

The findings from the tests proved that nanoclay modification helped to increase rutting resistance (at 40^{O}C and 60 ^{O}C) of bitumen. The modification also helped to increase the ageing resistance of bitumen. However, the nanoclay modifications were observed to negatively influence the fatigue resistance parameter of bitumen.

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1. Introduction

1.1 Bitumen

Bitumen has many different names like binder, performance graded asphalt cement (PGAC), tar and asphalt. According to the American Association of State Highway and Transportation Officials (AASHTO) asphalt binder is defined as an "asphalt based cement that is produced from petroleum residue either with or without the addition of non-particulate organic modifiers". [1]

Bitumen is a dark-brown to black, highly viscous material obtained from the residue of processing crude oils. Chemically it's a complex mixture of aliphatic, aromatic and naphthenic hydrocarbons in combination with mono-, di- and poly- substituted heterocycles and hetero- substituted chains of varying molecular weight. Predominantly hetero atoms present are oxygen, nitrogen and sulfur.[2]

1.1.1 Constitution

Usually, bitumen constituents are categorized into four groups depending on the solubility in selected solvents: Saturates, Aromatics, Resins and Asphaltenes (SARA).[3]

Saturates: They consist of straight and branch chain aliphatic hydrocarbons together with alkyl – naphthenes and some alkyl- aromatics. Their average molecular weight is in the region of 300 to 2000. [3]

Aromatics: They comprise the lowest molecular weight naphthenic aromatic compounds and represent the major proportion of dispersion medium for asphaltenes. Their average molecular weight is in the region of 300 to 2000.[3]

Resins: These are soluble in n-heptane. They are largely composed of hydrogen and carbon and contain small amounts of oxygen, sulfur and nitrogen. Their average molecular weight is in the region of 500 to 50000.[3]

Asphaltenes: These are n-heptane insoluble black or brown amorphous solids containing, in addition to carbon and hydrogen, some nitrogen, sulfur and oxygen. The asphaltene content has a large effect on rheological characteristics of bitumen. Their average molecular weight is in the region of 1000 to 100000.[3]

1.2 Need for High Performance Bitumen

Bitumen is used in road pavements as the binder of aggregates in a great extent all around the world. Bitumen pavements must undergo heavy loads and unfavorable environmental conditions for an acceptable period of time. High temperature rutting and low temperature cracking are the most considerable limitations of unmodified and pure bitumen.

Fatigue Cracking: This distress occurs due to repeated traffic loads. As a result of this there are large numbers of relatively short cracks generated creating roughness and allowing moisture to penetrate the structure. Repairing of this type of distress is ineffective since the distress usually reappears within short periods after the repair.[1]

Rutting: This can be observed as surface depression in the wheel path. This could be due to insufficient compaction during the construction and then heavy traffic load damages it more. It can be hazardous as it pulls vehicles towards the rut path only. Repair is possible by leveling up the deeper ruts or by overlaying a new lift of asphalt concrete. However, ruts that form in lower layers of the pavement will quickly return after a single lift overlay.[1]

Ageing: Bitumen ageing is a very complex process resulting in hardening of bitumen and embrittlement, both in application and in service, which contributes greatly to the deterioration of paving applications. Because of the ageing processes, a variation of both chemical composition and colloidal structure is observed: the asphaltenes oxidation and the structuring processes of molecules and clusters are considered the principal factors responsible for such variations. The loss of volatile oily components is less important than both the previous ones. The evolution of the colloidal structure has a very large effect on viscoelastic properties of bitumen.[4]

Therefore, modification and reinforcement of bitumen is necessary so that problems like rutting, fatigue cracking and ageing can be taken care of.

1.3 Introduction to clays:

Clays are natural materials (montmorrilonites, kaolinite, hydrotalcites), which have a sheet-like (layered) structure and can be organically modified into organo clays. The clay modification is generally achieved through an ion exchange process, replacing the natural CO3-2/OH- ions by organophilic ions which are present between the clay layers.[5] In our study we have used hydrotalcite clays which are commonly represented by the formula

$$[M^{2+}{}_{1-x}M^{3+}{}_{x}\,(OH)_2]^{q+}(X^{n-})_{q/n}\cdot yH_2O$$

Most commonly, z = 2, and $M^{2+} = Ca^{2+}, Mg^{2+}, Mn^{2+}$ and $M^{3+} = Al^{3+}$. In this case q = 2x – 1, X represents a generic anion and the value of y is normally found to be between 0.5 – 4 & x =0.1 ≤ x ≤ 0.5.

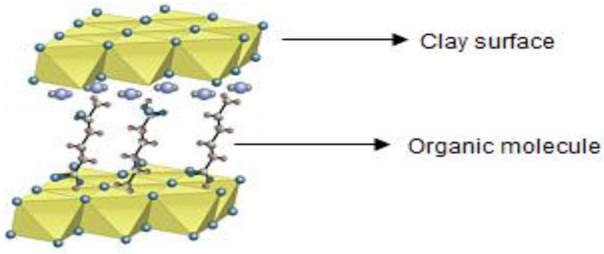

Figure 1.3.a. A representation of organically modified clay

Clay discs are positively charged, but stay together in a clay particle because of the negative ions between the clay discs. In this way the clay particle as a whole is neutral. In addition, unmodified hydrotalcite clays are generally highly hydrophilic species and therefore naturally incompatible with bitumen. To improve the interaction between clay and bitumen, clay can also be compatibilized with a polymer. A necessary prerequisite for successful formation of polymer-clay nanocomposite is therefore to alter the clay polarity by making the clay ‘organophilic’. To achieve a fine dispersion of clay, mechanical forces alone are not enough; there should be a thermodynamic driving force as well to separate the layers into individual sheets. This thermodynamic driving force is introduced by inserting a certain coating of surfactants or some selective ions on each individual layer. These molecules increase the inter-layer distance, improve the compatibility with the polymer and can give an increase in entropy because they can mix with the polymer. To enable each layer to be coated with the ion, the layers should be accessible for the ion from the solution, and for this reason the clay layers need to swell or exfoliate in the solvent. For example smectite clay, such as montmorillonite, is negatively charged and swells in water, and can therefore be coated with a cationic surfactant in an aqueous suspension. The ion provides a hydrophobic nature to the silicate surface, which causes the layers to precipitate as organophilic clay, also known as organoclay.[6]

The mixing of a few percentage of nanoclay in bitumen may lead to an improvement in its properties such as mechanical strength, durability and thermal stability. However, if the clay platelets are not well dispersed within bitumen medium then the expected improvements may not be realized.

The correct selection of modified clay is essential to ensure effective penetration of the polymer and then bitumen into the interlayer spacing of the clay resulting in the desired exfoliated or intercalated composite. In intercalate structure, the organic component is inserted between the layers of the clay such that the interlayer spacing is expanded, but the layers still bear a well-defined spatial relationship to each other. In an exfoliated structure (Figure 2), the layers of the clay have been completely separated and the individual layers are distributed throughout the organic matrix [7].

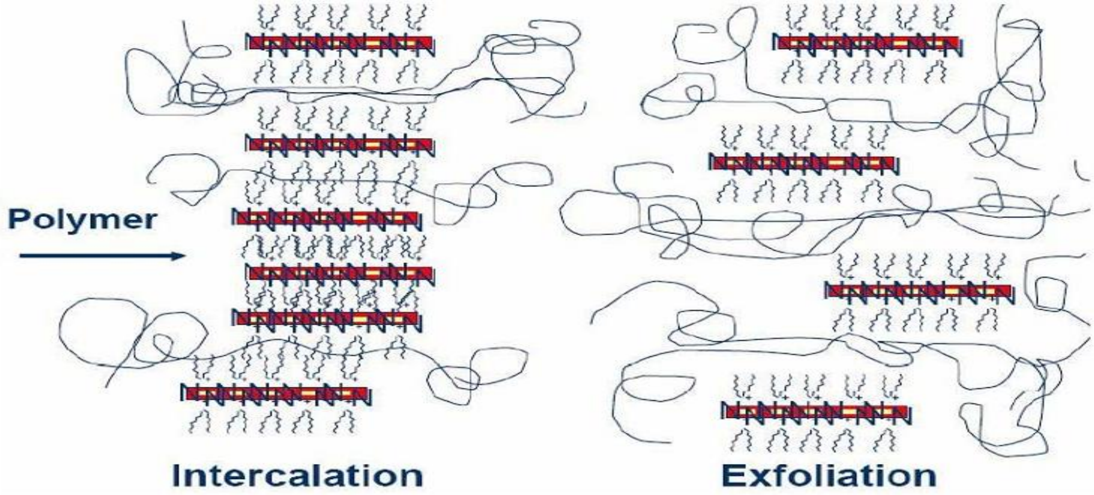

Figure 1.3.b .Intercalated and exfoliated nanocomposite

1.4 Scope of Study

In the current study we have investigated the characteristics of nanoclay modifiers and the rheological properties of modified bitumen in comparison to standard and fresh bitumen. In the study we have used 3 different types of hydrotalcite clays as modifiers using one type of bitumen (VG10, having a pen grade of 80/100). The proportions of the nanoclay modifiers considered in the study work are 1%, 2% and 5 wt% in relation to the binder. In addition, the clays are compatibilized with a natural rubber polymer where necessary to have a better interaction with the bitumen.

2. METHODS

2.1. Experimental Section

2.1.1 Materials Used

In all the experiments only one type of bitumen (VG10, having a pen grade of 80/100) is used .Three different types of hydrotalcite clays based on the type of anion (organic component) are used in this study:

a) Carbonate ion (CO_3)
b) 3-amino benzene sulfonate ion (3-ABS)
c) Do-decyl benzene sulfonate ion (DDBS)

A commercial grade of epoxidized natural rubber (ENR) is used as a compatibilizer between clay particles and bitumen. ENR can be prepared by performic epoxidation of natural rubber which converts 50% of double bonds in natural rubber to epoxides[8].

ENR was chosen as a compatibilizer since it is expected to interact well with the anion present in the clay because of the presence of a highly strained epoxide ring. Toluene was used as a solvent medium to dissolve ENR. Styrene butadiene styrene (SBS) was used to make the benchmark sample VG10 + SBS.

2.1.2 Drying of clays

All clays were dried at 100 ^{O}C under vacuum oven for 6 hours prior to its use. The drying was done to reduce the amount of water molecules trapped in between the clay layers so that clay can have better interaction with bitumen.

2.1.3 Solution mixing

ENR was first dissolved in toluene. The ratio of ENR to solvent was 1:10, weight by volume[9]. The solution was mixed using a high shear IKA mixer at 3000 rpm for 2 hours at room temperature. Subsequently 100 phr (10, 4 & 2 grams for 5%, 2% and 1% respectively) of nanoclay with respect to ENR was mixed to the solution and the mixing was continued for 1 more hour at 3000 rpm and room temperature. The resultant solution was then cast over in a thoroughly cleaned plane glass plate. The sample was kept in the same condition until the solvent evaporated completely. The obtained film was transparent which confirms that the dispersion of clays in ENR is good.

Figure 2.1.3: Image of a transparent film (after evaporation of toluene) of, a) ENR mixed with DDBS clay, b) ENR mixed with 3-ABS clay, c) ENR mixed with CO_3 clay.

The film was prepared just to confirm that if the clay is well dispersed in the ENR solution and is not used for any sample preparation afterwards.

2.1.4 Preparation of modified bitumen

The modified bitumen samples were prepared at 150 °C. First, 200 g bitumen was heated in an SS container in order to turn into fluid; then the measured amounts (1, 2, 5 weight %) of clays and compatibilized clays (clays mixed with ENR in 1:1 ratio) were gradually added into 200 gm of the base bitumen. The mixtures were blended at 3000 rpm rotational speed for about 2 h using a Silverson-L5M high shear mixer[10].

Preparation of benchmarked sample VG10 + SBS was done at 180 ^{0}C. Measured amounts of SBS (1, 2, 5 weight % w.r.t. bitumen) were gradually mixed with 200 g preheated bitumen and blended at 3000 rpm for 1 hour using a Silverson-L5M high shear mixer.

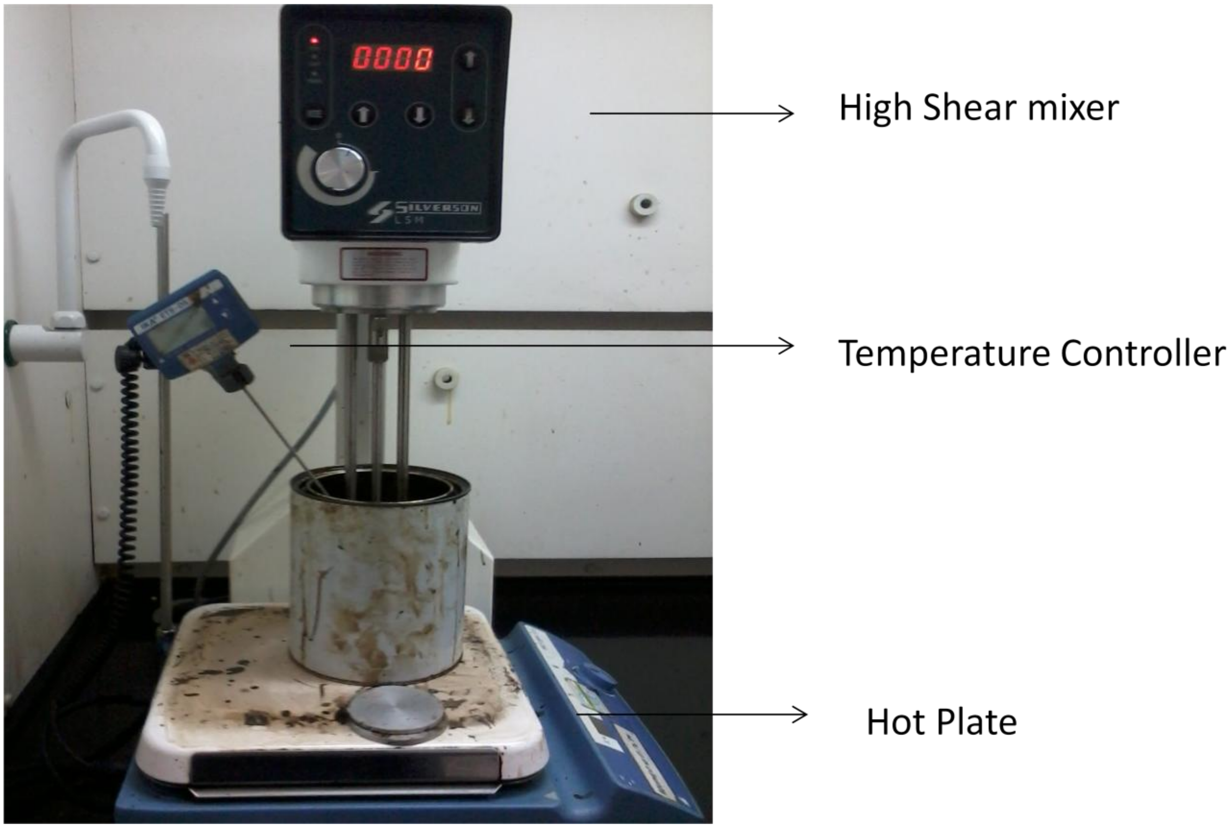

Figure2.1.4. Experimental setup for preparation of modified bitumen

Sample Name	Clay Amount(gm)			Polymer(ENR/SBS) amount(gm)		
	5%	2 %	1%	5%	2 %	1 %
VG10 + ENR	-	-	-	10	4	2
VG10 + Carbonate	10	4	2	-	-	-
VG10 +Carbonate + ENR	10	4	2	10	4	2
VG10+ DDBS + ENR	10	4	2	10	4	2
VG10 + DDBS	10	4	2	-	-	-
VG10 + 3-ABS + ENR	10	4	2	10	4	2
VG10 + 3-ABS	10	4	2	-	-	-
VG10 + SBS	-	-	-	10	4	2

Table 2.1: Concentrations of clays and polymers used for making nanocomposites of VG10 grade bitumen.

2.2 Testing Methods

2.2.1 Penetration Test

The consistency of a penetration grade or oxidized bitumen measured by the penetration test[11, 12] .In this test, a needle of specified dimensions is allowed to penetrate a sample of bitumen, under a known load (100 g), at a fixed temperature (25 ^{O}C), for a known time (5s) [3].The test apparatus is shown in figure 2.2.1.

The penetration is defined as the distance travelled by the needle into the bitumen. It is measured in tens of millimeter (decimillimetre, dmm). Lower the value of penetration, harder the bitumen. Conversely, higher the value of penetration, softer is the bitumen. For penetration less than 30 dmm, the bitumen is said to be hard. Penetration values higher than 100 dmm correspond to soft bitumen [13].

For each test, three individual measurements of penetration are made. The average of the three values is recorded. The recorded penetration is reported if the difference between the individual three measurements does not exceed a specified limit.

The acceptable repeatability values given in BS 1426: 2000[12] for penetration test are.

- If the penetration is <50 2 dmm
- If the penetration is ≥50 4% of the mean of the results

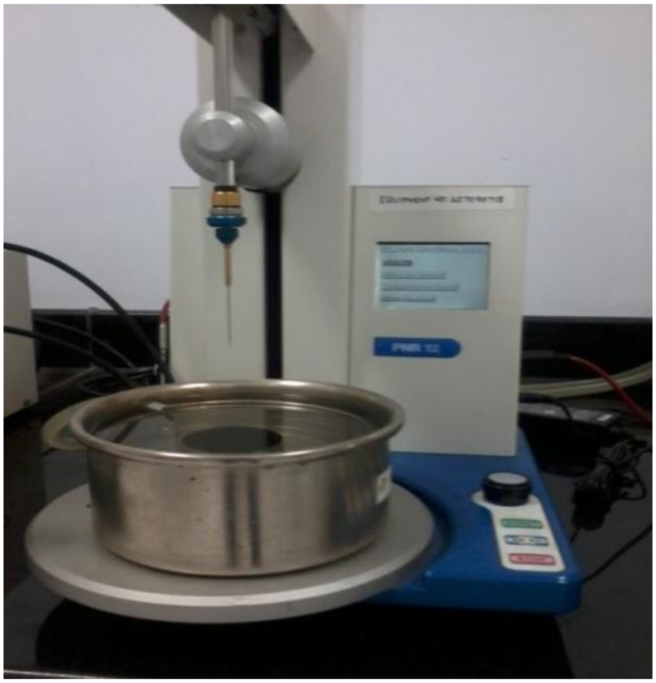

Figure 2.2.1: Petrotest PNR-12 Penetrometer

2.2.2 Retained penetration

When bitumen gets aged it increases its hardness and the retained penetration value helps checking the increase in hardness in relation to the previous value obtained on unaged material. It is computed as:

Retained penetration (%) = (aged penetration/ unaged penetration) x 100

A lower retained penetration value means that the material is more susceptible to ageing.[6]

2.2.3 Softening Point Test

The consistency of a penetration grade or oxidized bitumen can also be measured by determining its softening point[14, 15]. In this test, a steel ball (weight 3.5 g) is placed on a sample of bitumen contained in a brass ring that is then suspended in a water or glycerine bath. The apparatus is shown in figure 2.2.3.

Water is used for bitumen with a softening point of 80 ^{O}C or below and glycerine is used for softening points greater than 80 ^{O}C. In our case a water bath is used as all of our samples were supposed to have softening point below 80^{O}C. The bath temperature is raised at 5 ^{O}C per minute, the bitumen softens and eventually deforms slowly with the ball through the ring. At the moment the bitumen and the steel ball touch a base plate 25mm below the ring the temperature of the water is recorded. The test is performed twice and the mean of two measured temperature is reported. If the difference between the two results exceeds 1 ^{O}C, the test must be repeated. The reported temperature is designated softening point of bitumen.[3]

The acceptable repeatability limits given in BS EN 1427:2000[14] for the softening point test are :

- For unmodified bitumens in water: 1.0^{O}C
- For modified bitumens in water: 1.5^{O}C

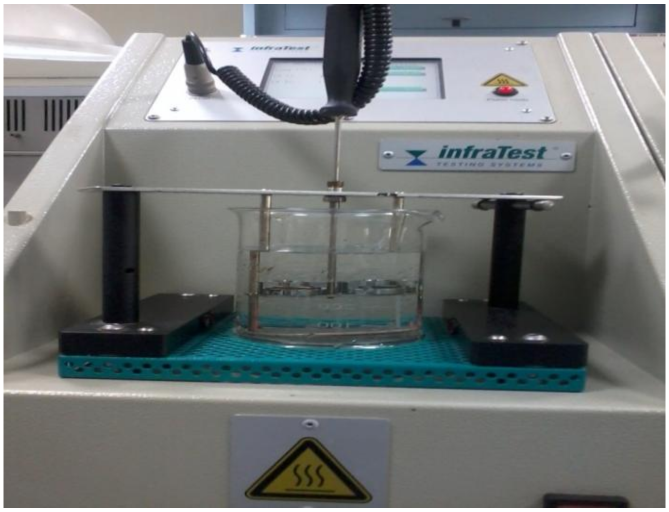

Figure 2.2.3: Infratest 20-2200 Ring and Ball apparatus

2.2.4 Increment in softening point:

Similar to retained penetration value the increment in softening point can be a help in checking susceptibility of the material to ageing. It is computed as:

Increment in softening point (^{O}C) = aged softening point (^{O}C) - unaged softening point

A smaller increment in softening point means the material is less susceptible to ageing.[6, 16]

2.2.5 Rolling Thin-Film Oven Test (RTFOT) (ASTM D2872)

The rolling thin-film oven test[17] is an ageing test and measures hardening by both oxidation and evaporation. The apparatus for this test is shown in figure 2.2.5. In this test, a thin film of bitumen is continuously rotated around the inner surface of a glass jar at 163 ^{O}C for 90 minutes, with an injection of hot air into the jar every 3 to 4 seconds. The amount of bitumen hardening during the test, i.e. drop in penetration, increase in softening point correlates well with that observed during manufacture of an asphalt.

Figure 2.2.5: Koehler K88001P RTFOT instrument

2.2.6 Dynamic Shear Rheometry (DSR)

This type of test applies an oscillatory shear force to a bitumen sample sandwiched between two parallel plates. The typical arrangement of DSR is of a fixed lower plate and an oscillating upper plate through which the shear force is applied to the specimen as shown in figure 2.2.6. The centre line of the upper plate described by point A in figure 2.2.6, moves to point B then passes through its original position to point C and then returns to point A, representing one cycle. This movement is then repeated continuously throughout the duration of the test. The most common DSR test is strain controlled.

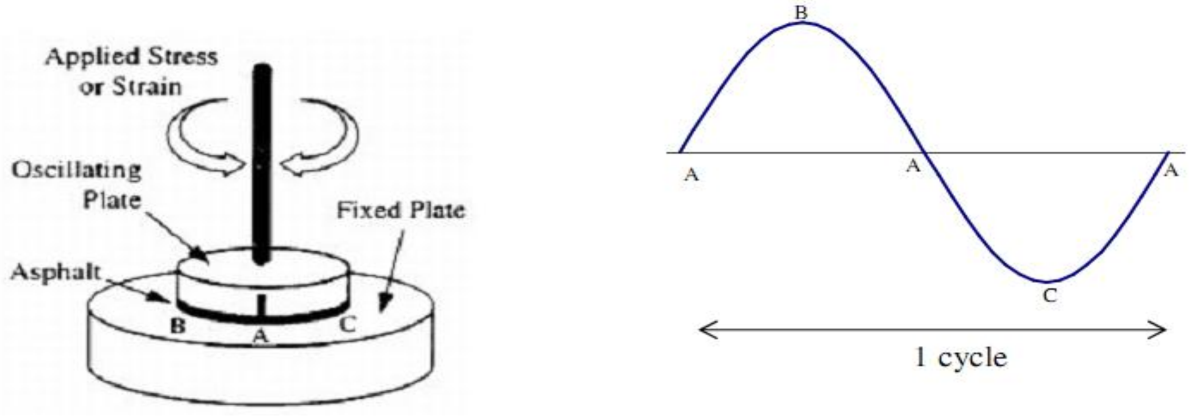

Figure 2.2.6 a: Dynamic Shear Rheometer

The DSR can be used to characterize both viscous and elastic behavior of bitumen by measuring the complex shear modulus G* , and the phase angle , δ, from a single test run at a given temperature, loading frequency, and strain magnitude as defined by the binder film thickness and the rotation amplitude.

Dynamic complex shear modulus, G*

The dynamic complex shear modulus G* is a measure of the total resistance of the binder to deformation when repeatedly sheared. For visco-elastic materials like bitumen, the complex shear modulus is composed of a loss modulus (viscous component, G") and a storage modulus (elastic component, G'), the relative magnitude of which dictates how the material responds to applied loads. Materials with higher storage moduli have greater ability to recover from deformation, and materials with higher loss moduli have greater ability to resist deformation at any prescribed frequency. The relationship between the two components is shown graphically in figure 2.2.6 b.

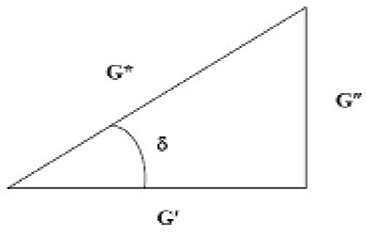

Figure 2.2.6 b. Relationship between G*, G’, G” and δ

2.2.7 TGA Analysis of clays

TGA analysis of all clays(calcined and uncalcined) was done at a heating rate 10 ^{O}C per minute under nitrogen environment and a flow rate of 120 ml per minute over a range of temperature starting from 25 ^{O}C up to 700 ^{O}C using TGA Q5000, TA instruments.

2.2.8 Powder XRD

Wide angle X-ray diffraction (WAXD) of the clays and modified bitumens was performed using X’pert Pro PANalytical 7602EA ALMELO, Cu K radiation (λ = 0.154 nm). The scanned range was from 2° to 30° in the 2θ with a scanning rate of 1.2°min^{-1}.

3. Results and discussions

3.1 TGA Results

All the clay samples were calcined at 450 ^{O}C in muffle furnace for 5 hours and then kept at dwelling for 48 hours and then TGA of calcined and uncalcined samples was performed using procedure mentioned above.

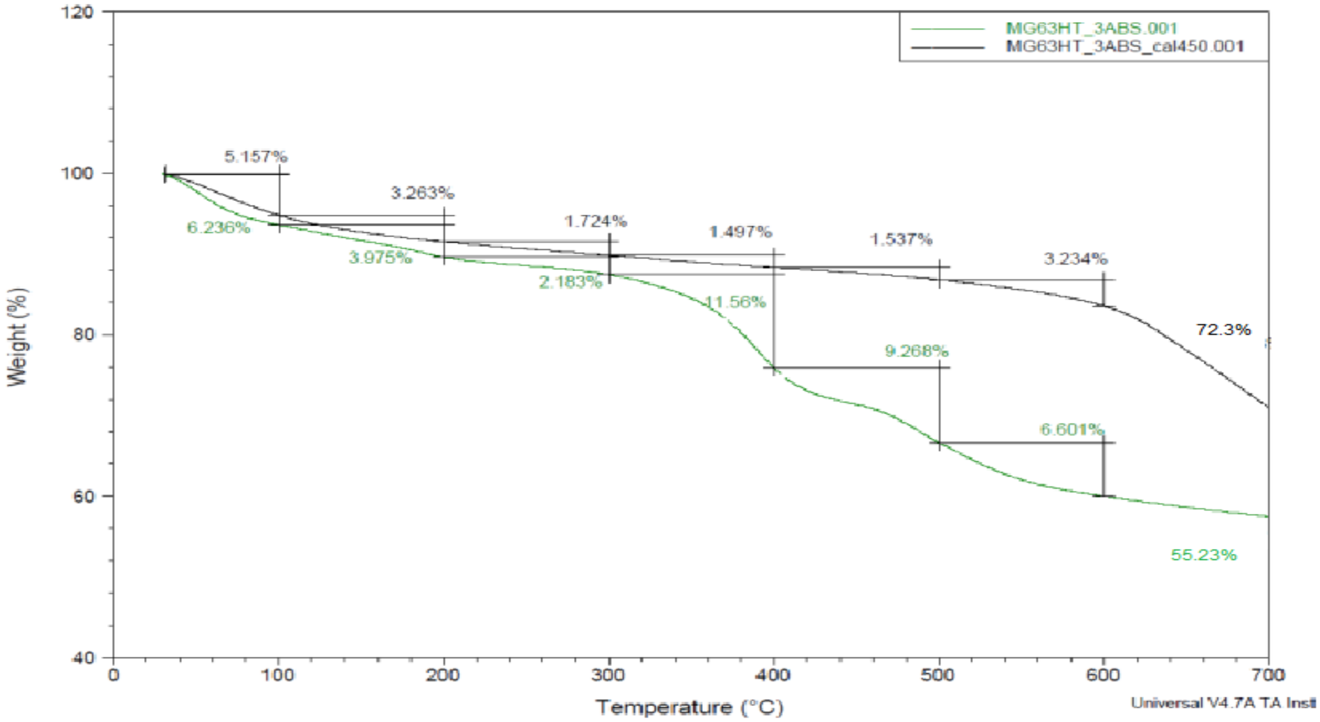

Figure 3.1: TGA Profile of Calcined and Uncalcined 3-ABS clay

Temperature (^{0}C)	Weight loss(3-ABS) (%)	
	Uncalcined	Calcined
25-100	6.2	5.2
100-200	3.9	3.3
200-300	2.2	1.7
300-400	11.6	1.5
400-500	9.3	1.5
500-600	6.6	3.2
0-700	44.8	27.7

Table 3.1 Weight loss values of calcined and uncalcined 3-ABS clay

For uncalcined clay weight loss up to 200 ^{0}C is due to removal of interlayer water molecules. The weight loss between 300 and 400 ^{o}C is due to degradation of 3-ABS anion. The weight loss between 400 and 500 ^{0}C is due to the removal of water molecules through dehydroxylation process.

For calcined clay the weight loss from 25 ^{0}C to 200 ^{0}C is due to the removal of water molecules.

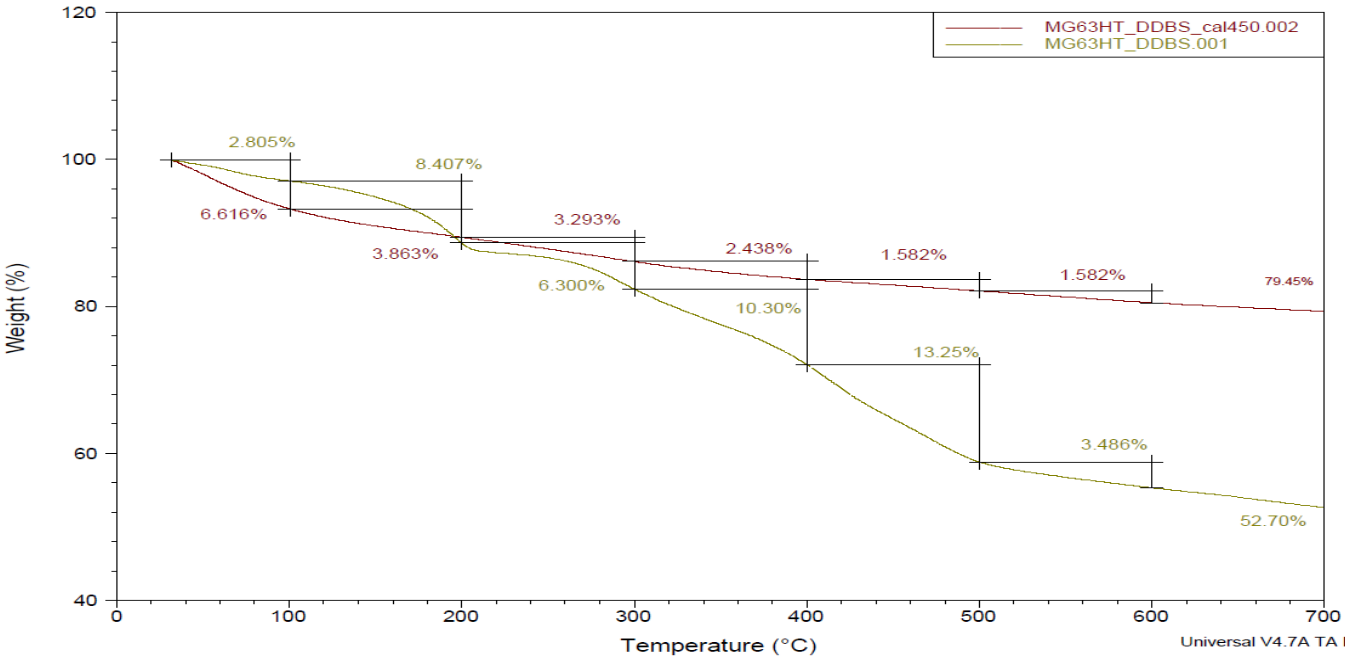

Figure 3.2: TGA Profile of Calcined and Uncalcined DDBS Clay

Temperature (^{0}C)	Weight loss(DDBS) (%)	
	Uncalcined	Calcined
25-100	2.8	6.6
100-200	8.4	3.9
200-300	6.3	3.3
300-400	10.3	2.4
400-500	13.3	1.6
500-600	3.5	1.6
0-700	47.3	20.6

Table 3.2 weight loss values of calcined and uncalcined DDBS clay

For uncalcined clay weight loss up to 200 ^{0}C is due to removal of interlayer water molecules. Weight loss between 200 and 300 ^{0}C is due to degradation of DDBS anions. Weight loss from 300 to 500 ^{0}C is due to removal of water molecules through dehydroxylation process.

For calcined clay weight loss from 25 ^{0}C to 200 ^{0}C is due to removal of water molecules.

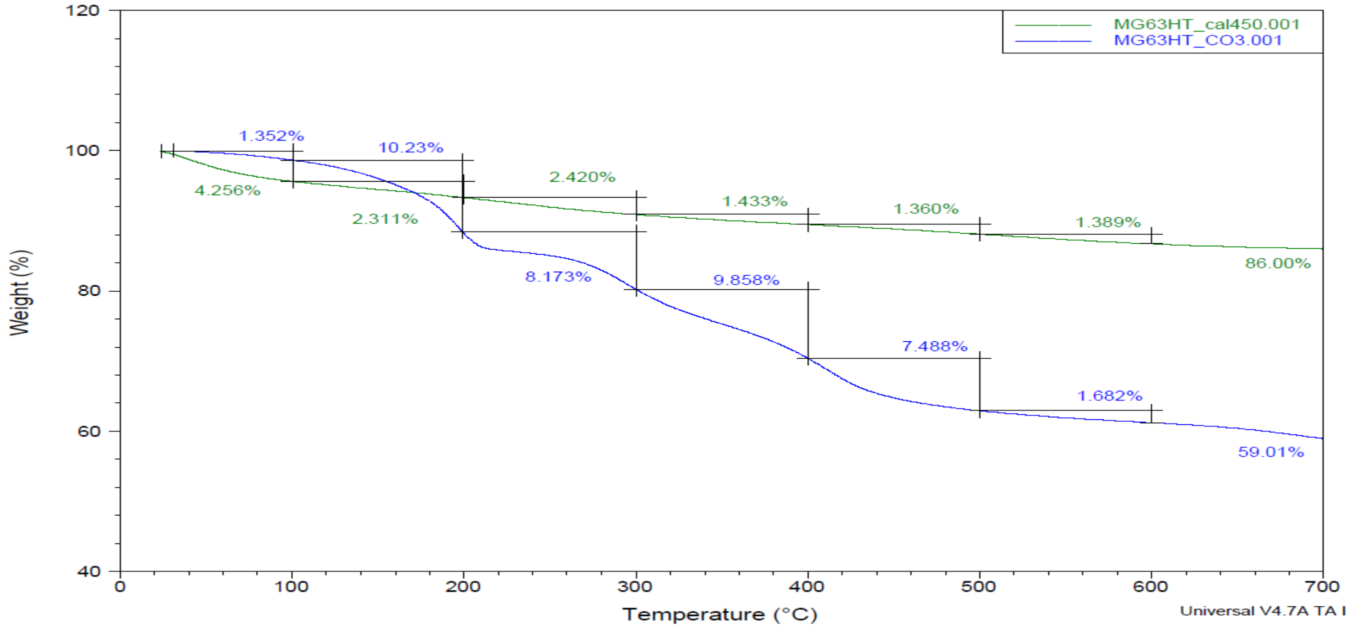

Figure 3.3 TGA Profile of Calcined and Uncalcined Carbonate Clay

Temperature (^{0}C)	Weight loss(CO_3) (%)	
	Uncalcined	Calcined
25-100	1.4	4.3
100-200	10.2	2.3
200-300	8.2	2.4
300-400	9.9	1.4
400-500	7.5	1.4
500-600	1.7	1.4
0-700	41	14

Table 3.3: weight loss values of calcined and uncalcined carbonate clay

For uncalcined clay weight up to 200 ^{0}C is due to removal of interlayer water molecules. Weight loss from 200 to 400 is due to removal of water molecules through dehydroxylation process. And last step that is from 400 to 500^{0}C onwards is degradation of carbonate interlayer anions.

For calcined clay weight loss from 25 ^{0}C to 100 ^{0}C is due to removal of water molecules.

3.2 X ray Diffraction results

XRD patterns were recorded for clays before and after mixing with bitumen and ENR. We expect that if there is any exfoliation or intercalation of the clay occurring in bitumen medium, this should increase in the d spacing and hence the crystalline XRD peaks available in clay spectrum should shift towards left i. e. their 2θ value should decrease (Bragg's law). But in some cases crystalline peaks can also disappear which means that the layered platelet structure is exfoliated or expanded beyond the XRD detection limit[18]. However, this needs further investigation using other microscopic techniques to confirm this.

All samples for X-ray diffraction measurements were prepared at 5 % loading of clays and 5 % loading of ENR.

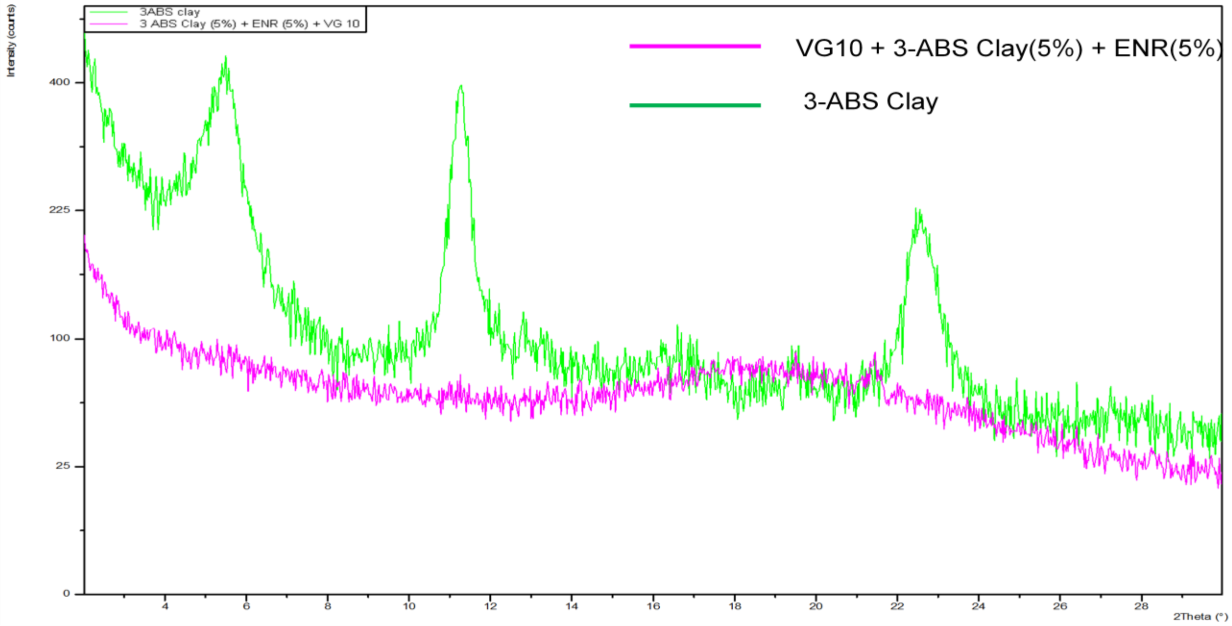

Figure 3.4 XRD of 3-ABS clay compared with 3-ABS+ VG10 +ENR nanocomposite

As the crystalline peaks observed in as-used clay (figure 3.4) are no longer visible in the nanocomposite, suggests that the layers of 3-ABS clay have been delaminated and the nanocomposite may form a exfoliated clay structure. However, this needs to be further investigated and evidence to be obtained using techniques such as AFM or TEM.

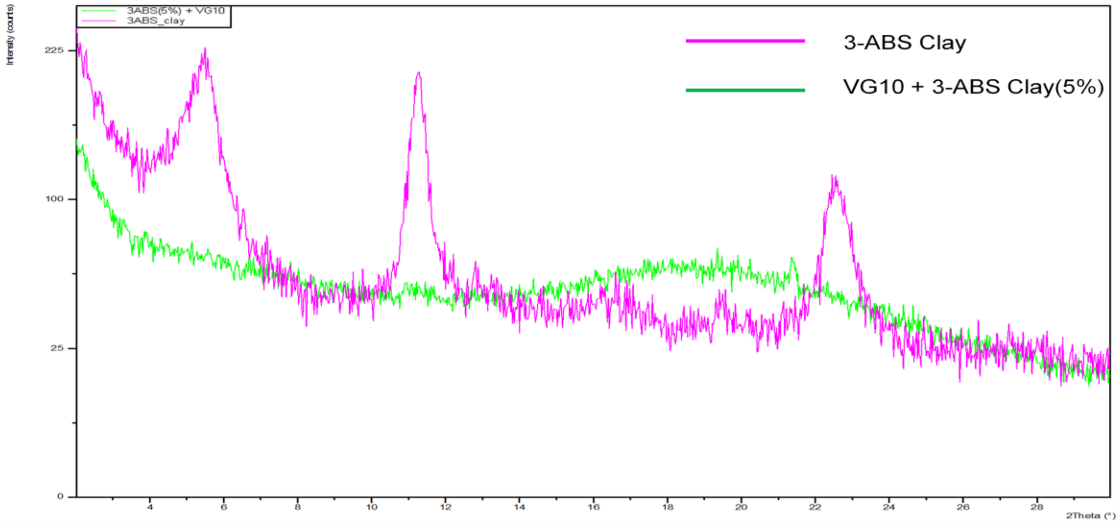

Figure 3.5 XRD of 3-ABS clay compared with 3-ABS+ VG10 nanocomposite

As crystalline peaks observed in clay (figure 3.5) are no longer visible in nanocomposite this may suggest that the layer of 3-ABS clay has been delaminated and the nanocomposite may form a exfoliated structure.

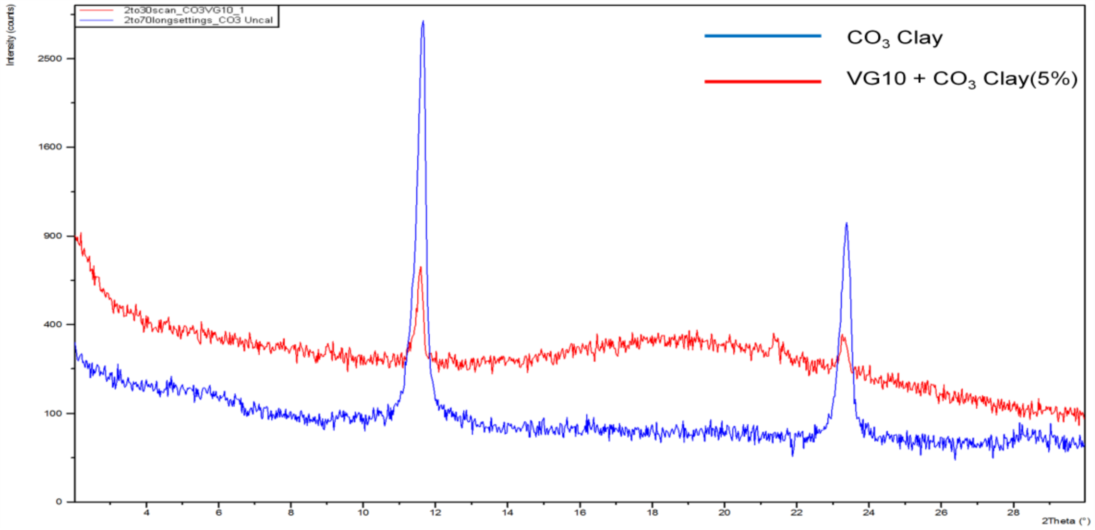

Figure 3.6 XRD of carbonate clay compared with carbonate clay+ VG10 nanocomposite

As crystalline peaks observed in clay (figure 3.6) are still present in nanocomposite and there is no shift of peaks this may suggest that there has been no exfoliation of clay.

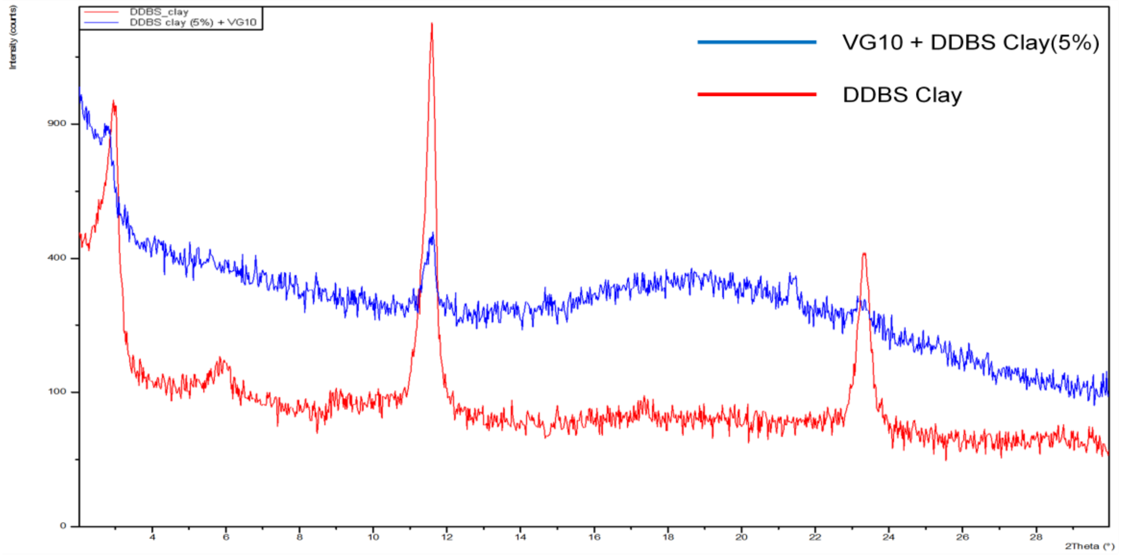

Figure 3.7 XRD of DDBS clay compared with DDBS clay+ VG10 nanocomposite

As crystalline peaks observed in clay (figure 3.7) are still present in nanocomposite and there is no shift of peaks this may suggest that there has been no exfoliation of clay.

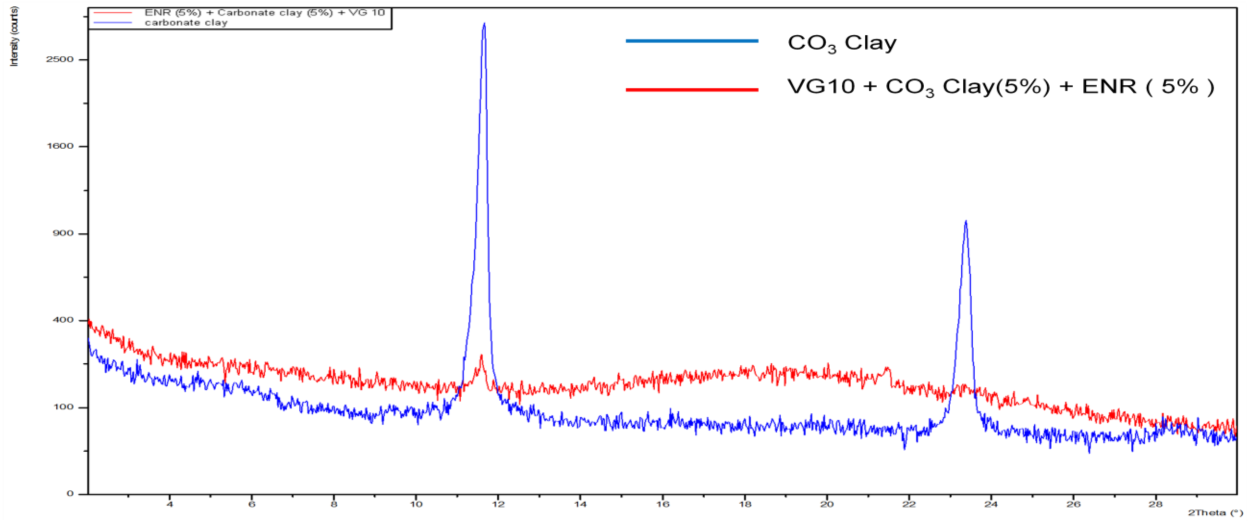

Figure 3.8 XRD of carbonate clay compared with CO_3 clay +VG10+ENR nanocomposite

As one of the crystalline peaks observed in clay (figure 3.8) is still visible in nanocomposite this may suggest that clay might not be exfoliated.

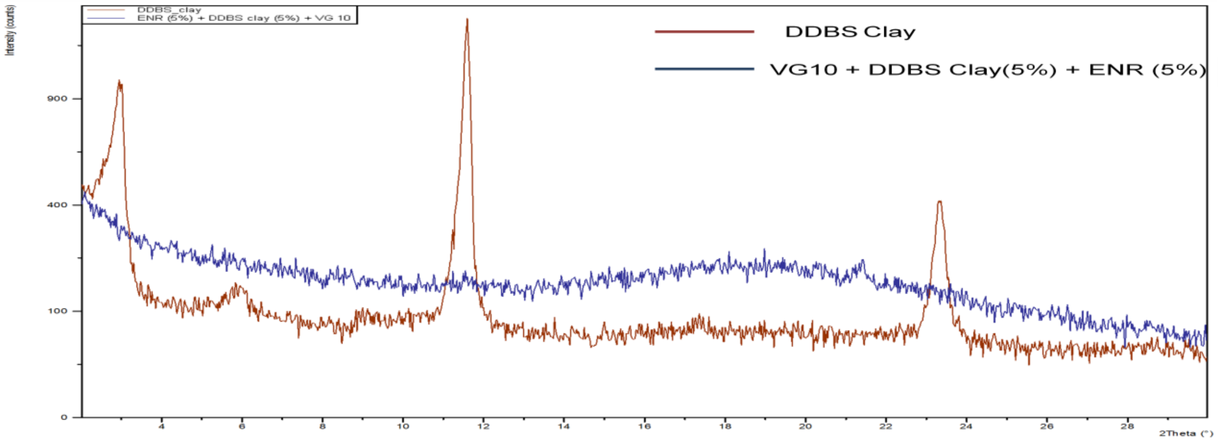

Figure 3.9 XRD of DDBS clay compared with DDBS+ VG10+ ENR nanocomposite

As crystalline peaks observed in clay (figure 3.9) are no longer visible in nanocomposite this may suggest that the layer of DDBS clay has been delaminated and the nanocomposite may form an exfoliated structure.

3.3 Penetration and softening point values

Sample Name	Penetration(dmm)			Softening Point(°C)		
VG 10	69			48		
	5%	2%	1%	5%	2%	1%
ENR + VG10	55.3	51	65.3	52.1	53.5	49.5
VG10 + CO_3	76.3	65.7	-	50	50.7	-
ENR + VG10 + CO_3	39.7	46	42.7	56.5	52.6	54.8
ENR +VG10+ DDBS	41.6	49.3	-	55.0	51.8	-
VG10 + DDBS	72.7	-	-	49.6	-	-
ENR + VG10 + 3-ABS	50	-	-	55.4	-	-
VG10 + 3-ABS	74.7	-	-	48.8	-	-
VG10 + SBS	50	51	65	59.5	52.9	49.5

Table 3.4: Penetration and softening point values

From above table these conclusions can be made:

1. On addition of ENR (5%) penetration value is reduced by 14 and softening point is increased by 5.5 units. This means that addition of ENR alone also affects penetration and softening point of bitumen.
2. Addition of uncompatibilized clays to bitumen does not have much influence on penetration and softening point values.
3. Addition of compatibilized clay reduces penetration of bitumen by significant amount (up to 30 units in case of ENR + VG10 +Carbonate(5%) and ENR +VG10+ DDBS(5%)) i. e. makes them harder and increases softening point of all three samples prepared using compatibilized clays by approximately 8 units.
4. Reduction in penetration values of nanocomposites (VG10 + ENR + Clay) is more than reduction in penetration values of our benchmark sample which is VG10 + SBS but increment in softening point is less than the benchmark.
5. At lower loading (2%) reduction in penetration is still considerable but is comparable to the benchmark (VG10 + SBS) but increment in softening point values of nanocomposites is not considerable at 2% loading.
6. At 1% loading ENR + VG10 +Carbonate sample surprisingly shows more reduction and more increment in softening point than benchmark and VG10 + ENR both samples.

3.4 Retained penetration and increment in softening point (ΔS)

Fresh modified and unmodified bitumen samples were aged using RTFOT test at 163 ^{O}C for 90 minutes and then penetration and softening point tests were performed on those aged samples. Retained penetration and increment in softening point values were obtained using pen and softening point data of fresh and aged bitumen samples.

Sample Name	Penetration Value (dmm)		Retained Penetration	Softening Point(^{0}C)		ΔS(Increment in softening point ^{0}C)
	Aged	Fresh		Aged	Fresh	
VG 10	51	69	73.9	53.6	48	5.6
ENR + VG10	32	51	62.7	56.5	53.6	2.9
VG10 + CO_3	43	65.7	65.5	53.6	50.7	2.8
ENR + VG10 + CO_3	36	46	78.3	56.2	52.6	3.6
ENR +VG10+ DDBS	37	49.3	75	56	51.8	4.2

Table 3.5 Retained penetration and increment in softening point (ΔS) values

As we know that higher retained penetration values show that the sample is less susceptible to ageing so sample ENR + VG10 +Carbonate is least susceptible to ageing and also lower ΔS values also suggest that a sample is less susceptible to ageing so ENR + VG10 and VG10 + Carbonate are least susceptible to ageing in terms of softening point.

3.5 Dynamic Shear Rheometer Results

3.5.1 Frequency sweep DSR test results

A typical frequency sweep gives values of complex modulus G* over a selected range of frequency. In our case a frequency range of 0.01 Hz to 100 Hz was selected.

3.5.2 Rutting and fatigue resistance parameter

In the viscoelastic region, the complex shear modulus (G*) and phase angle (δ) are indicators of the bitumen resistance to shear deformation that can predict the potential of rutting and fatigue resistance of hot asphalt mixture. At high temperatures(40^{O}C and 60^{O}C), the complex shear modulus and phase angle are proven indicators of the rutting susceptibility of the pavement measured by rutting parameter (G*/sinδ), similarly at medium temperatures(25^{O}C) they may be used to predict fatigue cracking measured by fatigue resistance parameter (G*sinδ)[16].

Lower frequency of oscillations in DSR means lower traffic loading time or slower moving vehicles and higher frequency of oscillations mans higher traffic loading time or faster moving vehicles[19].

We have made graphs of fatigue resistance parameter over a frequency range of 0.01Hz to 100Hz (at 25 ^{O}C) and rutting parameter over a frequency range of 0.01Hz to 100Hz (at 40 ^{O}C and 60 ^{O}C) to see how fatigue resistance parameter and rutting parameter change with respect to fast moving and slow moving vehicle.

3.5.3 Fatigue Resistance Parameter vs Frequency Results

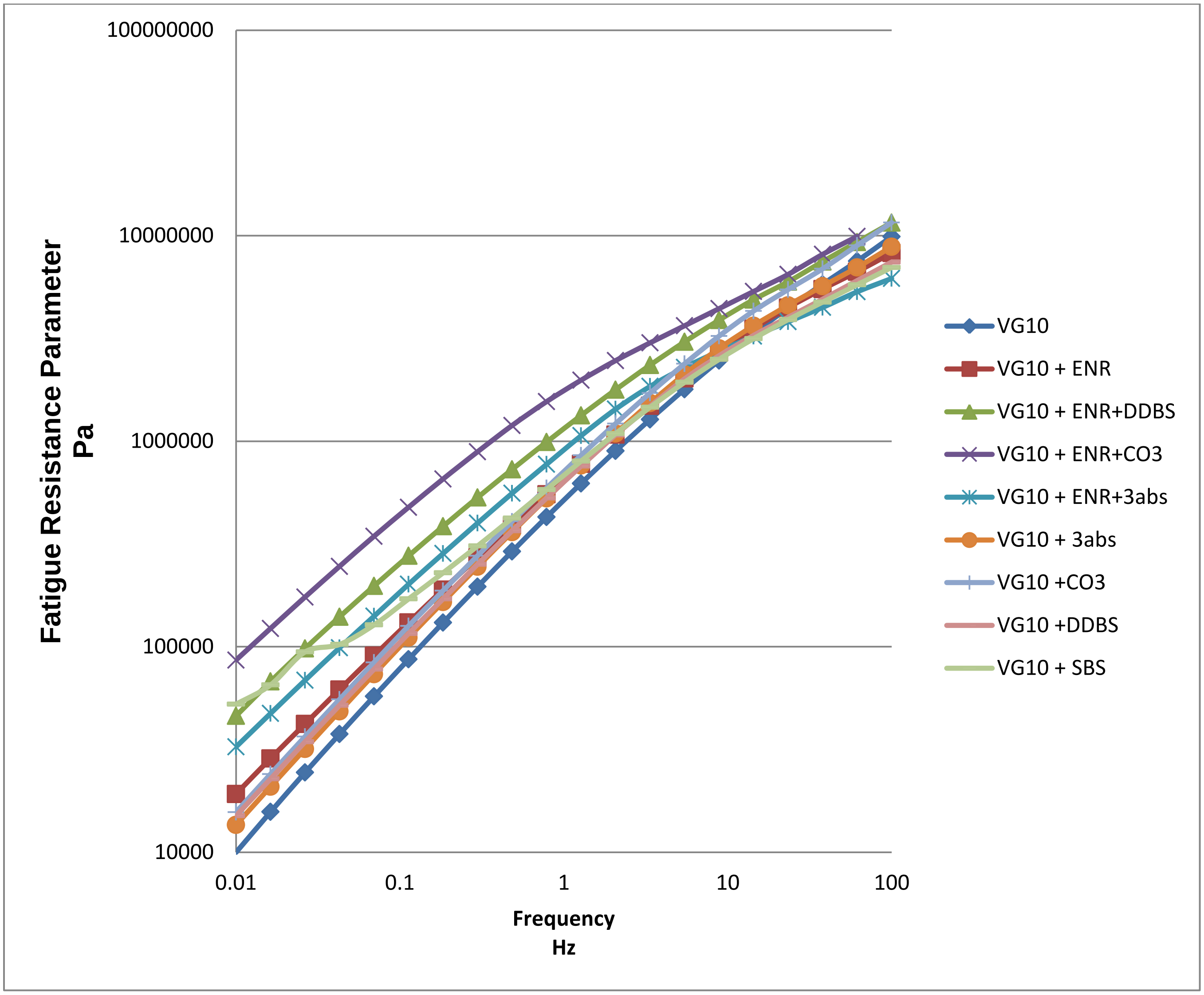

Figure 3.5.1 Fatigue Resistance Parameter vs Frequency at 25 ^{O}C & 5 % loading

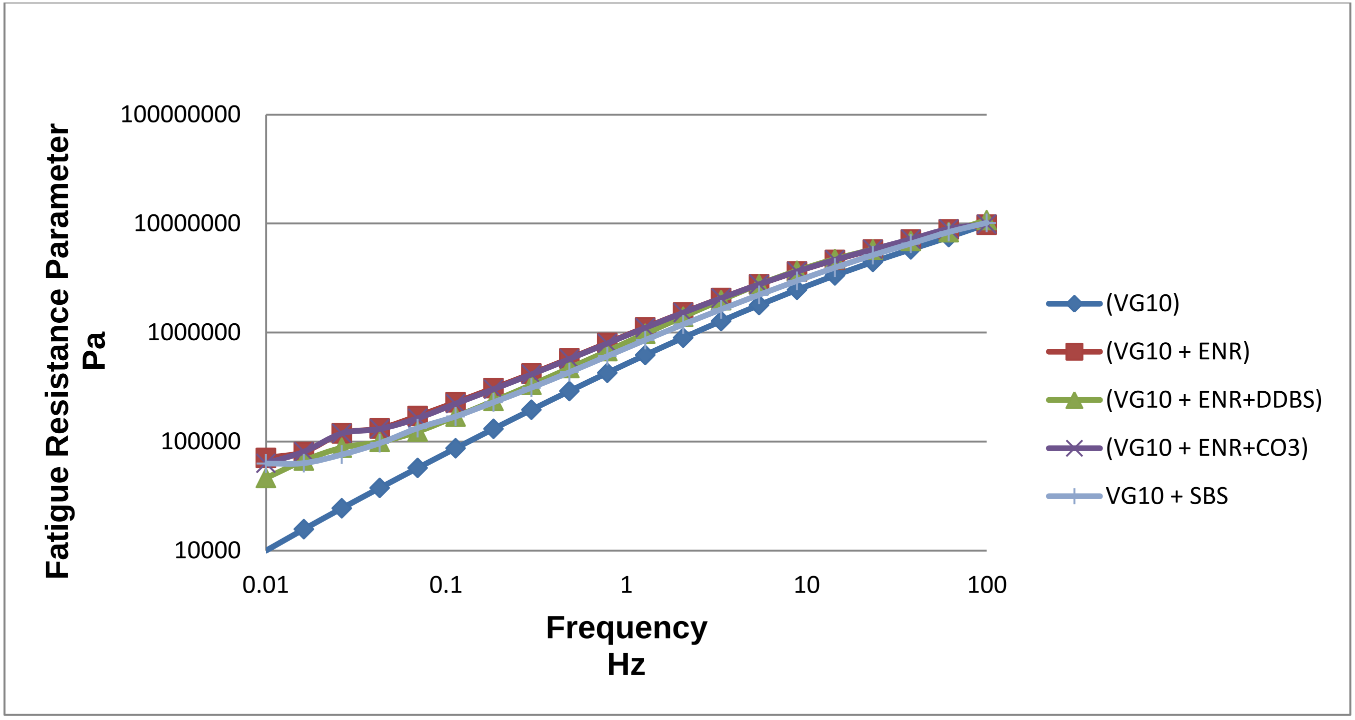

Figure 3.5.2 Fatigue Resistance Parameter vs Frequency at 25 ^{O}C & 2 % loading

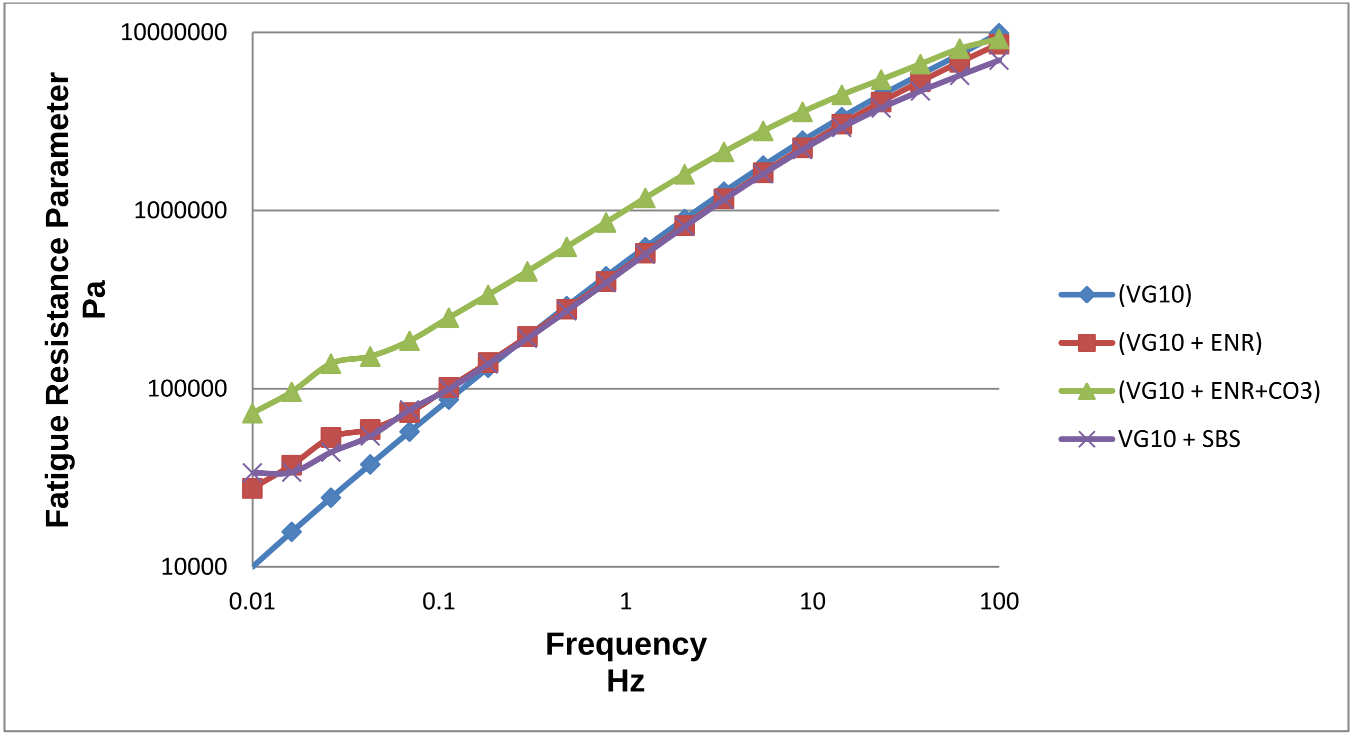

Figure 3.5.3 Fatigue resistance Parameter vs Frequency at 25 ^{O}C & 1 % loading

Analysis in Figure 3.5.1 shows that, there is significant increment in fatigue resistance parameter (G*Sinδ) of VG10 + ENR + CO_3 (carbonate clay) sample (at 5% loading) compared to unmodified bitumen, VG10 + ENR and benchmarked sample VG10 + SBS at higher frequencies but at lower frequencies the increment is very small. . These differences decree in 2% modification in all conditions (Figure 3.5.2) and VG10 + ENR + CO3 (carbonate clay) sample shows almost same fatigue resistance parameter over all range of frequencies .At 1 % loading (Figure 3.5.3)VG10 + ENR + CO_3 sample again shows significant increments at frequencies lower than 10 Hz as compared to pure VG10, VG10 + SBS and VG10 + ENR but the increment reduces at higher frequencies Thus, the analysis shows that addition of carbonate clay and ENR reduces the fatigue life of bitumen at 25 ^{O}C. although the reduction in fatigue is bigger when the amount of carbonate clay and ENR is higher in the bitumen.

3.5.4 Rutting resistance vs frequency results at 40^{O}C

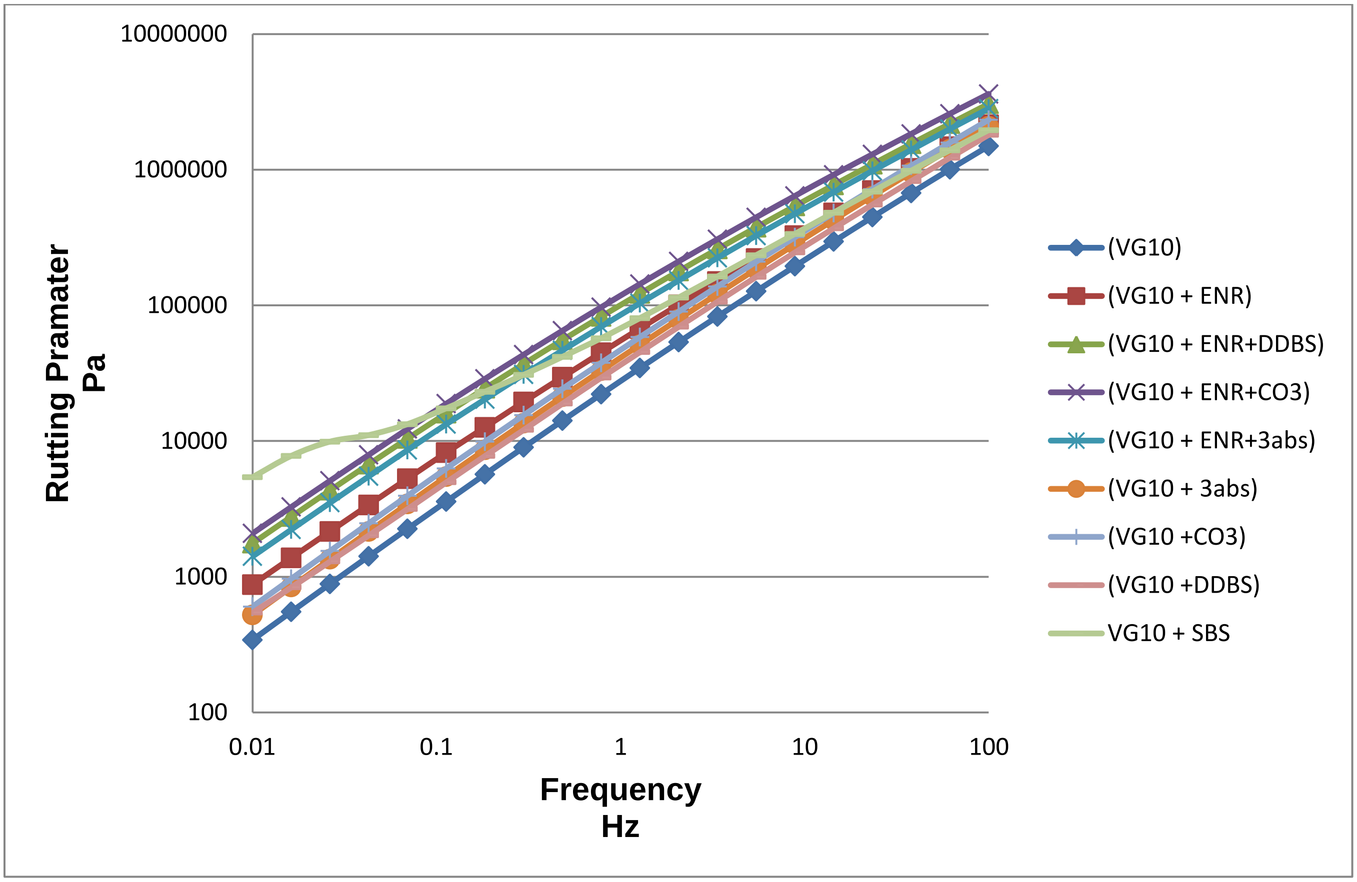

Figure 3.5.4 Rutting Parameter vs Frequency at 40 ^{O}C & 5 % loading

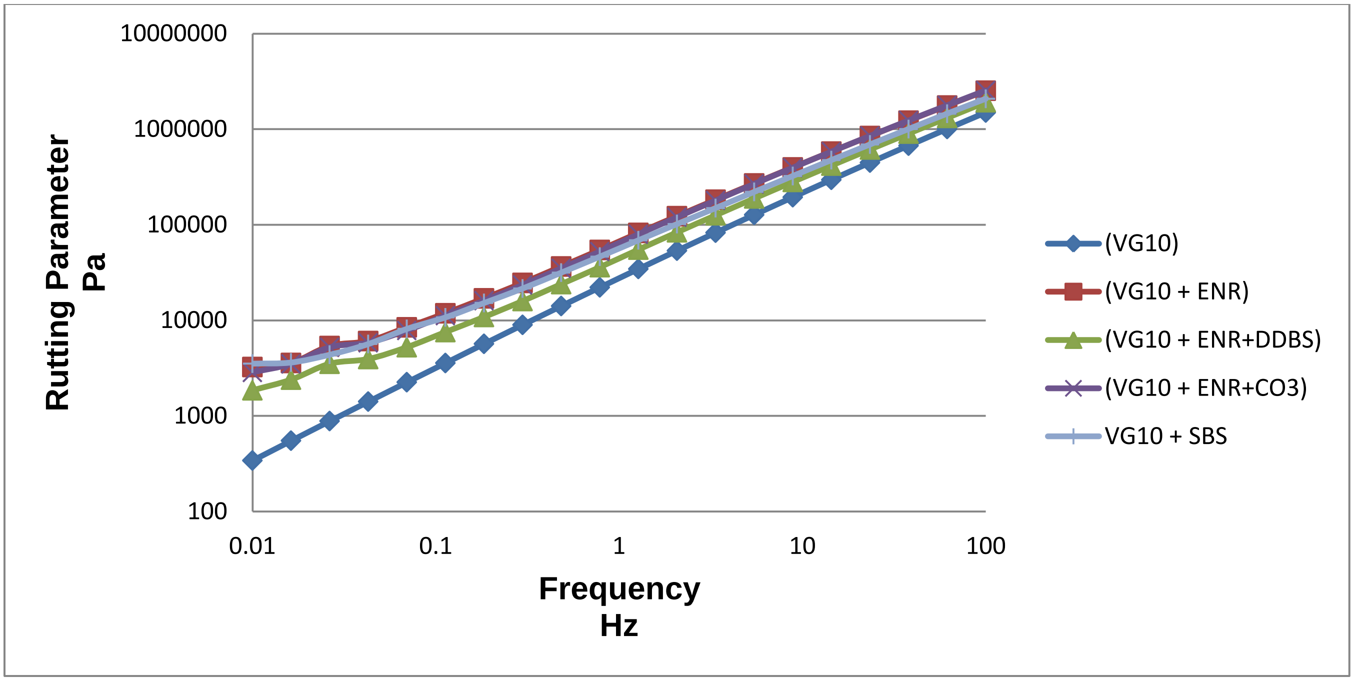

Figure 3.5.5 Rutting Parameter vs Frequency at 40 ^{O}C & 2 % loading

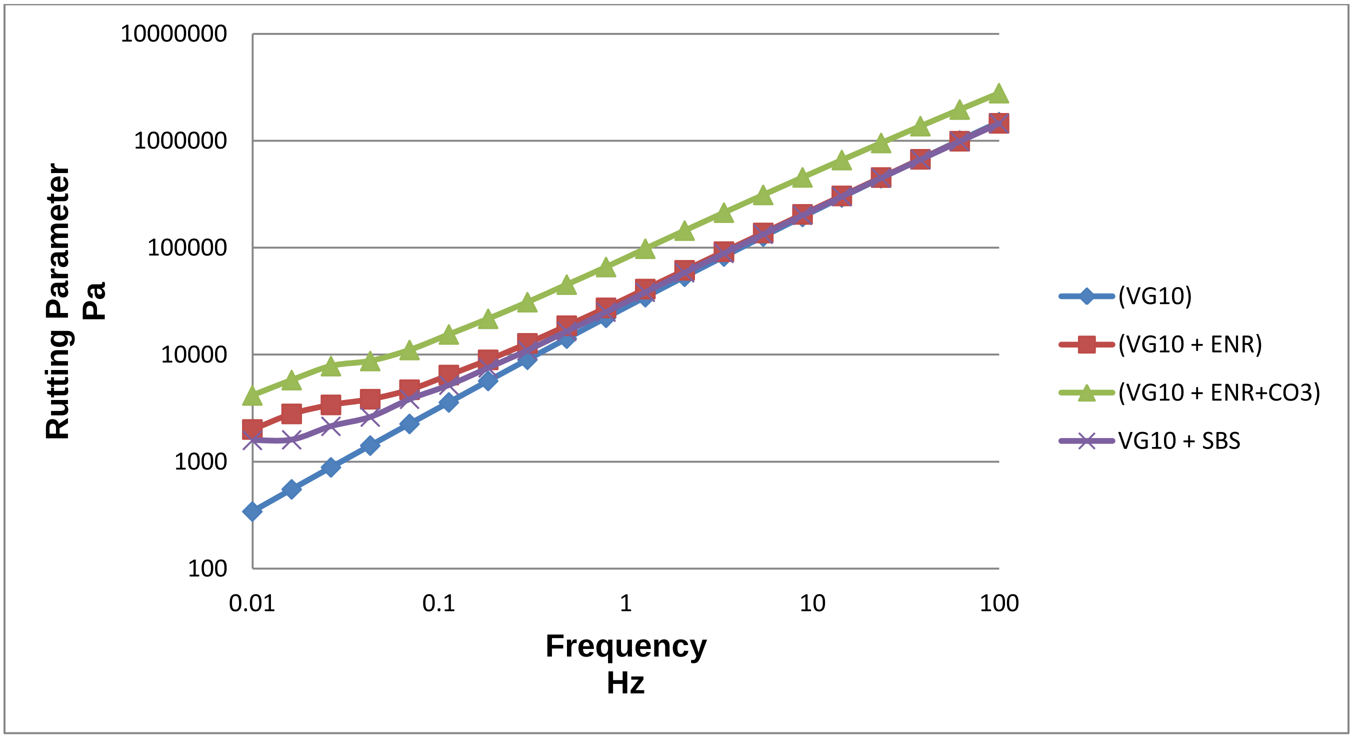

Figure 3.5.6 Rutting Parameter vs Frequency at 40 ^{O}C & 1 % loading

Analysis in Figure 3.5.4 shows that, there is significant improvement in rutting resistance parameter (G*/Sinδ) of VG10 + ENR + CO_3 (carbonate clay) sample (at 5% loading)compared to unmodified bitumen, VG10 + ENR and benchmarked sample VG10 + SBS at all higher frequencies but at frequencies lower than 0.1 Hz benchmark sample VG10 + SBS shows best results. These differences decree in 2% modification in all conditions (Figure 3.5.5) and VG10 + ENR + CO3 (carbonate clay) sample shows almost same rutting resistance parameter over all range of frequencies .At 1 % loading (Figure 3.5.6) VG10 + ENR + CO3 sample again shows significant improvements at all range of frequencies as compared to pure VG10, VG10 + SBS and VG10 + ENR. Thus, the analysis shows that addition of carbonate clay and ENR improves rutting resistance of bitumen at 40 ^{O}C but in some selected conditions.

3.5.5 Rutting resistance vs frequency results at 60 ^{O}C

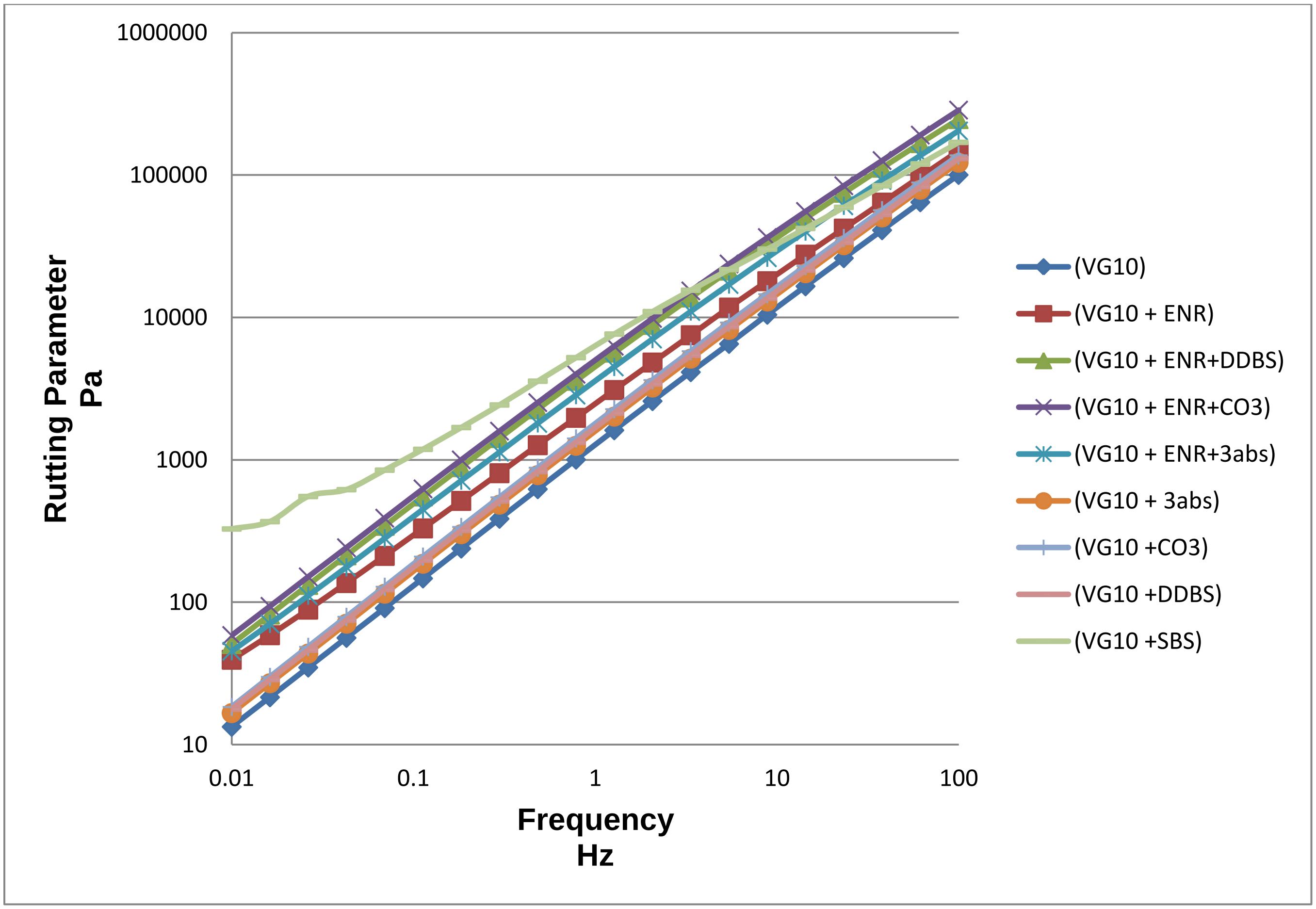

Figure 3.5.7 Rutting Parameter vs Frequency at 60 ^{O}C & 5 % loading

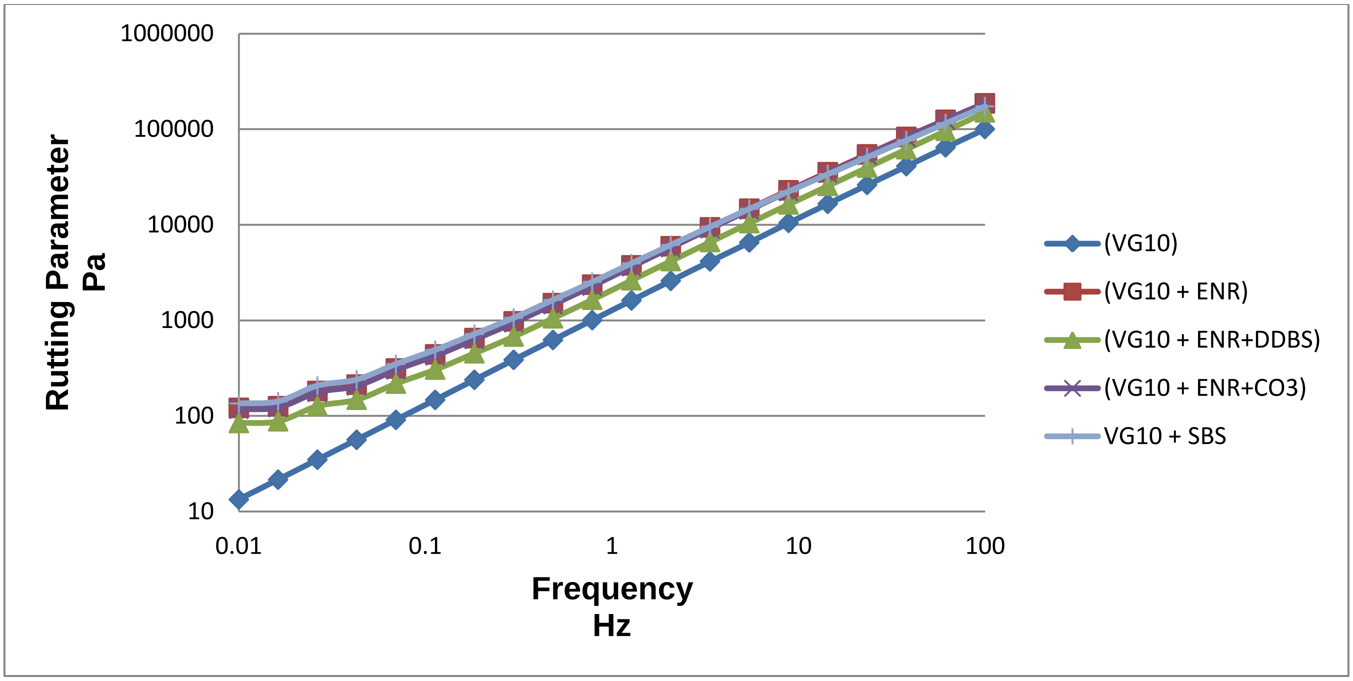

Figure 3.5.8 Rutting Parameter vs Frequency at 60 ^{O}C & 2 % loading

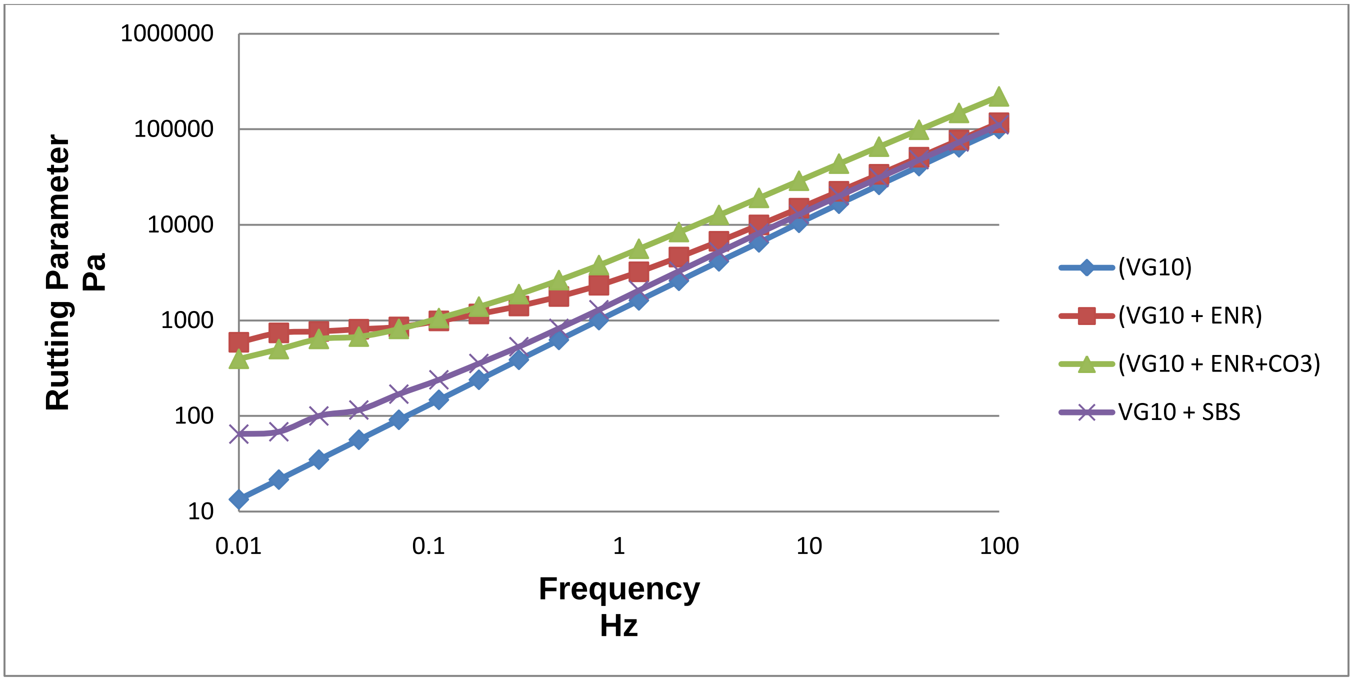

Figure 3.5.9 Rutting Parameter vs Frequency at 60 ^{O}C & 1 % loading

Analysis in Figure 3.5.7 shows that, there is significant improvement in rutting resistance parameter (G*/Sinδ) of VG10 + ENR + CO_3 (carbonate clay) sample (at 5% loading)compared to unmodified bitumen, VG10 + ENR and benchmarked sample VG10 + SBS at all higher frequencies but at frequencies lower than 10 Hz benchmark sample VG10 + SBS shows best results. These differences decree in 2% modification in all conditions (Figure 3.5.8) and VG10 + ENR + CO3 (carbonate clay) sample shows almost same rutting resistance parameter over all range of frequencies .At 1 % loading (Figure 3.5.9) VG10 + ENR + CO_3 sample again shows significant improvements at frequencies more than 0.1 Hz as compared to pure VG10, VG10 + SBS and VG10 + ENR but at frequencies lower than 0.1 Hz VG10 + ENR sample shows better rutting resistance. Thus, the analysis shows that addition of carbonate clay and ENR improves rutting resistance of bitumen at 60^{O}C but in some selected conditions.

4. Conclusions:

The tests performed on bitumen proved that the nanoclay modification in presence of a polymeric compatibilizer helped to improve the rutting resistance of the standard VG10 grade bitumen. This is especially true when bitumen was modified with carbonate clay and ENR polymer as compatibilizer. The nanoclay modification helped to improve the ageing resistance (retained penetration and increment in softening point) of the VG10 binder in the short term ageing.

However, the nanoclay modifications were observed to negatively influence the fatigue resistance performance of bitumen (at 25 ^{O}C). An overall conclusion from these findings is that the nanoclay modification with polymeric compatibilizer helped to improve some characteristics of bitumen but at this level they are not at a stage to justify application at large scale.

Hence, further studies on the chemistry of the nanoclay and bitumen and further development of the nanoclay technology is recommended to utilize the full potential of the nanoclay modified bitumen.

ENR	Epoxidized Natural Rubber
DDBS	Dodecyl Benzene Sulfonate
3-ABS	3- amino benzene sulfonate
CO3	Carbonate
VG10	Viscosity Grade 10
Dmm	decimillimetre
SBS	Styrene butadiene styrene

Table 3.6: Abbreviations used

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