

Laboratory Study on Nano Clay Modified Asphalt Pavement

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Abstract

In the present paper, the potential benefits of using Nanoclay powder and SBS in asphalt mixtures used in pavements is reported. The Nanoclay modified binder (NCMB) viz. five types namely VG 30+5.5% SBS+0.5 PPA designated as 1, VG 30+5.5% SBS+0.5 PPA+0.125% NC as 2, VG 30+5.5% SBS+0.5 PPA+0.25% NC as 3, VG 30+5.5% SBS+0.5 PPA+0.50% NC as 4 respectively. Microscopic analysis namely Scanning Electron Microscope test (SEM), Fourier Transform Spectroscopy (FTIR), and Differential Scanning Calorimetric test (DSC) and Thermo-Gravimetric Analysis (TGA) on the modified binder were carried out. Marshall Samples were prepared by the modified and unmodified asphalt binders. Additionally, workability tests (Marshall Stability, indirect tensile strength, tensile strength ratio and indirect tensile stiffness modulus) were conducted. The results of this investigation indicated that the asphalt mixture modified by 5.5% SBS plus 0.5% Nano clay powder could give the best results in the tests carried out in the current study so that this modification can increase physical and mechanical properties of asphalt binder and mixtures.

Keywords: Nano clay, poly phosphoric acid, Styrene Butadiene Styrene, Marshall Method of mix design

Introduction

Increasing traffic loads and traffic volume, combined with the rising cost of asphalt, have led to an urgent need to improve the durability, safety and efficiency of asphalt pavements through asphalt modification. Temperature susceptibility characteristics and physical properties of asphalt binder at high and low field operating temperatures

can affect the final performance of the mixture. To improve the performance of bitumen and asphalt concrete mixtures, the addition of modifiers such as polymers has become popular in recent years. Polymeric Nano composites are one of the most exciting of materials discovered recently and the physical properties are successfully enhanced when a polymer is modified with small amounts of Nano clay, on the condition that the clay is dispersed at nanoscopic level [1, 2]. Nano clay(NC) is one of the most affordable materials that have shown promising results on polymers, [3]. Because Nano clays are micro-scale fillers which would make polymers efficient as reinforcement, many researches showed that Nano clay modification can improve mechanical behavior properties of mixtures such as indirect tensile strength, creep and fatigue resistance[4, 5]. Nano clay is made from Montmorillonite (MMT) mineral deposits with average dimension of 1 nm thick and 70-150 nm wide. Nano clays are known to enhance properties of many polymers such as epoxy, PET, PE and PP leading to better clarity, stiffness and thermal stability. Also, in recent years there has been many interests in developing Nano clay reinforced composites due to their improved performance at high temperatures under various loading conditions including impact [6, 7]. Jahromi, [8], gave a detailed study concerning the engineering properties of Nano clay modified asphalt concrete mixtures. The investigation showed that Nano clay can improve properties such as stability, resilient modulus and direct tensile strength. Superior performance under dynamic effect was noticed compared to that of unmodified bitumen under dynamic creep. Also, the study showed that the optimum binder content and void in total mixture increased by adding Nano clay to bitumen. Lam [9], showed that layered Montmorillonite (MMT) as a newly invented Nano filler can extraordinarily improve the mechanical behaviors of polymer matrix.

Nanomaterial's have at least one dimension measuring less than 10 nanometer (nm) at least. Due to their small size, usually nanomaterial's have the higher reactivity ability and special surface properties, which can be used for industry products. Due to the special properties of the above-mentioned, nanomaterials, they are good candidates for implementation into asphalt pavements. In recent studies where Nano clay material was added to modify the base asphalt binder, it was found that Nano clay could increase the shear complex modulus and reduce the strain failure rate of base asphalt. Furthermore, the addition of Nano clay in the base asphalt binder could weaken the moisture susceptibility of asphalt mixture [10].

Asphalt is usually employed as an organic binding material for waterproofing, moisture resistance and corrosion protection. Modification of base asphalt is required to improve the material's performance (e.g. adhesion, temperature sensitivity, friction properties, oxidation resistance, aging resistance and durability). There are many kinds of asphalt modifiers, including various resins, rubbers, polymers, sulfur, metal complexes, fibers and chemical agents. In recent years, nanotechnology has gradually been incorporated into the field of modified asphalt with various kinds of nanomaterial's being used to modify asphalt [11-20].

2. Materials and Methods

2.1 Bentonite Clay

Bentonite is smectite group clay formed the alteration of siliceous, Glass –rich volcanic rocks such as tuffs and ash deposits. The major mineral in bentonite is montmorillonite, having hydrated sodium, calcium, and magnesium and aluminium silicate. Sodium and calcium are interchangeable ions giving montmorillonite a high ion exchange capacity. It is used in a wide range of applications such as water proofing and sealant. Bentonite has excellent rheological and adsorption properties. The properties of bentonite are listed in Table 1.

Table 1. Properties of Bentonite Clay

Elements	Net Counts	Weight %	Atom %
C	3292	16.67	27.92
O	35279	32.42	40.76
Na	3177	1.38	1.21
Mg	2795	0.69	0.57
Si	78237	20.68	14.81
Cl	1171	0.47	0.26
K	2066	0.93	0.48
Ca	2367	1.22	0.61
Ti	2436	1.87	0.78
Fe	9086	13.11	4.72
Al	41544	10.55	7.86

2.2 Polyphosphoric Acid

Polyphosphoric acid ($H_{n+2}P_nO_{3n+1}$) is a polymer of orthophosphoric acid (H_3PO_4). Polyphosphoric acid offered commercially is a mixture of orthophosphoric acid with pyro phosphoric acid, triphosphoric and higher acids. This eliminates issues of foaming and corrosion at the refinery or terminal. PPA's major applications are surfactant production, water treatment, pharmaceutical synthesis, pigment production, flame proofing, metals finishing and asphalt modification.

2.3 Styrene Butadiene Styrene (SBS)

The commercially available SBS was procured. The property of SBS is given in Table 2.

Table 2. Properties of Styrene Butadiene Styrene

Polymer Properties	SBS (Calprene 501)
Molecular structure	Linear
Volatile matter, % max 0.4	0.4
Total styrene (on polymer), %	31
Specific gravity	0.94
Hardness, Shore A	76
Elongation, %	880

2.4 Bitumen

The VG 30 (Viscosity Grade) bitumen supplied by the Mathura Refinery is used in this study.

2.5 Aggregate

Series of test has been carried out to ensure the suitability of aggregate to be used in the mix design. The aggregate should be hard and tough enough to resist crushing, degradation and disintegration which can be determined by impact and abrasion test. Particle shape and texture are important for proper compaction, load resistance and workability. Flakiness and elongation index are carried out to determine proportion of flaky and elongated aggregate present it. The higher proportion of it may cause failure of the pavement. The results are shown in Table 3.

Table 3 Laboratory test result for aggregate

Property	IS specified values	Test Value
Specific gravity	2.5 – 3.0	2.8
Aggregate Impact test	30 % (max)	21%
Flakiness Index	30% (max)	30%
Elongation Index	-	29%
Abrasion	30% (max)	31%

2.6 Preparation of Nano clay modified binder (NCMB)

Bitumen (VG 30) is heated up to 160 ± 5 °C in a small container until it flowed fully. Initially a small amount of SBS (5.5% of weight of bitumen) is gradually added (5 gm/min) into the melted asphalt under high shear mixer at 3000 rpm for 1 hr. It was observed that the polymer particles did not actually blend in a homogeneous manner. So to attain the homogeneous mix, 0.5% of Polyphosphoric acid (PPA) is added into the 3.5%, 5.5%, and 7.5% of SBS and blended for 1 & 1/2 hour. The percent recovery for the PPA SBS combination is always greater than just the SBS. The SBS is destined to separate from the bitumen when stored at a high temperature because of the poor compatibility between SBS and bitumen. Observing the best result in the elastic recovery, 5.5% SBS+0.5%PPA is selected for improvement and modification

with various mass proportions of Nano clay (SBS/OMMT = 100/12.5, 100/25 and 100/50). For this purpose, Nano clay is added into PMB at 180 ± 5 C and the mixture blended at the fixed speed of 4000 rpm for 45 min.

The Results of properties of Modified Bitumen are given in Table 4.

Table 4. Results of properties of Modified Bitumen

Properties	Penetration	Softening Point($^{\circ}$C)	Ductility (cm)	Elastic Recovery
Binders				
Recommended Values as per IRC	60-70	45-60	Min 70	-
60/70 Grade Bitumen	64	54	84	-
60/70+5.5%SBS	42	55	70	60
60/70+3.5%SBS+0.5%PPA	35	56	93	50
60/70+5.5%SBS+0.5%PPA	34	57	64	65
60/70+5.5%SBS+0.5%PPA+0.125%NANOCLAY	44	53	80	70
60/70+5.5%SBS+0.5%PPA+0.25%NANOCLAY	33	58	82	75
60/70+5.5%SBS+0.5%PPA+0.5%NANOCLAY	46	51	75	60

2.7 Instrumental Analysis

The NC modified binder viz. five types namely VG 30+5.5% SBS+0.5 PPA designated as 1, VG 30+5.5% SBS+0.5 PPA+0.125% NC as 2, VG 30+5.5% SBS+0.5 PPA+0.25% NC as 3, VG 30+5.5% SBS+0.5 PPA+0.50% NC as 4 respectively. Several instrumental analysis namely Scanning Electron Microscope test (SEM), Fourier Transform Spectroscopy (FTIR), and Differential Scanning Calorimetric test (DSC) and Thermo-Gravimetric Analysis (TGA) were carried out on modified binders.

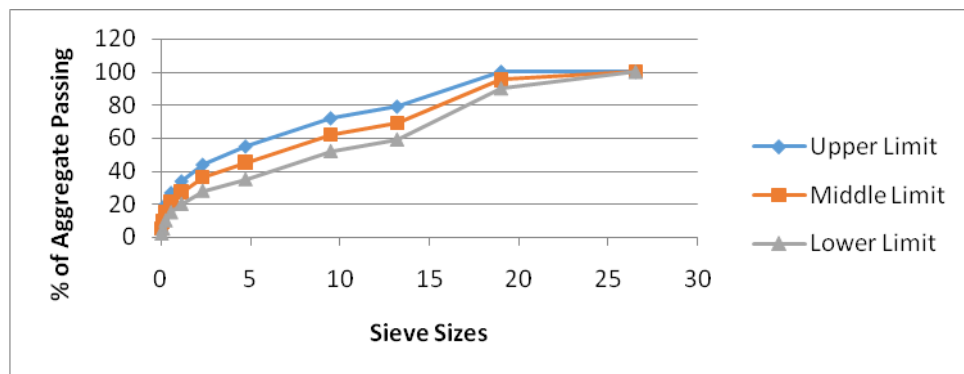
2.8 Mix Design

The conventional gradation for Bituminous Concrete as per the MoRTH specification was chosen in which the size of aggregate Varies From 26.5 mm to 0.0075 mm as shown in Table 5 and Figure 1.

Table5. Bituminous Concrete Gradation 1

SIEVE SIZES	U.L	M.L	L.L
26.5	100	100	100
19	100	95	90
13.2	79	69	59
9.5	72	62	52
4.75	55	45	35
2.36	44	36	28
1.18	34	27	20
0.6	27	21	15
0.3	20	15	10
0.15	13	9	5
0.075	8	5	2

Minimum Binder Content	= 5.2% (Normal Bitumen)
	= 5.4% (Modified Bitumen)
Percentage of Air Voids	= 3-5%
Percentage of voids filled with Bitumen	= 65-75
Tensile Strength Ratio	= 80% (Minimum)

**Fig .1 Gradation of Aggregate**

2.9 Volumetric Analysis

Fundamentally, mix design is meant to determine the volume of bitumen binder and aggregates necessary to produce a mixture with the desired properties. The properties that are to be considered, include the bulk specific gravity of the mix, percentage air voids, percentage volume of bitumen, percentage void in mineral aggregate VMA and percentage voids filled with bitumen VFB. The optimum binder content for the mix design is determined by taking average value of the Binder content corresponding to maximum stability, maximum bulk specific gravity and the median of designed limits of percent air voids (V_v) in the total mix (i.e. 4%) and voids filled with bitumen (VFB). In order to find out the optimum binder content, graphs has been plotted for

binder content against bulk specific gravity, air voids and stability and this has been shown in Figure 2.

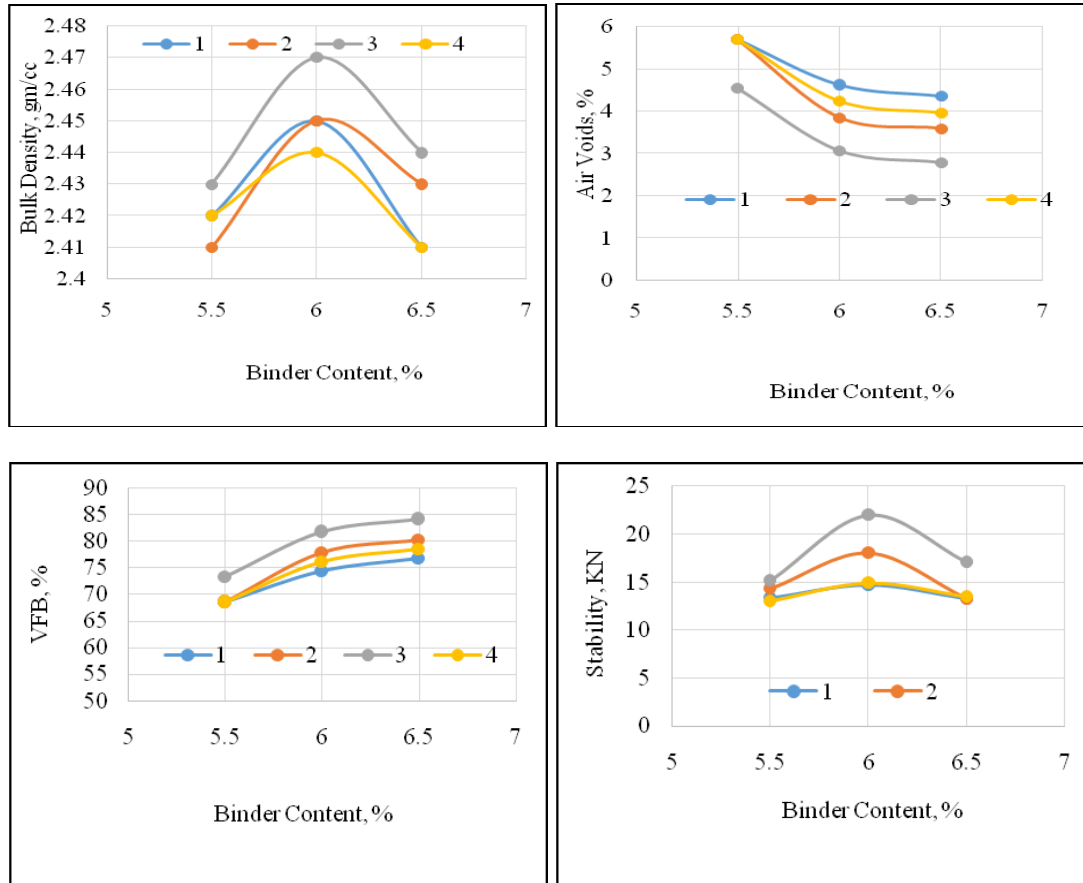


Figure 2. Volumetric properties of Nano clay modified binder

2.10 Resistance to Moisture Damage (AASHTO: T-283)

One set of Marshall Specimens (wet) were immersed in a water bath at 60°C for a period of 24 hours. The same samples were then removed from the water bath and kept at a temperature of 25°C for a period of 2 hours. Other set of samples (Dry) were kept at a temperature of 25°C for a period of 2 hours. These specimens were placed into the indirect tensile strength test assembly by loading along the axis of the specimen, with the two faces being restrained from movement. The entire assembly was then mounted on the conventional Marshall testing apparatus and the load at which the failure takes place was recorded. The indirect tensile strength (ITS) of the specimen was then calculated by using the given formula as below.

$$\sigma_x = 2P/\pi DT \text{ (kg/cm}^2\text{)} \quad \dots \quad (1)$$

Where,

P = load at failure, kg
 D = Mean diameter of the specimen, cm
 T = Mean height of the specimen, cm
 σ_x = Indirect tensile strength, kg/cm²

The indirect tensile strength ratio (TSR), which is a measure of water sensitivity, is calculated using the following formula; and represented in Figure 3.

$$\text{TSR, per cent} = 100 \times \frac{\text{Average tensile strength of wet sample}}{\text{Average tensile strength of dry sample}}$$

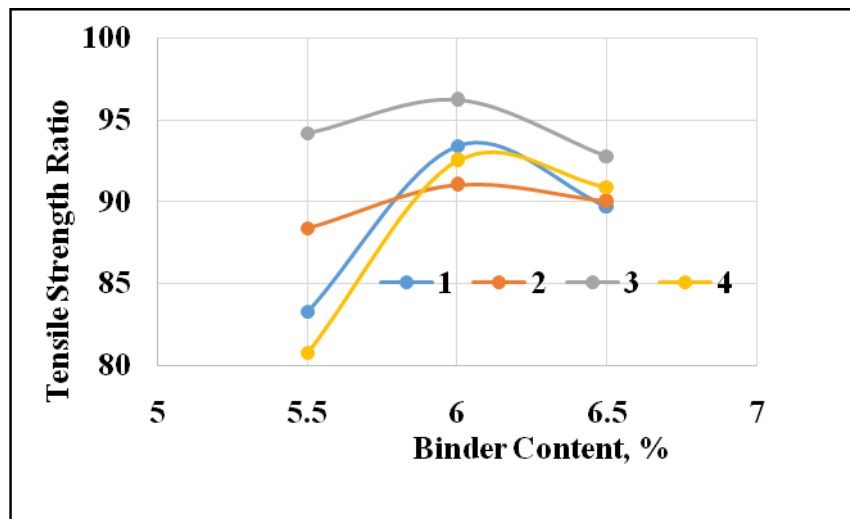


Figure 3. Tensile strength ratio of Nano clay modified binder

3. Characterization of Nano clay modified binder

3.1 Scanning Electron Microscopic Analysis(SEM)

The Scanning Electron Microscope (SEM) uses a focused beam of high energy electrons to generate a variety of signals at the surface of solid specimens (Figure4). The morphology of NC shows the crystalline structure (a), VG 30 appears to be plain and homogeneous (b). The addition of polymer in the VG 30 changes its internal structure of the blended bitumen. This is observed from the SEM analysis. The polymer phase appears light and hard, while the asphalt phase appears dark. Also, significant differences in morphology can be seen. The SBS-modified asphalts without Nano clay have phase separation and the SBS aggregates to form bigger particles (C). The addition of Nano clay has a significant effect on the compatibility of SBS-modified asphalts. The fine white SBS particles are dispersed in the asphalt matrix. This means that the blends with Nano clay can be stored at a high temperature (d, e and f).

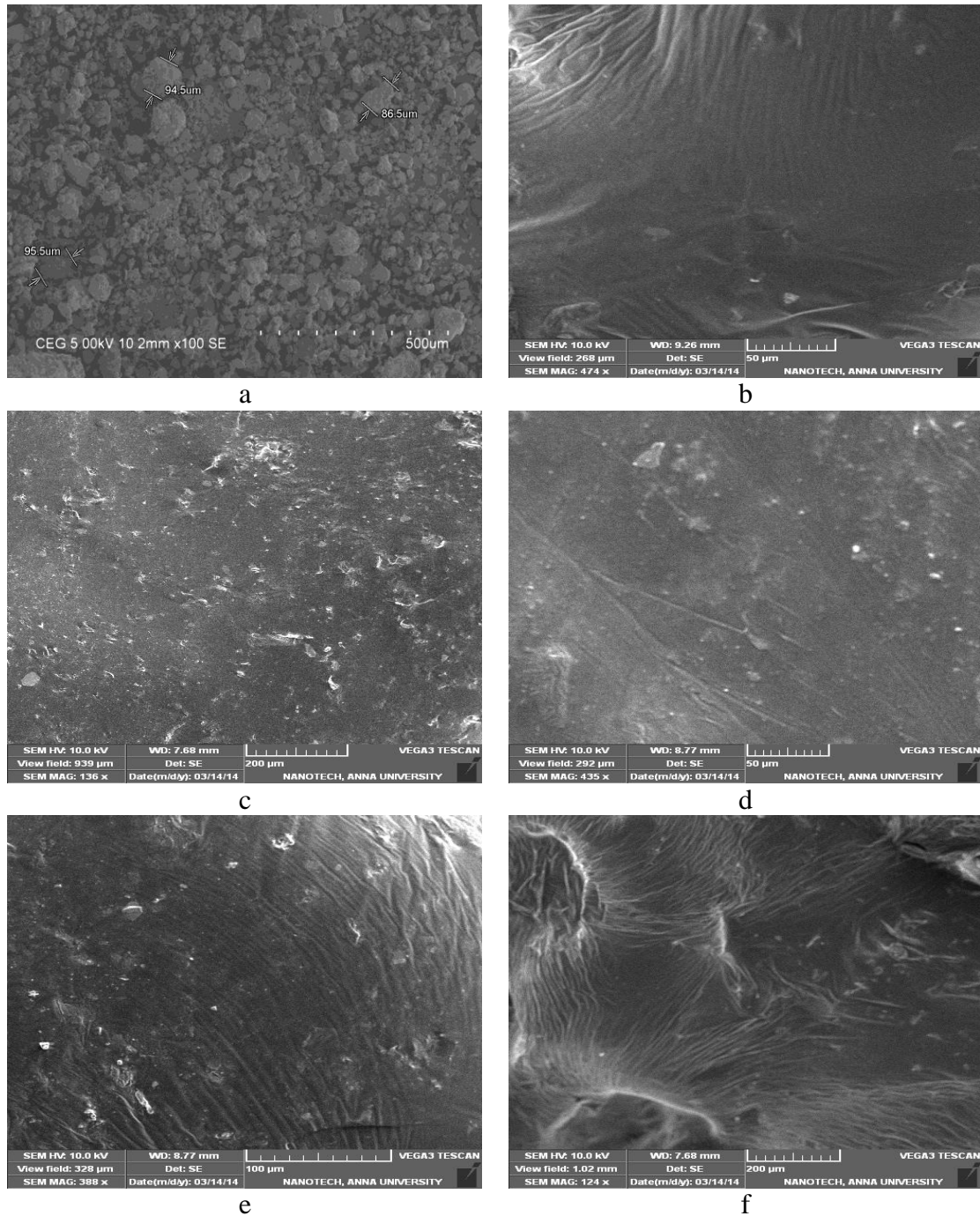


Figure 4. Morphology of (a) NC, (b) VG 30, (c) Sample 1, (d) Sample 2, (e) Sample 3, (f) Sample 4

3.2 Thermo Gravimetric Analysis (DSC/TGA)

The DSC curve of Nano clay modified binder shown in Figure 3, infers that the initial transition takes place at a temperature of 40° C due to the presence of polymer and the

physical property of the material changes at this temperature and it occurs with the absorption of energy. The next transition takes place at a temperature 77° C. The peak endothermic point is 150° C at which the material melts. ThermoGravimetric Analysis was done for all the five samples. Figure 5 and Figure 6 shows that modified bitumen decomposed at 255° C. The weight is reduced from 3.434 mg to 0.475 mg.s. Figure 6 (a) shows that modified bitumen decomposed at 255° C. The weight is reduced from 3.754 mg to 0.404 mg. Fig. 4.9 shows that modified bitumen decomposed at 297.29° C. The weight is reduced from 19.02 mg to 2.87 mg. Figure 6 (b) shows that modified bitumen decomposed at 354.91° C. The weight is reduced from 41 mg to 5.18 mg (Table 6).

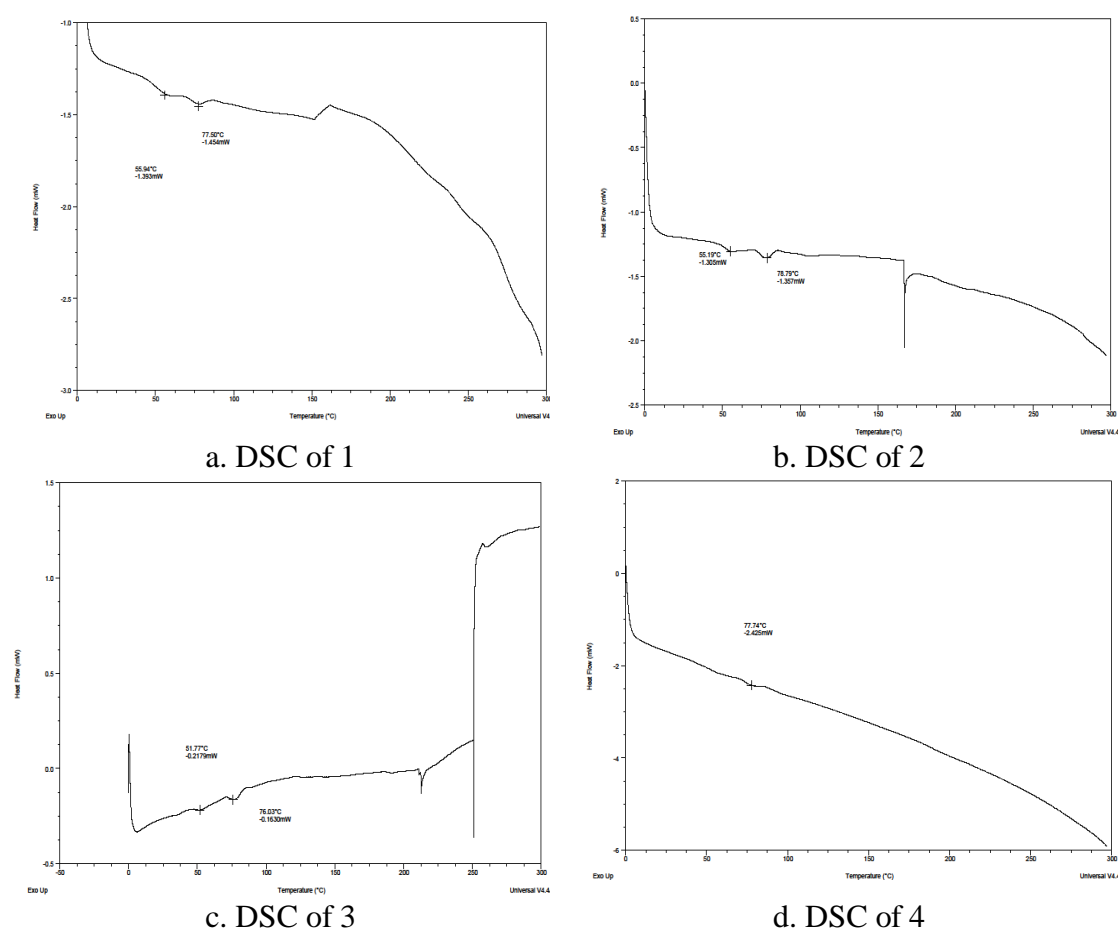


Figure 5. DSC analysis of NCMB

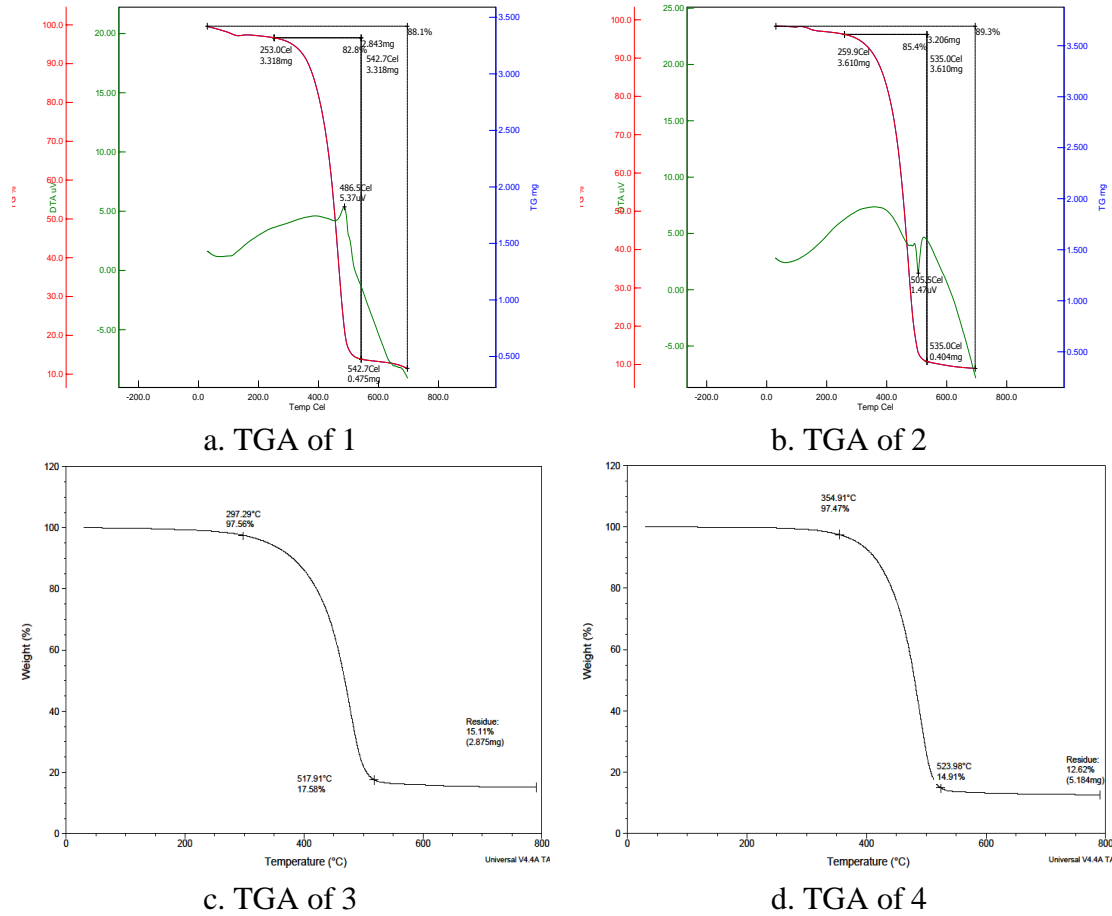


Figure 6. TGA analysis of NCMB

Table 6 TGA Test Results of the Binders

Name of the Sample	60/70 bitumen	60/70+5.5% SBS+0.5% PPA	60/70+5.5% SBS+0.5% PPA+100/12.5 NC	60/70+5.5% SBS+0.5% PPA+100/25 NC	60/70+5.5% SBS+0.5% PPA+100/50 NC
Original Weight(mg)	25.8	3.434	3.754	19.02	41
Residual Weight	3.52	0.475	0.404	2.875	5.18
% Lost	86.35	86	89	84	87
Temperature at which transition starts(°C)	296	253	259.9	297.29	354.91
Temperature at which transition stops(°C)	530.25	542.7	535	517.91	523.98

3.3 FTIR

Sample 1 has peaks in the region 3014 cm⁻¹, 2925 cm⁻¹, 2856 cm⁻¹, 1457 cm⁻¹, 1375

cm^{-1} , 1214 cm^{-1} , 751 cm^{-1} and 669 cm^{-1} and they represent Amine N-H, Alkenyl C-H, Aromatic C-H, Amines C-N, and C-H groups respectively. The Nano Modified bitumen (0.125% NC) has peaks in the region 2924.52 cm^{-1} , 2855.1 cm^{-1} , 1457.92 cm^{-1} , 1375.96 cm^{-1} , 1215.9 cm^{-1} , 754.995 cm^{-1} , 669.178 cm^{-1} and they represent Carboxylic Acid O-H, Alkanes C-H, Amines C-N, C-H groups respectively. The Nano Modified bitumen (0.25% NC) has peaks in the region and they represent 3726.76 cm^{-1} , 2927.41 cm^{-1} , 2857.99 cm^{-1} , 1458.89 cm^{-1} , 747.281 cm^{-1} , they represent Amide N-H, Alkyl C-H, Alkanes, Phenyl Ring Substitution Bands respectively. The Nano Modified bitumen (0.5% NC) has peaks in the region and they represent 3725.8 cm^{-1} , 3018.05 cm^{-1} , 2926.45 cm^{-1} , 1214.93 cm^{-1} , 749.209 cm^{-1} , 669.178 cm^{-1} , they represent Amide N-H, Carboxylic Acid, Alkanes C-H, Carboxylic acids C-O, C-H Phenyl Ring Substitution Bands, Alkenes C-H groups respectively.

The Y-axis is the percentage transmitted and x axis is the wave number. Each group like alcohol, aromatics, carbonyl have characteristic peaks. 700-1400 region is the skeletal region of the scan. The groups which characterize the compound are which comes after 1400. Functional groups corresponding to some of the wave numbers are shown in Table. 7 and Figure 7.

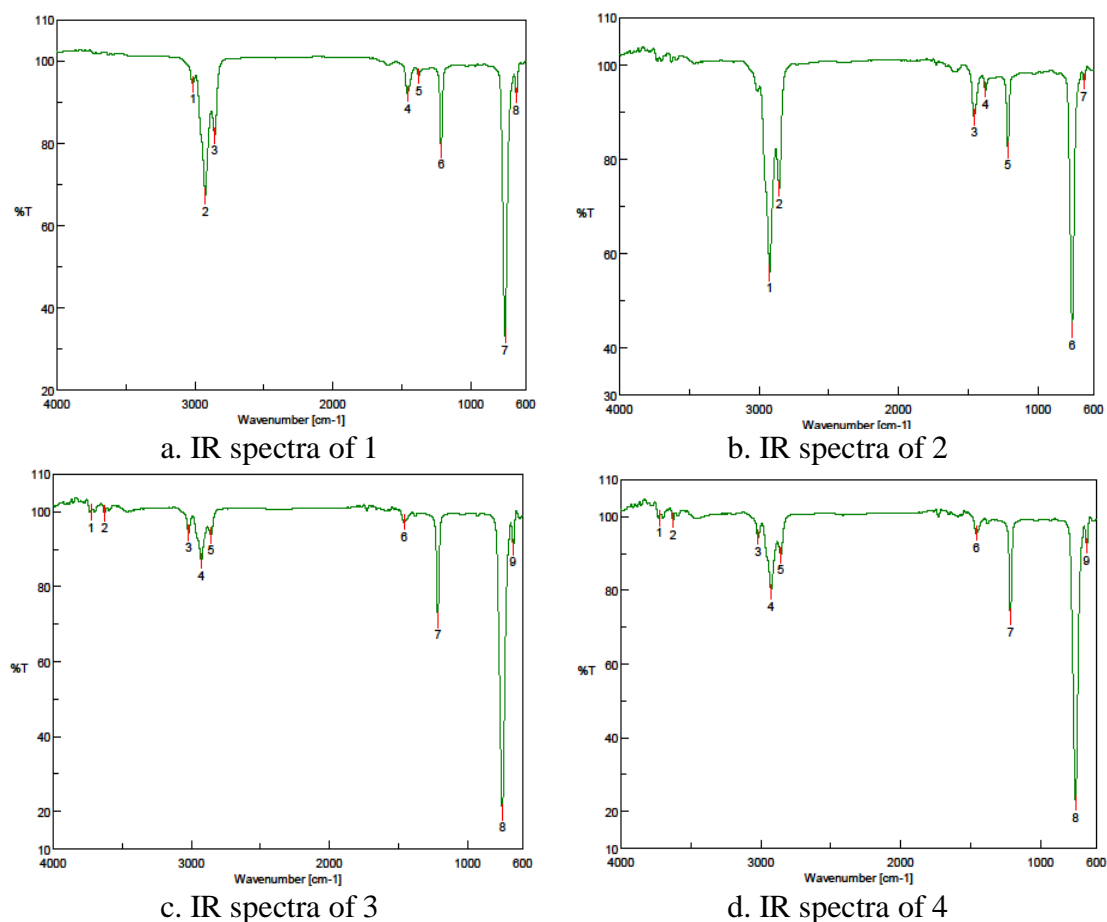


Figure 7

Table 7. Functional Groups Corresponding to Wave Number

Wave Number (cm ⁻¹)	Assignments of the Main Absorption Bands
722	(CH ₂) _n , n>4
746,814 ,874	C-H in substituted aromatics
1030	S=O
1160	C-O-C (anhydrides)
1650	C=O
2860	C-H (CH ₂)
2960	C-H (CH ₃)
3400	O-H

Source: Lucena et al (2007)

The asphalt binder presented physical and chemical changes when subjected to thermal oxidative process. This can be caused by the loss of volatiles or specimens of low molecular weight or even by the formation of hydrogen bonds.

In base bitumen an increase in the intensity of the bands in the region 1600-1700 cm⁻¹ regarding the carbonyl group (C=O) as a consequence of the oxidation process. Some other indication of the structural changes in the base bitumen on addition of polymer and Nano clay is disappearance of some peaks (which is predominant in base bitumen) and appearance of some new peaks in the modified bitumen. This shows that structural changes have been taken place on modification. Appearance of new peaks in modified form can be due to some chemical reaction taking place between bitumen and components of rubber.

Peaks around 2900-2500 cm⁻¹ found in base bitumen is due to C-H stretching of groups like CH-CH₂ and CH-CH₃ present in bitumen. In modified forms these peaks are less intense, so some of fraction of bitumen may undergo changes during mixing process. For Nano modified bitumen (0.125% and 0.25% and 0.5%) peaks around 3800-3500 cm⁻¹. Some of these observations cannot be assigned with 100% accuracy as matrix is complex.

Summary and Conclusion

The base bitumen of penetration grade 60-70 was modified using Nano Clay, SBS and PPA. It was observed that, when SBS was added into the base bitumen it gave sufficient strength even though the mix was heterogeneous. In order to obtain a homogeneous mix, small amount of PPA was added into the SBS modified bitumen. It was observed that the SBS was destined to separate from the bitumen when stored at a high temperature because of the poor compatibility between SBS and bitumen. To overcome this problem, Nano clay was added into the modified bitumen. Clays could decrease the density difference between SBS and base bitumen as the driving force of separation. Because of the best result in the elastic recovery, 5.5% SBS+0.5% PPA is selected for improvement and modification with various mass proportions of Nano clay (SBS/OMMT = 100/12.5, 100/25 and 100/50).

The conventional properties of Penetration, Softening Point, and elastic recovery were conducted on plain bitumen and on blended bitumen. Penetration value for (100/25) SBS/Nano clay modified bitumen was observed that 33 which is better than base bitumen which was 64. There is a significant decrease in the penetration value indicating the improvement in the temperature susceptibility resistant characteristics. Softening Point value for (100/25) SBS/Nano Clay modified bitumen was observed that 58°C which is better than base bitumen which was 54°C. The Softening point improvement can be the indicator to measure the degree of ageing. It is observed that the bulk density and stability values (2.47 and 21.9 KN) are better for Nanocomposite (100/25) (SBS/Nano Clay) bitumen compared to PMA and base bitumen which was 2.46 and 14.67 KN. Nanoclay proportions 100/12.5, 100/25, 100/50 were taken. It was found that (base bitumen+5.5 %SBS+0.5%PPA+100/25 Nano clay) combination gives better results in Penetration, Softening Point ,Elastic Recovery ,Stability values. From the study on TGA, it is observed that percentage loss in weight of the material (84%) is less for Nano clay modified bitumen compared to base bitumen (86.35%). This indicates that the addition of Nano Clay will give more resistance against thermal condition.

FTIR spectra at 2925 cm^{-1} , 2856 cm^{-1} , 1457 cm^{-1} , 1375 cm^{-1} , 1214 cm^{-1} , 751 cm^{-1} and 669 cm^{-1} and they represent Amine N-H, Alkenyl C-H, Aromatic C-H, Amines C-N, C-H groups remained in all the samples which shows better homogeneity of Nano clay with SBS in the bitumen. The physical and mechanical properties give the better result for the Nano clay modified bitumen. It is observed that on Nano clay modified bitumen there is an increase in the intensity of Amide N-H groups which result in the thermal stability and binding stability.

From SEM analysis it can be inferred that the optimum percentage of Nano clay (100/25) gives more homogeneity than the others. Excess amount of nanoparticles in PMA could cause agglomeration of Nano-particles and destruct the intercalate structure in triple Nano composite. The Indirect Tensile Strength test was done for all combination of mix. It was determined that the ITS value 96.2% for 100/25 Nano Clay modified bitumen which was more than the other combinations.

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