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Experimental Investigations on Nanoclay (Cloisite-15A) Modified Bitumen

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Abstract**—**This study investigated the influence of Cloisite-15A nanoclay on the physical, performance, and mechanical properties of bitumen binder. Cloisite-15A was blended in the bitumen in variegated percentages from 1% to 9% with increment of 2%. The blended bitumen was characterized using penetration, softening point, and dynamic viscosity using rotational viscometer, and compared with unmodified bitumen equally penetration grade 60/70. The rheological parameters were investigated using Dynamic Shear Rheometer (DSR), and mechanical properties were investigated by using Marshall Stability test. The results indicated an increase in softening point, dynamic viscosity and decrease in binder penetration. Rheological properties of bitumen increase complex modulus, decrease phase angle and improve rutting resistances as well. There was significant improvement in Marshall Stability, rather marginal improvement in flow value. The best improvement in the modified binder was obtained with 5% Cloisite-15A nanoclay.

Keywords**—**Cloisite-15A, complex shear modulus, phase angle, rutting resistance.

I. Introduction

IN a developing country like India, where about 98% roads are black topped [16], there is a wide range of temperature changes due to seasonal variation, and a great deal of attention is required to improve the performance of the bituminous mixes in order to diminish the maintenance cost and improve pavement life. Hence, to improve the performance of bituminous concrete mixtures and solve the problem of premature failure, the use of modifiers like polymers has been in trend recently. Among them, nanocomposites formed from the polymers are used by the transportation engineers and the researchers. When nanoclay is mixed in bitumen, which is itself a polymer, nanocomposite is formed on the condition that nanoclay is dispersed throughout the volume of bitumen at nanoscopic level. This nanocomposite has enhanced the physical properties of polymers and has the ability to improve the performance of pavements rendering it more resistant to deformations. Cloisite-15A, as a modifier, is among the most attracting and exciting materials recently discovered which is based on the nanotechnology.

Thermal and mechanical properties of clay/epoxy Nano-composites at various temperatures were studied. Two different types of modifier, Nanomer-I.28E and Cloisite-30B, were used and it was found that both the monomers were quite significant and improved the elastic modulus [14].

Nanoclays are very effective and greatly influence the rheology of bitumen and performance of bituminous mixes. At 3% of Cloisite-15A content, stiffness along with resistance against rutting and indirect tensile strength (IDT) is improved. On the other hand, nanofill at 6% improved both short and long term ageing-resistance [6].

Methods for formation of polymer-clay nanocomposites were discussed. They considered both the abstract point of view and practical methods for the synthesis of nanocomposites. They studied different methods like monomer modification, monomer intercalation, melt-intercalation, and common solvent methods. They discussed various models which explained that the mechanical properties are greatly improved by using nanomaterial [4].

Silicate nanoparticles were used to modify asphalt. They used bentonite clay (BT) and organically modified bentonite clay (OBT), mixed was prepared with bitumen at 160 ^{o}C and 4000 rpm (1-6%). They used also solicitor for better dispersion. Softening point and viscosity were increased more by OBT then by BT. On the other hand, ductility is reduced more by BT as compared to OBT. The rutting resistance improved as shown by the DSR tests. The BBR test data showed that, for aged specimens (RTFO & PAV), both the modifiers greatly improved rheological properties and cracking of asphalt low temperatures [12].

Asphalt was modified with montmorillonite nanoclay at 2% and 4%. The sample was prepared at high temperature and rotation in order to get desired exfoliation. The mixing of modifier with asphalt was done at 160 ^{o}C and 2500 rpm for 3 hour. The tests carried out were super pave rotational viscosity, DSR and Direct tension test. Complex modulus (G*) and viscosity increased after the modification whereas the results of Direct Tension Test showed better low temperature cracking resistance [15].

Engineering properties of asphalt concrete mixtures modified with Cloisite-15A and nanofill were discussed. They conducted different rheological and mechanical tests on asphalt and asphalt concrete mixtures. Both Cloisite-15A and nanofill were indicated to improve stiffness, rutting resistance, IDT, resilient modulus, and Marshall Stability [2].

Both macroclay and nanoclay affect the performance of bitumen. Softening point increased, whereas penetration decreased. Kinematic viscosity and tensile strength value increased to a greater extent. The best improvement was observed at 6% nanoclay [5].

The effect of nanoclay on the moisture susceptibility of bitumen was studied and also the cost analysis of nanoclay modified bitumen was carried out. Obtained results were compared with mostly used Polymer Modified Bitumen (PMBs) for the up-gradation and improvement in the

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performance of binder. They used two different types of nanoclay Cloisite-15A and Cloisite-11B to find their effect on most commonly used PG 64-22 binder using surface science approach. They showed that though the addition of nanoclay posed a reverse effect on moisture resistance of plain binder, it could improve the performance of bitumen in respect of stiffness and save the money[7].

The cost of PG 64-22 binder per metric ton was about U.S. $532.50. Using PMBs, the cost per metric ton of PG 70-28 and PG 76-28 binders were U.S. $798 (i.e., 50% more than PG 64-22) and U.S. $1,064 (i.e., 100% more than PG 64-22), respectively. But, nanoclay when manufactured in large amount (minimum 22 metric ton) costs only US $4.96/kg. And, nanoclay at 2 and 4% can yield PG 70-28 and PG 76-28 binders respectively at the rate of U.S. $622 and U.S. $712 per metric ton. Hence, it could save 22-33% when compared to PMBs in improving the performance of bitumen [7].

Walters et al. (2014) used two types of nanoparticles viz. nanoclay (Cloisite30B) and Bio-char grinded to Nano-scales. The nanoclay was mixed with asphalt at 2 and 4% with and without Bio-char (5% taken with respect to dry mass). Rotational viscosity tests and XRD tests were conducted on pure and modified asphalt. The test result showed that such Nano-modifiers could be very effective in diminishing temperature susceptibility [13].

There are varieties of naturally occurring clay viz. montmorillonite, bentonite, kaolinite etc. The montmorillonite is abundantly available in nature and with slight modifications it can be used to form nanocomposite. There are two steps that are followed to convert it into nanocomposite.

Step-1 states that the clay is originally hydrophilic which means it has affinity for water. So, in order to mix it with bitumen, which is a polymer, its polarity needs to be altered to make the clay 'organophilic'. Surfactants are agents which decrease surface tension for example detergents. They are used to separate the layer to achieve the fine dispersion of clay. These molecules of surfactant increase the distance between layers to separate them in the scale of nanometres and also exchange their cations to form organophilic clay. [10]

Organophilic clay is obtained, when hydrophilic clay is added to surfactants (12-aminododecanoic acid) and octadecanoic alkyl trim ethyl (quaternary ammonium salt). The formation of organophilic or hydrophobic nanoclay is shown in Fig. 1 [11].

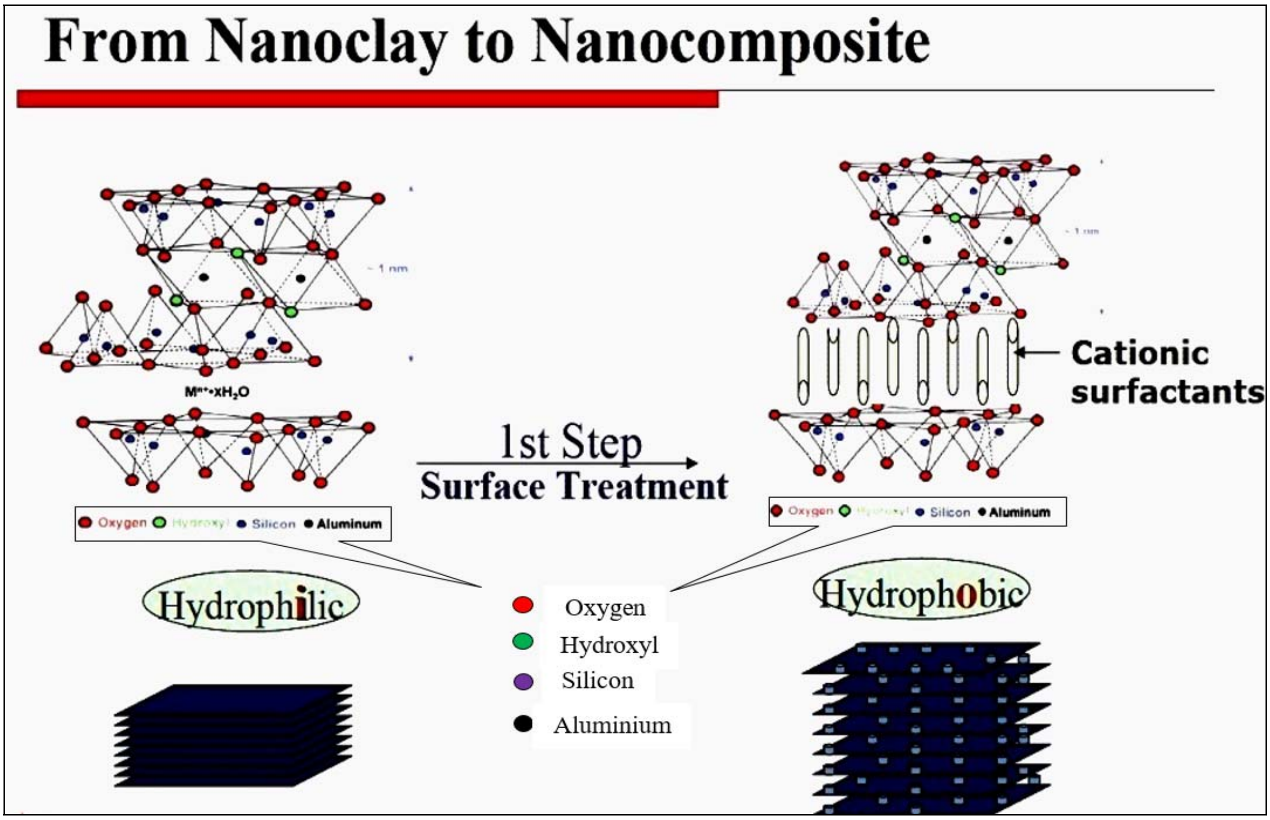

Fig. 1 Surface treatment of nanoclay

Step-2 states that modified clay at sufficient temperature, rotation and duration is mixed with bitumen. It causes effective dispersion of nanoclay throughout the bitumen which results in the formation of nanocomposite [11] as shown in Fig. 2. This nanocomposite so formed is really more stable and resistant, which can be very fruitful for improving pavement life when used as a binder in surface course.

The main objective of this study is to conduct a comparative test program on binders and bitumen mixtures containing standard and nanoclay modified bitumen and assess the effects of bitumen properties on pavement performance.

II. Materials and Methods

A. Bitumen

Bitumen is a common binder used for constructing flexible pavement. It is mainly derived as a by-product in petroleum refineries. It is defined as the black or dark brown sticky material which has high adhesive properties. It is a viscoelastic material showing elastic properties at low temperature and behaving as the viscous liquid at high temperature. The bitumen of 60/70 penetration grade was used for this study.

Fig. 2 Formation of nanocomposite

B. Cloisite-15A

In this project, a specific type of nanoclay, i.e. Cloisite-15A, was used to form Nano composite by mixing it with hot bitumen. The nanoclay is taken from Intelligent Materials Pvt. Ltd. which is in collaboration with Nano shell LLC Wilmington DE-19808 USA as shown in Fig. 3. It is a montmorillonite-based nanoclay modified by using a surfactant MT2ETOH (methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium) which makes it organophilic from its original nature of being hydrophilic. This modified organophilic nanoclay is compatible with polymers and has an affinity for it. The attributes of Cloisite-15A are given in Table I.

Fig. 3 Cloisite-15A in powdered form

In order to find out the suitability of modified bitumen, different physical conventional and non-conventional tests were performed.

C. Sample Preparation

Nanoclay (Cloisite-15A) was mixed with bitumen at temperature 130 oC and applied 2500 rpm torque for 30 minutes so that it may get dispersed homogenously throughout the bitumen, and melt intercalation may take place to form polymeric nanocomposite. Bitumen was modified with Cloisite-15A by adding 1%, 3%, 5%, 7%, and 9% by weight. Three samples were prepared to all considered content of modifier for all tests, and average of these is presented herewith.

TABLE I
Attributes of Cloisite-15 A

Treatment/Properties		Cloisite-15 A
Base		MT2ETOH (methyl, tallow, bis-2-hydroxyethyl,quaternary ammonium)
Moisture		<2%
Particle Size	10% less than	2μm
	50% less than	6μm
	90% less than	3μm
Density, g/cm^3		1.66
Plasticity Index		88%
Colour		Off-White

III. Results and Discussion

Experimental investigations were carried out using empirical test like penetration, softening point, and viscosity test along with performance test like rheology and Marshall Stability test. Outcomes are presented graphically in the following subsections.

A. Effect of Cloisite-15A on Penetration and Softening Point

This test provides a measure of the consistency or hardness of the bitumen. The penetration test is the most common control test for penetration grade bitumen. 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 oC), for a known time (5 s). It is measured in tenths of a millimeter. The lower the value of the penetration the harder the bitumen is and vice-versa [8].

It is observed that penetration value initially decreases and then after increases with the increase of modifier content. Minimum value is obtained at 5% of modifier content as shown in Fig. 4.

The ring and ball test is a test to determine the temperature at which a specific viscosity of the bitumen is reached at some point during its transition from solid to liquid. In this test, a ball (weight 3.5 g) is placed on a sample of bitumen contained in a brass ring that is then suspended in water bath. The bath temperature is raised at 5 ^{o}C per minute, the bitumen softens and eventually deforms slowly with the ball moving through the ring. This temperature is designated as the softening point of the bitumen and represents an equi-viscous temperature [9].

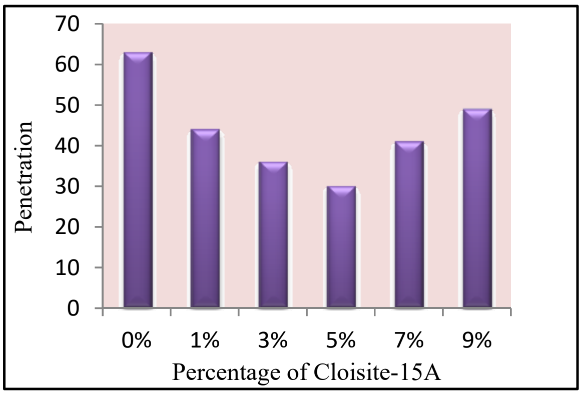

Fig. 4 Effect of Cloisite-15A on penetration

Softening point initially increases and then after decreases with increase of modifier content. Maximum value is obtained at 5% of modifier content as shown in Fig. 5.

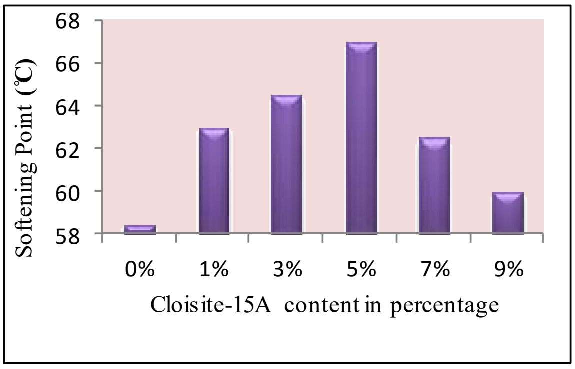

Fig. 5 Effect of Cloisite-15A on softening point

The 5% Cloisite-15A modification shows higher increment in softening point and higher decrement in penetration value of the fresh 60/70 binder. This behaviour may be due to the chemical reaction and change in chemical structures.

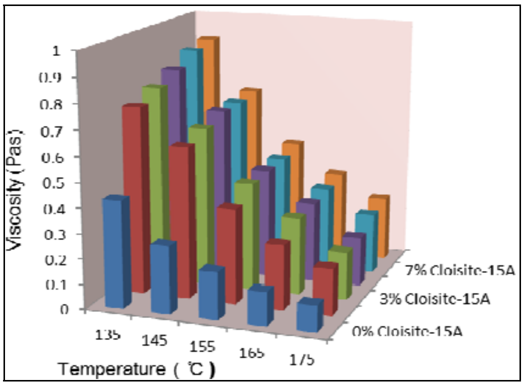

Fig. 6 Effect of Cloisite-15A on viscosity

B. Effect of Cloisite-15A on Viscosity of the Bitumen

The rotational coaxial viscometer test was used to evaluate the viscous property of modified binder (AASHTO T 316 and ASTM D 4402). The temperatures over which the viscosity test was conducted are 135, 145,155, 165, and 175 oC as shown in Fig. 6. Viscosity increases with increase of Cloisite-15A content over the temperature range. It was found that with the addition of 9% Cloisite-15A at 135 oC, the maximum value observed was 0.899 Pa.s which is still below the specified value 3 Pa.s. [3] This increase in viscosity may be attributed to the behaviour of Coisite-15A to form a nanocomposite with the bitumen which is more compact and more viscous. Hence, an increase in viscosity decreases its workability and mix ability, and more heat energy would have to be invested to get the desired workability.

C. Rheology Test

The DSR was used to characterize the mechanical properties of the modified bitumen under temperatures ranging from 40 oC to 90 oC and loading frequency of 0.01 Hz. The DSR measures the viscous and elastic behaviour of the bitumen as represented by the complex shear modulus (G*) and phase angle (δ), both used to evaluate performance parameter of rutting-resistance [1].

1. Effect on Complex Modulus (G*)

Complex modulus is the measure of the total resistance of the binder to deformation when repeatedly sheared. Binders which have higher elastic (storage) modulus show greater ability to recover from deformation, and which have higher viscous (loss) modulus show greater ability to resist deformation at any prescribed frequency.

Higher value of G* indicates higher stiffness, this reflects that the bituminous pavement is stiffer. G* decreases with increase of temperature over the range. At a particular temperature, G* increases with the increase of modifier content. It attains a maximum value at 5% modifier content. Afterwards, the value of G* decreased.

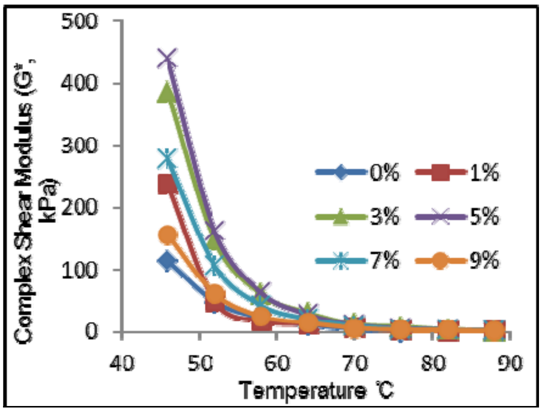

Fig. 7 Effect of Cloisite-15A on complex shear modulus

2. Phase Angle (δ)

The phase angle represents the immediate elastic and the delayed viscous responses of the binder that is obtained from the lag between the applied shear stresses and the resulting shear strains. The phase angle lies between 0o to 90o, where zero degree implies purely elastic and ninety degree implies purely viscous. Fig. 8 shows the trend of phase angle that represents with increase of temperature, phase angle increases. It is also observed that, with the increase of modifier content phase, angle decreased generally over the range of the temperature. Phase angle varied from lower to higher temperature indicates transition from elastic behaviour to viscous behaviour. The lower value of phase angle is good, from fatigue resistance point of view as this would lower down the value of G*sinδ.

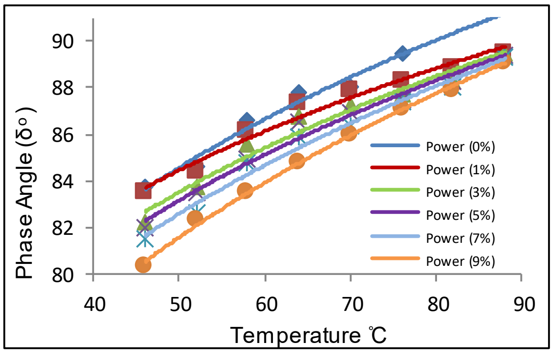

Fig. 8 Effect of Cloisite-15A on phase angle

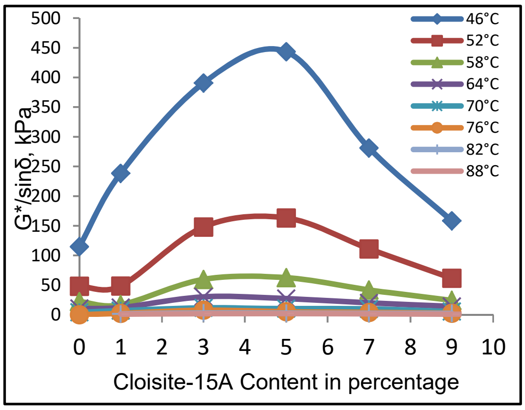

Fig. 9 Effect of Cloisite-15A on rutting resistance

3. Rutting Resistance Parameter (G*/Sinδ)

Rutting is formed due to repetition of axle loads along the wheel path, cyclic loading phenomenon. During each repetition of axle loads, certain amount of work is being done to deform the surface layer. Part of the work done is recovered in the elastic rebound of the surface layer, while the remaining work is dissipated through permanent deformation. To reduce rutting phenomena, work dissipated in each application of axle load can be minimized. Fig. 9 shows the variation of rutting resistance parameter with increase of modifier content at different temperature point. Rutting resistance parameter initially increased and then decreased, this trend indicates an optimum value. Optimum value of rutting resistance parameter is found at 5% of modifier content. There is a drastic change in rutting resistance when temperature increased from 46 °C to 52 °C and further slowly decreased with increase of temperature. Therefore, higher value of rutting resistance parameter at 46 °C may performs better than another one with small value of G*/sinδ .

D. Effect of Cloisite-15A on Marshall's Stability, Flow Value and Others

It is found that 5% modifier content shows maximum value of empirical test results except viscosity test. Also, performance tests result shows maximum value at 5% of modifier content. Hence, Marshall Test was conducted after modifying the bitumen by 5% of Cloisite-15A.This modified bitumen was used to prepare bitumen-aggregate mix for bituminous concrete surfacing course, and the test was conducted as per ASTM D 1559. The outcomes of Marshall Test showed that the stability value increased by about 56%. On the other hand, flow value reduced slightly and density showed a small increase in its value. Volume of voids decreased where as volume filled with bitumen increased slightly.

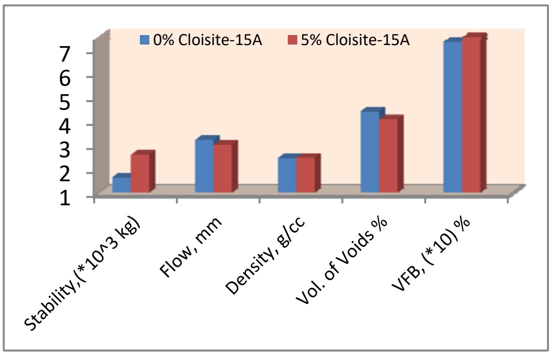

Fig. 10 Marshall Test results

IV. Conclusion

The lowest value of penetration at 5% of Cloisite-15A may indicate better improvement in shear resistance at high temperatures. Antipode, the highest value of softening point at 5% of Cloisite-15A may indicate better improvement in resistance to deformation. Hence, this modified bitumen binder can be considered suitable to be used in the places where the climate remains hot.

Viscosity of Cloisite-15A modified bitumen increases with the increase of modifier content while keeping temperature constant. This shows increment in cohesion force which will flow resistant. To make it flow-able, more energy will be required.

An acquired value of complex modulus extent is about 114 to 439 kPa, whereas the phase angle extent is about 80o to 90o over the temperature range for unaged modified bitumen. This higher value of phase angle suggests about the more viscous material. Complex modulus and phase angle are used as predictors of hot bituminous mix performance.

Rutting resistance parameter enhanced from 1.82 to 443 kPa at almost 5% addition of Cloisite-15A, when temperature decreased from 88 to 46 oC. Rutting resistance parameter found at 52 oC and 46 oC is greater than 100 kPa. Hence, this can pertinent to resistance to rutting. Also, the results obtained in the present study are greater than or equal to 1.0 kPa as specified [3].

Addition of 5% Cloisite-15A increases the stability by about 55% but flow value decreased by only 6.25%. Whereas, no significant change in other factors. This may manifest resistance against permanent deformations such as rutting, corrugation, and local settlement.

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