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Use of Nano-Clay in Asphalt Binder Modification

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Abstract: *-In order to increase the life of bituminous pavement, performance of bitumen needs to be modified. The study was carried out to explore the addition effect of nanoclay on physical and mechanical propertieslike stiffness, fatigue resistance, strength, and aging resistance. In this paper potential of modified bitumen with nanoclay is tested, rheological test and mechanical test containing unmodified and nanomodified bitumen were carried out. Impact of nanoclay on aging and rheology of binder is discussed. The impact of nanoclay modifiers on unaged&aged bitumen was measured with Dynamic Shear Rheometer (DSR)and on asphalt mixture with the direct tensile strength, fatigue, resilience modulus test at lower temperature and dynamic creep test at high temperatures and addition of nanoclayin asphalt mixture, the results showed remarkable improvement in the nanoclay modified asphalt binder inmechanical properties & aging resistanceperformance.*

Keywords*: Asphalt Mixture, Modified Asphalt,Modified bitumen, Nanotechnology, Nanoclay, Nanomaterials.*

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I. Introduction

The use of nanomaterial in asphalt pavement, started relatively late but in recent years, many research studies have started to work on the improvement of asphalt materials with addition of nanomaterials in asphalt cement and emulsions. There are various nanomaterials which are used in asphalt modification; such as nanoclay, nanosilica, nano-hydrated lime, nano-sized plastic powders, or polymerized powders, nano fibers, and nano tubes. Nanotechnology has been explored as the solution for problems in design, construction, and utilization of functional structures. Therefore Nanotechnology, allows the design of systems with high functional density, high sensitivity, special surface effects, large surface area, high strain resistance, and catalytic effects. This paper deals with review on the nanomodification of asphalt binder with particular focus on asphalt pavements in transportation infrastructure by involving the use of nanoclay for preparation of asphalt mix for enhancing field performance of asphalt mixture. [1]Asphalt has been widely utilized as a binder in construction of road pavement, highway and freeway for a long time due to viscous properties. Bitumen is an organic mixture of various chemical compounds, whose chemical structure changes when exposed to oxygen, heat and ultraviolet (UV) light which is called as process of aging. Temperature gradient characteristic of asphalt binder affects the final performance of mixture. To improve the performance of bitumen and asphalt mixtures, the addition of modifiers such as nanoclay isbeen popular in recent years and the physical propertiesare successfully enhanced when asphalt is modified with small amount of nanoclay, on that condition that clay is dispersed at nanoscopic level.

II. Literature Review

a) Development in Clay

The essential raw material of nanoclayis montmorillonite, a wider group of minerals in clay; however,in chemistry, all clay minerals may simply be described as hydrous silicates, Clay minerals may be divided into four major groups, (as

Table **1**) mainly variation in terms of layered structure. These include the kaolinite group, the montmorillonite/ smectite group, the illite group, and the chlorite group. The kaolinite group has three members, including kaolinite, dickite, and nacrite, each with a formula of $Al_2Si_2O_5(OH)_4$.

Table 1: Major Groups of Clay Minerals

S.No	Group Name	Member Minerals	General Formula	Remarks
1	Kaolinite	Kaolinite, Dickite, Nacrite	$Al_2Si_2O_5 (OH)_4$	Members are polymorphs (composed of the same formula and different structure)

2	Montmorill-oniteor Smectite	Montmorillonite, Pyrophyllite, Talc, Vermiculite, Sauconite,Saponite, Nontronite	$(Ca,Na,H)(Al,Mg,Fe,Zn)_2 (Si,Al)_4O_{10}(OH)_2\text{-}XH_2O$	X indicates varying level of water in mineral type
3	Illite	Illite	$(K,H)Al_2 (Si,Al)_4 O_{10}(OH)_2\text{-}XH_2O$	X indicates varying level of water in mineral type
4	Chlorite	(i) Amesite, (ii)Chamosite, (iii) Cookeite, (iv) Nimite etc.	(i)$(Mg,Fe)_4Al_4Si_2O_{10}(OH)_8$ (ii)$(Fe,Mg)_3 Fe_3 AlSi_3O_{10}(OH)_8$ (iii) $LiAl_5 Si_3O_{10} (OH)_8$ (iv)$(Ni,Mg,Fe,Al)_6AlSi_3O_{10}(OH)_8$	Each member mineral has separateformula; this group has relativelylarger member minerals and issometimes considered as a separate group, not as part of clays

Source: Metallurgical and materials transections, Volume 39A, December 2008- 2805

Montmorillonite, talc, pyrophyllite, saponite, and nontronite are a few members of the larger smectiteclay group. The general formula for the chemical structure of this group is $(Ca,Na,H)(Al,Mg,Fe,Zn)_2(Si,Al)_4O_{10}(OH)_2XH_2O$.The illite group is represented by the mineral, illite, the only common clay type. The general formula is $(K,H)Al_2(Si,Al)_4O_{10}(OH)_2XH_2O$.[2]

b) Nanoclays

Nanoclays are nanoparticles of layered mineral silicates. Depending on chemical composition and nanoparticle morphology, nanoclays are organized into several classes such as montmorillonite, bentonite, kaolinite, hectorite, and halloysite. Organically-modified nanoclays (organoclays) are an attractive class of hybrid organic-inorganic nanomaterials with potential uses in polymer nanocomposites, as rheological modifiers, gas absorbents and drug delivery carriers.Nanoparticles are in platelet form with thickness of 1 nm and width of 70-150nm. This high aspect ratio of 100-150 imparts some anisotropic characteristics to form the film, and the specific surface area is of the order of 700-800 sq m/gm. Therefore loading of only a few percentage (2-7%) of nanoclay into a polymer matrix drastically alters the properties due to high interfacial interaction.[3]Common clays are naturally occurring minerals and are, thus, subject to natural variation in their constitution. Many types of clay are alumina-silicates, which have a sheet-like (layered) structure, and consist of silica SiO_4 tetrahedron bonded to alumina AlO_6 octahedron in a variety of ways. Nanocomposite properties are highly dependent on the chemical nature of organic cations and polymer chains, as well as the method used to disperse (process) the clay to form the nanocomposite. [4]Nanoclays are knownto enhance the properties of many polymers and are used to improve modulus and tensile strength, flame resistance and thermal and structural properties of many materials.

Golestani-et-al.2012 indicates that proper selection of modified clay is essential for effective penetration of the polymer into the interlayer spacing of the clay desired for exfoliated or intercalated product. In an intercalate structure, the organic component is inserted between the clay layers in a way that the interlayer spacing is expanded but the layers still bear a well-defined spatial relationship to each other. In an exfoliated structure the layers of the clay have been completely separated and the individual layers are distributed throughout the organic matrix as shown in Figure 1.[5]

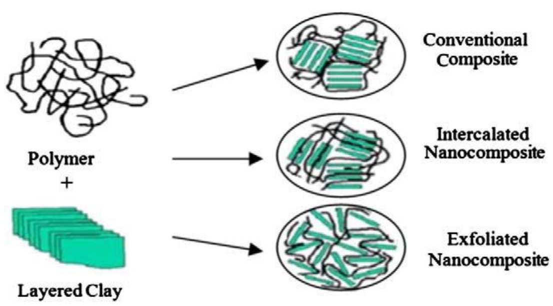

Figure 1: Schematic of structures of polymer nanocomposites (Golestani et al. 2012)

Source: Golestani B., Nejad F.M., Galooyak S.S., (2012) Performance Evaluation of Linear and Nonlinear Nanocomposite Modified Asphalts, Construction and Building Materials, 35, 197–203.

c) Chemical constituents and conversion effects of asphalt

Molecules of asphalt consist of carbon and hydrogen and have one or more element of nitrogen, sulfur or oxygen. In the asphalt molecule, carbon atoms typically get replaced by heteroatoms; the interaction of heteroatoms and the unique physical and chemical properties of various asphalt mixtures leads by the hydrocarbons.Based on the solubility, asphalt molecules are classified in two major fractions that are asphaltenes and maltenes. Aliphatics, cyclic, and aromatics are the three basic constituents of molecules of asphalt.[7]Ghile, (2006), conducted a research, suggested that modification by nanoclay in asphalt, improves some characteristics of asphalt binder and asphalt mixture .[6]Lamya M. J. Mahdi et al. (2013), indicates, when sodium montmorillonite (Na-MMT) and organophilicmontmorillonite (OMMT) blended in different percentage in asphalt, it was found that viscosity of SBS-modified asphalt increases by addition of Na-MMT and OMMT. When asphalt is modified by nanoclay, it gained lower phase angle, higher complex modulus and indicates stiffer and more elastic asphalt.Therefore, the nanoclay-modified asphaltbinders have good rutting resistance in comparison to original asphalt. [8]

d) Organic conversion of nanoclay fabrication

Montmorillonite (MMT) is the most frequently used layered silicates (nanoclay). A 2:1ratio of the tetrahedron to the octahedron sandwiching an alumina octahedron results in mineral clays of which the most common is montmorilloniteas shown in Figure 2. [1]

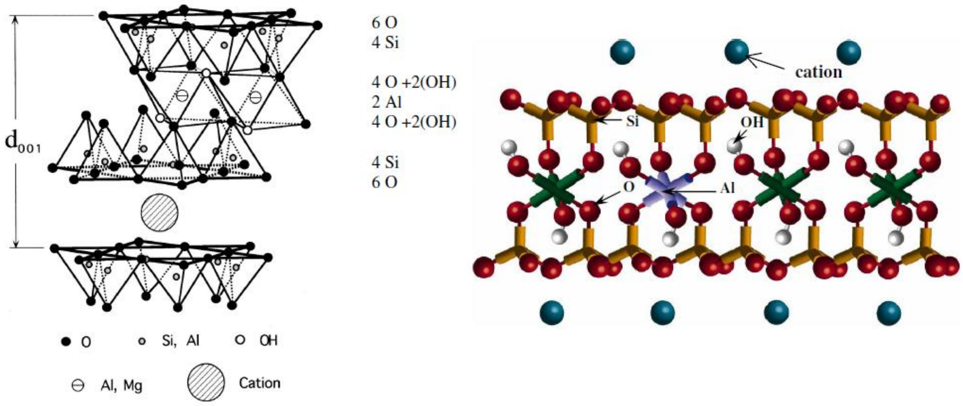

Figure 2: Schematic and Pictorial *Representation of montmorillonite*

Source: Saeed Ghaffajahromi, BehroozAndalibizade and shahramVossough (2009,)engineering properties of nanoclay modified asphalt concrete mixture, Arabian Journal for Science and engineering, Vol. 35 November 1B

By adding a small percent of nanoclay by weight,the compressive and shear strength of thermoplastic polymers are enhanced and gallery spacing increases,when the polymer penetrates between the adjacent layers of the nanoclay.[7] An exfoliated morphology occurs,if the clay platelets are completely separated due to thorough polymer penetration by various dispersion techniques.

e) Composition of asphalt nanocomposite

The wet modified nanoclay was dispersed byan organic solvent and the desired amount of coupling agent was added with continuous stirring in a water bath until the solvent was completely evaporated and then dried in vacuum at 80˚C. The wet-modified nanoclay in combination with the coupling agent was then dispersed in the asphalt. Through a high-shear mixture asphalt nanocomposite was fabricated. The asphalt was first heated to 160˚C till fluid state and the wet-modified nanoclay, A or B, was added and mixed at 2500 rpm for 3 hours to disperse the intercalation of compound of MMT nanoclay. Figure 3illustrates the chemical structure of Nanoclay. Nanoclays A and B are similar in terms of the structure.

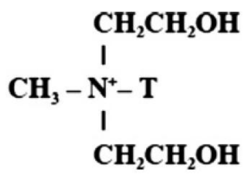

Figure 3: Chemical structure of nanoclay

Source: You Z et al. Nanoclay-modified asphalt materials: Preparation and characterization. Constr Build Mater (2010),

A higher rate of dispersion is required since nanoclays have a tendency to adhere to each other due to their inherent electrostatic charge.

III. Evaluation of nanoclaymodified asphalt

To characterize the mechanical properties of the modified and baseline asphalts prepared under controlled temperatures, the dynamic shear rheometer (DSR) was applied. The DSR measures the elastic behavior and viscosity of the binder which is represented by the complex shear modulus (G*) and phase angle (d), both are used to evaluate for rutting-resistance and fatigue cracking of the binder [7]

The rotational viscometer (RV) test was used to evaluate the difference in viscous behavior between the baseline asphalt binder and the nanoclaymodified asphalt binder. Tensile strength tests were performed on the neat binder and nanoclay-composite modified asphalt specimens. Direct tensile test (DTT) was applied to characterize the tensile strength of the modified and non-modified binders. The DTT measures the low temperature ultimate tensile strain/stress of asphalt. Dynamic shear Rheometer was used to investigate the fatigue properties of nanoclay modified asphalt binder and to avoid the steric hardening, the higher stress levels were applied in the test.Rolling Thin Film Oven Test was used to simulate short term aging of the nanoclay modified asphalt binder.[8]

IV. Influence of nanoclay in Asphalt Mixtures

Physical properties

The effect of nano clay in physical properties like penetration, softening point, penetration index and ductility of modified asphalt binder resulted in improvementas compared to base asphalt binder which has been studied by several researchers.Common types of nanoclay, organoclay (OMMT), Cloisite-15A, Nanofill-15 were used in this study. Viscosity got increased at higher temperature by adding upto 8% of nanoclay (OMMT) by M. El-Shafieet. al. which is good property of rutting resistance.[9],[10]It was seen by Zhanping You et. althat the addition of 2% of Nanoclay, in the asphalt, the rotational viscosity increase by an average of 41% for modified asphalt binder.[7]

The effect of nanoclay on the softening point of nanoclay (OMMT) and by adding 7% nanofill (Cloisite-15A) was seen by Saeed Ghaffaet. al.[1]Modified asphalts are less sensitive to high temperature changes and give a higher impact on softening temperature by an average of 4 to 13˚C and resistant to plastic deformation (rutting) compared to base asphalt by M. El-Shafie et. al.

Polacco et al. 2008 indicates that the viscosity of the styrene–butadiene–styrene (SBS) modified asphalt was increased and the phase angle decreased with increase in the stiffness while by adding the sodium montmorillonite (Na-MMT) and organophilicmontmorillonite (OMMT) nanoclays in asphalt, results are an indication that the Na-MMT and OMMT nanoclays have potential to reduce the permanent deformation or rutting of asphalt pavements.[11]

It can be seen that use of nanoclay(cloisite-15A) has high impact in reduction of ductility of asphalt binder which may be the result of chemical reactions and change in chemical structure by Ghaffarpouret. al (2009)[1]

Dynamic Rheological Properties

Several researches [7],[9]have studied the viscoelastic behavior of asphalt binders at medium to high temperatures using the Dynamic Shear Rheometer (DSR). The 4% Nanoclay-A strengthener in binder, increasedthe shear complex modulus by 125% and Z. You et. al. concluded that their convergence as the frequencyincreases from 0.01 Hz to 100 Hz. [7]The effect of OMMT modified bitumen showed high value of complex modulus through the temperature, compared with base asphalt binder and G* value of modified asphalt increase with increasing of organic montmorillonie content and phase angle δ decreased significantly, higher G* and lower δ values indicates greater stiffness property of asphalt binder which gradually increased with increasing concentration of nanoclay content was investigated by RatnasamyMuniandy et. al. [10]It can be seen from the study of Lamya M. J. Mahdi et. al. that the DSR test results increase in complex shear modulus G* and decrease in phase angle δ to the unmodified asphalt binder which gives improvement in rutting factor $G^*/\sin\delta$, that indicates the organic montmorillonie modified binder had a higher resistance to shear deformation when rutting is concerned. The aging resistance of organic montmorillonie modified binder, the dispersion of the layered silicate inside bitumen molecules that restrict the penetration of the oxygen from atmosphere, so at least delay the aging effect of binder. [8]

Direct Tension Test

Z. You et. al. conclude that use of nano clay provide reinforcement in tensile strengthpropertiesof asphalt binder and increase the potential for low temperature cracking, Z. You et. al. showed that the addition of 2% and 4% nanoclay A and nanoclay B, decrease in strain failure 78% to 64% respectively and stiffness behavior of nanoclay produced bond chain within the binderthat produced increases in toughness as increases percentage of nanoclay in asphalt binder.[7]If nanoclay increased up to 8% compared with the controlled binder, the tensile stress value showed significant increase with addition of nanoclayin asphalt binder and similar strain value were decreased with increasing the nanoclay content in asphalt binder showed by the M. El-Shafie et. al.[9]

Fatigue Properties

Saeed Ghaffe., (2009) et. al. conclude that at low temperatures (5°C), unmodified asphalt performed better under fatigue compared to nanoclay modified asphalt mixtures and average fatigue life ratio between the modified and unmodified asphalt mixtures is about 93% for nanofill-15 and about 80% for Cloisite-15A and also at high temperatures (25°C), for all loading conditions, the modified asphalt mixture performed better under fatigue when compared to the unmodified asphalt mixtures. [1]Shaopeng Wu, et. al. (2010), et. al indicated that According to the linear relationship, classical stress fatigue equation $N_f = K(1/\tau)^n$ Where, N_f is the loading time when the sample is failure and τ is the shear stress, K and n are material parameters. The smaller value of N_f meant the better fatigue resistance. OMMT modified binder had smaller than original asphalt, which showed that the OMMT modified binder exhibited better fatigue resistance.[15]Generally, lower $G^*/\sin\delta$ values are considered to fatigue cracking resistance. From the results, MMT modified asphalt binder has slightly lower resistance in term of fatigue cracking at intermediate temperature compared to the base binder, predicted by MohdEzree Abdullah, et. al. (2014).[12]

Storage stability

MohdEzree Abdullah et. al. showed that difference between softening point of the top and the bottom of control sample are 0.47% and meanwhile, nanoclay modified asphalt with WAA are 0.86% . It seems to be the sample has stable storage, which is a very important parameter for modified polymer asphalt.According to Stock's law, during storage at elevated temperatures, SBS-modified asphalt binder was not stable when stored at high temperature after one hour later storage, When the SBS/OMMT content in the triple nanocomposite was 100/50, the storage stability was significantly improved.[12]

V. Feasibility of Using Nano-asphalts in Cold Regions

According to Khodaii's research, the addition of nanoclay modifiers to bitumen has increased the indirect tensile strength and improvement in aging resistance. At high temperature, elasticity of the modified bitumen has increased and the dissipation of energy decreased due to claydispersion at the nanoscopic level. [13]

Durability and the service life of the asphalt pavements get improved by above properties and made the bitumen easy to work in high temperature areas, because viscosity increases. Some studies have shown that nanoclay modified asphalt bitumen has an increased anti-aging and anti- deformability properties under low temperature. One important advantage of nanoclay modified asphalt binder is its improvement in tensile strength and reduction in susceptibility to water indicated by Goh et al, 2011.[14]This is very useful in cold regions where many asphalt paved roads are susceptible to snow.

VI. Benefits of Nanoclay in Asphalt Mixtures

In general, in particular to asphalt and asphalt mixture properties, Nanoclay asphalt mixture has the following known benefits:-

- Improve the storage stability in polymer modified asphalt
- Increase the resistance to UV aging
- Reduce the moisture susceptibility under water, snow and deicers
- Improve the properties of asphalt mixtures at low temperature
- Improve the durability of asphalt pavements
- Save energy and cost
- Decrease maintenance requirements

VII. Conclusion

Adding Nanoclay in asphalts normally increases the viscosity of asphalt binders and improves the rutting and fatigue resistance of asphalt mixtures. One specific type of montmorillonitenano-clay doesn't affect the stiffness and viscosity of asphalt binder. Using Nano-particles can improve the storage stability of polymer modified asphalts.Nano-modified asphalt performs well in cold regions with many benefits by optimization of nano-materials in asphalt binder. From the DSR test results, it concludes, the Phase Angle (δ) decreased and Complex Shear Modulus (G^*) increased compared to the base asphalt which led to improvement in Rutting Factor ($G^*/\sin\delta$), as the quantity of nanoclay (OMMT) increased in asphalt binder result in dispersion of nanoclay particles in bitumen which made it less deformed and consequently reduced rutting. OMMTs modified asphalt delays the aging effect and reduce the deformation and rutting distress.Nanoclay modified asphalt binder exhibits better fatigue resistance and high temperature performance to base asphalt binder and by adding low percentages of nanoclay(cloisite-15A and nanofill-15) to bitumen changes rheological properties, decreases penetration and ductility, and increases softening point and aging. The cloisite-15A and nanofill-15 modifications increase the stiffness and improve the rutting resistance, indirect tensile strength;however, fatigue performance decreases at low temperatures.

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