Identification Effect of Nanoclay on Engineering Properties of Asphalt Mixtures

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ABSTRACT

Nanoclays are new generation of processed clays of interest in a wide range of high performance composites. In other words, nanoclay is defined as a clay that can be modified to make the clay complexes compatible with organic monomers and polymers. Here, it can be said that the polymeric nanocomposites are among the most exciting and promising classes of materials discovered recently. A number of physical properties are enhanced successfully when a polymer is modified with small amount of nanoclay on condition that the clay is dispersed at nanoscopic level. This research has accomplished a comparative rheological test on binders as well as a mechanical test on asphalt mixtures containing unmodified and nanoclay modified bitumen. For that matter, two types of nanoclay were used: Nanofil-15 and Cloisite-15A. While, the rheological test on binder were penetration, softening point, ductility and aging effect, mechanical test on asphalt mixture were marshal stability, indirect tensile strength, resilient modulus, diametric fatigue and dynamic creep test. Test results show that, nanoclay can improve properties like stability, resilient modulus and indirect tensile strength and possess better behavior compared with unmodified bitumen under dynamic creep although it does not seem to have beneficial effect on fatigue behavior in low temperature. Optimum binder content and void in total mixture (VTM) increase by adding nanoclay to bitumen.

KEYWORDS

Asphalt Mixture, Bitumen Modifies, Nanoclay, Mechanical properties.

1. INTRODUCTION

Temperature susceptibility characteristics and the 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, addition of modifiers such as polymers have become popular in recent years. As a matter of fact, polymeric nanocomposites are one of the most exciting of materials discovered recently and physical properties are successfully enhanced when a polymer is modified with small amount of nanoclay on condition that the clay is dispersed at nanoscopic level [1].

Many studies have been conducted on nanoclay modified polymers, though, relatively little published information is available about nanoclay modified bitumen. Material variables, which can be controlled and can have a profound influence on the nature and properties of the final nanocomposite include the type of clay, the choice of clay pre-treatment, the selection of polymer components and the way in which the polymer is incorporated into the nanocomposite [1]. thus subjected to natural variation in their formation. The purity of the clay can affect the final nanocomposite properties. 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. A 2:1 ratio of the tetrahedron to the octahedron results in mineral clays, the most common of which is montmorillonite (Figure 1). The thickness of the montmorillonite layers (platelets) is 1 nm with high aspect ratios, typically 100-1500 [2]. The expansion of montmorillonite is determined by their ion (e.g. cation) exchange capacities, which can vary widely. One of the characteristics of these types of clay is the cation exchange capacity (CEC), which is a number for the amount of cations between the surfaces. The CEC of montmorillonite ranges from 80 to 120 meq/100g (milliequivalents per 100 grams) whereas, kaolinite have CEC values ranging between 3 and 5.

The expansion pressure of montmorillonite is very high in which sodium ions constitute the majority of the adsorbed cations (called Na-montmorillonite), leading to exfoliation and dispersion of the crystal in the form of fine particles or even single layers. When Ca²⁺, Mg²⁺ and ammonium are the dominant exchangeable cations,

Common clays are the naturally occurring minerals and

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dispersion is low and the size of the particle is relatively large. Separation of clay discs from each other results in a nanoclay with a huge active surface area (it can be as high as 700 to 800 m² per gram). This helps an intensive interaction between the nanoclay and its environment (bitumen in our case). The process to realize the separation (surface treatment) depends upon the type of material to be mixed [3].

A necessary prerequisite for successful formation of polymer-clay nanocomposite is therefore alteration of the clay polarity to make it 'organophilic'. To achieve fine dispersion, mechanical forces alone are not sufficient; rather there should be a thermodynamic driving force to separate the layers into the primary silicate sheets. This thermodynamic driving force is being introduced by inserting a certain coating of surfactants (an agent such as detergent, which reduces surface tension) on each individual layer [4]. These surfactant molecules increase the layer distance, improve the compatibility with the polymer and can give an increase in entropy because they can mix with the polymer. Organophilic clay can be produced normally from hydrophilic clay by ion exchange with an organic cation. The organic reagents are quaternary ammonium salt with alkyl chains such as 12aminododecanoic acid (ADA), octadecanoic alkyl trimethyl quaternary ammonium salt. The reaction process is described as:

$$\begin{aligned} M\text{-}CLAY + CH_3(CH_2)_n NR_3 X &\to CH_3(CH_2)_n NR_3 \text{-}Clay + MX \\ (R = -H, -CH_3; X = -Cl, -Br, -I; M = Na^+, Ca^{2+}, Mg^{2+}) \end{aligned}$$

Addition of a positively loaded surface active material will in this case form an ADA layer around each clay disc, which changes from a hydrophilic into a hydrophobic disc. These modified clay discs will be separated automatically in water and can be used as nanoparticles. Figure 2 shows the surface treatment process of the nanoclay material [5]. The proper selection of modified clay is essential to ensure effective penetration of the polymer into the interlayer spacing of the clay and as such resulting in the desired exfoliated or intercalated product. In 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 (Figure 3), the layers of the clay have been completely separated and the individual layers are distributed throughout the organic matrix [6].

With dispersing nanoclay in a thermoplastic material (a material that is plastic or deformable, melts to a liquid when heated, and freezes to a brittle, glassy state when cooled sufficiently) stiffness and tensile strength, tensile modulus, flexural strength and modulus and thermal stability will increase [7].

Structure of bitumen and polymers are different with bitumen being a very complex polymer and not stable. The structure of asphaltenes on bitumen depends on the temperature and chemical composition of the binder. The asphaltenes are highly associated to each other in gel type, but they are not associated to each other in sol type, and as such have poor network and lower asphaltenes proportions and need different approaches of clay and bitumen interaction that probably limit the successes obtained in bitumen-nanoclay modifications.



Many researches were conducted on nanoclay modified polymers, but little published information is available about nanoclay modified bitumen. Some researches were also performed on bitumen modification by polymer materials such as SBS (Styrene Butadiene Styrene Block Copolymer), SBR (Styrene Butadiene Rubber Latex) and EVA (Ethyl Vinyl Acetate). A study by Chen and others on SBS shows that, SBS improves the rheological properties of asphalt binder due to the polymer network formation in the binder. This network forms in two stages: at low concentrations, the SBS acts as a dispersed polymer and does not significantly affect the properties; at higher concentrations, local SBS networks begins to form and are accompanied by a sharp increase in the complex modulus, softening point temperatures, and toughness[8]. Radziszewski studied the mechanical properties of asphalt mixtures containing elastomer, plastomer and fine rubber modified binders. His concluded that asphalt mixtures behave differently in terms of rutting and creeping, when it is being exposed to simulated short-term and long-term ageing. Here, ageing causes more stiffness with unmodified binder mixtures than with polymer or rubberized bitumen modified binder mixtures. Permanent deformation depends on the type of asphalt mixture and the binder used in the process. Asphalt concrete with rubberized bitumen, asphalt concrete with 7 % polymer modified binders and SMA as well as Superpave mixtures with unmodified binders appear to be the most resistant to the permanent deformations after long-term laboratory ageing [9].

Recently, nanoscale inorganic fillers have attracted much of the attentions as theoretically these significantly improve the properties of pristine polymers such as bitumen with relatively small percent of additive [10-15]. Nanoclays are micro-scale fillers which possibly make polymers efficient as filler reinforcements. Ghile performed mechanical tests on asphalt mixture modified by cloisite. The result showed that nanoclay modification improves mechanical behavior properties of mixture such as indirect tensile strength, creep and fatigue resistance [16]. Chow et al, investigated surface modified montmorillonite nanoclay and compatibilizer, and came to the conclusion that the strength and stiffness of polyamide polypropylene nanocomposites improves due to synergistic effects of surface modified montmorillonite nanoclay and compatibilizer [17]. Yasmin et al found that the addition of Nanomer I.28E and Cloisite 30B into some pure epoxy polymers produce materials with higher elastic modulus than that of the pure epoxy [18].

2-Material and Methods

The aggregates used in this study were crushed limestone aggregates with 12.5mm nominal size (according to Pavement Guidelines in Iran) and limestone mineral filler. Physical properties of both coarse and fine aggregate, together with mineral filler are given in Table 1 and aggregate gradation is shown in Figure 4. Bitumen had 60/70 penetration grade (AC-10) whose properties are shown in Table 2. Two types of common nanoclays used in this research are Cloisite-15A and Nanofil-15. Tables 3 & 4 highlight the properties of nanoclays.

Empirical tests were used for modified and unmodified bitumen to show penetration, ductility, softening point. Marshall Test and performance-based tests such as indirect tensile strength, resilient modulus test, fatigue resistance test and dynamic creep test were carried out on the mixture samples. Specimen preparation and compaction were carried out in accordance with ASTM D1559 [19]. All performance-based tests were done on marshall size samples.



Figure 4: Aggregate grading

Table 1: Aggregate Properties			
Coarse aggregate (ASTM C 127)			
Bulk specific gravity, g/cm3	2.698		
Apparent specific gravity, g/cm3	2.714		
Absorption, %	0.33		
Fine aggregate (ASTM C 128)			
Bulk specific gravity, g/cm3	2.683		
Apparent specific gravity, g/cm3	2.735		
Absorption, %	0.62		
Filler (ASTM D 854)			
Apparent specific gravity, g/cm3	2.743		
L.A. Abrasion, %, (ASTM C 131)	23.57		
Polishing value (BS 813)	0.47		

Table 2: Bitumen's Properties				
Softening point		54		
Penetration grade @25°C		63		
Flash Point		243		
Penetration index		+0.4		
Ductility @ 25°C		>100 Cm		
Fraass Breaking Point		14		
Loss of Heating		0.05 %		
Density		1.035		
-	at 50°C	250000		
Viscosity	at 60°C	100000		
-	at 72°C	20000		
Maltens		75 %		
asphaltenes		27.2 %		

Table 3: Properties Cloisite-15A				
Treatment/Properties:		Cloisite-15A		
Organic Modifier		MT2EtOH (methyl,		
		tallow, bis-2-		
		hydroxyethyl,		
		quaternary ammonium)		
	Base	Montmorillonite		
Modifie	er Concentration	90 meq/100g clay		
	Moisture	< 2%		
Weight Loss on Ignition		30%		
Anion		Chloride		
Particle Sizes	10% less than:	2μm		
	50% less than:	6µm		
	90% less than:	13µm		
	Color:	Off White		
Loos	e Bulk, kg/ m ³	230		
Packe	d Bulk, kg/ m³	364		
De	ensity, gr/cc	1.98		
X Ray Results:		d = 18.5Å		
Plastic Index		88%		

 Table 4: Properties Nanofil-15



3- Empirical Rheological Tests and Results

Empirical rheological tests on unmodified and modified bitumen with different nanoclay content were penetration, softening point and ductility tests. The modification of bitumen with nanoclay was performed at nanoscale level by thermodynamic driving force. The empirical tests were performed following the standard test procedures. The nanoclay contents selected during the above test were 0.2%, 0.4% and 0.7% by weight of bitumen. The results are shown in Figs. 5, 6 and 7.

From these results, it must be concluded that nanofil-15 modification brings little change on penetration and softening point of the unmodified 60/70 pen bitumen. A few percent of nanofil-15, increased penetration at 25 but increasing Cloisite-15A content led to decrease in penetration. Nanofil-15 have little effect on softening point; because the softening point increases only by 3% with the addition of 7% nanofil,. In contrast, Cloisite-15A has relatively higher effects on penetration and softening point of bitumen. With the increasing Cloisite-15A content, penetration decreases (from 63 to 45) and softening point increases from 54 to 61 depending on Cloisite-15A content. Also, both the nanoclays reduce ductility of binder but Cloisite-15A has more pronounced effect in reducing ductility. This behavior may be the result of chemical reaction and change in chemical structure as also pointed by Chile [16].



Figure 5: Penetration Test Results and Nanoclay Content



Figure 6: Softening Point Test Result and Nanoclay Content



Figure 7: Ductility Test Result and Nanoclay Content When bitumen gets older, it becomes harder, retained penetration (RP) and increase softening point (ISP) values as defined below:

 $RP(\%) = \frac{aged \ penetration}{unaged \ penetration} \times 100$

 $ISP(^{\circ}C) = (aged \ softennig \ point-unaged \ softennig \ point)$

A lower RP value and higher ISP reflect more ageing of the binder. Long-term ageing was performed for 20 hours at 90°C and atmospheric pressure. The retained penetration and increase in softening point were computed and presented in Figures 8 and 9. It can be observed that there are some improvements in the resistance to ageing in the long-term due to the nanofil-15 modification and therefore probably suffer less when contact with hot air or hot oxygen.



Figure 8: Retained Penetration and Nanoclay Content



Figure 9: Increase in Softening Point and Nanoclay Content

4- Mechanical Tests on Asphalt Mixtures

4.1. Specimen Preparation

The specimens prepare for the different tests were marshall tablets with an average height of 60–65mm and 100-102 mm diameter (ASTM D1559) [19]. Compaction of dense mixture specimens were by 2*75 blows. As mention before, since Cloisite-15A reduces the viscosity of modified binder, it is not fluid enough at the normal mixing temperature used for the standard binder (140°C).

Hence, a high mixing temperature needed for the preparation of the modified mixtures and as such the temperature was increased to 155°C. The Cloisite-15A content was 0.2%, 0.4% and 0.7% according to the weight of bitumen.

During the preparation of specimen, the modified binder smelled differently with more viscous at 185°C. Modified binder was relatively less sticky to the mixing pan and to the molds compared to the specimens of the standard mixes. All these tests were performed in a closed and temperature controlled cabinets. In addition, all specimens selected for the different tests were stored in a temperature controlled cabinet to the target temperature for a minimum of three hours before commencing any test. Table 5 shows the loading control and input parameters used in tests.

4.2. Marshal Stability, Flow and VTM

To compare the effects of different nanoclays in the mixes, marshall stability, optimum binder and VMA test results are shown in Figures 10, 11 and 12. It was found that marshall stability, optimum binder and VMA increase with the addition of nanoclays.

It is worth mentioning that nanoclay is active filler that improves strength properties of bitumen. By adding 2% Cloisite-15A, stability increases by 15% but nanofil-15 increases the stability to about 6%. Optimum binder increases due to large surface area of nanoclay modified mixture. Even 1 % nanoclay could increase the optimum binder by 0.3-0.35% as compare to unmodified mixtures. Further, as compared to nanofil-15, Cloisite-15A reduces the viscosity of modified binder thus, in compaction process, nanofil mixtures compact better than cloisite, and the VTM in cloisite mixture increases as well.

	Loading Properties		Displacement	Duplication	Temperatur e
Marshal stability	Displacement Controlled		Vertical	3	60 ⁰ C
Indirect Tensile Strength	Displacement Controlled, 0.85mm/s		Vertical	3	5, 25, 40°C
Resilient Modulus	Pulses Number	5			
	Pulse Form	Half Sine, 0.5HZ, Loading Period, 500ms Recovery Time, 1500ms	Horizontal	3	5, 25, 40°C
Dynamic Creep	Compressive Stress Controlled, 100, 200, 300, 400KPa				
	Pulse Form	Half Sine, 1HZ Loading Time, 200ms Recovery Time, 800ms	Vertical	2	40,50°C
Fatigue Test	Stress Contro	lled, varying between 150-1800 KPa			
	at at 2:	Half sine Pulse, Loading Period, 150ms 5°C, without Rest Period 5°C, with 50ms Rest Period	Vertical	2	5, 25°C

Table 5: Loading Properties and Test Temperatures

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Figure10: Stability and Nanoclay Content



Figure11: Optimum Binder and Nanoclay Content



Figure 12: VTM and Nanoclay Content

4.3. Indirect Tensile Strength Test

The tests were conducted at three different temperatures (5°C, 25°C and 40°). The indirect tensile strength has been computed at the maximum compressive force measured during the test at failure. Results in Figures 13 and 14 show increasing strength at different temperatures. Results show that modified specimens have higher strength at all test temperatures. Increasing Cloisite-15A content, from 2% to 7%, augment the indirect tensile strength values from 8% to 40% and the percentage of increase is seen larger for the higher testing temperatures. There seem to be no major difference in the effects of added nanofil and cloisite when these were tested at 5 or 25°C. However, such test at 40°C or specially when 7% nanoclay is added, Cloisite-15A increased the IDT to almost two fold compared to nanofil-15

In the ITS test, the area under force versus vertical displacement curve led the dissipated energy to crack or fracture the specimen. Two fracture energy values can be defined as: *Fracture energy until* failure; the energy dissipated before the specimen could start failing and, *Total Fracture energy*; the total energy dissipated in order to destroy the specimen completely (Figure 15).

Figs. 16 & 17 show that additions of nanoclay increase the total energy and the fracture energy as defined above. This increase in the total energy ranges between 55% and 95% for nanofil and 26% to 2% for cloisite. It is observed that, modified mixtures need more energy to start the cracking initiation at low temperatures (5°C), as compared to the standard mixture but when the cracks gets started, less energy is required to destroy the specimen. The fracture energy reduces at high temperature (40°C) due to visco-elasto-plastic behavior of bitumen.



Figure 13: Increase in Strength and Temperature for Cloisite-15A



Figure 14: Increase in Strength and Temperature for Nanofil-15





Figure 16: Total Fracture Energy for Cloisite-15A



Figure 17: Total Fracture Energy for Nanofil-15

4.4. Resilient Modulus Test

The present study applied the resilient modulus (Mr) test method detailed in the ASTM (D-4123). The specimens were tested at 5, 25 and 40°C respectively and 0.5 HZ was the loading frequency selected for each temperature. Pulse period and recovery time were set at 500 and 1500 ms, respectively. Resilient modulus depends on the test temperature and the loading frequency [20]. Figs. 18 & 19 show comparison of the average resilient modulus between Cloisite-15A and nanofil-15 modified mixtures with unmodified dense mixture for each test temperature and their values are given in tables.

Increasing stiffness as plotted in Figs. 18 & 19 shows that nanoclay modified mixture has greater stiffness than the unmodified mixture at all test temperatures. Depending on the test temperature, stiffness varies from 8% to 40% for Cloisite-15A and from 3% to 18% for nanofil-15, with the addition of 2% to 7% of nanoclay modification.



Figure 18: Resilient modulus and Cloisite Content



Figure 19: Resilient modulus and Nanofil Content

4.5. Dynamic Creep Tests

Creep test is used to evaluate the permanent deformation of the unmodified and modified mixtures at high temperatures. Accumulated permanent axial strain has three distinct stages with increasing number of cycles. *Primary stage*, with relatively large deformation during a short number of cycles; *Secondary stage*, when the rate of accumulation of permanent deformation remains constant and; *Tertiary stage*, the final stage when the rate of deformation accelerates until lead to the complete failure. The last stage is usually associated with the formation of cracks, and as such the start of the tertiary stage is usually represented by the flow number FN. This number is used as a rutting resistance indicator of asphalt mixtures (Fig. 20).



Figure 20: Cumulative permanent strain under loading cycles

In this test, only modified mixture was used with 7% nanoclay and the result was compared with the unmodified mixture. The loading pulse was half sine with duration of 200ms and a rest period of 800ms. The specimens were tested at the temperature of 40 and 60°C and results are show in Figs. 21 & 22.

At 40°C (Fig. 21) temperature, it can be seen that none of the modified and unmodified mixtures reach the tertiary stage before 6500 load repetition, for the applied load levels of 100KPa and 200KPa. As a matter of fact, the unmodified mixture reached the tertiary stage at about 3200 pulses, for the applied load levels of 400KPa. The modified mixture could not reach to the tertiary stage earlier than 6500 pulses. Excessive deformation was seen in unmodified mixture at 400KPa, and specimens failed before the 6500 maximum pulse limit. Modified mixture did not show shear deformation failure until 6500 pulse and the primary deformations of unmodified mixture are bigger at all applied load levels compared to those of the modified mixture samples.

At 50°C (Fig. 22), it can be seen that, after the 6500 pulses, none of the nanoclay modified mixtures reach the tertiary stage for applied load levels of 100KPa and 200KPa. All types of mixtures reach the tertiary stage if applied load was 300KPa. However, the unmodified mixtures reached to that stage after about 3000 pulses as against the nanofil-15 and Cloisite-15A modified mixtures that reached the tertiary stage after about 4100

and 5500 pulses, respectively. Unmodified mixture specimens possessed bigger deformations at the primary stage and failed by excessive deformation about 3800 pulse counts whereas the Cloisite-15A and nanofil-15-A modified mixtures specimens at 300KPa loading did not fail completely at 5300 and 6500 pulse counts, respectively.

4.6. Fatigue Resistance Test

Indirect tensile test with diametric compressive load was used to evaluate the fatigue resistance of unmodified and modified mixtures. A constant repetitive load was applied and the vertical deflection was measured with respect to the pulse counts. The fatigue life is defined as the number of load repetitions at specimen fracture. Like the creep tests, only modified mixture with 7% nanoclay was used to compare with the unmodified mixture. Fatigue resistance test was performed at 5°C and 25°C and results are shown in Figs. 23 & 24. The result shows a linear fit between N_f and σ at 5 and 25°C. The R² values are very close to 1 for all mixture types. The slope of the fatigue line at 5°C for the modified mixture while unmodified mixture while unmodified mixture had smaller slope.

According to the results found in Fig.23, the unmodified mixture performed better under fatigue at low temperatures (5°C) and almost for all loading conditions, compared to nanoclay modified mixtures. The average fatigue life ratio between modified and unmodified mixtures for nanofil-15 and Cloisite-15A is about 93% and 80%, respectively. At lower loading stress, the fatigue life ratio for the modified mixture is about 1.0 and at higher loading stress, the ratio decreases to 85% (Fig.23). At high temperatures (25°C), the modified mixture performed better under fatigue for all loading conditions, compared to the unmodified mixtures.

The average fatigue life ratio of the modified mixtures for Cloisite-15A and nanofil-15 is about 1.70 and 1.45, respectively. The fatigue life ratio depends upon the stress level and as such, the life ratio decreases at high stress levels (Fig. 24). This could be the result of rest period of loading applied in the tests at 25° C.





Figure 22: Dynamic Creep Test at 50°C



Figure 23: Fatigue test Result at 5°C



Figure 24: Fatigue test Result at 25°C

5. Discussion and Conclusions

Tests performed on binders and dense asphalt mixtures proved that the nanoclay modifications helped to increase the stiffness and improve the rutting resistance. When bitumen is modified with small amount of nanoclay; its physical properties are successfully enhanced on the condition that the clay is dispersed at nanoscopic level. Nanoclay materials possess big aspect ratio and large surface area and their particles are also not uniform in size and arrangement. Nanofil-15 particles are curly and smaller in size, compare to the cloisite-15A particles. The plastic limit shows that nanoclay is the expansive type of clay materials. Low percent of nanoclay in bitumen leads to the changes in rheological parameter, the decrease in penetration and ductility as well as the increase in softening point and aging. Tests performed on binders and dense asphalt mixtures show that the cloisite-15A and

nanofil-15 modifications increase the stiffness and improve the rutting resistance, indirect tensile strength, resilient modulus and marshall stability but fatigue performance decreases at low temperatures.

By adding nanoclay, stability increases by 6-15% and optimum binder increases due to large surface area of nanoclay modified mixture. Indirect tensile strength test results show that at high temperatures (40°C) strength values up to 40% increase but there is no major difference in the effects of added nanoclay at 5 or 25°C. Depending on the test temperature and nanoclay content, stiffness increase from 8% to 40% for Cloisite-15A and from 3% to 18% for nanofil-15. Creep test results at 40 °C and 60 ⁰C show that on modified mixtures, shear deformation failure occur at higher pulse compared to unmodified mixtures. Primary deformations of unmodified mixture are bigger at all applied load levels compared to the modified mixture samples. Unmodified mixture performed better under fatigue at low temperatures (5°C) but at high temperatures (25°C), the modified mixture performed better under fatigue for all loading conditions, compared to the unmodified mixtures. This results show that adding nanoclay can increase brittle behavior of bitumen.

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