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IMPROVEMENT PERFORMANCE OF MODIFIED ASPHALT BY ADDING CLAY/NANOCLAY

Eman A. Emam

Department of Petroleum Refining Eng. and Petrochemicals, Faculty of Petroleum and Mining Eng., Suez University, Suez, Egypt

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Abstract

Asphalt is a byproduct of crude oil during petroleum refining process and it is a complex heterogeneous mixture of hydrocarbons. It has many properties, which can be altered due to exposure to heavy loads and unfavorable environmental conditions such as heat, oxygen and ultraviolet light, resulting the reduction of the quality and performance of asphalt. There are many applications of asphalt such as paving and roofing. To maintain of the quality and obtain the best performance of asphalt for a long time, the use of asphalt modifiers may help address various problems of asphalt applications. Clays are cheap and abundant in nature, mostly consist of aluminosilicates. Clays can use as a asphalt modifier in macro and nanoscale. The present paper reviews the using of clay as a modifier to improve the performance of asphalt. This review summarizes the studies of the modification of asphalt by using clay, nanoclay, clay/nanoclay as a second modifier with polymer, clay/nanoclay with other materials. Results proved that, the overall performance of clay/nanoclay modified asphalt improved the different properties of asphalt such as increased softening point and viscosity, decreased penetration, improved rutting and fatigue cracking resistance, etc. Furthermore, many other modifiers can combine with clay/nanoclay in the manufacture of asphalt to lower bitumen viscosity, reduce carbon emissions, lower energy consumption, enhance the aging resistance and improve bitumen workability.

***Keywords**: Asphalt, Modified asphalt, Clay, Nanoclay, Montmorillonite, Polymer, Nanocomposite.*

1. Introduction

Asphalt (or bitumen) is a byproduct found from crude oil during petroleum refining process. Asphalt composes of a complex heterogeneous mixture of hydrocarbons [1]. It is a dark brown to black, cement-like semisolid or solid or viscous liquid. It has good adhesive and viscoelastic properties, for example, at high temperatures it flows, at room temperature it is flexible, and at lower temperatures it is rigid and brittle [1-2]. There are several applications of asphalt such as construction of roads, paving of airfield, waterproofing agent, thermal and acoustic insulation, corrosion protection of metals by coating, etc. while, the main division of applications are about 90% for paving and the remaining 10% for roofing material [1,3].

During the applications, asphalt exposes to different loads and environmental conditions such as heat, oxygen and ultraviolet light, etc., for a period of time, its chemical and physical properties can change, resulting the reduction of the quality and performance of asphalt [3-5]. Different and repeated loads can decrease strength because of fatigue [6]. Oxidation causes pavement degradation and consequent moisture damage to binder, which influences the aging of asphalt and leads to cracking [5,7]. Rainwater can affect the adhesion between asphalt and the aggregate, while the brittleness of asphalt at low temperatures often causes thermal cracking [2,8]. Asphalt becomes soft with a low stiffness and susceptible to permanent deformation at high temperatures [8]. All these factors can lower the performance of asphalt [1-2]. Furthermore, asphalt cost continuously increases due to the reduction of petroleum reserves [9]. As a result, modification and reinforcement of asphalt are essential. In the asphalt industry many modifiers can be used with the goal of improving asphalt performance, reducing carbon emissions, save energy consumption, and cost, improving the durability of asphalt and decrease maintenance requirements [1-4,8-10].

Many modifiers can be used in the manufacture of asphalt such as polymers, clay, nanoparticles [1-4,8-9]. Clays include montmorillonite (MMT), vermiculite, rectorite and kaolinite, they are cheap and abundant in nature, mostly consist of aluminosilicates. The separation of the clay layers produces a nanoclay with a special active specific surface area (700-800 m^2 g^{-1}) [1,11]. The addition of nanoparticles like nanoclay in asphalts increases the viscosity and enhances the rutting and fatigue resistance of asphalt [6-7]. Nanoclay can also be used as the second modifier in polymer modified asphalts either as an agent to enhance the polymer physical and mechanical properties or as a filler to decrease the used amount of polymer [8,12-15]. Other properties could be improved such as thermal and storage stability, the aging resistance, high gas barrier and flame retardation [3,10-11]. The aim of this review is to summarize the results of studies to improve the performance of the modified asphalt by adding clay, nanoclay, clay/nanoclay as a second modifier with polymer, clay/nanoclay with other materials.

2. Experimental procedures

2.1. Materials

Asphalt conventional penetration grades were used in the most studies. Several types of clays are used to modify asphalt such as kaolin [16], sodium bentonite [6] and vermiculite [12]. Montmorillonite (MMT) is the most important clay of bentonite. MMT is abundantly available in nature and with some modifications it can be used to generate different forms of nanoclays such as Cloisite-15A [1,5,17,18], Cloisite 20-A [19], Cloisite-30B [10], Nanofil-15 [1], and Nanofil-116 [5]. Cloisite and Nanofil are the common types of nanoclays which are most applicable as the modifiers of asphalt [1,5,10,17-19]. Several types of polymers can be used to modify asphalt and produce nanocomposites with the nanoclay, such as styrene-butadiene-styrene (SBS) [8,14-20], styrene-ethylene-butylene-styrene (SEBS) [21], styrene-butadiene-rubber (SBR) [22], ethylene-vinyl-acetate (EVA) [13], and polyethylene [23].

2.2. Preparation of modified asphalt

Generally, some nanoparticles are known to aggregate during mix with the asphalt [24]. Some researchers showed that the properties of asphalt such as stiffness and hardness could be improved depending on the mixing procedure, temperature and clay concentration [4,18,19,24-26]. In order to obtain a homogenous mixture of the asphalt and modifier, it is essential to select the appropriate mixing process [24].

To prepare the clay/nanoclay modified asphalt, the base asphalt is firstly heated to about 140°C and stirred for about 5 min [4]. Then, the temperature is raised for a wide range from 150 to 180°C according to the nature of the research [4,18,19,26], for about 2 or 3 hrs to reach a fluid state. The heated base asphalt is then stirred with a high speeds and heated during the slowly addition of the different percentages of clay/nanoclay. The temperature and mixing speed and time are adjusted to control the quality of the modified asphalt. Common types of mixers are mechanical, high shear, and ultrasonic. The prepared asphalt is left to cool at room temperature.

To prepare the modified asphalt with clay/nanoclay and polymer, in general, there are two mixing procedures refer to the different mixing sequences. The first one is the physical mixing by adding the first modifier (polymer or clay) to the asphalt, then adding the second modifier (clay or polymer) to the mix. While in the second one the polymer is primarily mixed with clay, thereby forming a polymer nanocomposite, then the nanocomposite is added to the base asphalt [12,19,27].

2.3. Asphalt tests

There are many numbers of tests to evaluate the different properties of modified asphalt, the most common tests are listed as the following:

- Physical properties, can be measured by: penetration, softening point, ductility, viscosity [17-18];
- Rheological properties, can be measured by: dynamic rheological parameters, dynamic shear rheometer (DSR) [1,14,17-18,28];
- The ageing index, can be measured by: Fourier Transform Infrared Spectroscopy (FTIR) [14,28];
- Mechanical properties, can be measured by: Marshall stability test [1,16-17,29];
- Storage stability test, can be measured by the difference between softening point of the top and the bottom sections of the sample, could be regarded as storage stable blend [1,3,27,30];
- Microscope methodology, can be measured by: Atomic Force Microscopy (AFM), X-ray diffraction (XRD), Transform Infrared Spectroscopy (FTIR) [26];
- Moisture resistance [29].

3. Results and discussion

3.1. Clay modified asphalt

Many types of clays can be used as asphalt modifiers [6,12,16,31-32]. Bentonite clay is a natural material with high ductility. The low cost of bentonite makes it logically, economically and industrially attractive for wider applications [33]. Shahabadi [6] studied to modify AC 60-70 asphalt binder with sodium bentonite clay (BT) and organically modified sodium bentonite (OBT) (in the concentrations range from 0 to 6 wt%) by melt processing under sonication and shearing stresses. The suggested structures of BT and OBT modified asphalt were an intercalated and exfoliated, respectively. The result proved that BT and OBT modified asphalts increased softening point and viscosity, while ductility reduced more by BT as compared to OBT. Adding BT and OBT significantly improved the dynamic rheological properties through higher complex modulus, lower phase angle and higher rutting parameter [6]. Asphalt cement tests were investigated the characteristics of modified bitumen using about 10 to 30% content of BT [34]. Results showed that the addition of BT improved the mechanical properties and Marshall parameters of bitumen. At adding 20% BT (wt% of bitumen), it is considered as optimum BT content and leaded to increase softening point and decrease penetration, and ductility [34]. In another study, addition of BT can increase the rutting resistance and the shear strength of hot mix asphalt (HMA). Moreover, the fatigue life of modified asphalt mixtures was longer than that of the conventional HMAs [33]. Furthermore, the dissipated energy of the bitumen containing 10% and 15% of BT is higher than the control bitumen. However the increasing trend declined at higher percentages of BT [35].

The most important clay mineral of bentonite is montmorillonite (MMT). Yu *et al.*, [36] modified asphalt using MMT and organically modified montmorillonite (OMMT). X-Ray diffraction analyses showed that MMT and OMMT modified bitumen had an intercalated and exfoliated structures, respectively. Results demonstrated that both MMT and OMMT increased viscosity, softening point, improved the rheological properties of the bitumen and increased the resistance at high temperature. At adding less than 3% of both MMT and OMMT, stable results were obtained for storage stability [36]. Whereas, the addition of OMMT decreased the effect of UV ageing and after short and long term ageing ductility retention rate increased [37].

Kaolin is an another type of clay. Kaolin can influence the physical and rheological properties of asphalt and its effect on the performance of porous asphalt mixture was investigated [16]. Results showed that the addition of kaolin macro-clay reduced temperature susceptibility and hardened the bitumen. It also improved strength and durabili 4% of macro-clay [16]. Also, the addition effect of kaolin clay on the hot-mix asphalt (HMA) was studied using a Marshall stability and flow testes, including stiffness, density, voids in total mix, and voids in filled with asphalt. Results showed that adding 2% of kaolin clay enhanced HMA properties such as good stability and stiffness by using it as filler [38].

The effects of Batu Pahat soft clay (BPSC) on the performance of HMA mixture was evaluated. The 4% of BPSC modified bitumen increased the strength of asphalt mixes, decreased the susceptibility to moisture damage and gave a better resistance to deformation than the controlled asphalt mixture [31]. In addition, BPSC modified asphalt binder can improve the rheological and physical properties, which means, BPSC could be considered as an appropriate modifier to improve the properties of asphalt binder [31-32].

3.2. Nanoclay modified asphalt

Nanoparticles definite as materials with at least one dimension in the range between 1 and 100 nm. According to the small size and high surface area, the property of nanoparticles is much different from normal size particles. The performance enhancement of asphalt modification using nanoparticles can be expected, according to the high surface-to-volume ratio of nanoparticles, and the modification required much lower concentrations to achieve equivalent properties, compared to conventional, normal size particles [4].

In general, the addition of nanoclay to asphalt decreased the mixture susceptibility to moisture damage, improved tensile strength and reduced susceptibility to water and deicers [39-40]. Van de Ven *et al.* [41] found that the addition of nanoclay in asphalt mixture increased the viscosity of the binder and thus ageing resistance was high since only less contact with air and in particular oxygen. Yang and Tighe [42] reported that an increase of the viscosity, rutting and fatigue resistance of the asphalt mixture was achieved by adding nanoclay. Many advantages of asphalt modified with nanoparticles in low temperatures as well as in high temperatures were observed, despite the disadvantage of having a low resistance to fatigue [6].

Montmorillonite (MMT) nanoclay was selected to modify bitumen with different weight percent as the 2:1 type layer structure makes it more compatible with others material. MMT and organic montmorillonite (OMMT) nanoclays have been studied to modify asphalt. The sodium montmorillonite (Na-MMT) and OMMT nanoclays can promise potential to reduce the permanent deformation or rutting of asphalt [43]. The improvement in aging properties of the OMMT nanoclay modified bitumen was obtained [44]. Yu *et al.* [45] reported that the improvement degree of the adding three different organic modifiers of OMMT nanoclay to bitumen depends on the type of the organic modifier. Also, the results showed an enhancement in rutting resistance of the aged modified binder, resulting better resistance to permanent deformation at high and intermediate temperatures [45]. The excellent fatigue resistance of modified asphalt containing OMMT was concluded [46]. Mahdi *et al.* [28] concluded that the adding about 9% OMMT nanoclay in bitumen resulted less penetration, while softening point and viscosity increased comparing to 3% and 5% nanoclay in bitumen. In general, the organic clay modified asphalts has the best properties which may be according to: (i) a better dispersion of the exfoliated structure of the organic clay platelets modified asphalts, (ii) the compatibility of organic clay nanoparticles with the organic molecules of the asphalt matrix is better [6,34].

There are several researches conducted to use and compare Cloisite and Nanofil nanoclays to modify asphalt. Cloisite-15A particles are larger in size as compared to the Nanofil-15 particles [5]. Both Cloisite-15A and Nanofil can improve stiffness, rutting resistance, indirect tensile strength, resilient modulus, and Marshall stability [47]. Ghile [48] evaluated the mechanical properties of an asphalt binder by adding Nanofil and Cloisite nanoclays. The results showed that both nanoclays were greatly significant the influence the rheology of bitumen and performance of bituminous mixes. Stiffness along with resistance against rutting and indirect tensile strength improved by adding 3% of Cloisite-15A. At 6% Nanofil, an improvement of both short and long term ageing-resistance was obtained [48]. The fatigue cracking resistance of the binder reduced and viscosity increased with Nanofil and Cloisite nanoclays [26], which will save money for maintenance and repairs, and also made the bitumen easy to work with in hot places. However, at low temperatures, the fatigue resistance of nanoclay modified bitumen was lower than the unmodified bitumen [48].

Jahromi *et al.* [49] studied to modify PEN 60/70 asphalt by adding Nanofil-15 and Cloisite-15A nanoclays. Results showed that the modified asphalt by nanoclay increased the stiffness and enhanced resistance to aging. Additionally, a low percent of nanoclay in asphalt could be modify in rheological parameter, decreasing penetration and ductility as well as increasing softening point and ageing resistance. At low temperatures, fatigue cracking performance decreased [49]. The research by Nazzal *et al.* [26] showed that Cloisite-20A nanoclay significantly increased the dynamic shear complex modulus values of the tested asphalt when prepared at high temperature (at 160°C) and rotation (2500 rpm) for 3 hrs in order to get desired exfoliation. Results of the direct tension test showed that the strain failure rate reduced by adding nanclay in asphalt, while the secant or direct tension moduli increased [26].

Kumar and Suman [17] investigated the influence of the blending 1% to 9% of Cloisite-15A nanoclay on the physical and mechanical properties of bitumen binder. The results showed an improvement of rutting resistances, an increase in softening point, dynamic viscosity and complex modulus, while a decrease in binder penetration, phase angle. Results also showed a significant improvement in Marshall stability and insignificant enhancement in flow value. 5% Cloisite-15A nanoclay gave the best improvement in the modified binder [17]. While, Blom *et al.* [18] concluded that in a hard bitumen, nanoclay addition has no effect on the penetration value, because the bitumen is already so hard. But, a slight increase of stiffness and elasticity obtained through the addition of 5% nanoclay in bitumen at low frequencies. Cloisite-15 has good storage stability in the bitumen [18]. Varun and Gehlot [1] reported about the improvement of the physical properties such as penetration, softening point, penetration index and ductility of modified asphalt binder by using common types of nanoclay, organoclay (OMMT), Cloisite-15A, Nanofil-15, through the wet-modified nanoclay in combination with the coupling agent then dispersed in the asphalt.

Bagshaw *et al.* [2] prepared nanoclay (Nanomer 1.44P)/bitumen nanocomposites to decide whether expensive and time-consuming blending was essential to reach important changes in the properties of the bitumen composites. Blending for longer times and/or higher shearing speeds resulted an increase of the dispersion and exfoliation of the nanomer clay, but, no significant effect on the physico-chemical and rheological properties of the modified bitumen. Simple paddle mixing was sufficient to disperse the nanomer to improve the physical properties of the modified bitumen. Nanomer dispersion into the softer bitumen grade caused larger apparent changes than blending into the stiffer grade. As a result, the use of simple, low-cost blending methods could be possible to manufacture effective clay-bitumen nanocomposites [2].

The effect of clay sizes such as macro- and nano-size on the performance of bitumen was studied [4,17]. El-Shafie *et al.* [4] compared between the effect of unmodified clay (macro-scale) and organically modified nanoclay on the physical and mechanical properties of asphalt binders. The results showed an increase in softening point; kinematics viscosity and decrease in penetration. The tensile strength of modified asphalt enhanced at all percentages by a comparison with both macroclay and unmodified asphalt. 6% nanoclay obtained the best improvements in the modified asphalt [4]. The physical and mechanical properties of asphalt were significantly improved compared to the control asphalt as follows: (i) an increase of softening temperature was 12°C, kinematic viscosity values increased by about 222% and 179% at 135 and 150°C, respectively, the stress values increased by about 179% and 370% at -7°C and 25°C, respectively, (ii) a decrease of about 25% was in the penetration value, the strain values decreased by about 41% and 35% at -7°C and 25°C, respectively [4].

3.3. Clay/nanoclay and polymer modified asphalt

Polymer modified asphalt has increasingly used to improve the flexibility, deformation stability, durability and other properties of asphalt [23]. The most common polymers used in asphalt modification are styrene-butadiene-styrene (SBS), styrene-butadiene-rubber (SBR), ethylene-vinyl-acetate (EVA), and polyethylene. A significant improvement of properties are achieved by using the clay as a second modifier in polymer modified asphalt [8,13-23]. For example, a small amount of nanoclay reinforcement can enhance the compressive and shear strength of thermoplastic polymers [4]. The gallery spacing increased and the resulting morphology was an intercalated structure, when the polymer dispersed between the layers of the nanoclay [50]. Another morphology is an exfoliated, produces when the clay layers are extensively delaminated and completely separated thorough polymer penetration using different dispersion methods [27,43,50]. The silicate layers also can be prevent the diffusion of oxygen through polymer modified asphalt, enhancing the aging resistance [12]. This enhancement realized at the addition of the clay either separately or premixed with the polymer in the asphalt [27,43,50].

Many studies were investigated the clay/nanoclay with polymers modified asphalt. Khodary [15] evaluated the properties of SBS-clay nanocomposite modified bitumen and mixtures. Results showed that both penetration and softening point of all modified bitumen improved by adding SBS-clay nanocomposite. Tensile strength of modified mixtures was higher than unmodified mixtures by about three times with 5% SBS and 6% nanoclay. Fatigue life of SBS-clay modified mixtures was about 3.4 times higher than unmodified bitumen [15]. Ouyang *et al.* [21] added kaolinite (KC) to styrene-ethylene-butylene-styrene (SEBS) to modify asphalt. Results showed that the ratio of SEBS/KC in the mix has a significant effect on the storage behavior at high-temperature. At the SEBS/KC ratio of about 2, the modified asphalt was stable. The compatibility of asphalt/polymer was changed by adding clay with direct implications on storage stability, mechanical and thermal properties [21].

MMT nanoclay and organic modification of nanoclay layered silicates has been successfully used in the modification of polymer to significantly improve the thermal stability, mechanical and barrier properties of asphalt [14,23]. Jasso *et al.* [51] examined the addition effects of MMT to SBS modified bitumen binders. Results demonstrated that MMT addition to SBS modified bitumen enhanced rheological benefits. Furthermore, it was concluded that the addition of the nanoclays increased the viscosity, improved the complex modulus, and decreased the phase angle of the SBS-modified asphalt, by the formation of an intercalated and exfoliated structures in the SBS modified asphalt binder using the Na-MMT and OMMT nanoclays, respectively [45]. On the other hand, Zhang *et al.* [20] found that OMMT could enhance the UV ageing resistance of asphalt by modifying SBS-asphalt with OMMT. Baochang *et al.* [22] found that SBR/MMT modified asphalt was very stable in a different content range of SBR/MMT and formed an ideal fine network structure. Additionally, SBR/MMT improved viscoelastic properties and resistance to rutting in modified asphalts at high temperature with higher complex modulus and lower damping factor exhibited [22]. Yao *et al.* [52] studied the rheological properties effects by using only MMT nanoclay and combined with polymers in bitumen binder. Results showed a significantly increase of viscosity and complex shear modulus values by adding nanoclay to bitumen, but, nanoclay combined polymer decreased these values slightly. However, better results for fatigue crack and rutting by using nanoclay combined polymer modified bitumen was achieved [52].

Yasmin *et al.* [53] obtained that the produced materials had higher elastic modulus than that of the pure epoxy when Nanomer I.28E and Cloisite-30B added into epoxy polymers. Furthermore, the physical and rheological properties of bitumen and polymer modified bitumen could be significantly enhanced by the addition of OMMT [4]. Sureshkumar *et al.* [13] also concluded that organomodified Cloisite or dellite clay had a high compatibilizing effect on asphalt and EVA copolymer can lead to the better dispersion of the polymer in the asphalt. In another study, the ternary blends of MMT clay and triblock copolymer (SBS, SIS, or SEBS) to the asphalt showed a relatively higher complex modulus and enhanced viscoelastic properties, which improved its resistance to rutting at high temperatures [27]. The optical microscopy of morphology exhibited the significant compatibility between triblock asphalt/polymer/MMT, thus influencing the final rheological properties of asphalt [27]. Pamplona *et al.* [12] observed an improvement on the physical and rheological properties, probably due to the intercalation of the asphalt in the nanoclay layers. A similar behavior of the asphalt modified by 2.5% and 4% of SBS with 2.5% of OMMT clays and organically modified vermiculite (OVMT). The addition of OMMT and OVMT in the binder leaded to save the required polymer. The black diagrams also showed the similar effect of nanoclays (OVMT and OMMT) as Cloisite®20A. The addition of OVMT enhanced the storage stability of SBS modified asphalt [12].

Polacco [43] investigated the addition procedures effect of Cloisite-20A as a third component in SBS polymer modified asphalts. The X-ray analysis showed that the mixing procedure had no significant effect on the formation of an intercalation between the interlayer distance of clay. The mixing procedure also seemed not to be affected the low-temperature glass transitions. Moreover, the final rheological properties were significantly affected by the mixing procedure [43]. Merusia *et al.* [19] studied asphalt modification produced from binary and ternary preparation procedures using linear SBS copolymer and Cloisite-20A clay. Ternary blends produced strong mechanical response of the system and significantly influenced by the nanocomposite modification. In case of bitumen was initially blended with clay and then with the polymer, the mechanical properties significantly improved but the general rheological properties remained as the same that of the bitumen/SBS binary blend [19].

The modified effect of Cloisite-15A and Cloisite-11B nanoclays on the moisture susceptibility and the cost analysis of PG 64-22 bitumen was studied and compared with polymer modified bitumen [54]. Results showed that the nanoclay addition gave a reverse influence on moisture resistance of plain binder, which enhanced the performance of bitumen in respect of stiffness and saved the money. At 2 and 4% nanoclay could save 22-33% of the cost when compared to polymer modified bitumen [54].

3.4. Clay/nanoclay and others modifiers

Every year, much amount of waste polymers are produced. Hence the waste polymers could be used as a good alternative to the new polymers for asphalt modification, as it will economical and might solve the problem of waste disposal to some extent [23]. The significant improvement in the Marshall stability of the modified bitumen by using MMT nanoclay and waste low density polyethylene (LDPE) and polypropylene (PP) obtained from waste carry bag, crumb rubber found from waste tire (CR). The highest stability value is obtained at 1% MMT and 4% of LDPE/PP [23]. Yu *et al.* [55] reported that asphalt rubber (AR) was prepared by blending crumb rubber and bitumen, gave various advantages such as superior rutting resistance, lower road-tire noise and longer service life, but it had poor storage stability, which in turn limits its wider application. Hence, they dispersed three types of nanoclays into hot AR binder by high shear blending. Results showed that the selected nanoclays had insignificant influences on workability, rutting and fatigue properties, but providing superior storage stability. The best storage stability of AR obtained by using pure MMT nanoclay with Na^+ inorganic group, which has an intermediate hydrophilic property and middle layer gap [55]. Mahalakshmi *et al.* [56] studied the modification of bitumen using both plastic waste (LDPE) and nanoclay individually and as a composite. Results showed that LDPE modified bitumen is preferred if the high temperature is reached on roads. But nanoclay is preferred in cold climatic regions, because it has much resistance for temperature susceptibility. For mixed climatic regions, composites of LDPE and nanoclay enhanced the properties of mix like strength and durability [56].

For environmental concerns, the asphalt industry interests to the promotion of green asphalt technologies [5]. Several researchers studied the application of bio-based asphalt binder to use as a modifier or alternative for bituminous asphalt [5,10,25]. The study results by Hosseinnezhad *et al.* [5] showed a significant reduction in the aging rate of modified asphalt binder with bio-binder (derived from swine manure) and Nanofil-116 nanoclay. The highest increase in gallery spacing was obtained at the equal ratio of bio-binder and clay, resulted from the interactions between amide functional groups of bio-binder and the silicate layer of nanoclay [5]. Walters *et al.* [10] studied the modified effect of Cloisite-30B nanoclay and bio-char grinded to nano-scales on asphalt rheological properties. Results showed that the addition of nanoclay and bio-char to modify asphalt binder improved the high temperature performance and aging resistance of asphalt. These results were mainly attributed to the modify of layer spacing in nanoclay as observed by XRD [10]. The authors also concluded that Cloisite-11 nanoclay leaded to a higher increase in viscosity compared to Cloisite-15A nanoclay of asphalt binder and enhancement of asphalt aging resistance. Further enhancement of asphalt properties when bio-char added to nanoclay modifiers to assist silicate platelets dispersion by decreasing electrostatic forces between the nanoparticles. Moreover, 3% Cloisite-11 found to be as effective as 6% Cloisite-11 combined with 3% bio-char to enhance aging resistance of base asphalt [25].

Modification of asphalt using other different types of modifiers and clay/nanoclay was studied. The addition of nanoclay and two different warm asphalt additives (WAA), Rediset® and

Cecabase® increased the softening point and viscosity, and improved the temperature susceptibility and physical properties of the asphalt [3]. The addition of nanoclay or synthesized nanosilica improved the performance of the asphalt binder by decreasing penetration, increasing softening point and viscosity. By increasing nanosilica percentage increased brookfield rotational viscosity (RV) at temperature of 135°C and up to 150°C, but, at small percentages of nanoclay increased the RV, while at higher temperature up to 165°C, RV values did not change significantly by using both nanomodifiers [24].

Yalçın *et al.* [9] reported that the conventional properties of asphalt binder improved with the addition of MMT nanoclay contains 35-45 wt% dimethyl dialkyl amine (DANC). Results of dynamic shear rheometer showed that the temperature and the frequency had a significant effect on the complex modulus of MMT and DANC modified asphalt. Results also indicated that the DANC has promising potential to decrease the permanent deformation or rutting of asphalt pavements [9].

Yao *et al*. [7] studied to improve the rutting and fatigue cracking resistance of asphalt binders by the addition of micro- and nanomaterials (Nanomer I.44P, carbon microfiber, nonmodified nanoclay and polymer modified nanoclay). The addition of nano or micro modifiers to asphalt binders increased the complex shear modulus and improved the performance of resistance to rutting. Whereas, the addition of polymer modified nanoclay increased the resistance to fatigue crack and decreased complex shear modulus. Moreover, the aging and oxidation effect can be delay and weaken by adding of four modifiers to the asphalt binder [7]. They also concluded that the dynamic modulus of micro- and nanomodified asphalt mixtures enhanced significantly and the rutting susceptibility reduced [57].

Bonati *et al.* [58] and Pei *et al.* [59] studied to limit the fire reaction of asphalt. Results of nano calorimeter test showed that aluminum hydroxide gave the best results for heat and smoke released and nanocomposite use provided benefits [58]. The addition of 1% OMMT and 3% alumina-trihydrate gave the best results for fire reaction. According to the results, the use of both additives together gave less gas emissions during fire and sustained better thermal stability compared to pure bitumen [59].

The interlayer space of MMT and OMMT increased from 1.41 nm to 1.95 nm and 2.08 nm to 2.42 nm through the fictionalization the clays by isophorone diisocyanate (IPDI) and hydrogenated diphenylmethane diisocyanate (HMDI), respectively. The modified asphalt with fictionalized clays by IPDI and HMDI gave a maximum softening point of about 57°C and 62°C, initial decomposition temperature of about 360°C and 370°C, respectively and possessed good storage stability [30].

One of the commonly occurring distresses in asphalt pavements is a moisture damage. The addition of nanoclay and carbon microfiber enhanced the performance of the mixture's moisture susceptibility or decreased the moisture damage potential [40]. The effects of nanoclay and nanohydrated lime on moisture susceptibility of a continuously graded asphalt mix were investigated. Results demonstrated that the addition of 5 wt% nanohydrated lime and 2 wt% of nanoclay increased tensile strength ratio of asphalt mixes by 52 and 49%, respectively [29]. On the other hand, the modifications of the asphalt with layered double hydroxides (LDHs), OMMT and carbon black (CB) improved the anti-UV ageing asphalt. LDHs decreased the ageing rate of asphalt most effectively, followed by OMMT then CB [14].

Zhang *et al.* [8] selected kaolin, carbon white, sulfur (S), tetramethylthiuram disulfide (TMTD), zinc oxide (ZnO), and butylated hydroxytoluene (BHT) to improve the performance of the SBS-modified bitumen stabilizer powder. The presence of S, TMTD, ZnO, and BHT significantly improved the storage stability and aging resistance of SBS-modified bitumen. These components also improved the softening point and viscosity and decreased the penetration. Furthermore, kaolin, carbon white significantly improved the storage stability of SBS-modified bitumen [8].

4. Conclusions

Using clays as modifiers considered to be very important, efficient and economical in asphalt industry. Different types of clays such as bentonite, kaolin and vermiculite are obtainable and used as asphalt modifier in different sizes. The addition of clay/nanoclay in asphalt improved several properties. The BT and OBT modified asphalts increased softening point and viscosity and significantly improved the dynamic rheological properties through higher complex modulus, lower phase angle and higher rutting parameter. OMMT modified asphalt decreased the effect of UV ageing. Nanoclay modified asphalt decreased the mixture susceptibility to moisture damage. Both Cloisite and Nanofil nanoclays can improve stiffness, rutting resistance, indirect tensile strength, resilient modulus, and Marshall stability of asphalt. A significant improvement of properties are obtained by adding clay/nanoclay as a second modifier in polymer modified asphalt. Clay/nanoclay can combine with many different types of materials used as modifiers of asphalt such as waste polymers, bio-char, different types nanomaterials, etc.

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To whom correspondence should be addressed: Dr. Eman A. Emam, Department of Petroleum Refining Eng. and Petrochemicals, Faculty of Petroleum and Mining Eng., Suez University, Suez, Egypt, E-mail: emamtah@yahoo.com