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Nanoparticle in Asphalt Binder: A State-of-The-Art Review

P J Ramadhansyah[1], K A Masri[1], A H Norhidayah[2], M R Hainin[2], M W Muhammad Naqiuddin[2], Y Haryati[2], M K I M Satar[2] and A Juraidah[3]

[1]Faculty of Civil Engineering Technology, Universiti Malaysia Pahang, 26300 Gambang, Pahang, Malaysia
[2]Faculty of Engineering, School of Civil Engineering, Universiti Teknologi Malaysia, 81310 Johor Bahru, Malaysia
[3]Faculty of Civil Engineering, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia

Abstract. Increasing traffic volumes and the rising cost of bitumen making it necessary to improve the performance of asphalt binder through bitumen modification. Various types of modifiers have been employed as bitumen binders in order to improve the bitumen mixture, particularly with regard to its resistance to aging, cracks due to fatigue and thermal conditions, moisture-induced damage and permanent deformation. This review study summarizes the performance of nanoparticles as an asphalt modifier. Several relevant literatures were reviewed, which related to the matter associated with nanomaterials such as nano-silica, carbon nano-tubes and nano-titanium dioxide. Recent studies showed that the utilisation of nanoparticle gave great benefits in many ways.For instance, nano kaolin as a mineral clay promises non-hazardous effects to road users. This can result in a healthy environment and help towards increasing the application of green technology road construction.

Content

1. Nanotechnology in Asphalt Binder

Recently, increased traffic volumes, larger and heavier trucks, and higher tire pressures have aggravated the severity of the condition upon the pavement system, resulting in rutting, stripping and fatigue cracking [1]. Therefore, the concept of new technology, named nanotechnology has been introduced as an alternative to enhance the physical and rheological behaviours of asphalt binders, resulting in enhanced performance of the asphalt mixture [2]. Improvements in asphalt binder and mixture performance through other types of modifier at macro-scale and micro-scale have been

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achieved, yet it is interesting to explore what nanotechnology offers in terms of improving asphalt pavement performance. Therefore, the application of nanotechnology in the binder was widely explored and reported all around the world. Nanotechnology is considered to be the latest knowledge for pavement in order to develop a safe and sustainable pavement infrastructure. Although researchers, material producers, and engineers have explored the potential for many years, nanotechnology usage has been limited. Therefore, new efforts and exploration of the development of nanomaterials for pavement application that improve the nanoscale mechanical and physical properties as well as durability of the mixture were further investigated.

2. Nanomaterials in Asphalt Binder Modification

The previous study proved that various kinds of modifiers such as a polymer, crumb rubber, fibers are introduced to improve performances of asphalt binder. These performances include moisture susceptibility, permanent deformation, fatigue life, anti-ageing, and so on. From all these modifiers, polymer was the most widely used in binder modification. However, one of the major shortcomings of pure polymer modifiers is that most of the polymers are thermodynamically incompatibility with asphalt binder due to the large differences of density, polarity, molecular weight and solubility between the polymer and the asphalt binder. This can result in delamination of the composite during thermal storage, which is not readily apparent and adversely affects the material when it is used in construction. Therefore, more and more researchers concentrate on the introduction of nanomaterials to modify the asphalt binder due to the rapid development of nanotechnology and overcome this issue. The nanomaterial is described as a material with at least one dimension within 1 – 100 nm [3]. Based on previous research, the properties of nano-composites such as physics, chemistry and biology were significantly different from their initial ones [4]. Due to the unique characteristic of nanomaterials such as the tunnel effect of macroscopic quantum and surface effect were also found attributing to the natures of its large surface area and small particles size. It is noted that nanomaterials exhibited high-temperature sensitivity, high ductility, large surface area, high strain resistance, and low electrical resistivity [5,6]. There are various types of nanomaterials that commonly used in binder modification such as nano-silica, carbon nanotubes (CNTs), nano titanium dioxide (TiO_2) and nano clay. The following section discussed the application of nanomaterials in binder modification in term of their properties and performance.

3. Nano-silica

Silica is an abundant compound worldwide that is largely employed in industries to produce silica gels, colloidal silica, fumed silica and etc. [7]. While nano-silica is an inorganic material was produced mainly from silica precursors. There are few methods to produce nano-silica which are vapour phase method, sol-gel methods and other methods, however, among them, the sol-gel process method is considered as the most widely applied method for its mild condition and pure products [8]. Nano-sized silica is interesting because it is applied in emerging areas like medicine and drug delivery. Amorphous nano-silica is qualified as a nano-bio pesticide. The advantage of these nanomaterials resides in a low cost of production and the high-performance features. According to Yao *et al.* [9], nano-silica is also a material with a huge surface area, strong absorption, good dispersal ability, high chemical purity and excellent stability. Therefore, it is expected that the utilisation of nano-silica enhances the performance properties of the asphalt binder and mixture. Table 1 shows the main physical and chemical properties of nano-silica.

Table 1. Properties of nano-silica [4,9]

Color	White				
True density, g/cm^3	2.4				
Surface area, m^2/g	180-600				
Bulk density, g/cm^3	<0.10				
Purity, %	+99				
Chemical properties	SiO_2	Ti	Ca	Na	Fe
	>99%	<120 ppm	<70 ppm	<50 ppm	<20 ppm

3.1. Application of Nano-silica in Modified Binder
The study on the utilisation of nano-silica in binder modification was performed to improve the performance of asphalt binder in terms of physical, rheological and mechanical properties. A laboratory evaluation conducted by Md. Yusoff *et al.* [10] reported that the addition of nano-silica improves the resistance to rutting at high temperature and fatigue deformation at intermediate temperature as compared to the control mixture. The study was performed using polymer modified asphalt mixture (PMA) with 0%, 2% and 4% of nano-silica by weight of asphalt binder. Figure 1 shows the results of the resilient modulus test at 25 ºC. The result shows that PMA mixed with 4% nano-silica shows least susceptibility to fatigue deformation with highest resilient modulus value. Similar trends can also be observed for aged samples. This indicated that the addition of nano-silica would improve resistance to fatigue deformation at intermediate temperatures, both for un-aged and aged samples. In addition, another finding was also can be observed at which as temperature increases, the difference in resilient modulus is more notable, with a decline in stiffness at temperature of 40 ºC as shown in Figure 2. By considering the difference in the resilient modulus value at higher temperatures, this indicates that PMA mixed with 4% nano-silica is the least susceptible to rutting compared to control mix. These findings coincide with previous studies done by Yao *et al.* [9], and You *et al.* [11], who found that the rut depths of nanomaterial modified asphalt mixtures decrease compared to the control mixture, and a smaller rutting depth was observed for a greater percentage of nanomaterials in mixtures. Another finding on the improvement of rutting resistance can also be observed through dynamic creep test as shown in Figure 3. The result indicates that the addition of nano-silica can reduce the rutting depth by almost half as compared to the control mixture with 4% nano-silica mixed with PMA shows the lowest permanent deformation values.

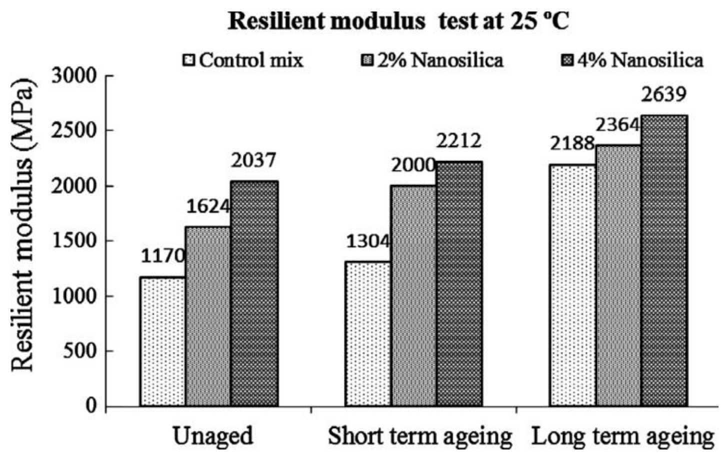

Figure 1. Resilient modulus test at 25 ºC [10]

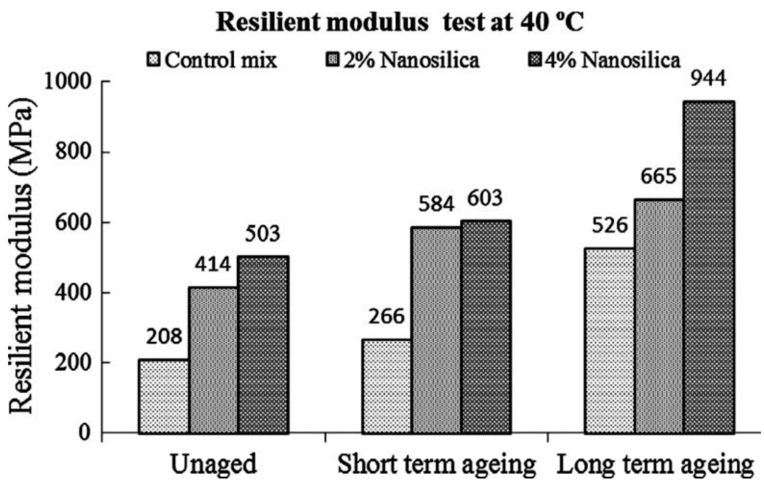

Figure 2. Resilient modulus test at 40 ºC [10]

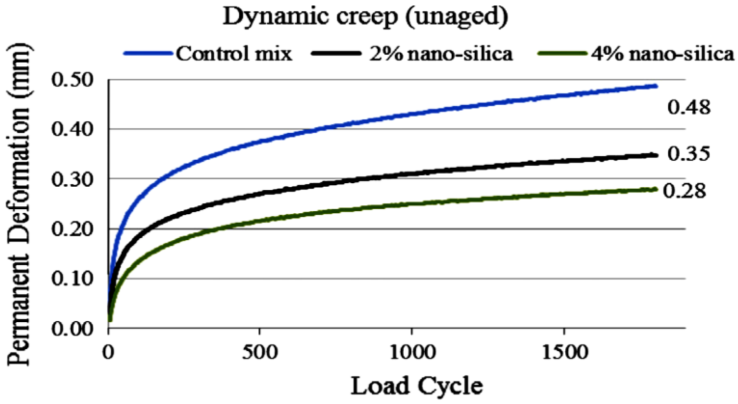

Figure 3. Dynamic creep test result for un-aged mixtures [10]

In 2015, Masri *et al.* [12] conducted research on the porous asphalt mixture incorporating nano-silica. This study was performed to investigate the effect of nano-silica modified binder on binder-drain down of porous asphalt. Binder drain-down was one of the main problems of porous asphalt because is having a high air void content which allowed the binder to flow through those air voids. This leads to the binder being drained off from the mixture. Different proportions of nano-silica ranging from 1 to 6% by weight of binder were used in this study. The nano-silica used was in colloidal form with the average size between 10 and 15 nanometres (nm). Table 2 tabulated the results obtained from the Cantabro and drain-down tests. The result shows that the Cantabro decreased as well as binder drain-down until the optimum percentage of nano-silica content which is 4% by weight of the binder. This indicates that the existence of nano-silica is capable of enhancing the performance of porous asphalt mixture in terms of abrasion resistance and binder drain-down. It can be concluded that the performance of anti-stripping property of nano-silica modified binder was significantly enhanced.

Table 2. Cantabro and drain-down test results for different proportions of nano-silica [12]

Nano-silica (%)	Cantabro (%)	Drain-down (%)	Drain-down (g)
0	17	0.324	3.564
1	13	0.277	3.047
2	12	0.222	2.442
3	10	0.197	2.167
4	9	0.186	2.046
5	11	0.234	2.574
6	14	0.285	3.135

4. Carbon Nanotubes (CNTs)

A carbon nanotube (CNT) is a one-atom-thick sheet of graphite rolled up into seamless hollow cylinders which have a diameter starting from one nanometre. CNTs were discovered by Iijima [13], who first reported the arc-discharge synthesis and characterisation of helical microtubules, formed by molecular-scale fibres with structures related to fullerenes. Since then, an enormous amount of research has been conducted in the area of CNT production and their applications due to the superiority of their electronic and mechanical properties [14]. CNTs are divided into two different types which are single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs), based on the number of grapheme sheets. However, as a modifier, MWCNTs are better than SWCNTs as they are stiffer, easier and cheaper to produce on a large scale [15]. Currently, several techniques are available to produce CNTs. The three common methods are arc discharge, laser ablation and chemical vapour deposition (CVD) [16]. Table 3 shows the properties and characteristics of MWCNTs.

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Table 3. Properties of MWCNTs [17]

Property	Value
Colour	Black
Purity, (%)	>90
Outside diameter, nm	10 – 30
Inside diameter, nm	5 – 10
Length, µm	10 – 30
Density, g/cm^3	2.1
Surface area, m^2/g	>200

Dispersion of CNTs has been one of the largest challenges due to the aggregation of the nanotubes [18]. Due to the strong, cohesive forces of CNTs, it can easily cluster together when added to asphalt binder. Therefore, for modified asphalt binder with CNT particles, the mixing process is a key factor. Improvement of material properties can be achieved by a proper dispersion technique. Improper dispersion leads to nanotubes damage and size break down, which deteriorate the material properties. Shirakawa *et al.* [19] used asphalt emulsion as solvent to disperse CNT and stated in their studied that CNT disperses better in anionic and non-ionic emulsion than cationic emulsion. Microstructure analysis performed by Faramarzi *et al.* [20] using Scanning Electron Microscope (SEM) analysis show that CNTs has strong tendency for aggregation with formation of random network of contacting aggregate as shown in Figure 4. Meanwhile, the morphology structure of CNT modified binder is shown in Figure 5, which presents a continuous matrix with uniform distributing nanometre phase. Both figures were observed using the same scale reference which is at 5 µm. In this study two process of dispersion in asphalt binder were performed: simple mixing and wet mixing. In simple mixing, CNTs was manually added into binder and mixed using mechanical stirrer at a speed of 1550 rpm for 40 minutes to reach the required homogeneity. While wet mixing involved the dispersed of CNTs in the solvent by means of sonication process and high shear mixing. Kerosene was chosen as solvent because it was petroleum-based product, cheap and easily available. Based on the morphology structure of CNTs modified asphalt binder, simple mixing CNT modified asphalt binder shows some large accumulated particles as shown in Figure 5(a). Meanwhile, Figure 5(b) shows CNTs particle distribute uniformly with a few mass accumulated particle for wet mixing. This indicated that utilising the wet mixing can lead to a decrease in the accumulating tendency of CNTs and consequently the increase in the mechanical properties as compared to simple mixing. Since CNTs exhibit great mechanical properties, it is expected to produce significantly stronger and more improved bituminous composites than conventional reinforcing materials such as glass fibers, carbon fibers and so on.

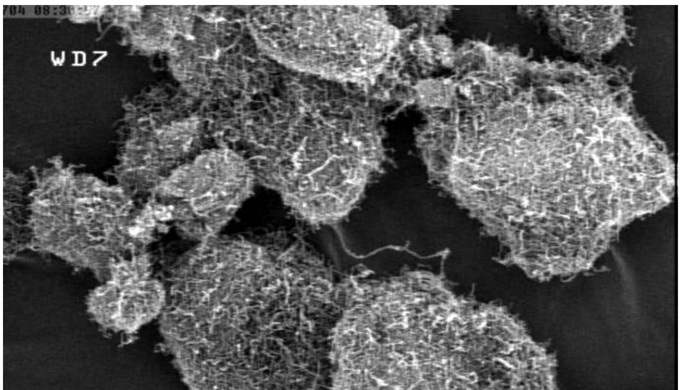

Figure 4. SEM images of carbon nanotubes [20]

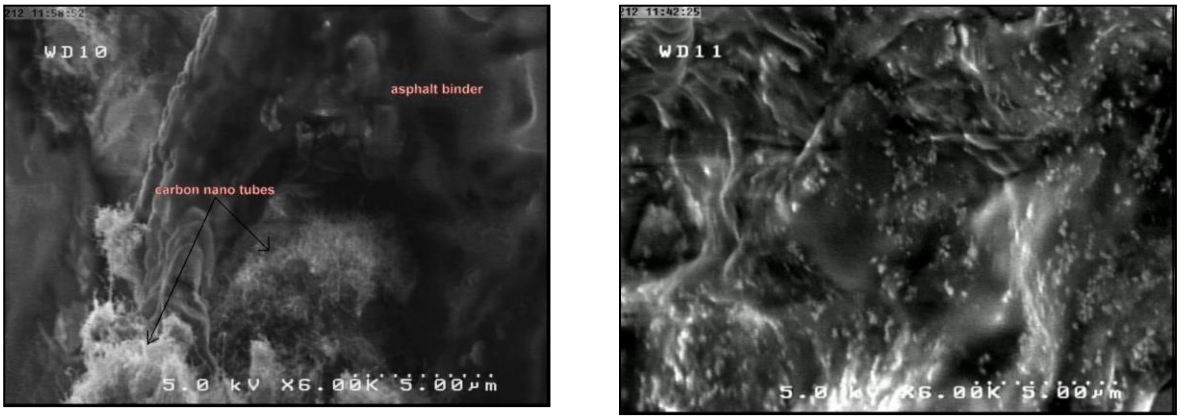

Figure 5. Simple mixing CNT-modified asphalt binder (left) and wet mixing CNT-modified asphalt binder (right) [20]

4.1. Application of CNTs in Modified Binder

One of the most desired properties of nanomaterials in road construction is their capability to confer a mechanical reinforcement to bituminous materials. While a large number of research studies have been carried out in the last decade on modification of asphalt binder by different nanoparticles, very few studies have been conducted in the area of CNTs modified binders and mixtures. Theoretically, the addition of CNTs in asphalt binder resulted in a reduction of penetration value and increased softening point due to increasing of binder stiffness. This was supported by Amin *et al.* [17], which found that the softening point value increased significantly with the increasing of CNTs content in the binder. This indicated that the modified binder with CNTs shows stiffer and lower temperature susceptibility. These characteristics are considered important especially when significant fluctuation in temperature occur during the day or in areas with heavy traffic. In addition, laboratory evaluation conducted by Amin *et al.* [17] reported that the addition of CNTs in binder enhanced the rheological properties of binder by increased the rutting factor, thus enhancing the pavement resistance to permanent deformation. Furthermore, rheological properties of binder in aging condition were also investigated in their study. A similar trend as un-aged condition was observed which it can be noticed that rutting factor significantly increased as amount of modifier increased. However, they found that modified binder with 0.5% of CNTs content or less did not cause a significant improvement. This finding was supported by Santagata *et al.* [21] where modifying asphalt binder with high percentages of CNTs (high than 0.5% of asphalt binder content) positively improve the rheological characteristics of the binder. These characteristic improvements lead to decrease asphalt pavement rutting in high temperature and thermal cracking at low temperature. Therefore, the selection percentage of modifier is one of the main parameters to produce the optimum performance of binder.

5. Nano-Titanium Dioxide (nano-TiO_2)

Titanium dioxide is the naturally occurred oxide of titanium and usually found in the form of rutile, anatase and brookite. TiO_2 has been known as a useful photocatalytic material that is attributed to the several characteristics includes high photocatalytic activity compared with other metal oxides, and it's compatible with conventional bituminous materials without changing any original performance. Its chemical formula is TiO_2 which it belongs to the family of transition metal oxides [22]. Nano-TiO_2 is produced from the oxidation of titanium precursor at a high temperature. It consists of 80% anatase and 20% rutile. Table 4 shows the main properties of nano-TiO_2. Generally, there are two main production methods to obtain nano-TiO_2 which are using sulfate process and chloride process. However, both methods have potential to cause negative impacts on environment. For instance, the sulfate process produced a large number of acidic wastes, while chloride process may result in a lot of solid, liquid and mineral wastes [23]. The characteristics of nano-TiO_2 are large surface area, small diameter and very low opacity as compared to ordinary TiO_2. Because of the unique properties, it is expected that nano-TiO_2 can improve the performance of modified asphalt binder and mixture.

Table 4. Properties of nano-TiO_2 [22,23,24]

Property	Value
Colour	White
Purity, (%)	>99.8
Particle size, nm	20-60
Density, g/cm^3	3.9
Bulk density, g/cm^3	0.08
Surface area, m^2/g	50-80

5.1. Application of Nano-TiO_2 in Modified Binder
Many kinds of research are carried out to investigate the properties of the modified binder with nanomaterial. For example, Buhari *et al.* [22] performed laboratory evaluation on physical and rheological properties of modified asphalt binder with nano-TiO_2 R15. The studies carried out using 2%, 4%, 6%, 8% and 10% of nano-TiO_2 content by weight of binder. The result shows that the addition of nano-TiO_2 has significantly reduced the penetration value and increased the softening point temperature. This demonstrated the improvement on the stiffness of the binder and also better temperature susceptibility as compared to control binder. In addition, viscosity value reduced as nano-TiO_2 content increased. This indicated that nano-TiO_2 modified binder has lower mixing and compaction temperature. Therefore, it can be considered that nano-TiO_2 modified binder is the environmental friendly because of less energy consumption during preparation of the mixture. Furthermore, the decreasing in viscosity value leads to improve the workability of the binder. In term of rheological properties, addition of nano-TiO_2 did not show positive improvement on the rutting factor ($G^*/\sin\delta$) as compared to control binder even though it is still in the same performance grade which is 64 °C. This finding was in contradictory with Fang *et al.* [25], where they stated that rutting factor and the elasticity of the nano-TiO_2 modified binder were increased. Thus the resistance to permanent deformation was enhanced, and the service life of modified asphalt mixture was prolonged. The studies performed by Shafabakhsh *et al.* [24] proved that the utilisation of nano-TiO_2 in bituminous material does not only improve the properties of binder but also in the mixture. The studies were carried out to investigate the properties of hot mix asphalt (HMA) with different percentages of nano-TiO_2 content (1%, 3%, 5% and 7% by weight of binder). The mechanical property of the mixture was evaluated in term of fatigue performance of both control mixture and nano-TiO_2 modified mixture. Based on the laboratory works, they found that nano-TiO_2 modified mixture tend to have longer fatigue life as compared to control mixture. This indicated that nano-TiO_2 reduced the generation and propagation rate of micro-cracks which can lead to high tensile strength in the modified mixture. Therefore, it can be concluded that utilisation of nano-TiO_2 can improve the fatigue life of mixture by prevents tensile and vertical cracks from being easily generated by horizontal tensile stresses and prevents them from propagating.

6. Nano clay
Amongst the potential nanoparticle, nano clay received much attention as a modifier due to the expectation to strengthen and enhance the physical and rheological properties of the asphalt binder. Nanoclay is a layered silicate that has a layer thickness between 1 and 100 nm and widely used in the binder modification to improve mechanical and thermal properties. In addition, nano clay is the most commonly used nanomaterials to modify bituminous material due to their low cost of production and abundance in nature. There are four main groups of clays which are kaolinite, montmorillonite, Illite and chloride. Generally, there are two main categories of nano clay used in asphalt binder, which is non-modified nano clay (NMN) and polymer modified nano clay (PMN). NMN is the most frequently used with 2-to-1 layered structure clay consisting of one octahedral alumina sheet sandwiched between two tetrahedral silica [26]. Based on previous studies, it has been proved that the utilisation of nano clay in bituminous material shows positive improvement in both rheological and mechanical properties of modified asphalt binder. However, no research was reported on the utilisation of NKC in

terms of the physical and rheological properties of the asphalt binder as well as mechanical properties of asphalt mixture while this study was performed.

7. Conclusion

This review focuses on the performances and possible use of the nanoparticle as an asphalt modifier. Polymer modified asphalt binders have been immensely popular; the high cost and thermal instability thereof encouraged researchers to explore new materials to improve their performance. Many studies agreed that the usage of nanoparticle could enhance the physical, rheological and mechanical properties of asphalt binder and mixtures. The utilisation of nanoparticle in the asphalt binder has been introduced. The summary of the issues are presented below:

a) The performance application of nanomaterials for asphalt binder to improve the physical and chemical properties are inadequate, especially under durability context.
b) The existing research on the anti-aging performance of nanoparticle as the modified binder is inadequate.
c) The fundamental effect of nanoparticle with other modifiers to improve asphalt performance is needed.

Certainly, further investigation is needed to better understand the utilization of nanoparticle as bitumen modifier in the fundamental level along with its field performance.

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