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A Review on The Exploration of Nanomaterials Application in Pavement Engineering

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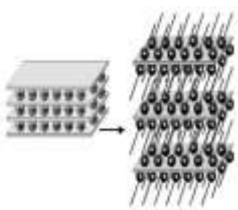

Nanoclay surface treatment

Abstract

In order to improve the performance of asphalt mixture, the virgin asphalt binder needs to be modified with suitable modifiers. There are various types of modifiers available in market and it is clearly stated and established in most of pavement standard specification. Nowadays, pavement technologist and researchers had put their interests on nanotechnology and they had found that polymeric nanocomposites have shown its effectiveness through the modification of virgin asphalt binder with certain portion of nanomaterials. In addition, many studies have demonstrated that nanomaterials have significant effects in improving the engineering properties of asphalt binder and mixture. Therefore, a thorough literature review on the current research of nanomaterials in pavement engineering for the past decades can enhance understanding and guaranteed something beneficial findings in the future. This paper described the theory of nanotechnology and its historical development including the method used among researchers in evaluation the structural and morphological characteristics of modified binder with nanoparticles. Also, the effect of different types of nanoparticles, suitable dosages, modifying procedures, problems and benefits on asphalt binder and mixture were explained. It is expected that in future the implementations of nanotechnology would have major impacts for better pavement performance.

Keywords: Nanotechnology, nanoparticles, modified asphalt binder, pavement engineering

1.0 INTRODUCTION

Since the 1990s there has been a very rapid increase in the implementation areas of nanotechnology such as science and education; materials and construction; manufacturing; nanoelectronics and computer information technology; medicine and healthcare; aeronautics and space exploration; environment and energy; biotechnology and agriculture; and national security [1-5]. Recently, nanotechnology has become one of the major interests among experts, engineers, media as well as public community. It is essentially about new ways of making things through understanding and control over the fundamental building blocks (i.e. atoms, molecules and nanostructures) of all physical things. The applications of nanotechnology are promising to have a major impact in our lives and cultures in the coming decades. Furthermore, with the backing of unprecedented funding, nanotechnology is emerging rapidly as the industrial revolution of the 21st century [2, 6-7]. This is likely to change the way almost everything is designed and made. This chapter presents a detail review on nanotechnology concept and its historical development, structural characterisation and types of nanomaterial used in pavement engineering.

1.1 Definition of Nanotechnology

Nanotechnology can be defined as the science and engineering involved in the design, synthesis, characterisation and application of materials and devices which smallest functional organisation in at least one dimension is on the nanometer scale that is one billionth of a meter (10-9 m) [1].
In general, nanomaterials may have globular, plate-like, rod like or more complex geometries. Typically, near-spherical particles which are smaller than 10 nm are called clusters. The number of atoms in a cluster increases greatly with its diameter. At 1 nm diameter there are 13 atoms in a cluster and at 100 nm diameter the cluster can accommodate more than 107 atoms. Clusters may have a symmetrical structure which is, however, often different in symmetry from that of the bulk.

They may also have an irregular or amorphous shape. As the number of atoms in a cluster increases, there is a critical size which a particular bond geometry that is characteristic of the extended bulk [7-8].

In highway research and construction normal practice, an addition of microparticles material either modified using wet or dry method is a common method applied for highway improvement. However, recently there has been an eager among experts and engineers to explore the performance of highway properties by using nano scale materials. Figure 1 illustrates the evolution of

length scales of flexible pavement material in macro scale to quantum scales. Nevertheless, nanoparticles also have a high surface area to volume ratio which are providing for a tremendously potential chemical reactivity.
Figure 2 shows particle sizes and specific surface area related to concrete materials. More than anything else, nanotechnology is being considered as a key technology and allowing us to do new things in almost every conceivable technological discipline. This transformation can change almost all aspects of human society due to the development of sustainable materials, constructions and many other technological advances [1-2, 10-12]

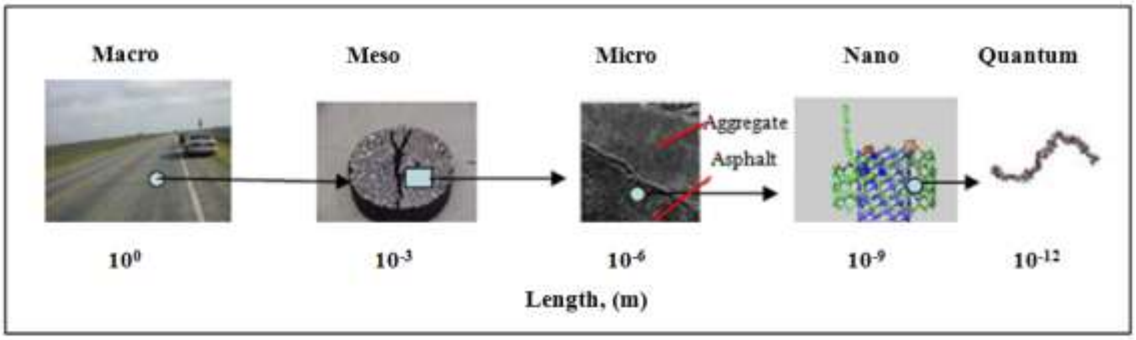

Figure 1 Evolution image of different asphalt dimensions [9]

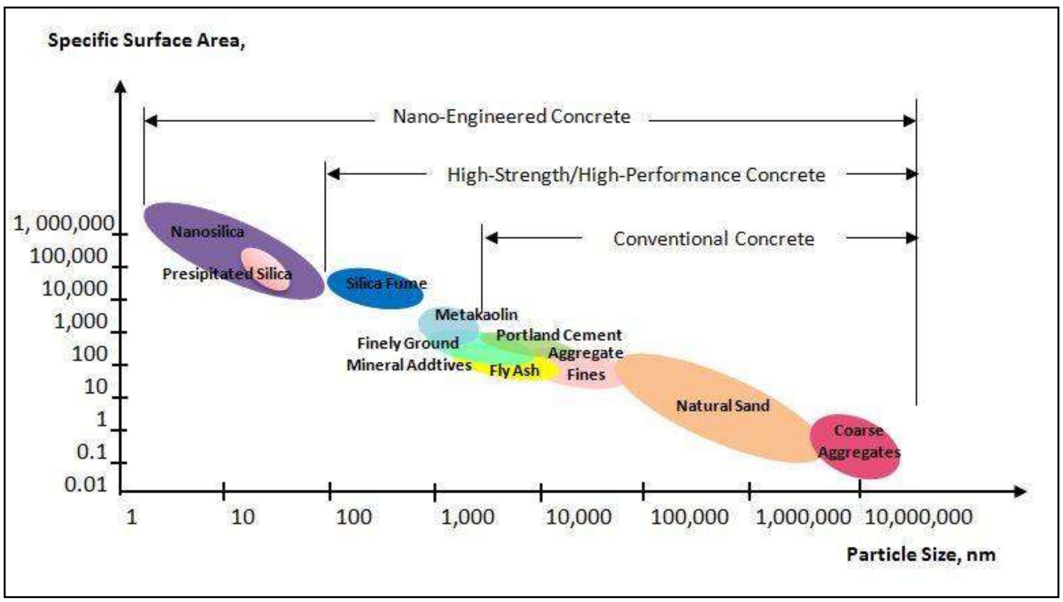

Figure 1 Examples of particle size related to concrete materials [5]

■2.0 HISTORICAL DEVELOPMENT OF NANOTECHNOLOGY

The term nanotechnology was first introduced by a Japanese engineer, Norio Taniguchi [13]. He described the precision manufacture of parts with finishes and tolerances in the range of 0.1 to 100 nm. The term originally implied a new technology that went beyond controlling materials and engineering on the micrometer scale. Then, in 1981, Drexler [14] pointed out a new approach which is more related to the meaning and application today. He corresponded to the atom-by-atom manipulative, hardtech processing methodology [1-2, 4, 8, 12, 15-18].

Today, the growing interest in nanostructured materials is the natural consequence of advances and refinements of knowledge about the creative manipulation of materials on the nanometer scale in order to perform functions or obtain characteristics which could not otherwise be achieved. Researchers [2, 19] stated that the more precisely nanomaterial properties are magnified, the more unusual and unexpected features emerged.

■3.0 STRUCTURAL CHARACTERISATION OF NANOPARTICLES

One of the critical challenges faced by researches in the nanotechnology area is the understanding of instrumentation with various potential of applications to observe, measure and manipulate the individual nanomaterials and nanostructures in pavement. Characterization of nanomaterials and nanostructures has been largely based on the surface analysis technique and conventional characterization methods developed for bulk materials. The most widely used in characterizing nanomaterials and nanostructures in pavement engineering are X-ray diffraction (XRD), various electron microscopy (EM) including scanning electron microscopy (SEM) and Field Emission Scanning Electron Microscopy (FE-SEM) [15, 20].

3.1 X-Ray Diffraction (XRD) Analysis

XRD is a very important experiment technique that has long been used to address all issues related to the crystal structure of solids, including lattice constant and geometry, identification of unknown materials, orientation of single crystals, preferred orientation of polycrystals, defects, stresses, etc. In XRD, a collimated beam of X-rays, with a wavelength typically ranging from 0.7 to 2 A, is incident on a specimen and is diffracted by the crystalline phases in the specimen. This diffraction pattern is used to identify the specimen's crystalline phases and to measure its structural properties [15]. XRD is non-destructive testing and also a powerful technique for investigating the following [21]:

(i) Crystallinity
(ii) Polymorphism (crystalline phase identification)
(iii) Additives, pigments and fillers identification
(iv) Active compounds and excipients
(v) Preferred orientation or texture
(vi) Residual stress and strain

The XRD analysis method can be applied to materials in powder form, or to manufactured parts, films, plaques, fibers, cured components, coatings, wafers or multilayer systems. Measurements can be made in reflection, transmission and grazing (glancing) angle modes. Temperature experiments allow the study of phase transitions for each crystalline structure present in the material. Analysis of preferred orientation in plastics, coatings, or metals can be studied by pole figure measurements, through texture coefficient measurements, or using camera attachment [21-26].

3.2 Scanning Electron Microscope (SEM)

SEM is a type of electron microscope that images the sample surface topography composition and other properties by a source of focused electrons into a beam, with a very fine spot size of 5 nm and having energy ranging from a few hundred eV to 50 KeV, which is raster over the surface of the specimen by deflection coils. As the electrons strike and penetrate the surface, a number of interactions occur that result in the emission of electron and protons from sample, and SEM images are produced by collecting the emitted electrons on a cathode ray tube (CRT). The resolution of the SEM approaches a few nanometers, and the instruments can operate at the magnifications that are easily adjusted from 10 to over 300000 nm [15, 21, 27].

The types of signals produced by SEM include secondary electron images, back-scattered electron images and elemental X-ray maps. When a high-energy primary electron interacts with an atom, it undergoes either inelastic scattering with atomic electrons or elastic scattering with the atomic nucleus. Due to the very narrow electron beam, SEM micrographs have a large depth of field yielding a characteristic three-dimensional appearance useful for understanding the surface structure of a sample. This is exemplified by the micrograph of pollen (shown to the right). A wide range of magnifications is possible, from about 10 times (about equivalent to that of a powerful hand-lens) to more than 500000 times. Not only does the SEM produce topographical information as optical microscopes do, it also provides the chemical composition information near the surface [15, 21, 27-29].

3.3 Field Emission Scanning Electron Microscopy (FE-SEM)

Field emission (FE) is the emission of electrons from the surface of a conductor caused by a strong electric field. An extremely thin and sharp tungsten needle (tip diameter 10 to 100 nm) works as a cathode. The FE source reasonably combines with scanning electron microscopes (SEMs) whose development has been supported by advances in secondary electron detector technology. The FE-SEM is an advance equipment as compare to SEM for surface imaging and morphological characteristic for any types material. The sample need to meet the setting condition of FE-SEM before decided to further test it. Commonly, the acceleration voltage between cathode and anode is with the magnitude of 0.5 to 30 kV, and the apparatus requires an extreme vacuum (10 to 6 Pa) in the column of the microscope. Since the electron beam produced by the FE source is about 1000 times smaller than a standard microscope with a thermal electron gun, the image quality will be markedly improved. The main advantage of the FE-SEM comes from its high resolution and long working length between magnetic lens and sample, which is unobtainable from a state-of-the-art optical microscope [29-32].

The FE-SEM images a sample surface by raster scanning over it with a high-energy beam of electrons. The electrons interact with the atoms comprising the sample to produce signals that contain informations about surface topography, composition and other properties, such as electrical conductivity. Features can be characterized at length scales from millimeters to around 10 nanometers. Therefore, the FE-SEM is a very useful tool for high resolution surface imaging in the field of nanomaterials science and its applications include [21]:

(i) Thickness measurement of thin coatings and films
(ii) Correlation of surface appearance and surface morphology
(iii) Characterisation of size, size distribution, shape and dispersion of additives, particulates and fibers in composites and blends
(iv) Measurement of height and lateral dimensions of nanometer-sized objects
(v) Characterisation of cell size and size distribution in foam materials
(vi) Elemental analysis of micron-sized features
(vii) Fracture and failure analysis
(viii) Defect analysis

■4.0 RESEARCH AND DEVELOPMENT ON THE APPLICATION OF NANOMATERIALS IN PAVEMENT ENGINEERING

At present, nanomaterials are utilised extensively to improve the performance in pavement research especially on modification of asphalt binder for flexible pavement. Much of the work to date in flexible pavement engineering involved the modification of virgin asphalt binder with various types of nanomaterials such as nanoclay (MMT), nano-hydrated lime and carbon nanoparticles. Meanwhile, in rigid pavement, study on the implementation of nanomaterial only focused on modification of surface treatment of concrete layer using nano-titanium oxide (nano-TiO_2).

4.1 Nanoclay

Nanoclay (layered silicates) is naturally occurring minerals and subject to natural variability in their constitution. The purity of the clay can affect the final nanocomposite properties. Clay mostly consist of alumina–silicates, which have a layered structure, and consist of silica SiO_4 tetrahedron bonded to alumina AlO_6 octahedron in various ways. One of the most frequently used layered silicates is montmorillonite (MMT), which has a 2:1 layered structure with two silica tetrahedron sandwiching an alumina octahedron. The thickness of the MMT layers (platelets) is 1 nm with a large active surface area that can have an intensive interaction between asphalt and depends upon the type of material mixed. MMT is also commonly used because it is environmentally friendly, readily available and its structure and chemistry have been well studied [9, 33-35].

In addition, Figure 3 shows the surface treatment process of the nanoclay materials. The proper selection of modified clay is essential to ensure effective penetration of the polymer into the interlayer spacing of the clay and so resulting in the desired exfoliated product [34].

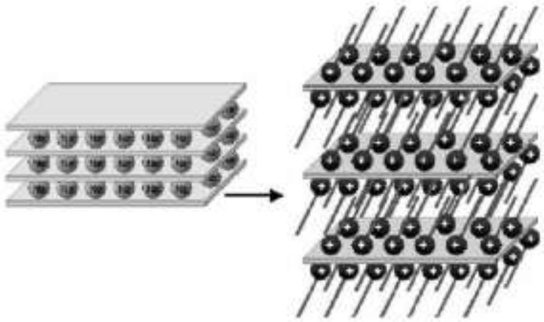

Figure 3 Nanoclay surface treatment [34]

In an intercalate structure as shown in Figure 4, 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, layers of the clay have been completely separated and the individual layers are distributed throughout the organic matrix. 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. These surfactant molecules increase the layer distance. They, moreover, improve the compatibility with the polymer and can enhance the bonding of nanoclay because they can be mixed with the polymer [9, 34-35].

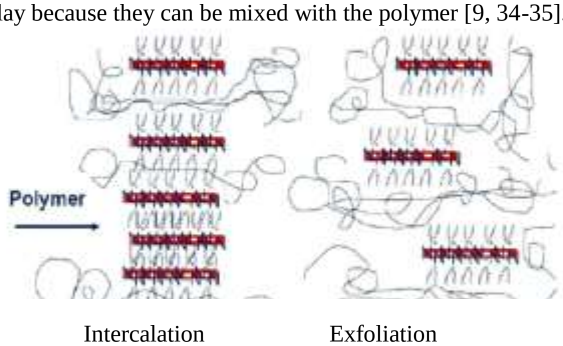

Figure 4 Intercalated and exfoliated nanocomposite [34]

Currently, many studies have been conducted on the performance of asphalt binder modified with nanoclay because it consists of high purity and compatible MMT particles. Most researchers have been using nanoclay at the range of 3 to 6% by weight of the asphalt binder [9, 33-41]. The SEM image of MMT is shown in Figure 5.

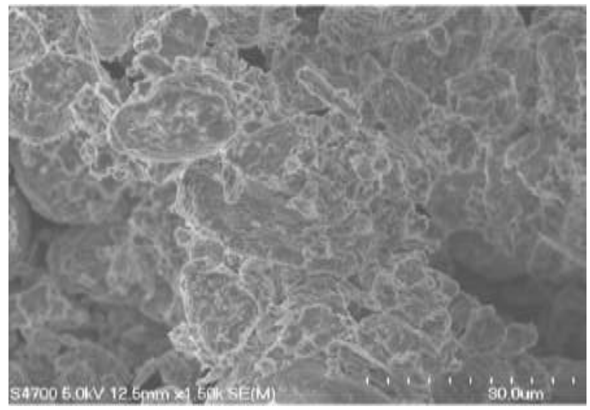

Figure 5 SEM image of Nanomer nanoclays [39]

In China, Yu et al. [42] have used different contents of MMT and organomodified montmorillonite (OMMT) in modified binders. Results showed that the softening point and viscosity of the modified binders were increased at high temperatures. Furthermore, the modified binders exhibited higher complex modulus and had lower phase angle. They also claimed that the MMT and OMMT modified binders enhanced viscoelastic properties, which improve its resistance to rutting at high temperatures. Also, in their recent work, Yu et al. [36] investigated the effect of OMMT on thermo-oxidative and UV aging properties of asphalt. They showed that the MMT and OMMT modified asphalts have higher rutting resistance and very good storage stability.

In addition, series of research works on the effectiveness of nanoclay (MMT base) modified binders had been conducted in United States of America. Findings stated by You et al. [9] described that nanoclay can improve the complex shear modulus, viscosity and has better low-temperature cracking resistance. Meanwhile, Yao et al. [39] showed the morphological images of asphalt binder modified with nanoclay as shown in Figure 6 and rheological findings indicated similar trend from previous researchers. In addition, they also suggested that the nanoclay has a potential effect as anti-oxidation which can reduce oxidation reaction the oxidation reaction when the modified binders are exposed to heat and daylight.

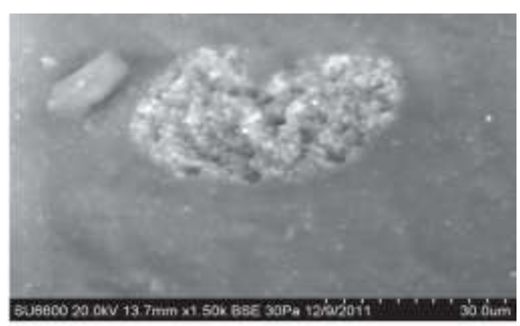

Figure 6 FE-SEM microstructure images of nanoclay modified binder [39]

In other research, the effect of styrene–butadiene–rubber/montmorillonite (SBR/MMT) modification on the characteristics and properties of asphalt were been investigated. Research conducted by Zhang et al. [41] indicated that the addition of SBR/MMT increased both the softening point and viscosity and decreased the penetration of the modified asphalts at high temperatures. They also stated that modified asphalts exhibited higher complex modulus (G*) and lower damping factor (tan δ). It implied that SBR/MMT displayed improved viscoelastic properties, resulting in enhancing its resistance to rutting at high temperature. Meanwhile, Galooyak et al. [37] had studied the effect of styrene–butadiene–styrene/organomodified montmorillonite (SBS/OMMT) modified asphalt mixtures. Results showed that the presence of nanoclay improves the storage stability of PMB significantly.

On the other hand, Zare-Shahabadi et al. [40] studied the use of bentonite clay (BT) and organically modified bentonite (OBT) to reinforce and modify a bituminous paving asphalt binder. They found that the modified asphalts have higher rutting resistance when tested by dynamic shear rheological. It was also indicated that the adding of BT and OBT can significantly improve low temperature of rheological properties and cracking of asphalt. The effect of nanoclay (nanofil-15 and cloisite-15A) on rheological properties of binders have also been studied by Jahromi and Khodaii [35]. They stated that the tests performed on modified binders had proven that the nanoclay modifications help to increase the stiffness and aging resistances. Further experimental works on the effect of nanoclay modified binders on mixtures performance also been conducted among researchers. In Netherland, Ghile [34] had performed mechanical tests on asphalt mixture modified by cloisite. The results showed that nanoclay modification improves mechanical behaviour properties of mixture such as indirect tensile strength, creep and fatigue resistance.

In the other research, Jahromi et al. [38] conducted rheological tests on binders and mechanical tests on asphalt mixture. They also used the same types of nanoclay. Test results showed that nanoclay can improve properties such as stability, resilient modulus, and indirect tensile strength, and result in superior performance under dynamic creep. However, they stated that nanoclays do not have a beneficial effect on fatigue behaviour in low temperature. Optimum binder content and void in total mixture (VTM) increased by adding nanoclay to asphalt.

4.2 Nano Hydrated Lime

Many construction industries used hydrated lime in asphalt mixtures to mitigate moisture-related damage and increase the performance of asphalt mixtures. Figure 7 shows the sub nano-sized hydrated lime (SNHL) with particle average size of 660 nm, which was produced by Los Angeles abrasion machine in a construction material laboratory. Then, SNHL powder was dispersed in acetone by sonicating for 20 minutes. The resulting suspension was dropped onto a clean Si substrate and air-dried. When lime is added to the mixture, it reacted with the aggregate and strengthens the bond between the asphalt and the aggregate interface. Lime reacted with highly polar molecules to inhibit the formation of water-soluble soaps that promote stripping. When those molecules reacted with lime, they formed insoluble salts that no longer attract water [43-47].

Numerous studies have demonstrated that hydrated lime in asphalt mixtures can reduce pavement rut-depth because of its distinct stiffening effects, moisture-associated damage by improving the aggregate–asphalt bonding, and long-term oxidative aging potential. The ability of hydrated lime to make an asphalt mix stiffer, tougher, and more resistance to rutting, is a reflection of its superior performance due to active and beneficial effects of mineral filler [43-47]. Recently, Cheng et al. [44] investigated the use of a super fine hydrated lime as sub nano-sized as anti-stripping properties of asphalt mixtures. They found that the modified asphalts using SNHL have higher values of ITS and TSR.

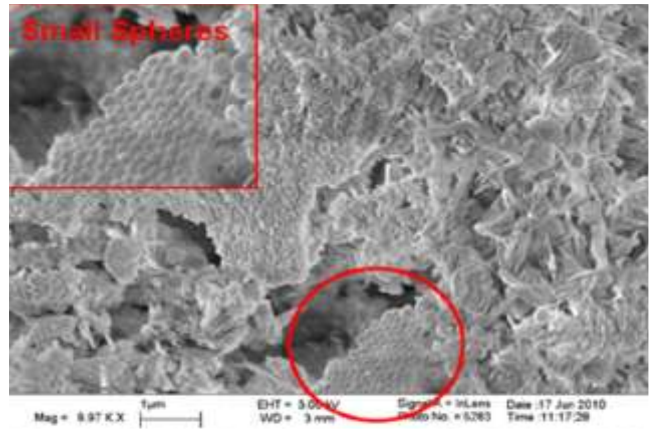

Figure 7 SEM image of nano-sized hydrated lime

4.3 Carbon Nanoparticles

Carbon nanoparticle as shown in Figure 3.8 used in the asphalt binder modification among researchers is basically come with black powder with a tube shape. In nanotechnology application, carbon nanoparticle is also known as carbon nanotubes which are made from sheets of graphite that have rolled up to form a tubular structure. In general, a fine particle of carbon nanotubes consists of many molecule structures with varieties in length, thickness, and number of layers which contribute huge surface area as particle per gramme. Carbon nanotubes can be categorised by its particle structure and currently, there are three types of nanotubes: single-walled nanotubes (SWNTs), multi-walled nanotubes (MWNTs) and double-wall nanotubes (DWNT). However, researchers had stated that MWNTs are easier and cheaper to produce compared with the other nanotubes. In addition, MWNTs can efficiently be dispersed when modified with virgin asphalt binder due to its individual molecules structure [48-51].

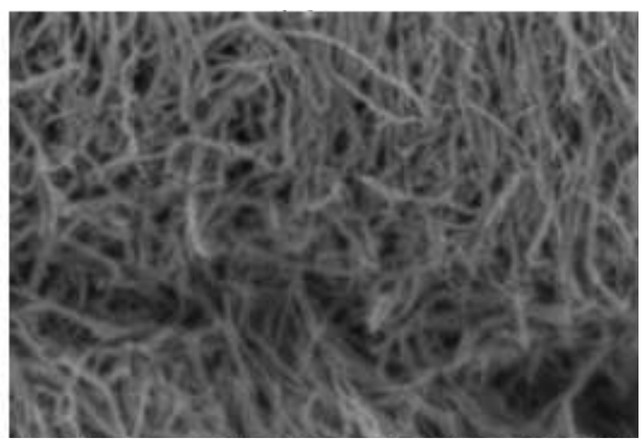

Figure 8 SEM images of carbon nanotube at 1 µm [48]

Previous studies found that the addition of MWNTs contributes to an improvement of rutting resistance at a higher performance temperature and increases the failure temperature, viscosity and elastic modulus when modified with any provided virgin binders. In addition, researchers also identified the highest complex modulus and the lowest phase angle values when virgin asphalt binder modified with MWNTs at the range between 1.0 to 1.5% by weight of virgin binder. In general, asphalt binder modified with MWNTs can increase the performance grade and can improve rutting resistance at pavement service temperature [48, 51].

4.4 Titanium Dioxide (TIO_2)

TiO_2 has been known as a useful photocatalytic material that is attributed to the following characteristics: (a) relatively inexpensive, safe, chemically stable; (b) high photocatalytic activity compared with other metal oxide photocatalysts; (c) compatible with traditional construction materials, such as cement, without changing any original performance; (d) effective under weak solar irradiation in ambient atmospheric environment. The concept of titanium dioxide as a photocatalyst is similar to plant photosynthesis which allows the decomposition of water into oxygen and hydrogen in the presence of Ultra Violet (UV) rays (320 to 400 nm). Based on this heterogeneous photocatalytic oxidation process, nitrogen oxides are oxidized into water-soluble nitrates while sulphur dioxide is oxidized into water-soluble sulfates; these substances can be washed away by rainfall [52-54]

The bulk material of TiO_2 is well known to have three crystal structures: anatase, rutile and brookite. The anatase type is more widely used because it has a higher photoactivity than the other types of TiO_2. Among them, the TiO_2 exists mostly as rutile and anatase phases and both phases have tetragonal structures. Rutile is a high-temperature stable phase and has an optical energy band gap of 3.0 eV (415 nm), while anatase is formed at a lower temperature with an optical energy band gap of 3.2 eV (380 nm) as well as refractive index of 2.3. It is well known that generally, the TiO_2-based photocatalyst with anatase phase shows more excellent photocatalytic effect than that with rutile phase, and the anatase phase can be transformed into the rutile phase at above 800°C [53].

There were various researchers that had been conducted using these nanomaterials. In China, the abrasion resistance and the flexural fatigue performance of concrete containing nano-TiO_2 as additives for pavement is experimentally studied. Li et al. [55-56] and Zhang et al. [57] indicated that the abrasion resistance of modified concrete pavement was increased with increasing compressive strength and also improved the fatigue performance. The sensitivity of their fatigue lives to the change of stress is also increased. Besides that, the addition of nano-TiO_2 also refined the pore structure of concrete and enhanced the resistance to chloride penetration on concrete.

Hassan et al. [52] investigated the used of TiO_2 particles as coating for concrete pavement where these particles can trapped and decomposed organic and inorganic air pollutants by a photocatalytic process. They stated that the wearing of the samples with 3% TiO_2 slightly improved the nitrogen oxides, NO_x ($NO+NO_2$) removal efficiency. They also claimed that the use of TiO_2 coating as a photocatalytic compound would provide acceptable durability and wear resistance. In Tokyo, Fujishima et al. [58] had coated several road areas with cement mixtures containing TiO_2 colloidal solutions. The results obtained in an area of 300 m2 showed 50 to 60 mg/day NO_x degradation.

In other research, Chen and Liu [59] reported the potential of heterogeneous photocatalysis as an advanced oxidation technology for NO_X removal from vehicle emissions by using TiO_2 as a photocatalyst immobilized on the surface of asphalt road. Based on asphalt road material porous characteristic, they utilized permeability technology to make asphalt nano-TiO_2 to be environmental protection materials. Results of experiment revealed that decontaminating rate of the productions ranged from 6 to 12% and this kind of photochemical catalysis environmental protection material has good environment purification function.

5.0 CONCLUSION

Nanotechnology has the potential for improvements in the field of pavement material and construction in future. In flexible pavement application, researchers focused on the modification of binder using nanoclay, nano-hydrated lime and carbon nanoparticles [60-63]. In general, all nanomaterials have stable in storage and can be effectively used as a modifier to improve the physical and rheological properties of virgin asphalt binders. In terms of physical properties, nanomaterials can decrease penetration and ductility, and increase softening point value. Meanwhile, the rheological properties such as performance grade, rutting resistance, low-temperature cracking resistance and aging resistance also showed better improvements. In addition, the engineering properties of mixtures incorporating asphalt binders modified with nanomaterials were significantly improved particularly in the areas of stiffness, rutting resistance, indirect tensile strength and resilient modulus.

On the other hand, the application of nano-TiO_2 as nanomaterial modifier in rigid pavement also indicates positive effects. The concrete containing nano-TiO_2 shows higher compressive strength which indicates higher abrasion resistance [64-65]. In terms of flexural fatigue performance, result shows that the modified concrete has higher fatigue life as compared with control concrete. In addition, the use of TiO_2 photocatalyst in combination with rigid pavement had shown an improved on NO_x removal efficiency. The use of TiO_2 coating as a photocatalytic compound would also provide acceptable durability and wear resistance.

In conclusion, most researchers had found many benefits or good potential of nanoclay when it was modified with virgin asphalt binder for flexible pavement applications. Since there are many types of nanoclay available in the market, it is recommended that the researchers can explore more on the the production process of nanoclay with optimum cost besides investigate the effectiveness of nanoclay as a modifier for WMA mixtures. With the advances in instrumentation and computational science, it could say that nanotechnology will exploit the improvement of pavement material properties and construction process in the future.

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