Journal of Civil Engineering Research 2015, 5(2): 21-27
DOI: 10.5923/j.jce.20150502.01

State-of-the-Art Review of the Applications of Nanotechnology in Pavement Materials

Faruqi M.*, Castillo L., Sai J.

Department of Civil and Architectural Engineering, Texas A&M University-Kingsville, Kingsville, USA

Abstract Nanotechnology is the understanding and control of matter at the nanoscale of dimensions between approximately 1 and 100 nanometers, where unique phenomena enable novel applications. The use of nanotechnology in pavement materials is an area that shows great promise and the potential to change commonly used materials. The overall objective of this paper is to present a state-of-the-art literature review of nanoscience based principles to improve the performance of transportation construction materials. The article is organized into six sections, namely: applications of nanotechnology in concrete pavements, application of nanotechnology in asphalt pavements, application of nanotechno-logy in soils, cost-benefit, challenges, and trends to the future. It is observed from this review that nanoscience can help improve the performance of transportation construction materials and this may eventually lead to the extension of their life cycle.

Keywords Nanotechnology, Pavements Cost-benefit, Challenges, Future

1. Introduction

Even as traffic on the Nation's highways has increased from 65 million cars and trucks in 1955 to almost 246 million today, the condition of U.S highways and bridges has deteriorated. According to estimates by the U.S. Department of Transportation, the current backlog of unfunded but needed repairs and improvements total $495 billion. The increased traffic volume has generated an escalating need for high-performance, durable construction materials for roadway pavements. This need, in turn, is driving research to develop the next generation of materials [1]. Nanotechnology is in its infancy, especially as a road science, but super concretes, smart aggregates, and self-healing structures are coming [2]. The typical expectations of nanotechnology based innovations in pavement materials is that they will change the properties of the materials such as the negative effects of environment and traffic loading (i.e. temperature and moisture sensitivity, fatigue cracking and rutting) can be minimized or reversed [3]. Nanoscience and nanotechnologies represent a new revolutionary approach in the way of thinking and producing, as they somehow revert to the traditional scientific approach and production process, from "big" to "small" [4]. The development of improved materials using nanotechnology based techniques can be very beneficial in pavement engineering.

Pavement engineers use a wide range of materials that are modified using products such as bitumen, cement and other chemical admixtures. The bulk of the materials, however; remains naturally occurring aggregates and soils. Problems often exist in the application of these materials for specific conditions, i.e. incompatibility between certain aggregates and binders (bituminous or cementitious), deterioration of the material during environmental conditions (i.e. water susceptibility of granular materials and temperature sensitivity of bituminous materials) and deterioration with use (i.e. fatigue due to overloading) [5]. Concrete and asphalt pavements are widely used throughout the world, however; they are expensive materials. Applying nanotechnology innovations with these materials can improve performance and increase durability, which in the long run can lead to a cost effective solution.

2. Nanotechnology

Nanotechnology is the understanding and control of matter at the nanoscale of dimensions between approximately 1 and100 nanometers, where uniq-ue phenomena enable novel applications. Encompassing nanoscale science, engineering and technology involves imaging, measuring, modeling, and manipulating matter at this length scale [6]. We have seen that the majority of the nanotechnological developments are occurring in areas such as chemistry, physics, and in electrical engineering.

Matter can exhibit unusual physical, chemical, and biological properties at the nanoscale, differing in important ways from properties of bulk materials and single atom or molecules. Some nanostructured materials are stronger or have different magnetic properties compared to other forms

* Corresponding author:
Mohammed.Faruqi@tamuk.edu (Faruqi M.)
Published online at http://journal.sapub.org/jce

or sizes of the same material. Others are better at conducting heat and electricity. They may become more chemically reactive or reflect light better or change color as their size or structured is altered. Nanotechnology is not simply working at ever-smaller dimensions; rather, working at the nanoscale enables scientists to utilize the unique physical, chemical, mechanical, and optical properties of materials that naturally occur at that scale [7].

For our society to get an impact from this great development, there has been strives to apply nanotechnology into pavement materials. Nanotechnology has led to advanced characterizations, prediction and control of material properties at submicron level. This technology has enhanced the understanding of "origins" of key properties of everyday materials and interactions between materials, structures, external elements and internal components [8]. Therefore, this works makes an attempt to present a state-of-the-art literature review of nanoscience based principles to improve the performance of transportation construction materials.

3. Previous Studies

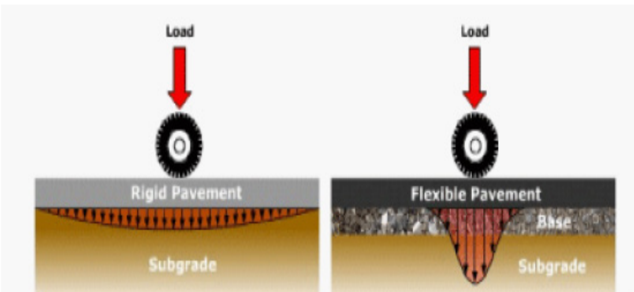

Figure 1. Typical stress distribution under a rigid and flexible pavement [10]

Pavements consist of a combination of engineered materials that generally provide all-weather access to a vehicle to travel in a safe economical way. The layers of materials used are selected and engineered to provide a structure which can withstand the applied vehicular loads under a range of environmental conditions for a defined minimum life [9]. There are two types of pavements, namely: concrete and asphalt. The primary structural difference between a concrete and asphalt pavement is the manner in which each type of pavement distributes traffic loads over the subgrade. A concrete pavement (rigid) also known as Portland Cement Concrete (PCC) has high stiffness and distributes loads over a relatively wide area of subgrade, a major portion of the structural capacity is contributed by the slab itself [10]. With a whopping consumption of over 11 billion metric ton per year, PCC is the most widely manufactured and extensively utilized product in the construction industries throughout the world. Despite its widespread use, a considerable portion of the physical/mechanical properties of cementitious products, specially concrete, have remained ambiguous and unexplained. The other common type is asphalt pavement (flexible). Asphalt pavement is one of America's building blocks. The United States has more than 2 million miles of paved roads and highways, and 94 percent of those are surfaced with asphalt [11]. The load carrying capacity of an asphalt pavement is derived from the load-distributing characteristics of a layered system [12]. Fig. 1 shows stress distribution under rigid and flexible pavements.

Tests and research have been conducted over the past several years in an attempt to understand interaction of nanotechnology in pavement materials. The application of nanotechnology in concrete, asphalt, soils cost-benefit, challenges and trends to the future are described below:

Application of Nanotechnology in Concrete Pavements

There is ongoing research for the application of nanotechnology in concrete pavements. Current applications of nanotechnology in concrete include: a) self-healing materials, b) crack-preventive materials, c) self-cleaning materials, d) shape alloy (SMA) materials, and e) Alkali-silicate reaction (ASR) gels. These applications are briefly described in the following sections.

Self – healing materials

Kumar and Curtin [13] evaluated crack and microstructure interaction with a discussion on the understanding of initiation of cracks in metal. This idea can easily be adapted to improve the nanoscale understanding of crack development in bituminous binder and cracking on concrete pavement. Balazs and Kessler [14, 15] investigated the modeling of self-healing materials, starting with biological examples, which can may potentially be expanded to infrastructures, where cracks that develop in the pavement layers may self-heal based on the introduction of microcapsules in the cement matrix. Similarly [2] described self healing polymers that included a microencapsulated agent and a catalytic chemical trigger when broken by a crack the healing agent is released into the crack along with a catalyst.

Although work is still under way, researchers have developed a polymer material that has the ability to automatically heal cracks. Autonomic (spontaneous) healing is accomplished in this program by incorporating a microencapsulated healing agent and a catalytic chemical trigger within an epoxy matrix. An approaching crack ruptures embedded microcapsules, releasing the healing agent into the crack plane through capillary action. Polymerization of the healing agent is triggered by contact with the embedded catalyst, bonding the crack faces [16]. A preliminary work on assessing the self healing performance has been carried out [17]. This work assess the self-healing performance of cementitious composites using microcapsules (PSMs) with oil and silica gel. The microcapsules were dispersed in fresh cement mortar along with carbon nano fibers and silica fumes. EIS (electrochemical analyses) was used to characterize micro-structural properties and self-healing effect of the fiber-reinforced cement mortars. The EIS data suggested that the inclusion of PSMs enabled the mortar composite to heal at least part of the artificially induced microcracks [7]. A similar process has been described in which micro-sized hollow fibers would also break and release sealant. This would be especially applicable for bridge piers and columns suffering from micro cracking and requiring costly epoxy injection and the ability to self-heal may not be limited to encapsulated microcapsules or fibers [2].

Crack-preventive materials

Self-healing materials are able to automatically heal structures cracks. A concept of crack-preventive materials presumably can prevent pavement cracking. It has been found that carbon nanotubes can have distinct properties depending on their atomic structure, i.e., they can be stiffer than steel, and can also be resistant to damage from physical forces [18]. Carbon nanotubes (CNTs) are considered to be one of the most beneficial nano reinforcement materials. The combination of high aspect ratio, small size, low density, and unique physical and chemical properties make them perfect candidates as reinforcements in multifunctional and smart cement-based materials [19]. The interfacial interactions between CNTs and cement hydrates produce high bond strength. CNTs act as bridges across cracks and voids, which ensures load-transfer in tension [2]. When an external force is applied to the tip of a nanotube, the nanotube bends; when force is removed, it recovers its original shape. Specially designed nanotubes used to build new core/shell micro particles in which the core is made of nanotubes and the thin outer shell is made of bonding materials [18]. The size and aspect ratio of CNTs mean that they can be distributed on a much finer scale than commonly used micro reinforcing fibers. As a result, micro-cracks are interrupted much more quickly during propagation in a nanoreinforced matrix, producing much lower crack widths at the point of first contact between the moving crack front and the reinforcement [20]. When construction material, like cement, is incorporated with a large quantity of strong, firm, rigid micro particles, it forms a new composite material with great strength, equivalent to rebar-frame reinforced concrete at micro scale, a crack-free material [18]. Fig. 2 shows the structure of CNTs.

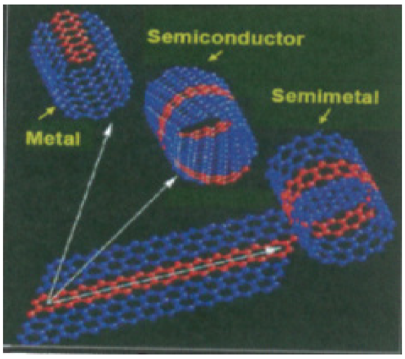

Figure 2. Typical stress distribution under a rigid and rigid and flexible pavement [19]

Self-cleaning materials

Another type of nanoparticle that can be applied to concrete is TiO_2 (titanium dioxide). Camden [21] has incorporated TiO_2 into concrete to render the concrete a material that can perform certain photocatalytic activities. The photocatalytic reaction is typically applied for the provision of self-cleaning surfaces and when incorporated into concrete pavements it can substantially reduce concentrations of airborne pollutants. Hassan [22] conducted a life cycle impact assessment on TiO_2 for concrete pavements and found that it had a positive effect on smog formation, acidification, and air pollutants. TiO_2 is a potent photocatalyst that can break down almost any organic compound it touches when exposed to sunlight in the presence of water vapor [23]. Additionally, it is hydrophilic and therefore provides self cleaning properties to surfaces to which it is applied. TiO_2 is attached to the surface and forms sheets which collect the pollutants and dirt particles previously broken down and washes them off [24].

Shape memory alloy (SMA) material

Differential settlement between bridges and pavements causes bumps or uneven joints at the bridge ends. When vehicles, especially heavy trucks, approach and leave bridges, the bumps cause large impact loads to the bridges and pavements. It is well known that these uneven joints can cause pavement and bridge deterioration, damage automobiles, or cause accidents. The damage includes separation of pavement topping from its base, spalling of joints, fatigue cracking of pavements, and fatigue damage to bridges [25]. SMA nanomaterials are very helpful in counteracting these problems.

Alkali-silicate reaction (ASR) gels

Much has been learned about the cause and prevention of ASR. ASR still continues to be a problem. Distresses caused by ASR have been noted in concrete structures that are over 100 years old and in structures that are only a few days old. The problem of ASR is not limited to certain types of structures, but has occurred in large structures, bridges and pavements [26]. ASR occurs between alkalis from cement and a reactive form of silica from the wrong aggregates, which can results in an alkali/silica gel. If there is enough moisture, the gel will expand, damaging the concrete. The Federal Highway Administration's work involves fundamental research into the chemical and physical processes that cause ASR gel damage. The research includes the application of neutron scattering and positron annihilation spectroscopy to measure nanoscale and sub-nanoscale changes in gel microstructures as a function of gel chemistry, temperature, and relative humidity. This is an innovative way to control ASR [27].

Application of Nanotechnology in Asphalt Pavements

United States has around 4,000 asphalt plants, at least one in every congressional district. Each year, these plants produce 500 to 550 million tons of asphalt pavement material worth in excess of $30 billion [11]. In the United States, transportation infrastructure investment accounts for 77% of the Gross Domestic Product (GDP). Increasing traffic loads and traffic volume, combined with the rising cost of asphalt, have led to an urgent need to improve the durability, safety, and efficiency of asphalt pavements through asphalt modification [28]. Asphalt is the most recycled material. Therefore, it is one of the main ingredients in a sustainable pavement.

In spite of the fact that bituminous materials, such as asphalt, are mainly used on a large scale and in huge quantities for road constructions, the mechanical behavior of these materials depend to a great extent on structural elements and phenomena which are effective on a micro and nano-scale [28]. So far nanotechnology has found hardly any attention from engineers and material producers, but since it is emerging in other fields, the possibility has found a new leap forward. The use of nanotechnology to improve asphalt pavements will result in a longer lasting more durable pavement for airfields, ports, and highways. This is achieved by adding nanoclay in the modification of polymer matrices to realize significant improvement in mechanical, thermal, and thermal barrier properties. Other applications for asphalt pavements include are in the field of material manufacturing, design, properties, testing, monitoring, and modeling.

A schematic overview of focus areas where nanoscience and technology could improve asphalt pavement technology is shown in Fig. 3 [28].

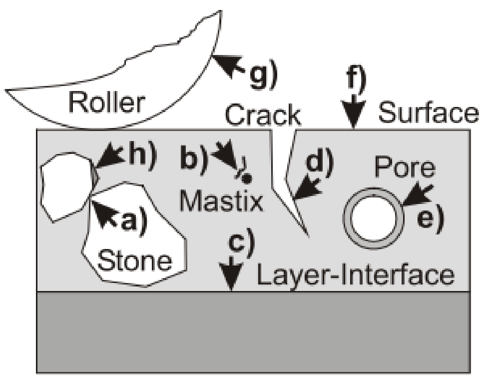

Figure 3. Schema to visualize focus areas for nanoscience and technology with respect to asphalt pavement structures:
a) Bond between stones (shear and tension)
b) Mastic (stiffening, cohesion, durability, compaction improvers)
c) Bond between layers (tack coats)
d) Self-repair (healing) and rejuvenating agents
e) Oxidation of binder films and binder inhomogeneities
f) Surface properties (friction, optical properties, water repellent, abrasion resistant, self-cleaning), sealcoats for surface protection
g) Anti-adhesion surface for rollers during compaction
h) Bond, adhesion between stone and mastic

Additional applications of nanotechnology in asphalt include sulfur-extended asphalt, nanoclay, and carbon microfibers. These are described below:

Sulfur-Extended Asphalt

Shell is marketing Shell Thiopave® to modify asphalt binder properties that would improve the performance of the extended asphalt concrete mixtures. The Thiopave modifier consists of small pellets of sulfur modifier that are added to the asphalt mixtures during the mixing process [29]. These pellets melt rapidly with the hot mix and is dispersed throughout the mixture. In addition to lowering the virgin binder requirements for a given asphalt mixture, the addition of Thiopave can significantly alter the performance properties. It is dependent both on (1) the percentage of virgin binder that is substituted with Thiopave; and (2) the amount of time the specimen is allowed to cure prior to performance testing.

Literature has shown that the addition of Thiopave has been shown to significantly increase the Marshall Stability and deformation resistance of asphalt mixtures in the laboratory after a two week curing period. [30-31] The Thiopave material also had little negative impact in area that were thought to be problematic, such as fatigue cracking resistance, low temperature cracking resistance, and moisture susceptibility [32].

Nanoclay and Carbon Microfibers

Recent research suggests that the use of nanoclay improves some characteristics of asphalt mixtures and asphalt binders, but there is still more research to be done before it can be applied on a large scale. Zhanping You and his colleagues have studied the addition of nanoclay (montmorillonite) and the effect that it has on asphalt. Layered silicates (nanoclay) are widely used in the modification of polymer matrices to realize significant improvement in mechanical, thermal, and barrier properties [33]. The addition of nanoclay to the asphalt mixture has seen an improvement to the toughness of this material. The toughness of each tested material was determined by using the area under the stress and strain curve for the direct tensile test. Fig. 4 shows that the nanoclay modification of 2% and 4% increases the toughness of the asphalt binder compared to the original binder.

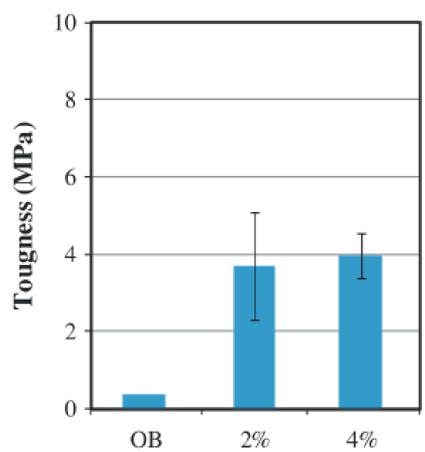

Figure 4. Toughness results for the original binder, nanoclay at 2%, and nanoclay at 4% [33]

The preliminary results from this research indicate that nanomodified asphalt binders hold promise to improving the performance. The addition of nanoclay increased the toughness compared to the original binder. The ongoing research will focus on the low-temperature cracking performance and fatigue resistance of the nanoclay-modified binder as well as the asphalt concrete mixtures made with nanoclay-modified asphalt [33].

Application of Nanotechnology in Soils

Although it was not officially termed as such, many geotechnical materials can be defined as nanomaterials and their behavior has for many years been studied on a nano level [4]. Soil is in essence a particulate material which encompasses a wide variety of particles with dimension of less than 1 nm to 75 mm [34]. Such a wide range of particle sizes, i.e., more than 6 orders of magnitude, has made soil one of the most complicated materials to be studied, modeled, and utilized [35]. Typically, soils are classified into four different categories (gravel, sand, silt, and clay). Natural soils and gravels can also be termed unbound materials, and they consist of soil material selected for its specific properties. Typically, water is added to these materials to ensure optimal contents, and then the material is compacted and forms the sub-grade, subbase or (in selected cases) base layer of the pavement structure. The behavior of these materials is typically affected by changes in moisture content [4].

A big change that a mineral undergoes when used at the nanoscale is that the surface area to volume ratio typically increases drastically. One of the materials that is often encounterd in pavement engineering is naturally occurring clay. These clays pose very specific problems to the pavement engineering field as their response to changes in moisture content and the platelet structure of the material cause most clay to have low friction angles and some to be expansive [4]. Current main application is self-cleaning soil. A self-clean material involves polycyclic aromatic hydrocarbons, and it is especially effective in decontaminating soil. Using polymeric nanoparticles, it could be an efficient tool to deal with soil particles with tightly adherent contaminants [36]. In addition; it can be made for a particular type of soil-decontamination conditions.

4. Cost-Benefit

The costs of most nanotechnology equipment and materials are currently relatively high. This is partly due to the novelty of the technology, but also due to the complexity of the equipment. However, in the case of the nanomaterials, costs have shown to decrease over time and the expectations are that, as manufacturing technologies improve, the costs of the materials will decrease [4]. Since 1990 the cost of producing CNTs has fallen 100-fold and can be expected to fall further [19]. Whether such decreases will render the materials as run-of-the-mill pavement engineering materials will have to be seen. Current opinion is that in special cases, the materials will enable unique solutions to complicated problems that cause them to be cost effective, which will lead to large scale applications of these specific technologies. In other cases the traditional methods for treating the problem may still remain the most cost effective. As indicated earlier, the job of the engineer is to solve real-world problems and provide a facility to the general public at a reasonable cost [19]. Furthermore, it is expected that the multifunctional and smart CNTs reinforced cement-based materials will feature high performance price ratio and low life cycle cost. Therefore, the cost of CNTs should no longer be the critical issue [19].

For asphalt pavements, bitumen is a by-product of the production of fuel from crude oil. In typical asphalt pavements the bitumen comprises about 0.5 percent of the mass and between 5 and 17 percent of the cost of the road. Internationally, the reserves of crude oil are viewed as being decreasing. The direct implication for pavement engineering is that the price of bitumen may increase drastically in future as the availability decreases [4]. Therefore, nanotechnology will play a role in alleviating this problem.

5. Challenges

Some of the main challenges that can be imposed are the health, safety, and environmental impacts. Although a large number of potential ideas and applications for nanotechnology and pavement engineering exist, it is also important to remain realistic and identify and accept the current limitations and challenges inherent in this field [9]. With the advent of new technologies, including nanotechnology, one should consider the potential unintended consequence to human health and the environment that might accompany development and use of the technology [37]. Users of nano-particles should endeavor to mitigate the potential risks of nanoparticles during the design stage rather than downstream during manufacturing or customer use (i.e. when the material is already embedded in the pavement) [4]. Five principles to design safe nanotechnologies are summarized below [38]:

- Reduction (evaluate the option to use smaller quantities of nanoparticles in the product while maintaining functionality).
- Encapsulation (enclose a potential hazardous nanoparticle with a material that is less hazardous).
- Functionalization (bond molecules to nanoparticles to change the properties that can reduce the hazard potential while preserving the desired product properties).
- Alternative materials (identify an alternative material that can be used to replace the hazardous nanoparticle).
- Size, surface, and structure (change the size, surface, or structure to reduce the hazard potential of the nanoparticle while maintaining its functionality).

Another major challenge to implement nanotechnology is the scale effect. Applying this technology to materials and making these nanomodified materials work in infrastructures can be difficult. The unique environment of the pavement engineer who works with large volumes of material should always be appreciated when evaluating potential applications of nanotechnology. The effects on manufacturing capacity and performance of the nanomaterials when combined with bulk aggregates and binders should be evaluated to ensure that the beneficial (nanoscale) properties are still applicable and cost-and-energy-efficient at these scales [4].

6. Trends to the Future

Based on this literature review, we may find that there are many characteristics of nanotechnology that can be applied to pavements to provide a better performance. However, successful nanotechnology application may need 5 or 10 years to be commercialized.

Some of the potential future directions are listed below [39]:

- Engineered materials using nanotechnology will allow maximum use of locally available materials and avoid unnecessary transport.
- Design ductile, flexible, breathable, permeable or impermeable concrete properties on demand.
- Design concrete and asphalt mixes which are resistant to freeze-thaw, corrosion, sulfate, ASR, and other environmental attacks.
- Develop specialty products such as products with blast resistant, conductive properties as well as temperature, moisture, and stress-sensing abilities.

Future nanotechnology applications will lead to reduce maintenance costs, increase pavement lifespan, reduce accidents, and increase construction efficiency.

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