The Tenth International Conference on Construction in the 21st Century (CITC-10)
July 2nd-4th, 2018, Colombo, Sri Lanka

Applications of Nanomaterials in Pavement Engineering: A Review

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Abstract
Various types of bituminous mixtures are used in the construction of flexible pavements, depending on the requirements of the project. Asphalt is a body of solid dark color substance, refined from crude oil. By mixing asphalt with additives like sand, stone and gravel, asphalt binds all of them together into what is called asphalt pavement. A systematic effort has been made to develop asphalt mixtures with improved properties. Although bituminous materials are mainly used on a large scale and in bulky quantities, the macroscopic mechanical behavior of these materials continues to essentially depend on the extent of microstructure and physical properties in micro and nano-scale. Nowadays, one of the most interesting areas of asphalt research involves the use of nanomaterials. New research efforts regarding the development of nanomaterials for use in asphalt indicate the potential for improvement in durability, mechanical and physical properties resulting thus in new multidisciplinary research fields with synergy of academia and industrial retrospective partners. This paper presents several types of nanomaterials with their properties, the ways that they can be integrated in new asphalt mixture development, potential applications in pavement engineering and pavement charactristic improvements, and finaly current trends and challenges in obtaining such results.

Keywords
nanomaterials, asphalt, pavement, material properties

1. Introduction

Nanotechnology is the consideration and control of matter at the nanoscale. More specifically, nanotechnology is manipulation of matter on an atomic, molecular, and supramolecular scale. A common description of nanotechnology refers to the particular technological goal of precisely manipulating atoms and molecules for fabrication of macroscale products (Drexler, 1992). According to Whatmore and Corbett (1995), the subject of nanotechnology includes “almost any materials or devices which are structured on the nanometer scale in order to perform functions or obtain characteristics which could not otherwise be achieved”. Nanotechnology is not just a science that deals with materials in very minor dimensions, but a science that exploits the unique physical, chemical, mechanical and optical properties of materials on this scale. Some nanostructured materials are stronger or have different magnetic properties compared to other shapes or dimensions of the same material. Some others, present better performance as far as the heat and electricity conductivity are concerned. They can also become chemically more drastic or reflect slightly better or even change color as their size or structure changes. As that, the utilization of nanotechnology in pavement materials is considered an area with high potentiality, strong enough to amend commonly used materials (Faruqi *et al*., 2015).

2. Nanotechnology in asphalt pavements

The continious increasing traffic loads and volume in conjuction with the rising cost of asphalt as a byproduct of crude oil, makes the need for improved durability, safety and efficiency of asphalt pavements imperative and this can be done by means of asphalt modification (Partl, 2004). Nanotechnology gradually is enganged more and more into the field of asphalt modification. Dreamlike effects of nanomaterials have now been brought to enhance and augment the perfromance of asphalt. Several trials and efforts have been initiated in the scope of preparation of modified asphalt for realizing the mechanism of modification and the subsequent improvement in performance (Changqing *et al*., 2013). In pavement engineering reasearch, nanotechnology is employed as a form of new material, device and system at the molecular level. It is anticipated that the use of nanotechnology in the improvement of asphalt pavements will craft the conditions for manufacturing of more durable and longer lasting pavements that can be utilized to key infrastructure projects like airfields, ports and highways. That can be done by adding various nanoparticles, the production of which is continously under reaserach and development for making them easier in mix process and more competive in cost (Faruqi, 2015). As nanotechnology reaseach follows a fast-track path, introduction of nanomaterials in asphalt pavements advances in a parallel hish ascending pathway. More than that, the unique qualities that nanomaterials exhibit, such as high temperature sensitivity, high ductility, large surface area, high strain resistance along with low electrical resistivity, create additional reasons for such soaring development (Yang *et al*., 2010 and Veytskin, 2015).

3. Nanomaterials in use for modified asphalt pavements

Nanomaterials, due to their nature, exert specific dimension properties. As a result, they exhibit specific characteristics, qualities and unique features compared to commonly used materials, making likewise feasible their integration as additives in asphalt pavements. Ordinary pavement materials can hardly meet the operational requirements for present and future highways as well as pavement construction technology. Consequently, pavement materials of enhanced quality, increased safety, higher realibility and more environmental friendly features, are in high demand. The dispersion of nanomaterials within asphalt materials may considerably enhance certain properties of asphalt constituents, e.g., visco-elasticity, high temperature effects, resistance to aging, fatigue and moisture (Ruoyu, 2017). The nanomaterials applied in asphalt pavement engineering with their specific properties are categorized in the next sections.

3.1 Carbon nanotubes (CNT)

Amid various nanoparticles that have been considered as potential asphalt binder modifiers, *Carbon Nanotubes (CNTs)* have attracted an increasing interest (Yang, 2013). CNTs belong to nanocarbons which are among the most promising materials developed in recent years. Nanocarbons also include fullerenes, nanodiamond, onions, various hybrid forms and 3-dimensional structures based on these. Several years ago, these materials were available in milligram-scale quantities while now many of them are produced by tones per year. Carbon nanotubes (CNTs) are allotropes of carbon with a cylindrical nanostructure. These cylindrical carbon molecules exhibit uncommon properties yet valuable for nanotechnology and other fields of material science and technology. On account of the material exceptional strength and stiffness, nanotubes have been constructed with length-to-diameter ratio of up to 132.000.000:1, significantly larger than for any other material (Wang, 2009).

3.2 Nano-clay

Nanoclays are nanoparticles of layered mineral silicates. As layered silicate is termed the clay that has a layer thickness ranging from 1 to 100 nm and is broadly utilized in the modification of matrices to improve mechanical and thermal properties. Depending on chemical composition and nanoparticle morphology, nanoclays are ordered into a number of classes such as *montmorillonite, bentonite, kaolinite, hectorite, and halloysite* (Sigma-Aldrich, 2018a). It is the sort of nano-particles mostly used for material modification, due to their low cost of production and ample availability in nature.

Two main types of nano-clays are utilized for modifying asphalt binder. The first is the Non Modified Nano-clay (NMN) asphalt and the other one is the the Polymer Modified Nano-clay (PMN) asphalt. Out of two nano-clays, the NMN is the most commonly layered silicate used, with a 2 to 1 layered configuration clay consisting of one octahedral alumina sheet sandwiched in the middle of two tetrahedral silica that was proposed by Ray and Okamoto (Ray and Okamoto, 2003) .

3.3 Nano-fibers

Nanofibers are fibers with diameters in the nanometer range. Nanofibers can be produced from different polymers (natural or synthetic) and, thus, have different physical properties and application potential while they belong also to the wider family of nanocarbons (Khajavi *et al.*, 2016). The diameters of nanofibers depend on the type of polymer used and the method of production. All polymer nanofibers are unique due to their large surface area-to-volume ratio, high porosity, appreciable mechanical strength, and flexibility in functionalization compared to their microfiber equivalents.

Carbon Nano-Fibers (CNFs), apart from having large surface area and high aspect ratio (like all nanomaterials), present also good interfacial bonding and high tensile modulus. Carbon nanofibers are discontinuous, highly graphitic, highly compatible with most polymer processing techniques, and can be dispersed in an isotropic or anisotropic mode. Also, they have excellent mechanical properties, high electrical conductivity, and high thermal conductivity, which can be imparted to a wide range of matrices including thermoplastics, thermosets, elastomers, ceramics, and metals. Carbon nanofibers have a unique surface state, which facilitates functionalization and other surface modification techniques to tailor/engineer the nanofiber to the host polymer or application. Carbon nanofibers are available in a free-flowing powder form - typically 99% mass is in a fibrous form (Sigma-Aldrich, 2018b).

3.4 Nano-Silica (S_iO_2)

Silicon dioxide, also known as silica (from the Latin silex), is an inorganic material, namely an oxide of silicon with the chemical formula S_iO_2, most commonly found in nature as quartz and in various living organisms. In many areas all over the earth, silica is the main constituent of sand while primarily it is produced from silica precursors. Silica is one of the most complex and most abundant families of materials, existing as a compound of several minerals and as synthetic product. Silica nanoparticles have been utilized in industrial applications for reinforcing the elastomers as a rheological solute (Chrissafis *et al.,* 2008). The main advantage of this nanomaterial is the low production cost compared to its high performance prospect.

3.5 Nano-T_iO_2

Titanium dioxide nanoparticles, also called ultrafine titanium dioxide, are particles of titanium dioxide (T_iO_2) with diameters less than 100 nm. Ultrafine TiO_2 is regarded as one of the three most produced nanomaterials, along with silicon dioxide nanoparticles and zinc oxide nanoparticles. It is the second most marketed nanomaterial in consumer products, after silver nanoparticles.

In nature, titanium dioxide is minly found in the form of rutile, anatase and brookite. In particular, nanoscale titanium dioxide consists of 80% anatase and 20% of rutile. Nano titanium dioxide, compared to ordinary one, exerts very large surface area, very small diameter and significatly low opacity. Due to these distinctive properties, nano titanium dioxide is utilized by researchers as performance improvement additive in modified asphalts (Chen, 2010).

3.6 Nanophosphors

Nanophosphors are nanoscale crystalline structures with a size depedent bandgap that can be altered to change the color of light. Nanophosphors can be defined as nanoparticles of transparent dielectrics (hosts) doped with optically active ions (activators), so that the emission of light happens due to the electronic transitions between the levels of the impurity ions inside the bandgap of the host (characteristic luminescence) (Kelsall *et al.*, 2004).

3.7 Graphene and Graphene Oxide (GO)

Graphene and *Graphene Oxide (GO)* are regarded as two of the most promising materials because of their surface area size along with exceptional electrical and physical properties. Given their considerable production and purchasing cost, they were hardly studied in the traditional material science. Nowdays, as both nanotechnology and nanomaterial development are subjects of high concern and graphene and GO are much cheaper than before, due to their production process improvement, these materials are progessively introduced in the construction industry. Graphene plays a key role in the families of nano-materials, following its excellent physical and electrical properties, and lately is used to improve polymer properties.

4. Applications of Nanotechnology in Pavements

The construction industry pays special attention to nanotechnology and nanomaterial developments and innovations appreciating novel advances that can trigger market growth. It appears that the products generated out of the nanotechnology research and development can considerably treat contemporary construction difficulties and may alternate the requirement of the construction process. The major applications in pavements engineering are presented in the folowing sections.

4.1 Pavement surface characteristics improvement

Using nanosilica in the base asphalt binder, the viscosity indexes of nanomodified asphalt binder are slightly reduced. Reduced viscosity of the binder indicates a lower compaction temperature and lower energy consumption. Mixing of nanosilica into the asphalt can enhance the recovery ability of asphalt binders. The anti-aging and fatigue cracking performance of nanosilica-modified asphalt binder and mixture are improved as well as the rutting resistance and anti-stripping property. Yet, adding nanosilica into asphalt binder does not greatly affect the low-temperature properties of asphalt binders and mixtures (Yao *et al.,* 2012).

4.2 Physical properties enhancement

The use of CNTs to bituminous binders and mixtures have an impact to various properties of them. In particular, it can significantly extent its rheological properties (Khattak *et al.,* 2012). Furthermore, it results in underlayer thichness reduction and, therefore, stone material consumption (Motlagh *et al.,* 2012). Moreover, it can contribute in rutting resistance enhancement (Amirkhanian *et al.,* 2011) and to reduced sensitivity to oxidatives (Santagata *et al.,* 2012).Various physical properties of the bitumen (such as stiffness and tensile strength, tensile modulus, flexural strength and modulus thermal stability) can be enhanced when it is modified with small amounts of nano-clay, on the condition that the clay is dispersed at the nano-scopic level. Generally, the elasticity of the nanoclay modified bitumen is much higher and the dissipation of mechanical energy is much lower than in the case of unmodified bitumen (Jahromi and Khodaii 2009). Adding nanoclay in asphalt normally increases the viscosity of asphalt binders and improves the rutting and fatigue resistance of asphalt mixtures. Research has shown that even a small percentage of nanoclay could significantly improve the compressive and shear strength of thermoplastic materials (Ruoyu, 2017). Adding T_iO_2 to bitumen, results in higher softening point than the base bitumen. It is clearly observed that the bitumen performance is improved againt rutting, while its visco-elastic behavior is improved at higher temperatures. Moreover, it results in a decrease of penetration value compared to the control bitumen as well as in an increase of viscosity due to the improved bond between bitumen particles, which is developed by the integration of nano particles. Finally, the enhanced performance of bitumen in the softening point tests makes it more sensitive to the temperature changes (Sadeghnejad, 2016).

4.3 Micro-cracks prevention

It is thought that the high aspect ratio of fiber can produce a good network of nanocomposite. As that, the bridge-link effect of nanofibers can effectively prevent the development of micro-cracks under the interaction of heavy vehicle loading. Accordingly, using CNFs in asphalt binder enhances its mechanical and rheological properties.

4.4 Safety improvement

Nanophosphors can be added to traditional pavement materials such as concrete, bitumen and road paint to enable these materials to become luminescent after exposure to light. If the road can act as the source of the light it can play a role in improving road safety as the source of the light is not depedent on external power.

4.5 Sensoring

One of the widely-mentioned in research potential of nanomaterials is the development of sensors that act as part of the substrate that is being observed, thereby allowing very fine measurements on a small scale and obviating the need to add external sensors to a system (Goddard *et al.,* 2007). The application of CNTs in traffic monitoring is an example of such application (Shi and Chung 1999). In this type of applications, data transfer from sensor to a data acquisition device and data analysis still require further work, especially if the sensors are being distributed inside a pavement of several kilometers length. Also, supported graphene layers and various forms of graphene films offer the ultimate sensitivity to detect tiny stimuli (from low concentrations) due to their large surface-to-volume ratio, while graphene membrane sensors can also benefit from their excellent mechanical properties, e.g., high rigidity, flexibility and strength. Another important parameter of sensors is specificity which refers to the detection of just one specific substance and no other. To do so, the graphene surface needs to be functionalized.

5. Nanomaterial cost

The cost of most nanotechnology equipment and materials are currently relatively high. This is partly due to the novelty of the technology but also to the complexity of the equipment. However, in the case of the nanomaterials, costs have shown to decrease over time. The expectation is that as manufacturing technologies improve, the costs of the materials will decrease. For example, since 1990 the cost of producing CNTs has dropped by the order of 100 and may reach lower prices in the future.

For asphalt pavements, bitumen is a by-product of fuel production 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 asphalt concrete. As the crude oil reserves are being globaly depleted, the price of bitumen may increase drastically in the future. Therefore, nanotechnology can play a role in alleviating this problem (Gopalakrishnan *et. al.,* 2011). Furthermore, when dealing with the potential of nanomaterial application in pavement engineering, both construction and maintenance costs needs to be evaluated with focus on the short term, long term and life cycle cost aspects. In terms of maintenance costs, actions that can ensure minimum maintenance of pavements have a direct impact on the life-cycle cost as well as on delay impacts during the maintenance period, which can be prevented by the development of automatic crack filters and treatment corrosion of reinforcement. Also, the pavemant service life can in general be increased through the improvement of pavement resistance to environmental acts. Developing stronger materials, the required material quantities are reduced (e.g., thinner pavement layers), affecting accordingly the construction cost. Life-cycle effects in terms of pavement durability enhancement and reduced maintenance requirements should be included in any cost evaluation.

6. Trends and Challenges

Nanomaterials (especially Graphene-based ones) are expected to bring new solutions to current industrial challenges related to coomunication, energy generation and storage applications. Asphalt pavements are excellent materials when it comes to solar energy utilization. They are bare surfaces exposed directly to sun and, because of their low thermal conductivity and large heat capacity, they present considerable temperature increase. This is the point where the superior thermal properties of graphene can be nicely exploited. Adding a small amount of graphene would have a negligible impact on heat capacity, increasing conductivity and making the pavement an efficient heat transfer mechanism. Adding the potential of future graphene-based production of light and flexible PV cells, highly sustainable biomimic PV cells, light electrical storage systems, as well as light hydrogen storage systems, 'smart roads' could be develped. For example graphene based energy harvesting systems and in-road energy storage can create powerful solutions for 'while on the move' vehicles charging systems (Ghavanini *et. al.,*2015).

Along with the promising trends of nanomaterials, there are also some issues to be considered. Unintended consequences to human health and the environment that might accompany development and use of nanomaterials should be considered and mitigate the potential risks during the design stage rather than downstream during manufacturing or customer use (e.g., when the material is already embedded in the pavement) (NNI, 2014). Another major challenge to implement nanotechnology is the scale effect. The unique pavement engineering environment with large volumes of material should always be considered for the evaluation of 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 value adding at these scales.

7. Conclusions

It is clearly shown that the addition of nanomaterials can improve the performance of asphalt binders. In particular, properties like softening point and kinematics viscosity can be improved (increased) along with bitumen penetration (decreased). Furthermore, the tensile strength of the modified bitumen is improved compared to the non-modified one. The same applies for the rutting resistance which is considerably better than the standard one. So far, nanoparticles (considered as additives) were not very attractive for investigation by researchers due to their relatively higher cost compared to usual additives (e.g., polymers). Nowadays, the continious engangement of more and more researchers in the nanotechnology field has resulted in the development of many new innovative and low cost production methods for nanomaterials, making them also appropriate for use in materials like asphalt binders, providing promising results in the direction of being integrated to them. There are still many sophisticated applications under research and development for nanomaterial-modified asphalt mixtures in order to meet several expectancies in pavement engineering, such as health monitoring, traffic monitoring, developing materials with luminescent properties, electricity production & storage, and information transferring.

8. References

Amirkhanian, N.A., Xiao, F., and Amirkhanian, N.S., (2011). “Characterization of unaged asphalt binder with carbon nano particle*”. International Journal of Pavement Research and Technology*, Vol. 4, pp 281-286

Chen, M., and Liu, Y. (2010). “No_x removal from vehicle emissions by functionality surface of asphalt road”. *Journal of Hazardous Materials*, Vol. 174, pp 375 - 379

Chrissafis K., Paraskevopoulos, K.M., Papageorgiou, G.Z, and Bikiaris, D.N. (2008). “Thermal and dynamic mechanical behavior of bionanocomposites: fumed silica nanoparticles dispersed in poly (vinyl pyrrolidone), chitosan, and poly(vinylalcohol)”. *Journal of Applied Polymer Science*, Vol.100,pp 1739-1749

Drexler, and K. Eric (1992). *Nanosystems: Molecular Machinery, Manufacturing, and Computation*. New York: John Wiley & Sons. ISBN 0-471-57547-X.Faruqi M., Castillo L., and Sai, J (2015).”State-of-the-Art Review of the Applications of Nanotechnology in Pavement materials. *Journal of Civil Engineering Research,*Vol.5, pp 21-27

Ghavanini, F., and Theander, H. (2015). "Graphene feasibility and foresight study for transport infrastructures" Chalmers Industriteknik ,Retrieved from https://www.chalmers.se/

Goddard, W. A., III, Brenner, D. W., Lyshevski, S. E., and Iafrate, G. J. 2007. Handbook of nanoscience, engineering, and technology, 2nd Ed., CRC, Boca Raton, Fla.

Gopalakrishnan, K. (1) et al, (2011) (eds): "Nanotechnology in civil infrastructure", Application of Nanotechnology in Road Pavement Engineering, Springer-Verlag Berlin Heidelberg, pp 49-83.

Jahromi S., Ghaffarpour, K.A. (2009). Effects of Nanoclay on Rheological Properties of Bitumen Binder. Construction and Building Materials, 23, 2894–2904.

Kelsall, R. W., Hamley, I. W., and Geoghegan, M. 2004. “Nanoscale science and technology.” Wiley, Chisester, England.

Khajavi, R., Abbasipour, M., and Bahador, A. (2016). "Electrospun biodegradable nanofibers scaffolds for bone tissue engineering". *Journal of Applied Polymer Science,* Vol.133, pp 1–19

Khattak, M.J., Khattab, A., Rizvi, H.R., and Zhang, P. (2012). “The impact of carbon nano-fiber modification on asphalt binder rheology”. *Construction and Building Materials*,Vol.30, pp 257-264

Motlagh, A., Kiasat, A., Mirzaei, E., and Birgani, F.O. (2012). “Bitumen Modification Using Carbon Nanotubes”. *World Applied Sciences Journal*, Vol. 18, pp 594-599

NNI, (2014), "Environmental, health, and safety issues", National Nanotechnology Initiative, (n.d), Web 02.Feb.2014, Retrieved from http:// nano.gov/you/envir-onmental-healthsafety.

Ray, S.S., and Okamoto, M. (2003). “Polymer layered silicate nanocomposites: a review from preparation to processing”. *Progress in Polymer Science*, Vol. 28, pp 1539-1641

Ruoyu, L., Feipeng, X., Serji., A., Zhanping., Y., and Jia., H. (2017). “Developments of nano materials and technologies on asphalt materials – A review”. *Construction and Building Materials*, Vol.143, pp 633-648

Sadeghnjad, M., and Shafabakhsh, G. (2016). “Experimental Study on the Physical and Rheological Properties of Bitumen Modified with Different Nano Materials (Nano S_iO_2 & Nano T_iO_2)”. *International Journal of Nanoscience and Nanotechnology*, Vol.13, pp 253-263

Santagata, E., Baglieri, O., Tsantilis, L., and Dalmazzo, D. (2012). “Rheological characterization of bituminous binders modified with carbon nanotubes”. *Procedia - Social and Behavioral Sciences*, Vol.53, pp 546-555

Shi, Z.-Q., and Chung, D. D. L. 1999. “Carbon fiber-reinforced concrete for traffic monitoring and weighing in motion.” Cem. Concr. Res., 29, 435–439.

Sigma-Aldrich (2018a). “Nano Minerals: Nanoclays”. Online at: https://www.sigmaaldrich.com/technical-documents/articles/materials-science/nanomaterials/nano-minerals-nanoclays.html. Accesed on February 2, 2018

Sigma-Aldrich (2018b). “Carbon Nanofiber Applications & Properties”. Online at: https://www.sigmaaldrich.com/technical-documents/articles/materials-science/nanomaterials/carbon-nanofibers.html. Accesed on February 2, 2018

Teraoka, I. (2002). *Polymer Solutions: An Introduction to Physical Properties*. John Wiley & Sons, Inc., New York, ISBN 0-471-22451-0

Veytskin, Y., Bobko, C., Castorena, C., and Kim, R., Y. (2015). “Nanoindentation investigation of asphalt binder and mastic cohesion”. *Construction and Building Materials,* Vol.100, pp 163-171

Wang, X., Li, Q., Xie, J., Jin, Z., Wang, J., Li, Y., Jiang, K., and Fan, S. (2009). " Fabrication of ultralong and electrically uniform single-walled carbon nanotubes on clean substrates". *Nano Letters, Vol. 9*, doi:10.1021/nl901260b , pp 3137–3141

Whatmore, R.W., and Corbett, J. (1995).”Nanotechnology in the Marketplace”. *Computing and Control Engineering Journal,* Volume 6, Issue3, June 1995, pp 106-107

Yang, J., and Tighe, S. (2013). “*A Review of Advances of Nanotechnology in Asphalt Mixtures”*. *Procedia Social and Behavioral Sciences*, Vol 96, pp 1269-1276

Yang, Z., Hollar, X., and Shi, X. (2010). “Surface-sulfonated polystyrene microspheres improve crack resistance of carbon microfiber-reinforced Portland cement mortar”. *Journal of Materials Science*, Vol.45, pp 3497-3505

Yao, H., Zhanping, Y., Liang, L., Lee, C.H., Wingard, D., Yap., Y.K., Shi, X., and Goh, S.W. (2013). “Properties and Chemical Bonding of Asphalt and Asphalt Mixtures Modified with Nanosilica”. *Journal of Materials in Civil Engineering,* Vol. 25, pp 1619-1630