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A review of advances of Nanotechnology in asphalt mixtures

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Abstract

This paper reviews the advances in using nano-materials in hot mix asphalt. The clay nano-particles are the primary materials applying in asphalt construction. Adding nano-particles like nanoclay, nanosilica, and nanotubes in asphalts normally increase the viscosity of asphalt binders and improves the rutting and fatigue resistance of asphalt mixtures. Using nanoclay as the second modifier in polymer modified asphalts can improve the storage stability and the aging resistance of polymer modified asphalts. Various Atomic Force Microscopy (AFM) techniques (e.g. tapping mode imaging, force spectroscopy, and nano-indentation) as well as X-ray diffraction (XRD) experiments can be conducted on modified asphalt binders to characterize the micro or nano-scale structures of nano-asphalts. Through the reasonable selection of nano-materials used in asphalt, nano-modified asphalt can offer many benefits in cold regions.

Keywords: Nanotechnology; Nanoclay; Nanosilica; Nanotubes; Asphalt Mixture

1. Introduction

Nanotechnology has been explored to a considerable degree to address the problems in design, construction, and utilization of functional structures with at least one characteristic dimension measured in nanometers (Kelsall et al. 2005). The U.S. National Nanotechnology Initiative stipulates that "Nanotechnology involves research and technology development at the atomic, molecular, or macromolecular levels, the length scale of approximately 1 to 100 nm (nanometer) range, to provide a fundamental understanding of phenomena and materials at the nano-scale and to create and use structures, devices, and systems that have novel properties and functions because of their small and/ or intermediate size" (Mann 2006). Nanotechnology therefore allows the design of systems with high functional density, high sensitivity, special surface effects, large surface area, high strain resistance, and catalytic effects. All attributes are directly or indirectly the result of the small dimensions of nano-particles (Parviz 2011, Teizer 2012).

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In spite of the fact that bituminous materials, such as asphalt, are mainly used on a large scale and in huge quantities for road construction, the macroscopic mechanical behavior of these materials still depends to a great extent on microstructure and physical properties on a micro- and nano-scale (Partl 2003). Although researchers, material producers, and engineers have explored the potential for many years, nanotechnology usage has been limited. New efforts and exploration of the development of nanomaterials for pavement application that improve the nano - scale mechanical and physical properties as well as durability of this important group of construction materials provide a considerable prospect.

2. Nano Materials in Asphalt Mixtures and Performances

A nano particle is a miniaturized particle that is measured in nanometers (nm) and is often defined as a particle with at least one dimension that is less than 100 nm. The physics and chemistry of nano-sized particles differ from those of conventional materials, primarily because of the increased surface area-to-volume ratio of nanometer-sized grains, cylinders, plates, and because of the quantum effects resulting from spatial confinement (Parviz 2011, Teizer 2012). The clay nano particles are the primary materials that could have application in asphalt construction based on a literature review of nano particles and nano materials. Carbon nano tubes (CNT), silica, alumina, magnesium, calcium, and titanium dioxide (TiO2) nano particles can also have a significant effect on asphalt performance.

2.1. Nanoclay

Nanoclay is clay that can be modified to make the clay compatible with organic monomers and polymers. These nano-composites consist of a blend of one or more polymers with layered silicates that have a layer thickness in the order of one nm and a very high aspect ratio. Common clays are naturally occurring minerals and subject to natural variation in their formation. Separation of clay discs from each other results in a nano-clay with a large active surface area (up to 700-800 m2/g). This results in an intensive interaction between the nanoclay and the bitumen.

While the stiffness and viscosity of specific bitumen were not affected by the addition of one specific type of montmorillonite nano-clay, another type of montmorillonite nano-clay did affect stiffness and viscosity. However, the short and long term aging resistance of the bitumen was improved for one of the nano-clays (Van de Ven et al 2008). Various physical properties (such as stiffness and tensile strength, tensile modulus, flexural strength and modulus thermal stability) of the bitumen 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).

Bentonite clay (BT) and organically modified bentonite (OBT) were used to reinforce and modify an asphalt binder. The modified asphalt binders were produced by melt processing under sonication and shearing stresses. The modified asphalts had a higher rutting resistance. Adding BT and OBT significantly improved the low temperature rheological properties and the resistance to cracking of asphalt (Zare-Shahabadi et al 2010; Ganesh 2012).

In asphalt paving technology, the styrene- butadiene-styrene (SBS) copolymer has been used as a modifier for producing high performing mixtures (Hanyu et al. 2005; Chen et al. 2006, Fu et al. 2007; Yildirim, 2007). Polymeric nano composites are one of the most exciting materials discovered recently and the physical properties are successfully enhanced when a polymer is modified with small amounts of nanoclay, on the condition that the clay is dispersed at the nanoscopic level (Jahromi and Khodii 2009; Mittal et al. 2012). Nanoclays have been used as a secondary modifier to further enhance the performance properties of SBS copolymer modified asphalt (Yu et al. 2007b; Polacco et al. 2008; Yao et al. 2012a). The sodium montmorillonite (Na-MMT) and organophilic montmorillonite (OMMT) nanoclays have promising potential to reduce the permanent deformation or rutting of asphalt pavements. In particular, the clay had a compatibilizing effect on asphalt and polymer, and a high compatibility between clay and polymer led to a better dispersion of the polymer in the asphalt, thus influencing the final rheological properties of the studied systems (Polacco et al. 2008). Furthermore, Nanofil-15 and Cloiste-15A have the potential to reduce the aging characteristics of the asphalt binder (Jahromi and Khodaii 2009).

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 or intercalated product. In an intercalate structure, 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 the layers of the clay have been completely separated and the individual layers are distributed throughout the organic matrix (Polacco et al. 2008), shown in Fig. 1.

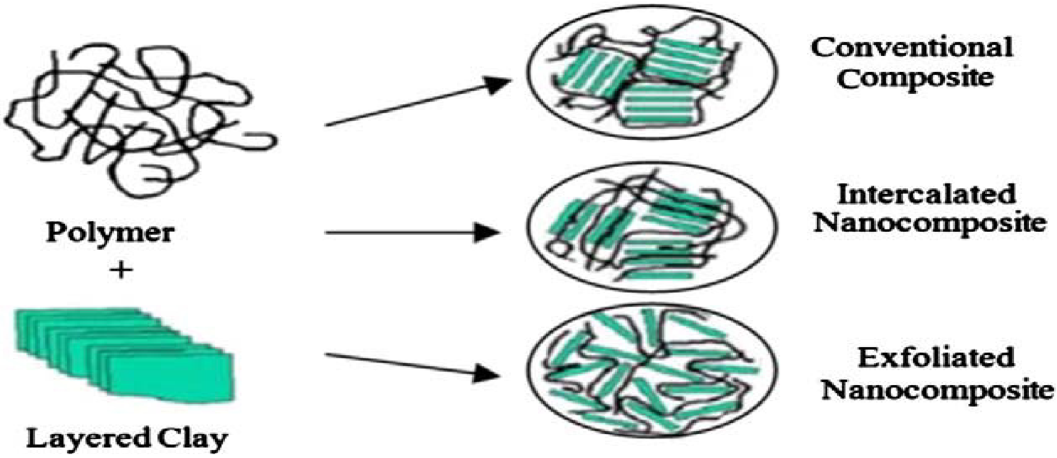

Fig. 1. Schematic of structures of polymer nanocomposites (Golestani et al. 2012)

2.2. Carbon nanotubes

A CNT is a one-atom thick sheet of graphite rolled up into a seamless hollow cylinder with a diameter of the order of one nanometer. CNTs were discovered by Iijima (1991), who first reported the arc-discharge synthesis and characterization of helical microtubules, formed by molecular-scale fibres with structures related to fullerenes. CNTs are characterized by superior mechanical properties when compared with other construction materials. Depending on the radius of the tube, the Young's modulus of a CNT can be as high as 1,000 GPa (Treacy et al. 1996) and the tensile strength can reach 150 GPa (de Heer, 2004). Two different types of CNT exist respectively in the form of single tubes (called single-wall CNTs) and coaxial tubes (multiple-wall CNTs). Multi-wall CNTs are less expensive and easier to produce but exhibit lower strength and stiffness than single-wall CNTs (Bai & Allaoui 2003). Very few studies have been conducted in the area of bituminous binders and mixtures. When CNTs are added with a sufficiently high percentage (> 1%) to base bitumen, they can significantly affect rheological properties (Xiao et al. 2011a; Xiao et al. 2011b; Khattak et al. 2012). Using carbon nanotubes equals to 0.001 of weight bitumen in asphalt mixtures, in addition to improving asphalt pavement properties, will decrease thickness of under layers and as a result reduce stone materials consumption (Motlagh et al. 2012). CNTs provide an enhancement of rutting resistance potential (Amirkhanian et al. 2011a; Amirkhanian et al. 2011b) and of resistance to thermal cracking. Moreover, susceptibility to oxidative aging is reduced with further advantages that are expected in the long-term performance of bituminous mixtures (Santagata et al. 2012).

2.3. Nanosilica

Silica is an abundant compound over the earth that is largely employed in industries to produce silica gels, colloidal silica, fumed silica and so on. The nanosized silicas are interesting particles because they are applied in emerging areas like medicine and drug delivery (Barik et al. 2008). Amorphous nanosilica is qualified as nanobiopesticides. Silica nanoparticles have been used in the industry to reinforce the elastomers as a rheological solute (Chrissafis et al. 2008) and cement concrete mixtures (Quercia & Brouwers, 2010). Silica nanocomposites have been attracting some scientific interest as well. The advantage of these nanomaterials resides in the low cost of production and in the high performance features (Lazzara et al. 2010).

With the addition of nanosilica in the base asphalt binder, the viscosity values of nanomodified asphalt binder decreased slightly. Lower viscosity of the binder indicates that a lower compaction temperature or lower energy consumption of the construction process will be achieved. The addition of nanosilica into the control asphalt improved the recovery ability of asphalt binders. The low-temperature grade of nanosilica modified asphalt binder was the same as the control asphalt binder, and the properties and stress relaxation capacity of nanosilica modified asphalt binder was the same as the control asphalt. The anti-aging performance and fatigue cracking performance of nanosilica modified asphalt binder and mixture were enhanced and the rutting resistance and anti-stripping property of nanosilica modified asphalt mixture were also enhanced significantly. Meanwhile, the addition of nanosilica into the control asphalt binder did not greatly affect the low-temperature properties of asphalt binders and mixtures (Yao et al. 2012b).

The asphalt binder modified by 1% nano powdered rubber VP401 has better performance in resistance to low temperature crack and rutting, compared to other nanomaterial modified asphalt binder (Chen et al. 2012). Spraying TiO2 and ZnO fog to the surface of asphalt slabs show lower aging rates (Steyn 2009; Gopalakrishnan 2011). The asphalt mixture modified by 5% SBS plus 2% nano-SiO2 powder can increase the physical and mechanical properties of asphalt binder and mixtures (Ghasemia et al 2012). The addition of nanoclay and carbon microfiber would improve a mixture's moisture susceptibility in most cases under water or de-icing chemicals (NaCl, MgCl2 and CaCl2), and even freeze-thaw cycles (Goh, et al 2010).

3. Microscope Research Methodology on Nano-asphalts

In order to characterize the nano and micro-structure and the mechanical behavior of asphalt clay nano-composites, various Atomic Force Microscopy (AFM) techniques (i.e. tapping mode imaging, force spectroscopy, and nano-indentation) as well as X-ray diffraction (XRD) experiments were conducted on asphalt binders modified with different contents of a nano-clay material. The AFM images and XRD results indicated that the nano-clay had an exfoliated structure within the nano-composite. In addition, the AFM images showed better interaction between the nano-clay layers and the distinct asphalt domains containing the so-called "bee-like" structures as compared to the flat asphalt matrix. The results of the force spectroscopy experiments indicated that the inclusion of the nano-clay material significantly enhanced the adhesive forces of asphalt materials, while it had a slightly adverse effect on the cohesive forces (Nazzal et al 2012).

The OMMT/SBS modified bitumen is found to have a good ultraviolet (UV) aging resistance through characterizing the microstructures of OMMT/SBS modified bitumen by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and atomic force microscopy (AFM) (Zhang et al. 2011).The interlayer spacing of silicate layers in bentonite, organically modified bentonite and the modified asphalt binders were analyzed through wide angle X-ray diffraction (WAXD) by Zare-Shahabadi et al (2010). Intercalated and exfoliated structures in the modified asphalt binder system were found (Zare-Shahabadi et al 2010).

The Na-MMT and OMMT were detected to have formed an intercalated and exfoliated structure within the SBS copolymer modified asphalt binder system (Yu et al. 2007a; Yu et al. 2007c; Polacco et al. 2008). Linear SBS-nanocomposite modified asphalt may form an exfoliated structure, whereas the Branch SBS-nanocomposite modified asphalt may form an intercalated structure, based on the X-ray diffraction (XRD) results (Golestani et al 2012). The spectra by X-ray diffraction (XRD) indicated that proper dispersion of OMMT in SBS leads to a homogenous exfoliated structure blend, and OMMT can improve the storage stability of polymer modified bitumen (Saeed et al. 2010).

A good dispersion of nanosilica particles in the asphalt binder matrix was observed by Scanning Electron Microscopy (SEM) images (Yao et al. 2012).

Fluorescence optical microscope and electron microscope were used to analyze the microstructure of the nanometer ZnO and SBS modified asphalt. If the nanometer ZnO /SBS modified asphalt was made by the solvent method, it can make full use of ZnO's benefits to make SBS on a micrometer scale in the modified asphalt, and improve the combinative ability on the interface of the SBS and asphalt. It is a complex physical and chemical process in making the nanometer ZnO /SBS modified asphalt, the major character of SBS and asphalt is a physical reaction, while the major character of nanometer ZnO and SBS is a chemical reaction (Xiao et al 2006).

4. Feasibility of Using Nano-asphalts in Cold Regions

According to Ghile's research, the addition of nanoclay modifiers to bitumen has increased the stiffness of the asphalt, which has improved the rutting resistance (Ghile 2006). Consistent research conclusions were achieved by Yu et al (2007b) and Polacco et al (2008). The indirect tensile strength has also increased due to the input of nanoclay modifiers, which has improved the aging resistance. The elasticity of the modified bitumen increased in high temperatures, and the dissipation of energy decreased because the clay is dispersed at the nanoscopic level (Jahromi and Khodaii 2009). These improvements have increased the durability and the useful life of the asphalt pavements, which will save money for maintenance and repairs, and also made the bitumen easy to work with in hot areas, since the viscosity has increased. However, there are possibly some disadvantages of nano material modified pavement under low temperatures. Research shows that the fatigue resistance of nanoclay modified bitumen is lower than the unmodified bitumen at low temperatures (Ghile, 2006). Although, according to the study by Prof. You and his team at Michigan Technological University, a nanoclay modified asphalt pavement trial was built recently in the USA in cold weather (Marcia Goodrich, 2012 May).

Despite the disadvantage of having a low resistance to fatigue, bitumen modified with nano materials have many advantages in low temperatures as well as in high temperatures. Studies have also shown that bitumen modified with nano CaCO3 has an increased anti-deformability and anti-aging properties under low temperature (NPCC-701 For Modified Asphalt, 2010). Another important advantage of nanoclay modified asphalt is its improved tensile strength and the reduced susceptibility to water and deicers (Goh et al, 2010). This is important because in cold regions, where most asphalt paved roads are susceptible to snow, deicers used on roads usually erode and damage the pavements. By having a modified pavement that is less susceptible to damage by deicers, a great amount of energy and money would be saved from less maintenance.

5. Benefits of Nanotechnology in Asphalt Mixtures

In general, Nanotechnology will produce benefits in two ways – by making existing products and processes more cost effective, durable and efficient and by creating entirely new products.

In particular to asphalt and asphalt mixture properties, Nanotechnology has the following known benefits:

- Improve the storage stability in polymer modified asphalt
- Increase the resistance to UV aging
- Reduce the moisture susceptibility under water, snow and deicers
- Improve the properties of asphalt mixtures at low temperature
- Improve the durability of asphalt pavements
- Save energy and cost
- Decrease maintenance requirements

6. Conclusions and Recommendations

- Adding Nanoclay in asphalts normally increases the viscosity of asphalt binders and improves the rutting and fatigue resistance of asphalt mixtures. One specific type of montmorillonite nano-clay doesn't affect the stiffness and viscosity of asphalt binder. Applying Nanoclay can improve the aging resistance of asphalt mixes.

- Polymer nano composites are one of the most exciting materials because of the nano-particle addition and nanoscale dispersion. Using Nano-particles can improve the storage stability of polymer modified asphalts.

- CNTs provide an enhancement of rutting resistance potential and of resistance to thermal cracking.

- The anti-aging performance, fatigue cracking performance, rutting resistance, and anti-stripping property of nanosilica modified asphalt binder and mixture are enhanced. Meanwhile, the addition of nanosilica into the control asphalt binder did not greatly affect the low-temperature properties of asphalt binders and mixtures.

- Various Atomic Force Microscopy (AFM) techniques (i.e. tapping mode imaging, force spectroscopy, and nano-indentation) as well as X-ray diffraction (XRD) experiments can be conducted on modified asphalt binders to characterize the micro or nano-scale structures of nano-asphalts. The major character of SBS and asphalt is a physical reaction, while the major character of nano-particle and SBS is a chemical reaction, which should be paid the further investigations.

- Through the engineering selection and optimization of nano-materials used in asphalt, nano-modified asphalt can perform well in cold regions with many benefits.

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