

Nanomaterials' Effect on Asphalt Mixtures

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The desire for high-performance and long-lasting asphalt pavements significantly pushed the modification of the conventional paving asphalt binders. To cope with such demand, the use of nanomaterials for the asphalt binder modification seems promising, as with a small amount of modification an important enhancement of the asphalt mixture mechanical performance can be attained. Several studies already evaluated the effects of the modifications with nanomaterials, mostly focusing on the asphalt binder properties and rheology, and the positive findings encouraged the study of modified asphalt mixtures.

modified bitumen

nanomaterials

nanosilica

nanoclay

nanoiron

asphalt mixtures

mechanical performance

aging sensitivity

1. Introduction

The asphalt binder, i.e., the bitumen, is a material widely used for road construction worldwide. Generally, the bitumen is obtained from refining crude oil and its final properties are dependent on crude oil origin and refining processes. Bitumen can be described as a thermoplastic, viscous-elastic material that behaves as a solid at low/intermediate temperatures (under 25 °C) and as a semi-solid/liquid at higher temperatures (typically above 60 °C) ^{[1][2]}. This property allows its use in road construction, where firstly, the bitumen is heated to properly mix with the aggregates and, finally, after the compaction process and cooling to ambient temperature, the bitumen will act as the binder of the aggregates. Nevertheless, the bitumen temperature sensitivity causes several problems for the asphalt pavement in service. The permanent deformation and cracking mechanics are highly related to high and low service temperatures, respectively.

While in service, the asphalt pavement has to withstand a wide range of environmental conditions and traffic loads. In many cases, the conventional penetration grade bitumen no longer ensures the desired performance over the service life, and early conservation work or reconstruction may be needed. In addition, the bitumen is a material sensitive to aging, and its properties deteriorate over the service life. The aged bitumen becomes stiffer and more brittle, thus affecting the performance of the asphalt mixture ^[1]. Aging effect is particularly severe in surface layers that are exposed to environmental conditions such as UV radiation, moisture, oxygen, and larger thermal amplitude ^[3]. Thus, the service life of the asphalt mixture is highly dependent on its aging resistance ^[4].

Over the years, several types of additives have been studied to modify the properties of the asphalt mixtures, generally, focusing on the improvement of mechanical performance. The additives studied more frequently were

adhesion improvers, fibers, rubber, to use warm mix asphalt (WMA) technology, and a wide variety of polymers [5]. In the last one or two decades, following the developments in the field of nanotechnology, the study of nanomaterials broadened and its application as asphalt mixture additive was considered.

The definition of nanomaterial group a wide variety of different materials, generally, designated according to their specific properties or structures (e.g. nanoparticles, nanotubes, nanowires, nanoplatelets, nanorods, and nanoporous). Nano is a unit prefix name, represented by the symbol n, which corresponds to the submultiple 10^{-9} . Thus, the materials that have their dimensions in the nanoscale, generally 1 nm to 100 nm, are often designated as nanomaterials. The European Commission Recommendation (2011/696/EU) [6] provides a more concise definition for nanomaterial: "Natural, incidental or manufactured material containing particles, in an unbounded state or as an aggregate or as an agglomerate and where, for 50% or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm to 100 nm". Fairly similar description is provided by the American Society for Testing and Materials (ASTM) in ASTM E2456-06 2012 [7].

The nanoscale allows the material to behave differently than its macroscopic counterpart. Such behavior can be triggered by two effects: The surface to volume ratio (specific surface area) and spatial confinement [8]. The specific surface area increases as the particle size decreases, becoming significantly large in the nanoscale. For example, in the case of a single spherical particle the surface to volume ratio is 3 mm^{-1} , $3 \times 10^3 \text{ mm}^{-1}$, and $3 \times 10^6 \text{ mm}^{-1}$, for the sphere radius of 1 mm, 1 μm , and 1 nm, respectively. Thus, considering the same volume unit, the use of nanoparticles instead of microparticles will allow a much larger available surface area. Nanomaterials can play a significant role in enhancing the performance of the existing materials by providing better resistance to traffic and environmental loads or mitigating incompatibility between some natural aggregates and asphalt binder, enabling more sustainable and durable pavement solutions [9].

2. Nanomaterials

2.1. Type of Nanomaterials

Theoretically, any material can be synthesized in the nanometric scale, generically, by processing macroparticles of the respective material. The nanomaterials more studied for asphalt binder and asphalt mixture modification are types of nanosilica and of nanoclay.

2.2. Modification of the Asphalt Binder with Nanomaterials

In the majority of the studies found in literature, the modification of asphalt mixtures with nanomaterials is initially done at the binder level, i.e., the asphalt binder is modified with the nanomaterials, and then, the modified binder is used to produce the asphalt mixture. The optimum dosage of nanomaterial in the asphalt binder will be dependent on the type of nanomaterial, type of asphalt binder, and the methodology used, i.e., type of testing selected. Generally, the nanomaterials are blended with asphalt binder in small percentages, around 2 to 6% by mass of asphalt binder [10]. In some cases, besides the nanomaterial, a polymer modification is also done, or the binder

being modified is a polymer-modified binder (PMB). Generally, for the modification of the asphalt binder with nanomaterials in the laboratory, one out of two methods is used: The dry blending method or the solvent blending method [\[11\]\[12\]\[13\]\[14\]](#).

3. Effect of the Modification with Nanomaterials in the Asphalt Binder

The nanosilica-modified binder presented a decrease in penetration, increase in viscosity, and increase in softening point [\[15\]\[16\]\[17\]\[18\]\[19\]\[20\]](#). Regarding the rheological behavior, evaluated using the dynamic shear rheometer (DSR), the modified binders present higher complex modulus and lower phase angle [\[16\]\[21\]\[19\]\[22\]](#). Authors evaluating the binder fatigue with DSR tests, concluded that the nanosilica modifications showed superior fatigue resistance [\[23\]\[24\]\[25\]](#).

At the level of fundamental characterization, the nanoclay-modified binder presented a decrease in penetration, increase in softening point, and increase in viscosity [\[14\]\[15\]\[17\]\[18\]\[26\]\[27\]\[28\]\[22\]\[29\]\[30\]\[31\]\[32\]\[33\]\[34\]\[35\]\[36\]](#). And consistently, regarding rheology, the nanoclay modified binders present an increase in complex shear modulus and decrease in phase angle [\[14\]\[28\]\[33\]\[34\]\[37\]\[38\]\[39\]\[40\]](#). The existing studies mostly focused on organically modified montmorillonite, due to the expectation of obtaining exfoliated structures in the modified binders and higher performance improvements. The raw nanoclays, in their hydrophilic natural form, may form only intercalated structures, although, some authors studying raw nanoclays [\[28\]\[38\]\[39\]\[41\]\[42\]](#) also obtained considerable performance improvements.

The type of nanoclay used in the modification has an important effect on the results, i.e., in the modified binder performance. Although the overall trends were the same, the authors that studied more than one nanoclay type obtained different results, regardless of using the same control binder. A study [\[28\]](#) about the modification of 60/70 asphalt binder with nanoclays, sodium bentonite and organically modified sodium bentonite, revealed that both modifications caused reduction of the phase angle and increased viscosity, softening point, and complex shear modulus. The effects were correlated with the dosage of nanoclay introduced and, in all cases, the effects of the organically modified clay were stronger. The exfoliated structure of the organically modified nanoclay, which promotes a better dispersion in the asphalt matrix, can explain these effects. On the other hand, in another study [\[14\]](#), the authors studied the modification of a PG 64-28 with two organically modified nanoclays with similar structure (nanoclay A and nanoclay B) and observed different effects. For example, regarding viscosity, the modifications caused an increase of 41% and 112% with 2% of nanoclay A and 2% of nanoclay B, respectively, and regarding complex shear modulus, the modifications caused an increase of 66% and 184% with 2% of nanoclay A and 2% of nanoclay B, respectively. Jahromi and Khodaii [\[37\]](#) studied the effects of two organically modified nanoclays (Nanofil-15 and Cloisite-15A) on the properties of the 60/70 asphalt binder and, found the effects of the second stronger than those of the first. In the cases that authors studied the same dosage and nanomodification in different control binder, they reported that the effects in softer binders are stronger than those in stiffer binders [\[43\]\[44\]](#).

4. Effect of the Modification with Nanomaterials in the Mechanical Performance of Asphalt Mixtures

4.1. Nanosilica

The authors that conducted studies about nanosilica modified asphalt mixtures, reported important improvements in the mechanical performance of the mixture. To evaluate the asphalt mixture performance, the mechanical tests most found in the literature were Marshall stability, water sensitivity (using the indirect tensile strength ratio or the retained Marshall stability), permanent deformation, and stiffness. The nanosilica modified asphalt mixtures presented higher Marshall stability, higher indirect tensile strength, higher stiffness modulus, enhanced water sensitivity (indicated by higher indirect tensile strength ratio and higher retained Marshall stability), lower permanent deformation and better fatigue resistance.

4.2. Nanoclay

In the studies of asphalt mixtures modified with nanoclays, several improvements in the mechanical performance were identified. Generally, the effect reported by the authors were: Increase in Marshall stability, reduction in permanent deformation, lower water sensitivity (increase in indirect tensile strength ratio and/or retained Marshall stability), increase in stiffness modulus/resilient modulus, and better resistance to fatigue. Although the findings are generally consistent, the big variety of materials leads to different effects in mechanical performance. The nanoclay type, the modification of raw nanoclay with organo-modifiers, the nanoclay dosage and the original asphalt binder properties can have a strong influence on the results.

4.3. Nanoiron

The authors studying the use of nanoiron to modify the asphalt mixture indicate several improvements in mechanical performance, such as, higher Marshall stability, higher indirect tensile strength, enhanced water sensitivity (indicated by higher indirect tensile strength ratio and higher retained Marshall stability), lower permanent deformation, better fatigue, and fracture resistance.

5. Conclusion

The studies about the modification of asphalt binders with nanomaterials (nanosilica, nanoclay and nanoiron) showed that if a correct dispersion of the nanomaterials in the asphalt matrix is attained, several properties can be improved. Regarding the properties of the asphalt binders, the modifications with nanomaterials brought a reduction in penetration value and an increase of viscosity and softening point, as well as, increase in complex modulus and a decrease in phase angle. The effects of the modifications are dependent on the type and dosage of the nanomaterial, as well as, on the properties of the original asphalt binder to be modified. The optimum nanomaterial dosage may be dependent on the mechanical property to be enhanced, as well as the cost of the

modification. For example, softer binders attained higher gains in resistance to permanent deformation than stiffer binders.

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