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Review

Behavior Evaluation of Bituminous Mixtures Reinforced with Nano-Sized Additives: A Review

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Abstract: This article presents a comparative review of the most commonly used nano-additives for bituminous mixtures: nanoclays (NC), nanosilicates, carbon nanotubes (CNTs), graphene nanoplatelets (GNPs), nano-calcium oxide (CaO), and nano-titanium dioxide (TiO_2). In this study, the mechanical behavior of the obtained additive mixture is evaluated. According to the revised literature, the results strongly depend on type, concentration, and dispersal of used nano-additive. In fact, it has been seen that simple shear mixing followed by sonication homogenizes the distribution of the nanoparticles within the bituminous matrix and favors the bonds' formation. The viscosity of the mixture of bitumen with nanoparticles improves with the increase of the percentage of additive added: it indicates a potential improvement to permanent deformation and rutting. Another benefit is an increased resistance of the binder to aging. Furthermore, it has been shown that the nanoparticles are able to prolong the service life of a bituminous mixture by means of various interdependent chemical–physical mechanisms that can influence the resistance to fatigue failure or the ability to self-heal. However, the effectiveness of these improvements depends on the particle type, added quantity and mixing technique, and the tests carried out.

Keywords: bituminous mixtures; nano-additives; nanoclay; carbon nanotubes; graphene nanoplatelets; nano-calcium oxide; nano-titanium dioxide; sonication; fatigue performance; self-healing

1. Introduction

Bitumens are natural or artificial mixtures of solid or semi-solid hydrocarbons, obtained from asphaltic rocks or natural oils; they are used to provide waterproofing and protective coating and as binders in road construction [1]. Bitumen's components are usually grouped into two categories: asphaltenes and maltens. These two can be subdivided into saturates, aromatics, and resins [1]. Bitumen is modeled as a colloid composed of asphaltene micelles covered by a stabilizing phase of polar resins; this phase forms the interface with a continuous oily maltenic medium [1,2].

Different factors affect the physical and mechanical behavior of bituminous mastics, including temperature and loading time. The compound is liquid or solid at high or low temperatures, respectively. Therefore, when asphalt is used for road pavements, cracks at low temperatures or rutting at high temperatures may occur. Moreover, oxygen, ultraviolet (UV) light of sun, and heat affect both the physical properties and chemical structure of asphalt, and cause a phenomenon called aging [3]. Another enemy of the asphalt binder is moisture: it causes the progressive loss of functionality of the material due to loss of the adhesive bond between the asphalt binder and the aggregate surface [4]. Penetration of moisture in asphalt mixtures reduces strength and stiffness of asphalt mixtures and makes the mixtures prone to develop premature pavement distresses (e.g., stripping, raveling, and hydraulic scour [5,6]; rutting, alligator cracking, and potholes [4]). The presence of water in pavements can be detrimental if combined with other environmental factors such as freeze–thaw cycling over extended periods: chemical and physical interactions between bitumen and aggregate at the interface influence the adhesive strength [5]. Moreover, repetitive vehicular loads cause fatigue cracking distress in asphalt pavements. Fatigue in asphalt pavements consists of two consecutive phases. At first (pre-localization), micro-cracks are generated; these grow followed by the formation of macro-cracks during post-localization due to critical stresses or strains [7]. Finally, permanent deformations (i.e., rutting) affect asphalt pavements; they are caused by deformation or consolidation of pavement layers, especially if they are thermosusceptible as asphalt ones are. Several factors influence rutting of asphalt pavement: overloading, low-speed trucks, substance properties, and climate conditions (i.e., high-temperature areas). As traffic loading and tire pressure increase, permanent deformation at the top layer of pavement surface also increases [4]. Service life of the pavement drastically declines because of rutting: when in ruts, asphalt becomes a hydroplaning hazard.

In recent years, increased traffic levels (both volume and load) entailed the need to enhance performance of used asphaltic materials. In addition, both a better understanding of behavior and characteristics of binders and the greater development of technology have encouraged and enabled researchers to examine the benefits of introducing additives and modifiers into the asphalt [8,9]. Available modifiers fit into various categories (e.g., naturally occurring materials, industrial by-products and waste materials, and engineered products). Some of the most common categories include reclaimed rubber products, fillers, fibers, catalysts, polymers (natural and synthetic), and extenders. Among them, a blend of asphalt with polymer is the most often currently used to improve performances of asphalt (and asphalt mixes) [10,11]. Polymer-modified asphalt has been used for many years with mixes and its usage will probably increase in the immediate future. Polymer-modified asphalt improves resistance to rutting, abrasion, cracking, fatigue, stripping, bleeding, and aging at high temperatures, and flexibility at low temperatures [10]. In addition, the structural thickness of asphalt pavement could be reduced. According to some research [12], different types of polymers can be mixed with asphalt: there is no universally superior polymer type and therefore its selection depends on specific needs. Moreover, its effectiveness depends on polymer characteristics, polymer content, and the nature of the asphalt.

In addition to traditional modifiers such as polymers, in recent years various alternative materials have been considered. Particularly, the emergence of nano-technologies has motivated a number of researchers in evaluating the use of nano-materials for such a purpose [13]. Nanotechnology is the study of the control of matter on an atomic and molecular scale: it deals with structures of the size 100 nm or smaller and involves developing materials or devices within that size. The application of nanomaterial technology in asphalt mixtures is a relatively new topic; it has rapidly evolved since the buckminsterfullerene discovery [14]. Nanotechnology allows us to create new materials and devices to be used in many fields of science and applied technology [15]. In the road pavement sector, due to their mechanical properties and large surface area to volume ratio, carbon nanotubes (CNTs) [16] and nanoclays (NCs) are some of the most promising modifiers [17–19]. According to Steyn [20], nanotechnology can play a role in improving existing and available materials to enhance the mechanical characteristics of asphalt binders. Several studies have been carried out on the capability of nano-sized particles to improve rheological characteristics of bitumens, while limited works have focused on the effects on fatigue and healing properties. Khattak et al. [21] demonstrated that carbon nano-fibers could enhance the fatigue resistance of bituminous materials by means of crack bridging and pull-out mechanisms. Santagata et al. [22] showed that the adoption of a proper dispersion of carbon nanotubes in bituminous mastics could have effect against cracking. According to Liu et al. and Wu et al. [23,24], both chemical characteristics of the nanoclay surfactant and an adequate interfacial interaction between bitumen and nanoclay particles can improve fatigue resistance.

However, aspects must be clarified concerning the costs–benefits of nano-reinforced materials and the industrial-scale implementation of bituminous mixtures with nano-additives' production. According to preliminary investigations, it is envisioned that nanotechnologies in the road sector may open undiscovered scenarios in the development of new smart, multifunctional, and high-performance products.

2. Research Methodology

In this study, the systematic literature review (SLR) defined by Kitchenham was performed [25]. It allows identification, analysis, and interpretation of available data about a research question, area, or investigated phenomenon. According to the evidence of reference materials, the goal of the study is to identify and analyze research into the use of nanoparticles as additives in bituminous conglomerates: manuscripts that contribute to SLR are primary studies, while this manuscript is a secondary study.

Peer-reviewed articles on the use of nanotechnology in road pavement, published between 2007 and 2018, were included. The main search strategy was automatic and involved the peer-reviewed databases Scopus, Web of Science, and Google Scholar. Furthermore, a manual search activity was performed as consequence of the results obtained in the automatic process and involved papers published since 2003. This activity involved both peer-reviewed, and not, documents. Finally, classical sources, standards, and regulations were considered, whatever their publication year.

Planning, conduction, and reporting results are the three main phases of the systematic literature review. They include:

1. Planning: Identification of the need which justifies the systematic literature review. Particularly, the research questions are:
    - What are the types of nano-additives considered, and the methods and technological solutions investigated at international level?
    - What are the performance improvements of bituminous mixtures additives with nanoparticles?
    - What is the extent of the self-repairing capacity of bituminous mixtures with the addition of nanoparticles compared to those without additives?
2. Conduction: Implementation of a search strategy compliant with the protocol defined in the previous phase;
3. Reporting results: Description of the results, answers to the goal of the study, and discussion of the results.

After the final application of the work selection strategy, 81 documents were identified: 69 are primary studies (i.e., peer-reviewed indexed research papers), 4 are secondary studies (i.e., reviews), and 8 are classical sources, standards, and regulations.

These works allowed the authors to make a critical assessment of the state of the art and answer the research questions.

3. Materials and Methods

3.1. Materials

3.1.1. Nanoclay

Nanoclays are hydrated aluminosilicates belonging to the class of phyllosilicates such as montmorillonite or caolinite. The nanoclays are composed of nanometric flakes with high specific surface area and aspect ratio: their dispersion in a polymeric matrix gives the nanocomposite increased barrier properties and greater resistance [26]. In general, nanoclays are able to modify profoundly the rheological properties of different materials. Extensive research has been dedicated to the use of nanoclay to reinforce asphalt binders. Although some types of nanoclay did not affect the stiffness or viscosity of the bitumen, other types of nanoclay showed encouraging results. Various physical properties such as stiffness, tensile strength, tension module, flexural strength, and bitumen thermal stability modulus can be improved when a small amount of nanoclay is microscopically dispersed. Generally, the elastic modulus increases for the modified bitumen with the added nanoclay, while the dissipation of the mechanical energy with respect to the unmodified bitumen is lower [26]. Jahromi and Khodaii [26] used bentonite clay (BT) and a chemically modified bentonite (OBT) to modify asphalt binders using the mixing process "sonication and shearing stresses". The modified asphalts had a higher resistance to rutting as well as a significant improvement in behavior at low temperatures with an increase in cracking resistance [27,28]. The improvement in terms of stiffness and resistance of the modified bitumen depends on the temperature and the percentage of added nanoclay. Nanoclay is also used as a second additive to improve the performance of bitumen modified with styrene–butiadene–styrene (SBS) [29–31].

Recent studies have shown an increase in the rutting trigger factor according to Superpave (SUperior PERforming asphalt PAVEments) standard [32], while the rotational viscosity tests indicated a significant increase in viscosity [33,34]. Among other benefits, nanoclays have also shown the ability to improve the resistance to aging of asphalt mixtures [35,36].

3.1.2. Nanosilica

Silica nanoparticles are used in medicine and pharmaceutical industries [37] for diagnostics and treatment of many pathologies, in industry to reinforce elastomers as a rheological solute [38], and in cement mixtures [39]. Similar to nanoclay, they have low production costs and high performance. Indeed, asphalt binders modified with nanosilicates have a lower viscosity value that reduces the compaction temperature or the energy dispersion during the construction process. The addition of nanosilica improves the recovery capacity of asphalt binders and enhances anti-aging capabilities, cracking resistance, resistance against rutting, and anti-stripping properties [27]. On the other hand, the addition of nanosilica does not influence the low-temperature properties of the modified bitumen [31].

According to Yusoff et al. [11], nanosilica could reduce susceptibility to moisture damage and increase resistance to fatigue and rutting of bituminous binders [11].

3.1.3. Carbon NanoTube

Under specific conditions, carbon atoms make up spherical structures, the fellurenes whose structure, after a subsequent relaxation, tends to roll up on itself, resulting in the typical cylindrical structure of carbon nanotubes [16]. Nanotubes are commonly divided into two types:

- single-walled nanotubes or SWCNTs (single-walled carbon nanotubes): consisting of a single graphite sheet wrapped around itself;
- multi-walled nanotubes or MWCNTs (multi-walled carbon nanotubes): formed by multiple sheets coaxially wound one on the other.

The high ratio between the length and diameter of carbon nanotubes gives them mechanical properties that are superior to those of other construction materials. When CNTs are added to bituminous binder mixtures with a sufficient percentage (>1% by bitumen weight), they can have significant effects on their rheological properties [21,40]. With the addition of CNTs to asphalt, an increase in adhesive strength was noted as well as increased susceptibility to moisture [41]. Moreover, the addition of CNTS produces positive effects on fatigue and rutting resistance compared to the not-additivated bituminous binders. [42,43]. Furthermore, the susceptibility to thermal cracking [35] and oxidative aging is reduced in bituminous mixtures [22].

3.1.4. Graphene Nanoplatelets

Graphene nanoplatelets (GNPs) consist of stacks of graphene sheets (Figure 1) (material consisting of a monoatomic layer of hexagonally arranged carbon atoms) that can be characterized by diameter of sub-micrometers and thickness of the order of nanometers. Graphene nanoplatelets exhibit superior mechanical properties if compared to nanoclay and nanosilica. They have the advantage of having a lower cost compared to CNTs. Having regard to cement mortar, GNP could effectively improve the electrical conductivity and reduce the critical pore diameter of cement mortars [44] with a significant impact on its durability [44]. Experiments have also shown that the addition of GNP would increase mechanical performances of cement mortars and contribute to the self-healing properties of bituminous mixtures [44,45].

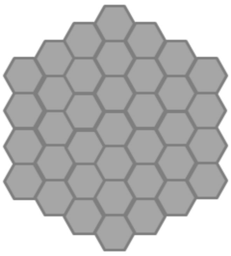

Figure 1. Graphene nanoplatelet (GNP) sheet.

3.1.5. Nano-Oxides

This category includes a wide variety of spherical or aggregate forms of nanoparticles. It includes metal oxides, semiconductors, and ultrafine inorganic compounds, produced through various chemical processes or through pyrolytic processes and the recovery of combustion waste in industrial processes. It is a type of particle whose dimensions are quite variable, particularly suitable for production in large quantities and on an industrial scale compared to other types [46].

Nano-oxides have greater thermal and chemical resistance and mechanical stability; greater resistance to atmospheric agents and greater resistance to aging.

In the infrastructure sector, mainly calcium oxide and titanium dioxide are used.

Nano-Calcium Oxide (CaO)

According to recent studies [47,48], the addition of nano-calcium oxide (CaO) in bituminous binder produces:

- A reduction of the penetration value by 7%, which directly relates to resistance to high temperature [47];
- An increase of softening point's value by 45% with resilience modulus value increased by 1.7 times that of neat bitumen [47];
- An improvement of bitumen's characteristics in colder regions to avoid thermal cracking when added at 4% and 6% of weight of bitumen [48].

Nano-Titanium Dioxide (TiO_2)

According to recent studies [49–51], the addition of titanium dioxide (TiO_2) to a bituminous binder can:

- improve fatigue resistance, permanent deformation, and oxidative aging of the binder [49–51];
- in association with other modifiers, such as polymers, it can improve the softening point and the ductility of the binder [52];
- have the ability to remove air pollutants [53];
- degrade most pollutants from automobile exhaust [54];
- improve creep comportment and prevent vertical cracks (added in 5% of bitumen mass) [49];
- improve fatigue life and flexural stiffness [55].

3.2. Methods

In the literature, the presented additives have been added to a bituminous base compliant with AASHTO M 320 [56]. The added percentage by weight of bitumen varies between 0.1% and 1% for CNTs and GNP, and between 3% and 6% for nanoclays and nanosilica; in any case dosage of nanoclays and nanosilica is higher than that of CNTs [22,57–60]. The added percentage by weight of bitumen varies between 4% and 6% for nano-calcium oxide [47] and between 1% and 7% for nano-titanium dioxide. In the latter case, for many authors the optimum content of TiO_2 is 5% of binder mass [61].

Both the dosage of added nano-additive and the mixing techniques used for preparing the mixture influence the bitumen's behavior [62,63].

3.2.1. Mixing Techniques

Usually two mixing techniques are used:

- The first is based on a simple shear mixing procedure [22,57,64,65] and consists of two phases. In the first phase, the nano-additives are manually added to the bitumen. A second phase follows this (pre-mixing) one; a mechanical stirrer (Figure 2) with heating mixes at 1550 rpm and a constant temperature of 150 °C the additivated bitumen for 90 min. This technique is not only the most convenient to use in laboratory, but is easily transferable on industrial scale in hot-mix asphalt plants.

Figure 2. Mechanical stirrer.

- The second mixing procedure consists of three phases: a third phase (i.e., ultrasonic sonication) is added to those of the first procedure. In one research project [63], a UP 200S ultrasonic homogenizer (200 W and 24 kHz) equipped with a titanium cylindrical sonotrode (7 mm diameter) was used. When it was immersed in the fluid mixture at a constant temperature of 150 °C, the generated ultrasounds propagated inside the material. The transmitted compression waves allowed separation of individual nanoparticles from the existing agglomerations and ensured a greater homogeneity of dispersion [60]. In order to improve the dispersion, several researchers tested duration and amplitude of the waves during sonication [27,66,67]. Finally, the effects of sonication on the distribution of nanoparticles were evaluated directly by microscope or indirectly through rheometric methods. Particularly, the storage modulus was sensitive to dispersion of nanoparticles: it increases with increasing energy spent during homogenization (both sonication duration and wave amplitude [68]).

The rotation rate and the power of the mixer were varied for high shear, mechanical, and ultrasonic mixers (Figure 3) [69].

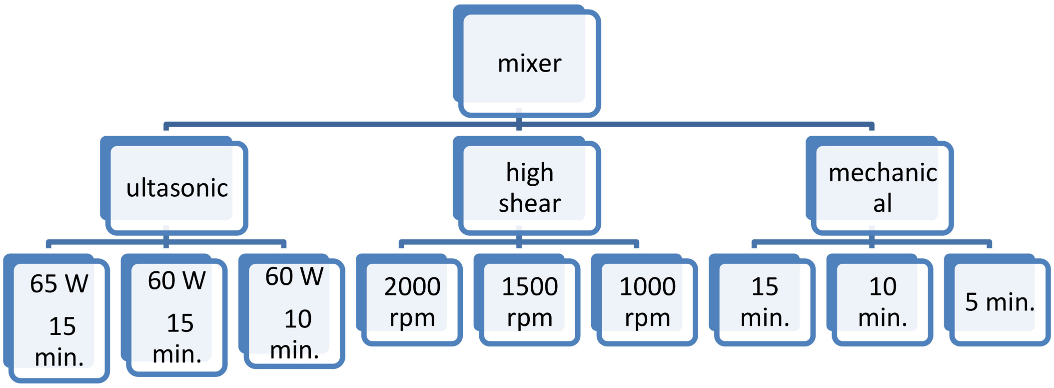

Figure 3. Alternative mixing techniques reproduced from [69].

3.2.2. Testing Program

To study the distribution of the various nanocomposites in the bituminous matrix, researchers have commonly used atomic force microscopy (AFM), X-ray diffraction spectroscopy (XRD), scanning electron microscopy (SEM), and tunneling electron microscopy (TEM). These tests are also useful to understand the effect of nanocomposites on the mechanical and rheological properties of the modified bitumen [70].

Having regard to the three critical phases in bitumen life (i.e., storage and transport; mixture production and laying, and aging), laboratory tests analyzed non-aged short-lived and long-lasting specimens [71,72]. The carried out laboratory tests concerned:

1. Viscosity tests according to AASHTO T316-04 [73].
2. Through the use of the DSR (dynamic shear rheometer), OSL (oscillatory shear loading) and MSCR (multiple stress creep recovering) tests were carried out, increasing stresses from 0.1 to 3.2 kPa and different temperature values according to AASHTO TP 70-10 [74]. By applying a shear stress, the equipment measures the binder's response in shear-cut terminations. Through the relationship between the applied cutting force and the obtained deformation, the rheometer allows us to obtain the following parameters:
    - G* (complex modulus);
    - δ (phase angle);
    - G*/sinδ (parameter correlated to rutting);
    - G* sinδ (parameter correlated to fatigue).
3. Fatigue tests according to AASHTO T 315 [75].

4. Self-repair tests performed by means of cyclic load tests of the time sweep type interrupted by multiple rest periods; the test ends when a reduction in initial dissipation energy of 5%, 10%, 30%, and 50% is reached.

4. Conclusions

This document presents a review of the nano-additives most commonly used to modify bitumen: it analyzes and compares their mixing conditions and their influence on the mechanical characteristics of the binder. Performances of bitumen additivated with nanoclays, nanosilica, carbon nanotubes, graphene nanoplatelets, and nano-oxides were considered having regard to different distresses (i.e., fatigue resistance, rutting, and self-healing processes).

Given the results in the literature, simple shear mixing technique is potentially more easily transferable to the industrial production of hot bituminous mixes, while the dispersion of nanoparticles in the bituminous matrix improves through the ultrasonic mixing technique.

In fact, with reference to storage modulus that is highly sensitive to nanoparticle dispersion and interfacial interaction, by increasing the energy input for homogenization, either by extending sonication duration or by expanding wave amplitude, the storage modulus increases. It can be seen that similar trends were recorded regardless of the considered additive type. This is also supported by the results obtained under the microscope and by other characterization techniques such as AFM, TEM, SEM [68–70].

The addition of a sufficient amount of CNTs (>0.5% by weight of bitumen) significantly increases the stiffness and elasticity of the bituminous base at low frequencies and high temperatures: it could result in a potential improvement in resistance to bending. Binders containing CNT have revealed a high sensitivity to the level of damage. In addition, there is a different fatigue behavior depending on the mixing technique adopted to disperse the CNTs in the bituminous matrix; an improvement is noted with the increase in sonication times or with the modification of the amplitude of the ultrasonic waves.

As indicated by the upward displacement of the corresponding curves τ–NDERmax [59], the mixtures with NC have shown better performance in terms of fatigue than net bitumen in the entire spectrum of loading and damage conditions simulated in laboratory [76–79].

CNT helps in improving tensile strength, flexural strength, and rutting resistance, and reduces thermal cracking.

In terms of self-repair, the recoverable damage component depends on both the load history and the type of bitumen considered. By increasing the degree of damage suffered by the sample, the repair potential tends to decrease; on the other hand, materials containing nano-additives show a higher recovery component than that of net bitumen.

In particular, the higher viscosity of the admixed mixtures can delay the process of formation of the surface cracks which represents the initial step for the self-repair process [64,65,80].

While NCs improve the self-repairing ability of net bitumen when limited damage occurs, CNTs make an even more significant contribution after high-load levels.

Nano-TiO_2/SiO_2 have also been reported to be used as an additive to improve the rheological properties of conventional bitumen [4]. The nano-modified bitumen showed improved adhesive bonding of aggregate, better interlock between aggregates, reduced deformation, improved fatigue life of pavement, low phase angle value, high complex modulus value at low temperatures, and high rutting resistance [4].

The test results indicate that modified asphalt binders show an increase in the complex modulus and a decrease in the phase angle compared to unmodified asphalt binders.

The phase angles of both unmodified and nano-modified asphalt increase as the temperature increases.

In comparison, the nano-modified asphalt was less sensitive to temperature changes. In other words, the modified asphalt binders demonstrate a higher ability to maintain elastic/viscous capability than the unmodified asphalt [4].

Bitumen composites synthesized with nano-additives exhibit improved properties in hotter and colder regions [70].

In conclusion, the efficacy as bitumen modifiers of additives of nanometric dimensions strongly depends both on the volume within the mixtures (due to a simple filling effect) and on the interactions that can arise with the continuous bituminous matrix (depending on the surface specification and compatibility).

The use of nano-additives for bituminous binders promises a series of advantages, with particular attention to bitumen durability. But their use in bituminous mixes still has many aspects to be clarified and optimized. The first problem is the lack of univocal procedures that makes it difficult to compare data coming from different laboratories [81].

Moreover, according to the opinion of several researchers, the interactions at nanoscale can lead to a new generation of bituminous nanocomposites with tailored chemical–physical properties.

Other specific aspects of binder behavior should be subjected to analysis, possibly by introducing in the evaluation a cost–benefit analysis in order to stimulate applications at the industrial scale. In addition, the possibility of creating a bituminous binder with nano-additives and 100% recycled aggregates should be considered in order to obtain high-performance mixtures and reduce environmental impacts and maintenance costs.

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