



Mechanical performance of asphalt concrete modified with nanoparticles: Nanosilica, zero-valent iron and nanoclay

João Miguel Lopes Crucho^{a,*}, José Manuel Coelho das Neves^a, Silvino Dias Capitão^{a,b}, Luís Guilherme de Picado-Santos^a

^a CERIS, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais 1, 1049-001 Lisboa, Portugal

^b Instituto Politécnico de Coimbra, Instituto Superior de Engenharia de Coimbra, Rua Pedro Nunes, 3030-199 Coimbra, Portugal

HIGHLIGHTS

- The nanomodifications improved the mechanical performance of asphalt mixtures.
- Nanosilica modification presented the best global performance.
- Zero-valent iron exhibited high improvement in the water sensitivity.
- Nanoclay improved fatigue resistance and elastic behavior.
- The nanomodifications may improve the durability of the asphalt mixtures.

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ABSTRACT

The objective of this study is to evaluate the effects of nanomodifications in the asphalt mixture performance. Three types of nanoparticles were used: silica, zero-valent iron and bentonite. The correspondent mixtures were tested for stiffness, fatigue, permanent deformation and water sensitivity. The results showed that nanomodifications lead to improvements in the performance. (1) nanosilica improved stiffness and permanent deformation; (2) zero-valent iron presented better water sensitivity; (3) and bentonite improved fatigue life and elastic behavior. An analysis of the nanomodifications based on all the mechanical performance indicators was performed and revealed that the silica modification achieved the best global performance.

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1. Introduction

The importance of maintaining the road infrastructure in good condition, the increasing lifespan needed, and larger payloads to resist, are demanding factors for better binders which can make mixtures resist for a longer time to all the more demanding factors related to degradation mechanisms of pavements. Binder modification will play a key role in improving or maintaining the mixture's performance. The nanoparticles seem very promising to enhance the properties of the asphalt binders [1–6]. The physicochemical interactions and reactivity of the nanoparticles are typically higher compared to particles of the same material at the macroscale [7].

Also, their very specific properties, such as high surface area, enable such a behavior. The recent developments in technology allow for more applications and better characterization of nanoparticles and modified materials. Although some studies about the use of nanoparticles in asphalt binders were already done, the number of studies about asphalt mixtures performance is very limited [2,8], and particularly scarce when stiff binders are considered. This is the case of 35/50 penetration grade asphalt binder often used in certain conditions [9–11], that current uncertainty on nanomodification effects demand more studies in this field. In the existing studies nanoclays [7,12–33] and nanosilicas [7,31–39] received special attention.

The objective of this study is to evaluate the influence of three different nanomodifications on the performance of an asphalt mixture using a conventional stiff grade binder, the 35/50 penetration

* Corresponding author.

E-mail addresses: joao.crucho@tecnico.ulisboa.pt (J.M.L. Crucho), jose.manuel.neves@tecnico.ulisboa.pt (J.M.C.d. Neves), capitao@isec.pt (S.D. Capitão), luispicadosantos@tecnico.ulisboa.pt (L.G.d. Picado-Santos).

grade. The nanoparticles selected for this study were nanosilica, zero-valent iron (ZVI) and nanoclay (hydrophilic bentonite).

The nanosilica, standard silicon dioxide, has demonstrated important improvements on the modification of softer grade binders, thus, its effects on the stiff 35/50 binder will be evaluated.

The zero-valent nanoiron is a dry air-stable ferrous powder of non-valent chain. Their properties such as reactivity and high specific surface may cause an important impact on the properties of the modified binder. Currently, the ZVI is applicable in reduction technologies, such as ground-water remediation and wastewater treatment. When alone, in the presence of water the ZVI particles will produce iron oxides, hydroxides, and hydrogen. Potentially, because of this, it can offer some aging protection to the asphalt binder. The ZVI has a reducing activity and due to the high specific surface of the nanoparticles will rapidly oxidize to iron oxides reducing the effective concentration of dissolved oxygen in the asphalt binder so it can act, at least in the first months, to reduce the oxidation of the asphalt binder. Later on, the stable Fe_2O_3 is a much worst catalyst because its mobility in the asphalt matrix is very limited and the oxidation reaction is second order, therefore reducing drastically the oxidation kinetics. The preliminary work of the authors using ZVI modification of asphalt mixture [40] obtained improvement in water sensitivity.

The nanoclays are hydrophilic in nature and their hydrophilic properties may cause difficulties to disperse into the asphalt matrix [41], thus, to avoid this difficulty the interlayer cations can be replaced with quarternized ammonium or phosphonium cations, preferably with long alkyl chains originating an organo-modified or organophilic nanoclay. The additional clay-modification process helps to increase complexity and cost of these nanomodifications, making them less prone to be scaled to the pavement engineering environment. Therefore, the nanoclay selected for this study is a raw nanoclay, hydrophilic bentonite, more similar to its form in nature.

The study starts from the binder modification and is developed up to characterization of asphalt mixture in laboratory. The experimental program included materials' characterization, mixture testing to obtain performance indicators and testing to assess the effect of water damage by conducting water sensitivity tests.

2. Background on the nanomodifications of asphalt

Among the nanomaterials, nanoclays and nanosilicas are the most studied materials for asphalt binders modification.

Table 1 presents a summary of the research studies developed on the effects of nanomodifications on the asphalt mixtures performance. Different nanoparticles and percentages were considered in the composition of the asphalt mixtures: nanosilica, nanoclay (raw nanoclays, such as montmorillonite and bentonite), polysiloxane-modified montmorillonite and organophilic montmorillonite (organo-modified montmorillonite). Majority of the mentioned authors considered a nanoparticle content between 1% and 6% per weight of binder. The use of such nanoparticle content for the nanomodification of the asphalt binder should be high enough to present some effect on the final performance of the asphalt mixture. The positive (improvement) and negative (degradation) effects of the nanomodifications were based on the Marshall stability, water sensitivity, stiffness, permanent deformation and fatigue.

The authors studying modifications of asphalt binders with nanosilica reported a decrease in penetration and an increase in softening point [33,35], higher complex modulus and lower phase angle [31,35,39]. Dynamic shear rheometer (DSR) tests on nanosilica-modified binders showed superior fatigue resistance [36,37] but in bending beam rheometer (BBR) tests presented higher creep stiffness and lower m -value [31]. Thus, underperformance at PG low temperature is expected. In studies of asphalt mixtures modified with nanosilica (Table 1), authors reported an improvement in Marshall stability [32,34], water sensitivity [34,38], stiffness [34,37,38] and permanent deformation [37,38].

Concerning nanoclays, the increase in complex shear modulus and decrease in phase angle are the most commonly reported effects [14,15,18,19,25,27], and, consistently, the reduction in penetration value, increase in softening point temperature [23,26,28,33] and increase in viscosity [14,15,31,33]. For the asphalt mixtures (Table 1), authors reported: improvement in permanent deformation [13,16,20,24,30], improved water sensitivity [13,21,22,24,28,30] and higher stiffness [20,22,24,28]. Although the findings are generally consistent, the big variety of nanoclays

Table 1
Studies related to the effects of nanomodifications on the asphalt mixtures performance.

Nanomodification		Binder type	Effects on performance		Refs.
Nanoparticle	Percentage		Positive	Negative	
Nanosilica	4%	35/50	Marshall stability	–	[32]
	4%	PG 76	Water sensitivity; Stiffness; Permanent deformation	–	[38]
	4%; 6%	PG 58–34 with ABS	Permanent deformation; Stiffness	–	[37]
	2%	60/70 with 5% SBS	Marshall stability; Water sensitivity; Stiffness	–	[34]
Nanoclay	1%; 3%; 5%	PG 58–28; PG 64–28	Permanent deformation	–	[16]
	2%; 4%	PG 58–34	Stiffness; Permanent deformation	Water sensitivity	[20]
Polysiloxane-modified montmorillonite	2%	PG 58–28	Water sensitivity	Indirect tensile strength (dry)	[21]
	2%; 4%	PG 58–34	Stiffness; Permanent deformation	Water sensitivity	[20]
Organophilic montmorillonite	2%; 4%; 7%	60/70	Water sensitivity; Stiffness	–	[22]
	6%	40/60	Water sensitivity; Stiffness; Permanent deformation	Fatigue life	[13]
	3%	PG 58–22	Water sensitivity; Stiffness; Fatigue life; Permanent deformation	–	[24]
	1.5%	PG 58–10 with 6% SBS	Water sensitivity; Stiffness	–	[28]
	2%; 3.5%; 5%	50/70 Type A	Marshall stability; Permanent deformation; Indirect tensile strength (dry) at 25 °C	Indirect tensile strength (dry) at 15 °C	[30]
	2%; 3.5%; 5%	50/70 Type B	Marshall stability; Permanent deformation; Indirect tensile strength (dry) at 25 °C	Indirect tensile strength (dry) at 15 °C	[30]
2%; 3.5%; 5%	50/70 Type C	Permanent deformation	Indirect tensile strength (dry) at 15 °C and 25 °C	[30]	

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