Performance Characteristics of Nano-Modified Asphalt Mixtures

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Performance characteristics of nano-modified asphalt mixtures

Lucia Tsantilis, Giuseppe Chiappinelli, Orazio Baglieri, Pier Paolo Riviera, Fabrizio Miglietta, Ezio Santagata

Department of Environment, Land and Infrastructure Engineering, Politecnico di Torino,

24, Corso Duca degli Abruzzi, 10129, Torino, Italy

The growing need for high quality paving materials has aroused an increasing interest in innovative reinforcing agents, such as those characterized by nanometric dimensions. The experimental study presented in this paper focused on the use in asphalt mixtures of nanoclays and multiwall carbon nanotubes as bitumen modifiers. The performance characteristics of asphalt mixtures containing these nano-sized additives and those of a reference neat mixture were compared in a wide array of temperature and loading conditions. The testing program included the assessment of linear viscoelastic characteristics, anti-rutting potential and crack propagation resistance, by means of stiffness modulus, flow number and semi-circular bending tests, respectively. Results highlighted that both types of nano-additives have the potential to improve the performance properties of neat asphalt mixtures, with nanoclays yielding a superior reinforcing action.

Keywords: asphalt mixture, nanoclays, multiwall carbon nanotubes, rutting, cracking.

1 Introduction

Nanotechnology has become increasingly popular in recent years in many areas of materials science and engineering, as it allows phenomena that occur at the nanometre scale to be exploited for design, characterization and production purposes (Ramsden, 2011). Among the various forms and applications of nanotechnology, the fine-tuning of advanced composite materials obtained by making use of nano-additives has opened up new perspectives in the pavement research community (Gopalakrishnan et al., 2011; Li et al., 2017).

In the case of bound layers of flexible pavements, several nano-sized products have been considered in order to improve the physicochemical properties of both neat and polymer-modified bituminous matrices. In such a context, nanoclays and carbon nanotubes actually represent the most promising reinforcing agents against rutting and fatigue cracking distresses (Yang and Tighe, 2103, Santagata et al., 2016b; 2016c, Tsantilis et al., 2019). However, as synthesized in the following, the substantial diversity between nanoclays and carbon nanotubes in terms of origin, geometry and physicochemical nature, leads to completely different interactive mechanisms occurring at the nanoscale.

Layered silicates used as nano-additives, the so-called nanoclays, have been given widespread consideration since the 1980s, when Toyota researchers reported on the strengthening action yielded in composites by clay platelets via intercalation and/or exfoliation mechanisms. Intercalation occurs when matrix molecules penetrate within clay sheets which, nevertheless, still maintain a predefined basal spacing. On the other hand, exfoliation occurs when penetration leads to a complete breakdown of the original crystallographic structure of clay, with a consequent random distribution of platelets in the composite material. When considering organic matrices such as bitumen, detachment of platelets cannot be easily achieved as a consequence of the combined effect of layer stacking phenomena and of the hydrophilic character of clays. Therefore, specific surfactant coatings, characterized by hydrophilic heads and hydrophobic tails, are used to organically modify the pristine clay with the twofold objective of changing the overall polarity of the layered particles and of expanding clay galleries. Due to their high charge density and cation exchange capacity, montmorillonites are the most suitable minerals to be employed in the manufacture of organophilic clays. Moreover, their abundance in nature limits production costs and causes only minor environmental concerns related to the exploitation of resources (Pavlidou and Papaspyrides, 2008).

Carbon nanotubes were first discovered by Iijima in 1991, as a product of carbon-arc discharge experiments in fullerene soot. They are one-dimensional carbon materials composed of rolled-up hexagonal networks of carbon atoms in sp^2 hybridization, arranged in the form of hollow cylinders of nanometric diameters and micrometric lengths. Depending on the number of coaxial tubular layers of which they are composed, that can typically vary between 1 and 50, commercial carbon nanotubes can be found in either single-wall or multi-wall configurations. These peculiar structural features lead to outstanding mechanical properties, that potentially make carbon nanotubes excellent candidates to be used as reinforcing agents in composite materials. Furthermore, sustainable technologies to produce carbon nanotubes, based on the use of waste materials or green synthesis methods, are currently being developed in addition to classical processes such as the electrical arc discharge, chemical vapour deposition, and laser ablation (Dresselhaus et al., 2001; Deng et al., 2016).

Several research studies have been carried out for the evaluation of the physicochemical properties of bituminous binders containing nanoclays and carbon nanotubes. However, scarce data have been reported on the performance characteristics of corresponding nano-reinforced asphalt mixtures.

This paper focuses on the effects of organophilic clays and carbon nanotubes used in mixtures as bitumen modifiers. The experimental investigation which is discussed in the following sections included the assessment of linear viscoelastic characteristics, anti-rutting potential and crack propagation resistance by means of stiffness modulus, flow number and semi-circular bending tests, respectively.

2 Materials and methods

The materials used in the experimental investigation included a reference asphalt mixture (B), containing neat bitumen, and two nano-modified mixtures (NC and CNT), in which the same bitumen used for B was reinforced with two different types of nano-sized additives, nanoclays and carbon nanotubes, respectively.
The nanoclay employed in the study was a natural montmorillonite organically modified via an ion exchange reaction. The surfactant agent used to change the hydrophilic nature of the clay in its virgin state to the hydrophobic character of the employed additive, was a quaternary ammonium salt composed of two methyl groups and two alkyl chains bonded to a positively charged nitrogen atom. Carbon nanotubes were obtained by means of the catalysed chemical vapour deposition process in multiwall structures of nanometric diameter. The main characteristics of the two commercially available products are reported in **Tables 1** and **2**.

Table 1 Physical characteristics of the nanoclay

Basal spacing [nm]	Cation exchange capacity (CEC) [meq/100 g]	Density [g/cm^3]	Anion
3.15	125	1.66	Chloride

Table 2 Physical characteristics of carbon nanotubes

Average diameter [nm]	Average length [μm]	Density [g/cm^3]	Carbon purity [%]
9.5	1.5	1.72	90

The neat binder was a 70/100 penetration grade bitumen belonging to Performance Grade (PG) 58-22. Nano-reinforced blends were prepared in the laboratory combining the same neat bitumen with fixed dosages of nanoclays and carbon nanotubes. Based on the results obtained from previous investigations (Santagata et al., 2016a; 2015a), percentages of nanoparticles of 3 % and 0.5 %, by weight of base bitumen, were chosen for nanoclays and carbon nanotubes, respectively. Blending was performed at 150 °C following a protocol which combines shear mixing and sonication. Shear mixing was carried out with a mechanical stirrer for 90 minutes operating at 1550 rpm, while ultrasounds were applied by means of an ultrasonic homogenizer for 60 minutes operating at 24 kHz with a wave amplitude of 157.5 μm (Santagata et al., 2015b).
For the preparation of asphalt mixtures, the three binders were mixed with siliceous aggregates, with the same reference gradation (**Fig. 1**), at a constant binder content of 4.8 % by weight of dry aggregates. Cylindrical specimens of 150 mm diameter and variable height (equal to either 170 mm or 50 mm), with a target void content of 4 % ± 0.5 %, were obtained by making use of a gyratory shear compactor. Based on the different rheological properties of the employed binders, mixing and compaction temperatures were changed from one case to the other as detailed in **Table 3**.

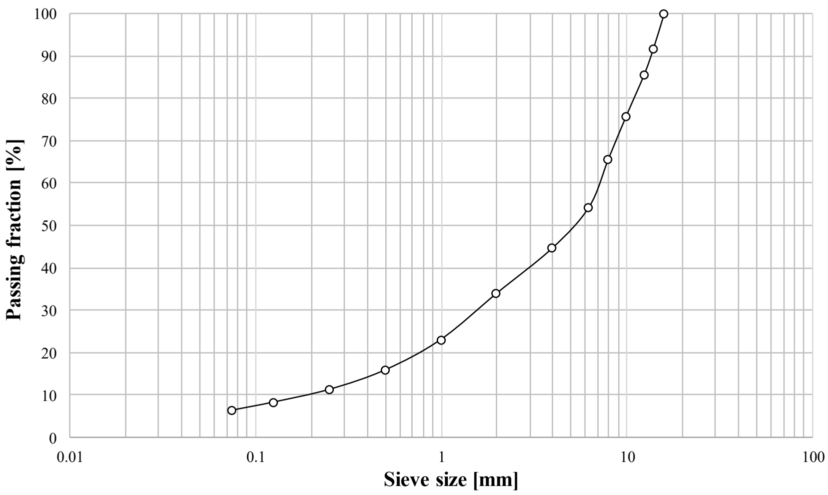

Fig. 1 Aggregate gradation of asphalt mixtures

Table 3 Mixing and compaction temperatures of asphalt mixtures

Mixture	Mixing temperature [°C]	Compaction temperature [°C]
B	150	140
NC	180	170
CNT	165	155

The testing program included the assessment of linear viscoelastic characteristics, anti-rutting potential and crack propagation resistance by means of stiffness modulus, flow number and semi-circular bending tests, respectively.

Stiffness modulus measurements (EN 12697-26) were performed at testing temperatures of 5 °C, 20 °C and 30 °C on cylindrical specimens of 150 mm diameter and 50 mm height. Indirect tension was induced in the specimens by applying repeated load pulses characterized by a pulse repetition period of 3 s and by different values of rise time, selected in the range of 60 ms to 160 ms.

Flow number tests (AASHTO T378) were carried out on cylindrical specimens of 100 mm diameter and 150 mm height obtained by coring and sawing the larger gyratory specimens. Haversine axial compressive load pulses with a duration of 0.1 s were applied every 1.0 s in unconfined conditions with a fixed deviator stress equal to 600 kPa at a testing temperature set equal to 58 °C.

Semi-circular bending tests (EN 12697-44) were performed at 20 °C on half cylinder test pieces of 150 mm diameter and 50 mm height (obtained by sawing gyratory compacted specimens), with a 10 mm midspan notch. Specimens were loaded in the three-point bending configuration by imposing a constant deformation rate of 5 mm/min.

3 Results and discussion

3.1 Stiffness modulus tests

The effects of nano-sized additives on the linear viscoelastic response of asphalt mixtures were assessed by means of stiffness modulus tests performed by simulating relevant in-service conditions in terms of temperature and traffic loading. The outcomes of these tests are presented in **Fig. 2**, which allows direct comparisons to be made among mixtures at 5 °C, 20 °C and 30 °C and at several rise-time durations.

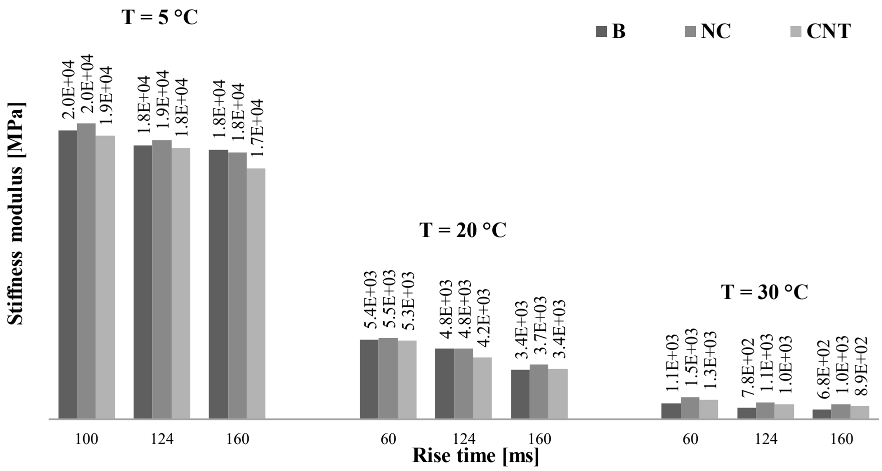

Fig. 2 Stiffness moduli of asphalt mixtures

From a general overview of the results it can be seen that, regardless of the loading duration, the presence of nano-particles in the mixtures did not cause dramatic changes at 5 °C and 20 °C. This is proven by the values of the relative variations in stiffness, calculated with respect to the reference mixture, that never exceed 15 %. On the contrary, at 30 °C such variations were found to be higher, with an increase in stiffness that reached values of 48 % and 30 % for NC and CNT mixtures, respectively.

When focusing on the minor changes in modulus which occurred at 5 °C and 20 °C, it is worth noting that, on the whole, the two additives showed a diverging effect on the response of the neat asphalt mixture. While nanoclays in most cases exhibited a stiffening action, carbon nanotubes generally induced a stiffness reduction which was greater at the lowest temperature. These findings, although unexpected, are consistent with those obtained from the linear viscoelastic characterization of carbon nanotubes-bitumen blends (Santagata et al., 2012).

When considering the effect of different loading durations, it is interesting to observe that at the highest temperature (30 °C) the viscoelastic response of the nano-modified mixtures showed a lower time-dependency when compared with the reference mixture, thus indicating an enhancement of the degree of elasticity.

3.2 Flow number tests

The results of flow number tests performed at the reference temperature of 58 °C are displayed in **Fig. 3**, where the evolution of cumulative permanent strain is plotted versus the number of loading cycles. In line with typical outcomes reported in the literature for both neat and modified mixtures (Santagata et al., 2017), all asphalt mixtures exhibited three distinct stages of response under repeated loading: a primary stage, characterized by a progressively decreasing rate of strain, a secondary stage in which the rate of strain is almost constant, and a final stage of tertiary flow, during which the rate of strain accumulation dramatically increases with load repetitions.

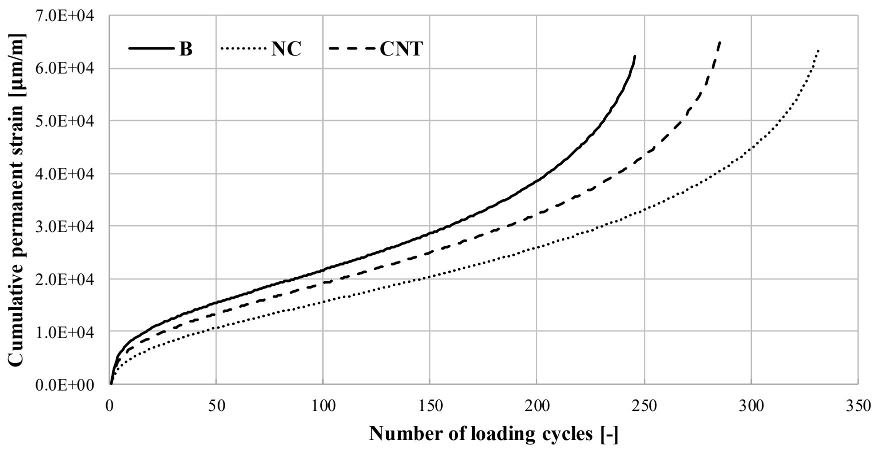

Fig. 3 Typical curves obtained in flow number tests

Table 4 Average flow number values of asphalt mixtures

Mixture	Flow number [-]
B	111
NC	146
CNT	132

The flow number is defined as the number of loading cycles which corresponds to the transition between the secondary and tertiary stage. It is also associated to the point of minimum rate of change of permanent strain. Average flow number values, calculated from experimental curves fitted to the analytical model proposed by Franken, are listed in **Table 4** for the three mixtures included in the study.

In good agreement with previous studies performed at the binder scale (Santagata et al., 2013, 2015b; 2016b), also at the mixture scale nano-modified materials were found to be less susceptible to permanent deformation accumulation under repeated loadings, the best performance being exhibited by NC. These observations, which are consistent with the enhancements in stiffness and elasticity found in the linear viscoelastic response, reveal that nano-sized additives yielded a reinforcing action in the mixture that was also effective in the domain of large deformations.

3.3 Semi-circular bending tests

Semi-circular bending tests were carried out at 20 °C in order to evaluate the impact of nano-modification on the resistance to crack propagation. Typical outputs of tests are presented in **Fig. 4** as load-versus-displacement curves. Average experimental results are summarized in **Table 5** in terms of fracture toughness (K_{Ic}), strain at maximum load (ε_{max}), maximum stress at failure (σ_{max}), and strain energy to failure (U). This last parameter is calculated as the area under the load-versus-deflection curve up to peak load.

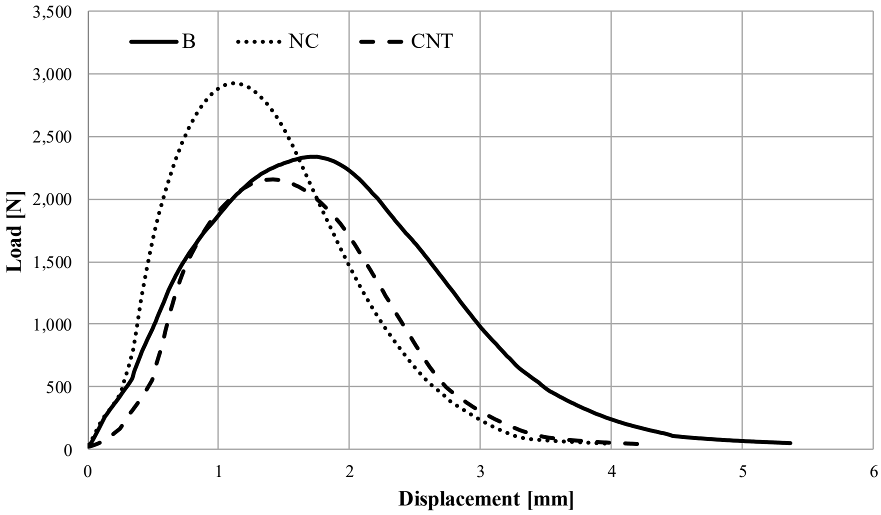

Fig. 4 Typical load-versus-displacement curves obtained in semi-circular bending tests

Table 5 Average results of semi-circular bending tests

Mixture type	K_{Ic} [N/mm$^{3/2}$]	ε_{max} [%]	σ_{max} [N/mm^2]	U [kJ]
B	7.78	2.09	1.31	2.01E+03
NC	9.56	1.73	1.61	2.05E+03
CNT	7.61	1.99	1.28	1.94E+03

When considering the effect of nano-modification with organophilic clays, a non-negligible improvement in fracture toughness was exhibited by mixture NC with respect to reference mixture B. Moreover, changes in fracture properties were revealed by the higher values of both maximum stress and strain energy to failure, and by the lower value of strain at maximum load recorded during tests. Based on these experimental outcomes and by taking into account the encouraging enhancements in fatigue resistance found in previous studies by means of indirect tension cyclic tests (Miglietta et al., 2018; Santagata et al., 2019), it can be inferred that organophilic clays can play an important role in preventing distresses related to fatigue cracking phenomena.
On the other hand, modification with carbon nanotubes was not effective in improving the fracture properties of the reference asphalt mixture. This is shown by the limited variations in fracture toughness, strain at maximum load and maximum stress at failure which were recorded during the investigation. It is interesting to note that as a result of the presence of carbon nanotubes, strain energy to failure decreased. Such a finding is in general disagreement with the results obtained by other researchers who performed semi-circular bending tests on mixtures containing the same dosage of carbon nanotubes (Ameri et al., 2016). Further work is certainly needed to clarify the cause of this apparent discrepancy in results.

4 Conclusions

Based on the results presented in this paper, it can be concluded that nano-sized additives have the potential to positively affect the performance properties of neat asphalt mixtures, with organophilic clays yielding a superior reinforcing action when compared to carbon nanotubes. However, the general effectiveness of such improvements should be carefully evaluated by means of a cost- and environmental-based analysis.
Considering the mechanical behaviour of the mixtures in their linear viscoelastic domain, no major changes were generated by both types of nano-particles. However, at the highest investigated temperature a moderate increase in stiffness and elasticity was highlighted in the case of the nano-modified mixture.
With respect to their anti-rutting performance, the two nano-modified mixtures showed a superior resistance to accumulation of permanent deformations under repeated loading when compared to the reference neat material. In particular, the best performance was exhibited by the mixture reinforced with nanoclays.
When focusing on the resistance to crack propagation, beneficial effects associated to nanomodification were found only in the case of nanoclays, thus suggesting that for the considered mixture employed carbon nanotubes may have an inadequate scale length for crack bridging contributions.

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