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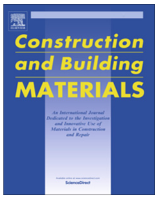

Low-temperature properties of bituminous nanocomposites for road applications

Lucia Tsantilis *, Orazio Baglieri, Ezio Santagata

Department of Environment, Land and Infrastructure Engineering, Politecnico di Torino, 24, c.so Duca degli Abruzzi, 10129 Turin, Italy

HIGHLIGHTS

- A wide array of materials and testing conditions were considered in the study.
- Analyses focused on rheological properties and on an energy parameter.
- Effects of nano-modification were dependent on base materials and additive dosage.
- Use of nanocomposites in pavements should be carefully evaluated in cold climates.

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ABSTRACT

This paper focuses on low-temperature performance of bituminous nanocomposites for road paving applications. In the experimental investigation, one type of carbon nanotubes and two types of nanoclays were combined with three base bitumens at various dosages by following a protocol based on the use of shear mixing and sonication. All rheological measurements were carried out by means of a Bending Beam Rheometer at temperatures comprised between −6 and −24 °C. Results, which were interpreted by combining different analysis models, showed that the effectiveness of nano-modification is strictly influenced by the combination of base binder, additive type and dosage.

1. Introduction

Low-temperature cracking is one of the most critical failure modes of flexible pavements which are observed in cold regions as well as in areas characterized by significant daily temperature variations. The occurrence of this distress depends on the combination of several factors such as environmental conditions, pavement structural features and materials properties. In particular, it has been widely recognized that the characteristics of the bituminous binder employed in wearing courses play a key role in controlling crack initiation and propagation phenomena [1,2]. Due to its viscoelastic nature, bitumen has the capability to relax tensions which arise as a consequence of thermal actions; unless these stresses are not dissipated, they can be released by crack initiation once the tensile strength of the binder has been exceeded. The ability to relax stresses is governed by the array of molecular species that constitute bitumen, which can gradually change their relative positions and interactions by re-orientation of intermolecular bonds [3].

In recent years, the use of nano-sized materials for the manufacturing of composites with tailored physicochemical properties has attracted an increasing interest in the community of paving technologists. Among the products that have been considered for a selective modification of bituminous materials at the nanoscale, carbon nanotubes (CNTs) and organo-modified clays, also known as nanoclays (NCs), currently represent the most promising additives [4]. CNTs are one-dimensional carbon materials that consist of graphene sheets rolled-up in seamless hollow structures with a nanometric diameter. They can be characterized either by single-wall or multi-wall configurations. While single-wall CNTs are composed of a tubular graphene structure with only one atom in thickness, multi-wall CNTs are composed of two or more coaxial graphene layers [5,6]. NCs are layered silicate minerals in which the hydrophilic character of clays has been changed to hydrophobic by replacing the surface inorganic exchange cations with surfactants containing organic tails. This treatment promotes the diffusion of organic molecules within gallery spaces, thus

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* Corresponding author.
E-mail address: lucia.tsantilis@polito.it (L. Tsantilis).

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generating intercalated or exfoliated clay structures. Intercalation occurs when penetration of molecules produces an expansion of galleries, whereas exfoliation is the result of a complete clay sheet detachment [7–9].

A number of research works showed that nano-sized additives can enhance the performance-related properties of bituminous materials in terms of permanent deformation and fatigue cracking resistance at high and intermediate in-service temperatures, respectively [10–19]. However, few studies addressed the problem of low-temperature properties. De Melo et al. [20] investigated the mechanical characteristics of bituminous binders containing multi-wall CNTs (dosages of 1 and 2%). They showed that at both −12 and −18 °C the presence of CNTs caused a stiffness increase and a creep rate reduction, making the nanocomposites more susceptible to thermal cracking. Wang et al. [21] explored the performance of polymer-modified binders reinforced with functionalized multi-wall CNTs (dosages 0.02, 0.5 and 1%) at temperatures equal to −12, −18 and −24 °C. Positive effects, consisting in a stiffness reduction and creep rate increase, were observed only with the use of a CNT percentage of 0.5%, thus indicating the importance of a proper choice of additive dosage. However, notwithstanding that such rheological improvements were recorded at −12 and −24 °C, at −18 °C conflicting outcomes were obtained, thus indicating that there still remains a need for clarification. With regard to the effects of NCs, Zare-Shahabadi [22] observed that organically modified bentonite clay (5% dosage) caused a beneficial stiffness reduction at a temperature of −12 °C. On the other hand, a detrimental effect on the relaxation capability was found, as proven by the lower value of creep rate. Abdullah et al. [23] studied the rheological response of bituminous binders modified with two types of montmorillonite NCs (dosages comprised between 3 and 5%). Tests performed at −18 °C showed that addition of the nano-additives resulted in an increase in stiffness and in a reduced relaxation capability, thus indicating a lower resistance to low-temperature cracking.

Given the scarcity of research studies currently available on this topic and due to the inconsistency of reported findings, this work focused on the effects of nano-sized additives on the low-temperature properties of bituminous binders by considering a wide array of materials and testing conditions. One type of CNTs and two types of NCs were combined with three base bitumens at various dosages. All rheological measurements were carried out with a Bending Beam Rheometer (BBR) at temperatures comprised between −6 and −24 °C.

2. Base materials and blend preparation

With the purpose of highlighting the role played by the physicochemical nature of base components in the preparation of nanocomposites, three different neat bitumens and three different nano-sized additives were considered in the present investigation.

Neat bitumens were provided by two refineries which operate on crudes of various origins according to different fractionation and processing schemes, thereby allowing the use of materials characterized by significant differences in terms of chemical composition and microstructure. The former refinery provided a 70/100 penetration grade bitumen, labelled in the study as A1, while the latter provided a 70/100 and a 50/70, labelled as B1 and B2, respectively.

For each bitumen, the relative amounts of saturates, aromatics, resins, and asphaltenes were evaluated by means of the combined use of a thin layer chromatography and a flame ionization detection. Moreover, preliminary rheological characterization was performed by determining softening point ($T_{R\&B}$, EN 1427-07), penetration at 25 °C (Pen_{25}, EN 1426-07), dynamic viscosity (η, AASHTO T316-10) and performance grade (PG, AASHTO M 320-10).

Results of the preliminary characterization of neat bitumens are presented in Tables 1–3 and Fig. 1. It is worth noting that bitumens B1 and B2, which were provided by the same refinery, showed a similar chemical structure but completely different rheological properties. On the contrary, bitumens A1 and B1, which were supplied by different refineries but belong to the same penetration and performance grades, were found to be quite different in terms of chemical composition.

The nano-sized additives employed to reinforce the neat bitumens were three commercially available products: one type of carbon nanotubes (CNT) and two types of nanoclays (NCA and NCB). Carbon nanotubes were produced by means of the catalyzed chemical vapour deposition process in thin multi-wall structures. The two nanoclays were natural montmorillonites which were organically modified by means of different surfactant coatings. Main characteristics of the three additives are reported in Tables 4 and 5.

Based on the results of previous investigations performed by the authors [13,24], the three modifying products were added to the neat binders in different dosages by following a procedure which combines the effects of shear mixing and sonication. Dosages were selected equal to 0.5 and 1% for CNTs and equal to 3 and 6% for the two nanoclays (NCA and NCB). Hence, from the factorial combination of base bitumen, additive type and dosage, 18 nano-reinforced blends were produced in the laboratory.

Mixing operations were all performed by maintaining binder temperature at 150 °C. The procedure begins with an initial phase of hand-mixing of the additive into the bitumen performed in order to completely embed the nano-particles into the binder phase. The blend is then homogenised by means of a mechanical stirrer operated at a speed of 1550 rpm for a total time of 90 min. The mechanical stirrer employed in this investigation was a Heidolph RZR 2041, equipped with a special handmade disintegrating head consisting of a ringed propeller-type impeller with shaft, coupled with a fixed perforated plate. This device promotes the deagglomeration of particles by means of the high shear forces generated by the axial flow through the plate holes. After shear mixing the blends are subjected to the action of ultrasounds for a total time of 60 min by employing the ultrasonic homogeniser UP200S from Hielscher. Continuous ultrasonic waves characterized by an amplitude of 157.5 μm and a frequency of 24 kHz are transmitted throughout the volume of the binder by means of a titanium sonotrode of 7 mm in diameter in order to further disintegrate agglomerations.

Nano-reinforced binders were coded as XX-YYY-Z, where XX indicates the base bitumen (A1, B1, B2), YYY indicates the additive type (CNT, NCA, NCB) and Z indicates, by referring to each specific additive type, the lower or higher dosage (L in case of the lower dosage, H in case of the higher dosage).

The three base bitumens and the 18 nano-reinforced blends were subjected to low-temperature rheological characterization in their long-term aged state which was simulated in the laboratory by means of the Pressure Ageing Vessel (PAV) as prescribed by AASHTO R28-09. As required by standard procedures, before PAV-ageing the binders were short-term aged by means of the Rolling Thin Film Oven (RTFO) as per AASHTO T240-09.

3. Testing

Mechanical characteristics of the binders after long-term ageing simulation were attained by carrying out three-point bending tests in the creep mode with a Bending Beam Rheometer (BBR), according to AASHTO T313-10. Midpoint deflection of the beam caused by a constant load of 980 mN was recorded at 8, 15, 30, 60, 120 and