Low-temperature properties of bituminous nanocomposites for road applications

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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.

Keywords

Bituminous binder; nanoclay; carbon nanotube; rheology; low-temperature cracking

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 nano-scale, 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 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 characterised 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 Figure 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.

Table 1. Chemical analysis of neat bitumens.

Base bitumen	Saturates (%)	Aromatics (%)	Resins (%)	Asphaltenes (%)
A1	5.5	38.1	42.0	14.4
B1	3.0	65.3	16.0	15.8
B2	2.4	63.4	17.5	16.7

Table 2. Softening point and penetration at 25 °C of neat bitumens.

Base bitumen	$T_{R\&B}$ [°C]	Pen_{25} [dmm]
A1	45.2	98
B1	44.6	95
B2	47.7	63

Table 3. Performance grade of neat bitumens.

Ageing conditions	PG characteristic rheological point	Measured parameter		
		A1 PG58-22	B1 PG58-22	B2 PG64-22
Original	η@T=135 °C	0.375 Pa·s	0.347 Pa·s	0.472 Pa·s
	T@G*/sinδ = 1 kPa	63.2 °C	63.3 °C	67.5 °C
RTFO	T@G*/sinδ= 2.2 kPa	64.0 °C	63.8 °C	66.0 °C
	T@G*·sinδ = 5000 kPa	19.9 °C	22.0 °C	24.0 °C
PAV	T@m = 0.300	-16.6 °C	-14.3 °C	-13.0 °C
	T@S = 300 MPa	-17.6 °C	-16.2 °C	-14.5 °C

RTFO: Rolling Thin Film Oven; PAV: Pressure Ageing Vessel; η: dynamic viscosity (Brookfield viscometer); T: test temperature; |G*| and δ: norm and phase angle of the complex modulus (Dynamic Shear Rheometer); m and S: creep rate and creep stiffness (Bending Beam Rheometer).

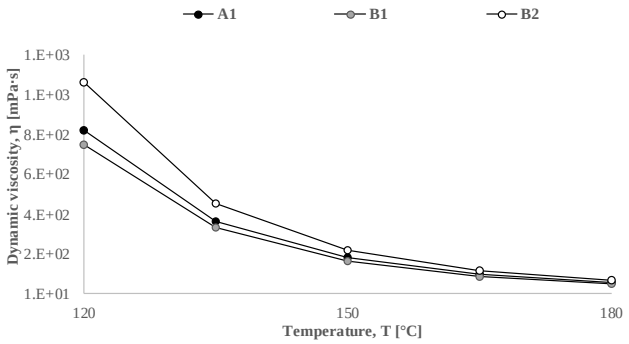

Fig. 1. Dynamic viscosity of neat bitumens.

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.

Table 4. Main characteristics of carbon nanotubes.

Additive	Average diameter [nm]	Average length [μm]	Surface area [m^2/g]	Carbon purity (%)	Density [g/cm^3]
CNT	9.5	1.5	250-300	90	1.72

Table 5. Main characteristics of nanoclays.

Additive	Organic modifier	Anion	Basal spacing [nm]	Cation Exchange Capacity (CEC) [meq/100g]	Density [g/cm^3]
NCA	Dimethyl, dihydrogenatedtallow, quaternary ammonium	Chloride	3.15	125	1.66
NCB	Methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium	Chloride	1.85	90	1.98

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 minutes. 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 minutes by employing the ultrasonic homogeniser UP200S from Hielscher. Continuous ultrasonic waves characterised 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 240 s at temperatures of -6, -12, -18 and -24 °C in order to determine creep stiffness and creep rate. At least two runs were performed for each test condition and average data were considered in the analysis. As indicated by AASHTO T313-10, results were considered acceptable when the difference between the two replicates, expressed as a percentage of their mean, did not exceed 7.2 and 2.9 % for creep stiffness and creep rate, respectively.

4 RESULTS AND ANALYSIS

4.1 Creep stiffness and creep rate

From the data recorded during BBR testing, flexural creep stiffness S(t) was calculated as indicated in Equation 1, applying the elementary Bernulli-Euler theory of elastic bending, but replacing elastic modulus E with time-dependent stiffness S(t) [25]:

$$S(t) = \frac{PL^3}{4bh^3\delta(t)} \qquad (1)$$

where P is the constant load, L is the span length, b is the width of the beam, h is the height of the beam and δ(t) is the time-dependent beam deflection at the midspan.

Creep-rate parameter m(t), which is the absolute value of the slope of stiffness versus time in a bi-logarithmic scale, was calculated as follows (Equation 2):

$$m(t) = \left| \frac{d\left(\mathrm{Log}S(t)\right)}{d(\mathrm{Log}t)} \right| \qquad (2)$$

Outputs of the performed creep tests are shown in Figures 2-4, where the overall response of blends is presented in terms of flexural creep stiffness (S) and creep rate (m) evaluated at 60 seconds. Such a loading time is traditionally used in low-temperature binder characterization consistently with the approach proposed within the SUPERPAVE system developed during the SHRP research program [26].

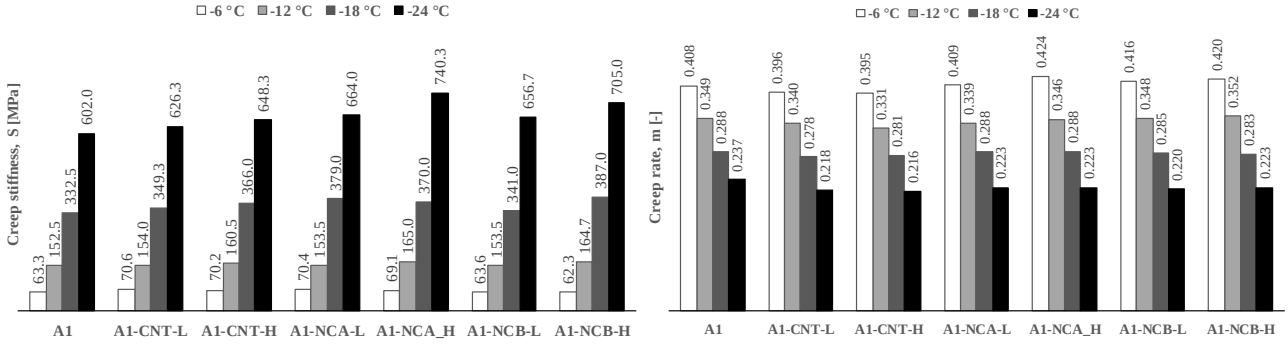

Fig. 2. S and m parameters for A1 blends.

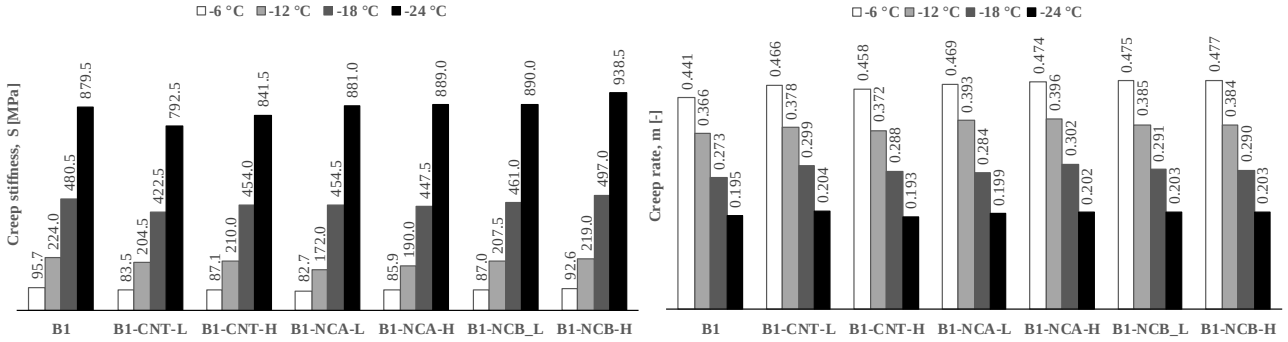

Fig. 3. S and m parameters for B1 blends.

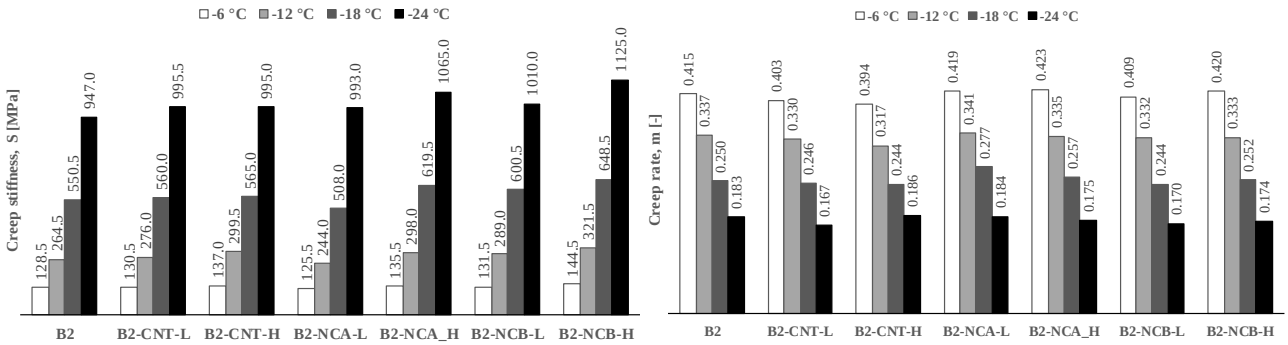

Fig. 4. S and m parameters for B2 blends.

Experimental results clearly indicate that the presence of nano-particles changes the rheological response of bitumen with effects that are significantly dependent on base bitumen, additive type and additive dosage. However, such variations never exceed 25 %. It is worth noting that this general outcome, obtained in low-temperature conditions, is in contrast with results previously reported on the same blends at both high-temperatures, with regard to the evaluation of anti-rutting potential, and at intermediate temperatures, with regard to fatigue behaviour, which showed variations in control parameters with respect to unmodified bitumen that exceeded in both cases 250 % [13, 17].

In agreement with the general findings of investigations carried out on the same blends at high in-service temperatures [13], modification of bitumen A1 always resulted in an increase in low-temperature stiffness. The relative variation in stiffness of the nano-reinforced blends with respect to neat bitumen was dependent on the specific combination of additive

and dosage, while it was only marginally affected by temperature. In this regard, a weak trend was noticed which seems to indicate a general amplification of the stiffening effect produced by the nano-particles at decreasing temperatures (as indicated by average rates of stiffness change of 2.5 and 5.1 MPa/°C at low and high dosages, respectively). When CNTs were used to reinforce bitumen A1, stiffness moderately increased when increasing dosage. The same effect was observed in the case of modification with both types of nanoclays, even though the amount of stiffening yielded by the layered nano-particles was higher than that observed with CNT modification (e.g. at -24 °C the stiffness increments at the lower and higher dosages were 4 and 8 % for CNT, while they were around 10 and 20 % for nanoclays).

Binders containing CNTs highlighted a more elastic behaviour than that of the reference bitumen, as indicated by the lower creep-rate values. This effect seems to be amplified for decreasing temperatures and, coherently with the results obtained in terms of stiffness, is more evident at the higher dosage. By contrast, the NCB-bitumen blends at both dosages showed an overall response that drastically changed with temperature. In fact, there was a definite increase and decrease of the relaxation capability with respect to neat binder at -6 and -24 °C, respectively. Similar outputs were also obtained for the NCA-bitumen blends at the higher dosage, whereas in the case of the lower dosage results indicated an overall increase in elasticity for decreasing temperatures. While an increase in elasticity triggered by nano-particles was somehow expected [15, 27], it is fairly surprising that some of the blends containing layered structures showed an increase in the relaxation capability as far as temperature remained above a specific threshold, after which relaxation phenomena that occur in the base bitumen seem to be hindered by the presence of the nano-platelets. Since it is well known that intercalated and/or exfoliated silicates can generate a shift in the glass transition temperature of bituminous matrices [28] or, more in general, of viscoelastic polymers [29], the observation reported above is indicative of an effective interaction between bitumen molecules and clay structures.

When considering the blends prepared with bitumen B1, the presence of nano-particles determined a general decrease in stiffness. In the case of modification with CNTs, it is interesting to observe that even if the decrease in stiffness was found at all investigated temperatures and dosages, it was more evident at the lower dosage. This finding is in line with results of tests previously performed at intermediate temperatures [17], which demonstrated that the performance of nanocomposites is strictly related to the networking action of CNTs, that, in turn, is dependent on the level of dispersion reached by nano-particles within the matrix. Hence, it can be assumed that in the case of blends prepared with the higher dosage of CNTs, the energy input provided during mixing operations was not sufficient to fully exploit the potential of nano-reinforcement. Nanoclays also produced a decrease in stiffness that was usually greater at the lower dosage. However, this effect seems to be lost in the lower range of investigated temperatures (at -18 °C for NCB-H, and at -24 °C for NCA-L, NCA-H, and NCB-L), thus confirming the strict correlation existing between the rheological behaviour of bitumen at low temperatures and interaction phenomena which occur between clay platelets and the bituminous phase.

Moreover, by comparing blends containing the two types of layered additive, it can be seen that nanoclay NCA produced a softening effect that was superior than that produced by nanoclay NCB, probably as a consequence of the greater values of both basal spacing and cation exchange capacity (Table 5), characteristics that can significantly promote intercalation and/or exfoliation of platelets [30].

In line with the stiffness results, it was found that creep rate increased with the presence of nano-particles, regardless of additive type. However, the effect that dosage had on the degree of enhancement of relaxation potential was strictly connected to the nature of the additive. In the case of CNT-bitumen blends, higher values of the m-parameter were found when the lower dosage of CNTs was used. By contrast, in the case of nanoclays it was highlighted that NCA was more effective when added at the higher percentage of modification, while NCB was not significantly sensitive to dosage variations. Hence, by combining information obtained in terms of the S and m parameters for blends prepared with base bitumen B1, it can be stated that in the case of CNTs better low-temperature performance were always obtained by using the lower dosage for modification. On the other hand, the evaluation of the effect of dosage for nanoclays led, in many cases, to contradictory outcomes when comparing results obtained from the analysis of the stiffness and those obtained in terms of elasticity.

Blends prepared with base bitumen B2 showed an increase in stiffness after modification, with a superior growth in the S parameter at higher percentages of nano-particles. The only exception was found in the case of NCA-bitumen blends at the lower dosage, which showed a reduction in stiffness in the range of temperatures between -6 and -18 °C.

Modification of bitumen B2 with CNTs generally caused a reduction in the creep-rate parameter that was intensified at the higher dosage. By contrast, there was no clear trend in the creep rate pattern of NCA- and NCB-bitumen blends with respect to both dosage and temperature. Hence, as described in section 4.2 further analysis was necessary in order to interpret experimental data.

4.2 Energy ratio

Given the contradictory nature of a part of the outcomes obtained from the S and m parameters for the assessment of the low-temperature performance of the binders, experimental data were also analysed by means of a synthetic energy parameter based on the evaluation of the combined effect of dissipation and storage potential [3, 31-32].

Raw data collected during BBR tests were interpolated via a non-linear regression analysis by means of the Burgers model, which combines a Maxwell and a Kelvin element in series [33]. According to this model, under a constant stress σ the total strain $\varepsilon(t)$ is composed of an instantaneous elastic strain, a viscous strain and a retarded elastic strain, as indicated in Equation 3:

$$\varepsilon(t) = \frac{\sigma}{E_1} + \frac{\sigma}{\eta_1} t + \frac{\sigma}{E_2}\left(1 - e^{-\frac{E_2}{\eta_2}t}\right) \quad (3)$$

where E_1 is the instantaneous elastic modulus, E_2 is the delayed elastic modulus, η_1 and η_2 are viscous coefficients and t is loading time. Burgers parameters E_1 , E_2, η_1, and η_2, which in contrast to creep stiffness and creep rate are time independent, were estimated from the time-dependent evolution of creep compliance D(t) during the entire loading period of BBR tests (240 s) using a least-squares regression analysis. D(t), which is defined as the ratio between time-dependent strain and constant stress (Equation 4), was calculated as the inverse of the flexural creep stiffness S(t) obtained from the experimental data by means of Equation 1.

$$D(t) = \frac{1}{S(t)} = \frac{\varepsilon(t)}{\sigma} = \frac{1}{E_1} + \frac{t}{\eta_1} + \frac{1}{E_2}\left(1 - e^{-\frac{E_2}{\eta_2}t}\right) \quad (4)$$

Examples of creep-compliance data plotted as a function of time are shown in Figure 5a, where both experimental results and data fitted with the Burgers model are presented. A comparison between modelled and experimental data is given in Figure 5b, where creep compliance values at 6 loading times and 4 temperatures are considered for all the 21 materials of the investigation. The coefficient of determination R^2 corresponding to the displayed relationship was found equal to 0.999.

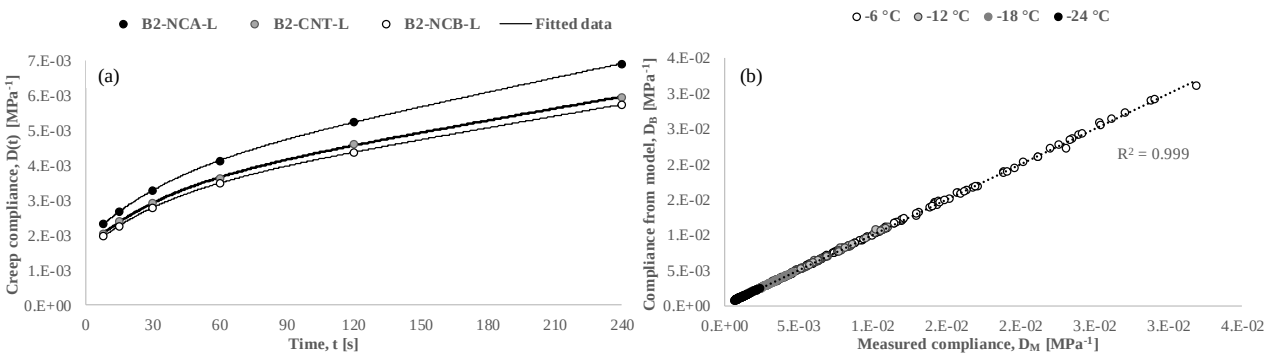

Fig. 5. Comparison between modelled and experimental data.

By integrating the energy per volume (W) (Equation 5) for each spring or dashpot element of the Burger model, formulas of the dissipated (W_d) and stored (W_s) energy were obtained (Equations 6-7). Hence, the corresponding values of W_d and W_s were calculated for each creep test and their ratio, indicated as energy ratio ER, was thereafter computed (Equation 8).

$$W = \int \sigma \cdot d\varepsilon \quad (5)$$

$$W_d(t) = \sigma^2\left(\frac{t}{\eta_1} + \frac{1}{2E_2}\left(1 - e^{-\frac{2E_2}{\eta_2}t}\right)\right) \quad (6)$$

$$W_s(t) = \sigma^2\left(\frac{t}{2E_1} + \frac{1}{2E_2}\left(1 - 2e^{-\frac{E_2}{\eta_2}t} + e^{-\frac{2E_2}{\eta_2}t}\right)\right) \quad (7)$$

$$ER = \frac{W_d}{W_s} \quad (8)$$

In order to better highlight the effects produced by nano-particles, the energy ratio found for each blend ($ER_{XX\text{-}YYY\text{-}Z}$) was normalised with respect to the value of the corresponding base bitumen (ER_{XX}), thus obtaining parameter ΔER (Equation 8).

$$\Delta ER = \frac{ER_{XX-YYY-Z}}{ER_{XX}} \qquad (9)$$

Results obtained by means of the energy approach described above are shown in Figures 6-8, which, for the sake of clarity, display ΔER values recorded only at the extreme temperatures investigated (-6 and -24 °C).

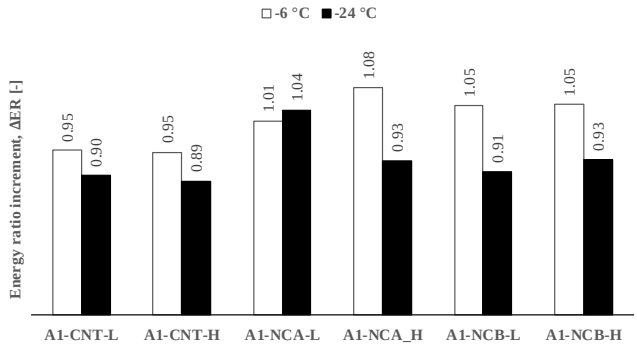

Fig. 6. ΔER parameter for A1 blends.

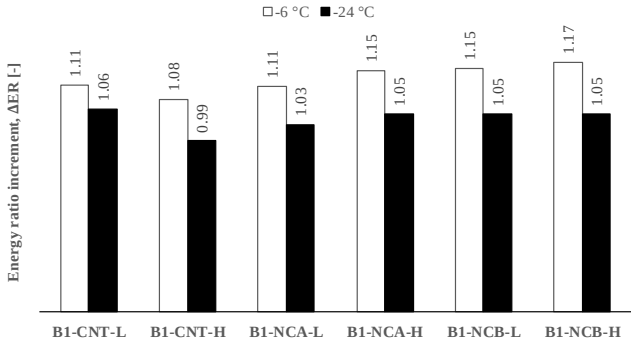

Fig. 7. ΔER parameter for B1 blends.

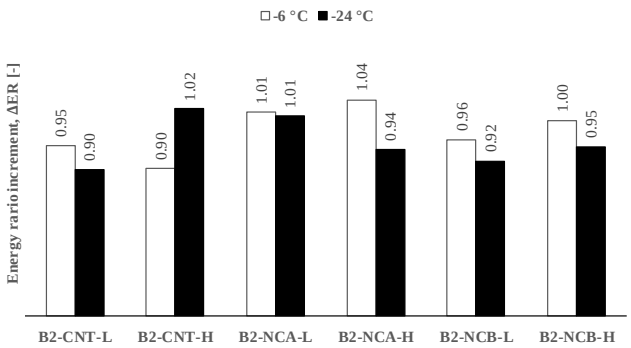

Fig. 8. ΔER parameter for B2 blends.

From a general overview of the results it can be observed that the adopted energy approach, which combines elastic and non-elastic response in a single parameter, further reduces the effects caused by nano-modification. This is proven by the

fact that in all cases ΔER is close to the unit value and is comprised, for the entire set of tested materials, between 0.89 and 1.17.

By referring to the ΔER values, it was found that neither the nature of the additive nor its dosage significantly affected the low-temperature properties of the nano-modified blends. However, it can be clearly pointed out that only blends prepared by using B1 showed a moderate increase in the energy dissipation capability with respect to base bitumen, thus indicating an enhancement of the low-temperature performance of these binders. On the other hand, the use of both bitumens A1 and B2 led to a general reduction of the energy dissipation capability of the nano-modified blends. Such a dependency of nano-modification effects upon base bitumen may be explained by referring to the outcomes of preliminary characterization tests carried out on the neat binders (Tables 1-3 and Figure 1). Quite surprisingly, it can be noticed that the chemical structure of B1 did not differ significantly with respect to that of B2 (that was supplied from the same refinery), while the overall rheological properties of B1 were quite similar to those of A1 (same penetration- and performance-grade). Nevertheless, it is worth noting that B1 is the binder characterized by the lowest value of viscosity at the mixing temperature, and that differences between A1 and B2 at 150 °C are lower than 10 %. This observation supports the idea that small variations in viscosity can significantly impact on the final dispersion of nano-particles within the bituminous matrix and, hence, on the performance properties of binders. However, future studies need to be performed to thoroughly explore this preliminary hypothesis and to characterize base binders by means of a more advanced chemical characterization.

5 CONCLUSIONS

Based on the experimental outcomes presented in this paper, it can be concluded that nano-sized additives, such as carbon nanotubes and nanoclays, only marginally affect the rheological behaviour of bituminous binders at low in-service temperatures. This was verified by combining different analysis approaches that were applied to the results of three-point bending tests performed by using a Bending Beam Rheometer (BBR).

Effectiveness of nano-modification was found to be strictly influenced by the combination of base binder, additive type and dosage. However, among these factors, the physicochemical nature of base bitumen seems to play a role of primary importance in the definition of the viscoelastic properties of final blends. Hence, the use of bituminous nanocomposites for paving applications should be carefully evaluated in climates in which thermal cracking represents a potential failure mode.

Further studies are certainly needed to combine the viscoelastic characterization performed in low-strain conditions via the BBR apparatus with the performance properties in the high-strain domain, necessary to explore the fracture behaviour of nanocomposites at low temperatures.

Acknowledgements

The study reported in this paper is part of the FIRB research project on “Innovative nano-structured and polymer-modified bituminous materials” funded by the Italian Ministry of Education, University and Research (MIUR).

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