Effect of sonication on high temperature properties of bituminous binders reinforced with nano-additives

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EFFECT OF SONICATION ON HIGH TEMPERATURE PROPERTIES OF BITUMINOUS BINDERS REINFORCED WITH NANO-ADDITIVES

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ABSTRACT

The study focused on the effect of sonication on high temperature properties of bituminous binders containing carbon nanotubes and nanoclays. Blends at various dosages were prepared in the laboratory according to two techniques, based on sonication and/or shear mixing. Rheological behaviour of binders was investigated, in the unaged and short-term aged state, by means of oscillatory and creep-recovery tests. Experimental results were found to be coherent with interaction phenomena occurring at the nano-scale and indicate that effects caused by sonication on nano-modified blends are not univocal, but are highly dependent on additive type.

KEYWORDS: Carbon nanotubes, nanoclays, bituminous binders, sonication, rheology, rutting.

1 INTRODUCTION

Nanotechnology has aroused, in recent decades, a great deal of interest in a wide variety of scientific disciplines, including biology, physics, chemistry and materials engineering [**1-4**].

Among the nano-sized additives that have been taken into account in literature, carbon nanotubes and nanoclays currently represent the most promising products. Carbon nanotubes were discovered by Iijima in 1991, as cathode deposit in electrical arc experiments [**5**]. They basically consist of graphene sheets, made of hexagonal networks of carbon atoms, which are rolled up into cylinders and capped with a half fullerene molecule. Carbon nanotubes can be found in either single-wall or multi-wall configurations, constituting a tubular shell with only one atom in thickness or multiple coaxial tubes of increasing diameter, respectively [**6**]. Nanoclays are sheet-like structures that are capable of yielding a huge surface area by means of clay platelet separation. The most common nanoclays are obtained from 2:1 phyllosilicates, the crystal lattice of which is made of a central octahedral sheet sandwiched between two external silica tetrahedrons. In order to give a hydrophobic character to phyllosilicates, which are typically hydrophilic, clays can be organically modified by means of specific surfactants, thus obtaining the so-called organoclays [**7,8**].

In the area of bituminous binders and mixtures employed in road paving applications, use of nano-sized additives is quite new and a relatively limited number of studies have been conducted by researchers worldwide. Some authors have highlighted the capability of nano-sized particles to improve rheological properties of bitumens, especially at high in-service temperatures [**9-15**]. However, in most cases, the full potential of nano-sized products has been limited by the difficulty of achieving a homogeneous dispersion, which ensures their effectiveness at the nano-level. Consequent performance-related benefits of modification, even if significant, are far below theoretical expectations.

The unique properties of nano-particles, which are associated to their large surface area to volume ratio, can be fully exploited only if an efficient homogenization and disaggregation of individual units is obtained within the bituminous matrix. In the case of carbon nanotubes, these phenomena depend upon entanglement, which arises as a consequence of the synthesis process, and agglomeration, due to intermolecular van der Waals forces [**16,17**]. In the case of organoclays, apart from agglomeration concerns, the degree of penetration of bitumen molecules between silicate layers plays a key role in defining the final properties of the composite binder. A successful bitumen-clay interaction may generate intercalated or exfoliated morphologies. Intercalation occurs when the galleries between the layers are expanded but silicate platelets still retain a well-defined spacing, whereas exfoliation results from complete separation and random dispersion of clay sheets [**18,19**].

In the effort of maximizing interactions between nano-particles and bitumen, encouraging outcomes have been obtained by means of ultrasound energy. Experimental results published by Zare-Shahabadi et al. [**20**] indicate that the combined use of sonication and shear stresses during mixing may lead to intercalated or exfoliated structures, depending on the type of employed silicate. Khattak et al. [**21**] showed that preliminary sonication treatment of carbon nano-fibers in a solvent may be beneficial to enhance visco-elastic and fatigue characteristics of bitumen. Santagata et al. [**22**] demonstrated that an actual reinforcement effect against fatigue cracking can be achieved in binders modified with carbon nanotubes when dispersion is performed by means of ultrasounds.

On the basis of the promising results provided by sonication, the study presented in this paper focused on the effect of ultrasounds on high temperature properties of bituminous binders containing carbon nanotubes and nanoclays. Several blends at various dosages were prepared in the laboratory according to two processing techniques, based on sonication and/or simple shear mixing. Rheological behaviour of binders was investigated by means of tests performed in both the oscillatory and creep-recovery mode. Experimental results were analysed with the specific goal of highlighting the effects of the dispersion technique on high-temperature performance properties of such innovative materials.

2 EXPERIMENTAL INVESTIGATION

2.1 Base materials

A single base bitumen was employed in the present work. Based on the results of preliminary rheological tests carried out according to AASHTO M 320 (Table 1), it was classified as a PG58-22. Chemical analysis, performed by means of the combined use of Thin Layer Chromatography and Flame Ionization Detection, yielded the relative amounts of

Saturates, Aromatics, Resins and Asphaltenes shown in Figure 1 (where measured electric potential difference ΔV is plotted as a function of time).

Three commercially available nano-sized additives were considered in the investigation: one type of carbon nanotubes (CNT), and two types of nanoclay (NC_A and NC_B). Carbon nanotubes were produced by means of the Catalyzed Chemical Vapour Deposition (CCVD) process in thin multi-wall structures, which have the advantage of guaranteeing a satisfactory aspect ratio (>150) while limiting production costs. The two nanoclays were originated from natural montmorillonites by inserting within clay platelets specific surfactant coatings, constituted by different types of quaternary ammonium salts. This allowed polarity to be altered, thus providing an organophilic character to the silicate surface. Main characteristics of the additives, based on manufacturers' technical specifications, are reported in Tables 2 and 3.

Aging condition	Temperature [°C]	Rheological characteristic
Unaged	135.0	η = 0.375 Pa·s
	63.2	$G^*/\sin\delta$ = 1 kPa
Short-term aged	64.0	$G^*/\sin\delta$ = 2.2 kPa
Long-term aged	19.9	$G^*\cdot\sin\delta$ = 5000 kPa
	-16.6	m = 0.300
	-17.6	S = 300 MPa

Table 1. *Rheological characterization of base bitumen*

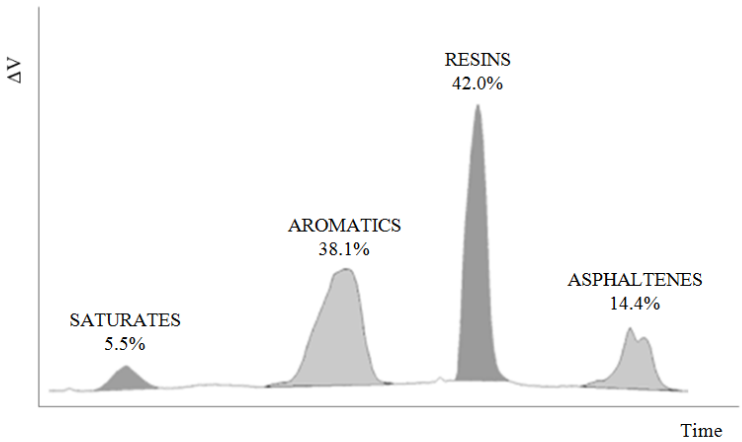

Figure 1. *Chemical analysis of base bitumen*

Average diameter [nm]	Average length [μm]	Surface area [m^2/g]	Density [g/cm^3]	Carbon purity (%)	Metal oxide (%)
9.5	1.5	250-300	0.0427	90	10

Table 2. *Main properties of multiwall carbon nanotubes*

NC type	Surfactant	Anion	Basal spacing [nm]	Cation Exchange Capacity (CEC) [meq/100g]	Density [g/cm^3]
NC_A	Dimethyl, dihydrogenatedtallow, quaternary ammonium	Chloride	3.15	125	1.66
NC_B	Methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium	Chloride	1.85	90	1.98

Table 3. *Main properties of nanoclays*

2.2 Preparation of nano-reinforced blends

The base bitumen and additives described in section 2.1 were employed for the laboratory preparation of several nano-reinforced blends. Experimental factors which were kept variable in the study were additive dosage and mixing technique.

Dosages of the nano-sized additives were defined by taking into account the significant differences in terms of volumetric properties of carbon nanotubes and nanoclays. Thus, percentages by weight of the base bitumen were fixed at 0.5% and 1% for carbon nanotubes and at 3% and 6% for nanoclays. These dosages were selected on the basis of previous investigations [**12,13,22**] which showed that they are sufficient to affect the rheological response of neat bitumen. Moreover, they are compatible with the needs of limiting costs (of base materials) and of avoiding excessive viscosity of blends at mixing temperatures.

Since mixing operations can influence the rheological behaviour of nano-reinforced materials [**16,18**], two mixing techniques were compared in the whole study. The first one is based on a simple shear mixing protocol previously developed by the Authors [**12, 13**]. The procedure begins with initial hand-mixing of the additive in the preheated binder, followed by a phase during which the blend is mixed with a mechanical stirrer, operated at a speed of 1,550 rpm for a total time of 90 minutes at a temperature of 150°C, kept constant by means of a thermostatic oil bath. The second protocol consists in the addition of a sonication phase to the shear mixing procedure described above. This further phase is carried out by employing the ultrasonic homogeneizer UP200S from Hielscher GmbH (200 W and 24 kHz), equipped with a cylindrical titanium sonotrode (7 mm diameter). This element is immersed in the blend which is kept in a fluid state at a constant temperature of 150°C. Ultrasounds are then generated, propagating within the material in the form of compression attenuated waves. As a consequence, separation of individual nanoparticles from existing agglomerates is promoted, thus leading to a more homogeneous dispersion [**16**].

In order to choose sonication parameters which lead to an adequate dispersion of nano-particles, a preliminary set of tests dedicated to the evaluation of the effect of sonication duration and wave amplitude was performed on a reduced set of nano-reinforced blends. Values of these parameters were respectively fixed at 30 and 60 minutes and at 87.5 and 157.5 μm. In the case of sonication duration, these values were adapted from those proposed elsewhere for carbon nano-fibers and nanoclays dispersions [**20,21,23**]. Selected amplitudes correspond to 50% and 90% of the maximum value that can be attained by the equipment. They were chosen in the attempt of maximizing the overall efficiency of the system and of limiting wearing phenomena which may occur at the tip of the sonotrode in the case of high viscous media.

The effect of sonication parameters on distribution of nano-particles may be assessed via microscopic inspections or indirect estimative techniques. Even if microscopy represents the only way to obtain direct information on morphology, it requires a stringent protocol for specimen preparation that cannot be easily adopted in the case of bituminous materials. Moreover, microscopy provides information that is limited to the cross-section of the sample, whereas results obtained from the use of indirect rheological methods are related to the bulk properties of considered specimens [**17**]. In the light of these observations and of the numerous works which have established a correlation between microscopic inspections and dynamic rheological measurements [**17,24-27**], in this study the efficiency of the sonication protocol on dispersion of nano-sized additives was indirectly assessed with a rheometric approach. Since storage modulus is highly sensitive to nano-particle dispersion and interfacial interactions which take place in complex compounds [**17,28,29**], this parameter was monitored in a wide range of strains by means of amplitude sweeps. Tests were carried out by covering the strain range comprised between 0.01% and 100%, at ambient temperature (20°C) and at a constant frequency of 10 Hz.

Figure 2 shows the response of blends containing 1% CNT and 6% NC_A, prepared by using the shear mixing procedure only (0 min of sonication), and by applying, in addition to shear mixing, a further phase of sonication. This further step of preparation lasted for 30 or 60 minutes and was characterised by an ultrasound wave of 50% or 90% of maximum amplitude (marked as A50 and A90, respectively).

It can be noticed that similar trends were recorded regardless of the considered additive type. By increasing the energy input for homogenization, either by extending sonication duration or by expanding wave amplitude, the storage modulus increases. Such an effect can be attributed to disintegration of clusters of nano-particles which makes a greater surface available for interactions and three-dimensional networking [**30,31**].

A drop of mechanical properties was never measured by increasing dispersion energy. It can thus be assumed that damage to outer shells of nanotubes [**32**] or partial dissolution of montmorillonites [**33**], which may be caused by high pressure fields or prolonged sonication durations, were negligible. In any case, the possibility of carrying out mixing with a higher sonication energy was discarded based on equipment limitations and economic considerations.

As a result of these observations, a sonication duration of 60 minutes with a wave amplitude of 157.5 μm was used for the preparation of all sonicated blends considered in the rest of the experimental investigation.

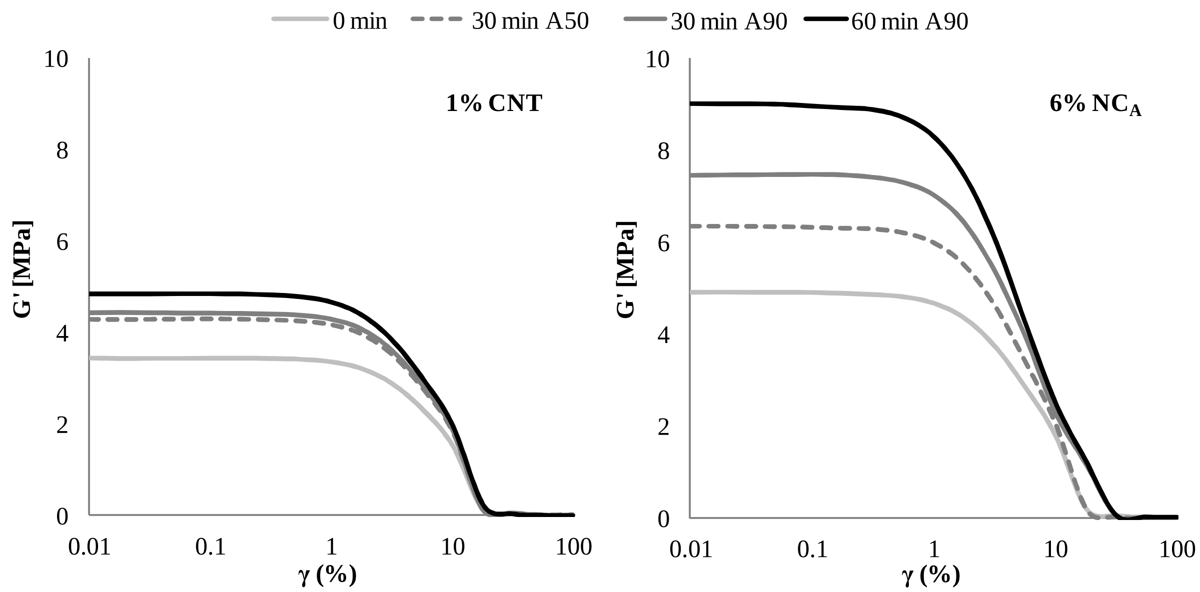

Figure 2. *Effect of sonication parameters on storage modulus of blends containing 6% NC$_A$ and 1% CNT*

2.3 Testing

A thorough rheological characterization at high in-service temperatures was carried out on all blends in the unaged state and after short-term ageing (AASHTO T 240-2009), simulated in the laboratory by means of the Rolling Thin Film Oven (RTFO) test.

Equipment used for binder characterization was a Physica MCR 301 DSR from Anton Paar Inc., an air-bearing stress-controlled device equipped with a permanent magnet synchronous drive (minimum torque = 0.1 μNm, torque resolution < 0.1 μNm) and an optical incremental encoder for the measurement of angular rotation (resolution < 1 μrad). A 25-mm parallel plate sensor system was used with a 1-mm gap between the plates.

A first screening of the effect of nano-reinforcement was initially obtained by means of frequency sweeps carried out on unaged binders. Norm and phase angle of the complex modulus were monitored in a broad spectrum of testing conditions, by covering two log decades of frequency, from 1 to 100 rad/s, and by adopting test temperatures comprised between 34 and 82°C (with 6°C increments between each measurement step). Shear strains applied to test specimens were varied depending upon temperature and frequency, allowing rheological properties to be always evaluated within the linear visco-elastic domain.

A successive phase of the experimental investigation focused on the evaluation of specific rutting parameters obtained by means of both oscillatory shear loading tests and creep-recovery tests, performed at three different temperatures (58, 64 and 70°C). Rutting resistance factor $|G^*|/sin\delta$ was obtained according to AASHTO T 315-10, at a frequency of 10 rad/s, on binders tested in both unaged and RTFO-aged states. Non-recoverable creep compliance (*Jnr*) and percent strain recovery (*R*) were determined by carrying out Multiple Stress Creep Recovery (MSCR) tests performed according to AASHTO TP 70-10. These tests were conducted on short-term aged blends, by applying ten creep-recovery cycles at two stress levels, equal to 0.1 and 3.2 kPa.

A minimum of two replicates were run for each test and average data were used in the analysis.

3 RESULTS AND DISCUSSION

3.1 Black diagrams

Norm and phase angle values of the complex modulus gathered from frequency sweep tests are showed in Figures 3-5 in the form of Black diagrams. Such a representation allows oscillatory data collected in a wide range of time-temperature conditions to be presented in a single diagram without any manipulation of raw data, thus providing a portrayal of the overall mechanical response. Moreover, Black diagrams permit an assessment of thermo-rheological behaviour. While in the case of neat bitumens commonly employed in pavement applications thermo-rheological behaviour can be associated to a sufficient degree of simplicity on account of the time-temperature equivalence, this needs to be verified for innovative binders [**34**].

In the case of blends containing carbon nanotubes (Figure 3), it can be observed that results seem to be highly sensitive to both additive dosage and mixing technique. In particular, an increase of the amount of reinforcement and/or of the energy employed for dispersion of nano-particles induces a shifting of rheological data towards lower phase angles and higher moduli. In physical terms this translates into an enhancement of stiffness and elasticity.

Data collected from non-sonicated compounds indicate that 0.5% addition of CNT produces a fairly low increase in elasticity, while at 1% dosage the improvement becomes considerable. This is evident from the different asymptotes that can be identified for the two blends in the high temperature-low frequency domain. It can therefore be postulated that a sufficiently high amount of carbon nanotubes hinders the transition to Newtonian flow, which in the same temperature and frequency conditions occurs in the case of neat bitumen.

Results discussed above differ from those found elsewhere [**13**], where a CNT dosage of 0.5% was sufficient to cause a marked reduction of phase angle values in the low frequency-high temperature domain. This discrepancy may be related to the different chemical structure of the neat bitumens employed in the two studies. Such an issue should be thoroughly investigated in future research.

A further improvement in stiffness and elasticity is recorded in blends treated with ultrasonic waves at either considered dosages. This finding can be explained by the beneficial effect of de-agglomeration of nanotube clusters, that allows a great deal of interactions to take place along the huge interfacial areas.

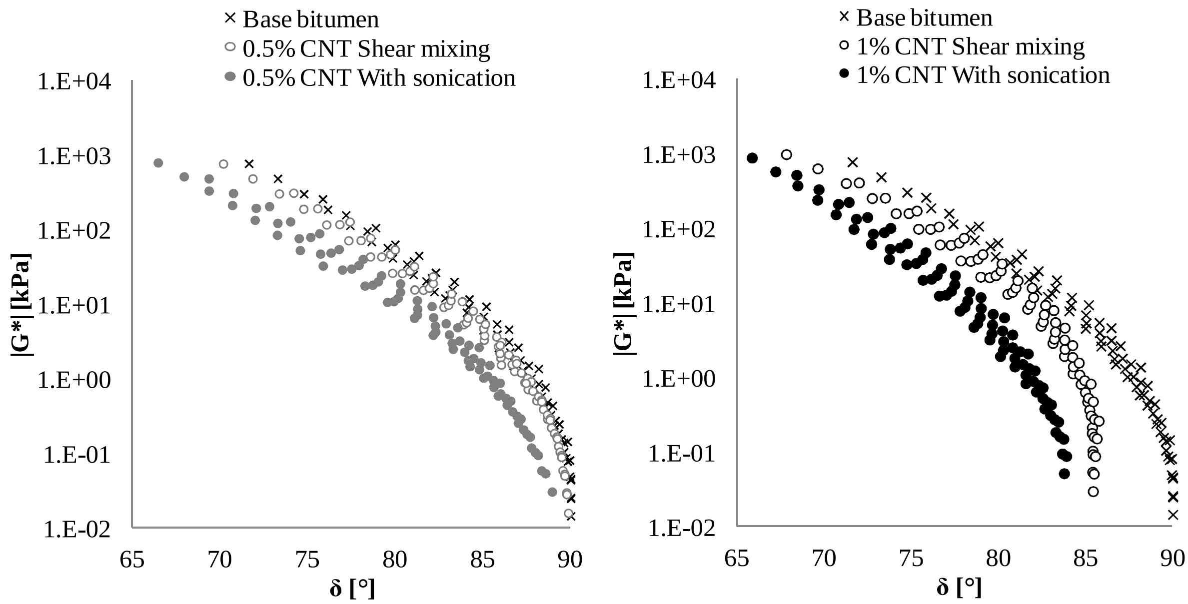

Figure 3. *Black diagrams of blends reinforced with CNT*

Results obtained from tests carried out on binders containing nanoclays are shown in Figures 4 and 5, which highlight the relevant effects associated to the specific properties of each considered nanoclay.

On the whole, Black diagrams of nanoclay-bitumen blends obtained by means of high shear mixing are very similar to that of base bitumen. This indicates that, even if modification alters the mechanical response in specific time-temperature conditions, it does not affect overall rheological behaviour.

Completely different considerations can be made by analysing the results obtained on binders prepared with the aid of ultrasounds and by employing nanoclay NC_A. In particular, for such blends nano-modification produces a variation of elasticity which is particularly high at 6% dosage. As a result of its different properties, use of nanoclay NC_B does not yield the same rheological effects, with Black diagrams that are similar to those of non-sonicated blends and are almost overlapping with that of base bitumen.

It may be reasonable to hypothesize that, once local energy provided by sonication allows nanoclay particles to break free from the adjoining restraining forces of agglomerates, the possibility of bitumen to intercalate within nanoclay galleries is largely governed by nanoclay peculiarities. In particular, degree of bitumen intercalation is guided by polarity of the surfactant and by the gap existing between layers, which in turn is largely influenced by the length of surfactant chains and by clay charge density [**8**]. Thus, in the case of the two nanoclays employed in this study it can be inferred that the lower values of basal spacing and cation exchange capacity (CEC) of nanoclay NC_B (Table 3) may be responsible for the reduced reinforcing effects transferred to the bituminous matrix.

Based on these observations it can be concluded that the effects generated by sonication treatment are not univocal, but are highly dependent on additive type. In the case of CNT blends, the action of ultrasounds emphasizes the positive effects that are already noticeable for compounds obtained by simple shear mixing. In the case of NC_A blends, potentiality of the additive seems to be fully exploited only after sonication; in the case of NC_B blends, no substantial benefit can be attributed to nano-modification.

It is noteworthy that when an increase in stiffness and elasticity occurs in any of the considered blends, this is always accompanied by a loss of thermo-rheological simplicity, as indicated by discontinuities in Black curves. This means that a change in temperature does not correspond to a variation in loading frequency since temperature does not alter only the absolute value of relaxation times by a simple shifting toward lower or higher values, but affects the overall relaxation function [**35**]. Such a behaviour is typical of high wax content and polymer modified bitumen, due to the presence of crystalline arrangements, or of gel type bitumen, as a consequence of the numerous interconnected asphaltene micelles. In the case of nano-modified binders, lack of thermo-rheological simplicity can be associated to a deep structuring of nano-particles within the dispersing medium [**34,36**].

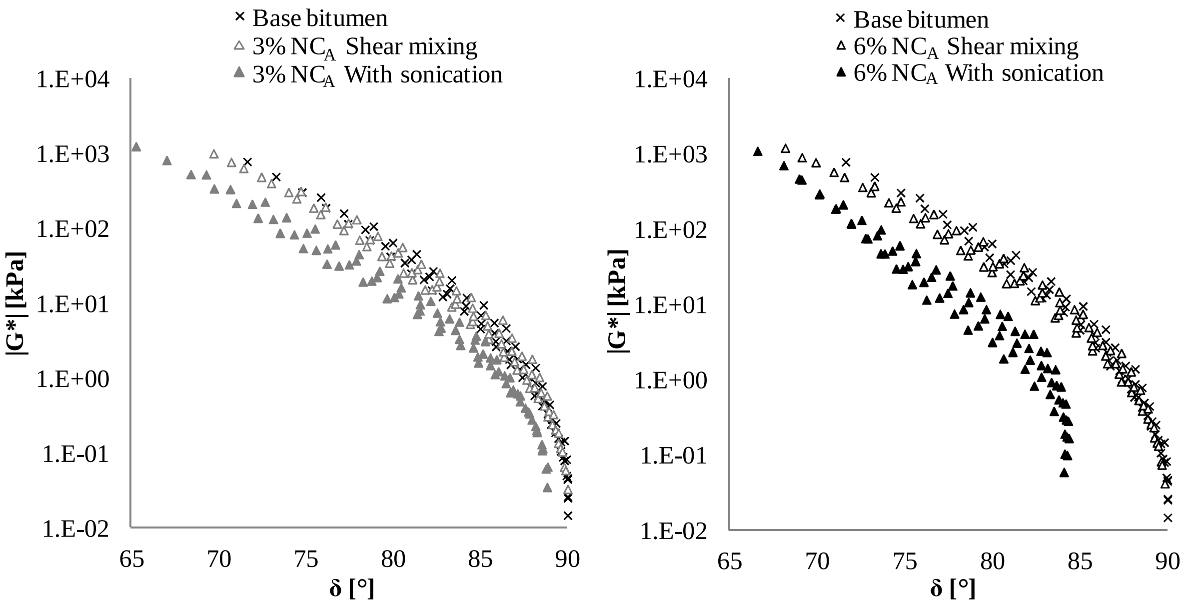

Figure 4. *Black diagrams of blends reinforced with* NC_A

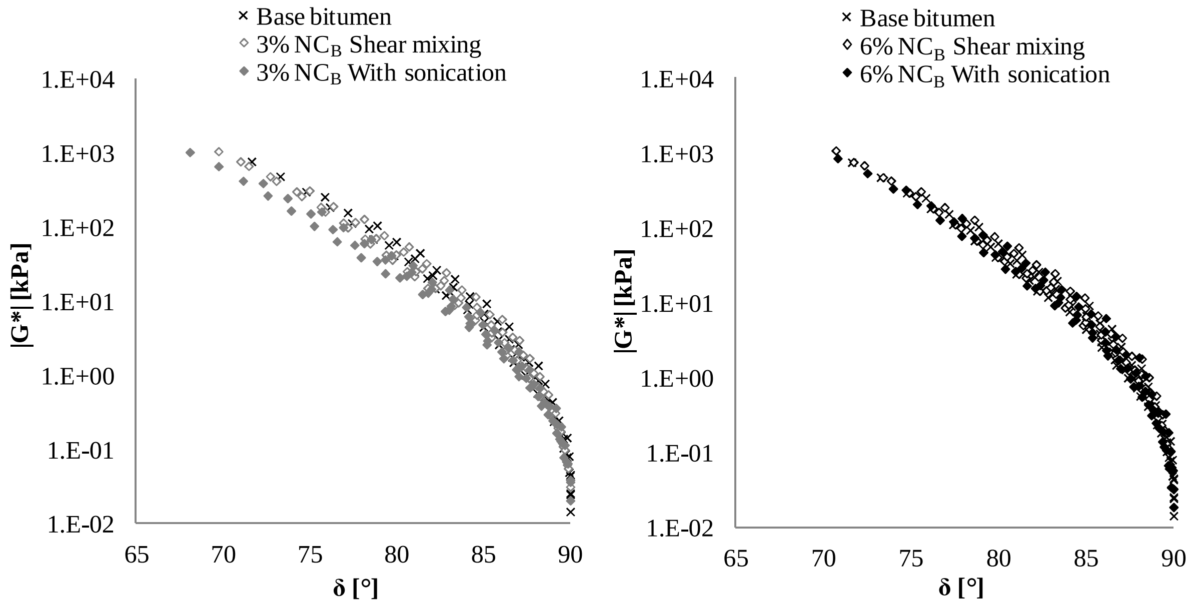

Figure 5. *Black diagrams of blends reinforced with NC_B*

3.2 SHRP rutting parameter

SHRP rutting parameter $|G^*|/sin\delta$ was determined from data retrieved from oscillatory shear loading tests carried out on base bitumen and on all blends containing nano-additives. This parameter, that represents the reciprocal of loss compliance, can be correlated to the fraction of non-recoverable deformation accumulated in a pavement that is ascribable to the bituminous binder [**37**]. The relative variation of $|G^*|/sin\delta$ caused by modification of neat bitumen was calculated according to Eq. 1

$$\Delta(|G^*|/sin\delta) = \frac{(|G^*|/sin\delta)_x - (|G^*|/sin\delta)_B}{(|G^*|/sin\delta)_B} \qquad \text{Eq. 1}$$

where $(|G^*|/sin\delta)_B$ and $(|G^*|/sin\delta)_x$ indicate the rutting resistance factor of base bitumen and of blends obtained by means of nano-particle addition, respectively. As shown in Figures 6 and 7, the enhancement in anti-rutting performance expressed in terms of $\Delta(|G^*|/sin\delta)$ was evaluated for unaged and short-term aged materials.

In the case of unaged blends (Figure 6), even though addition of nano-additives always leads to an enhancement in resistance to permanent deformation of base bitumen, the degree of enhancement is found to be highly dependent upon additive type, dosage and mixing technique.

On the whole, the most critical factor in controlling final performance of blends containing nano-particles is the adopted mixing protocol. In view of the huge differences that can be observed by comparing materials obtained by means of shear mixing only and those subjected to a further sonication phase, it can be inferred that the thorough homogenization provided by ultrasounds is necessary in order to make full use of the potentiality of nano-scale reinforcements.

Inspection of the influence of additive type indicates that the best anti-rutting performances are found by employing CNT and NC_A, whereas NC_B shows a much lower capability to affect rheological properties of neat bitumen regardless of the mixing technique. Such a result seems to corroborate the idea that a lower extent of intercalation of bitumen molecules within the nanoclay platelets takes place in the case of NC_B.

It is noteworthy that, even though the higher dosages of CNT and NC (respectively equal to 1% and 6%) lead to higher values of the SHRP rutting resistance factor, ultrasounds are more effective in improving high temperature properties of blends with lower additive dosages (0.5% CNT and 3% NC). This is proven by the greater ratio between enhancements obtained after and before sonication, which is around 5 for lower dosages and approximately 3.5 for the higher ones.

From the comparison between data gathered for unaged materials (Figure 6) and those subjected to the RTFO process (Figure 7), it can be deduced that the nature of additive type plays a key role in influencing the performance of blends after ageing.

Enhancement of high temperature properties of binders containing CNT after short-term ageing is comparable to that recorded in unaged conditions. This suggests that neither the structure of carbon nano-particles is affected by the ageing process nor CNT-bitumen compatibility is jeopardized by the substantial chemical changes which occur in the bituminous medium.

Quite different considerations can be made for materials reinforced with nanoclays. In agreement with the findings of other studies [**38**], after RTFO treatment both adopted nanoclays show a lower effectiveness in improving the rutting resistance factor of base bitumen, if compared with enhancements exhibited before ageing.

When binders containing NC_A are considered, such an evidence may be attributed to the well known barrier properties of silicate layers [**20,39-41**]. In fact, in the case of highly intercalated and/or exfoliated structures, dispersed platelets are capable of hindering permeability of gas molecules as a consequence of the combined effect of their peculiar chemical properties and of the geometrical constraints related to their complex distribution within bitumen. Hence, on the one hand, they limit oxygen penetration by increasing its average path length, and, on the other hand, they reduce loss of volatile components of bitumen. Due to this strong anti-ageing mechanism provided by nanoclay layers, hardening of bitumen is somewhat hampered, thus leading to a reduction of anti-rutting effectiveness.

Rheological properties of unaged materials modified with NC_B seem to indicate a negligible degree of intercalation. A possible cause for this unique performance may lie in a partial degradation of the organic portion of the nanoclay, due to the thermo-oxidative action provoked during the RTFO test [**38**]. As suggested in literature [**12,38**], a further explanation of nanoclay-bitumen performance worsening can derive from the degree of nano-particle dispersion. Thus, nanoclays in the form of clusters may be more prone to degradation phenomena, probably as a consequence of the limited shielding action provided by bitumen. However, this hypothesis seems to be not fully confirmed in the case of blends containing 6% NC_B, which highlight the ineffectiveness of sonication in enhancing the mechanical properties of base bitumen.

It is interesting to note that in the case of aged materials, effectiveness of sonication was observed to be extremely variable, with no clear trend of the ratio between enhancements obtained after and before sonication.

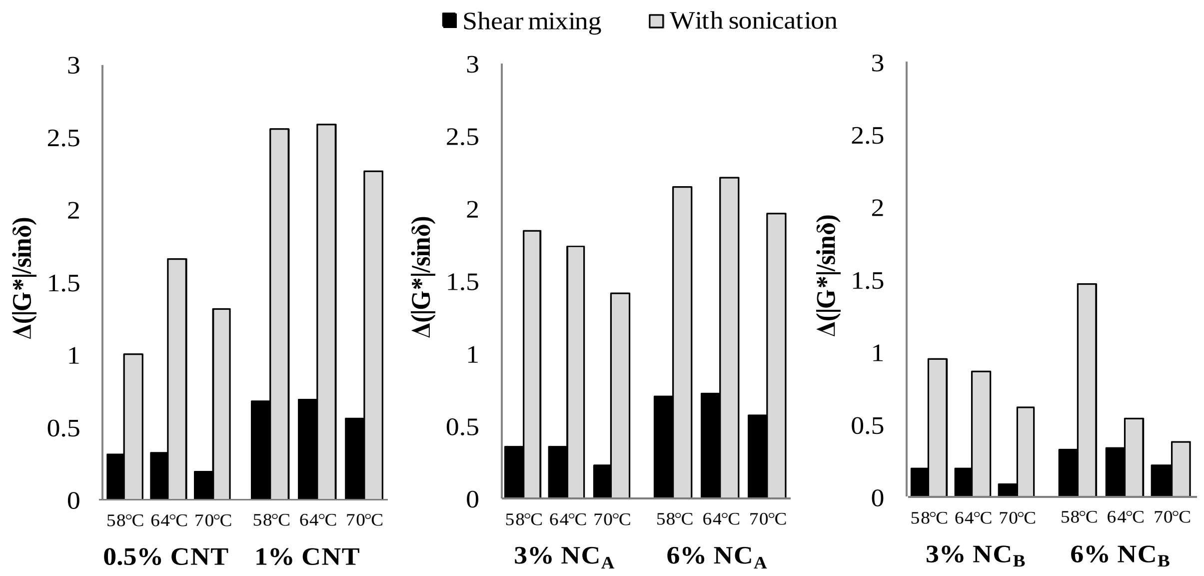

Figure 6. *Relative variation of rutting resistance factor obtained for unaged blends*

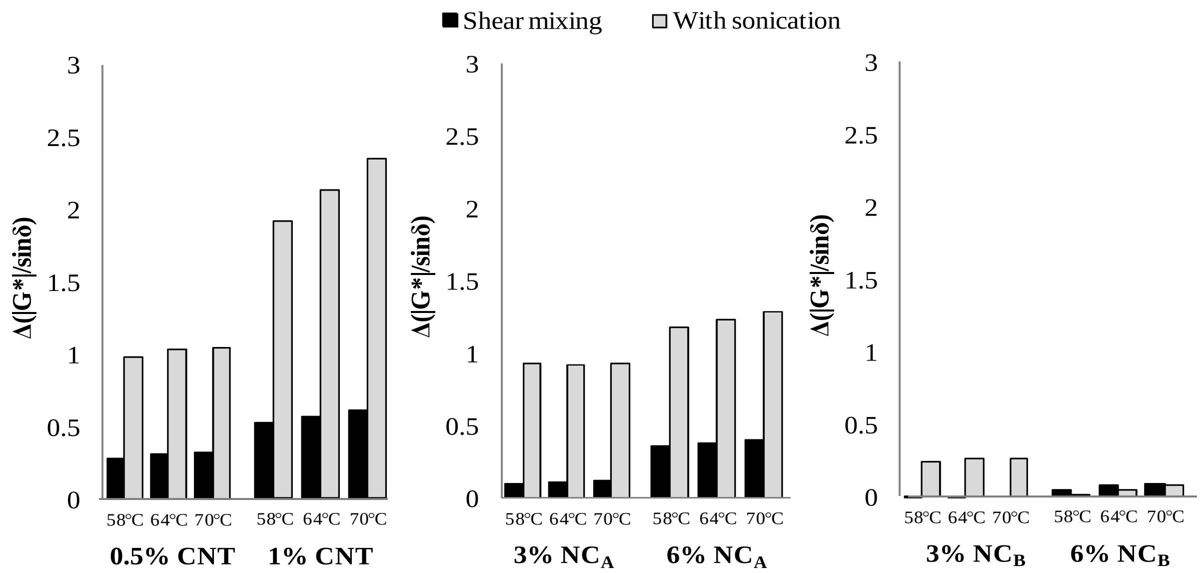

Figure 7. *Relative variation of rutting resistance factor obtained for short-term aged blends*

3.3 Non-recoverable creep compliance and percent strain recovery

By adopting the same approach followed in section 3.2, parameters gathered from MSCR tests were expressed by referring to their relative variation caused by the use of nano-sized additives. In particular, non-recoverable creep compliance (*Jnr*) and percent strain recovery (*R*) data were processed by means of the following equations:

$$\Delta Jnr = \frac{(Jnr)_x - (Jnr)_B}{(Jnr)_B} \qquad \text{Eq. 2}$$

$$\Delta R = \frac{(R)_x - (R)_B}{(R)_B} \qquad \text{Eq. 3}$$

where symbols denoted with pedex (*x*) refer to the generic blend containing a nano-sized additive, while those with pedex (*B*) are relative to base bitumen.

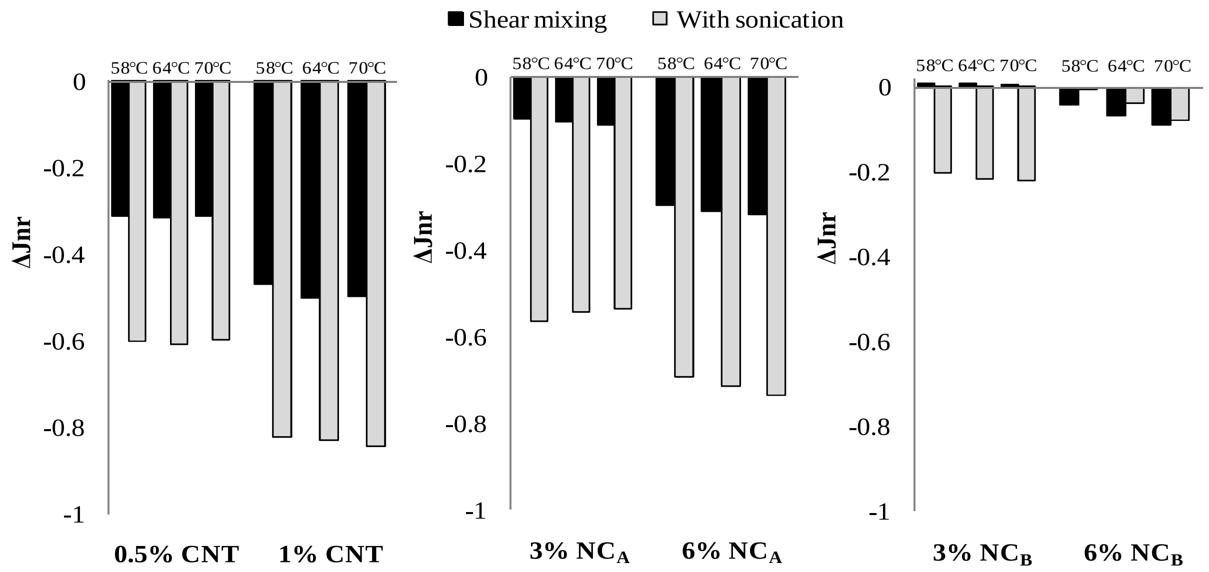

Figure 8. *Relative variation of Jnr at 0.1 kPa stress level*

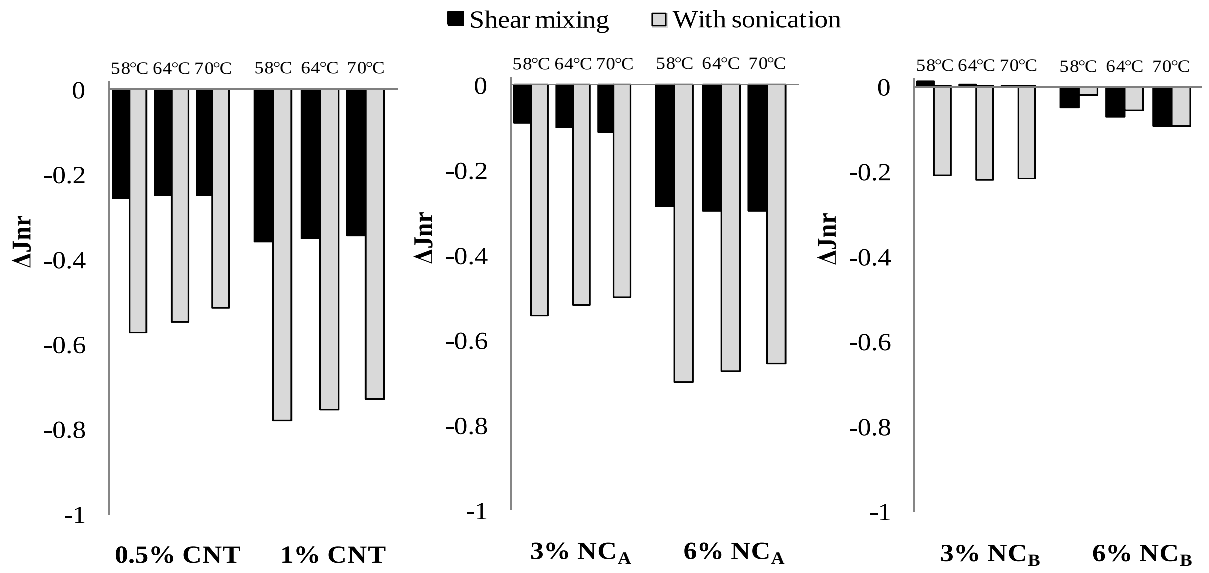

Figure 9. *Relative variation of Jnr at 3.2 kPa stress level*

ΔJnr values calculated for each stress level considered in creep-recovery tests (0.1 and 3.2 kPa), are presented in Figures 8 and 9. Once again it can be seen that the benefit resulting from the presence of nano-particles is markedly dependent on mixing technique, additive type and dosage. Effects recorded at each stress level are comparable, thus indicating a marginal change in stress dependency caused by modification of neat bitumen.

If the effects of preparation technique are considered, it can be observed that the better dispersion provided by ultrasounds always leads to a significant reduction of non-recoverable strain, with the only exception of blends containing 6% NC_B.

By comparing results obtained for different types of additives it can be stated that the greatest enhancement of resistance to permanent deformation is obtained by means of CNT. This indicates that the effect of the intrinsic mechanical properties of the additive, combined with an adequate surface interaction, provide an efficient reinforcement action that allows a great deal of load transfer to take place even in the high strain domain.

When analysing effects produced by the two organoclays, it can be noticed that NC_A is significantly more efficient in reducing the non-recoverable creep compliance of base bitumen. Such an evidence suggests that when sufficient interaction between binder and nanoclay occurs, flow of bitumen is extensively obstructed by the presence of exfoliated platelets and by confinement of bitumen molecule chains within the galleries of intercalated structures [**39,40,42**].

In agreement with the information derived from the SHRP rutting parameter, a relatively high dosage of both CNT and NC_A yields a higher deformation resistance. This is also true in the case of NC_B for blends obtained by shear mixing, while materials treated with the ultrasound process perform better at the lower dosage (3%).

In Figures 10 and 11 the variation of percent strain recovery is presented at the two stress levels adopted in the investigation. On the whole, differences in terms of anti-rutting performance highlighted by analysing non-recoverable creep compliance seem to be amplified when the recovery ability of binders is considered.

The best elastic behaviour is exhibited by CNT-bitumen blends, which show improvements by increasing the dosage as well as by intensifying nano-particle dispersion by means of sonication. It is worth observing that while for sonicated blends similar results are obtained at 0.1 and 3.2 kPa, materials prepared by shear mixing show a non-negligible sensitivity to stress level applied during the creep phase.

As expected, nanoclay NC_B only marginally affects the elastic response of base bitumen, with a slight improvement or worsening that is dependent upon additive dosage and mixing technique.

On the other hand, data gathered for binders containing nanoclay NC_A confirm the potential of this nano-sized additive to effectively interact with the bituminous matrix when accurately dispersed by sonication, with the better performance displayed at the higher dosage at both 0.1 and 3.2 kPa.

As in the case of the SHRP rutting parameter obtained for aged materials, results gathered from MSCR tests did not highlight the influence of additive dosage on the effectiveness of sonication.

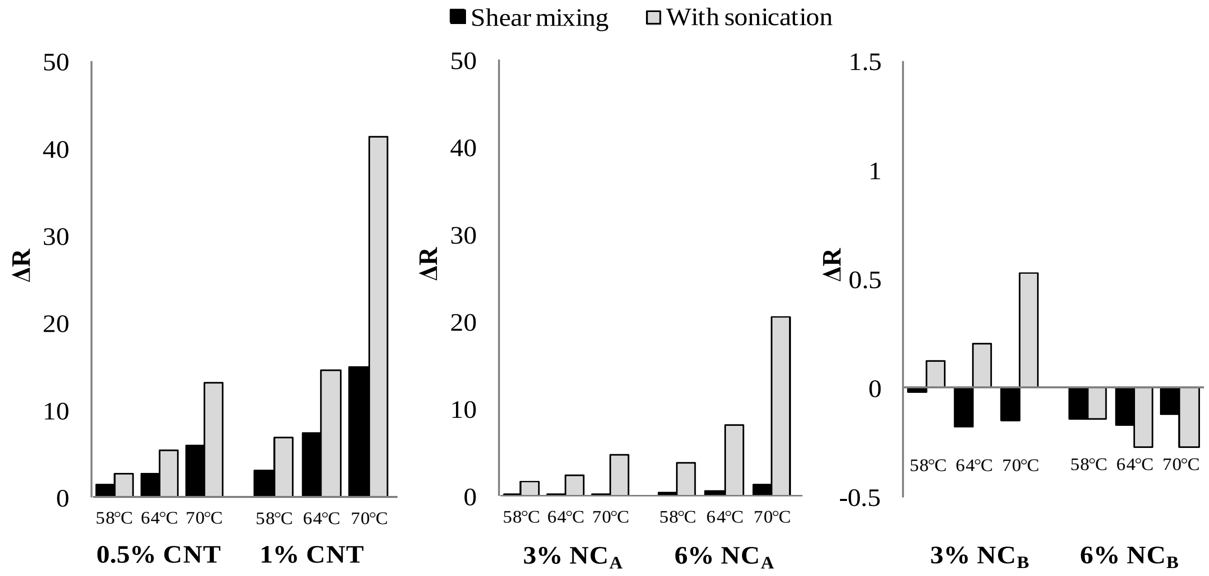

Figure 10. *Relative variation of R at 0.1 kPa stress level*

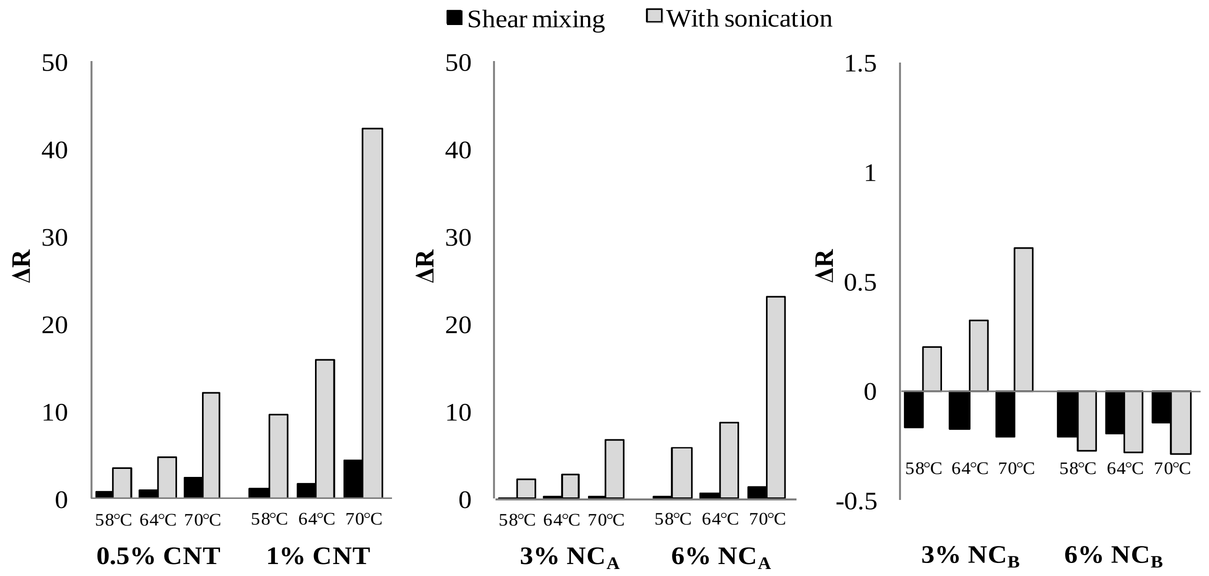

Figure 11. *Relative variation of R at 3.2 kPa stress level*

4 CONCLUSIONS

Based on the results obtained in the experimental investigation described in this paper, it can be concluded that sonication may be a key element for the preparation of nano-reinforced bituminous binders characterized by superior performance. This was verified with respect to high in-service temperature properties of binders which were evaluated by adopting several rheological approaches in order to assess resistance to permanent deformation. Results were found to be coherent with interaction phenomena which occur at the nano-scale. In particular, assessment of rheological properties of sonicated blends suggests that damage to outer shells of nanotubes or partial dissolution of nanoclay, if existing, are negligible and do not jeopardize the beneficial effects of agglomerate disaggregation.

In general terms it can be stated that the effects caused on nano-modified blends by sonication treatments are not univocal, but are highly dependent on additive type. In particular, it was observed that ultrasounds may emphasize the positive reinforcing effects produced by carbon nanotubes and can fully reveal the potentiality of nanoclay modification. This second aspect, however, requires nanoclays to be fully compatible with bitumen as a result of their aptitude to be subjected to intercalation and/or exfoliation.

Further research is needed to generalize the outcomes of this study and to directly verify the mechanisms by means of which modifying effects are obtained. This should be done by extending investigations to other temperature conditions and by addressing a variety of performance-related issues (not limited to rutting only). Moreover, mixing techniques should be subjected to optimization by introducing in the evaluation a cost-benefit analysis applied to the industrial scale.

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