

Bituminous-based nanocomposites with improved high-temperature properties

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Corresponding Author: Prof. Ezio Santagata,

Corresponding Author's Institution: Politecnico di Torino

First Author: Ezio Santagata

Order of Authors: Ezio Santagata; Orazio Baglieri; Lucia Tsantilis; Giuseppe Chiappinelli; Davide Dalmazzo

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## Bituminous-based nanocomposites with improved high-temperature properties

Ezio Santagata<sup>\*</sup>, Orazio Baglieri, Lucia Tsantilis, Giuseppe Chiappinelli, Davide Dalmazzo

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

Italy

(\*). Corresponding author, Tel. +39 0110905633; fax: +39 0110905614; e-mail address:

ezio.santagata@polito.it

### Abstract

This research work focused on high-temperature properties of bituminous binders nano-reinforced by means of organoclays. A commercial organophilic montmorillonite was used as a second component to nano-reinforce a reference neat bitumen, and as a third component in a polymer-modified binder which was derived from the combination of the reference neat bitumen and a polyisoprene-based additive. Several mixing protocols were followed for blend preparation.

Rheological behaviour of the binders was investigated by means of oscillatory and creep-recovery tests carried out with a dynamic shear rheometer. Results indicate that final properties of binders nano-reinforced with layered silicates are strongly affected by the mixing protocol adopted for blend preparation as a result of the key role played by the morphological configuration that nano-particles assume within the bituminous matrix.

### Keywords

A. Bitumen; A. Nano-structures; B. High-temperature properties; D. Mechanical testing

### 1. Introduction

Nanotechnology involves the fine-tuning of systems at the atomic and molecular scale. In recent decades this new technology has aroused interest across a wide array of disciplines, ranging from basic sciences such as biology, chemistry and physics, to their corresponding engineering applications [1]. In the area of materials engineering, noteworthy advantages in terms of both

1 mechanical properties and durability have been attained by using nano-sized particles in  
2 polymeric matrices [2,3]. These outcomes have attracted the attention of paving technologists  
3 with regard to the creation of bituminous-based nanocomposites capable of yielding novel  
4 scenarios in the overall performance of flexible pavements. Among the nano-sized products that  
5 have been taken into account as binder reinforcing agents, layered silicates have been in the  
6 forefront of recent and ongoing scientific research [4-14].

7 Layered silicates consist of a series of thin platelets, usually bound by counter-ions, where the  
8 building blocks of each platelet are made of tetrahedral and octahedral sheets fused together in  
9 different crystallographic configurations. One of the most common layered silicates used for the  
10 synthesis of nanocomposites is montmorillonite clay. This type of clay is a naturally occurring  
11 2:1 phyllosilicate characterised by a central alumina octahedron sandwiched between two  
12 external silica tetrahedra, where the trivalent aluminium cations of the octahedral sheets are  
13 partially substituted by divalent magnesium cations. The overall negative charge resulting from  
14 this isomorphous substitution is balanced by exchangeable cations lying on the layers' surfaces.  
15 Therefore, when montmorillonite clays are used as reinforcements in composite materials, the  
16 presence of these exchangeable cations can promote the expansion of interlayers by means of  
17 diffusive phenomena, with the consequent establishment of nanoscale interactions between  
18 silicate platelets and surrounding environment [15]. On the basis of the degree of diffusion, a  
19 nanocomposite can assume different morphological configurations. Intercalated structures  
20 occur when the penetration of molecules produces an expansion of galleries, but silicate  
21 platelets still retain a well-defined spacing. Exfoliated structures result from a complete  
22 separation and random distribution of the clay sheets within the dispersing medium. Moreover,  
23 several hybrid configurations can occur as mixed intercalated-exfoliated morphologies [16].

24 Despite the remarkable expansion potential of montmorillonite clay, it should be emphasised  
25 that simple mixing of these silicate particles with organic matrices does not necessarily lead to  
26 formation of a nanocomposite material. Indeed, occurrence of nano-scale interactions depends  
27 on chemical composition and processing protocol [17].

28 With regard to the chemical compatibility between base components, it is recognised that the  
29 organic modification of hydrophilic clays into organoclays represents a fundamental prerequisite  
30

1 to promote interactions at bitumen-clay interfaces [18]. In fact, replacement of the inorganic  
2 exchange cations which lie in the clay galleries with alkylammonium surfactants provides the  
3 twofold advantage of changing the polarity of clay surfaces and expanding clay galleries. On the  
4  
5 other hand, addition of layered silicates as a third component in polymer-modified binders can  
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7 significantly alter the overall equilibrium between bitumen and polymer, thus leading to several  
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9 morphological arrangements of the silicate platelets within the complex organic matrix [19,20].  
10  
11 When considering the technique adopted for producing bituminous-based nanocomposites, it  
12  
13 has been found that both mixing technique and homogenisation energy have non-negligible  
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15 effects on the final internal structure assumed by the composite material and, therefore, on its  
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17 rheological behaviour [11,21].  
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20  
21 This research work aims to increase the knowledge about the potential use of layered silicates  
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23 in the production of bituminous-based nanocomposites with improved high-temperature  
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25 properties. Organophilic montmorillonite was employed as a second component in binary  
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27 bitumen/clay blends, and as a third component in ternary bitumen/polymer/clay blends.  
28  
29 Rheological behaviour of the binders was investigated by means of both oscillatory and creep-  
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31 recovery tests carried out with a dynamic shear rheometer. Results obtained from the  
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33 experimental investigation were specifically analysed in order to highlight the effect of  
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35 preparation protocol on final properties of such innovative materials.  
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## 40 **2. Experimental investigation**

### 41 **2.1 Base materials**

42  
43 Nano-reinforced bituminous blends considered in this research study were prepared by making  
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45 use of a single neat 70/100 penetration grade bitumen (B), characterised by a softening point of  
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47 45.2°C (EN 1427-07) and a penetration at 25°C of 98 dmm (EN 1426-07). Bitumen B was  
48  
49 subjected to preliminary characterisation including chemical analysis and rheological tests.  
50

51  
52 Chemical analysis was performed to attain an overall description in terms of saturates,  
53  
54 aromatics, resins and asphaltenes contents. The four fractions were separated via thin layer  
55  
56 chromatography and the corresponding relative amounts were quantitatively assessed by using  
57  
58 a flame ionization detector. Results obtained from analysis are shown in Figure 1. Rheological  
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1 measurements were carried out in order to determine temperatures which yielded rheological  
2 parameters equal to threshold values indicated in AASHTO M 320-10. Obtained results,  
3 reported in Table 1, showed that the Performance Grade (PG) of bitumen B is PG58-22.  
4  
5 Two different commercial products were employed to modify the base bitumen, a polymeric  
6 material (P) and a nanoclay (C). The polymeric material was a natural CIS 1.4 polyisoprene in  
7 aqueous dispersion, containing ammonium hydroxide (NH<sub>4</sub>OH) as a preserving agent. The  
8 nanoclay was a natural montmorillonite modified with a quaternary ammonium salt used to  
9 provide an organophilic character to the hydrophilic clay. The ammonium salt that was  
10 employed as a surfactant agent consisted of two methyl groups and two alkyl chains bonded to  
11 a positively charged nitrogen. Main characteristics of the two products, based on manufacturers'  
12 technical specifications, are provided in Tables 2 and 3.  
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## 25 **2.2 Blend preparation**

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27 By combining the base materials mentioned above, several binary bitumen/clay (BC) and  
28 ternary bitumen/polymer/clay (BPC) blends were produced in the laboratory. Their rheological  
29 characteristics were compared to those of neat bitumen (B) and of a reference polymer-  
30 modified binder (BP) derived from it by employing the selected polymeric additive (P). Thus,  
31 effects produced by incorporation of nanoclay were assessed both in the absence and presence  
32 of an underlying polymeric structure. Moreover, by including several mixing protocols in the  
33 experimental plan, the influence of blend preparation technique was also highlighted.  
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41 Binary BC blends were prepared by adopting a fixed nanoclay dosage, selected as 6% by  
42 weight of neat bitumen on account of encouraging outcomes obtained in previous studies  
43 [11,22]. Three different mixing protocols were followed: one based on shear mixing only (BCs0)  
44 and the other two based on the combination of shear mixing and sonication (BCs1 and BCs2).  
45  
46 The shear mixing procedure begins with the addition of nanoclay powder to base bitumen,  
47 which is preheated at a temperature of 150°C in order to reach a sufficiently fluid state. This  
48 preliminary step is performed while the binder is homogenised by means of a mechanical stirrer  
49 operating at low speed (500 rpm). Once the nano-additive is completely incorporated into  
50 bitumen, mixing speed is raised to 1550 rpm and kept constant for 90 minutes.  
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1 The mechanical stirrer employed in this investigation (Heidolph, RZR 2041) is equipped with a  
2 special handmade disintegrating head consisting of a ringed propeller-type impeller with shaft,  
3 coupled with a fixed perforated plate. With such a device axial flow is induced through the plate  
4 holes, with consequent high shear forces that promote particle dispersion.  
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9 In BCs1 and BCs2 protocols, after shear mixing, blends are subjected to the action of an  
10 ultrasonic homogeniser (UP200S, Hielscher GmbH) operated at a frequency of 24 kHz.  
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12 Continuous ultrasonic waves are transmitted throughout the volume of the binder by means of  
13 an immersed titanium sonotrode of 7 mm diameter. Ultrasounds are applied for a total time of  
14 30 minutes at two different wave amplitudes, fixed at 88  $\mu\text{m}$  and 158  $\mu\text{m}$  for protocols BCs1 and  
15 BCs2, respectively. These two values correspond to 50% and 90% of the maximum amplitude  
16 of the equipment. Also during this second stage of blend preparation, temperature was kept  
17 constant at 150°C by means of a heating plate and checked by making use of a temperature  
18 probe immersed in the sample.  
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27 Ternary BPC blends were prepared by adopting single percentages, by weight of base bitumen,  
28 of each additive. These dosages were fixed at 4% in the case of the polymeric additive (P) and  
29 at 2% in the case of the silicate additive (C). Two different ternary blends, labelled in the study  
30 as BPCa and BPCb, were produced according to two distinct protocols (protocol a and protocol  
31 b). Protocol a, that was followed to produce the BPCa blend, involved modification of the neat  
32 bitumen with both the polymer and the nanoclay, that were added separately. Protocol b, that  
33 was used to produce the BPCb blend, consisted in the modification of bitumen with a premixed  
34 nanoclay-reinforced polymeric additive.  
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44 In the case of protocol a, both the polymeric additive and the nanoclay are incorporated into the  
45 molten bitumen at a temperature of 180°C under the action of the abovementioned mechanical  
46 stirrer operating at low speed (500 rpm). Mixing temperature was selected in order to ensure full  
47 dispersion of the polymeric additive, which at lower temperatures led to the creation of a  
48 non-homogeneous binder. In the case of protocol b, nanoclay is preliminary added to the liquid  
49 polymeric emulsion, thus generating a solid composite material. This premixed master batch is  
50 then manually granulated and incorporated into bitumen with the aid of the mechanical stirrer  
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1 operating in the same temperature and speed conditions adopted in protocol a (180°C, 500  
2 rpm).  
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4 After incorporation of the additives into neat bitumen, according to both protocols blends are  
5 subjected to high-shear mixing and sonication. High-shear mixing is generated by the stirrer  
6 operating at a speed of 1550 rpm for 120 minutes at a temperature of 180°C. Ultrasound energy  
7 is provided by subjecting blends to waves with an amplitude of 158  $\mu\text{m}$  for 30 minutes at a  
8 temperature of 150°C. Such a temperature, lower than that adopted for mixing, was selected in  
9 order to reduce possible ageing effects during the additional sonication phase.  
10

11 In an attempt to isolate the rheological peculiarities of the ternary blends which can be ascribed  
12 to the presence of nanoclay, a reference polymer-modified bitumen (BP) was also produced by  
13 adopting the same polymer dosage (4%) and the same shear mixing and sonication procedures  
14 used for the preparation of both the BPCa and BPCb blends.  
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16 All binders considered in the present work are listed in Table 4, where their identification codes  
17 are defined as a function of additive type, dosage and mixing parameters.  
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### 19 **2.3 Testing program**

20 Rheological analysis of all blends was performed with the specific goal of evaluating their anti-  
21 rutting properties at high in-service temperatures. Two different approaches were followed,  
22 based on Oscillatory Shear Loading (OSL) and Multiple Stress Creep-Recovery (MSCR) tests  
23 carried out by employing a dynamic shear rheometer (Physica MCR 302 from Anton Paar Inc.)  
24 equipped with 25-mm parallel plates set with 1-mm gap. OSL tests were performed according to  
25 AASHTO T 315-12 on both unaged and short-term aged materials, at a frequency of 10 rad/s in  
26 the linear viscoelastic range. Short-term ageing was simulated in the laboratory by means of the  
27 Rolling Thin Film Oven (RTFO) test according to AASHTO T 240-13. MSCR tests were carried  
28 out according to AASHTO TP 70-10 on short-term aged blends only, by adopting two stress  
29 levels, equal to 0.1 and 3.2 kPa.  
30

31 Both the OSL and MSCR tests were carried out at several temperatures (with 6°C increments  
32 between each measurement step) over a temperature range comprised between 58 and 76°C  
33 for base bitumen (B) and binary BC blends (BCs0, BCs1, BCs2), and over a temperature range  
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1 comprised between 58 and 82°C for the reference polymer-modified bitumen (BP) and ternary  
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3 BPC blends (BPCa, BPCb).

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5 A minimum of two replicates were run for each test verifying that results were within acceptable  
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7 limits and average data were used in the following analysis.  
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### 10 **3. Results and discussion**

#### 11 **3.1 Binary BC blends**

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13 SHRP rutting parameter  $|G^*|/\sin\delta$  was determined from norm ( $|G^*|$ ) and phase angle ( $\delta$ ) values  
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15 of the complex modulus gathered during OSL tests. This parameter, that derives directly from  
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17 the definition of loss compliance, is associated to the part of non-recoverable deformation which  
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19 can be attributed to the binder phase of bituminous mixtures [23]. Figure 2 illustrates the data  
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21 obtained for neat bitumen and bitumen/clay blends in both unaged and short-term aged  
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23 conditions. It can be stated that, in agreement with the outcomes of previous studies, the  
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25 presence of the nano-additive always produced an increase of  $|G^*|/\sin\delta$ , which suggests an  
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27 improvement of rutting resistance [9,11,22,24,25]. In addition, degree of enhancement  
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29 appeared to be strongly dependent on the protocol followed for blend preparation and on ageing  
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31 conditions. Moreover, it was observed that relative improvements in expected performance do  
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33 not depend upon test temperature.  
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38 On the whole, by increasing mixing effort, higher values of the rutting parameter were always  
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40 attained. In the case of unaged materials, this was proven by a relative increment of  $|G^*|/\sin\delta$  of  
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42 around 60% for blends prepared by means of shear mixing only, and by increments of around  
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44 200% and 250% for blends treated with ultrasounds at the lower and higher amplitude,  
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46 respectively. After short-term ageing, binary blends showed improvements with respect to the  
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48 neat aged bitumen that were almost halved in comparison to those recorded for the  
49  
50 corresponding unaged binders. This finding indicates that the reinforcement action provided by  
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52 the nano-additive actually interfered with phenomena which typically occur during chemical  
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54 ageing as a result of the barrier properties of layered silicates. In fact, when gas-impermeable  
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56 platelets are randomly dispersed in the matrix, the permeating oxygen molecules are forced to  
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58 diffuse throughout the bulk by following more complex paths. Secondly, the geometrical  
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1 constraint dictated by the presence of clay sheets also hampers the loss of volatile components  
2 of bitumen [15]. Hence, this twofold anti-ageing action induced by silicate nano-particles actually  
3 minimises the component of anti-rutting that is ascribable to irreversible molecular changes  
4 which stem from oxidation and polymerization reactions and from the evaporation of lighter  
5 compounds.  
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10 Experimental results retrieved from MSCR tests performed on the RTFO-aged binders were  
11 processed in order to obtain information about the rheological response of the materials in  
12 terms of non-recoverable compliance and elasticity.  
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15 Values of non-recoverable creep compliance ( $J_{nr}$ ) determined at 0.1 and 3.2 kPa are presented  
16 in Figure 3. In line with observations drawn from OSL tests, the presence of silicate platelets  
17 always led to an enhancement of the resistance to permanent deformation, highlighted by a  
18 noticeable reduction of the  $J_{nr}$  parameter. Regardless of temperature and stress level, the non-  
19 recoverable creep component of damage decreased, with respect to neat bitumen, by about  
20 30% when nano-particles were homogenised by means of shear mixing only. Major changes in  
21 the rheological response were observed for blends prepared with sonication, which induced  
22 abatements of  $J_{nr}$  of around 55% and 65% for materials subjected to ultrasounds with lower  
23 and higher wave amplitude, respectively. In view of these results, it is clear that a more efficient  
24 reinforcement action against permanent deformation was achieved by increasing the energy  
25 input for homogenisation, with a definite improvement yielded by sonication. Such evidence can  
26 be associated with the change in the load transfer capacity that is probably triggered by de-  
27 agglomeration of clusters and intercalation of bitumen molecules between clay galleries [26-28].  
28

29  
30 Elastic properties of the blends were assessed by computing percent strain recovery (R) at the  
31 two stress levels adopted for creep loading (0.1 and 3.2 kPa). Corresponding results are  
32 summarised in Figure 4, where the effect of nanoclay modification can be evaluated at various  
33 temperatures by comparing the response of the blends obtained from different mixing protocols.  
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35  
36 In general, the R parameter was found to be more sensitive to test conditions and material  
37 features, hence allowing a more accurate discrimination among the anti-rutting performance of  
38 such innovative materials. In contrast with previous observations on the SHRP rutting  
39 parameter and the non-recoverable creep compliance, in this case the degree of enhancement  
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1 provided by nano-modification was strongly influenced by test temperature. At the lower  
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3 temperature, enhancements attributable to the presence of the nano-additive were in line with  
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5 those obtained from the analyses carried out with respect to the SHRP rutting parameter and to  
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7 non-recoverable creep compliance. However, at the higher test temperatures elastic  
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9 peculiarities of each blend were clearly revealed at both stress levels considered in the  
10  
11 experimental plan. This can be appreciated by considering the relative improvements in the  
12  
13 modified blends with respect to neat bitumen, that may change significantly as a function of  
14  
15 adopted preparation protocol. In particular, they increased by even one order of magnitude  
16  
17 when adding the sonication phase to initial shear mixing. Since the analysis of the response  
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19 under repeated loading in terms of strain recovery can be a useful tool to assess the ability of  
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21 modification agents to effectively interact with the bituminous matrix, these findings confirm the  
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23 beneficial effect of vibration energy for the preparation of nano-reinforced bituminous blends. In  
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25 fact, ultrasounds allow interactions to take place along the huge surface areas that are  
26  
27 potentially available between nano-platelets and bitumen, thus increasing the capability of these  
28  
29 composite materials to recover deformations induced by external loadings.  
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### 31 32 33 **3.2 Ternary BPC blends**

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35 Experimental results obtained for ternary blends in terms of the SHRP rutting parameter are  
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37 displayed in Figure 5, where bitumen/polymer/clay composites obtained by following the two  
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39 different preparation protocols (a and b) are compared with the reference polymer-modified  
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41 bitumen (BP). Both ternary blends exhibited better anti-rutting performance when compared  
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43 with the reference material for all temperatures and ageing conditions investigated.  
44  
45 Nevertheless, the extent of improvement ascribable to silicate platelets was drastically  
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47 increased when nanoclay was used as a modification agent of the polymeric phase (protocol b).  
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49 This was proven by relative increments of the rutting parameter with respect to the reference  
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51 material that were around 75% and 65% for the BPCb blend and around 20% and 10% for the  
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53 BPCa blend in unaged and RTFO-aged conditions, respectively. As expected, also in the case  
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55 of ternary blends, the layered structure of nanoclay showed non-negligible barrier properties. In  
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57 fact, while enhancement of the rutting parameter attributable to ageing was around 70% for the  
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1 reference polymer-modified bitumen, this value was lowered to around 55% for both the BPCa  
2 and BPCb materials. By combining information regarding the effects caused by the presence of  
3 the nano-additive with those regarding ageing, it can be stated that the enhancement in  
4 stiffness and elasticity observed in the aged BPCb blend was mainly caused by the structural  
5 effect provided by nanoclay rather than by the chemical ageing of the bituminous phase. In  
6 contrast, in the case of the aged BPCa blend, the component ascribable to chemical ageing  
7 prevailed with respect to that related to nano-modification. Since phenomena involved in  
8 chemical ageing are known as possible causes of premature crack-related distresses [29], it is  
9 believed that the enhancement of high-temperature properties by means of the nano-  
10 reinforcement action yielded by clay platelets, combined with the reduction of ageing sensitivity,  
11 can lead to an overall improvement of field performance.

12 Jnr values obtained from MSCR testing are presented in Figure 6 for different loading and  
13 temperature conditions. From the comparison of outcomes obtained at 0.1 and 3.2 kPa it is  
14 evident that nanoclays were more effective against non recoverable deformations when the  
15 higher value of shear stress was adopted. In the case of the BPCa blend, at 0.1 kPa marginal  
16 variations in Jnr values were caused by the presence of nano-particles, whereas at 3.2 kPa  
17 average abatements of around 30% were recorded. When considering the BPCb blend, the  
18 drop in non-recoverable creep compliance was found to be around 45% at 0.1 kPa and around  
19 60% at 3.2 kPa. Hence, if the effect of the mixing sequence is taken into account, results clearly  
20 show that lower values of non-recoverable deformation were obtained by modifying the base  
21 bitumen via a premixed master batch. It can be hypothesised that in the case of the BPCa  
22 blend, multiple isolated sites of both silicate and polymer contributed separately in the  
23 mechanical response of the binder. On the other hand, in the case of the BPCb blend the  
24 effects of modification seem to be mainly governed by an integrated system composed of  
25 rubbery molecular chains of polyisoprene cross-linked by hard clay domains. Similar  
26 conclusions were drawn by other Authors who focused on ternary bituminous blends produced  
27 by employing organo-montmorillonite clay in combination with either SBS (styrene-butadiene-  
28 styrene) or EVA (ethylene-co-vinyl-acetate) polymers [19-21].

1 Further information about the rheological behaviour of ternary bitumen/polymer/clay blends can  
2 be obtained from percent strain recovery (R) values coming from MSCR testing. Coherently with  
3 results collected for the Jnr parameter, inspection of Figure 7 indicates that in more severe  
4 loading conditions the elastic contribution provided by nanoclay was significantly higher, thus  
5 supporting the idea that in the case of ternary blends high stress levels were necessary in order  
6 to fully activate the reinforcement action of modification. At 0.1 kPa a noticeable enhancement  
7 in the R value was never recorded, regardless of the protocol adopted for blend preparation.  
8 Moreover, a clear tendency to a worsening of elastic behaviour by increasing test temperature  
9 was highlighted for both ternary blends when compared to the reference polymer-modified  
10 bitumen. At 3.2 kPa the BPCa blend showed almost no performance improvement with respect  
11 to BP. This outcome seems to suggest that neither the swelling phenomena occurring between  
12 bitumen and polymer, nor intercalation mechanisms which take place between bitumen and  
13 silicate platelets, were effective, on their own, to fully exploit the potential of the combined use  
14 of polymer modification and nano-reinforcement. On the other hand, the BPCb blend showed  
15 major improvements in elasticity, with relative increments caused by the presence of clay  
16 platelets that were more and more evident at increasing test temperatures. Hence, it can be  
17 hypothesised that the use of a premixed master batch allows a more continuous and  
18 homogeneous modifying phase to be active throughout the volume of the material, thus  
19 promoting the formation of a three-dimensional reinforcing network capable of substantially  
20 altering the overall elastic response of the plain bituminous matrix.  
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#### 43 **4. Conclusions**

44 Results presented in this paper indicate that bituminous-based nanocomposites with improved  
45 high-temperature properties can be obtained by employing organophilic clays as reinforcing  
46 agents, both in neat and in polymer-modified binders. However, the effectiveness of these  
47 silicate particles was found to be strongly dependent on the mixing protocol adopted for blend  
48 preparation, as a result of the crucial role played by the morphological arrangement of nano-  
49 platelets within the composite material.  
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1 In the case of binary bitumen/clay blends, it was observed that the effects caused by the silicate  
2 additive are extremely sensitive to variations of the energy employed for homogenisation. In this  
3 regard, the use of ultrasounds seems to be necessary in order to fully exploit its potential nano-  
4 scale reinforcement effect. When the organoclay was used as a third component in polymer-  
5 modified binders, rheological behaviour of the ternary blends was found to be significantly  
6 affected by mixing sequence. Use of nanoclay as a modification agent of the polymeric phase  
7 appears to promote the formation of a three-dimensional reinforcing network in the bituminous  
8 matrix, which is able to provide superior high-temperature properties to the neat binder.  
9 Further research will be performed in order to validate the conclusions of this preliminary  
10 investigation by considering a wider array of base materials and mixing protocols. Moreover,  
11 efforts will be made in order to assess the technical and economical feasibility of transferring the  
12 identified mixing protocols from the laboratory to the industrial production level.  
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28  
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### 37 **References**

- 38 1. Ramsden JJ. Nanotechnology: an introduction. Elsevier, Waltham, 2011.
- 39 2. Paul DR and Robeson LM. Polymer nanotechnology: nanocomposites. *Polymer* 2008;  
40 49(15):3187-3204.
- 41 3. Pinnavaia TJ and Beall GW Polymer-Clay. Nanocomposites. Wiley series in polymer science.  
42 Wiley, Chichester; 2000.
- 43 4. Yang J and Tighe S. A review of advances of Nanotechnology in asphalt mixtures, 13th  
44 COTA International Conference of Transportation Professionals (CICTP 2013), Procedia -  
45 Social and Behavioral Sciences 2013; 96:1269–1276.  
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- 1 5. Liu G, Wu S, Van de Ven MFC, Molenaar AAA., Besamusca J. Modification of bitumen with  
2 organic montmorillonite nanoclay. Third International Conference on Advances and trends in  
3 Engineering Materials and their Applications; 2009.
- 4  
5  
6  
7 6. Liu G, Wu S, van de Ven M, Yu J., Molenaar A. Influence of sodium and organo-  
8 montmorillonites on the properties of bitumen. Applied Clay Science 2010; 49(1-2):69-73.
- 9  
10 7. Liu G, Van De Ven M, Wu S, Yu J, Molenaar A. Influence of organo-montmorillonites on  
11 fatigue properties of bitumen and mortar. International Journal of Fatigue 2011; 33(12):1574-  
12 1582.
- 13  
14  
15  
16  
17 8. Zhang H, Shi C, Han J, Yu J. Effect of organic layered silicates on flame retardancy and  
18 aging properties of bitumen. Construction and Building Materials 2013; 40:1151–1155.
- 19  
20  
21 9. Zare-Shahabadi A, Shokuhfar A, Ebrahimi-Nejad S. Preparation and rheological  
22 characterization of asphalt binders reinforced with layered silicate nanoparticles.  
23 Construction and Building Materials 2010; 24:1239–1244.
- 24  
25  
26  
27 10. Santagata E, Baglieri O, Tsantilis L, Chiappinelli G. Fatigue and healing properties of nano-  
28 reinforced bituminous binders. International Journal of Fatigue 2015; 80:30-39.
- 29  
30  
31 11. Santagata E, Baglieri O, Tsantilis L, Chiappinelli G, Brignone Aimonetto I. Effect of  
32 sonication on high temperature properties of bituminous binders reinforced with nano-  
33 additives. Construction and Building Materials 2015; 75:395-403.
- 34  
35  
36  
37 12. Santagata E, Baglieri O, Tsantilis L, Chiappinelli G. Storage stability of bituminous binders  
38 reinforced with nano-additives. 8th RILEM International Symposium on Testing and  
39 Characterization on Sustainable and Innovative Bituminous Materials. Rilem Bookseries  
40 vol.11, Springer Netherlands; 2016.
- 41  
42  
43  
44  
45 13. Santagata E, Baglieri O, Tsantilis L, Chiappinelli G. Fatigue and healing properties of  
46 bituminous mastics reinforced with nano-sized additives. Mechanics of Time-Dependent  
47 Materials 2016, Special Issue on Time-Dependent Behaviour of Bituminous Materials: In  
48 Press.
- 49  
50  
51  
52  
53 14. Ortega FJ, Navarro FJ, Garcia-Morales M, McNelly T. Thermo-mechanical behaviour and  
54 structure of novel bitumen/nanoclay/MDI composites. Composites Part B 2015; 76: 192-200.
- 55  
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- 1 15. Pavlidou S and Paspaspyrides CD. A review on polymer-layered silicate nanocomposites.  
2  
3 Progress in Polymer Science 2008; 33:1119-1198.  
4
- 5 16. Le Baron PC, Wang Z, Pinnavaia TJ. Polymer-layered silicate nanocomposites: an  
6  
7 overview. Appl. Clay Science 1999; 15:11-29.  
8
- 9 17. Ray SS and Okamoto M. Polymer/layered silicate nanocomposites: a review from  
10  
11 preparation to processing. Progress in Polymer Science 2003; 28:1539-1641.  
12
- 13 18. Ghaffarpour Jahromi S and Khodaii A. Effects of nanoclay on rheological properties of  
14  
15 bitumen binder. Construction and Building Materials 2009; 23:2894-2904.  
16
- 17 19. Polacco G, Kříž P, Filippi S, Stastna J, Biondi , Zanzotto L. Rheological properties of  
18  
19 asphalt/SBS/clay blends. European Polymer Journal 2008; 44(11):3512-3521.  
20
- 21 20. Sureshkumar MS, Filippi S, Polacco G, Kazatchkov I, Stastna J, Zanzotto L. Internal  
22  
23 structure and linear viscoelastic properties of EVA/asphalt nanocomposites. European  
24  
25 Polymer Journal 2010 46:621–633.  
26
- 27 21. Merusi F, Giuliani F, Polacco G. Linear viscoelastic behavior of asphalt modified with  
28  
29 polymer/clay nanocomposites. Proceedings of the 5<sup>th</sup> International SIIV Congress 2012.  
30
- 31 22. Santagata E, Baglieri O, Tsantilis L, Chiappinelli G. Effects of nano-sized additives on the  
32  
33 high-temperature properties of bituminous binders: a comparative study. International RILEM  
34  
35 Symposium on Multi-Scale Modeling and Characterization of Infrastructure Materials,  
36  
37 Stockholm, 2013 pp 297-309.  
38
- 39 23. Kennedy TW, Huber GA, Harrigan ET, Cominsky RJ, Hughes CS, Von Quintus H, et al.  
40  
41 Superior performing asphalt pavements (SUPERPAVE): the product of the SHRP asphalt  
42  
43 research program. Washington, DC: Strategic Highway Research Program, National  
44  
45 Research Council;1994.  
46
- 47 24. Yu J, Zeng X, Wu S, Wang L, Liu G. Preparation and properties of montmorillonite modified  
48  
49 asphalts. Materials Science and Engineering A - Structural Materials Properties  
50  
51 Microstructure and Processing 2007; 447(1-2):233-238.  
52
- 53 25. Ghaffarpour Jahromi S, Ahmadi NA, Mortazavi SM, Vossough S. Rutting and fatigue  
54  
55 behavior of nanoclay modified bitumen. Iranian Journal of Science and Technology,  
56  
57 Transaction B: Engineering 2011; 35(C2):277-281.  
58  
59  
60  
61  
62  
63  
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65

- 1 26. Planellas M, Sacristán M, Rey L, Olmo C, Aymamí J, Casas MT, del Valle LJ, Franco L,  
2  
3 Puigallí J. Micro-molding with ultrasonic vibration energy: New method to disperse  
4  
5 nanoclays in polymer matrices. *Ultrasonics Sonochemistry* 2014; 21:1557-1569.  
6  
7 27. Lam C, K Lau K, Cheung H, Ling H. Effect of ultrasound sonication in nanoclay clusters of  
8  
9 nanoclay/epoxy composites. *Materials Letters* 2005; 59:1369-1372.  
10  
11 28. Isik I, Yilmazer U, Bayram G. Impact modified epoxy/montmorillonite nanocomposites:  
12  
13 synthesis and characterization. *Polymer* 2003; 44:6371-6377.  
14  
15 29. Robertson RE. Chemical properties of asphalts and their relationship to pavement  
16  
17 performance. SHRP-A/UWP-91-510. Strategic Highway Research Program (SHRP),  
18  
19 National Research Council. Washington, DC; 1991.  
20

21 Table 1. Rheological characterisation of base bitumen  
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Ageing condition	PG parameter	Measured value
Original	T=135°C	$\eta=0.375$ Pa·s
	$ G^* /\sin\delta = 1$ kPa	T=63.2°C
RTFO	$ G^* /\sin\delta = 2.2$ kPa	T=64.0°C
	$ G^*  \cdot \sin\delta = 5000$ kPa	T=19.9°C
PAV	m = 0.300	T=-19.6°C
	S = 300 MPa	T=-17.6°C
Performance Grade	PG58-22	

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32 RTFO: Rolling Thin Film Oven (short-term ageing); PAV: Pressure Ageing Vessel (long-term  
33 ageing);

34  $\eta$ : dynamic viscosity (Brookfield viscometer); T: test temperature;  $|G^*|$  and  $\delta$ : norm and phase  
35 angle of the complex modulus (Dynamic Shear Rheometer); m and S: creep rate and creep  
36 stiffness (Bending Beam Rheometer).  
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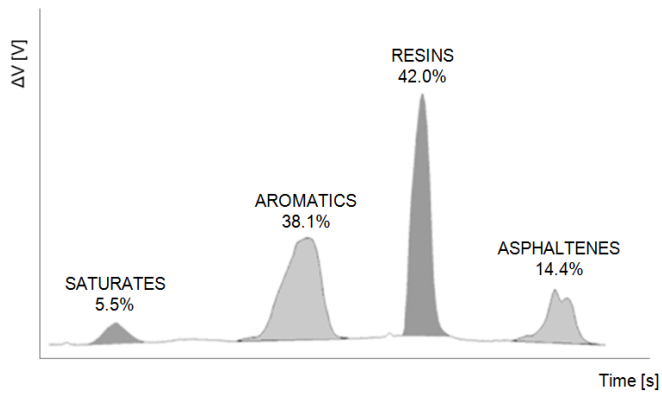


Figure 1. Chemical analysis of base bitumen (electrical potential difference  $\Delta V$  versus time)

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Table 2. Main properties of polymeric modifier

Latex content (%)	Ammonia content (%)	pH	Decomposition temperature [°C]	Density at 20°C [g/cm <sup>3</sup> ]
60	0.6-0.7	9.8-10.8	200	0.95

1 Table 3. Main properties of organoclay

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3 Surfactant	4 Anion	5 Basal spacing [nm]	6 Cation Exchange Capacity (CEC) [meq/100g]	7 Density [g/cm <sup>3</sup> ]
8 Dimethyl, dihydrogenated tallow, quaternary ammonium	9 Chloride	10 3.15	11 125	12 1.66

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1 Table 4. Binders considered in the study and corresponding blend preparation parameters

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Binder code	Dosage		Shear mixing parameters		Sonication parameters		
	C (%)	P (%)	Temperature [°C]	Time [min.]	Temperature [°C]	Time [min.]	Amplitude [μm]
B	0	0	-	-	-	-	-
BCs0	6	0	150	90	-	-	-
BCs1	6	0	150	90	150	30	88
BCs2	6	0	150	90	150	30	158
BP	0	4	180	120	150	30	158
BPCa	2	4	180	120	150	30	158
BPCb	2	4	180	120	150	30	158

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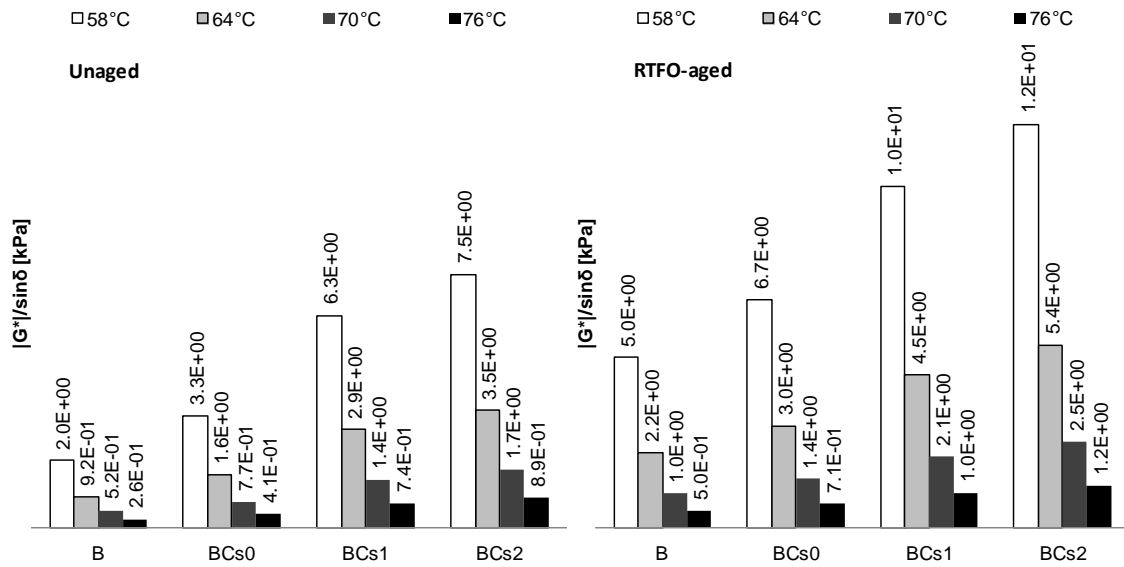


Figure 2. SHRP rutting parameter  $|G^*|/\sin\delta$  of neat bitumen (B) and binary blends (BC) in unaged and RTFO-aged conditions

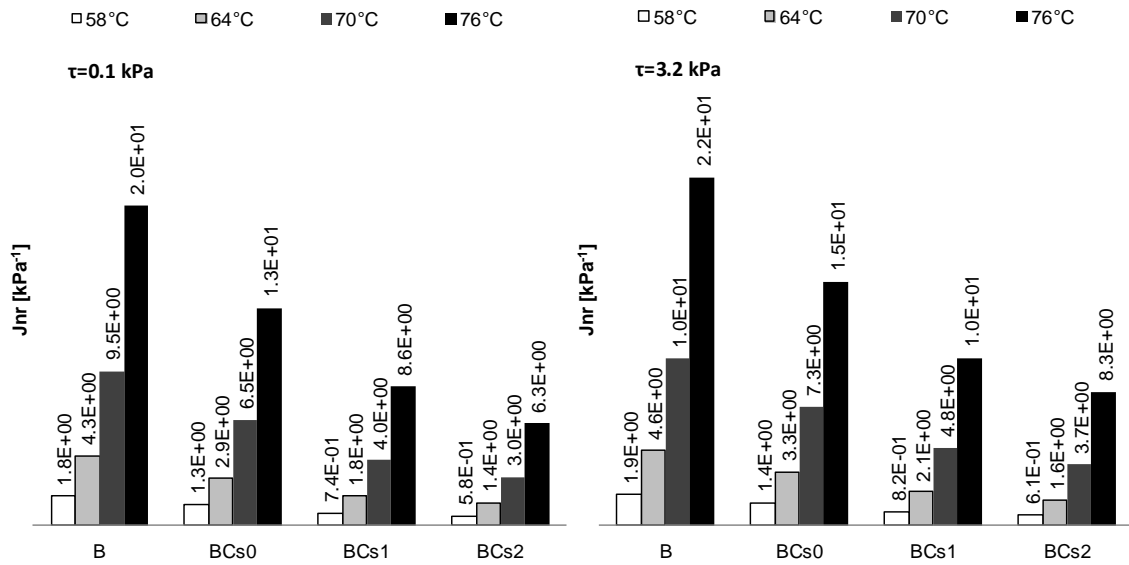


Figure 3. Non-recoverable creep compliance  $J_{nr}$  of neat bitumen (B) and binary blends (BC) at 0.1kPa and 3.2 kPa

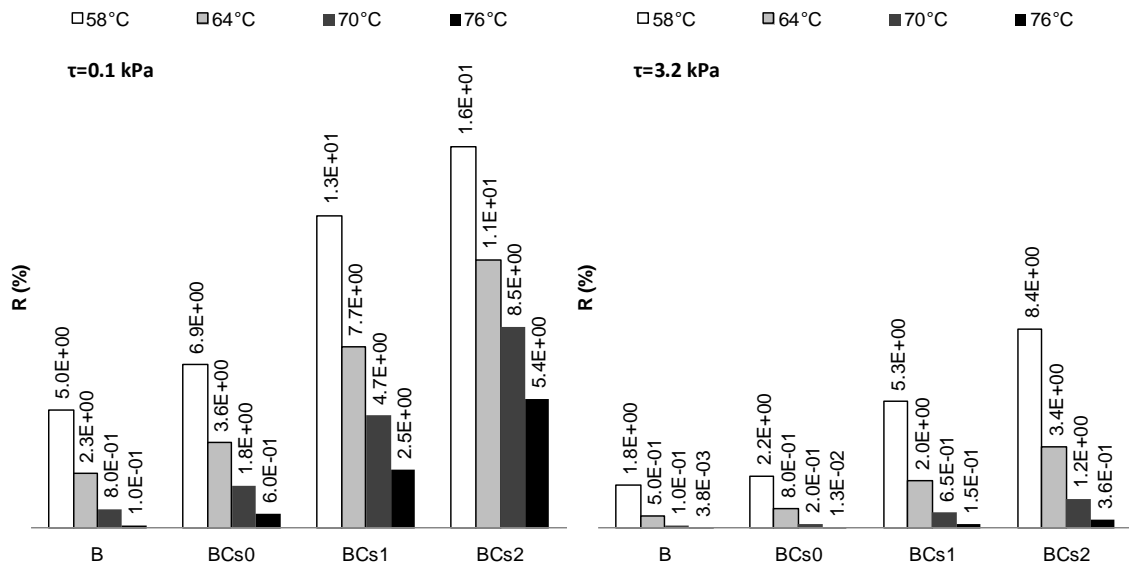


Figure 4. Percent strain recovery  $R$  of neat bitumen (B) and binary blends (BC) at 0.1 kPa and 3.2 kPa

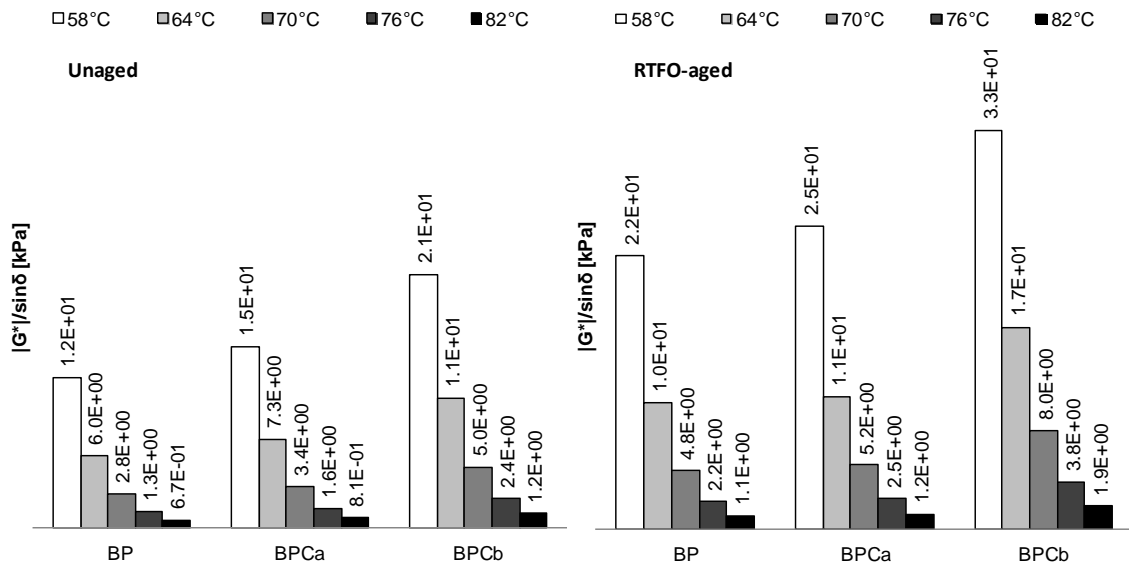


Figure 5. SHRP rutting parameter  $|G^*/\sin\delta$  of polymer-modified bitumen (BP) and ternary blends (BPC) in unaged and RTFO-aged conditions

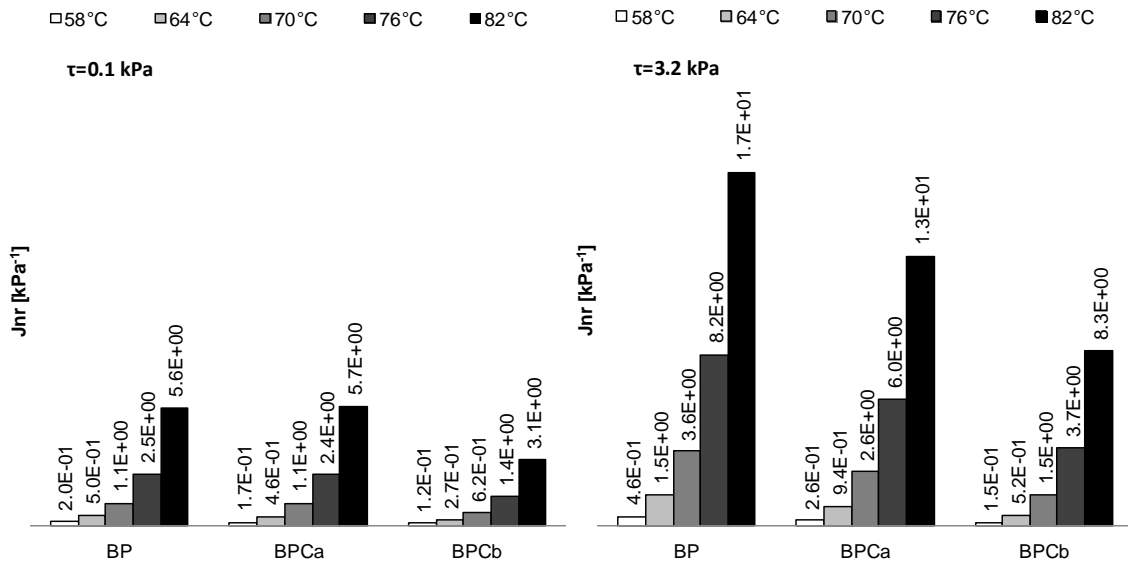


Figure 6. Non-recoverable creep compliance  $J_{nr}$  of polymer-modified bitumen (BP) and ternary blends (BPC) at 0.1 kPa and 3.2 kPa

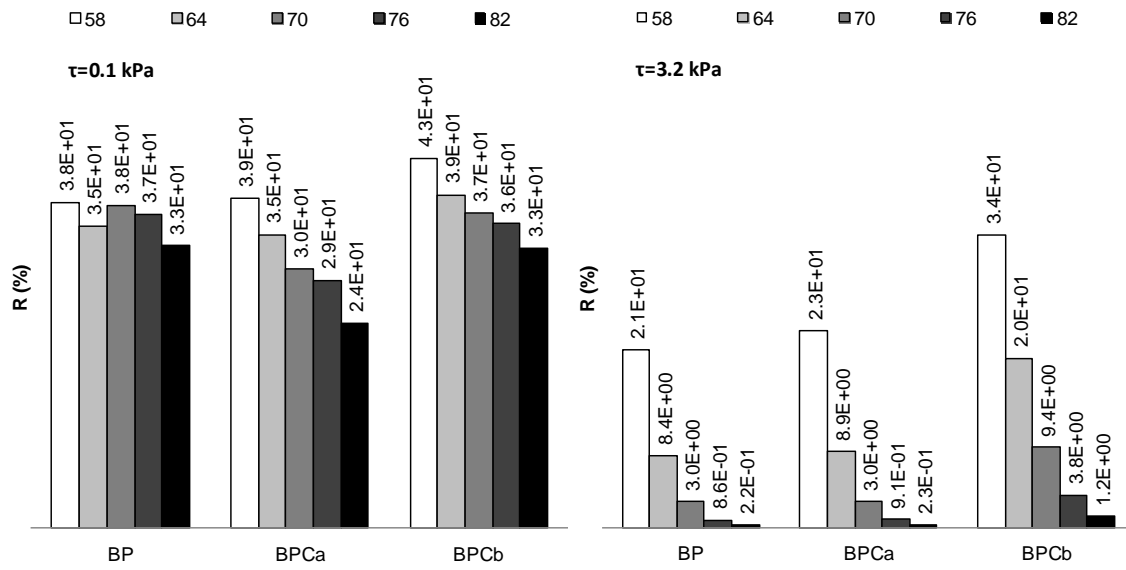


Figure 7. Percent strain recovery  $R$  of polymer-modified bitumen (BP) and ternary blends (BPC) at 0.1kPa and 3.2 kPa