EVALUATION OF RHEOLOGICAL BEHAVIOR AND PERFORMANCE TO
PERMANENT DEFORMATION OF NANOMODIFIED ASPHALT MIXTURES
WITH CARBON NANOTUBES (CNTs)

João Victor Staub de Melo¹; Glicério Trichês²

¹ Corresponding author: Professor of the Federal University of Santa Catarina, Department of Civil Engineering, Street João Pio Duarte Silva, nº 205, 88040-900, Florianópolis-SC, Brazil, Tel.: + 55 48 96631850, joao.victor@ufsc.br

² Professor of the Federal University of Santa Catarina, Department of Civil Engineering, Street João Pio Duarte Silva, nº 205, 88040-900, Florianópolis-SC, Brazil, Tel.: + 55 48 37217773, Brazil, glicerio.triches@ufsc.br
Abstract

Rutting is one of the most important issues associated with asphalt pavements. This defect leads to the accelerated degradation of the pavement and considerably reduces the level of road safety. This paper reports results obtained in the optimization of nanocomposites asphalt containing carbon nanotubes (CNTs) with regard to the resistance to permanent deformation. Nanocomposites asphalt were prepared with the addition of different proportions of CNTs. Based on a study on the empirical and rheological properties of the nanocomposites developed, optimization of the CNT content incorporated into the conventional asphalt binder was carry out. Then two asphalt mixtures were investigated, a reference mixture and a nanomodified mixture with CNTs (optimal content). The rheological evaluations were carry out on four-point fatigue equipment and the resistance to permanent deformation was tested in a traffic simulator (wheel tracking test). The results demonstrate the efficient contribution of the nanocomposite to the resistance to permanent deformation.

Keywords: Carbon Nanotubes; Nanocomposites Asphalt; Asphalt Mixtures; Rheological Behavior; Permanent Deformation.
1 INTRODUCTION

One of the structural defects most commonly encountered in asphalt pavements is permanent deformation. This can be defined as a depression in the wheel track with the possible occurrence of an elevation along the edges of this depression. Permanent deformation mainly originates from the instability of the asphalt concrete due to the excessive fluency of the mixture, aggravated by high temperatures, heavy traffic and the relief conditions (Ali 2006).

In this context, this phenomenon is one of the main problems in developing countries with a tropical climate, where an increase in the volume and aggressiveness of the traffic has been recorded and also better quality asphalt pavements and coatings are required (Melo and Trichês 2014).

This defect leads to the formation of an uneven pavement surface, increasing the irregularity, the discomfort to road users and in some cases a loss of drivability. On rainy days the accumulation of water in the wheel tracks can cause accidents due to the phenomenon of aquaplaning, which occurs when vehicles lose the tire/pavement adhesion required to maintain their stability.

The permanent deformation of an asphalt mixture can be considered as the simultaneous occurrence of viscous deformation of the asphalt binder and plastic deformation of the mineral structure of the asphalt mixture. From this perspective, both the aggregate and the asphalt binder play a role in the mechanical behavior of the asphalt mixture: the binder due to its consistency and rheology and the aggregate as a result of the internal friction forces between its particles (Joliet and Mallot 2000).

According to Hunter (2000), one way to ensure that the asphalt provides its contribution to the resistance to permanent deformation is the use of an asphalt binder which is not
only more rigid but also which behaves as an elastic solid in the pavement at high temperatures, minimizing the accumulation of deformation.

Based on this approach, the modification of asphalt binders can improve their performance and, consequently, that of the asphalt concrete mixtures. Several types of modifiers (elastomeric and plastomeric polymers, ground tire rubber, among others) have been employed as asphalt binders to improve the properties of asphalt concrete considering the main mechanisms of pavement degradation.

With regard to improving the properties of materials, a revolution has occurred in this field based on the use of nanomaterials as reinforcement in different matrixes. In this area, nanoscience offers great potential and new materials can be developed with properties superior to those of the existing ones. Nanocomposites are a new class of materials, in which at least one dimension of the dispersed particles lies within the nanometric scale (Ray et al. 2003).

Several types of nanoloads are currently being developed, for instance, metal oxide nanoparticles, carbon nanotubes and nanoclays. In the past two decades several authors (Santagata et al. 2012; You et al. 2011; Zare-Shahabadi et al. 2010; Leite et al. 2012; Jahromi and Khodaii 2009) have begun to study inorganic/organic nanocomposites, in particular nanocomposites of polymeric and asphalt matrices.

In this paper, the results of a study aimed at the development of nanocomposites asphalt containing carbon nanotubes (CNTs) with a high potential with regard to contributing to the resistance to permanent deformation of asphalt mixtures are reported.

2 MATERIALS AND METHODS

2.1 Materials
In this study the following materials were used: conventional asphalt binder (asphalt matrix) and carbon nanotubes (reinforcing load) for the preparation of nanocomposites asphalt, and aggregate minerals and hydrated lime for the production of the asphalt mixtures.

The base asphalt binder used in the study is classified according to the penetration as being within a range of 50-70 mm/10 and as PG 58-22 according to the Superpave classification. The carbon nanotubes are comprised of multiple layers with external diameter: 50-80 nm; internal diameter: 5-15 nm; length: 10-20 µm; specific surface area 60-80 m$^2$/g; and density: 2100 kg/m$^3$.

The aggregate mineral selected for the formulation of the asphalt mixtures is of basaltic origin and its properties are shown in Table 1.

The generation of the granulometric curve used in the formulation of asphalt mixtures adhered to the Superpave specification for a nominal maximum size of 19 mm, satisfying the criteria of control points and restricted zone (recommended). Based on the granulometric study of the aggregates the curve shown in Figure 1 was established. The granulometric curve is comprised of 43% coarse aggregate (19.1 mm), 15.5% fine aggregate (9.5 mm), 40% stone dust and 1.5% lime.

2.2 Methodology

In order to develop an optimized nanocomposite containing CNTs, with regard to its resistance to permanent deformation, asphalts with different contents of CNTs incorporated were produced. The definition of the optimum content of CNTs was based on an evaluation of the empirical and rheological properties of the nanocomposites produced in relation to the non-nanomodified (conventional) asphalt binder. After the
optimization of the nanocomposite containing CNTs the performance in relation to the permanent deformation of the asphalt mixtures produced with the optimized nanocomposite and with the conventional asphalt binder was evaluated.

2.2.1 Nanomodification of Conventional Asphalt Binder

The conventional asphalt binder was modified using a high shear mixer (Silverson model L5M-A). The nanomodification was carry out with asphalt binder at a temperature of 150 °C (rotational viscosity of 0.15 Pa.s), with a shear level of 5000 rpm and a mixing time of 100 min. Three nanocomposites asphalt were produced differentiated by the content of CNTs incorporated (1%, 2% and 3%, by weight of asphalt), having the following names: CNT-1%, CNT-2% and CNT-3%, respectively.

2.2.2 Optimization of Nanocomposite Containing CNTs

The definition of the optimum CNT content incorporated into the asphalt binder matrix was carry out through an evaluation of the properties of the nanocomposites produced. The traditional properties assessed were changes in the penetration (ASTM D 5), softening point (ASTM D 36) and penetration index (PI) (Pfeiffer and Van Doormaal). The rheological evaluation of virgin samples and short-term aged residues was conducted using a dynamic shear rheometer (DSR) applying the rolling thin-film oven test (RTFOT - ASTM D 2872). In these tests the complex shear modulus (|G*|) and the phase angle (δ) (ASTM D 7175) were determined at temperatures of 52 °C, 58 °C, 64 °C, 70 °C and 76 °C. The optimization of the nanocomposites containing CNTs was carry out based on an evaluation of the gains in the properties obtained with the addition
of CNTs in relation to the conventional asphalt binder. The aim was to develop nanocomposites asphalt which are less susceptible to temperature and more rigid and elastic.

2.2.3 Mix Design of Asphalt Mixture

The mix design of the asphalt mixture was carry out according to the Superpave methodology and with the use of a gyratory compactor. The procedures adopted in the mix design were those recommended in the standards AASHTO M 323 and AASHTO R 35. Three parameters were fixed for the modeling: compaction angle of 1.25°, compaction pressure of 0.6 MPa and gyration speed of 30 rpm. All specimens were molded into pieces with a diameter of 150 mm and a height of approximately 110 mm. The study on the mix design of the mixture was carry out for a high volume of traffic \( (N_{\text{initial}} = 9 \text{ gyrations}, N_{\text{design}} = 125 \text{ gyrations and } N_{\text{maximum}} = 205 \text{ gyrations}) \). The asphalt binder content of the mix design was defined as that which fulfilled the following Superpave mix design criteria: air voids percentage \( N_{\text{initial}} > 11\%\), \( N_{\text{design}} = 4\%\) and \( N_{\text{maximum}} > 2\%\); voids in the mineral aggregate \( \geq 13\%\); voids filled with asphalt between 65\% and 75\%; and dust proportion 0.8-1.6\%.

2.2.4 Evaluation of the Rheological Behavior of the Asphalt Mixtures

After the design of the asphalt mixture one slab (600 x 400 x 90 mm) of each sample studied was molded on a compactor table (IFSTTAR - l'Institut Français Des Sciences et Technologies Des Transports). The slabs were compacted according to the AFNOR NF P 98-250-2 specifications. After a period of 15 days of curing the slabs were cut...
with a saw into the prismatic specimens (381 x 50.8 x 63.5 mm) in order to carry out the rheological study on the four-point apparatus.

After the cutting, the specimens were characterized in terms of their geometry and specific mass. Based on this characterization, the three specimens of each mixture which showed the highest degree of homogenization were selected for the rheological evaluation.

In the study on the rheological behavior of the asphalt mixture produced, the complex modulus was determined at different test frequencies and temperatures on the four-point apparatus, according to the guidelines established in the European norm EN 12697-26. For each mixture studied, three specimens were tested and the result considered as the average of the values obtained.

The tests were conducted at frequencies of 0.1, 0.2, 0.5, 1, 2, 5, 10 and 20 Hz and at temperatures of 0, 5, 10, 15, 20, 25 and 30 °C, under controlled deformation with alternating sinusoidal load and with a maximum deformation by flexion of 50 µm/m.

2.2.5 Evaluation of Performance in Relation to Permanent Deformation of Asphalt Mixtures

For testing of permanent deformation, two slabs (500 x 180 x 50 mm) of each asphalt mixture studied were molded on an IFSTTAR compaction table. The slabs were compacted according to the specifications of AFNOR NF P 98-250-2. The performance of the asphalt mixtures with regard to their resistance to permanent deformation was evaluated using the French equipment Orniéreur, that its a laboratory wheel tracking test in compliance with Standard AFNOR NF EN 12697-22 and standard AFNOR NF P 98-253-1. In this test, the asphalt mixture slabs, at 60 °C, were submitted to the passage of
30000 cycles of a rolling axle with a frequency of 1 Hz, loading of 5 kN and tire inflation pressure 0.6 MPa. During the test the depth of the foundation of the wheel track in relation to the slab thickness was obtained for 100, 300, 1000, 3000, 10000 and 30000 cycles.

3 RESULTS AND DISCUSSION

3.1 Optimization of Nanocomposite Containing CNTs

Figure 2 shows the effect of the CNTs in the asphalt binder with regard to the penetration (25 °C, 100 g and 5 s), softening point and penetration index (PI) (Pfeiffer and van Doormaal) of the virgin samples.

Figure 2 verifies the reduction in the penetration and increase in the softening point with the addition of CNTs, resulting in greater sensitivity to variations in temperature, as observed from the penetration index (PI). A higher softening point and lower PI indicate asphalts with lower susceptibility to permanent deformation. However, the consistency and thermal susceptibility of the asphalt binders alone does not guarantee good performance with regard to the permanent deformation of the asphalt mixture, and these need to be determined together with the rheological properties of the material.

The viscoelastic properties of the virgin and RTFOT-aged asphalt binders were studied using a dynamic shear rheometer (DSR). The rheometry was carried out at high temperatures (52 °C up to 76 °C), and the evaluation was directed toward the complex shear modulus (|G*|) and phase angle (δ), in order to obtain the parameter associated with permanent deformation (|G*/sin δ).

The complex shear modulus (|G*|) and phase angle (δ) of asphalt binders indicate their contribution to the resistance to permanent deformation. At high temperatures, the
rheological study is carried out based on the $|G^*|/\sin \delta$ parameter established according to the dissipated energy approach, where a rigid and elastic asphalt binder is sought. Thus, high values for the complex shear modulus ($|G^*|$) are favorable, since these represent a high resistance to deformation, and low values for the phase angle ($\delta$) are desirable, since this reflects a greater elastic component of the total deformation. Permanent deformation is considered a phenomenon under controlled stress and the greater the value for the parameter $|G^*|/\sin \delta$ the lower the amount of energy dissipated during each load cycle, according to equations 1 and 2 for the dissipated energy approach.

\[
W_i = \pi \sigma_i \varepsilon_i \sin \delta_i \quad \text{(Equation 1)}
\]

In the case of controlled stress, we have: $\sigma_i = \sigma_o$ and $\varepsilon_i = \frac{\sigma_o}{|G^*|}$. Thus:

\[
W_i = \pi \sigma_i \varepsilon_i \sin \delta_i \rightarrow W_i = \pi \sigma_o^2 \left( \frac{1}{|G^*_i|/\sin \delta_i} \right) \quad \text{(Equation 2)}
\]

where:

- $W_i$ = energy dissipated in the load cycle $i$;
- $\sigma_i$ = stress in the load cycle $i$;
- $\sigma_o$ = initial stress (constant);
- $\varepsilon_i$ = strain in the load cycle $i$;
- $\delta_i$ = phase angle between the stress and strain signals in the load cycle $i$; and,
- $|G^*_i|$ = complex modulus in the load cycle $i$.

Figures 3 and 4 show the results for the parameter $|G^*|/\sin \delta$ as a function of the variation in the temperature for the virgin samples and the residues aged in the RTFOT, respectively.

The graphs in Figures 3 and 4 clearly show the influence of the addition of CNTs on the rheological behavior of the asphalt binder. For all of the nanomodified samples and
temperatures tested higher values were verified for the parameter \(|G^*/\sin \delta\) due to an increase in the complex shear modulus \((|G^*|)\) and a reduction in the phase angle \((\delta)\).

Table 2 shows the gains in the performance obtained for each nanocomposite asphalt in relation to the conventional binder, for both the virgin samples and the residues obtained by RTFOT. The gains are evaluated in terms of temperature \((^\circ C)\) and considered in relation to a \(|G^*/\sin \delta\) value of 1.0 kPa for the virgin samples and 2.2 kPa for the aged samples.

The data in Table 2 verify that the incorporation of CNTs resulted in an improved performance of the asphalt binder in terms of the \(|G^*/\sin \delta\) parameter. In this regard, the best performance is observed when the CNT content is increased from 1% to 2%. However, this gain is reduced with an increase in the content to 3%. The reduced performance could be related to the dispersion of the CNTs in the asphalt matrix, indicating that for contents of around 3% the dispersion is hindered, leading to the formation of agglomerates of CNTs in the matrix.

In this regard, Biercuk et al. (2007) and Liu and Wagner (2005) reported that good nanometric dispersion not only allows a better interaction with the matrix but also ensures that the agglomerates do not concentrate stresses, which affect the mechanical performance of the nanocomposites. In this context, several authors (Ma et al. 2007; Kosmidou et al. 2008; Ma et al. 2009) have also noted that a CNT concentration high hinders the dispersion of nanoparticles and leads to a reduction in the mechanical characteristics of the nanocomposites, which in some cases can be lower than of the pure matrix.

Thus, the rheological results show an optimum incorporation of around 2%, considering the rheological performance in terms of the \(|G^*/\sin \delta\) parameter. The asphalt binder with 2% addition of CNTs shows a maximum gain in performance grade (in high
temperatures) of 6.6 °C for the virgin samples and 4.6 °C for the aged samples when compared with the conventional asphalt. These performance gains, give an indication that nanomodified asphalt mixtures would have higher resistance to permanent deformation than conventional asphalt mixtures.

3.2 Mix Design of Asphalt Mixtures

Prior to the verification of the susceptibility to permanent deformation of the asphalt mixtures, the Superpave mix design of the asphalt mixture and the molding of the asphalt slabs were carry out. In this regard the mix design of the mixture was performed using the conventional asphalt binder. The contents defined in the mix design study were obtained by varying the estimated binder content (4.0%) by ± 0.5% and + 1.0%. Taking as the suitable binder content that which led to 4% of air voids at 125 gyrations ($N_{\text{design}}$), the design content of the mixture was defined as 4.35% of asphalt binder.

As mentioned above, a design content of 4.35% was arrived at for the conventional asphalt binder and in a complementary study (data not shown) a design content of 4.10% was obtained for the nanocomposite asphalt with 2% CNTs. However, the adoption of different contents of asphalt binders in the mixtures in order to investigate the changes in the mechanical characteristics due to the use of different types of binders introduces a variable which affects the results. In this regard, a variation in the proportion of materials is inherent to the use of different contents of asphalt binder.

Therefore, in order to guarantee the same proportion of the materials (content of binder and granulometric distribution) in the asphalt mixtures studied, the design binder
content of 4.35% was fixed for the conventional and nanomodified asphalt mixtures in the evaluation of permanent deformation.

3.3 Evaluation of Rheological Behavior of the Asphalt mixtures

In order to study the rheological behavior of the conventional and nanomodified (2% of CNTs) asphalt mixtures, a test to determine the complex modulus at different temperatures and load frequencies was carried out. The evaluation was directed toward two viscoelastic parameters: the complex modulus ($|E^*|$) and the phase angle ($\delta$). For each asphalt mixture, two prismatic specimens were tested. The average results obtained for each mixture are shown in the form of graphs and tables.

Figure 5 shows the isothermal curves for the conventional and nanomodified mixtures. The isotherms relate the complex modulus along the ordinate axis to the load frequency along the abscissa axis, both on a logarithmic scale, for each test temperature.

In Figure 6, the master curves for the mixtures studied at the reference temperatures (TR) of 15 °C and 20 °C can be observed, which were obtained from the horizontal translation of the isothermal curves. The factors of the horizontal translation were calculated using the Williams-Landel-Ferry (WLF) equation (equation 3).

\[
\log a_T[T] = \frac{C_1(T-T_{ref})}{C_2+T-T_{ref}} \tag{Equation 3}
\]

where:

- $a_T[T]$ = factor for the horizontal translation of the isothermal curve for temperature $T$;
- $C_1, C_2$ = model parameters, calculated by linear regression, dependent on the material;
- $T_{ref}$ = temperature of a certain isothermal curve ($^\circ$K); and,
$T_{ref} =$ reference temperature of an isothermal curve (°K).

The model parameters, C1 and C2, obtained for each asphalt mixture are: conventional 15 °C ($C_1 = -17.2661$ and $C_2 = 108.4144$); conventional 20 °C ($C_1 = -16.5049$ and $C_2 = 113.4144$); nanomodified 15 °C ($C_1 = -13.9706$ and $C_2 = 88.5277$); nanomodified 20 °C ($C_1 = -13.2237$ and $C_2 = 93.5277$).

In Figure 5 an increase in the value for the complex modulus of the asphalt mixture with CNT can be observed. The increase is characterized by a vertical upward shift in the isothermal curves for the nanomodified mixture in relation to the conventional mixture. It can be noted that at higher temperatures there are greater gains in the complex modulus. The isothermal curves also allow the lower thermal susceptibility of the nanomodified asphalt mixture to be observed. In these curves the gap (distance) between the isothermal curves for 0 °C and 30 °C is smaller for the nanomodified mixture, indicating that the effects of the temperature are weaker for this asphalt mixture. In this regard, more compact isothermal curves represent a lower thermal susceptibility of the asphalt mixture.

According to Figure 6, on comparing the master curves for the different mixtures, at the reference temperatures of 15 °C and 20 °C, it can be verified that the modulus for the nanomodified mixture was higher in relation to that for the conventional mixture, for all frequencies. In order to quantify this increase in the rigidity, Table 3 shows the increase in the complex modulus for the nanomodified asphalt mixture in relation to the conventional mixture in percentage terms.

In Table 3 the increase in the value for the complex modulus with the use of the nanomodified asphalt binder can be verified. As an example, at a frequency of 1 Hz, with the use of the nanocomposite there are increases in the complex modulus of the
asphalt mixture of 125%, 104% and 48%, for temperatures of 30 °C, 25 °C and 20 °C, respectively. In summary, the laboratory tests show that there is a greater increase in the complex modulus mainly at high temperatures and low load frequencies. It can be noted that the greatest increases occur under service conditions of the asphalt mixtures which favor the occurrence of the permanent deformation phenomenon, that is, in regions with hot climates (high temperatures) and on lanes with slow traffic (low load frequency). The incorporation of the CNTs into the asphalt binder, and consequently the asphalt mixture, leads to an increase in the rigidity of the mixture, providing greater resistance to the accumulation of plastic deformation of the asphalt coating during each load cycle (passing of a truck axle).

Figure 7 shows the curves of the phase angles versus the frequency for the reference and nanomodified asphalt mixtures. A vertical downward shift in the curves for the nanomodified mixture in relation to the conventional mixture can be observed in Figure 7, characterizing a reduction in the phase angle at all frequencies and temperatures tested. Table 4 shows the reduction in the phase angle (in percentage terms) when the nanocomposite asphalt is used in the asphalt mixture.

The results in Table 4 verify the reduction in the phase angle of the asphalt mixture, for all frequencies and temperatures applied in the test, when the nanocomposite asphalt was tested. At a frequency of 1 Hz, when the nanocomposite was used, there were reductions in the phase angle of 19%, 20% and 21%, at temperatures of 25 °C, 20 °C and 15 °C, respectively. A reduction in the phase angle indicates an asphalt mixture with a more viscous and elastic behavior, that is, with a greater capacity to recover completely from the deformation occurring in each load cycle (passing of a truck axle), reducing the accumulation of permanent deformations.
The complex modulus (|E*|) and phase angle (δ), are indicators of the resistance to permanent deformation of asphalt mixtures. In this regard, rheological analysis was carry out based on the parameter |E*|/sin δ, according to the dissipated energy approach (Equation 2). Figure 8 shows the results for parameter |E*|/sin δ as a function of the variation in the temperature for the two asphalt mixtures studied. The results for this parameter are related to the rheological tests conducted at 1 Hz. In the evaluation of the parameter |E*|/sin δ this load frequency was considered, since 1 Hz is the frequency used in the main tests (Asphalt Pavement Analyzer – APA, Hamburg Wheel Tracking Devices – HWTD and Orniéreur Equipment of IFSTTAR) for the verification of the performance of asphalt mixtures in terms of their resistance to deformation. This frequency represents low traffic speeds on the highways, which is a situation of concern in relation to the formation of wheel tracks (permanent deformation) in asphalt mixtures.

An increase in the parameter |E*|/sin δ for the nanomodified asphalt mixture in relation to the conventional asphalt mixture, for all of the test temperatures, can be observed in Figure 8. It can be noted that for a higher temperature there is a greater increase in the value for this parameter in the case of the nanomodified mixture. Thus, in terms of rheological behavior, the incorporation of 2% of CNTs improves the performance of the asphalt mixture in terms of its resistance to permanent deformation.

### 3.4 Evaluation of Permanent Deformation Performance of Asphalt Mixtures

After evaluating the rheological behavior of asphalt mixtures, two asphalt slabs were molded in the LCPC compactor for each mixture and were submitted to permanent deformation tests. The results obtained show that the incorporation of 2% CNTs significantly improves the performance of the asphalt mixtures in terms of their resistance to permanent deformation.
deformation tests. Figure 9 shows the results for the resistance to permanent deformation of the asphalt slabs tested in the laboratory traffic simulator.

In general, as shown in Figure 9, the nanomodified asphalt mixture obtained better performance than the conventional mixture. After 30,000 cycles the accumulated deformation of the conventional mixture was 9.5% in relation to the thickness of the slab while the mixture with the nanocomposite containing 2% of CNTs showed an accumulated deformation of 4.6%. Thus, the reduction in the permanent deformation at 30,000 cycles is 52% with the addition of 2% of CNTs. The results verify the beneficial effect of the addition of nanometric loads on the mechanical performance of the asphalt mixture, reducing the permanent deformation.

The permanent deformation of an asphalt coating layer is associated with several factors, mainly the formulation of the granulometric composition and the appropriate mix design of the mixture (binder content). However, the properties of the asphalt binder will also influence the behavior of the mixture. In this regard, the different responses of the behavior verified in Figure 9 are associated with the characteristics of the asphalt binder, since the binder content and the granulometric composition of the two mixtures did not change.

The improved behavior of the permanent deformation of the nanomodified asphalt mixtures is directly associated with the carbon nanotubes, which form an elastic network within the asphalt matrix. This network provides the decrease in phase angle and increase the elastic portion (or storage) of the complex modulus, as noted in the rheological results of the asphalt mixtures. Thus, with each passing of traffic the total deformation and also the viscous deformation of the asphalt binder are smaller.

4 CONCLUSIONS
This paper presents the results of research carried out to develop nanocomposites asphalt containing CNTs with a high potential for the resistance of permanent deformation. The main conclusion of this study is that the nanomaterials had a beneficial effect on the rheological behavior of asphalt binders and on the mechanical performance of the asphalt mixtures with regard to permanent deformation. The obtainment of asphalt mixtures with a high resistance to wheel track rutting based on the incorporation of carbon nanotubes was verified.

The incorporation of nanomaterials into the conventional asphalt binder led to an improvement in the empirical and rheological properties of these high temperature materials. With the addition of CNTs the softening point of the asphalt binder increased and the penetration decreased, leading to better thermal susceptibility, which is dependent on the content incorporated. The reduction in the sensitivity to temperature is greater with an increase in the CNT content incorporated. The complex shear modulus increased and the phase angle decreased at high temperatures with the addition of CNTs. The results show that the optimum content added is around 2%. However, it should be noted that the addition of around 3% of CNTs leads to a reduction in the rheological characteristics of the nanocomposites, possibly due to the formation of larger agglomerates of CNTs and a lack of interaction with the asphalt matrix.

The rheological study of asphalt mixtures clearly demonstrated the influence of the CNTs on the behavior of the mixture. It was verified that the nanomodified asphalt mixture (CNT-2%) had lower thermal susceptibility (as seen in isothermal curves), which is associated with an increase in the complex modulus (|E*|) and a reduction in the phase angle (δ) at all of the test temperatures. Consequently, there was an increase in the value for the parameter |E*|/sin δ. Based on the rheological alterations observed it
can be concluded that the nanomodified asphalt mixtures show greater resistance to permanent deformation than the conventional asphalt mixture.

The permanent deformation tests on asphalt mixtures confirm the prediction of rheological studies. The incorporation of 2% of CNTs in the asphalt binder reduced the permanent deformation of the mixture by 52%, indicating that in the field, particularly in tropical developing countries, a significant reduction in the appearance of this defect on highways could be achieved.

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ASTM - American Society for Testing and Materials. 2012. ASTM C 127: Standard test method for density, relative density (specific gravity), and absorption of coarse aggregate. USA.


Table 1 - Results obtained for the characterization of the aggregate.

<table>
<thead>
<tr>
<th>Properties*</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Apparent Specific Gravity (Gsa) of the coarse aggregate (ASTM C 127)</td>
<td>2953 kg/m³</td>
</tr>
<tr>
<td>Bulk Specific Gravity (Gsb) of the coarse aggregate (ASTM C 127)</td>
<td>2880 kg/m³</td>
</tr>
<tr>
<td>Absorption of coarse aggregate (ASTM C 127)</td>
<td>0.8%</td>
</tr>
<tr>
<td>Apparent Specific Gravity (Gsa) of fine aggregate (DNER-ME 084)</td>
<td>2974 kg/m³</td>
</tr>
<tr>
<td>Apparent Specific Gravity (Gsa) of dust (DNER-ME 085)</td>
<td>2804 kg/m³</td>
</tr>
<tr>
<td>Angularity of coarse aggregate (ASTM D 5821)</td>
<td>100%</td>
</tr>
<tr>
<td>Angularity of fine aggregate (ASTM C 1252)</td>
<td>49.2%</td>
</tr>
<tr>
<td>Flat, elongated particles (ABNT NBR 6954)</td>
<td>9.6%</td>
</tr>
<tr>
<td>Clay content (sand equivalent) (AASHTO T 176)</td>
<td>61.2%</td>
</tr>
<tr>
<td>Hardness (Los Angeles abrasion) (ASTM C 131)</td>
<td>11.6%</td>
</tr>
<tr>
<td>Soundness (ASTM C 88)</td>
<td>2.1%</td>
</tr>
<tr>
<td>Deleterious material (AASHTO T 112)</td>
<td>0%</td>
</tr>
</tbody>
</table>

*The coarse aggregate corresponds to the fraction which passes through a 19.1 mm sieve and is retained by a N° 4 ASTM sieve; fine aggregate represents the fraction which passes through a N° 4 ASMT sieve and is retained by a N° 200 ASTM sieve; the powdered material passes through a N° 200 ASTM sieve.
Table 2 - Performance of asphalt binders in relation to the parameter $|G^*|/\sin \delta$.

<table>
<thead>
<tr>
<th>Asphalt binders</th>
<th>Temperature ($^\circ$C)</th>
<th>Gain in performance ($^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Virgin $</td>
<td>G^*</td>
</tr>
<tr>
<td>Conventional</td>
<td>63.0</td>
<td>62.7</td>
</tr>
<tr>
<td>CNT-1%</td>
<td>64.8</td>
<td>63.4</td>
</tr>
<tr>
<td>CNT-2%</td>
<td>69.6</td>
<td>67.3</td>
</tr>
<tr>
<td>CNT-3%</td>
<td>67.2</td>
<td>65.0</td>
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</table>
Table 3 - Increase in the complex modulus for the nanomodified asphalt mixture in relation to the conventional asphalt mixture (in percentage terms).

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>0.1</th>
<th>0.2</th>
<th>0.5</th>
<th>1</th>
<th>2</th>
<th>5</th>
<th>10</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>91.56</td>
<td>122.89</td>
<td>167.51</td>
<td>124.68</td>
<td>121.83</td>
<td>102.01</td>
<td>83.12</td>
<td>69.31</td>
</tr>
<tr>
<td>25</td>
<td>162.30</td>
<td>126.14</td>
<td>125.69</td>
<td>103.86</td>
<td>80.55</td>
<td>61.15</td>
<td>54.81</td>
<td>45.12</td>
</tr>
<tr>
<td>20</td>
<td>83.76</td>
<td>68.31</td>
<td>65.04</td>
<td>47.83</td>
<td>39.62</td>
<td>29.64</td>
<td>24.64</td>
<td>19.99</td>
</tr>
<tr>
<td>15</td>
<td>62.20</td>
<td>57.98</td>
<td>42.71</td>
<td>33.45</td>
<td>28.24</td>
<td>23.74</td>
<td>19.01</td>
<td>17.36</td>
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<tr>
<td>10</td>
<td>37.46</td>
<td>32.75</td>
<td>26.18</td>
<td>21.34</td>
<td>18.61</td>
<td>17.58</td>
<td>14.56</td>
<td>14.48</td>
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<tr>
<td>5</td>
<td>27.02</td>
<td>21.45</td>
<td>19.06</td>
<td>16.64</td>
<td>14.46</td>
<td>13.47</td>
<td>12.59</td>
<td>11.87</td>
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<td>12.86</td>
<td>12.39</td>
<td>11.50</td>
<td>10.87</td>
<td>10.58</td>
<td>10.37</td>
<td>10.58</td>
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</tbody>
</table>
Table 4 - Reduction in the phase angle of the nanomodified asphalt mixture in relation to the conventional asphalt mixture (in percentage terms).

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>0.1</th>
<th>0.2</th>
<th>0.5</th>
<th>1</th>
<th>2</th>
<th>5</th>
<th>10</th>
<th>20</th>
</tr>
</thead>
<tbody>
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<td>30</td>
<td>-</td>
<td>-</td>
<td>3.93</td>
<td>9.43</td>
<td>15.16</td>
<td>19.53</td>
<td>23.09</td>
<td>26.13</td>
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<tr>
<td>5</td>
<td>20.00</td>
<td>19.37</td>
<td>18.47</td>
<td>16.79</td>
<td>15.13</td>
<td>14.14</td>
<td>12.79</td>
<td>13.16</td>
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<tr>
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<td>13.53</td>
<td>13.16</td>
<td>12.90</td>
<td>12.35</td>
<td>9.86</td>
<td>8.47</td>
<td>7.84</td>
<td>6.67</td>
</tr>
</tbody>
</table>
Figure Captions:

Figure 1 - Grain-size distribution.

Figure 2 - Penetration, Softening point and penetration index (PI) (Pfeiffer and van Doormaal) of virgin samples.

Figure 3 - Relation between |G*/sin δ and temperature for the virgin samples.

Figure 4 - Relation between |G*/sin δ and temperature for aged residues (RTFOT).

Figure 5 - Comparison of isothermal curves for the asphalt mixtures studied.
Figure 6 - Comparison of the master curves ($T_R = 15 \, ^\circ C$ and $T_R = 20 \, ^\circ C$) for the asphalt mixtures studied.

Figure 7 - Curves of the phase angles versus the frequency. Comparison between the conventional and nanomodified asphalt mixtures.

Figure 8 - Parameter $|E*/\sin \delta|$ as a function of the test temperature (test frequency of 1 Hz).

Figure 9 - Performance of permanent deformation of asphalt mixtures produced.
Figure 1. Grain-size distribution.
53x62mm (300 x 300 DPI)
Figure 2. Penetration, Softening point and penetration index (PI) (Pfeiffer and van Doormaal) of virgin samples.
27x16mm (300 x 300 DPI)
Figure 3. Relation between $|G^*|/\sin \delta$ and temperature for the virgin samples.

37x31mm (300 x 300 DPI)
Figure 4. Relation between $|G^*|/\sin \delta$ and temperature for aged residues (RTFOT).

37x31mm (300 x 300 DPI)
Figure 5. Comparison of isothermal curves for the asphalt mixtures studied.

84x158mm (300 x 300 DPI)
Figure 6. Comparison of the master curves (TR = 15 oC and TR = 20 oC) for the asphalt mixtures studied.
Figure 7. Curves of the phase angles versus the frequency. Comparison between the conventional and nanomodified asphalt mixtures.

79x140mm (300 x 300 DPI)
Figure 8. Parameter $|E^*|/\sin \delta$ as a function of the test temperature (test frequency of 1 Hz).

28x18mm (300 x 300 DPI)
Figure 9. Performance of permanent deformation of asphalt mixtures produced.