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# Carbon Nanotubes-modified Asphalt Binder: Preparation and Characterization

M. Faramarzi [1+], M. Arabani [1], A. K. Haghi [2], and V. Mottaghitalab [2]

**Abstract:** This study focuses on the exploratory analysis of the mixing procedure of carbon nanotubes (CNTs) with asphalt cement (AC) and discusses the viscoelastic characteristics of neat and CNT-modified AC binders. Two CNT-asphalt cement mixing procedures including simple and wet processes were investigated. Viscoelastic properties of modified AC incorporated with 0.1, 0.5, and 1 (%w/w) CNT were evaluated, considering bitumen penetration, softening point, ductility, rotational viscosity (RV), and dynamic shear rheometer (DSR) tests, then the results were compared to those of unmodified asphalt binder. It was found that the wet process technique can make a homogeneous CNT-asphalt binder mixture, while the simple process technique would not disperse CNTs as uniformly as the wet process, but it is easier and more practical. Moreover, adding carbon nano tubes (CNTs) provides an enhancement of rutting resistance potential along with the resistance to thermal cracking.

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***Key words**: Asphalt binder; Carbon nanotube; Mixing procedure; Visco-elastic.*

## Introduction

New plans must be experienced to improve quality, productivity, and durability of conventional pavements. Asphalt mixtures are composed of very irregular aggregates bound together with hydrocarbon-based asphalt, with a low volume fraction of voids dispersed within the matrix. Modified asphalts using variety of fillers have increasingly been used over the last decade to minimize low-temperature cracking and high-temperature rutting while improving the fatigue cracking resistance of asphalt concrete [1, 2].

Instead of using a large amount of micro size fillers, it's highly recommended to use nanomaterials, which are defined as restructuring of matter on the order of nanometers (i.e., less than 100 nm) to create materials with fundamentally new properties and functions. It is widely observed as having huge potential to bring benefits in diverse areas such as production of stronger and lighter materials [3].

### Nanotechnology and Current Development in Pavement Materials

The mechanical behavior of bituminous mixtures depends on structural elements and phenomena that occur in a micro and a nano scale. As a result, nanotechnology can modify the molecular structure of asphalt, which leads to improvement in the material's bulk properties. Nanotechnology can also improve the mechanical performance, durability, and sustainability of asphalt concrete. The revolutionary effects accompanying nanotechnology allow the development of cost-effective, high-performance, and long-lasting products of asphalt binder and asphalt concrete, which can then lead to unprecedented uses of such materials. One of the most desired properties of nanomaterials in the construction sector is their capability to confer a mechanical reinforcement to bituminous-based structural materials [4]. While a large amount of research studies have been carried out in the last decade on modification of asphalt binder by different nano particles like nano clay [5], nano zinc oxide [6], nano silicon dioxide [7], nano titanium oxide [7], carbon nano fibers (CNFs) [8], etc., very few studies have been conducted in the area of carbon nano tubes (CNT)-modified binders and mixtures.

Since CNTs exhibit great mechanical properties [9, 10] along with extremely high aspect ratios (length-to-diameter ratio) ranging from 30 to more than several thousand [11], they are expected to produce significantly stronger and more improved bituminous composites than traditional reinforcing materials (e.g., glass fibers or carbon fibers). The high specific strength, the chemical resistance, the electrical conductivity, and the thermal conductivity of carbon nanotubes (CNTs) make them attractive for use as reinforcement to develop superior bituminous composites [12, 13].

### CNT-Asphalt Binder Modification

Some research has been performed on mixing process of CNFs in asphalt binder, but not for CNTs, which are about 100 times smaller than CNFs and harder to disperse. Dispersion of CNTs has been one of the largest challenges due to the aggregation of the nanotubes [14]. Improvement of material properties can be achieved by a proper dispersion technique. Improper dispersion leads to nanotube damage and size break down, which deteriorate the material properties. There are still many challenges and difficulties to utilize these carbon nano particles to enhance the properties of construction materials. The interaction of unaged modified binders is not well understood from the standpoint of binder properties and field performance. Because of the complicated relationships of asphalt binders and carbon nano particles in the modified binders, detailed

[1] Dept. of Civil Engineering, University of Guilan, Rasht, I. R. Iran.
[2] Dept. of Textile Engineering, University of Guilan, Rasht, I. R. Iran.
[+] Corresponding Author: E-mail masoud.faramarzi67@gmail.com
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information will be beneficial to help obtain an optimum balance in the use of these materials. This paper focuses on the mixing procedure of CNT with asphalt and the effect of various dosages of CNT on the viscoelastic characteristics of the asphalt cement (AC).

## Literature Review

It has been indicated by Xiao et al. [15, 16] that CNFs would be beneficiary to the enhancement of the rheological properties of asphalt binders after short-term and long-term aging treatments. Elsewhere, Amirkhanian and his coworkers [17, 18], based on a study about unaged binder, recommended the use of a relatively high percentage of CNFs (>1%) to increase resistance to permanent deformation at high temperatures. Another study by Khattak et al. [8] concluded that neat asphalt binders modified by carbon nano-fibers would improve fatigue and rutting response by a certain amount, which depends on the mixing procedure manipulated for the dispersion of nano-fibers in the asphalt binder. The biggest challenge in developing nanocomposite is the dispersion of nanoparticles or chemical compatibility with matrix materials, which has been mentioned by Hussain et al. [19]. They have suggested that in order to improve the carbon nanofibers (CNFs)/matrix interfacial adhesion issue, it is necessary to achieve a complete dispersion to have the full potential of nano reinforced composite materials. Shirakawa et al. [20] used asphalt emulsion as solvent to disperse carbon nanotubes and indicated that carbon nanotubes disperse in anionic and non-ionic emulsion better than cationic emulsion. Also CNT-modified asphalt binder showed higher penetration degree and short wave absorption than carbon powder-modified asphalt binder. Elsewhere, the simple mixing procedure employed to disperse CNTs in asphalt binder indicated that modifying asphalt binder by high percentages (higher than 0.5% of asphalt binder content) of CNTs improve its rheological characteristics [21]. These characteristics' improvements lead to decrease of asphalt pavement rutting in high temperatures and thermal cracking in low temperatures. Liu Xiaoming et al. [22] investigated the effect of using graphite and CNFs as additives on mechanical characteristics of asphalt concrete, separately and together. It was proven that adding CNFs alone leads to an increase of marshal stability and a decrease of resistance against rutting, but using graphite and CNFs together made a noticeable improvement of both of these properties.

## Materials and Methods

### Material

Materials used in this experimental investigation included a neat asphalt binder 60/70-penetration grade from Tehran mineral oil refinery with the physical properties listed in Table 1. A commercially available multiwalled CNT (MWCNT) made by CVD (chemical vapor deposition) method supplied by Neutrino company was used without further purification. The characterization of CNTs is shown in Table 2. Commercially available kerosene was used as a solvent to disperse the CNTs and ultimately mixed with the AC binders. The specific gravity and boiling point of the kerosene are 0.75 and 155$^{o}$C, respectively.

### Experimental Procedure

In this study, wet and simple mixing procedures were performed for CNTs inclusion in AC. A simple process procedure was chosen because of low cost, easy process, and practicality, while the wet process was chosen because of better dispersion of CNTs aggregates in this technique. The following two techniques were employed to incorporate CNTs into the base asphalt binder.

#### *Simple Shear Mixing Process*

This technique is comprised of two steps. The first step is the addition of CNTs and its manual blending. Then, the asphalt binder-CNT blends are mixed with a mechanical stirrer operating at a speed of 1,550 rpm for an overall time of 40 minutes to reach the required homogeneity. Within the mixing periods, the temperature has been set at 160℃ and is kept constant by applying an oil bath heated by a hot plate.

The short-term aging effect is necessary to be evaluated; therefore, an unmodified AC sample was subjected to the same mixing circumstance as that of CNT modified AC.

#### *Wet Process*

The CNT was dispersed in the solvent by means of sonication process and high shear mixing. Kerosene was chosen as solvent because of the fact that it was a petroleum based product, cheap and

**Table 1.** Properties of Used Asphalt Binder.

| Properties | Purity Grade | Flash Point | Softening Point | Penetration Grade at 25$^{o}$C | Ductility at 25$^{o}$C | Viscosity | Density | Fraass Breaking Point | Loss of Heating |
|---|---|---|---|---|---|---|---|---|---|
| Unit | % | $^{o}$C | $^{o}$C | mm/10 | cm | mPa.s | - | $^{o}$C | % |
| Value | 99 | 262 | 49 | 61 | 125 | 330 | 1.03 | 14 | 0.05 |

**Table 2.** Carbon Nano-tubes (CNTs) Properties.

| Properties | Purity | Outer Diameter | Inner Diameter | Average Length | Special Surface Area | Colour | Tap Density | True Density | Electric Conductivity |
|---|---|---|---|---|---|---|---|---|---|
| Unit | % | Nm | nm | μm | m$^2$/g | - | g/cm$^3$ | g/cm$^3$ | s/cm |
| Value | >95 | 10-20 | 5-10 | 10-30 | >200 | Black | 0.22 | 2.1 | 100 |

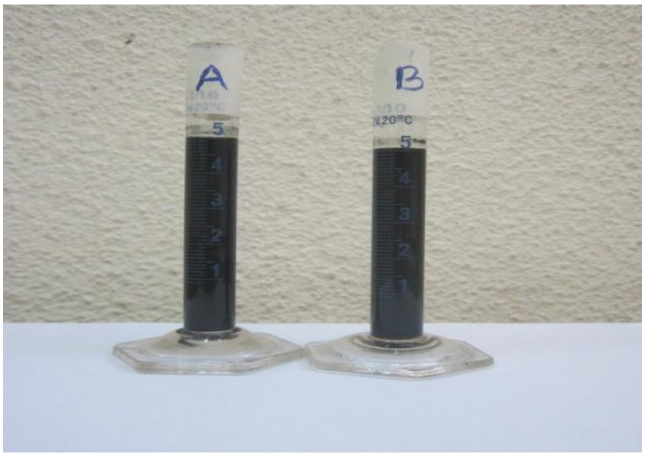



**Fig. 1.** Dispersion operation by sonication

**Fig. 2.** Dispersed CNTs in kerosene.

easily available. In this study, several samples of CNT-kerosene mixture were prepared by sonication (Fig. 1) and high shear mixing. Various duration lengths for sonication and high shear mixing were investigated, and comparisons were conducted for all the mixtures. Samples were compared based on the sedimentation level after the samples were allowed to settle for an extended period.

Comparison of various samples revealed that the optimum CNT dispersion with a homogenous distribution was obtained by applying the following procedure. Almost 84 gr (120 ml) of kerosene was placed in a measuring cylinder. Next, 1.28 gr of CNT was mixed and sonicated. During sonicating operation, the sonicator horn was placed at the center of the cylinder and inserted 40 mm deep into the CNT-kerosene mixture. The CNT were scattered by the sonication with a power of 240 watts at 50% pulse rate and the sonication time of 25 min, along with 2 min of high shear mixing at 2500 rpm. This procedure provides sufficient disaggregating energy to break the CNT aggregation without damaging the nanotubes. However, constantly proliferating dispersion energy would make CNT reagglomeration and cause a huge size break down. The CNT-solvent was mixed totally with AC using a low shear mixer while the temperature was set at 160℃, up to the time the intended amount of the solvent was vaporized. To determine the mixing time, the solvent-asphalt mixture mixed as long as the mass became the same as that of the neat AC binder. At this mixing time, about 1.5% kerosene content in AC was remaining that could be substituted to the evaporated lower molecular weight oils. As CNT-solvent has always been made in constant dosage, different amounts of CNT-solvent should be used to make CNT modified asphalt binder in different CNT percentages. Suitable mixing times were obtained by checking the weight of asphalt binder during the mixing process. As a result, 150, 165, and 180 min of mixing operation were the required times for making modified asphalt binder by 0.1, 0.5, and 1% CNT, respectively.

The short-term aging effect because of wet processing needs to be evaluated; therefore, an AC sample was subjected to the same mixing circumstance as that of CNT modified AC.

## Morphology of the Dispersed Nanotubes

The CNT-kerosene compound prepared by sonicator (Fig. 1) and high shear mixing showed a black color solution with high stability upon storage at room temperature for two weeks as shown in Fig. 2. It could be understood that because of suitable mixing process, CNT aggregates have disintegrated and become finer and lighter than before; as a result, CNT-solvent could stay stable  (Fig. 2).

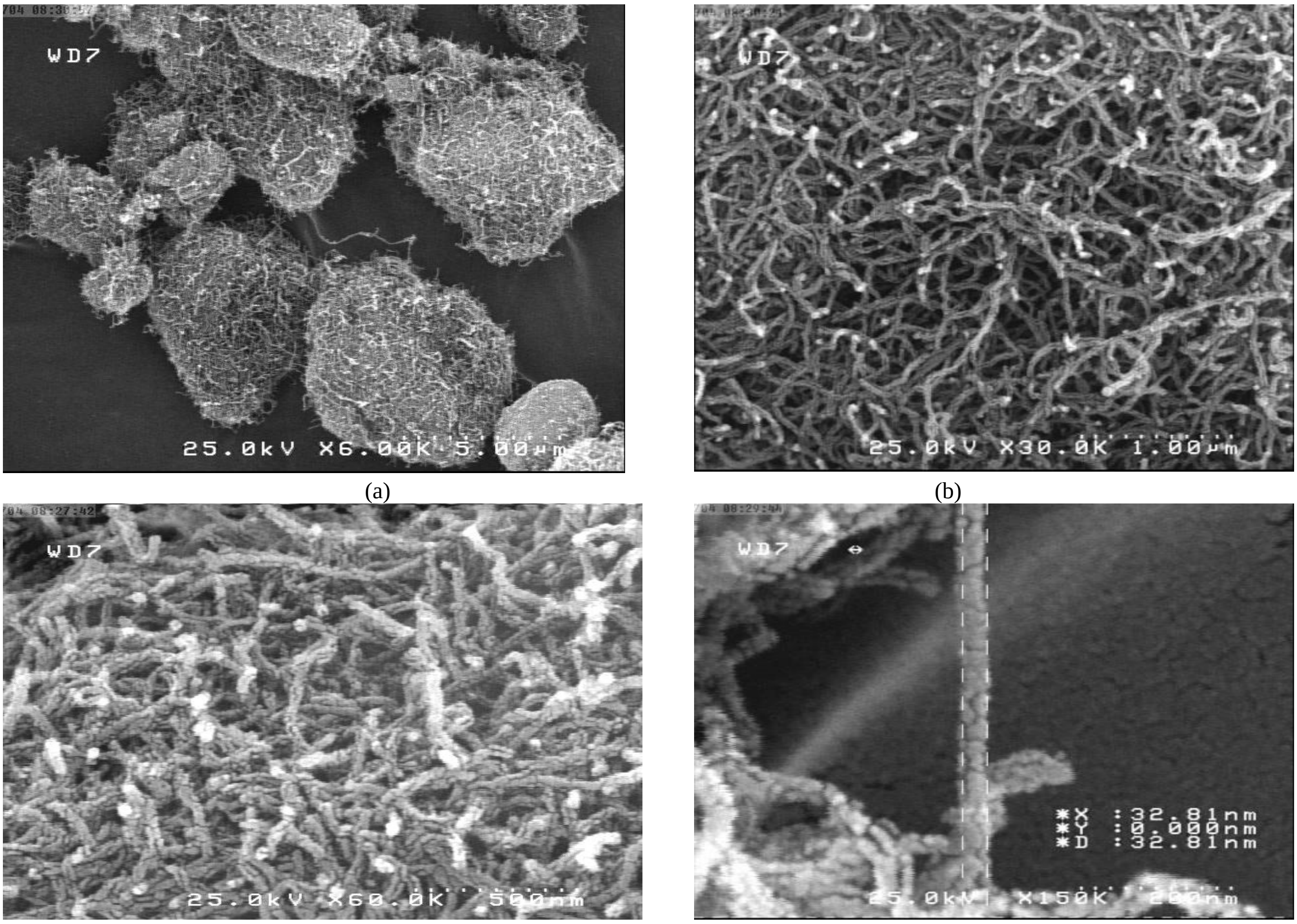
## Laboratory Tests

To determine the optimum content of CNTs and viscoelastic characterization of the base binder, empirical rheological tests carried out on conventional and modified asphalt binder with different CNTs content. In this study, empirical tests were performed according to the standard test procedures. The penetration test is an empirical test which measures the consistency (hardness) of asphalt binder at a specified test condition according to ASTM-D5 standard [23]. Also ASTM-D36 was used to determine the softening point of asphalt binder [24]. Ductility test was done and samples were drawn at 25℃ and with a speed of 5 cm/min, according to ASTM-D113 [25]. Viscosity tests were performed with a Brookfield rotational viscometer while temperature was set at 135℃ in accordance to AASHTO T316 [26]. A number 21 spindle and a specimen size of 8.5 grams were used for this study. Prior to pouring each sample, the container of modified binder was gently stirred for one minute to disperse the nano particles throughout the binder. To measure the high temperature rheological properties, a dynamic shear rheometer (DSR) was used according to AASHTO T315 [27]. Each binder specimen was measured in terms of the complex shear modulus (G*) and phase angle (δ) values at temperature of 60℃ and frequency of 1.59 Hz until failure according to superpave mix design specifications.

# Results and Analysis

## SEM Analysis Results

As shown in Fig. 3, CNTs show a strong tendency for aggregation with formation of random network of contacting aggregates. These bundles are clearly visible in Fig. 3, and in principle they can be mechanically removed for making the dispersion more homogeneous. Such “quasi-homogeneous” dispersions with minimized quantity and size of bundles can also be obtained by




(a) (b) (c) (d)

**Fig. 3**. SEM Images of Carbon Nanotubes, (a) 5 µm; (b) 1 µm; (c) 500 nm; (d) 200 nm.

careful sonication under certain optimized conditions.

The morphology of CNT-modified asphalt binder studied by SEM imaging is shown in Fig. 4, which presents a continuous matrix with uniform distributing nanometer phase. However, in simple processed CNT-modified asphalt binder, some large accumulated particles can be observed. For example, in Fig. 4(c) and 4(d), the average size of CNTs in the matrix is about 50–100 nm. CNTs distribute uniformly with a few mass accumulation particles. In Fig. 4(a) and 4(b) for simple processed CNT-modified asphalt binder, the average size of the particle increases, and some large accumulated particles can be observed. These results indicate that CNT is likely to accumulate in CNT-asphalt binder composites when simple procedure is used for the mixing operation. The large accumulation of CNTs in asphalt binder matrix becomes a breakdown point as result of stress concentration; therefore, the mechanical properties of materials decrease. For modified asphalt binder by CNT particles, the mixing procedure is a key factor. As wet procedure is chosen, CNTs distribute uniformly in the matrix, and particles do not accumulate; therefore, a higher strength of CNTs-modified asphalt binder is obtained. In the meantime, utilizing the simple procedure as part of the mixing protocol leads to an increase in the accumulating tendency of CNTs and consequently the decrease in the mechanical properties compared with wet procedure.

## Penetration Degree Test

Fig. 5 shows the acquired data regarding the penetration degree tests for neat and composite AC containing different amount of CNTs. It shows that there is insignificant difference between the neat and the processed composite AC. This is because of the negative effect of aging, which happens during mixing process in high temperatures. The addition of CNTs to asphalt binder decreases the penetration degree of asphalt binder. The higher the CNT content, the lower the penetration degree observed. Wet processed samples have shown a higher reducing rate than the simple process, possibly because of better dispersion of CNTs, and they make better CNT-asphalt binder matrix, which leads to harder asphalt binder. This reduction is due to the formation of powerful bound between chemical compositions of AC by CNTs with high specific surface. The bond formed between Asphaltene and Maltene nano particles prevents separation of ingredients of AC and leads to asphalt binder with better properties.

## Softening Point Test

The higher softening point for asphalt binder provides great opportunity for application in areas with high average annual temperature or areas with heavier traffic. Fig. 6 shows a graph of the

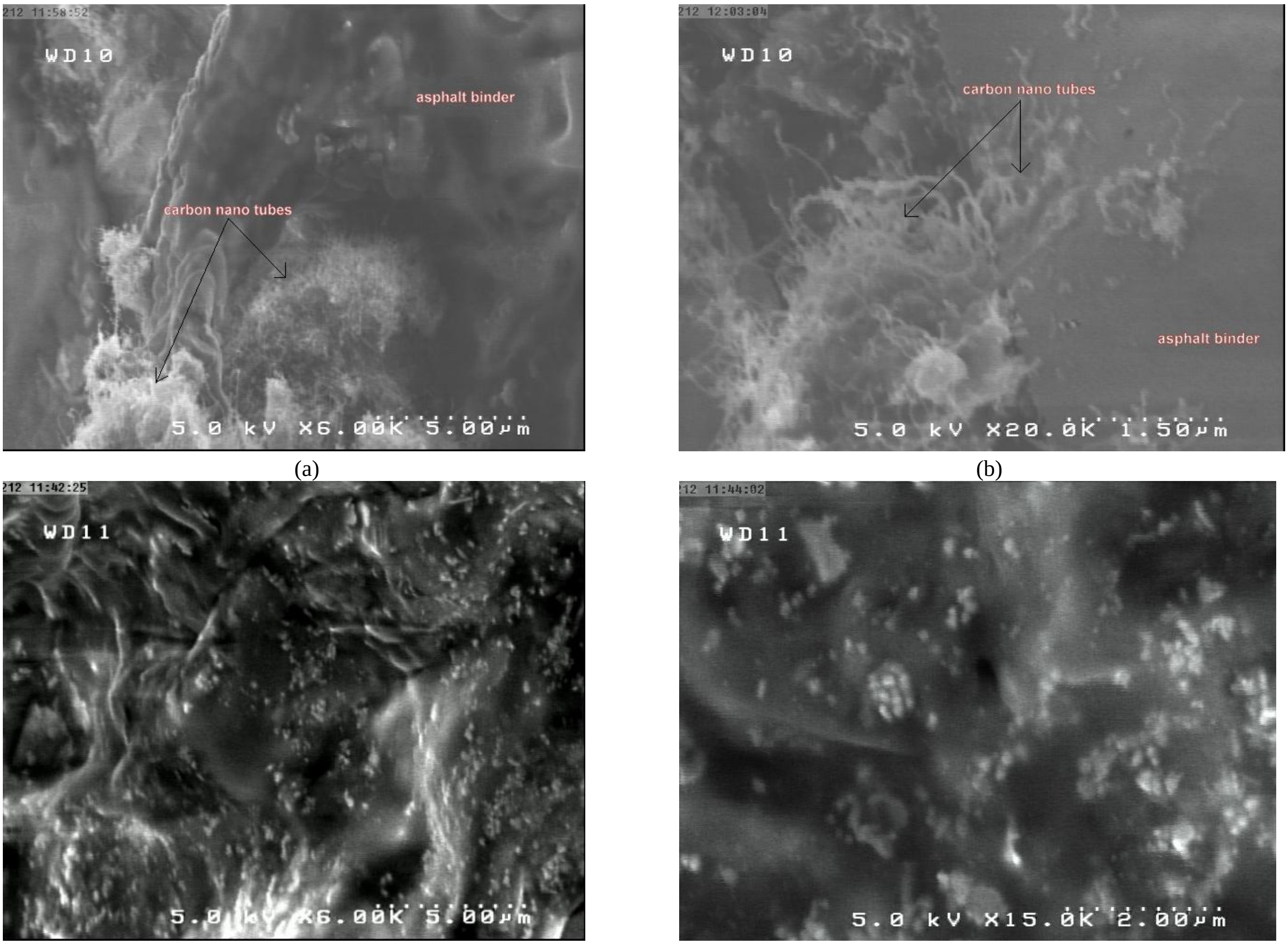



**Fig. 4.** SEM Images of Modified Asphalt Binder with Carbon Nanotubes, (a) Simple Processed CNT-modified Asphalt Binder – 5 µm; (b) Simple Processed CNT-modified Asphalt Binder - 1.5 µm; (c) Wet Processed CNT-modified Asphalt Binder – 5 µm; (d) Wet Processed CNT-Modified Asphalt Binder – 2 µm.

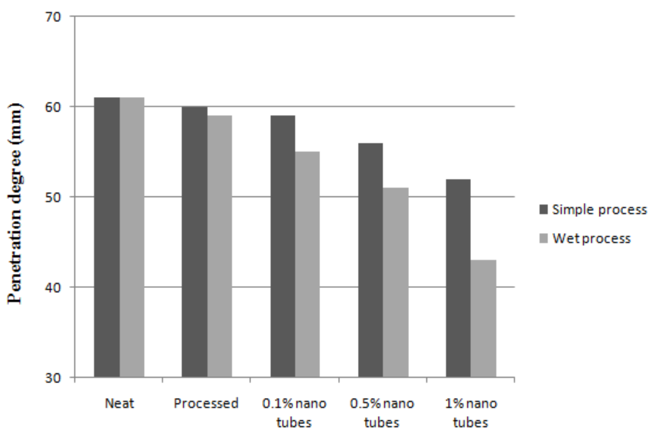



**Fig. 5.** Penetration at 25℃ as Function of CNT Dosage.

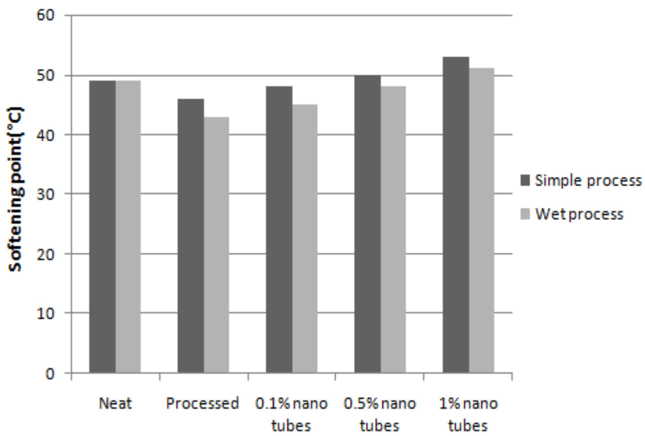



**Fig. 6.** Comparison of Softening Point Test Results for Different Samples.

softening point changes for the modified asphalt binder with different mixing process. For both modified asphalt binders, as a result of aging during the mixing process and its effect on the asphalt binder thermal sensitivity, a decrease is seen in the softening point for processed asphalt binder, but when CNTs are used, it has increased, leading to the improvement of softening point. As can be seen, for binder containing 1.0% CNTs, the softening point increased between 2℃ and 4℃ for wet and simple process, respectively.

It can be attributed to the formation of powerful bound between chemical compositions of AC by CNTs and also the high heat capacity of CNTs, which causes the asphalt binder to show more stability against the flowing, thus increase the softening point. Wet processed asphalt binder samples have lower softening points in comparison with dry processed samples. This trend is constant at all the different percentages. This is because in the wet process a little amount of kerosene (about 1.5%) remains in the asphalt binder making its thermal capacity decrease.

## Ductility Test

Asphalt binder that has acceptable ductility is more resistant to thermal cracking in low temperatures and shows good adherence, so could perfectly coat aggregates. Fig. 7 shows a graph of the ductility changes. Processed asphalt binder has lower ductility than neat ones because the mixing process at temperature of 160℃ has aged the AC due to the evaporation of lower molecular weight oils. In this case, by increasing carbon nanotubes, ductility properties will decrease much more for both simple and wet processed specimens. This behavior may be the result of chemical reaction and change in chemical structure, as also noted by Ghile [28]. As it could be understood from the diagram, wet processed modified asphalt binder has better ductility property than a simple processed one; it is possible that the effect of homogeneous CNT-asphalt binder matrix leads to a more ductile asphalt binder. Also the 1.5% remaining kerosene solvent could be a substitute of vaporized weight oil that had been removed during the mixing process. As a result, the aging effect has been decreased, leading to a more ductile asphalt binder in comparison to simple processed ones. According to ASTM-D113 [25], ductility of all these samples' asphalt binders, which has been modified by different percentages of CNT, seems to be higher than the minimum.

## Viscosity Test

The viscosity data of different samples including neat, processed, and composite AC containing different amount of CNTs at a temperature of 135℃ was collected by standard viscometery test (Fig. 8). It is obvious that regardless of mixing procedure, the viscosity values at 135℃ increase with the increase in CNT content. However, the rate of increase is a function of the mixing procedure used. The simple process of CNT mixing yielded a higher rate of increase in viscosities relative to the wet process of mixing. In general, the CNT-modified AC showed 3-4 times higher viscosity than the processed AC. It can be seen that the addition of the CNTs increased the viscosity of the binders at 135℃, but the binder with a low nano dosage percentage (e.g., 0.1% and 0.5%) only exhibited a slight increase in viscosity value. However, the statistical results indicate that the binder containing 1.0% CNTs has a significantly higher viscosity compared to the neat binder.

The noticeable point about higher viscosity is that the increase of mixing and compaction temperature can deteriorate bitumen properties, so the viscosity should not be more than the allowable limit. According to AASHTO (T-316) [26], the maximum amount for bitumen viscosity is 3000 mpa. All samples in this study have lower viscosity than this, and are placed in permissible intervals.

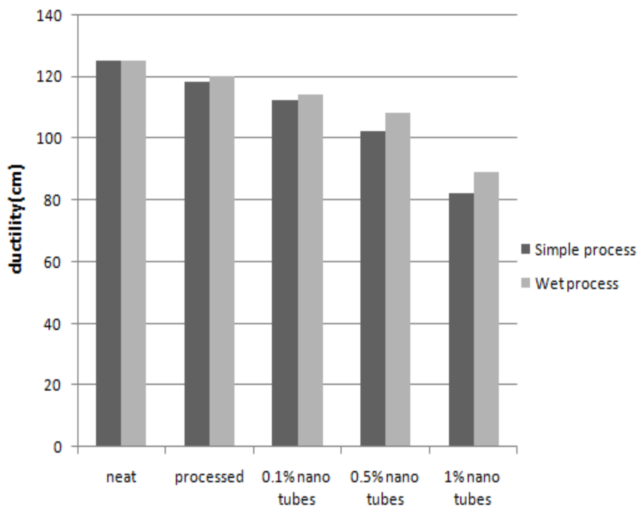



**Fig. 7.** Ductility at 25℃ as Function of CNT Dosage.

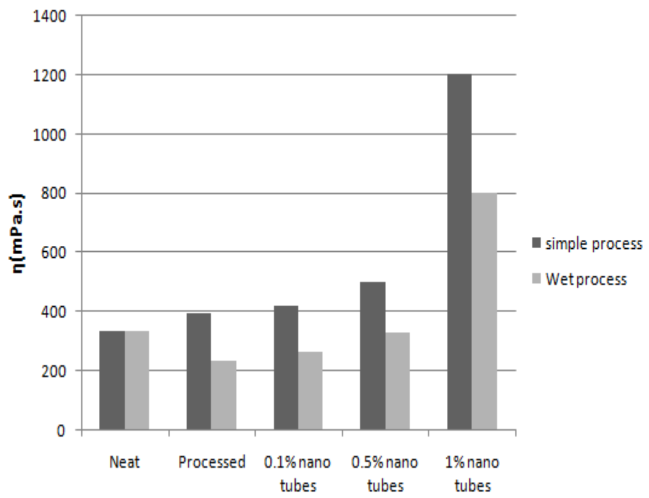



**Fig. 8.** Viscosity at 135℃ as Function of CNT Content.

## Dynamic Shear Rheometery Test

Dynamic shear test can be used to compare the temperature susceptibility of reinforced and original binder. During the dynamic shear test, a dynamic shear rheometer (namely DSR) was adopted to characterize the asphalt binder, and to determine the complex shear modulus (G*) and the phase angle (δ) of the asphalt binder at high and intermediate service temperatures. The asphalt control was repeatedly sheared in the DSR, and the resistance of binder to deformation is expressed in terms of a complex modulus. The phase angle δ must also be determined because it is possible for two asphalt binders to have the same numerical complex modulus, yet exhibit different amounts of elastic and viscous behaviour.

The rutting parameter, G*/sinδ indicates the permanent deformation resistance of asphalt binder. A high complex modulus (G*) and low phase angle (δ) benefit the high temperature performance of the asphalt binder, which reduces the high temperature flow deformation and increases the resistance to the permanent deformation visible in rutting. As a result of properties listed above, superpaving imposes requirements on G* and δ. The rutting parameter, G*/sinδ, is required to be a minimum of 1 kPa for

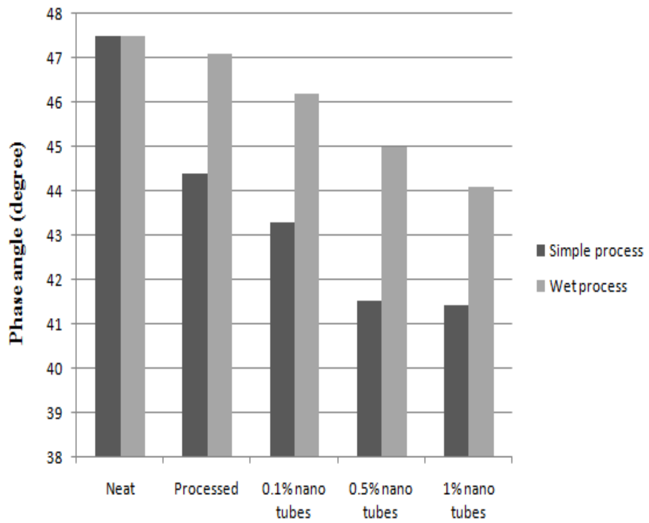



**Fig. 9.** δ Values at 60℃ as Function of CNT Dosage.

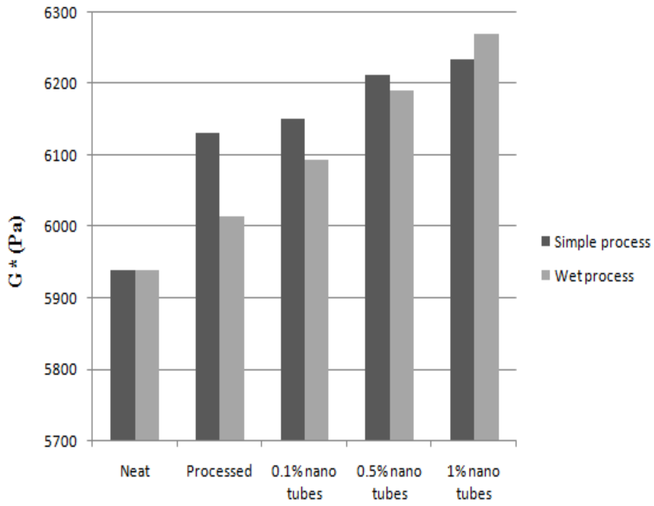



**Fig. 10.** G* Values at 60℃ as Function of CNT Dosage.

original binder and 2.2 kPa for rolling thin film oven (RTFO) aged binder. And according to requirements, the asphalt binder can reach a critical temperature used to divide asphalt to different grades. The higher the critical temperature, the stronger the resistance to high temperature flow deformation. Therefore, according to the test value of the rutting parameters (G*/sinδ) at the same temperature, the high temperature performance of CNT-asphalt binder can be evaluated.

As illustrated in Figs. 9 and 10, by increasing carbon nanotubes, phase angle will decrease and G* will increase much more for both simple and wet processed specimens. The higher the G* value, the stiffer the asphalt binder is (able to resist deformation), and the lower the δ value, the greater the elastic portion of G* is (able to recover its original shape after being deformed by a load).

Fig. 11 shows that when the test temperature remained invariable, the value of (G*/sinδ) also increased remarkably with the increase of nanotubes content. It indicates that the addition of CNTs resulted in the improvement of asphalt binder's high temperature stability, and as a result led to asphalt pavement more resistant to rutting phenomena. It is obvious that regardless of mixing procedure, (G*/sinδ) increases with the increase in CNT content. However, the rate of increase is a function of mixing procedure. The simple process of CNT mixing yielded to a higher rate of increase in (G*/sinδ) relative to the wet process of mixing. 1% CNTs modified specimens in comparison with neat bitumen show an increase of 11.8% for wet procedure and 17% for simple procedure. These improvements indicate high resistance to rutting for CNF modified asphalt binders. But in order to investigate the effect of CNTs modification on the rise of (G*/sinδ), modified binder should be compared with the processed one. In such circumstances when 1% CNT is used, the wet processed CNT-modified binder exhibited improvements up to 9.7% with respect to wet processed AC. On the other hand, simple processed CNT-modified binder showed only a 7.5% increase in the G*/sinδ values relative to simple processed AC. The higher improvement using the wet processes was mainly due to the even dispersion of CNT using the sonication techniques followed by the higher shear mixing.

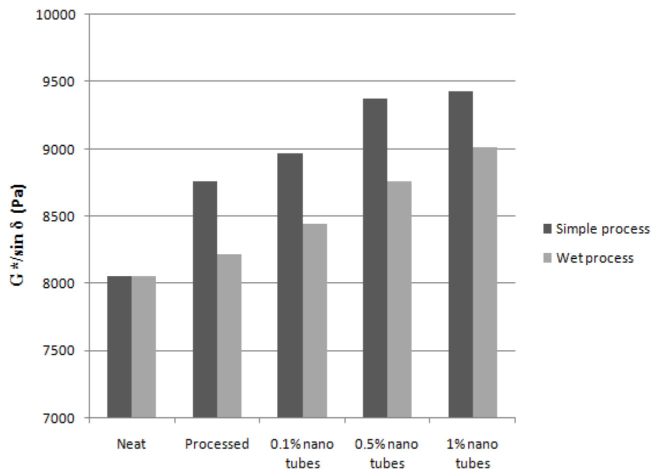



**Fig. 11.** G*/sinδ Values at 60℃ as Function of CNT Dosage.

## Conclusion

This study provides experimental analyses for mixing methods and various properties of CNT modified AC binders. The results obtained in the experimental study indicate that CNTs may considerably affect visco-elastic properties of bituminous binders if added to base asphalt binder with adequately high percentages (at least 0.5% by weight in the case of materials considered in this study). The recent laboratory procedure has presented the proof of the concept indicating that the homogenous dispersion of CNT makes good visco-elastic properties of CNT-modified AC binders. However, the mixing procedure has some limitations and challenges such as using a high amount of solvent to disperse a small amount of CNTs as well as the capability to be applied in the industrial scale. What seems to be considerable is identifying mixing and compaction temperatures, which may be higher than those generally applied for neat binders. This is a result of the viscosity increase produced by dispersed CNTs. In such a case, boundaries of the CNT dosage may be essential. Also, the chemical impact of solvent on the AC characteristics and the effect of CNT modification on the mechanistic features of HMA need to be investigated. Based on the experimental test results, the following conclusions can be drawn:

- As it was shown in FE-SEM pictures, wet procedure was a more efficient technique to mix CNTs in asphalt binder and make a uniform CNT-asphalt binder matrix.
- Wet processed modified asphalt binder showed better property improvement in penetration degree and ductility tests, while simple processed asphalt binder showed better improvement in softening point, viscosity, and dynamic shear rheometer tests.
- Despite the better dispersion of CNTs in wet mixing method, it was seen that simple process modified binder had higher improvement of $G^*/\sin\delta$ parameter. This was due to the lack of solvent in simple mixing method.
- Based on the laboratory tests, samples containing 1% and 0.5% carbon nanotubes by weight of asphalt binder, respectively, lead to more improvement of $G^*/\sin\delta$ parameter for both mixing methods; as result, permanent deformation resistance increased at higher CNTs contents.
- Although the wet process improves dispersion of CNTs aggregate, the simple process is more acceptable for large scale construction since wet process is more expensive and complicated than simple process.

Finally, more efforts are needed to generalize these results and understand the process by which modifying effects are obtained. Moreover, other specific aspects of binder behavior should be investigated, using the evaluation of a cost-benefit analysis in order to encourage applying at the industrial scale.

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