Evaluation of Different Conditions on The Mixing Bitumen and Carbon Nano-Tubes

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Abstract—Asphalt has been widely used for pavements building for long time. Actually, the increase in traffic loading and in the number of vehicles together with the adverse environmental conditions, conduce to a rapid structural damage of pavements. In order to enhance the mechanical properties and the long time behavior, a new generation of blend asphaltic has been developed through the incorporation of different kind of polymers. Nano-reinforced materials hold the potential to redefine the field of transportation materials both in terms of cost effectiveness and long term pavement performance. This study focuses on the exploratory analysis of the mixing procedure of carbon nanotubes (CNTs) with asphalt cement (AC). In this paper, the impact of different mixers on the mixture conditions of asphalt and carbon nano tube is investigated. CNT, having three percent of asphalt weight, and asphalt are mixed together by using mechanical, high shear and ultrasonic mixer, and then examined by a scanning electronic microscope. According to the pictures of different samples, the ultrasonic mixer creates the best form of asphalt and CNT mixture.

Index Term—Bitumen, Carbon Nano Tube (CNT), mixing, Scanning Electronic Microscope (SEM), Ultrasonic Mixer

1. INTRODUCTION

Asphalt has been widely used for pavements building for a long time. Actually, the increase in traffic loading and the number of vehicles together with the adverse environmental conditions, conduce to a rapid structural damage to pavements. In order to enhance the mechanical properties and the long time behavior, a new generation of blend asphaltic has been developed through the incorporation of different kinds of polymers [1–6]. The application of nanotechnology in various applied fields is receiving widespread attention. It is important to ensure that these applications address real questions to allow the technology to improve general well-being of the public, especially while evaluating application in the area of civil engineering [7]. Nanoreinforced materials hold the potential to redefine the field of traditional materials both in terms of performance and potential applications [8–13]. Hussain et al. [9] showed that the biggest challenge in developing nanocomposite is the dispersion of nanoparticles or chemical compatibility with matrix materials. They found out that the issue of improving the carbon nanofibers (CNFs)/matrix interfacial adhesion and complete dispersion must be resolved before achieving the full potential of nanoreinforced composite materials. Dispersion of nano-fibers has been one of the biggest challenges due to the aggregation of the nanofibers. Carbon nanotubes (CNTs) are considered to be one of the most beneficial nano-reinforcement materials. The combination of high aspect ratio, small size, low density, and unique physical and chemical properties makes them perfect candidates for reinforcement in multifunctional and smart cement-based materials. CNTs can be Structurally approximated to “rolled-up” sheets of graphite (Fig.1). In this graphite, sp2 hybridization occurs, where each carbon atom is evenly connected to the other three carbon atoms (120°) in the xy plane, and a weak π bond is present in the z axis. The sp2 set forms the hexagonal (honeycomb) lattice of a graphite sheet [14–16].

Nano clay modification improves some characteristics of asphalt binders and asphalt mixtures such as rutting. However, it has not mitigated the fatigue problem and hence, more research is required before it can be utilized on a large scale [18]. Research has shown that nanocalcium carbonate (nano-CaCO3) modified asphalt [19, 20] can enhance asphalt rutting resistance and improve its low-temperature toughness. Nanoclays such as sodium montmorillonite and organophilic montmorillonite have shown improvements in viscosity, complex shear modulus and phase angles of styrene–butadiene–styrene (SBS) copolymer modified asphalt [21]. Varieties of CNTs include single-walled nanotubes (SWNTs) and multi-walled nanotubes (MWN Ts). SWNTs only have one wall that constitutes a tube, whereas MWN Ts are made up of multiple walls that can slide against each other. The diameters of CNTs range from just a few nanometers in the case of SWNTs to several tens of nanometers for MWN Ts. The lengths of the tubes are usually in the micrometer range [14].

Fig. 1. The structure of CNTs [17].
This paper focuses on the mixing conditions of CNT with asphalt and the effect of various mixers on the CNF mixing with asphalt cement (AC).

2. MATERIAL AND METHODS

In the first stage, multi wall carbon nanotube, which its weight proportion to asphalt is three percent, and asphalt are mixed together. This mixture is divided into three smaller mixtures (samples). Each sample is mixed by using a different mixer and in different conditions. These mixers are mechanical, high shear and ultrasonic mixers.

| TABLE I
CHARACTERISTICS OF THE USED BITUMEN |
<table>
<thead>
<tr>
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</tr>
</thead>
<tbody>
<tr>
<td>Ductility (cm)</td>
<td>Softening point (°C)</td>
<td>Penetration at 25 °C (0.1mm)</td>
<td>Pure bitumen</td>
</tr>
<tr>
<td>Over 100</td>
<td>51</td>
<td>68</td>
<td>60/70</td>
</tr>
</tbody>
</table>

| TABLE II
CHARACTERISTICS OF THE USED CNT |
<table>
<thead>
<tr>
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</thead>
<tbody>
<tr>
<td>length</td>
<td>purity</td>
<td>ash</td>
</tr>
<tr>
<td>30 µm</td>
<td>&gt; 95%</td>
<td>&lt; 1.5%</td>
</tr>
<tr>
<td>SSA</td>
<td>Density</td>
<td></td>
</tr>
<tr>
<td>200 m²/gr</td>
<td>2.1 gr/cm²</td>
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Then, according to the capabilities of each mixer, which has a different performance of mixing materials, the combination conditions are considered different for each of them. Therefore, each mixer has its own specifications. For example, due to the constant combination rate of a mechanical mixer, its combination time is considered as a variable. The rotation rate and the power of the mixer are supposed to be variables for high shear and ultrasonic mixers, respectively.

2.1. Mechanical mixer

The mechanical mixers are often used in metallurgical and mechanical laboratories. This kind of mixer is used to mix several dry powder materials or combine solutions easily mixed together or solve a solid material in a solution. The mixer is used considering its time parameter a variable, while its motor rotation is constant in each minute. In other words, since the motor rotation is constant, the materials must be mixed as long as a homogenized mix is obtained. One should of course note that the time of mixing depends on the type of matured materials and the operator's opinion.

Fig. 2. The mixers which are used to mix asphalt and carbon nano tube (from right to left: mechanical mixer, high shear mixer and ultrasonic mixer [22, 23])

Fig. 3. Three kinds of mechanical mixer
2.2. High shear mixer
High shear mixers are of the most applicable mixers which are used in mixing asphalt and polymer. It is used to mix asphalt with polymers and other additives. Rotation rate of the mixer’s tip can be determined based on the kind of the polymer. This mixer is used in mixing asphalt and polymer because of the special structure of its tip. In fact, the special design of mixer tip makes the mixture enter and move rapidly through the space between two very close plates and leaves it through the space between embedded slots in outer layer. This procedure results in making the mixture of asphalt and polymer more homogeneous.

![Fig. 4. Quality of performance of high shear mixer [24]](image)

2.3. Ultrasonic mixer
The term of ultrasonic waves is used for mechanical waves whose oscillation frequencies are more than the upper limit of human’s hearing frequency range (20 Hz to 20 KHz). Performing a simple calculation, it can be found out that if a point oscillates with the frequency and amplitude of 25 KHz and 10 μm, respectively, its acceleration will be 25000 times as large as that of gravity. Such acceleration and, consequently, a high speed in liquids will result in cavitation and then, some bulbs with the pressure of about 200 bars and the temperature about 5000 K are formed during explosion. On the other hand, if a relative movement with above specifications forms between two solid surfaces, the resultant temperature increase makes these surfaces weld together, called “ultrasonic welding”. The applications of ultrasonic technology can include accelerating chemical reactions, increasing fuel efficiency, water purification, cell wall breaking and disinfection, combining nano particles with water and other solutions homogeneously and so on. In fact, this apparatus produces a huge amount of energy by creating ultrasonic waves and cavitation which can combine the mixture and also separate nano particles from each other and finally, make a completely homogeneous mixture.

![Fig. 5. Different parts of an ultrasonic mixer and quality of its performance [25].](image)

3. Providing samples
As previously mentioned, it is necessary to determine how the materials should be combined together. That is why, in this test, three different kinds of mixers, with different conditions considered for each of them, are used to mix CNT with asphalt. Then, after sampling the mixture, these samples must be tested by using a scanning electronic microscope to determine the combination conditions of asphalt and CNT and also the quality of dispersion of nano materials in nano scale.

![Fig. 6. The use of ultrasonic mixer in providing samples mixed with nano materials](image)

After providing samples according to graph 1 (different forms of mixture by using different mixers), all samples were tested by using a scanning electronic microscope to examine the quality of asphalt and nano material combination. It should be noted that the samples, before placing under the scanning electronic microscope, were placed in a vacuum reservoir and then covered with a thin layer of gold.

![Fig. 7. Part of provided samples after mixing by using the ultrasonic mixer in different mixing conditions (right: samples provided for element analysis Left: samples provided for delivering to scanning electronic microscope)](image)
Generally, the following points must be applied to observe the provided samples under the scanning electronic microscope.

Size: size limitation is determined by the design of scanning electronic microscopes. The samples whose sizes are 15 to 20 can be usually tested without sample movement.

Providing samples: Non-conductive materials are often covered with a thin layer of carbon, gold or gold alloy. It is necessary to make an electronic connection between sample and base and spread the fine samples, like powders, on a conductor film, like aluminum paint, and dry it completely. The samples must be free of any liquid with high vapor pressure like water, organic detergent solutions and residual oil films.

![Image of Asphalt sample](https://via.placeholder.com/150)

**Fig. 8.** Asphalt sample, before (right) and after (left) preparation for placing under the microscope (left sample: placement of sample in vacuum reservoir and covering with gold)

4. **RESULTS ANALYSIS**

The provided samples, with different mixers and in different conditions, are placed under the microscope to examine mixture conditions of asphalt and nano materials. Generally, these samples, based on the mixer type, could be categorized to three groups. The effect of mix by each mixer on the quality of dispersion of nano materials was absolutely apparent. Thus, the samples must be examined separately.

4.1. **Mechanical mixer**

Similar results were observed in almost all samples mixed by the mechanical mixer. While there was a concentration of nano materials in some parts of samples (Fig. 9, parts A, B, D), there was almost no nano materials concentration in some other samples (Fig. 9, part C). The concentration of nano materials indicates that the mechanical mixer is unable to separate nano materials from each other. Therefore, these materials were interlaced (Fig. 9, part D). In such conditions, there were some concentrated micro materials instead of nano dispersion. This indicates that the use of the mechanical mixers, to mix nano materials, leads to forming a heterogeneous mixture based on the materials dispersion in asphalt. In addition, it cannot prevent nano materials from becoming agglomerated.

![Image of Samples Mixed with Nano Materials](https://via.placeholder.com/150)

**Fig. 9.** Microscopic picture of samples mixed with nano materials by using a mechanical Mixer (heterogeneous dispersion of nano materials and agglomeration of nano materials)
4.2. High shear mixer

High shear mixer combined and provided the samples with three different angular velocities. First, asphalt and CNT were mixed by the mixer with the angular velocities of 1000, 1500 and 2000 rpm for 15 minutes at 120°C and then, the mixture were sampled. In contrast to the provided samples by the mechanical mixer, the dispersion of nano materials in the whole sample mixed by the high shear mixer (Fig. 10, parts A, B) was homogeneous. But unfortunately, this mixer, like the previous one, could not disperse nano materials in nano scale and these materials were dispersed in micro scale. Therefore, agglomeration of nano materials in the sample was observed (Fig. 10, part C, D).

High shear mixer is used to homogeneously mix asphalt and additive due to its nature and designed shape which combines the materials with high speed and pressure between two near plates (That is why it is used to mix asphalt and polymer). It should be noted that the materials used in this test are in nano scale. Consequently, they normally become agglomerated and approach micro scale. Therefore, this mixer cannot separate these nano materials from each other. Based on the observed samples under the scanning electronic microscope, it is clearly concluded that the high shear mixers are not capable of separating nano materials from each other. One should of course note that since this problem has been caused in the case of CNT, other nano materials may not encounter this problem. Thus, they would be considered useful for mixing with asphalt.

Fig. 10. microscopic picture of samples mixed with nano by using a high shear mixer (homogeneous dispersion of nano materials and their agglomeration)

4.3. Ultrasonic mixer

The samples mixed by an ultrasonic mixer are generally categorized into three groups. The samples provided with the power of 60 watt for 10 and 15 minutes and the one provided with the power of 65 watt for 15 minutes at 12°C are placed under the scanning electronic microscope. For these samples, and particularly for the sample provided with the power of 65 watt for 15 minutes, nano materials are observed homogeneously and separately dispersed in asphalt (without agglomeration) (Fig. 11, part A,B). Also, as it can be seen in Fig. 11, CNT particles are separated from each other and easily recognizable.
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carbon nanotube and bitumen.
percentage of carbon
composition as the second reagent to the reaction medium
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material
conducted on the present samples based upon
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employed
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data based on the percentage of these elements can be
hydrogen and nitrogen
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composition of elements and then
synthetic materials
Elemental analysis is a process during which the natural and
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are analyzed
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elements
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determine which
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does not without reaction with tar and bitumen to create a
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reason for
this test. Since appropriate conditions of
combination of asphalt and nano materials must be provided
to make a modified asphalt with CNT, three kinds of mixers and three mixture conditions for each mixer were considered.
Observing the samples obtained from nano materials and
asphalt combination under the scanning electronic microscope indicates that a mechanical mixer is not useful for mixing
these nano materials, because it not only cannot separate nano
materials from each other, but also cannot homogeneously
disperse this material in the asphalt samples.
High shear mixer, because of the type of the mixture, can
homogeneously disperse nano materials in asphalt, but like
mechanical mixer, it cannot separate the agglomerated nano
carbon tubes from each other.
In spite of two previous mixers, the ultrasonic mixer can make
a homogeneous mixture and separate nano particles from each
other. This is because of its capability in creating cavitations and producing energy throughout ultrasonic waves.
Samples elemental analysis shows that combining carbon
nanotubes with bitumen to increase the percentage of carbon
combined with carbon nanotube-based bitumen is typical. The
reason for this statement is that carbon nanotube as an additive
is not without reaction with tar and bitumen to create a
chemical reaction occurs with this material.

6. CONCLUSION
Polymeric and non-polymeric materials are used to improve
the characteristics of asphalt and its mixtures and consequently, to increase and improve their life and
performance. CNT, as a new material possessing some unique characteristics and having a similar molecular structure to
asphalt, was used in this test. Since appropriate conditions of
combination of asphalt and nano materials must be provided
to make a modified asphalt with CNT, three kinds of mixers and three mixture conditions for each mixer were considered.

5. ELEMENT ANALYSIS
Elemental analysis is a process during which the natural and
synthetic materials are analyzed to identify the isotopic
composition of elements and then to determine which analyzes
are available. The most common type of elemental analysis is
CHN method that is based on the percentage of the carbon, hydrogen and nitrogen elements in organic compounds. The
data based on the percentage of these elements can be employed as an approach to identify the structure and purity of
the used synthesized compounds. CHN elemental analysis was
conducted on the present samples based upon the percentage of carbon. This percent was reported 84/95 % in the raw
material. This high amount of carbon confirms it as the main
element in Bitumen. After adding carbon nano-tube composition as the second reagent to the reaction medium, the
percentage of carbon was increased to 85/72% and 85/24%.
This increase shows the formation of covalent bond between
carbon nanotube and bitumen. This bond is indicative of π-σ
bond with carbon bitumen and π-π between carbon nanotube
walls. This point shows that not only is the carbon nano-tube
an add-on to bitumen, but also it is capable of reacting to
bitumen molecules. As a result, final composition is not a
physical one.

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AhmadGoli
- PhD Student in Civil Engineering, Transportation Engineering.
- PhD Thesis title: Laboratory analysis of HMA mixes characteristics modified with Carbon Nano Tube (CNT).
- Extensive experience in preparing different test specimens and performing experimental tests to characterize the performance of different types of modified asphalt and use of CNT in other technology. In this research analysis of HMA mixes characteristics modified with Carbon Nano Tube (CNT).
- Research interests:
  - Bitumen modifier with different polymers
  - Mechanical and performance properties of asphalt concretes