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Effect of Functionalization and Mixing Process on the Rheological Properties of Asphalt Modified with Carbon Nanotubes

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Abstract The aim of this paper is to investigate the rheological properties of conventional asphalt modified with Multi- Walled Carbon Nano Tubes (MWCNTs). Pristine MWCNTs were chemically modified using acid functionalization process to introduce carboxylic acid groups onto the surface of MWCNTs. The pristine and functionalized MWCNTs were then characterized by Scanning Electron Microscope (SEM) and electron dispersion X-ray (EDX) analysis. A 3% (by weight of asphalt) of pristine and functionalized MWCNTs were each blended with a base asphalt at 120°C. The properties of the base and modified asphalts were evaluated using softening point, rotational viscometer and dynamic shear rheometer (DSR) for both original and short term aged asphalts using the rolling this film oven (RTFO) test. The results indicated that the use of MWCNTs as a modifier was helpful in improving the conventional and rheological properties of the asphalt. Generally, it was found that the softening point, as well as the rotational viscosity, were increased and the temperature susceptibility was improved. The results showed a remarkable improvement in the binder complex shear modulus, failure temperature, and rutting resistance. The rheological properties of the asphalt modified with pristine MWCNTs were better than the functionalized MWCNTs. Finally, the effect of mixing technique (high shear mixer and a manufactured mechanical mixer) of MWCNTs with asphalt was evaluated. Results showed that both mixers yielded similar properties based on the rotational viscosity testing.

Keywords: *CNTs, MWCNTs, DSR, RTFO, modified asphalt, rutting*

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1. Introduction

Over the last decades, there have been a variety of asphalt modifiers such as synthetic polymers, natural and crumb rubber used to improve asphalt physical and rheological properties. Recently, many researchers are interested in studying what nanotechnology can offer in improving characteristics and performance of asphalt pavement [1]. Nanotechnology is a relatively new science, which aims at understanding and controlling individual atoms and molecules (from 1 nm to 100 nm). One nanometer (nm) is a billionth of a meter (1 m = 10^9 nm). Thus it includes scanning, measuring, modeling, and manipulating matter at the nano-scale [2]. Nanoparticle is a particle that has at least one dimension (height, length or depth) less than 100 nm [3].

There are many types of nano-materials that are widely used in the modification of asphalt such as nanoclay, nano titanium oxide, nano silicon dioxide, nano zinc oxide, carbon nano fibers and nano- hydrated lime. Nanoclay is the most commonly used nano material for asphalt modification [4]. Some Studies concluded that nanoclay is a worthy material for asphalt modification because it improved asphalt performance [5,6,7]. Generally, using nanoclay leads to positive effect on the asphalt penetration, ductility and softening point, as well as increasing aging resistance. However, for low temperature cracking, the original asphalt yielded better performance compared to the nanoclay modified asphalt [6].

Many researchers have started to investigate and implement the use of carbon nanotubes (CNTs) in reinforcing concrete but only very few and limited research studies were conducted on carbon nanotubes (CNTs) as an asphalt modifier. Thus, research studies are still required in the area of carbon nanotubes modified asphalt before it can be applied on a large scale.

2. Literature Review

Carbon nanotubes look like long hollow cylinders of graphene (hexagonal rings of carbon atoms) sheets, which have a diameter ranging from 1 nm up to 50 nm as shown in Figure 1. They were discovered in 1991 by Sumio

Iijima who characterized them by High-Resolution Transmission Electron Microscope (TEM) [8].

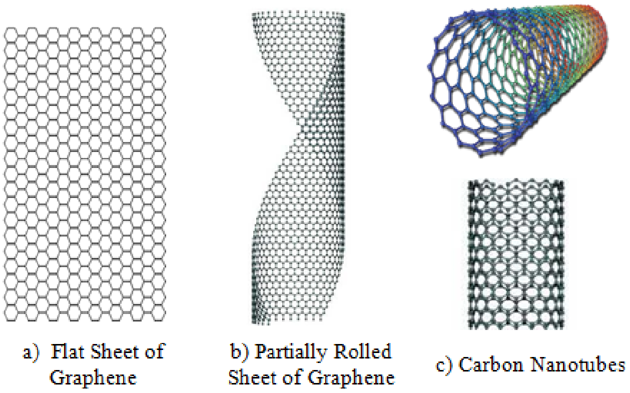


Figure 1. Schematic of a Graphene Sheet and Carbon Nanotubes [9,10]

There are many techniques to produce carbon nanotubes; however the three most commonly used techniques are: arc discharge, laser ablation and chemical vapor deposition (CVD). Based on the number of graphene sheets, CNTs are divided into single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). SWCNTs have a diameter ranging from 0.4 to 12 nm [11,12]. MWCNTs consist of multi rolled layers of graphene inserted one into the other. The number of graphene walls may reach more than 25 walls with spacing of 0.34 nm [13].

CNTs have Young's modulus greater than 1 TPa, tensile strength of 10 to 100 times that of steel while only having 16% of the steel density, making it the strongest and stiffest material on earth [14]. Because of CNTs outstanding mechanical properties shown in Table 1, they are expected to improve asphalt properties better than traditional modifiers and other nano reinforcing materials.

Table 1. Mechanical Properties of Carbon Nanotubes [15]

Material	Young's modulus (GPa)	Tensile strength (GPa)	Density (g/cm3)
MWCNT*	1200	150	2.6
SWCNT**	1054	75	1.3
Steel	208	0.4	7.8

As a material modification, MWCNTs is better than SWCNTs as it is stiffer, easier, and cheaper to produce on a large scale [16].

The most common use of CNTs is to disperse it in other material to promote its mechanical characteristics. However CNTs have strong cohesive forces (Van Der Waals forces) and easily bundle together when added to composite, causing defect sites in the composite where CNTs will be few or missing [17]. Thus a homogeneous dispersion of CNTs into the modified material is considered a big challenge in the area of carbon nanotube application. Therefore, some of the research studies conducted in the area of CNTs modified asphalt mainly focused on how the dispersion quality of CNTs in asphalt matrix or the properties of CNTs modified asphalt were affected by the CNTs mixing technique. Hasan et al., investigated the effect of mixing CNTs with asphalt using different procedures on dispersion efficiency in asphalt matrix [1]. A 3.0% of CNTs was blended with asphalt using three different types of mixers and each mixer used three different conditions of mixing according to the capability of each mixer. The used mixers were mechanical stirrer, high shear, and ultrasonic mixers. Modified samples were examined by Scanning Electron Microscope (SEM). SEM images showed that ultrasonic mixer yielded the best results as the CNTs were uniformly distributed and separated in asphalt without any agglomeration. High shear mixer and mechanical stirrer separated CNTs in micro scale but high shear mixer yielded more homogeneous asphalt than mechanical stirrer which produced different concentration of CNTs on asphalt surface. The study did not give a detailed information about mixers characteristics and mixing steps. For example, high shear mixing time, mechanical stirrer rotational rate and mixing temperature for all mixers which surely affecting on the quality of dispersion were not presented in the study. Santagata et al., investigated the effect of two different mixing techniques on the fatigue properties of binder reinforced with 0.5% and 1.0% of carbon nanotubes [18]. The first technique was the simple shear mixing through a mechanical stirrer with 1550 rpm for 90 min at 150ºC. The second technique, included first method followed by additional sonication phase (frequency 24 kHz and 200 W output power) to improve CNTs dispersion. Two different sonication times (30 and 60 min.) were adopted to determine the best mixing method. A Dynamic Shear Rheometer (DSR) stress controlled mode was used for fatigue analysis. Results indicated that blending technique and percentage of carbon nanotubes affected the asphalt fatigue life. Shear mixing plus sonication showed a significant increase in fatigue resistance than simple shear mixing technique only. Moreover, increasing sonication time improved asphalt fatigue response. Faramarzi et al., evaluated the effect of mixing techniques on dispersion quality of MWCNTs in asphalt matrix [3]. Three percentages of MWCNTs (0.1%, 0.5% and 1.0% by asphalt weight) were blended with asphalt using two different mixing techniques. First method called simple shear mixing process which used a mechanical stirrer with 1550 rpm at 160ºC for 40 minutes. Second method known as wet process using sonication process and high shear mixing. Wet process was divided in to two parts. Firstly, MWCNTs were dispersed in kerosene solvent then sonicated with a power of 240 watts at 50% pulse rate for 25 minutes along with using high shear mixer for 2 minutes at 2500 rpm. Secondly, using low shear mixer to evaporate the solvent at 160ºC and time depended on MWCNTs percentage in modified asphalt. Results showed that wet mixing process had better uniform dispersion of carbon nanotubes in asphalt matrix than simple shear mixing process. However, it had a negative effect on most of the mechanical and rheological properties of asphalt due to the use of kerosene solvent with asphalt. In addition, the wet mixing process is more complicated and not feasible from the economical point of view. As just presented, these studies focused on using different types of mixers or using solution mixing. Chemical treatment of CNTs surface is a technique used for improving the efficiency of dispersion between the CNTs and some polymers [19]. Thus, chemical surface treatment of CNTs (functionalization) may help in improving the dispersion efficiency of CNTs in asphalt thus enhancing the rheological properties of the modified asphalt.

3. Objectives and Scope

This study aims at evaluating and quantifying the properties of asphalt binder modified with MWCNTs. The specific objectives are to:

- Conduct chemical treatment of MWCNTs surface (Acid Functionalization).
- Compare between the effect of both pristine and functionalized MWCNTs on the routine and rheological properties of modified asphalt binders.
- Compare the mixing efficiency of a manufactured mechanical stirrer and the high shear mixer.

In this study, the experimental work was divided into three parts. The first part focused on the surface chemical treatment of MWCNTs. The second part focused on evaluating the performance of original and 3.0% modified asphalt with both pristine (P-MWCNTs) and functionalized Carbon Nanotubes (MWCNTs-COOH). The third part evaluated the effect of the mixing technique on the properties of modified asphalt binder. Figure 2 shows the outline of the conducted laboratory work.

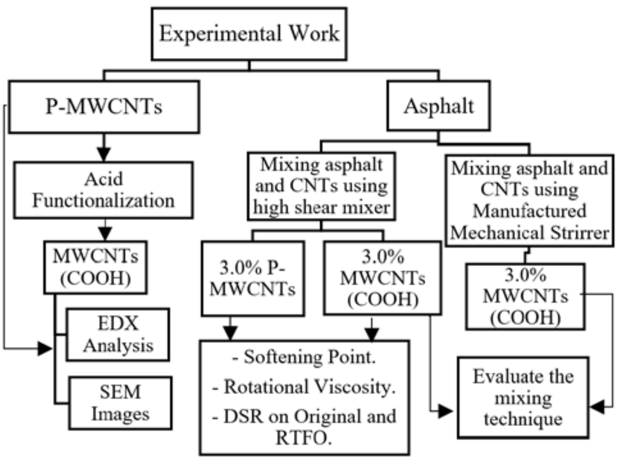


Figure 2. Experimental Program Outline

4. Materials

A base asphalt 60/70 penetration grade obtained from Al-Nasr Petroleum Company in Suez, Egypt was used in this study. The basic properties of the asphalt were determined in the laboratory and summarized in Table 2. MWCNTs purchased from the US Research Nanomaterials, Inc was used as the binder modifier. The main characteristics of MWCNTs, according to the manufacturer's sheets are listed in Table 3.

Table 2. Properties of Original Asphalt

Test	Result	Standard Test Method	Specification
Penetration at 25 °C (0.1 mm)	63	ASTM D5 / D5M - 13	60-70
Softening Point (°C)	42.4	ASTM D36 / D36M - 14	45-55
Viscosity at 135°C, (cP)	434.35	ASTM D4402 / D4402M - 12	-----
G*/sin δ at 67.6 °C, (kPa)	1.0	AASHTO T 315-12	-----

Table 3. Properties of MWCNTs According to the Manufacturer Characteristics

Property	Unit	Value
Purity	%	> 90 wt.% (carbon nanotubes)
Outside diameter	nm	10-30
Inside diameter	nm	5-10
Length	μm	10-30
Density	g/cm^3	2.1
Special Surface Area	m^2/g	> 200
Manufacturing method	Chemical Vapor Deposition (CVD)	

5. Laboratory Testing, Results, and Analysis

Chemical treatment of the MWCNTs was first performed. The pristine and functionalized MWCNTs were then characterized by Scanning Electron Microscope (SEM) and Electron Dispersion X-ray (EDX) analysis. Both MWCNTs were mixed with a 60-70 pen grade asphalt at 120 °C using two different mixers. The properties of the base asphalt and modified asphalts were evaluated using softening point, rotational viscosity and dynamic shear rheometer (DSR) at original and short term aging conditions.

5.1. Chemical Treatment of the MWCNTs

As mentioned before, agglomeration of CNTs is one of the drawbacks of using CNTs as a modification material. The surface of CNTs can be chemically modified to improve the compatibility of CNT and asphalt. This stage is defined as functionalization of the CNTs which means the formation of functional groups on the surface of the CNTs such as –OH, –NH3, –BR and –COOH [17]. This is shown in Figure 3. Different methods can be used to functionalize the surface of CNTs [22]. In this paper, the acid treatment technique using refluxing process to oxidize the surface and increase the concentration of carboxyl functional groups (-COOH) was tried.

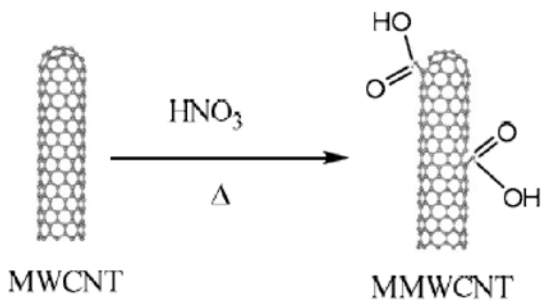


Figure 3. Chemical Modification of Carbon Nanotubes Surface (Functionalization) [23]

Acid functionalization process of MWCNTs was performed through three stages. Firstly, 10 gm of pristine multi-walled carbon nanotubes (P-MWCNTs) was refluxed in 100 ml 65% nitric acid and 30 ml sulfuric acid on bottom flask for 4 hours as shown in Figure 4. During refluxing period, the sulfuric acid (H_2SO_4) creates some defect sites on the surface of carbon nanotubes and nitric acid (HNO_3) oxidizes these sites by providing a functional group (Carboxylic group) [24]. Subsequently, the carbon was filtered off, placed in a filter with a 3 µm pore size and washed using deionized water multiple times until the pH of the washing water reached a value between 6 and 7, which is the pH of the used deionized water. The carbon was dried overnight under ambient conditions and then for 24 hours at 110°C. The functionalized carbon nanotubes are designated MWCNTs (COOH).

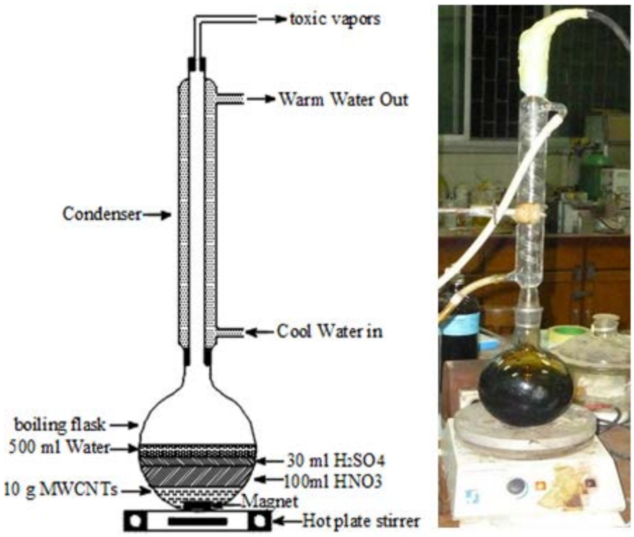


Figure 4. Reflux System used in Functionalization

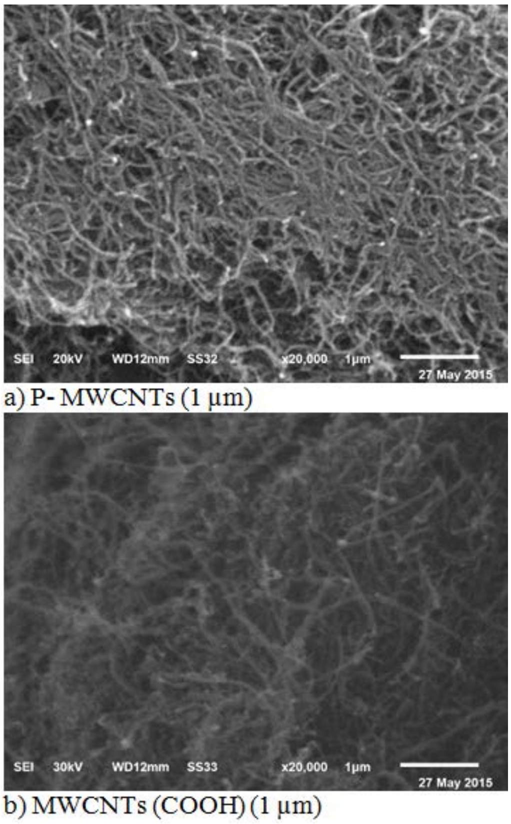


Figure 5. SEM Images of P-MWCNTs and MWCNTs(COOH)

The Scanning Electron Microscope (SEM) was used to investigate the morphology of the P-MWCNTs and functionalized MWCNTs (COOH) at an acceleration voltage of 20kV and 30kV, respectively. The agglomeration of carbon nanotubes bundles was observed but without distinct difference in morphology between P-MWCNTs and MWCNTs (COOH) as shown in Figure 5. The electron dispersion X-ray (EDX) analysis was used to measure the increase of oxygen atoms as a result of acid treatment. The EDX results showed that the functionalized MWCNTs (COOH) have more amount of oxygen atoms compared to P-MWCNTs which proved the occurrence of functional groups on carbon nanotubes surface as shown in Table 4.

Table 4. The Atomic Mass Percentage of Carbon and Oxygen of P-MWCNTs and MWCNTs (COOH).

Sample	Carbon (%)	Oxygen (%)
P- MWCNTs	91.27	8.51
MWCNTs (COOH)	89.97	9.58

5.2. Mixing Carbon Nanotubes with Asphalt

High shear mixer and mechanical stirrer are laboratory tools used for mixing asphalt with additives such as polymers and nanomaterials. In the mechanical stirrer mixing technique, the high speed rotary motion of the stirrer creates a high centrifugal force that helps blending asphalt with additives. The motor rotational speed is constant during the mixing period. The rotational speed depends on the type of additive and the operator's judgement. As for the high shear mixer, the special design of the tip makes the high shear mixer (HSM) different from other mixers. High shear mixers combines between the high degree of shear (speed) and low level of pumping and circulations [20]. High rotational speed pull the materials from the bottom of the vessel to the tip then a centrifugal force drives materials rapidly out through the stator screen in to lower velocity area of the mix. Velocity difference creates a hydraulic shearing force which creates a homogeneously mixed materials [21]. The working stages of HSM are shown in Figure 6.

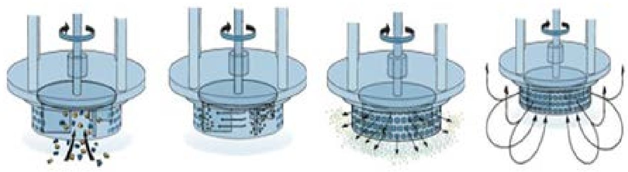


Figure 6. Schematic of Working Stages of HSM [21]

Figure 7. Mixing Asphalt with Carbon Nanotubes using High Shear Mixer

A 3.0 percent of both pristine (P-MWCNTs) and functionalized MWCNTs (MWCNTs (COOH)) by weight of asphalt were blended with fresh base asphalt using a high shear mixer as shown in Figure 7. The asphalt was preheated to 120°C in oven and then a high shear mixer with a speed of 2500 rpm was used for mixing the heated asphalt and the nanomaterial for 1 hour. Time was divided into two phases. First phase (about 30 minutes), MWCNTs were manually added to the asphalt at approximately constant rate (about 0.2 g/minute) while the mixer is running. Second phase, agglomerated MWCNTs were dispersed in the asphalt matrix to reduce the dispersion problem during the operation of the device. During the mixing period, the temperature was kept at 120°C by a hot plate as shown in Figure 7.

The mechanical stirrer is more appropriate than high shear mixer from the industrial viewpoint as it is easier, simpler, and cheaper. Thus, a mechanical stirrer was designed and manufactured for the purpose of blending CNTs with asphalt. The mechanical mixer has an operating speed up to 4,000 rpm and equipped with a tachometer to measure the actual rotational speed of the shaft. The operating time up to 120 minutes can be controlled using a timer and the temperature can reach 300°C. Moreover, the rotational direction of shaft can be reversed. The capacity of the mixer is 2.0 liters. The conceptual design and manufactured mixer are shown in Figure 8.

a) Conceptual Design

b) Manufactured Mixer

Figure 8. Mechanical Mixer

The MWCNTs (COOH) and asphalt were blended using the mechanical stirrer (MS) at a speed of 3000 rpm. The temperature was fixed at 120 °C and the time was set to 60 minutes. The mixing procedure using mechanical stirrer followed the same methodology used with the high shear mixer (HSM). The efficiency of the manufactured mechanical stirrer was evaluated by measuring the rotational viscosity of a 3.0% MWCNTs (COOH) modified asphalt mixed with the two different mixers. The results are illustrated in Figure 9. The results indicate that there was no significant difference between the 3.0% MWCNTs (COOH) modified asphalt viscosity mixed with mechanical mixer at all testing temperatures compared to that mixed with the high shear mixer. Thus one can surmise that there is no significant difference between the efficiency of the manufactured mechanical stirrer and the high shear mixer.

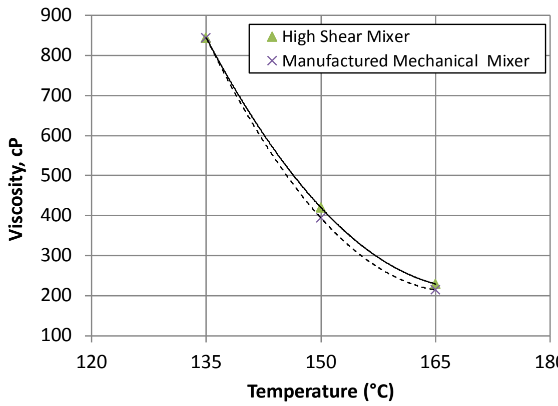


Figure 9. Viscosity of the 3.0% MWCNTs(COOH) Modified Asphalt Mixed with the Manufactured Mechanical Stirrer and a High Shear Mixer

5.3. Control and Modified Asphalts

5.3.1. Softening Point

The Ring and Ball Softening Point test was carried out according to (ASTM D36) [25]. The addition of MWCNTs yielded an increase in the softening point of the modified asphalts compared to the conventional pen 60/70 asphalt as shown in Figure 10. This improvement was expected as the high Young's modulus of carbon nanotubes enhanced the stability of asphalt against flow [26]. However, the improvement was better for the untreated (P-MWCNTs).

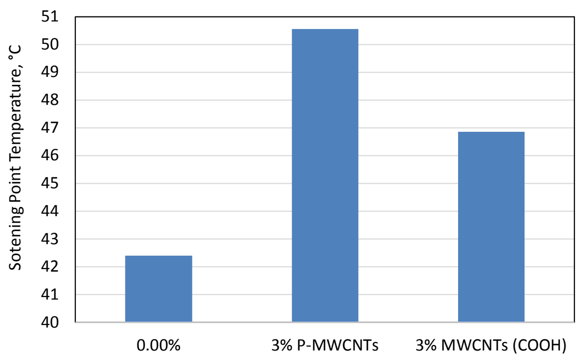


Figure 10. Comparison of Softening Point for Control, 3.0% P-MWCNTs and 3.0% MWCNTs(COOH)

5.3.2. Rotational Viscosity

The Brookfield rotational viscometer (RV) test was used to measure the viscosity difference between unmodified and modified asphalts at three temperatures (135^{o}C, 150^{o}C and 165^{o}C) in accordance with ASTM D4402 [27]. Figure 11 shows that using MWCNTs yielded a significant increase in viscosity at all temperatures. Results indicate that the 3.0% P-MWCNTs modified asphalt yielded the highest viscosity at all temperatures.

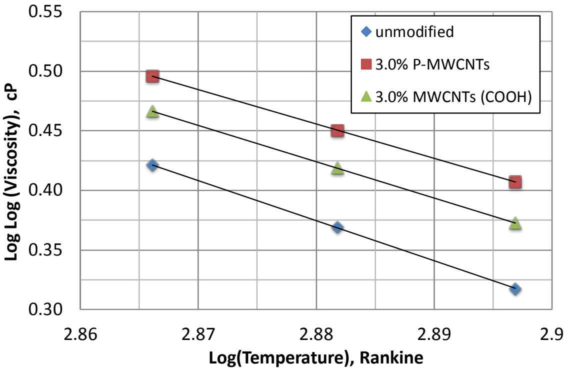


Figure 11. Viscosity Temperature Susceptibility for Control, 3.0% P-MWCNTs and 3.0% MWCNTs (COOH) Modified Asphalts

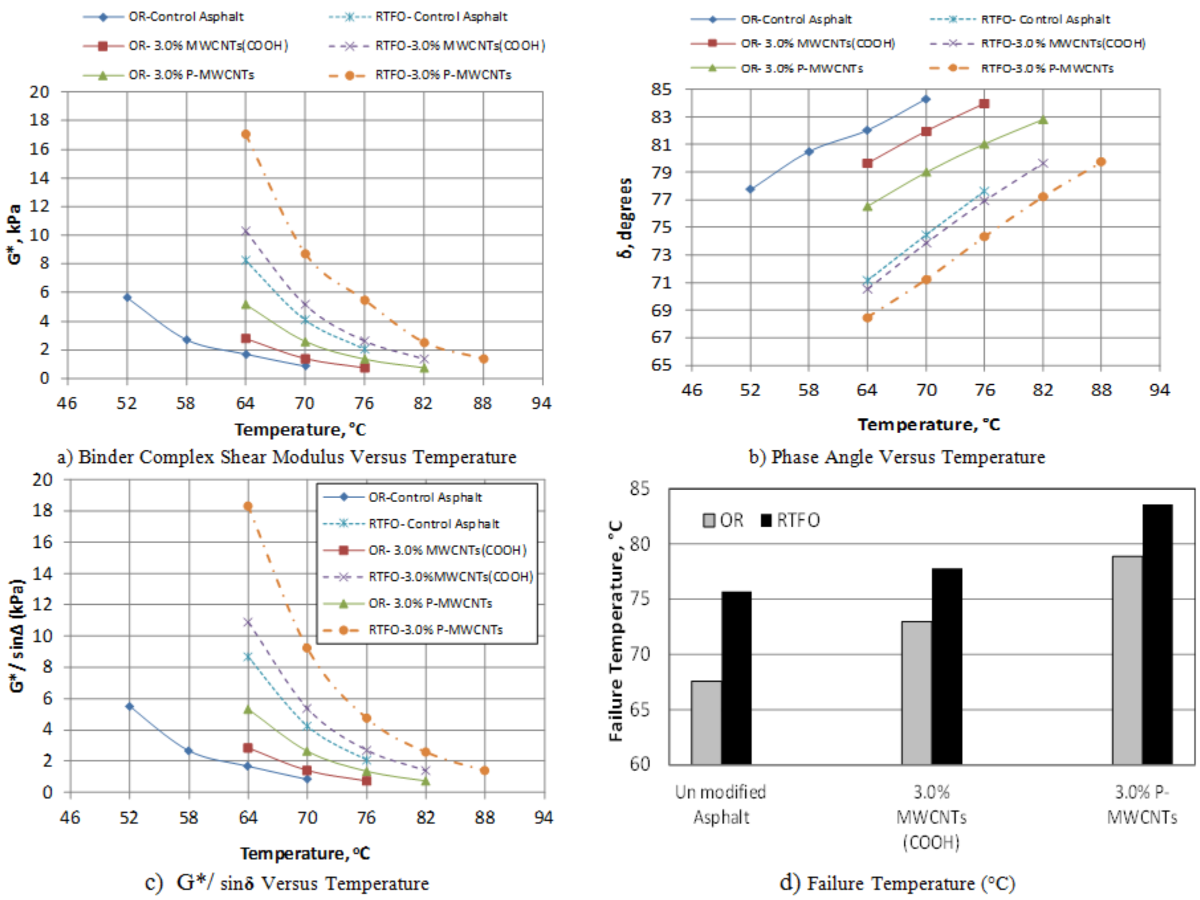
The temperature susceptibility of asphalt is considered as an important property used for evaluating asphalt modifiers. Asphalt with low susceptibility to temperature is required. The Viscosity Temperature Susceptibility (VTS) expresses temperature susceptibility of asphalt, the lower the magnitude of VTS values (the slopes of the regression lines shown in Figure 11), the less susceptible the asphalt is to changes in viscosity with temperature [28]. Table 5 summarizes VTS values for control and modified asphalts arranged in order of decreasing VTS (highest temperature susceptibility to lowest) along with the coefficients of determination (R^2). The VTS values along with Figure 11 showed reduced viscosity temperature susceptibility for the modified asphalts compared to the original asphalt. It should be noted that the functionalized carbon nanotubes showed higher susceptibility compared to the pristine carbon nanotubes.

Table 5. Viscosity Temperature Susceptibility (VTS) Values

Asphalt Type	Control (Unmodified)	3.0% MWCNTs (COOH)	3.0% P-MWCNTs
VTS	-3.363	-3.034	-2.876
R^2	1.0	1.0	0.999

5.3.3. Dynamic Shear Rheometer

The Dynamic Shear Rheometer (DSR) test was performed to measure the asphalt shear modulus (G*) and phase angle (δ) at intermediate and high temperatures according to ASTM D7175 - 08 [29]. DSR tests were conducted on unaged and short term aged samples using the Rolling Thin Film Oven (RTFO) test according to ASTM D2872-12 [30]. For unaged and RTFO aged asphalt, 1 mm thick and 25 mm in diameter samples were used. G* and δ were measured starting from 52°C then the temperature was increased to the next Performance Grade (PG) until sample failure. Once the sample reaches the target temperature, at least 15 minutes equilibrium time was allowed to ensure thermal equilibrium. The target shear strain values were 12% and 10% for the original and RTFO samples, respectively. Three replicates were tested for each asphalt binder. DSR oscillation rate of 10 rad/sec (1.59 Hz) to simulate the shearing action corresponding to a traffic speed of about 90 km/hr was used. Using CNTs led to an increase in G* values before and after asphalt aging which represents a higher resistance to deformation as shown in Figure 12(a).



a) Binder Complex Shear Modulus Versus Temperature

b) Phase Angle Versus Temperature

c) G*/ sinδ Versus Temperature

d) Failure Temperature (°C)

Figure 12. DSR Results for RTFO Control, MWCNTs (COOH) and P-MWCNTs Modified Asphalts

Figure 12(b) illustrates that decreased δ values with the modification making CNTs modified asphalt more elastic than the conventional asphalt which represents a better improvement of asphalt performance. The P-MWCNTs modified asphalt yielded a higher G* and lower δ values compared to MWCNTs-COOH throughout the temperature range.

According to Superpave specifications, G*/sinδ is defined as a rutting factor which represents a measure of the rutting resistance of asphalt binder. To minimize rutting, G*/sinδ must be less than 1.0 kPa for original asphalt binder and 2.2 kPa at high temperatures for RTFO asphalt [31]. As shown in Figure 12(c), adding CNTs to conventional asphalt increased the rutting factor G*/sinδ; thus enhancing pavement resistance to permanent deformation under repeated traffic loads.

The failure temperature for original and RTFO control and modified asphalt were determined through interpolation then the high temperature PG grade was observed. Figure 12 (d) illustrates that the failure temperature remarkably increased with the addition of CNTs to asphalt and the failure temperatures for all RTFO binders were higher than the minimum high critical temperature for original asphalts. Using CNTs as an asphalt modifier has a significant effect on asphalt high temperature PG grade. Based on the DSR results, the high temperature PG grade of the control asphalt is 64°C, 70 °C for the 3.0% MWCNTs-COOH and 76 °C for the 3.0% P-MWCNTs. Thus, adding 3% P-MWCNTs yielded a remarkable improvement in the high temperature of 2 grade pump compared to the MWCNTs-COOH which yielded only one grade pump. Pan and Xing reported that the surface functionalization of CNTs affects the wettability of CNTs surfaces and as a result CNTs become more hydrophilic and may increase the resistance of diffusion and decrease the adsorption with nonpolar hydrocarbons [32]. Based on this trend, the P-MWCNTs adsorption in asphalt matrix was better than MWCNTs-COOH as asphalt is a hydrocarbon material. Consequently, the rheological properties of the asphalt modified with pristine MWCNTs were better than the functionalized MWCNTs.

6. Summary and Conclusions

A surface chemical treatment of MWCNTs using sulfuric and nitric acids was conducted. The rheological properties of the pristine and functionalized MWCNTs were compared along with SEM images and EDX analysis. The effect of pristine and functionalized MWCNTs on the rheological properties of the conventional asphalt was evaluated. Finally, the effect of two different mixing techniques (high shear mixer and a manufactured mechanical mixer) of CNTs with asphalt based on the rotational viscosity testing was conducted. From the laboratory testing results and analyses, the following conclusions can be drawn:

1. The SEM observation showed that there is no distinct difference in morphology between P-MWCNTs and MWCNTs-COOH.
2. The surface functionalization of MWCNTs by carboxyl groups was not found effective for improving the rheological properties of asphalt binders.
3. Using MWCNTs as an asphalt modifier increased the softening point temperature and hence led to an asphalt which is stiffer and more stable against flowing especially in the hot climates.
4. Viscosity results indicated that the addition of MWCNTs increased the asphalt viscosity (stiffer binder). Temperature susceptibility of the asphalt was also improved significantly with the MWCNTs.
5. In terms of DSR test results for the original and RTFO asphalts, the asphalt stiffness and elasticity were increased with adding MWNT. The 3.0% P-MWCNTs increased the high temperature from 64°C to 76°C which is a significant improvement in asphalt resistance to permanent deformation. Thus making the asphalt more suitable for hot climates and higher traffic loads.
6. The manufactured mechanical stirrer which is cheaper and more practical especially in the field was found to produce blends of asphalt and MWCNTs with properties similar to those produced using the more expensive high shear mixer.

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