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EFFECT OF CARBON NANOTUBE ON THE RHEOLOGICAL PROPERTIES OF BITUMEN

Saeed Sadeghpour Galooyak[1i], Massoud Palassi[2], Hosein Zanjirani Farahani[2], Ahmad Goli[3]

[1]Refining Technology Development Division, Research Institute of Petroleum Industry, Tehran, Iran; [2]Department of Civil Engineering, University of Tehran, Tehran, Iran; [3]Department of Transportation, University of Isfahan, Isfahan, Iran

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Abstract

Carbon nanotubes are one of the most widely used Nanomaterial that have two main features of light-weight and high strength material for tensile, compressive, impact and thermal stresses. In this study, different contents of carbon nanotube are used for the modification of the conventional bitumen. For the samples prepared by the ultrasonic mixer, it is observed that the agglomerated Nano-materials are peeled off and uniformly dispersed in bitumen. Then classical experiments of bitumen, x ray analysis, and rheological tests using Dynamic Shear Rheometer, were conducted on the modified bitumen. Master curves are plotted, and the results depicted that addition of 1.2 wt% of carbon nanotubes to the bitumen have improved rheological properties of bitumen at high and low temperature service, significantly. Also addition of Nanotube was increased the stiffness and reduced the phase angle of base bitumen.

Keywords: Bitumen; Master Curve; Carbon Nanotube; Performance; Rheology.

1. Introduction

Bitumen has been widely used for road paving for long time. Actually, the increase in traffic loading and the number of vehicles along with the severe weather conditions, conduce to a quick structural damage of pavements. In order to enhance the mechanical properties and the aging behavior of asphalt concrete, a new generation of asphaltic blend has been developed through the incorporation of different kinds of modifiers [1-3] in bitumen.

In recent years, different kinds of polymers have been used to modify properties of hot mix asphalt. On the other hand, the use of Polymer Modified Asphalts (PMAs) allows the construction of safer roads and important reduction in maintenance cost [4-5]. Among the polymers, Styrene-butadiene- Styrene (SBS) is one of the most widely used, which would extremely improve the physical, mechanical and rheological properties of asphalt mixtures [6].

Polymeric materials like Polyethylene (PE), and Polypropylene (PP), are appropriate polymers for using as modifying materials in asphalt mixtures [7-10]. However, absence of a suitable documented design procedure for modified asphalt mixtures has reduced the confidence of highway engineers for using these materials in road paving. Modification of asphalt mixtures with polymers appears to have the well potential for successful application in flexible pavements. These benefits can be realized by extending the service life of the pavement, or reduction in asphalt concrete thickness [11].

Nanotechnology is the development of new materials, devices, and systems at the molecular level as phenomena associated with atomic and molecular interactions, strongly influence macroscopic material properties [12]. Nanoreinforced materials hold the potential to redefine the field of traditional materials both in terms of performance and applications [13-18]. Hussain *et al.* [14] illustrated the dispersion of Nanoparticles in matrix materials. They identified that improving the carbon Nanofibers (CNFs)/matrix interfacial adhesion issue and complete dispersion must be resolved before achieving the full potential of Nanoreinforced composite materials. Dispersion of Nano-fibers has been one of the largest challenges due to the association of the Nanofiber particles. Improvement of material properties can be achieved by a proper dispersion technique. Improper dispersion leads to Nanofiber damage and size break down which deteriorate the material properties. Ziari *et al.* [19] developed a technique for dispersion of Carbon Nanotube (CNT) in bitumen by comparing sonication, high shear and mechanical mixing techniques. In their study, several sonication periods with several power rates and mixing speeds were employed to optimize the dispersion process.

In this paper the effects of carbon nanotube on rheological properties of bitumen binder have been examined. Various qualification test methods were conducted on the prepared samples to determine the influence of CNT on the rheological and physical properties of base binder. Then the optimum content of CNT was obtained based on the rheological results.

2. Materials and experiments

2.1 Materials

The common bitumen grade (60/70 penetration grade) from Isfahan refinery (Iran), with the properties mentioned in Table 1, was used as the base binder in this research.

Table 1. Effect of CNT on the physical properties of bitumen

Properties	standard	CNT(wt%)					
		0	0.3	0.6	0.9	1.2	1.5
Penetration at 25 °C, dmm	ASTM-D5	65	64	59	55	51	49
Softening point, °C	ASTM-D36	52	53	55	56	60	61
Penetration index	---	-0.062	0.139	0.391	0.433	1.079	1.175

Carbon nanotube with length of 30 μm, specific surface area of 200 m^2/gr and density of 2.1 gr/cm^3 was prepared from RIPI (Research Institute of Petroleum Industry). The structure of CNT is shown in Fig. 1.

Fig.1 The structure of CNTs

2.2 Experiments

2.2.1 Providing samples

To investigate the effect of CNT on the bitumen, it was initially mixed with the standard bitumen with different weight percentages. The outcome of this mixing was 6 types of standard and modified bitumen including 0, 0.3, 0.6, 0.9, 1.2 and 1.5 weight percent of Carbon Nano Tube. As mentioned in previous work, three different kinds of mixers (including mechanical mixer, high shear mixer and ultrasonic device), with different conditions considered for each of them, were utilized to mix CNTs with asphalt [19-21]. Then, after preparation of samples, modified bitumen were tested 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.

For the samples prepared in high shear mixer and mechanical stirrer, agglomeration of CNTs were perceived immediately after discontinue blending (Fig. 2). From SEM analysis it was observed that (Fig. 3), for the samples prepared with the power of 65 watt for 15 minutes, nanomaterials were dispersed homogeneously in bitumen, without any agglomeration.

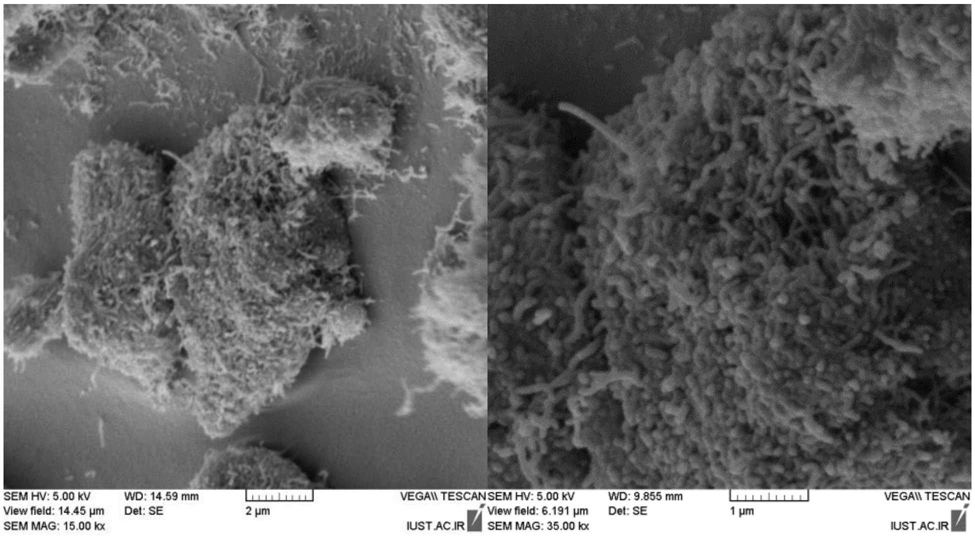

Fig.2 Microscopic picture of samples mixed with Nano by using a high shear mixer (homogeneous dispersion of nano materials and their agglomeration)

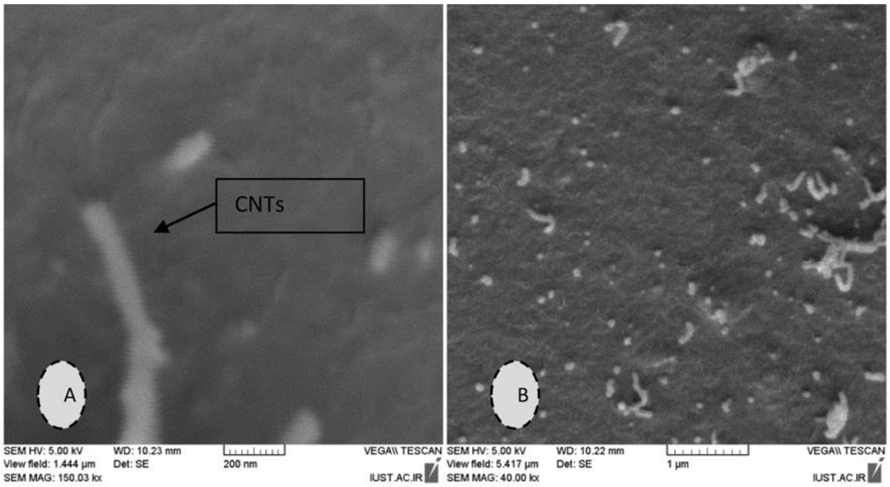

Fig.3 Microscopic picture of samples combining with nano materials by using of an ultrasonic mixer. (Homogeneous dispersion and Nano materials separation)

2.2.2 X-Ray spectroscopy

XRD is the most commonly used technique for examining the structure as well as for occasional study of the kinetics process of Nano composites. X-ray diffraction (XRD) spectra, were obtained using Philips model PW1840 diffractometer with Cu Kɑ radiation (k= 0.154 nm, 40 kV, 30 mA) at the room temperature. The scanning were performed from 15^{o} to 95^{o} in the 2h range in 0.02^{o} steps, at a scanning rate of 2^{o}/min.

2.3 Rheological analysis

Rheological characterization of the base binder and the bitumen-CNT blends considered in this study was carried out using a dynamic shear rheometer (DSR, MCR300, Anthon Paar Co.). Rheological analysis were performed under controlled strain condition in linear viscoelastic range. So, the frequencies were swept between 0.0001 and 1000 rad/s at fixed temperature and strain of 50°C and 1%, respectively. Under these conditions, rheological parameters such as complex modulus and phase angel were obtained for the evaluation of neat and modified bitumen.

2.4 Physical properties analysis

The physical analysis were performed using conventional tests including needle penetration at 25°C (ASTM D5), softening point (ASTM D36) and ductility at 4°C (ASTM D113). Also, viscosity of samples at temperatures of 120, 140, 160 and 180°C were measured according to ASTM D4402 using Brookfield viscometer.

3. Results

3.1 The classical experiment of bitumen

The needle penetration test at 25°C was performed to determine the relative stiffness of bitumen. According to table 1, it can be seen that an increase in the proportion of CNT to bitumen, was led to a reduction in the penetration degree of bitumen which is indicative of the decrease in fluency and the increase in the consolidation of bitumen at normal and high temperatures. Such modified samples of bitumen do not rut at high temperatures.

The softening point is the temperature at which bitumen becomes fluent. The bitumen with higher softening point is less sensitive to the variation in temperature and experiences less variation in its viscosity. As it is depicted in table 1, addition of CNT to bitumen, increases bitumen softening point.

In general, the variations in the penetration degree or viscosity of bitumen, resulted from the variation in its thermal conditions, is called the thermal sensitivity of bitumen. The thermal sensitivity of bitumen can be calculated in several ways. One of these approaches is by using Penetration Index, PI, which is introduced in the following correlation [20]:

$$A = \frac{\log 800 - \log(Pen at\, 25^0 C)}{T_{R\&B} - 25^0 C} \quad PI = \frac{20 - 500A}{1 + 50A} \tag{1}$$

$T_{R\&B}$ is the softening point of bituminous sample.

Adding CNT with different percentages to neat bitumen increases the PI of bitumen (Table 1). Despite the fact that bitumen possesses good adhesion, it has limited continuity. According to table 1, the use of this additive leads to the expansion in the endurable temperature range as well as continuity improvement of bitumen.

3.2 X-Ray analysis of carbon nanotube

The X-ray analysis of carbon nanotube is shown in Fig. 4. As it is indicated in this figure, the diffraction peaks at 26.1°, 42.8°, 54°, and 77.9° that have been observed in the diffraction of MWNTs can be attributed to the hexagonal graphite structures (002), (100), (004), and (110). The interlayer spacing of 0.18 nm was calculated according to Bragg law (d002).

$$n\lambda = 2d \sin\theta \tag{2}$$

where d is the interlayer spacing of MWCNT, λ is the wavelength of apparatus, and θ is the diffraction angle.

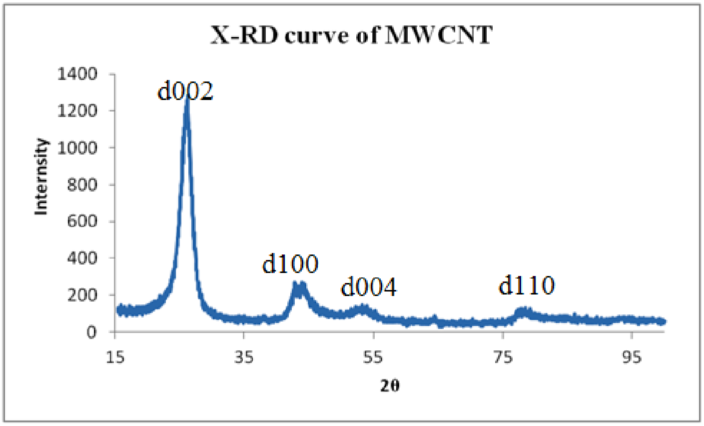

Fig.4 X-ray diffraction results on Carbon Nano tube

3.3 The effect of CNT on the viscosity of base binder

The rotational viscosity is determined at constant rotational speed by measuring the torque that has been applied on a cylindrical spindle while submerged in bitumen. Viscosity is criterion for the ability of bitumen in pumping and mixing with mineral aggregates. The effect of CNT on the viscosity of base binder at different temperatures are shown in Fig.5. As expected, nanotube increases the viscosity of bitumen. According to SHRP protocol, the viscosity of binders at 135°C should be less than 3 pa.s to could be pumped and blended with the aggregates at such a high temperature. As shown in Fig. 5, the viscosity of all of modified samples at 135°C are less than 3 pa.s which demonstrates the ability of CNT to modify the properties of bitumen at high temperature without any specific limitations. As can be seen in Fig.5., two samples containing 1.2% and 1.5% of the Nanotubes have showed a sever increase in viscosity of the bitumen.This demonstrates that these two samples have greater ability to withstand at high temperature of road service with the less permanent deformations. At very high temperatures (upper than 160^0C), CNTs have not significant impact on viscosity.

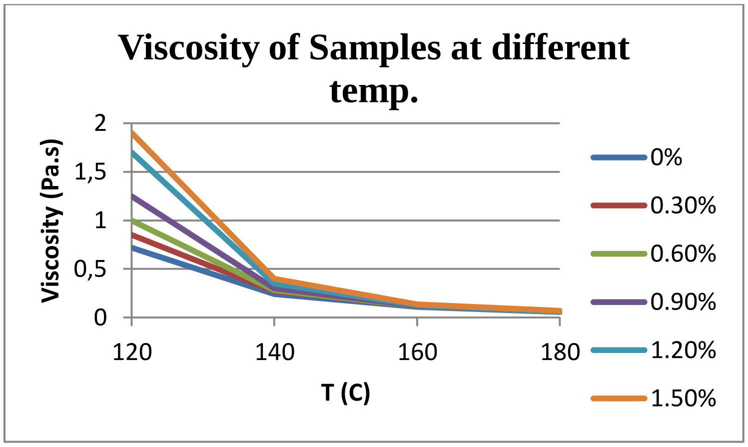

Fig.5 Viscosity of samples with different percentages of CNT at different temperatures

3.4 Fundamental rheological tests by dynamic shear rheometer (DSR)

The complex modulus is one of the main parameters describing the behavior of bitumen, which includes two parts of elastic and loss modulus.

$$G^{*2} = G'^{2} + iG''^{2} \qquad (3)$$

where G^* is the complex modulus, G' is the elastic modulus, and G" is the dissipative modulus of samples. The obtained results from Dynamic Shear Rheometer indicate that the use of CNT improves the performance of the complex modulus of bitumen.

As it is shown in Fig.6., the use of CNT improves the properties of modified bitumen in comparison to base binder in all loading frequencies. The value of complex modulus for CNT modified bitumen (1.2 wt% CNT) is more than neat bitumen (0% CNT) in all of the applied frequencies. This means that the performance of modified samples are improved in mid and high service temperatures.

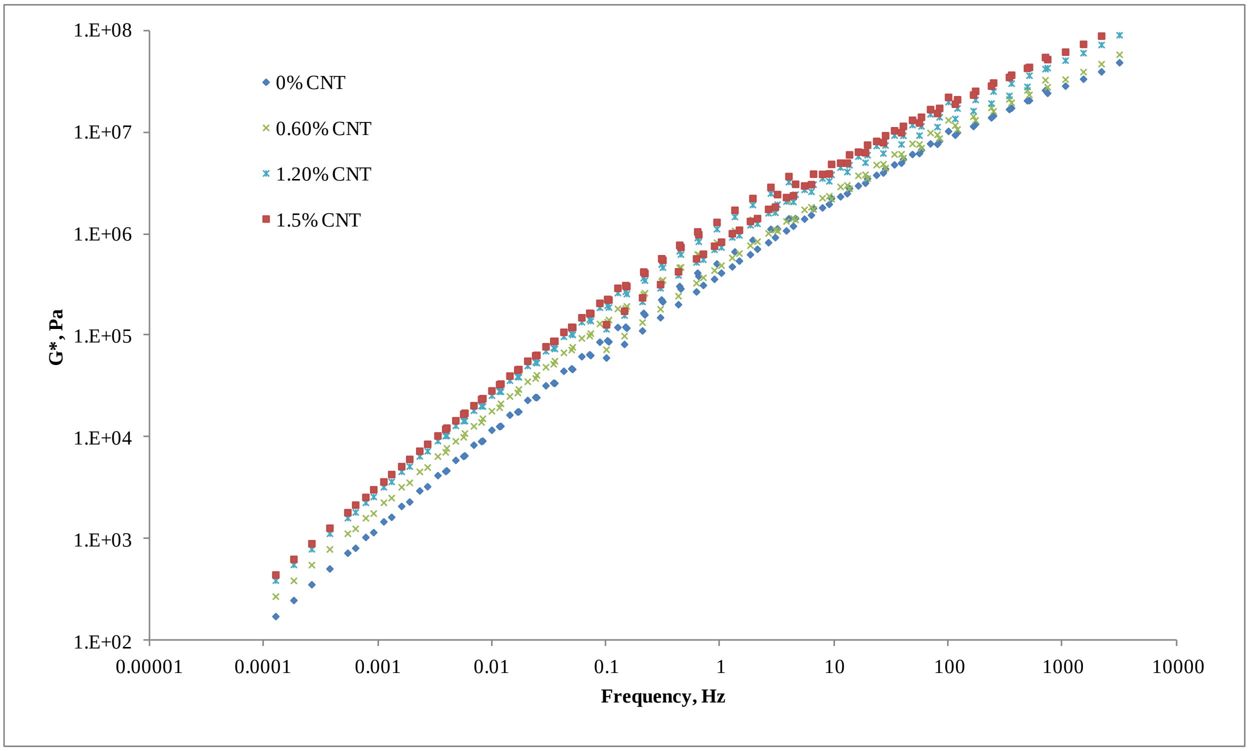

Fig.6 Master curve of complex modulus for modified bitumen with CNT and unmodified bitumen

Furthermore, the phase angle, as a significant parameter affecting the behavior of bitumen at a specific load frequency, is influenced by the applied loads on the road paving. This parameter is more sensitive than complex modulus to physical and chemical structure of samples. So, phase angle could show the rheological behavior of modified samples properly. The bitumen types with small phase angle possess a better performance, especially at high service temperatures. In addition to the fact that small phase angles are indicative of lower perdurable deformation in asphalt concrete, the slope of this diagram is pointing the performance of this material in hot weather conditions. As it is depicted in Fig.7., with increasing the percentage of CNT in bitumen, the phase angle of modified bitumen decreases which means that the modified bitumen has a greater performance at high service temperatures, or in heavy road traffic loading (for example, in summers). Lower frequency is related to heavy traffic loading condition or high service temperature, and higher frequency depicts the low traffic loading or lower temperature. For the modified bitumens with CNT, the slope of diagram as well as the phase angle have decreased, specially at low frequencies, which is indicative of more elastic behavior at high service temperature or heavy traffic loading.

One of the most important problems pavings is the large deformation of asphalt along the path of vehicles' wheels. This kind of failure is the consequence of large deformation of asphalt concretes due to the weakness of elastic properties of bitumen at high service temperature. This type of failure is called rutting. The parameter G*/Sinδ, rut factor, predicts this failure in high service temperature. As it is shown in Fig.8, adding 1.2 wt% CNT to bitumen has improved the rutting behavior of binder at low loading frequencies. This, implies a greater behavior of binder at high temperatures and a reduction in the failure resulted from the asphalt rutting.

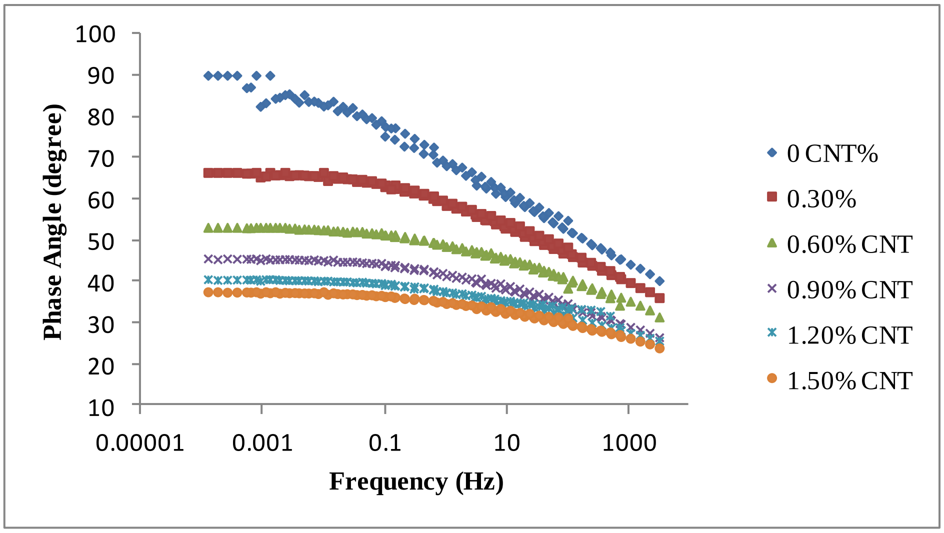

Fig.7 The Master curve of phase angle for modified bitumen with CNT and unmodified bitumen

Finally, by investigating the complex modulus, phase angle and rut factor curves it can be concluded that carbon nanotubes improve the performance of neat bitumen at high service temperatures and reduce the rutting and deformation of binder at these temperatures.

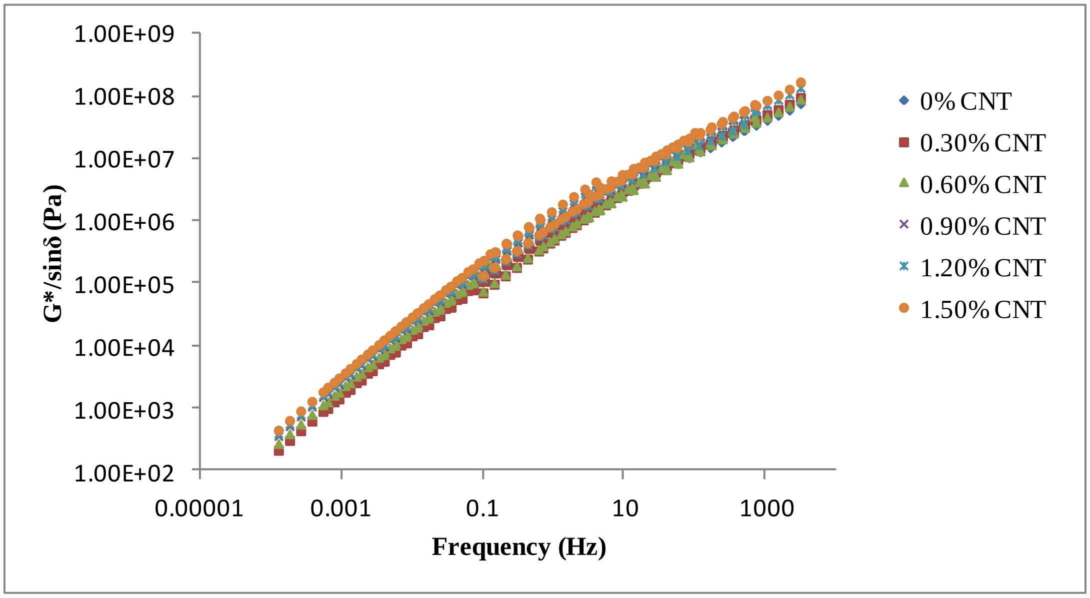

Fig.8 The Master curve of rutting parameter for modified bitumen with CNT and unmodified bitumen

Of course, choosing the appropriate combination of nanotubes is important. For example, the results of complex modulus shows that the sample containing 0.6 wt% can be useful for modifying bitumen (has not shown in this manuscript). As a result, elastic modulus shows that 0.6% of CNT has a small effect on base bitumen and it should be emphasized that the increase in the complex modulus of the sample containing 0.6 wt% nanotube is related to loss modulus and not to the elastic modulus of sample. Also the results of rut factor confirms this phenomena, because the sample containing 0.6 wt% nanotube acts like the base bitumen and this point refers to the more phase angle of this sample compared to other samples containing nanotubes. Thus, samples containing 0.9, 1.2, and 1.5 wt% of nano-tubes could improve the performance of base binder at the high temperatures excellently. It can be concluded that increasing CNT percent from 1.2 to 1.5%, has no significant effect on properties of bitumen, so the 1.2% CNT has been selected as optimum CNT percent.

3.5 Ductility

As can be seen in the Table 2, increase in percentage of nanotubes have no negative effect on the ductility at low temperature (4°C) and even some minor improvements are also observed. These results indicate that the nanotubes without having a negative effect on the performance of bitumen at low temperatures, can effectively improve the high temperature properties of bitumen, and this is the major advantage of Nanotubes according to other common modifiers.

Table 2 Ductility at temperature of 4°C

Percent of CNTs, %	0%	0.3%	0.6%	0.9%	1.2%	1.5%
Ductility @ 4°C, cm	4	4	4	4.5	5	5

4. Conclusion

Limitations of ordinary bitumen have caused to take steps for modifying the bitumen behavior and asphalt mixtures performance. In recent decades, different methods and a wide range of additive materials have been used in order to improve the properties and behavior of bitumen and as a result improvement of asphalt mixtures performance. The effects of these materials on behavioral of asphalt mixture are quite different. In this study, carbon nanotubes are used as a modifier of bitumen. The images taken using a scanning electron microscopy showed that in the samples mixed by the ultrasonic mixer, Nano-materials are dispersed uniformly in bitumen and separately from each other (without being agglomerated). So, the use of carbon nanotubes as additives has significantly improved the classical properties of bitumen (softening point, penetration, etc.) and performance of modified bitumen compared to base binder. Also by analyzing the master curves of complex modulus, Phase Angle, and rut factor, it was observed that the sample containing 1.2% of carbon nanotube has the best performance and this amount is selected as the optimal percentage of CNT. Finally, it can be concluded that modified bitumens have more stiffness modulus and less phase angle compared to basic bitumen. Also, temperature susceptibility of base binder has improved by adding CNT. Iincreasing the CNT content from 1.2 to 1.5 wt.%, has no significant effect on properties of bitumen, so the 1.2% CNT has been selected as optimum percent. Also, the results indicate that the nanotubes without having a negative effect on the performance of bitumen at low temperatures, can effectively improve the high temperature properties of binder and this is the major advantage of Nanotubes in compare to other common modifiers.

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