Journal of Geotechnical and Transportation Engineering
Volume 7 | Issue 1
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Received: November 2021
Accepted: December 2021
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The Effect of Carbon Nanotubes on the Mechanical and Rheological Properties of Asphalt and Bitumen

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Abstract

The current research assessed the effect of carbon nano tubes (CNTs) on the mechanical and rheological behavior of asphalt and bitumen samples. In this paper, different contents of CNTs are used for the modification of the asphalt and bitumen samples. For this study, softening point and penetration tests were done to evaluate the performance of different samples. CNTs was completely characterized in terms of morphological and structural properties. The effect of CNTs on the rheological behavior of samples was investigated by central composite design (CCD) experimental design and response surface methodology (RSM). The results of the Marshall test indicated that the stability of samples containing CNTs increased due to the more effective presence of CNTs in asphalt mixtures compared to the base asphalt. The results indicated that the use of CNTs as an additive has increased the softening point, reduced the degree of penetration and improved the performance characteristics of bitumen compared to base bitumen.

Keywords: Carbon Nanotubes, Bitumen, Asphalt, Central composite design, Rheological Properties.

1. Introduction

The quality of road asphalt layers, which plays an important role in protecting and transmitting road pressures from the top to the bottom layers, is one of the factors determining the safety and comfort of road drivers [1]. In designing asp halt paving materials, high durability, good performance and long life should be considered [2]. In recent years, the expansion of road transport, increasing traffic volume, as well as severe climate change, including heavy rains, heat and sudden cooling, have caused serious damage to road asphalt, resulting in increased road maintenance costs. Therefore, the use of new technologies to create asphalt pavement with more strength has always been considered [3, 4]. Polymer modification is usually used to obtain the desired quality asphalt. However, the disadvantages of polymer-modified asphalt include poor solubility of polymers, poor storage stability, sensitivity to separation at high temperatures, and low strength. Hence, the researchers turned their attention to nanotechnology. Nanotechnology examines materials as small as 100 nanometers or less at the level of atoms and molecules, and has changed perceptions about the properties of materials [4].
Carbon nanotube (CNT) among various nano-sized materials have been able to enhance the performance of materials well. CNT is a hollow, seamless cylinder 1 nm in diameter made by twisting a graphite sheet one-atom thick. CNT shows good mechanical properties compared to other materials. It can also improve the performance of other materials [4]. Therefore, CNT is a good option for improving bitumen in asphalt. Bitumen forms a major part of asphalt and helps to bond different layers of asphalt together. Bitumen is a material composed of crude oil and consists of an asphalting part with a larger and stronger molecular weight and a

molten part with small and liquid molecules. Bitumen is known as a temperature dependent material. And at high temperatures shows viscoelastic behavior. At hot temperatures, asphalt concrete cracks due to heavy traffic, creating grooves in the asphalt surface. It also loses its softness as the temperature decreases, especially in cold areas. Thus, the undesirable properties of bitumen cause a lot of damage in asphalt mixtures; including thermal cracks at low temperatures, deformation at high temperatures, low durability against heavy traffic and humidity. Preventing and postponing the common breakdowns of asphalt pavements, in order to increase the life of road asphalt, which reduces costs and also increases the safety of road asphalt, is more and more necessary today [5].

Bitumen can be modified using CNT. Many researchers have reported the use of CNTs as reinforcing additives to modify asphalt binders. Jiang and coworkers synthesized a CNT/PEA nanocomposite as an asphalt modifier and showed that CNT-modified asphalt has better advantages [4].

Faramarzian and coworkers improved the technical properties of bitumen using carbon nanotubes as additives [6].Santagata and coworkers found that the rheological function of the binder increased by adding a high percentage of CNTs. In addition, the use of CNT compared to Nano-additives shows better performance against rust [7]. Sadeghpour and coworkers shown that nanotubes can effectively improve high temperature properties without negatively affecting the performance of bitumen at low temperatures [8]. In a study, Wu and coworkers investigated the performance of two nanometer modifiers such as graphene (Gr) and CNTs in enhancing the thermal, physical, and rheological properties of asphalt binders [9]. On the other hand, Rossi and coworkers introduced a new type of carbon nanotube and studied its properties and showed that this new carbon nanotube also improves the performance of bitumen [10]. In a study by Wang and coworkers, Gr/CNT composite materials were used to reinforce the bitumen composite, which showed better dispersion, while promoting surface interactions between the carbon nanomaterials and the bitumen matrix [11]. For the first time, Barati and coworkers evaluated the rheological and mechanical properties of bitumen and asphalt with CNT and RGP [3]. Also, Wang and coworkers showed that CNT has a good effect on the physical properties, storage stability of rheological modified styrene-butadiene-styrene (SBS) asphalt [12]. In a project, Tsantilis and coworkers found that the aging resistance of SBS-modified asphalt was increased by adding the right amount of carbon nanotubes [13]. Najafi and coworkers studied the effect of desiccant materials on the moisture sensitivity of base asphalt mixtures modified by CNTs. The results showed that bitumen modification with CNTs led to an increase in non-stick energy (AFE) [14]. On the other hand, Najafi and coworkers investigated the effects of carbon nanofiber-modified asphalt binders and carbon nanotube-modified aggregates on the moisture sensitivity of asphalt mixtures simultaneously [15]. In a project, Kumar and coworkers investigated the effect of CNT on the low temperature properties of asphalt binders using the energy-based method [16]. Also, Kui Hu and coworkers studied the storage stability and low temperature properties of RPE-modified asphalt. They used CNTs as a reinforcing agent and simulated molecular dynamics to discover the reinforcing mechanism of CNTs in RPE-modified asphalt [17]. Mosir Shah and coworkers investigated the effect of multi-walled carbon nanotubes (MWCNT) on the adhesion properties of low viscosity asphalt and showed that the addition of MWCNT improves the high temperature performance of modified bitumen [18]. Chang and coworkers investigated the leveling mechanisms between the four components of base asphalt (asphalting, resin, aromatic and saturated), styrene-butadiene-styrene (SBS) and CNT by simulating the molecular dynamics of CNT [19]. Wang and coworkers designed and synthesized two types of CNTs and styrene-butadiene-styrene (SBS) to modify asphalt and used it to study the thermal stability of asphalt [20].

Therefore, in this paper, in the present work, we propose an approach for synergistically enhancing the rheological properties of asphalt and bitumen composites through the CNTs. For this purpose, different contents of CNTs are used for the modification of the samples. We considered the morphological features of the nanocomposite using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The influence of CNTs on the rheological behavior of samples was studied by response surface methodology (RSM).

2. Materials and Methods

2. 1. Raw Materials

All chemicals and solutions were of analytical reagent grade and used without further purification. Carbon nanotube (CNT) with length of 30 μm, real density of 2.1 g cm-2, specific surface area of 200 m2 g-1 and purity of 95% was prepared from JCNANO Company, Nanjing, China. The bitumen used in constructing the laboratory samples have been prepared from the Isfahan Oil Refinery. The measured values of the primary physical properties are tabulated in Table 1.

Table 1. Properties of matrix bitumen.

Properties	Penetration (25 °C)	Softening point (°C)	Flashing point (°C)	Solubility in tetrachloride carbon (%)	Ductility (cm)
Values	68	51	295	99.2	>100

2. 2. Characterization

A Kokusan centrifuge (Tokyo, Japen) was used for the phase separation.The reaction mixtures were shaken using a shaker (model GLF 3203; Hilab, Düsseldorf, Germany). The mixtures are sonicated by using an ultrasonic homogenizer (Bandelin Sonopuls HD3400). Marshall Stability of samples were tested by the Marshall Stability meter produced by Iran Soil Mechanics Industry, SMAS-4100. To estimate the morphological properties of CNT, scanning electron microscope (SEM, Gemini SUPRA 55VP-ZEISS) and transmission electron microscopy (TEM, JEM-2100F) tests were performed.

2. 3. Sample Preparation

For preparing of modified bitumen, at first, the raw bitumen was heated to 110 °C in a specific container and mixed with a shaker for 30 min at 5000 rpm. The resultant of this mixing was 3 types of standard and modified bitumen including 0.3, 0.6 and 0.9 weight percent of CNT. The mixture were sonicated at 1000, 2000 and 3000 rpm for 10, 20 and 30min at 110 °C. In the present study, asphalt samples have been made based on standard method ASTM. The asphalt samples immersed in water bath at 60°C for 30min. After that, various concentrations (0.3, 0.6 and 0.9%) of CNT were added to samples and were stirred at 3000 rpm with a stirrer. For the preparation of all samples, the temperature was kept constant through an electric heating jacket (Hualu SKM-2, Heze, China).

2. 4. Physical Properties Analysis

In this study, the physical analysis were done using conventional tests including softening point and penetration tests. Also, one of the significant factors in designing the asphalt mixtures is Marshall Stability. The Marshall test in the next section was evaluated.

2. 4. 1. Softening Point Tests

The softening point of samples can be measured by using a ring-and-ball apparatus immersed in double distilled water. The softening point is described as the mean of the temperatures at which the two plates soften enough to allow each ball, enveloped in sample, to fall a distance of 25 mm.

2. 4. 2 Penetration Tests

3/ Cool the prepared samples for 3h at room temperature.
4/ Put the samples in a thermostatic water-bath for 90min.

2. 5. Experimental Design

In order to obtain the best responses (softening and penetration points), the procedure was optimized using a central composite design (CCD). The statistical analyses were performed by using the software package Design-Expert 11 (Stat-Ease Inc., Minneapolis, MN, USA). In this paper, the most-effective independent parameters on softening points, such as amount of CNT (A), mixing time (B), and stirring rate (C) were chosen based on the literature and preliminary experiments. According to the design, each of the three parameters (A–C) was considered at three levels (Table 2). For this case, a total of 20 (=2K +2K+C0, where k is the number of variables, and C0 represents the number of center points) experiments incorporating six axial points, eight factorial points and six replicate at the center were suggested by the software (Table 3 and Table 4). The quadratic polynomial model was worked out using the following equation:

$$Y = \beta 0 \sum_{i=1}^{k} \beta i X i + \sum_{i=1}^{k} \sum_{j=1}^{k} \beta ij\, X i X j + \sum_{i=1}^{k} \beta ii\, X i^2$$

Here Y represents the dependent variable, β0 represents the constant coefficient, βi, βii and βij denote the linear, quadratic and interaction coefficients, respectively. Xi and Xj denote the coded values of the variables, respectively. K represents the number of the independent variables.

Table 2. The experimental range and levels of the factors in the CCD

Variables	Code	Unit	Coded variable levels -1	0	+1
Amount of CNT	A	%	0.3	0.6	0.9
Mixing time	B	min	10	20	30
Stirring rate	C	rpm	1000	2000	3000

Table 3. experimental data. CCD for softening point test using RSM

	Factor 1	Factor 2	Factor 3	**Response**
Run	A: Amount of CNT (%)	B: Mixing time (min)	C: Stirring rate (rpm)	**R (°C)**
1	0.3	10	1000	51
2	0.6	20	2000	55
3	0.3	30	1000	51
4	0.9	20	2000	50
5	0.6	20	1000	56
6	0.6	20	2000	55
7	0.9	30	3000	60
8	0.6	30	2000	54
9	0.9	10	3000	59
10	0.6	20	2000	55
11	0.6	20	2000	56
12	0.9	10	1000	59
13	0.4	10	3000	51
14	0.3	20	2000	61
15	0.3	30	3000	52
16	0.9	30	1000	59
17	0.6	20	2000	55
18	0.6	10	2000	55
19	0.6	20	2000	56
20	0.6	20	3000	51

3. Results and Discussion

3. 1. Morphological Observations

Microscopic morphology of CNTs was detected by SEM and TEM tests. Fig. 1a, b indicate the results of the morphological analysis carried out on the CNTs sample. As can be seen in Fig. 1a, CNTs has a tubular and one-dimensional structure. Also, the tubes were irregularly arranged and intertwined with each other. Furthermore, the analysis of the TEM image of the CNTs, indicated the presence entanglement of nanotubes (Fig. 1b).

3.2. Marshall Stability

The Marshall test was conducted to estimate water stability. The results of the Marshall test on asphalt was depicted in Fig.2. As shown in Fig. 2, addition of CNTs to asphalt samples results in increase of stability from 800 to 12000 Kg. The reason for this can be attributed to the specific characteristics of CNTs, including good tensile stability and high-density levels.

Table 4. CCD for penetration degree test using RSM and experimental data.

	Factor 1	Factor 2	Factor 3	Response
Run	A: Amount of CNT (%)	B: Mixing time (min)	C: Stirring rate (rpm)	R (°C)
1	0.3	10	1000	53
2	0.6	20	2000	61
3	0.3	30	1000	63
4	0.9	20	2000	51
5	0.6	20	1000	64
6	0.6	20	2000	64
7	0.9	30	3000	69
8	0.6	30	2000	61
9	0.9	10	3000	69
10	0.6	20	2000	62
11	0.6	20	2000	62
12	0.9	10	1000	68
13	0.4	10	3000	54
14	0.3	20	2000	70
15	0.3	30	3000	54
16	0.9	30	1000	68
17	0.6	20	2000	63
18	0.6	10	2000	64
19	0.6	20	2000	63
20	0.6	20	3000	61

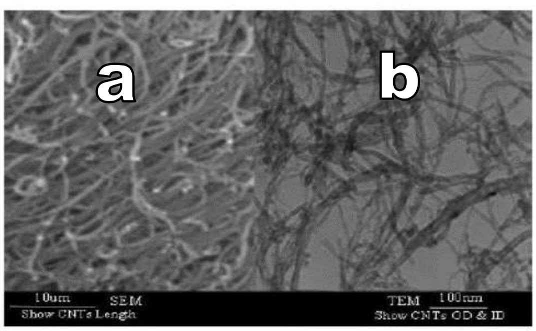

Fig. 1. a) SEM and b) TEM images of CNTs

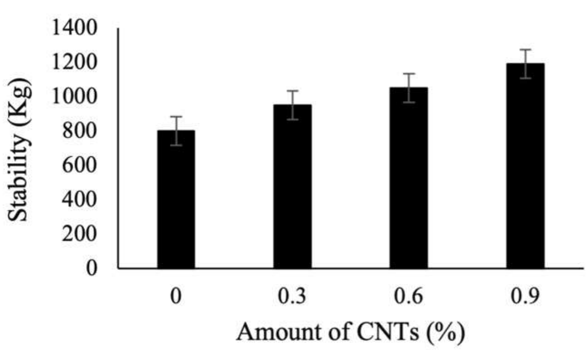

Fig.2. The results of Marshall Strength of different percent amounts of CNTs.

3. 3. Softening Point Test

The effects of amount of CNT, mixing time and stirring rate on the softening point for bitumen were determined in selected range of factors and results are expressed as contours plots. Fig. 3a indicates 2D contour plot of amount of CNT against the mixing time. The contour plot of amount of CNTs versus mixing time shown that the optimal conditions for softening point were in the dark green region, where CNTs amount ranged from 0.2 to 1% and mixing time from 5 to 35min. Fig. 3b indicates the interaction of amount of CNT with stirring rate. As can be seen in Fig. 3b, the softening point of the bitumen increases with increase in CNTs amount and it increases with increases stirring rate. As shown in Fig. 3c, the softening point of the bitumen increases with increase in mixing time and increases in stirring rate. Based on the results (Fig.3c), with increasing mixing time from 20 to 35min, the softening point was enhanced, reaching the maximum value at 0.6% of CNTs. Also, the analysis of variance (ANOVA) such as the regression (R2), predicted R2 and adjusted R2, were done to justify the efficiency and significant of the developed regression model. The R2 of the developed model was 0.966, indicating that 96.6% of the total variations in the results could be due to the studied parameters. Additionally, the R2 was very close to the adjusted R2 (0.935). Moreover, the difference between the predicted R2 (0.789) and adjusted R2 (0.935) is less than 0.2, which are in reasonable agreement to each other.

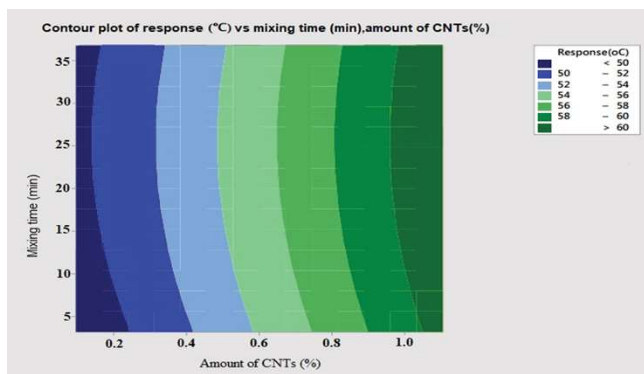

Fig.3. a. contour plots for the mutual effects of: (a) mixing time and amount of CNTs

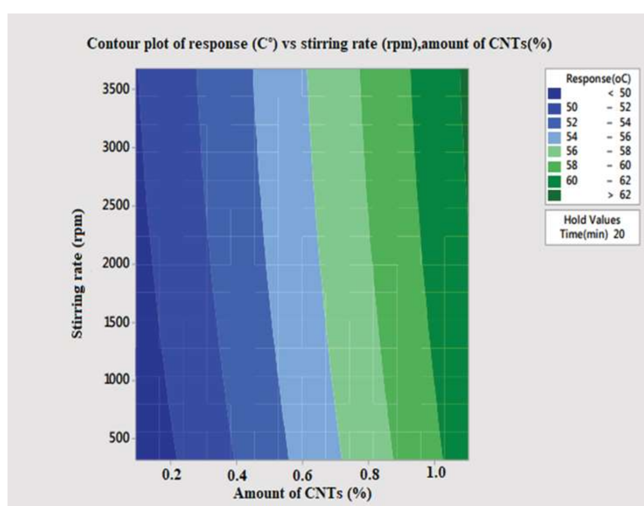

Fig.3. b. contour plots for the mutual effects of (b) stirring rate and amount of CNTs

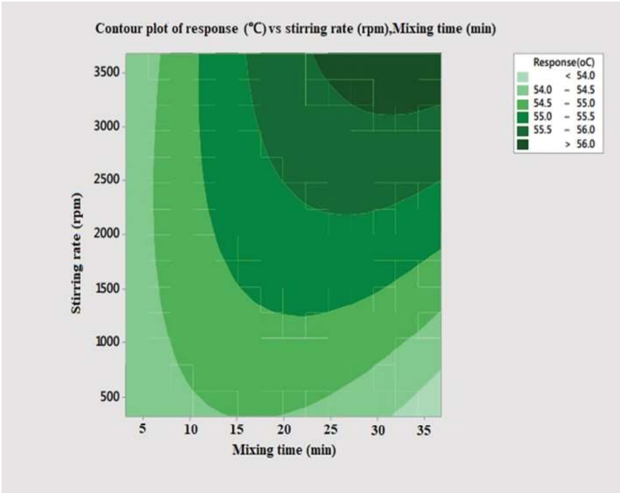

Fig.3. c. contour plots for the mutual effects of: (c) stirring rate and mixing time on the softening point test.

3. 4. Penetration Degree Test

The needle penetration experiment was carried out to determine the relative stiffness of bitumen. The special influences of each factor (amount of CNT, mixing time and stirring rate) on the penetration point for bitumen were considered by contours plots. Fig. 4a shows that the penetration point increased with amount of CNT and prolonging the mixing time when the stirring rate was fixed at 2000rpm. Fig. 4b indicates that when the amount of CNT increased and the stirring rate increased, the penetration point enhanced. As indicated in Fig.4c, it was observed that the penetration point increased with prolongation of the stirring rate and mixing time, when the amount of CNTs was fixed at 0.6%. On the other hand, a high value of the adjusted R2 (0.939) also indicated the high significance of the developed regression model. In this case, the adjusted R2 and R2 values were found to be very close. (R2= 0.971). Also, according to the results of ANOVA, the value of predicted R2 was 0.787.

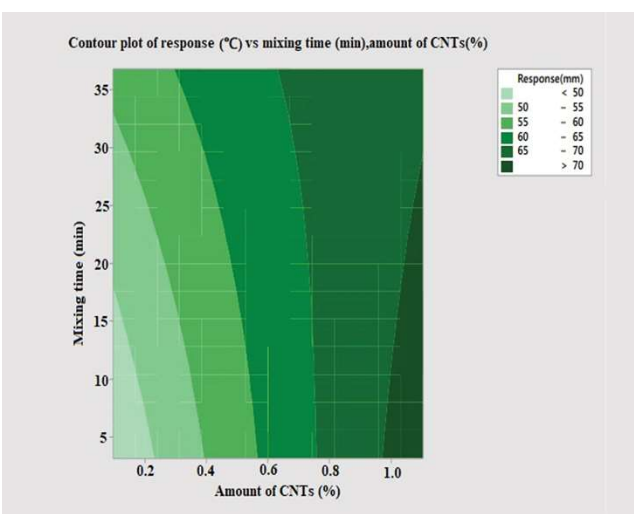

Fig. 4. a. contour plots for the mutual effects of: (a) mixing time and amount of CNTs

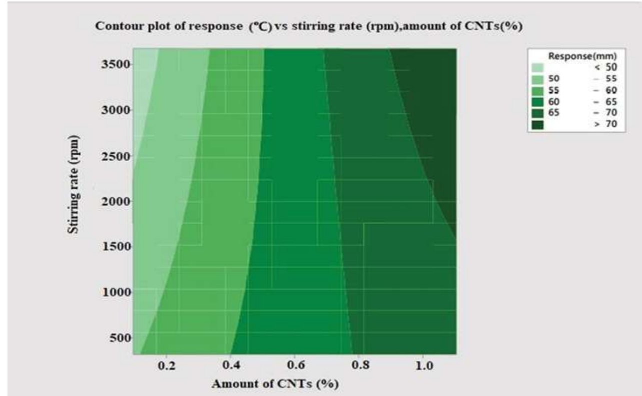

Fig. 4. b. contour plots for the mutual effects of (b) stirring rate and amount of CNTs

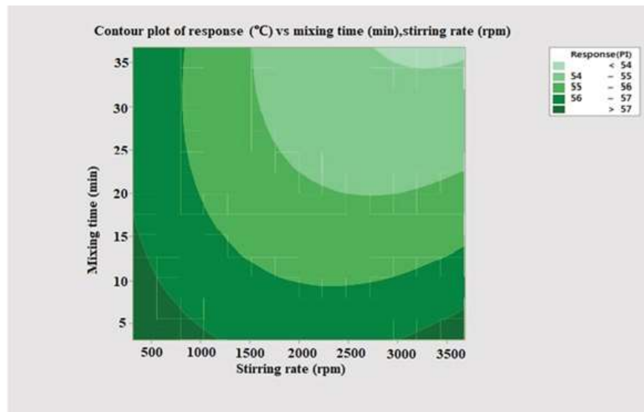

Fig. 4. c. contour plots for the mutual effects of: (c) stirring rate and mixing time on the softening point test.

4. Conclusion

Due to the increasing development of carbon nanotubes (CNTs) in the nanotechnology, we can use them as the special choice in asphalt mixtures. The effect of CNTs on rheological behavior and storage stability of modified samples were studied. The shape and morphology for modified samples were characterized by SEM and TEM, respectively. The effect of CNTs on the softening and penetration point of samples were examined by central composite design (CCD) experimental design and response surface methodology (RSM). CCD results proposed the rheological behavior to follow quadratic equation. Increasing the CNTs content from 0.3 to 0.9%, had significant effect on rheological properties of bitumen, so the 0.9% CNTs has been selected as optimum condition. Also, it was observed that the mixing time has the best performance and 30min was selected as an optimum mixing time. Rheological properties enhanced by increasing the stirring rate. The Marshall test had significantly increased by adding the percentage of CNTs to bitumen. CNTs had a significant effect on Marshall Ratio results due to increased stability. The experimental data showed that bitumen and asphalt mixture would be affected by CNTs.

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