Evaluation the Effect of Carbon Nanotube on the Rheological and Mechanical Properties of Bitumen and Hot Mix Asphalt (HMA)

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ABSTRACT: The technical characteristics of modified bitumen and asphalt have provided many study opportunities around the world. This article has assessed the effects of adding the Nanomaterial on the rheological specifications of bitumen by adding carbon nanotubes to bitumen and it also has evaluated the physical characteristics and bulk parameters of the surface (Topeka) layer of asphalt concrete sample by conducting Marshall Tests. In this regard, the technical characteristics of bitumen such as penetration grade, softening point, viscosity and thermal sensitivity were tested by adding carbon nanotubes with the amounts of 0.25, 0.50, 1 and 1.5 percent by weight of bitumen. The results show that adding carbon nanotube to the bitumen has been accompanied with a reduction in the penetration grade and an increase in softness of the bitumen, which improves the specifications of bitumen and therefore reduces asphalt tracking at high temperature. Following, the asphalt samples reinforced with carbon nanotubes evaluated for conducting Marshall Test. The results showed that the additive alters the Marshall Test parameters such as increasing the strength and decreasing the flow. Meanwhile, the specific gravity of asphalt mixture was increased and the void space percent of the aggregates was relatively decreased. Moreover, the void space of the asphalt mixture and the void space percent filled with bitumen were relatively increased. Economic analysis was evaluated for a 3-way path. Finally, according to the results and analysis of the Nanomaterial on the Nano specifications of bitumen and asphalt, technically, the results strongly suggest the use of carbon nanotubes. Although economically, the use of carbon nanotubes is limited.

Keywords: Carbon Nanotube, bitumen, asphalt, Marshall, economic analysis.

1 INTRODUCTION

Several factors affect the strength parameters of asphalt surfaces such as asphalt mixtures profile specifications, including the specifications of bitumen, aggregates used in asphalt mixtures and different percentages of its composition and also gradation type. Iran spends annually a considerable amount of its credits in the road and transportation sector on repairing or replacing the surface of the paths, which has not long passed since constructing its former coating; thus, creating asphalt roads using new technologies has always been considered for making more reinforced pavements.

Nanomaterial has been defined as a substance that at least one of its dimensions (length, width, and thickness) is less than 100 nm. Nano-materials of the structural elements and components of the bitumen and asphalt are in the form of micro at the Nano scale. Nanotechnology can be used to improve the specifications of these materials; some of these specifications may be asphalt resistance against damage from moisture, resistance and longevity, saving maintenance costs of asphalt or key specifications such as compressive strength, tensile strength and durability at high temperatures [1].

This paper has used nanotechnology to bolster the asphalt mixture. First, it will examine the effects of the additive on bitumen and then it will test the effect of this additive on the bitumen asphalt mixture by Marshall Test. Also, a dense graded asphalt mixture was used based on ASTM standard in order to prepare samples.

1.1. Literature Review

Adding materials is considered as one of the most suitable solutions for strengthening asphalt mixtures. Zarei and Zahedi, Zahedi and Zarei, Amir Tobakovic et al., Jens Groenniger et al., R. Zhen Fu et al., and Bharathi Murugan et al. have studied the effect of this additive on the asphalt mixes. The results indicate that the additives improve the specifications of the asphalt mixtures [2-8]. Regarding the superior mechanical specifications of nanotubes considering the tube radius, their Young's modulus and tensile strength can reach, respectively, 1000 and 1500 GPa [9].

Having specifications such as high specific surface $(gr/m^2 1000-700)$, high strength and exceptional electrical specifications, these materials are used as a catalyst base, mechanical reinforcement of polymers and composites, and manufacturing of electronic parts. They are 10 times stronger than steel, while their weight is one-sixth of the steel weight. This rating makes them the first choice to build bridges, planes and even spaceships [10].

After preparing some compositions containing carbon nanotube and evaluating the bitumen dispersion specifications, Shirakawa et al. (2012) found that adding nanotubes into the emulsion compositions is effective in the emulsion dispersion ability so that it is less effective in dispersion when adding it into the emulsion just in one step compared to the condition that the same amount of nanotube was gradually added into the emulsion and then was stirred [11].

Akbari Motlagh et al. (2012) used carbon nanotubes as an additive to the bitumen to enhance the technical specifications of bitumen and asphalt mixtures [12].

Figure 1 shows the changes in penetration grade, degree of softness and ductility property of the bitumen for samples with different percentages of nanotubes. In the condition that carbon nanotube is used, as the amount of nanotube has increased, the penetration grade has been further reduced and the changes in the degree of softness have also increased, and the modified bitumen shows more resistance against the flowing. Moreover, according to the chart, increasing the percentage of carbon nanotubes makes the bitumen more cohesion and it increases the amount of its plasticity, i.e., the ductility property of the bitumen has increased.



Figure 1. Changes of testing bitumen for samples of bitumen modified with carbon nanotube

According to the results, the technical specifications of asphalt mixture increases by increasing the amount of carbon nanotubes. As the sample that contains a nanotube equal to 0.001 of weight bitumen, has had the best results.

The sample was superior to the control sample in terms of Marshall Strength of 62.9%.

Santagata et al. (2012) have focused on the use of carbon nanotubes in the bitumen and its rheological specifications in different conditions. After testing the compounds, the viscosity amount has reduced with increasing temperature and the viscosity amount has also increased by increasing the carbon nanotubes percent in the combination; therefore, increasing viscosity is beneficial in improving resistance to permanent deformation at high temperatures [13].

Carbon nanotubes increases the potential for rutting resistance and thermal cracking resistance in the asphalt concrete as well as it reduces the aging ability of bitumen oxidation, which are effective in longterm performance of asphalt mixtures [14].

According to the surveys on resources about the effectiveness and the use of carbon nanotubes separately in the heated asphalt concrete, the results indicate that nanotubes has beneficial use in asphalt mixes due to the changes in the specifications of bitumen and upgrading the technical specifications of asphalt mixtures. So, the present study has tried to provide a chance for producing resistant asphalt mixtures by improving the specifications of bitumen and asphalt.

2 THE CONSUMABLE MATERIALS SPECIFICATIONS

2.1 Grading and Aggregate

The aggregates, which have used to make the laboratory samples, have prepared from the Ghazanchi asphalt plant in Kermanshah and it is fixed at all stages of testing. The mixing ratios of the aggregates in the asphalt mixtures for the Topeka layer are specified as in Table 1.

Table 1. Proportions	aggregate	asphalt	mixture
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Types of Aggre- gates	Medium gravel	Fine gravel	Sand
Grain size	4.75-25 Mm	0-19Mm	0-6 Mm
The percentage of mixture in aggregate	10	42	48

The grading curve, which has resulted from mixing the required weight percentages, in comparison to the grading used to prepare the samples, has drawn in Figure 1.



Figure 2. The Grading Resulted from Mixing Aggregates in the Asphalt Mixture for Topeka Layer

2.2 . Bitumen

The bitumen, which has blended in this mixture, has prepared from the Isfahan refinery, and the required tests have conducted on it. The most relevant results are listed in Table 2.

Table 2. The results of standard tests used in research on bitumen

Characteristic	standard	Results
	ASTM	_
Specific gravity at 25°C	D70	1.015
The penetration grade in 25°C	D5	64
(100 g-5 seconds), in 0.1 mm		
Softening point (ring and ball),	D36	49
in C		
the amount of stretch at 25°C	D113	More than
in cm		100
The degree of flammability	D92	289
(open-Cleveland), in Celsius		
The amount of stretch at 25°C,		More than
in cm		100

Carbon Nanotubes 2.3

The present study has used a multi-walled carbon nanotube according to the specifications given in Table 3.

According to the conducted surveys, this additive and the bitumen modifier are combined with it in four percentages (0.5, 1, 1.5 and 2) by weight of bitumen. To do this, an amount of bitumen with the desired amount of carbon nanotubes should be poured into the beaker by using a mechanical mixer and a heater is used for heating since the bitumen should be flowed to the extent that the mixing can be done easily. So, the heater is set to around 120 °C in order to avoid excessive heating of bitumen and then the mixing is done for an hour [12].

3 SAMPLING METHOD

The samples of conventional asphalt mixtures used in the present research tests have been cylindrical with a diameter of 4 inches (101.6mm) and a height of about 2.5 inches (63.5 mm) [13]. The samples are compressed by weighing the different components of the aggregates, mixing them in the tank, and then pouring the mixture into the Marshal mold and applying 75 strokes to each side (for simulating the heavy traffic). Samples, 24 h after compression, are taken out from the mold by using specific jacks and they get prepared for testing [16].

3.1 *Explaining and Analyzing the Results of* Bitumen Tests Modified with Different Percent of Carbon Nanotube

Various tests should be conducted on the bitumen to evaluate its performance. The physical, mechanical, morphology, rheology specifications of the bitumen can be determined by using these tests, which this section has examined the effect of carbon nanotubes on some fundamental specifications of the bitumen compared with the pure bitumen.

Table 3. The Properties of Multi-Walled Carbon Nanotube (MWCNTs)						
Method of production	External di- ameter	inner di- ameter	the length	Specific sur- face area (SSA)	Real den- sity	Purity
Epitaxial chemical vapor (CVD)	5-15 Nm	3-5Nm	50 Microm- eter	233m ² /g>	2.6g/cm ³	‰> 9 5

3.1.1 The Results and Analysis of Penetration Testing

Figure 3 shows the results of penetration grade testing for the bitumen modified with different percentages of carbon nanotubes. Increasing the percentage of carbon nanotubes in bitumen leads to reduced penetration grade so that its lowest amount has been reduced to 18.8 percent for a sample with 1.5% nanotubes. This is due to a very high surface density, strength, and high tensile strength of carbon nanotubes that cause resistance to needle penetration and thus reduce the penetration degree. Given that, in all the above cases, the penetration grade is reduced compared to the original bitumen, so the obtained bitumen can be used in the warmer weather or in areas with more frequent and heavier traffic; and therefore, it is already known that the stiffness modulus increases at temperature 25°C by increasing the amount of carbon nanotubes.



Figure 3. Comparison of the Penetration Grade Test Results for Samples with Different Percentages of Carbon Nanotubes



Figure 4. Comparison of the Test Results for Samples with Different Percentages of Carbon Nanotubes Softening Point

3.1.2 The Results and Analysis of Softening Point Testing

As it can be seen, the softening point subtly has enhanced by increasing the nanotube percent. The maximum amount of increase was obtained by adding 0.25% nanotube to bitumen just at the beginning of the chart, as compared to other percentages. The increase in the softening point is desirable, because the bitumen with high softening point may be less sensitive to temperature changes (rutting). It can also be expected that asphalt made from these types of bitumen have a more robust performance against permanent deformation and rutting in the wheel paths and ultimately its sustainability will be higher relative to the environment temperature changes.

3.1.3 The Results and Analysis of Kinematic Viscosity Testing at 135° C in terms of Centistokes (cSt)

The bitumen viscosity has been rising considerably with increasing nanotube percentage in bitumen. The slope of the chart is initially mild and it goes up by increasing the amount of additive, and it reaches the amount of 1482 cSt for the bitumen with 1.5% carbon nanotube from the amount of 387 cSt for the base bitumen, which is a tangible increase of 283% (Fig. 5). The viscosity testing is to determine flow specifications of bitumen at high temperatures and the performance of asphalt. Another noteworthy point is that the bitumen viscosity with asphalt stability has a direct relationship with temperature variations. That is, when the viscosity is low, the bitumen will get pasted in the summer heat and it causes the asphalt to become rugged under the traffic load and the bitumen oxidation phenomenon will occur. Moreover, the asphalts will crack in the winter coldness when the bitumen viscosity is high. Considering that the modified bitumen at higher temperatures had a higher level of viscosity than the base bitumen, so, it has higher strength and there will be less rutting [16].



Figure 5. Comparison of the Viscosity Test Results for Samples with Different Percentages of Carbon Nanotubes

3.1.4. The Results and Analysis of the Parameters Determining the Bitumen Thermal Sensitivity (PI and PVN)

Penetration index (PI) is a criterion for thermal sensitivity. The higher the penetration index, the bitumen sensitivity to temperatures is lower and consequently there will be less rutting, permanent deformation and thermal cracking on them. The PI value for the base bitumen is negative. This indicates their limited service temperatures and extreme sensitivity to the temperature. In the PI relationship, there is only penetration grade and softening point, which due to its slow changes along with an increase in the percentage of carbon nanotube, the penetration grade effect in this relationship is less than the softening point, i.e. the sensitivity of the PI relationship for the modified bitumen to the softening point is more than the penetration grade. Therefore, the excessive increase in PI is associated with the sharp rise in the softening point. As it can be seen in Fig.5, as a result of determining the PI values for the modified bitumen, at first, the PI will be increased and then it will have a downward trend by increasing the amount of the nanotube; so that the sample with 0.25% carbon nanotube, in terms of the highest amount, has the best performance among other samples.



The effect of carbon nanotubes on sign of penetration



Figure 6. Percent Carbon Nanotubes Shift with Increasing Penetration Index Bitumen

PVN is another parameter that determines the bitumen thermal sensitivity, which based on a formula defined in chapter 3, the calculated values for it are given in Table 4. As it can be seen, in contrast to the results obtained from the penetration index, the amount of PVN also increases by adding the amount of nanotube to the bitumen.

Table 4. Results of experiments with different percentages of carbon nanotube

Com- bine name	Pene- tration grade (tenth of a milli- meter)	Soften- ing point (° C)	Kine- matic viscos- ity tem- pera- ture ° C135	Ther- mal sen- sitivity	PI	PVN
control	65	49	387	0.0454	-0.825	0.741-
C0.25	64	50.4	459	0.0432	-0.506	0.513-
C0.50	62	50.5	666	0.0434	-0.535	0.021-
C1	57	50.7	1038	0.446	-0.712	0.503
C1.50	52	50.8	1482	0.0460	-0.909	0.881

4 THE OPTIMUM BITUMEN PERCENTAGE AND TYPICAL MARSHALL PARAMETERS

Based on the Marshall test results of the used mixture design, the optimum bitumen percentage of conventional asphalt samples for Topeka layer is formed 5.2% by weight of the 1200g sample, that is, 62.4g of sample weight, which as a result of performing the tests on samples with different percentages of bitumen and the obtained curves, the parameters resulted from the Marshall test for the sample made with optimum bitumen percentage (control sample) are according to table 5.

Param- eter	Strength (kg)	Flow (mm)	Spe- cific weight (grams per cu- bic centi- meter)	VMA (per- cent)	VTM (per- cent)	VFA (per- cent)
Amount	1005	3.1	2.290	%14.8	%3.5	%72

Table 5. Marshall Test results for the control sample.

4.1 Marshall test

The physical properties and bulk parameters of asphalt mixture such as Marshal strength, Marshall flow, specific gravity, void space percent of aggregates mixture, void space percent of compressed asphalt mixture and void space percent of aggregates mixture filled with bitumen are determined and studied by doing Marshall tests on the asphalt concrete samples constructed from glass powder and carbon nanotube simultaneously.

4.2 Describing and Analyzing the Marshall Strength Testing of Asphalt Mixture Samples Made with Carbon Nanotubes

Figure 6 shows the results of tests to determine the strength of different amounts of carbon nanotube containing compounds Marshall. According to the results, adding nanotubes to the bitumen in the asphalt concretes increases the Marshall strength and it had an increasing trend graph so that the least amount of strength to combine with 0.25 percent nanotubes and for a sample that 1.5% by weight of Nano material is used in its bitumen, the highest amount of strength is obtained and it is 69.75 per



The effect of carbon nanotubes on marshall stability

Figure 7. Marshall Resistance Changes in Carbon Nanotubes Added to the Bitumen

cent greater than the control sample. Also, with the nanotubes equal to 1% with 0.60% in asphalt mixtures, the strength became 1493.4 kg, which the rate of increase in strength was 48.54%. This is due to the fact that these are special specifications of carbon nanotubes, including the high density surface, high tensile strength and resistance.

5.2. Describing and analyzing the Marshall Flow Test for Asphalt Mixture Samples Made with Carbon Nanotubes

As it can be seen in Figure 8, adding carbon nanotubes to bitumen will reduce the flow in asphalt concrete. This means that the flow level increased by 22.58% for the sample with 0.25 % nanotubes and then the flow level increased by 3mm for the 50% composition, which its most important reason is the Young's modulus of carbon nanotubes; afterwards, the flow level has had a decreasing trend since other specifications of nanotube such as resistance and tensile strength have overcame the Young's modulus.

4.3 Describing and Analyzing Real Gravity Test Samples of Asphalt Mixture Made with Carbon Nanotubes



Figure 8. Marshall Flow Changes in Carbon Nanotubes Added to the Bitumen

According to the results, the specific gravity of all mixtures containing nanotubes is greater than the control sample So that the highest specific gravity of the sample containing 1% nanotube had increased by 1% compared to the sample without the additive. Among the samples containing nanotube, the lowest level of specific gravity relates to the asphalt mixture containing 0.5 percent by weight of bitumen of nanotube, which is equal to 2.304 gr/cm³ and it has had a 0.61 percent increase compared to the control sample. The specific gravity loss of this sample is caused by the high surface density of nanotube, but then the high



tensile strength and resistance have overcome the surface density, which led to increase the specific gravity (Figure 9).



Figure 9. Changes in the Specific Gravity of Carbon Nanotubes Added to the Bitumen

4.4 Describing and Analyzing the Results of the Voids in Mineral Aggregate (VMA) Samples of Asphalt Mixture Made with Carbon Nanotubes

The results presented for the voids in the mineral aggregates in Figure 9 shows that for all mixtures containing nanotube with different percentages, the lowest level of the 0.25% mixture is 14.46 and the highest amount of the 0.50% mixture is 14.68, which for these two compounds, respectively, 2.3 and 0.8 percent is less than the control sample. So, all the resulting values for voids of aggregates are less than the value obtained from control samples.



Figure 10. Changes of Voids in Mineral Aggregate in Carbon Nanotubes Added to the Bitumen

The effect of carbon nanotubes on VTM



Figure 11: Changes in the Voids in the Total Mixture Added to Bitumen Carbon Nanotubes

4.5 Describing and Analyzing the Results of Voids in the Total Mixture (VTM) for the Samples made with Carbon Nanotubes

According to Figure 11, it can be seen that the increase in carbon nanotubes increases the voids in the total mixture to 4.57 percentages higher than the control sample and this upward trend has continued to the sample with 0.50 percent by weight of bitumen. Then, the chart goes down in order to reach its lowest amount (3.53 percent) among the mixtures modified with the Nano material. It should be explained that the asphalt mixtures voids of all samples with nanotubes is more than of common laboratory samples and the amount is within the allowable range bylaws.

4.6 Describing and analyzing the Results of Voids Filled with Asphalt (VFA) for the Asphalt Mixture Samples Made with Carbon Nanotubes

According to the results in Figure 12, it can be seen that the volume of voids filled with asphalt mixture modified with nanotube is higher than the typical sample and it initially increases by 3.75 percent in 0.25% compound. Also, the lowest level of increase belongs to the mixture with 0.50% nanotube that is 1.91 percent more than the control sample. The amount of filled void for the sample that its bitumen



Figure 12. Changes in the Voids Filled with Asphalt in Condition Carbon Nanotubes Added to the Bitumen



contains 1% nanotube is equal to 75.37%, which is more than other samples and the simple sample; however, the maximum amount allowed for heavy traffic is 75%. So, the requirements of the regulation do not meet this feature.

5.7. Summary of Marshall Results Summary of the results is presented in Table 6.

Table 6. Results Summary

Com- bine name	Strengt h(kg)	Flo w(m m)	Spe- cial weigh t (Kg / cm3)	Voids in min- eral aggre- gate (VMA)	Void s in total mix (VT M)	Voids Filled with As- phalt (VFA)
con- trol	1005	3.1	2.29	14.8%	3.5%	72%
C0.25	1222.7	2.4	2.31	14.46%	3.66	74.70%
C0.50	1350	3	2.304	14.68%	3.91	73.37%
C1	1493.4	2.6	2.313	14.35%	3.53	75.37%
C1.5	1706	2.8	2.307	14.57%	3.78	74.03%

5 COST ANALYSIS

This article has studied the economic analysis of adding carbon nanotubes to asphalt mixtures according to the results of Zarei et al. and Mirbaha et al [17-20]. This section has evaluated the costs and savings (benefits from adding carbon Nanotube). To this end, construction of a 6-line path (each direction 3 lines) for 1 km was evaluated. The specific gravity of asphalt was considered y = 2.3 ton/m³ and the price of each ton of asphalt and carbon nanotube (per kg) were considered about 51\$ and 3250\$, respectively. The cost of adding additives is calculated using the following formula:

Benefit=1000*6*3.65* $\frac{D_i * 2.54}{100}$ * γ * asphalt price -1000*6*3.65* $\frac{D_0 * 2.54}{100}$ * γ * asphalt price (Eq.1)

Cost=1000*6*3.65* $\frac{D_i * 2.54}{100}$ * χ * 1000* $\frac{62.4}{1000}$ * additive percent*carbon nanotube price (Eq.2)

Table 6 and 7 show the results of design and economic analysis respectively:

Table /. Design result						
additive %	Marshall stability (Pound)	a1	Di			
0	0	0	0			
C 0.25	2694.021	0.483	4.078674948			
C 0.50	2976.21	0.496	3.971774194			
C1.0	3291.468	0.54	3.648148148			
C 1.5	3761.048	0.54	3.648148148			

Table8. Econ additive	nomical result Benefit	lt Cost	Benefit-Cost
7 <u>0</u>	0	0	0
C 0.25	47384.37	42398270	-42350885.27
C 0.50	54359.57	82574049	-82519689.78
C1.0	75475.94	1.52E+08	-151616111
C 1.5	75475.94	2.28E+08	-227461904.5

According to the table 8 and after performing the cost analysis on the effect of carbon nanotube, it was concluded that this type of additive should be used in restricted areas.

6 CONCLUSION

The main objective of this study is to provide solutions to construct pavements with functional properties and better resistance than conventional pavements and as the asphalt pavements are the national funds, and every year a lot of budget spent on road pavement construct, maintaining and improving the mechanical specifications of asphalt is concerned with maintaining economic aspects. The results are as follows:

- By increasing the percentage of carbon nanotube, penetration degree decreases and softening point and viscosity increases.
- By adding carbon nanotube, Penetration index (PI) increases and then decreases. On the other hand and by increasing the percentage of additive, Penetration viscosity number (PVN) increases.
- Thermal sensitivity decreases by increasing the percentage of additive. By increasing the percentage of the additive, the thermal sensitivity becomes greater than the base value.
- By adding carbon nanotube, stability increases and flow decreases relatively.
- By adding carbon nanotube, specific gravity increases.
- Voids in mineral aggregate (VMA) relatively decreases. However, voids in the total mixture

(VTM) and voids filled with asphalt (VFA) relatively increases.

• By adding carbon nanotubes to asphalt mixtures, the cost of asphalt mixture increases sharply.

After performing the tests and observing the results obtained regarding the technical and economic aspects, among all joint samples with glass powder and carbon nanotubes, for combination with 0.25 percent by weight of bitumen with the estimated carbon nanotubes limit regulation, have had the optimal specifications of the test results Marshall. Technically, the results strongly suggest the use of carbon nanotubes. Although economically, the use of carbon nanotubes is limited.

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