Using the Statistical Analysis of Carbon Nano-tubes Dispersion in Bitumen Employing Software MINITAB

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Abstract:

Nowadays, utilisation of Nano-materials as one of the most recent methods of bitumen modification has attracted attention of many researchers. However, not enough research has been pursued on their mixing with bitumen, because of their dimensions and specific properties. In this study, the carbon Nano-tubes were mixed with bitumen using different mixers and some images were recorded employing a scanning electron microscope. Then, different statistical analyses were carried out on the experiment of penetration degree performed on several samples. The recorded images of mixed samples and the statistical analyses show that the ultrasonic mixer has mixed the carbon Nano-tubes more homogeneously with bitumen compared to other mixers.

Keywords: Bitumen, CNT(Carbon Nano Tubes), SEM, mixers

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1. Introduction:

Bitumen, as the most applicable material in road pavements, has two major properties: adhesion and hydrophobic. Despite the fact that bitumen has a perfect performance, the weather and loading conditions might affect adversely on its efficiency. Therefore, many research works have been implemented to modify its specifications. These materials include polymeric and non-polymeric modifiers.

Bitumen is a complex mixture of aliphatic, aromatic and naphtenic hydrocarbons, with smaller quantities of other organic and metal organic compounds generally obtained from the vacuum residue of crude oil processing and mainly used as binders in road and airport pavements [Read and Whiteoak, 2009].

Bitumen has been widely used for pavement construction for a long time. Actually, the increase in traffic loading and in the number of vehicles together with the adverse environmental conditions, conduct to a rapid structural damage of pavements. In order to enhance the mechanical properties and the long time behavior, a new generation of blending bitumen materials have been developed through the incorporation of different kinds of polymers [Collins et.al, 1991, , Sengoz et.al, 2007 and Isacsson et.al, 2001].

On the other hand, use of polymer-modified asphalts (PMA) allows the construction of safer roads and leads to a major reduction in maintenance cost [Polacco et.al, 2005]; these advantages compensate the major cost of the PMA obtained. However, absence of a well-documented design procedure for modified flexible pavements has resulted in a low confidence in highway engineers while using these materials.

The aims of this paper are as follows:

(1) Recommendation of specification of best mixing condition of bitumen and Carbon Nano-Tubes (CNT).

(2).Verification of best mixing conditions by statistical analysis.

2. Literature Review

Nanotechnology has changed and will continue to change our vision, expectations and abilities to control the material world. These developments will definitely affect the field of construction and construction materials. Carbon Nanotubes (CNTs) are considered to be one of the most beneficial Nano-reinforcement materials. The combination of high ratio, small size, low density and unique physical and chemical properties make them perfect candidates as reinforcements in bitumen-based materials [Banthia, 2009 and Branner et.al, 2008].

Modifying the bitumen mixtures with polymers appears to have the greatest potential for successful application in the design of flexible pavements. These benefits can be realized by extending the service life of the pavement or reduction in asphalt concrete layer or base thickness. The necessary modifications can be brought about in the existing design procedure by using new materials for the pavement construction [Al-Hadidy and Tan, 2009].

Hussain et al. [Hussain et al, 2006] showed that the biggest challenge in developing nanocomposite is the dispersion of nanoparticles or chemical compatibility with matrix materials. They found out that the issue of improving the carbon nanofibers (CNFs)/ matrix interfacial adhesion and complete dispersion must be resolved before achieving the full potential of nanoreinforced composite materials.

Nanoclay modification improves some characteristics of asphalt binders and asphalt mixtures such as rutting. However, it has not mitigated the fatigue problem and hence, more research is required before it can be utilized on a large scale [Ghile DB, 2006]. Research has shown that Nano calcium carbonate (Nano-$CaCO_3$) modified asphalt can enhance asphalt rutting resistance and improve its low-temperature toughness. Nanoclays such as sodium montmorillonite and organophilic montmorillonite have shown improvements in viscosity, complex shear modulus and phase angles of styrene–butadiene–styrene (SBS) copolymer modified asphalt [Yu, J. et.al, 2007 and Ma, F. et.al, 2007].

3. Materials

The bitumen with PG58-16 degree of performance from Isfahan Refinery has been used to be mixed with carbon Nano-tube. Characteristics of bitumen and carbon Nano-tube are presented in Tables 1 and 2, respectively. For further experiments, bitumen containing three percent of multi-wall carbon Nano-tube was used and each sample was mixed using different mixers and under different circumstances in the first step. In this step, three types of mixers including mechanical mixer, high-shear mixer, and ultrasonic mixer were employed (Fig. 1).

Table 1.Characteristics of used bitumen.

Ductility (cm)	Softening point (^{0}c)	Penetration at 25 ^{0}c (0.1mm)	Pure bitumen
Over 100	51	68	60/70

Table 2.Characteristics of used CNT

length	purity	ash	SSA	Density
30 µm	> 95%	< 1.5 %	200 m2/gr	2.1 gr/cm2

3.1 mixers

The mechanical mixers are often used in metallurgical and mechanical laboratories. This kind of mixer is used to mix several dry powder ??? High shear mixers are among the most applicable mixers used in mixing asphalt and polymer. It is used to mix asphalt with polymers and other additives. Rotation rate of the mixer's tip can be determined according to the type of polymer. This mixer is used for mixing asphalt and polymer because of the special structure of its tip. In fact, the special design of mixer tip makes the mixture enter and move rapidly through the space between two very close plates and leaves it through the space between embedded slots in outer layer. This procedure results in making the mixture of asphalt and polymer more homogeneous.

This apparatus produces a huge amount of energy by creating ultrasonic waves and cavitation that can combine the mixture and also separate Nano particles from each other and finally, make a completely homogeneous mixture.

Then, based on the fact that while mixing materials, the performance of different mixers differ ,different mixing conditions were considered. For instance, the combination time has been considered to be variable for mechanical mixer since its speed of mixing is constant. The rotation speed and the power have been supposed to be variable for high-shear and ultrasonic mixers, respectively. Therefore, according to Figure 3, nine different types were prepared to mix bitumen and carbon Nano-tube.

After mixing carbon Nano-tubes and using different mixers under different circumstances, scanning electron microscope was employed to investigate the dispersion of carbon Nano-tubes in Nano-scale.

One should note that before placing samples under the microscope, they were put in a vacuum chamber and

Figure 1. Different types of mixers used for mixing bitumen and carbon Nano-tube (from the right: mechanical mixer, high-shear mixer, ultrasonic mixer)

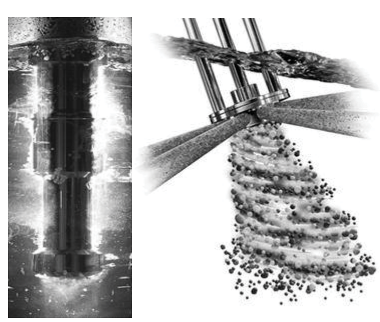

Figure 2. Quality of performance of high shear and ultrasonic mixers [directindustry and composites site]

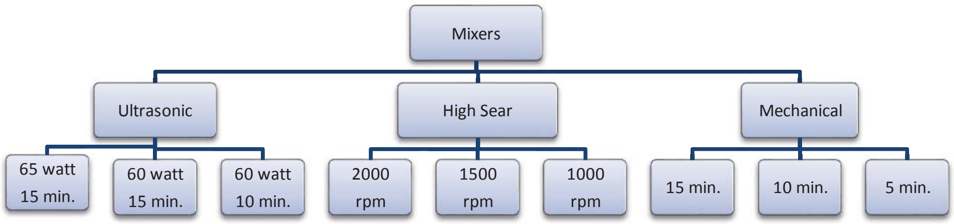

Figure 3. The considered conditions to mix bitumen with Nano-materials based on the type of mixer

were covered with a thin layer of gold (figure 4).

Figure 4. Bitumen sample, before (right) and after (left) preparation for being placed under microscope (the left sample: placing in vacuum chamber and covering with a thin layer of gold)

In addition, to verify the prepared samples mixed with carbon Nano-tube and to evaluate the accuracy of obtained images, a special experiment should be conducted. This experiment should be conducted without making any change in sample's state. It should also be able to be carried out at any point of the sample. Surveying all experiments regarding bitumen including both classic and SHRP ones; showed that the experiment of penetration degree was selected as the control test. Although this experiment is classic and is not widely used, it was chosen since it meets all the required needs.

In this stage, the experiment of penetration degree was conducted on the standard bitumen sample (case 1), the mixture of bitumen with carbon Nano-tube mixed by the mechanical mixer (case 2), high-shear mixer (case 3) and ultrasonic mixer (case 4). Results were then analyzed using software MINITAB.

4. Results analysis

Using different mixers and under different circumstances, the samples were prepared to be placed under the microscope in order to investigate the effect of mixing method. According to the type of mixer, the considered samples can be divided into three general groups (because the result of different cases of each mixer was similar) in each of which the impact of mixer's type on Nano-materials dispersion is conspicuous. Consequently, the samples prepared by each mixer (mechanical, high-shear, and ultrasonic mixers) are investigated separately.

4-1 Mechanical mixer

For nearly all the samples prepared by mechanical mixer, results were almost the same The concentration of Nano-materials was observed in some parts of samples (Figure 5, parts A,B,D). However, there was no trace of Nano-materials in some samples (Figure 5, part C) and also in some samples, the concentrated Nano-materials were observed in a part of sample ,indicating that the mechanical mixer has not been able to separate Nano-materials from each other. As a result, they were detected tangled (Figure 5, part D). Indeed, the dispersion of materials was in micro-scale instead of Nano-scale.

This matter shows that using mechanical mixers for mixing Nano-materials creates a non-homogenous mixture in terms of material dispersion in the bitumen. Furthermore, they cannot prevent Nano-materials from agglomeration.

4-2 High-shear mixer

Using the high-shear mixer, the samples have been prepared by three different angular speeds including 1000 rpm, 1500 rpm, and 2000 rpm while being mixed with bitumen for 15 minutes in 120°C. The sampling procedure was then performed on the obtained mixtures. Unlike the samples prepared by the mechanical mixer, those prepared by the high-shear mixer monitored homogenous dispersion of Nano-materials in the entire of the sample (Figure 6, part A and B). However, this mixer could not spread the Nano-materials in Nano-scale, but rather in micro-scale and the agglomeration phenomenon was observed in the samples (Figure 6, part C and D).

The configuration of the high-shear mixer due to which

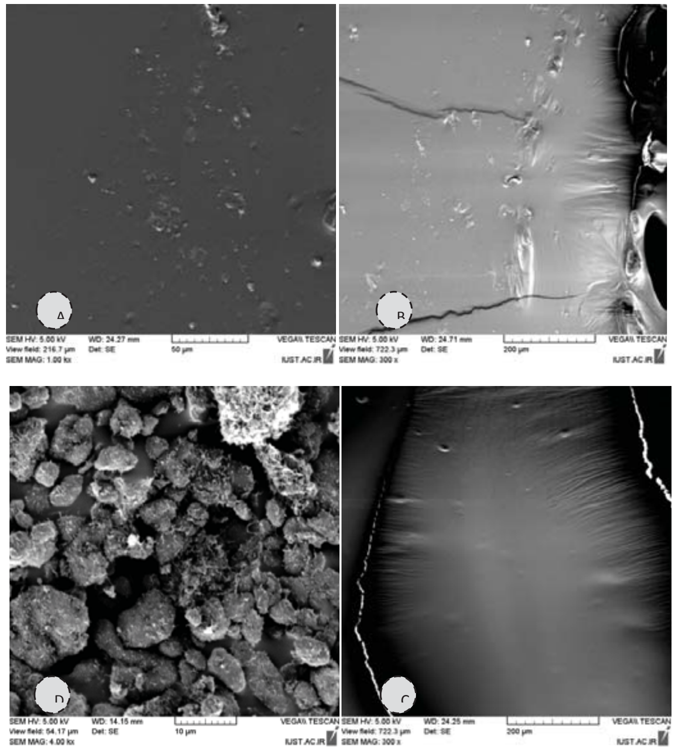

Figure 5. Microscopic images of mixed samples with Nano-materials by a mechanical mixer (non-homogenous dispersion and agglomeration of Nano-materials)

the materials are mixed between two adjacent planes at a high pressure and speed, makes a homogenous mixture of bitumen and additive material (for this reason, it is used for mixing bitumen and polymer). Nonetheless, since the material used in this study is in Nano-scale that can normally be agglomerated reaching micro-scale, the mixer should have the ability of homogenously mixing and separating these materials as well. However, it can be claimed that the high-shear mixer might not have the capability of separating Nano-materials according to the observed samples under scanning electron microscope. One should, of course, note that this problem concerns carbon Nano-tubes and it (materials agglomeration) might not take place while dealing with other types of Nano-materials and they could be appropriate for mixing bitumen with other Nano-materials.

4-3 Ultrasonic mixer

The prepared samples of bitumen and Nano-materials mixture employing the ultrasonic mixer can be divided into three general groups including; the samples prepared with 60 watt of power mixed with bitumen for 10 and 15 minutes and the sample prepared with 65 watt of power mixed with bitumen for 15 minutes in 120°C. For the samples mixed by the ultrasonic mixer, specifically the one mixed for 15 minutes with 65 watt of power, it was observed that the Nano-materials were spread throughout the bitumen uniformly, separately, and without any agglomeration (Figure 7, parts A and B). As it can be seen in Figure 6, the carbon Nano-materials are completely separated and can be discriminated.

5. Statistical analysis

One of the most important statistical analyses, usually performed on experiments, is variance analysis. In this experiment, the single-factor (one-way) variance analysis is conducted since there is only one influential parameter that is the type of mixer. The purpose of this kind of analysis is to investigate the impact of the considered parameter (the type of bitumen) and its quantity on the response variable (the penetration degree of the experiment). Initially, the variation of variable in different conditions and its effect on the response variable have been considered according to available statistical tests in variance analysis. In this work, there are one variable and four states. The variable is the type of

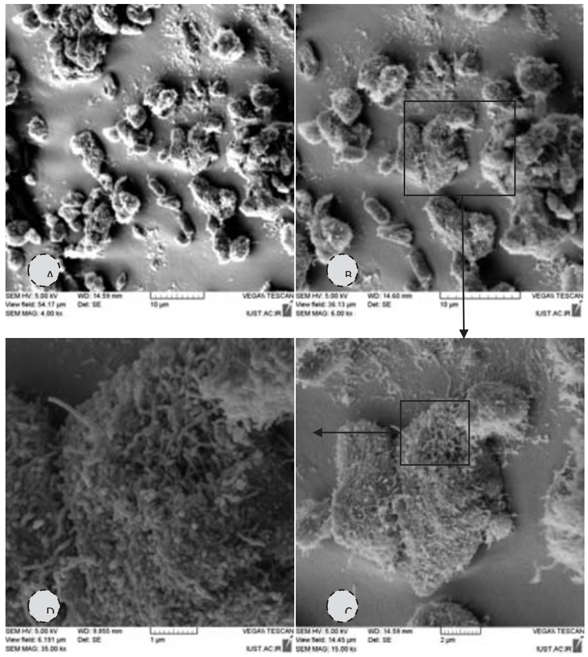

Figure 6. The microscopic image of prepared samples using a high-shear mixer (uniformity in Nano-materials dispersion and agglomeration)

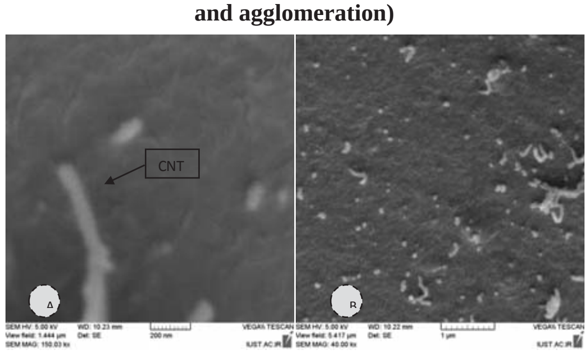

Figure 7. The microscopic image of samples mixed with Nano-materials by the ultrasonic mixer (uniformity in dispersion and separation of Nano-materials)

bitumen and the possible states are four types of bitumen: 1. Standard bitumen without additive materials. 2. Bitumen containing carbon Nano-tubes mixed by a mechanical mixer. 3. Bitumen containing carbon Nano-tubes mixed by a high-shear mixer 4. Bitumen containing carbon Nano-tubes mixed by an ultrasonic mixer

For F-test in variance analysis, it is assumed that the accidental errors have an independent and normal distribution that should be confirmed for this analysis. At first, the variance analysis is performed and then, the conditions are checked in terms of model's adequacy to assure they are satisfactory.

In this step, the data are entered into the software Minitab to conduct the single-factor (one-way) variance analysis (ANOVA). In this experiment, the type I error (the type I error is the rejection of a potentially true null hypothesis), α , is considered to be 0.05.

In variance analysis, the null and hypotheses are defined as:

$H_0: \mu_1 = \mu_2 = \mu_3 = \mu_4$: The mean-value is the same for all four types of bitumen.

H_1 : At least, two of the mean-values are different from each other

The results of the variance analysis are presented in table 3 and figure 8.

In results of the variance analysis, whenever P-value is less than 0.05, the null hypothesis is rejected. Based on the obtained results, it is observed that P-value is less than 0.05. Thus, the null hypothesis, i.e. the hypothesis of mean-values equality, is rejected. In addition, the fact that this number is zero up to three decimal places is indicative of the remarkable influence of different circumstances of variables presented in figure 9.

To reach the best of several types of bitumen, the model's adequacy, i.e. the accuracy of problem's conditions, is evaluated and then, if the conditions are satisfactory, one can claim that the results of the variance analysis are accurate and finally, the best mixing type is selected.

To evaluate the model's adequacy, the independency and normality assumptions of the experiment error values should be investigated. To evaluate the first issue, the plot of residuals vs. time is used. The positive and negative sequences are indicative of a positive correlation between residuals which rejects the independency assumption of errors. Figure 10 shows the plot of residuals vs. time.

As it is apparent from figure 10, there is neither positive nor negative sequence between residuals. This means that the plot has many changes in one side and does not show a familiar trend such as a sine plot. Therefore, it can be inferred that the errors are independent.

There are a number of methods to prove the normality of errors: 1. The errors' histogram should be like the normal plot. Obviously, the plot of figure 11 is in a strong similarity to the normal plot.

2. Using the probability plot: the more similar ????, the more accurate ????. In addition, if P-value is less than 0.05, the null assumption or the abnormality of errors is rejected. It can be seen from figure 12 that the plot has a considerable similarity to a straight line. Moreover, the major criterion, P-value, is less than 0.05. Hence, the normality assumption of the errors is confirmed, too.

Hence, results obtained from the variance analysis are accurate. Now, we are supposed to seek for the optimized answer. The best answer is the one which has the lowest penetration degree and variance or dispersion. According to the figure 13, the bitumen of the fourth type, containing carbon Nano-tube mixed by the ultrasonic mixer, has the lowest penetration degree.

Furthermore, it can be inferred from figures 13 and 14 that the bitumen of the fourth type, in addition to having the lowest penetration degree, has the lowest amount of dispersion in comparison to the third and second types which has a close mean-value to the fourth type bitumen.

For the bitumen of type four, the penetration degree and

Table 3. Results of the variance analysis

ne-way ANOVA: response versus type					
Source	DF	SS	MS	F	P-value
type	3	15332.4	5110.8	76.18	0.000
Error	248	16639	67.1		
Total	251	31971.4			
S = 8.191 R-Sq = 47.96% R-Sq(adj) = 47.33%					

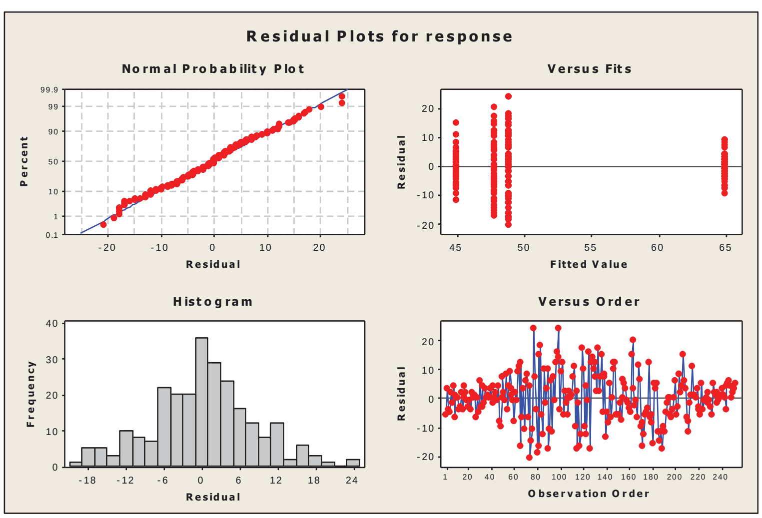

Figure 8.Variance analysis diagrams

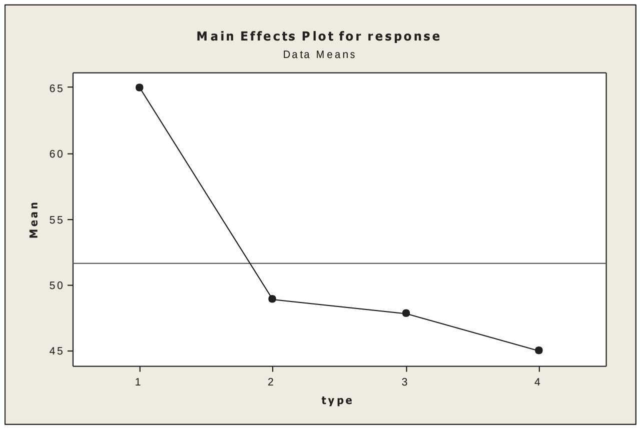

Figure 9.The plot of the variable's impact in different circumstances

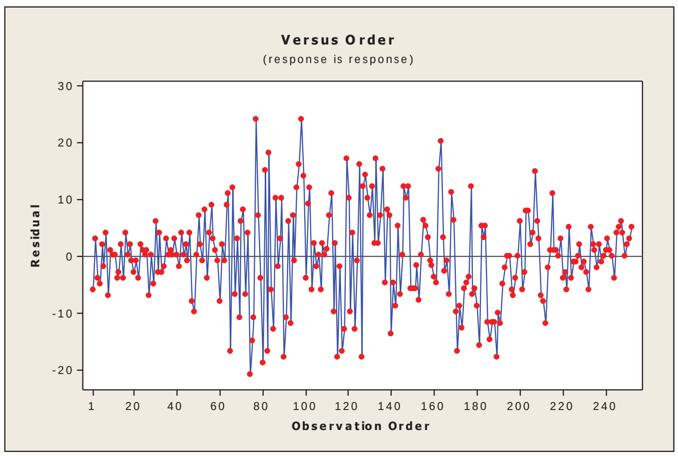

Figure 10. The plot of residuals vs. time

standard deviation are 44.968 and 5.11, respectively. Therefore, this type of bitumen is chosen as the best type.

Moreover, the problem can be analyzed in other ways without using variance analysis, as follows. Comparing the results of penetration degree experiment in figure 15, it can be seen that the lowest standard deviation is for the cases 1 (standard bitumen), and 4 (mixing by the ultrasonic mixer) which is indicative of similarity between the dispersion of these two types, and based on the fact that the standard bitumen has neither any kind of impurity nor any additive material, it can be deduced that the uniformity of the mixture prepared by the ultrasonic mixer is almost the same as that of the standard bitumen. Although adding Nano-materials reduces the penetration degree of this type, the data dispersion of penetration degree is lower than that of cases 2 (mixing by the mechanical mixer), and 3 (mixing by the high-shear mixer). This matter indicates that Nano-materials are more uniformly scattered by the ultrasonic mixer in comparison to other mixers.

In figure 16, each point signifies the result of a single penetration degree experiment. In case 4, for instance, the outcome of six penetration degree experiments is 45, across which 6 points are plotted. Investigating the data more carefully (figure 16) and the dispersion of experimental results separately, it can be inferred that the dispersion for the data regarding the ultrasonic mixer and the standard bitumen (cases 1 and 4) are almost the same. In terms of cumulation accumulation??? Did you mean this??, also, the data for cases 1 and 4, in the middle part (close to the average), are more cumulative in comparison to cases 2 and 3 (regarding samples prepared by the mechanical and high-shear mixers). This issue implies that the uniformity of Nano-materials dispersion in bitumen, prepared by the ultrasonic mixer is greater than that of other mixers. In a similar analysis for figure 17, the same results can be obtained since for cases 1 and 4, the penetration degrees are concentrated around some especial points, unlike cases 2 and 3 for which, the points are widely scattered.

For a better analysis of data, the 95 percent confidence method is also employed. In this approach, to evaluate

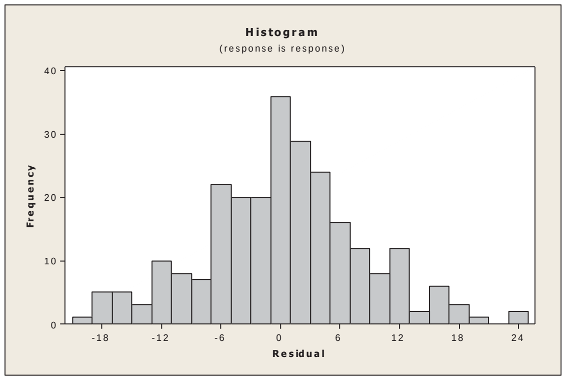

Figure 11. The histogram of residuals

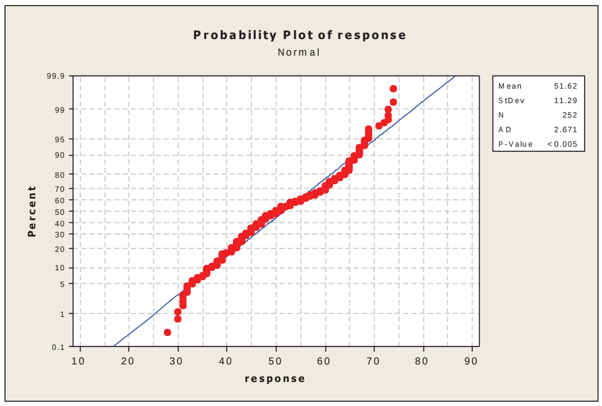

Figure 12. The probability diagram of total data

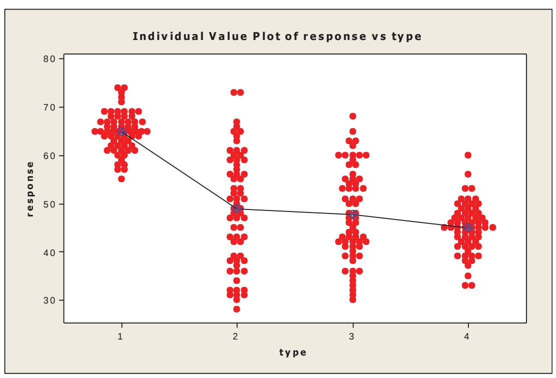

Figure 13. The diagram regarding the average and data distribution for types of bitumen

the data uniformity, the dispersion of 95 percent of medial data is investigated. As it is apparent from figure 18, the dispersion of 9 percent of data for cases 1(standard bitumen) and 4 (sample prepared by the ultrasonic mixer) is prominently less than that for cases 2 (sample prepared by the mechanical mixer) and 3 (sample prepared by the high-shear mixer). In addition, the samples mixed by mechanical mixer show greater dispersion than those mixed by the high-shear mixer. Generally, the dispersion of the samples mixed by the ultrasonic mixer is less than that of the samples mixed by the other mixers.

Figure 18 depicts the data distribution. None of the plots has a remarkable deviation from the normal plot. Yet, it can be seen that the data distribution for the first and fourth groups is in the way that they have a sharper slope than other two plots. This matter suggests that the plots of the first and fourth groups are more similar to the normal plot than other two plots.

At this stage, the normality evaluation of data is numerically dealt with. Considering all values for the standard

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Individual 95% CIs For Mean Based on    Pooled StDev

Level  N    Mean   StDev  ---------+---------+---------+---------+
1      63  64.905   4.059                       (--*--)
2      63  48.857  11.660        (--*--)
3      63  47.746   9.475       (--*--)
4      63  44.968   5.115  (--*--)
                         ---------+---------+---------+---------+
                              49.0      56.0      63.0      70.0

Pooled StDev = 8.191
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Figure 14. Mean value and standard deviation of data for four types of bitumen

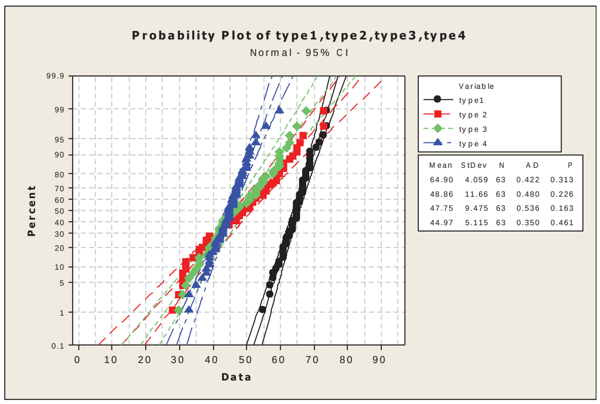

Figure 15. The probability plot for four types of bitumen

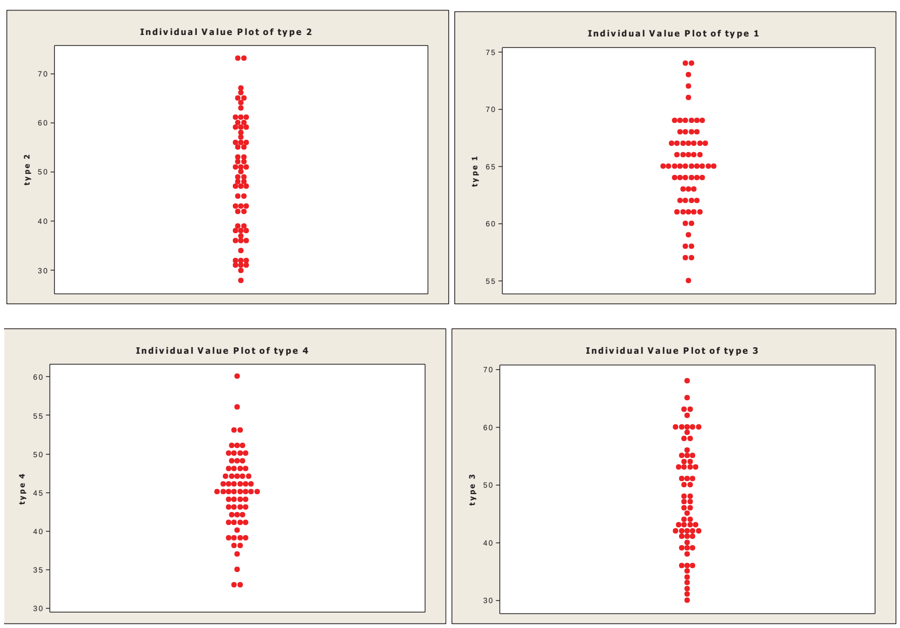

Figure 16. The dispersion diagram

deviation and the data dispersion seen beside each plot, it can be deduced that all four groups have normal data. Therefore, their abnormality assumption is rejected. As it is apparent from figure 8, the plots regarding groups 1 and 4 are in a stronger similarity.

6. Conclusion

Traditional bitumen produced in refineries has the capability of being used in most of the asphalt pavement. If this bitumen is consumed appropriately and while fulfilling all the needs for bitumen mixtures prepara-

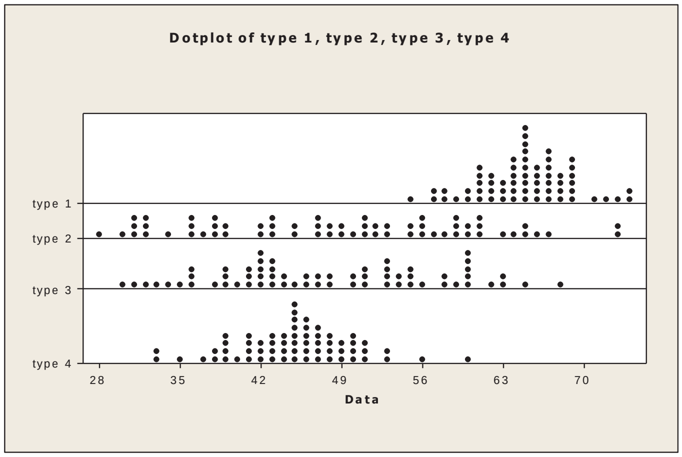

Figure 17. Dotplot diagram

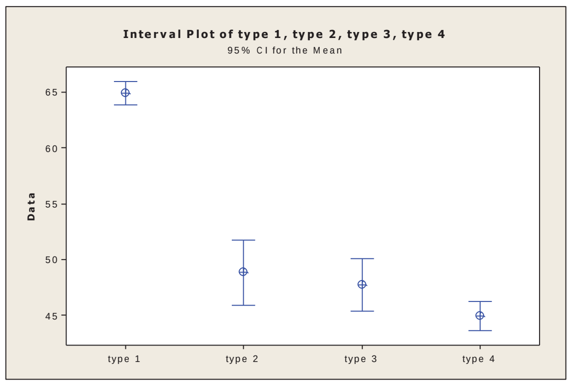

Figure 18. Interval plot

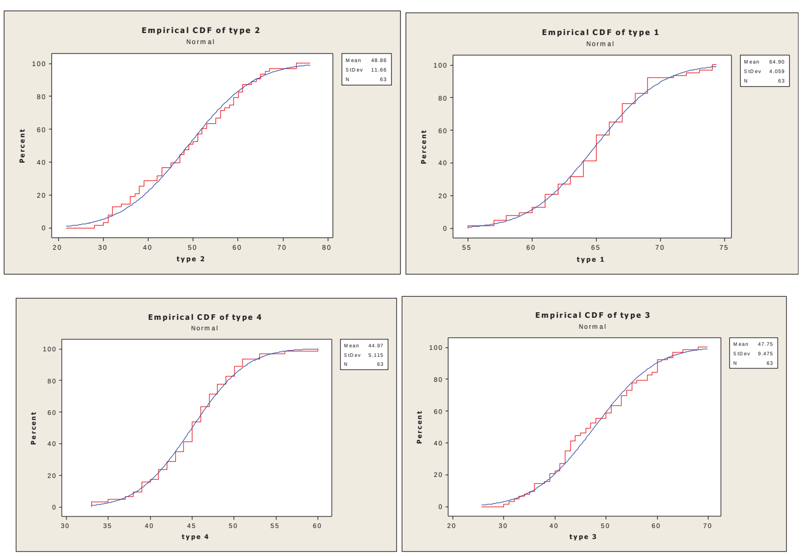

Figure 19. The normality evaluation of data for different mixing approaches

tion, they will have adequate mechanical properties compatible with the traffic and weather conditions. As a consequence of performance flaws in specific thermal and loading conditions, however, the researchers have always been trying to improve its properties.

Nowadays, Nano-materials are introduced as the newest bitumen modifiers. Nevertheless, the mixing conditions of these materials with bitumen are different from those of other modifiers due to their enormously small dimensions and special properties. In this study, carbon Nano-tubes were mixed with bitumen using different mixers and then, the dispersion of these materials throughout the bitumen was investigated using a scanning electron microscope. Furthermore, the accuracy of the recorded images by the mentioned microscope was confirmed by statistically analyzing the results of penetration degree experiment.

Use of mechanical mixers for mixing Nano-materials creates a non-homogenous mixture in terms of material dispersion in the bitumen. Furthermore, they cannot prevent Nano-materials from agglomeration. The high-shear mixer might not have the capability of separating Nano-materials according to the observed samples under scanning electron microscope, but the carbon Nano-materials are completely separated and can be discriminated with use of ultrasonic mixer.

The recorded images by the scanning electron microscope reveal that mixing carbon Nano-tubes with bitumen by the ultrasonic mixer provides a more uniform mixture compared to mechanical and high-shear mixers and agglomeration of Nano-tubes is prevented as well. As a result, these materials are scattered in bitumen in Nano-scale. Moreover, results of penetration degree experiment and statistical analysis indicate that the data dispersion of the experiments for the samples mixed by the ultrasonic mixer is much less than that of samples prepared by other mixers. This matter implies that the resultant mixture has a greater uniformity. Therefore, the best way of mixing bitumen with carbon Nano-tubes is by using the ultrasonic mixer.

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