Application of Taguchi Method for Optimizing of Mechanical Properties of Polystyrene-Carbon Nanotube Nanocomposite

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SUMMARY

Carbon nanotube (CNT) was selected as reinforcement agent to improve the mechanical properties of polystyrene (PS). PS–CNT nanocomposite was prepared by mixing CNT with a solution of PS. Taguchi experimental design method was used to determine the optimal conditions for preparation of the nanocomposite. The effects of six factors including the type of CNT (A), type of solvent (B), type of PS (C), drying temperature of nanocomposite film (D), the percentage of CNT (E) and duration of mixing after adding CNT (F) were investigated at different levels. The tensile strength values of PS-CNT nanocomposite films were used as the responses for the analysis of data using signal to noise (S/N) method. Using this method, the optimum conditions were obtained as: the type of CNT: functionalized single walled CNT (SWCNT), the percentage of SWCNT: 1.5%, the type of solution: tetrahydrofuran, the type of PS: GPPS 1460, drying temperature: 25 °C, duration of mixing: 1 hour. Based on the obtained values, the order of the effect of factors was CEADBF. The most effective and the least effective factors were C and F, respectively. The calculated F-ratio of each factor showed that at 95% confidence interval, the F values for all factors except factor F have significant effects on the response values. Also, the functionalization of the CNTs surfaces by –OH and –COOH groups confirmed by FTIR and SEM techniques.

Keywords: Polystyrene, Carbon nanotube, Nanocomposite, Taguchi, S/N Analysis method

1. INTRODUCTION

Despite the acceptable performance of composite technology in preparing materials with improved properties, the obtained composite materials fail to meet industrial needs, especially in terms of achieving desirable mechanical properties[1]. In recent years, researchers have become aware of the fact that if the material is prepared at small (nano) scale, its bonds with the adjacent phases will be much stronger than those of large-scale preparation. Therefore, a new variant of composites called nanocomposite has been introduced and developed. Nanocomposite is a compound in which the size of at least one of its phases has the dimension of 1 to 100 nanometres. The polymer based nanocomposites are a new type of nanocomposite materials in which nano-scale inorganic components with different structures and low weights (often less than 6%) are used as reinforcement agents in polymer matrices[2].

Therefore, polymer-based nanocomposites due to having both organic and inorganic materials properties together, have attracted the attention of many researchers. For example, nanocomposite preparation based on polymers like polyvinyl chloride, polystyrene and so on with nanostructures like carbon nanotubes (CNTs), silver, titanium dioxide and montmorillonite, has been reported (3-5). Meanwhile, CNTs are used as ideal additives for the preparation of polymer-based nanocomposites due to their extraordinary properties such as high mechanical strength, high aspect ratio, small diameter, light weight, high electrical and thermal conductivities, as well as high thermal and air stabilities. CNTs have long, hollow, cylindrical carbon structures which are obtained from the rolling of graphite sheets, and their diameter is up to 100 nanometres. CNTs are of two types: single-walled carbon nanotubes (SWCNT) and multi-walled carbon nanotubes (MWCNT); MWCNT is preferred to SWCNT because of its lower price[3].

The industrial polymers, including polystyrene (PS) are used to make many products due to advantages like cheapness, processability and lightness. However, their weak mechanical properties do not allow their use in the cases which need high mechanical strength. Therefore, PS and CNTs nanocomposites have been prepared by methods such as *in situ* emulsion polymerization[6], with the purpose of improving the properties of the product.

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For example, Safadi *et al.* mixed MWCNT with PS using ultrasonic waves. A study of the conductive and mechanical properties of the obtained nanocomposite confirmed the reinforcing effect of MWCNT[7]. Pham *et al.* prepared the nanocomposite of PS-SWCNT using solution method and studied the changes of the glass transition temperature (Tg) of the polymer. The obtained results confirmed an increase of 3 °C in the value of Tg [8]. Miftah *et al.* used emulsion method for preparing the PS-CNT nanocomposite. The innovation in their work was developing a combined approach of non-covalent and covalent CNT functionalization in order to improve their reactivity. The thermal and mechanical properties showed significant improvements over pure PS, even with modest CNT content[9].

Today, there is a tendency towards the use of efficient experimental design methods which are able to reduce the number of experiments required by mixing the variables and simultaneous study of their effects. The experimental design methods are also preferred because of their economy in terms of time and money[10,11].

Since optimization of the process of PS-CNT nanocomposite preparation needs several experiments due to the numerous parameters affecting the process of production, a Taguchi method was used for designing the needed experiments. Taguchi experimental design method is used for improving the quality of the product or the manufacturing process. Besides designing the experiments, this method includes analysis of the results. The Taguchi method examines the effect of the factors on the responses simultaneously, and it is one of the most important methods of combining the factors, so the number of the needed experiments decreases considerably[12,13]. Therefore, in the present study the focus was on preparing PS-CNT nanocomposite in order to improve the mechanical properties of PS to expand its applications. Because of the competition among the industries for producing products with high quality and low price, the Taguchi design method was used for optimizing the effective experimental parameters.

2. EXPERIMENTAL

2.1 Chemicals

SWCNT (≥70% carbon as SWCNT, 0.7-1.3 nm diameter) and MWCNT (multi-walled-carbon>95%, O.D. ×L6-9 nm×5 μm) were purchased from Sigma Aldrich Company. Toluene, tetrahydrofuran (THF), chloroform, HCl 37 % and H_2SO_4 98% all of laboratory grade, were purchased from Merck Company of Germany. All of the materials used in the study had high purity percentage, and were used without any purification. Two commercial grades of general-purpose polystyrene (GPPS) containing GPPS1540 with a density of approximately 1.04 g/cm^3 and MFI 11 g/10 min (type 1), and GPPS1460 with a density of approximately 1.04 g/cm^3 and MFI 6.5 g/10 min (type 2), were purchased from the Tabriz Petrochemical Company.

2.2 Characterization

A FTIR spectroscopy, Shimadzu 8400S (Japan) was used to investigate the functionalization process on CNTs surfaces. A scanning electron microscopy (SEM) LEO 1430VP (corporately made by Germany and England) was used to investigate the surface morphology of raw and functionalized CNT.

2.3 The Experimental Design

The Taguchi method is a systematic and efficient approach utilizes orthogonal arrays to study a large number of variables using a small number of experiments. Then, research and development costs can be reduced by simultaneously studying a large number of parameters. Analysis of variance (ANOVA) is used to analyze the results; it is applied for estimating error variance and for determining the relative importance of various factors. From the obtained results, the optimum setting of parameters is predicted[14].

The present study aimed at improving the mechanical properties of PS by preparing its nanocomposite with CNT. There was an attempt to investigate the effect of 6 factors including the type of CNT (A) with four levels, type of solvent (B) and CNT weight percentage (E) with three levels for each factor and type of PS (C), drying temperature of the nanocomposite film (D) and duration of the nanocomposite solution mixing (F) with two levels for each factor, as given in **Table 1**.

According to the factors and their selected levels, an L_{16} orthogonal array

Table 1. PS-CNT nanocomposite preparation factors

Factor	Level 1	Level 2	Level 3	Level 4
Type of CNT (A)	Functionalized-SWCNT	Functionalized-MWCNT	SWCNT	MWCNT
Type of solvent (B)	Toluen	THF	Chloroform	-
Type of PS (C)	Type 1	Type 2	-	-
Film drying temperature (D)	25	60	-	-
CNT weight percentage (E)	0.5	1.0	1.5	-
Mixing time duration (F)	1 h	2 h	-	-

(OA) was selected for this study. The experiments were conducted in the layout of this OA, and 16×2=32 data values were collected. To analyze the obtained results, DEMO version of Qualitek 4 version 7.2.0 was used. In Taguchi design, signal/noise (S/N) ratio was used for determining the optimum experimental conditions. Since the purpose of the present study is determining the conditions for preparing PS-CNT nanocomposite with better mechanical properties; therefore, the experiment quality characteristic of 'bigger is better' was selected for determining the S/N ratio. In this case, the ratio of $(S/N)_i$ for the i'th experiment was shown in Equation (1).

$$\left(\frac{S}{N}\right)_i = -10\,Log\left(\frac{1}{n}\sum_i\left(\frac{1}{y_i^2}\right)\right) \quad (1)$$

in which n and y_i show the number of experiments and the value of the response in the i'th experiment, respectively. Detailed information about the Taguchi method is explained in [14]. The main effect of factor A in the level of L () can be calculated as:

$$\overline{A}_L = \frac{\sum Y_i}{n} \quad (2)$$

Similarly to Equation (1), in which n and y_i show the number of responses and the value of the response in the i'th experiment, respectively, the sum of squares of factor A (S_A) is calculated as shown in Equation (3):

$$S_A = \frac{\sum_{i=1}^{N_{A1}} Y_{A1}^2}{N_{A1}} + \frac{\sum_{i=1}^{N_{A2}} Y_{A2}^2}{N_{A2}} + \cdots + CF \quad (3)$$

where Y_{An} and N_{An} are the response value and the experiment number in which the parameter A has its n^{th} level, respectively. Correction function (CF) is:

$$CF = \frac{\sum_{i=1}^{N} Y_i}{N} \quad (4)$$

where N is the total number of the experiment according to the orthogonal array and Y_i is the value of the response in i^{th} experiment. By considering f_A, degree of freedom of the factor A, the variance of factor A (V_A) is calculated from:

$$V_A = \frac{S_A}{f_A} \quad (5)$$

So, the portion of the effect of factor A (P_A) could be calculated according to the following equations:

$$P_A = \frac{S_A'}{S_T} \times 100 \quad (6)$$

$$S_A' = S_A - (f_A \times V_e) \quad (7)$$

$$S_T = \sum_{i=1}^{n}(Y_i - \overline{Y}) \quad (8)$$

where V_e is the variation of error and Y is the average response. The Fisher ratio (F_A) which determines the meaningfulness of a factor can be calculated by use of the equation below[14]:

$$F_A = \frac{V_A}{V_e} \quad (9)$$

Based on the selected OA, each experiment was performed twice to generate sufficient data to determine the effect of noise sources. The analysis of variance was used for analyzing the results in the Taguchi experimental design method. An F test was carried out on the results of mechanical properties of nanocomposite films to determine the most and the least effective factors.

2.4. Functionalization of CNT

In order to reduce the aggregation of CNTs and increase their effective dispersion in the matrix of the nanocomposite, functionalization of the surfaces of SWCNT and MWCNT by creating hydroxyl and carboxyl groups was carried out. For this, SWCNT and MWCNT were separately added to a mixture of sulfuric acid and nitric acid in 3:1 ratio. The obtained mixtures were sonicated and stirred for 3 h at a temperature of 50 °C followed by repeated washing with distilled water to reach neutral pH [15]. The presence of carboxyl and hydroxyl groups on surfaces of SWCNT and MWCNT was confirmed by FTIR.

2.5. Nanocomposite Preparation

The solution method was used to prepare nanocomposites. The experiments were conducted in the layout of L_{16} OA (presented in **Table 2**). Therefore, 0.6 g of PS (type 1 or type 2) was dissolved in 40 mL of the solvent (toluene, chloroform or THF). Then a specified amount of CNT (SWCNT, MWCNT, functionalized SWCNT or functionalized MWCNT) with a specific weight percentage in comparison with PS (0.5, 1.0, or 1.5%) was gradually (over 30 minutes) added to PS solution and mixed for a specified time (1 or 2 hours). Later, in order to improve the dispersibility of CNT in PS solution, ultrasonication was used for 30 minutes. Then, a solution-casting method was used to prepare PS-CNT nanocomposite films. Each experiment was performed two times and 16×2=32 nanocomposite films were collected.

3. RESULTS AND DISCUSSION

3.1 Mechanical Properties of Nanocomposite Films

The tensile test was used to determine the mechanical properties of PS-CNT nanocomposite films. The thickness of nanocomposite films was in the range of 1-2 μm. The tensile test was performed three times for each nanocomposite film and the average obtained value was reported as the tensile strength value for each film. According to Section 2.5, each PS-CNT nanocomposite film was prepared two times in similar conditions, and then two tensile strength values were reported in **Table 2**. According to this table, the film of number 10 showed better mechanical properties because of its higher tensile strength value than the other films.

3.2 Statistical Analysis

Using Equation (1), the amounts of S/N for each of 16 experiments were calculated, and they are given in **Table 2**. The results indicate that experiment (10) shows the greatest amount of S/N. The greater the S/N ratio, the better, since improvement of the tensile strength of the sample was the purpose of this research.

Using Equation (2), the main effects of the factors were calculated for four levels of factor A, 3 levels of factor E and B and two levels of factor C, D and F; the results are given in **Table 3**. Each level that had the higher value, was selected as the optimal level of the related factor. Therefore, the optimum levels are $A_3B_2C_2D_1E_3F_1$, which is given in **Table 4**. A comparison of the optimised parameters with the used L_{16} OA shows that the obtained conditions were according to those of experiment 10. In other words, the experiment 10 was carried out in optimal conditions.

Table 2. Experimental layout, factors and results

Expt. No.	A	B	C	D	E	F	Tensile Strength 1 (MPa)	Tensile Strength 2 (MPa)	S/N
1	1	1	1	1	1	1	34	35	30.75
2	2	2	1	1	2	1	35	37	31.11
3	1	3	2	2	3	1	41	40	32.14
4	2	1	2	2	1	1	34	34	30.62
5	2	3	2	1	1	2	38	39	31.70
6	1	1	2	1	2	2	35	36	31.00
7	2	1	1	2	3	1	41	39	32.03
8	1	2	1	2	1	2	41	40	32.14
9	1	1	1	2	1	3	43	42	32.56
10	2	3	1	2	2	3	47	47	33.24
11	1	2	2	1	3	3	35	36	31.00
12	2	1	2	1	1	3	35	34	30.75
13	2	2	2	2	1	4	37	35	31.11
14	1	1	2	2	2	4	38	39	31.70
15	2	1	1	1	3	3	33	34	30.49
16	1	3	1	1	1	4	36	37	31.24

Table 3. The main effects of factors, calculated for each level the absolute value of the difference between the highest and lowest values

Factors	L_1	L_2	L_3	L_4	$\lvert L_{max}-L_{min} \rvert$
A	31.16	31.72	31.89	31.14	0.75
B	31.36	31.76	31.42		0.40
C	31.00	31.94			0.94
D	31.70	31.25			0.44
E	31.24	31.34	32.08		0.84
F	31.57	31.38			0.18

Table 4. Optimal conditions of PS-CNT nanocomposite preparation

Factors	Levels	Description of levels
A	3	raw-SWCNT
B	2	THF
C	2	Type 2
D	1	25 °C
E	3	1.5
F	1	1h

According to **Table 4**, the optimum conditions were: type of CNT: functionalized SWCNT; percentage of SWCNT: 1.5 %; type of solvent: THF; type of PS: type 2; drying temperature of the film: 25 °C; and duration of mixing after adding SWCNT: 1 hour.

According to the results, functionalized SWCNT is the optimal level of Factor A (type of CNT) and the main effect of CNT percentage (factor E) increases with filler loading from 0.5 to 1.5 wt.%. It seems that the superior mechanical properties of SWCNT in comparison to MWCNT and the improved dispersibility of functionalized SWCNT in comparison to raw CNT cause better results.

Also, according to the obtained optimal conditions, PS of type 2 has a higher main effect value than type 1, which can be attributed to its higher molecular weight causing greater tensile strength. Among the selected solvents, THF has the highest main effect value and ANOVA analysis in Section 3.2.2 determined that factor F (mixing time duration) has no significant effect on responses and can be eliminated.

According to the last column of **Table 4**, the of the difference between the highest and lowest values ($\lvert L_{max}-L_{min} \rvert$) of the main effects of a factor was used to determine the most effective and the least effective factors. The obtained the order of the effect of factors was CEADBF.

3.2.2 Analysis of Variance

Analysis of variance (ANOVA) was used for studying which factors had a significant effect on the response value and determining the percentage (%) significance of the factors. The results of ANOVA (calculated using Equations

(3)-(9)) and calculated F-ratio of each factor are given in **Table 5**. The F-value for each factor is the ratio of the mean of the squared deviations to the mean of the squared error.

At 95% confidence interval, the F values given in **Table 5** for all factors except F are greater than the values obtained from the Fisher table. Therefore, all factors except F have significant effects on the response values. Moreover, with elimination of factor F, the optimum conditions are obtained as $A_3B_2C_2D_1E_3$.

The percentage contributions of the factors indicate that the type of PS, CNT weight percentage and type of CNT have significant effects on the tensile strength values. It can be observed from **Table 5** that factor (C) is the most significant factor and affect the tensile strength values of PS-CNT nanocomposite films with a percentage contribution of 37.75%. The next significant factors are factors (E) and (A) with percentage contributions of 19.90% and 16.75%, respectively.

3.3 Surface Morphology

Figure 1a and **b** shows the images of the purchased SWCNT and the functionalized SWCNT, respectively. As can be seen, the surface of the functionalized SWCNT was considerably rough. Moreover, the length of the modified SWCNT, as a result of functionalization, has decreased significantly. These changes as well as the increase in the diameter of the modified nanotubes confirm the functionalization of the SWCNT surface[16].

3.4 FTIR Spectroscopy

FTIR spectra from the as-received single-walled and multiwall carbon nanotubes and functionalized single-walled and multiwall carbon nanotubes are shown in **Figure 2**. FTIR spectra of functionalized single-walled and multiwall carbon nanotubes show broad peaks at around 3400-3700 cm^{-1}, which relate to the O-H of a carboxylic acid group. There are three new major peaks in the FTIR spectra of functionalized CNTs in comparison to raw CNTs, located at 3743, 3445, and 1541 cm^{-1}. The presence of a peak at around 3743 cm^{-1} represents free hydroxyl groups. The presence of a peak at around 3445 cm^{-1} can be attributed to the O-H stretch from O=C−OH and C−OH groups. Also, the presence of a peak at around 1541 cm^{-1} represents the carboxylate anion stretching mode. The peak at 1635 cm^{-1} represents the stretching of the carbon nanotube backbone. The peaks at around 2856 and 2923 cm^{-1} correspond to the H−C stretching modes of H−C=O in the carboxyl group[17].

Figure 1. SEM images of SWCNT (a) as purchased; (b) functionalized

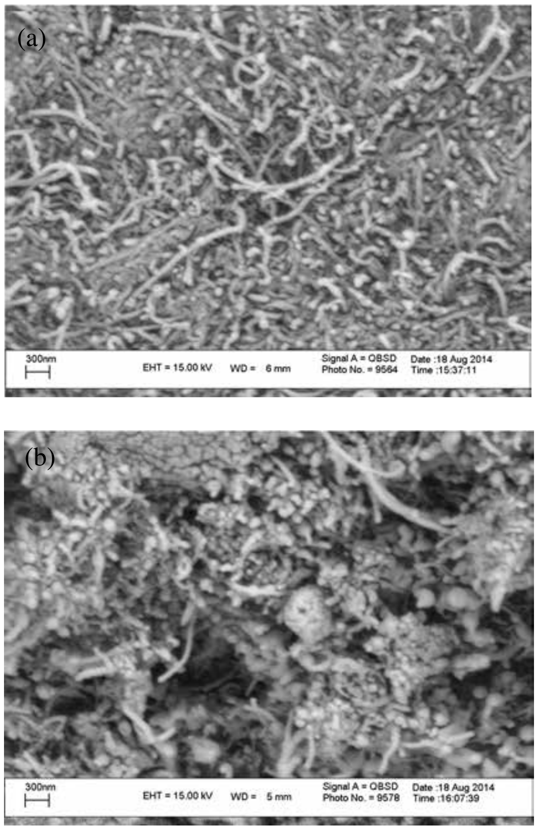
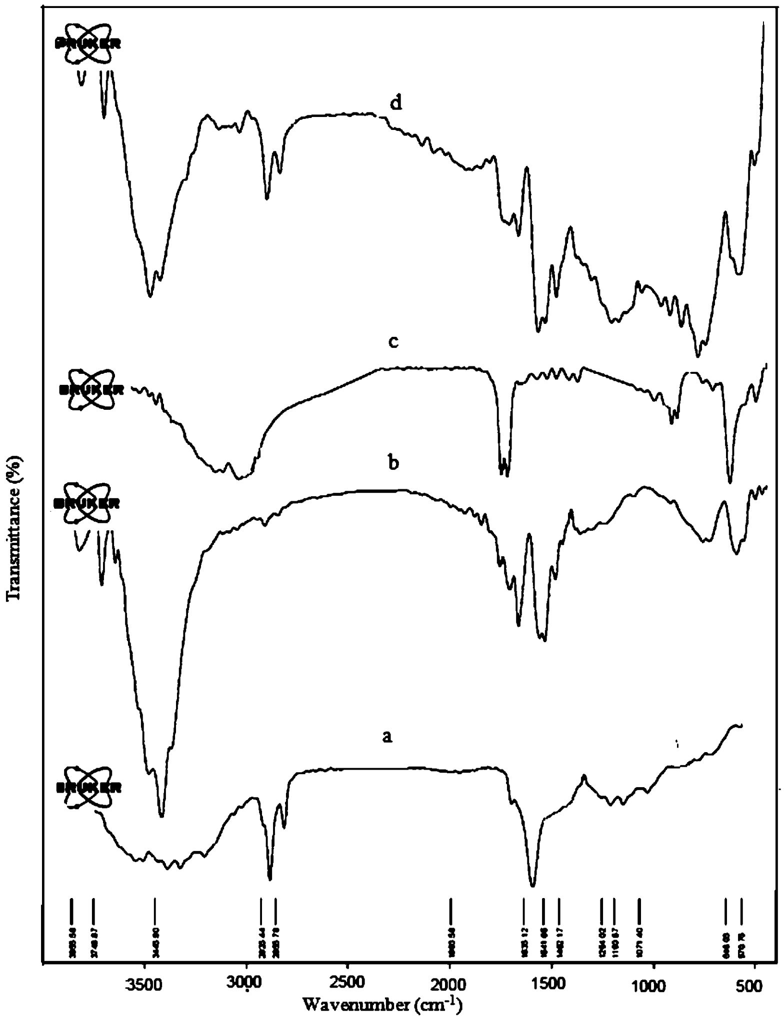


Table 5. The results of ANOVA and F-test in S/N method

Factors	Degrees of Freedom (DOF)	Sum of Squares (S)	Variance (V)	F-ratio (F)	P%
A	3	1.78	0.59	6.65	16.75
B	2	0.45	0.22	2.54	3.01
C	1	3.53	3.53	39.66	37.75
D	1	0.78	0.78	8.78	7.59
E	2	1.99	0.99	11.19	19.90
F	1	0.13	0.13	1.51	0.50
error	5	0.44	0.89		13.64
Total	15	9.12			100%

Figure 2. FTIR spectra of (a) raw SWCNT; (b) functionalized SWCNT; (c) raw MWCNT; (d) functionalized MWCNT



4. CONCLUSIONS

In order to improve the mechanical properties of PS, PS-CNT nanocomposite was prepared by considering the effects of six factors containing the type of CNT, type of PS, the type of solvent, the percentage of CNT, drying temperature of the nanocomposite film and the mixing time of the solution at different levels, using the Taguchi method, based on an L_{16} orthogonal array.

The mechanical properties of the obtained nanocomposite films were studied, and the tensile strength values of nanocomposite films were used as the results for the analysis of data using S/N method. Using S/N method, the optimum conditions were obtained as follows: type of CNT: functionalized SWCNT; percentage of SWCNT: 1.5%; type of solvent: THF; type of PS*:* type 2; drying temperature of the film: 25 *°C*; and mixing time of solution: 1 hour.

Based on the obtained values, the order of the effect of factors was CEADBF; i.e., the most effective and the least effective factors were C and F, respectively. Also, the factors C, E and A affected the tensile strength values of PS-CNT nanocomposite films with percentage contribution of 37.75%, 19.90% and 16.75%, respectively. The results of ANOVA and the calculated F-ratio of each factor showed that at 95% confidence interval, the F values for all the factors except F had significant effects on the response values. FTIR and SEM techniques were used to confirm the functionalization of the CNT surfaces by –OH and –COOH groups.

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