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Experimental and Statistical Study of Nonlinear Effect of Carbon Nanotube on Mechanical Properties of Polypropylene Composites

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Abstract**—**In this study concept of experimental design is successfully applied for the determination of optimum condition to produce PP/SWCNT (Polypropylene/Single wall carbon nanotube) nanocomposite. Central composite design as one of experimental design techniques is employed for the optimization and statistical determination of the significant factors influencing on the tensile modulus and yield stress as mechanical properties of this nanocomposite. The significant factors are SWCNT weight fraction and acid treatment time for functionalizing the nanoparticles. Optimum conditions are in 0.7 $_{\%}$ of SWCNT weight fraction and 210 $_{\text{min}}$ as acid treatment time for 1112.75 ± 28 $_{\text{MPa}}$ as maximum tensile modulus and in 216 $_{\text{min}}$ and 0.65 $_{\%}$ as acid treatment time and SWCNT weight fraction respectively for 40.26 ± 0.3 $_{\text{MPa}}$ as maximum yield stress. Also after setting new experiments for test these optimum conditions, found excelent agreement with predicted values.

Keywords**—**Polypropylene, carbon nanotube, nanocomposites, Central composite design

I. INTRODUCTION

POLYPROPYLENE is one of semi-crystalline thermoplastic materials that have many general uses. Completely obvious those physical properties of these materials such as Strength depend on their structure and morphology. In industry, polypropylene has several uses that these because of existence balance between the properties and the price of this material. So that process ability and low density are the tangible symbols of it. Since the discovery of CNTs by Ijima in 1991 [1], a lot of focus on the mechanical, electrical, thermal and chemical properties of these materials have been done. Both experimental and theoretical studies have shows CNTs exceptional properties. The tensile strength, modulus and Poisson's ratio of single walled carbon nanotubes (SWCNTs) have been reported to be in the range of 37- 100 GPa, 1-2 TPa and 0.14-0.28, respectively [2-5]. In our previous works due to the valuable properties of CNTs, some studies have been done on using these materials as nano-filler in polymer matrix [6-10]. The simplest way for length shortening and purification of CNTs is using acid treatment. These shortened CNTs were produced by carboxylic acid groups at the side walls and end of the nanotubes [11-14] and because of interfacial adhesion between CNTs and polymer matrix, cause mechanical and electrical properties Improvement [15].

Statistics is a scientific discipline devoted to the drawing of valid inferences from experimental or observational data. The study of variation, including the construction of experimental designs and the development of models which describe variation, characterizes research activities in the field of statistics [16]. According to surveys conducted in [17], in the titles of most articles used such words "optimization", "development" or "effect of", applied OVAT (one variable at time) model for studying the parameters in their experimental works and few of them like [18] for optimization use various models of "Experimental design". In our previous works [6-10] as same as OVAT model qualitative study without any special experimental design were done. The optimization has been done by OVAT model can not guarantee that optimum point will be happen and it because that this approach is correct when variables play a role in optimizing are completely independent from each other. By comparing the results obtained from OVAT model and experimental design model can be said that [14], the experimental design considers the interaction between variables, while OVAT doesn't; the experimental design provides a global knowledge of experiment domain, while OVAT provide a local knowledge, the number of tests needed by an OVAT is greater than the number of experiments performed with experimental design approach, the quality of responses obtained by experimental design is depend on various parameters such as domain of

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experiment, postulated model for experimental design, budget available, experimental limitations and etc.
Central Composite Design (CCD) [17] is a type of experimental designs that allows for estimating the constant, the linear terms, the interactions between variables, and the quadratic terms according to the following model for example for two parameters (***X₁*** and ***X₂***):

$$Y = b_0 + b_1 x_1 \quad b_2 x_2 + b_{12} x_1 x_2 + \\ + b_{11} x_1^2 + b_{22} x_2^2 \tag{1}$$

Where b_0 is constant, b_1, b_2 show the linear effect of x_1, x_2 respectively, b_{12} shows the interaction between parameters x_1, x_2 and b_{11}, b_{22} show the quadrative nonlinear effect of x_1, x_2 respectively.

The main purpose of this article is to optimize the mechanical properties, tensile modulus and yield strength, of Polypropylene composite samples reinforced with functionalized single wall carbon nanotubes by employing central composite design as an experimental design. The effective parameters are weight fraction of SWCNT and acid treatment time. Also Transmission Electron Microscopy (TEM) and electron dispersion X-ray (EDX) analysis on SWCNTs were studied.

II. EXPERIMENTAL DESIGN

A. Review Stage

Experimental methods are widely used in research as well as in industrial settings, however, sometimes for very different purposes. The primary goal in scientific research is usually to show the statistical significance of an effect that a particular factor exerts on the dependent variable of interest and the primary goal is usually to extract the maximum amount of unbiased information regarding the factors affecting a production process from as few (costly) observations as possible. In order to better understand the impact of various parameters on experiment results and also obtain the mathematical relationship between them, we use "Central composite design" as an experimental design model. As we know, in central composite design model, if the parameters change in quantitative levels, optimal point can be reached. In this research, the weight fraction of SWCNT and time of acid treatment will be studied as the parameters affecting the experiment results. Two parameters with three different levels were selected for experimental design, Table (1).

TABLE I
DESCRIPTION OF PARAMETERS AND THEIR LEVELS FOR CENTRAL

Parameters	Levels		
	-1	0	+1
SWCNT weight fraction	0.5%	0.75%	1%
Acid treatment time	2 hr	4 hr	6 hr

Note that, very often one single experimental design doesn't lead to the solution of the problem. In those cases the information obtained from first experimental design is used to removal of the non-significant variables, redefinition of the experimental domain and modification of the postulated model. Since the possibility of having to perform more than one single experimental design must always be taken into account, it is wise not to invest more than 40% of the available budget in the first set of experiments [17]. But in our study, the results obtained by statistical analyze, both involved parameters were effective parameters. Therefore according to central composite design model using Statistical design software i.e., Statistica 7, experimental matrix and experimental plan related to Table (I) reported in Table (II).

TABLE II
EXPERIMENTAL MATRIX, EXPERIMENTAL PLAN RELATED TO TABLE (I)

Exp. No.	***X₁***	***X₂***	SWCNT weight fraction	Acid treatment time
1	-1	-1	0.5 %	2 hr
2	-1	0	0.5 %	4 HR
3	-1	+1	0.5 %	6 HR
4	0	-1	0.75 %	2 hr
5	0	0	0.75 %	4 HR
6	0	+1	0.75 %	6 HR
7	+1	-1	1 %	2 hr
8	+1	0	1 %	4 HR
9	+1	+1	1 %	6 HR
10	0	0	0.75 %	4 HR

III. EXPERIMENTAL DETAILS

A.Raw materials

Isotactic polypropylene homopolymer, with a melt flow index of 8 g/10 min and a PP density of 0.902 g/cm^3, was supplied by Bandar Imam Petrochemical Co., Iran, as grade Poliran PI0800. SWCNTs were obtained from the Research Institute of Petroleum Industry (RIPI), Iran. The SWCNTs were prepared using a chemical vapor deposition (CVD) process using methane as a carbon source, a cobalt catalyst system, and a reaction temperature between 800 and 1000ºC. PP-g-MA (PB3150) from Uniroyal Chemical was used as a compatibilizer (Mw=330 kg/mol and maleic anhydride content = 0.5 wt %). Irganox 1010 supplied from Ciba was also added into PP matrix as a heat stabilizer.

B.Functionalization of SWCNTs

The process includes four steps. The untreated SWCNTs (200 g) were refluxed in 100 ml of 2.5 M hydrochloric acid for 24 h to take away metal particles and amorphous carbon for the first step. Purified SWCNTs were added to a 1:3

mixture of concentrated nitric acid/sulfuric acid (25 ml/75 ml) for the second step. For three different time periods: 2, 4, and 6 h the mixture was treated in an ultrasonic bath (40 kHz). The mixture was diluted with distilled water, followed by filtration thorough a 0.45 Poly Tetra Fluoro Ethylene filter (PTFE, Millipore) membrane, and then rinsed with ethanol until the PH of the filtrate was about 7 for the final step. The obtained filtrated sample was finally dried in a vacuum oven at 120°C overnight, generating acid treated.

C.Nanocomposites preparation

To take away any humidity before mixing with other parts, PP, PP-g-MA, and SWCNTs were dried under vacuum at 80°C for 12 h. The PP pellets, PP-g-MA, Irganox1010 (0.1 wt% of PP) and various amounts of untreated and acid treated SWCNTs were dry mixed together and then launched into the mixer where mixing continued for 10 min; mixing the parts was performed in an internal mixer (Haake Rheomix; HBI SYS90) with a rotor speed of 120 rpm at 180ºC. The composition of nanocomposites is given in tab.3. The mixture was compression molded after mixing. Square plaques (0.5 mm thick) of the mixture were prepared in a Toyoseiki Mini Test Hydraulic Press (Japan) at 190°C and 10Mpa for 5min. The sheets then were quenched in an ice-water mixture.

D.Tensile testing

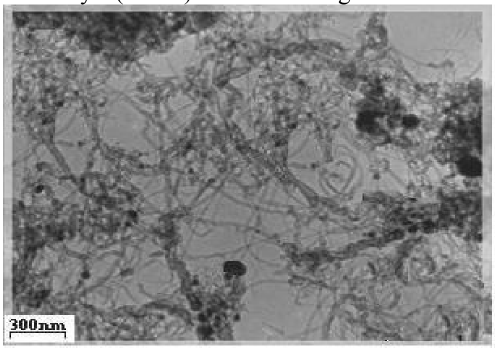
At room temperature tensile testing was performed on a MTS model 10/M. shape of test specimens were dumbbell(width of narrow section 6 mm, length of narrow section 36 mm, overall length 76 mm, and gauge length of 25 mm). Experiments to measure mechanical properties such as "Tensile modulus" and” yield strength" were carried out with a cross-head speed of 50 mm/min. Ten replicates of each sample were run to obtain averages.

E.Transmission electron microscopy (TEM) description

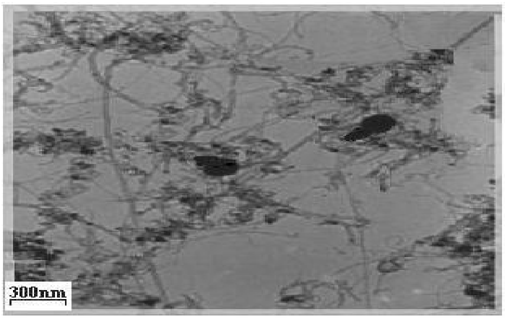
Transmission electron microscopy (TEM) images were achieved using a Philips CM-200 TEM microscope operating at an acceleration voltage of 120 kV to observe the nanoscale structure of SWCNTs and PP/SWCNTs nanocomposites. Ultrathin sections of PP/SWCNTs nanocomposites for TEM analysis were prepared by mounting the specimen in araldite resin and cutting with a diamond knife (a Riechert ultra microtome) to yield samples with a thickness of 40-80 nm. SWCNTs for TEM study were dispersed in ethanol by sonication for 1 min, and then one drop of this solution was placed on a carbon-coated copper microscope grid. The presence of catalysts and other elements derived from the functionalization step was displayed by electron dispersion X-ray (EDX) analysis.

F.TEM Analysis of functionalized SWCNTs

Fig.1 shows the TEM pictures of untreated SWCNTs and functionalized SWCNTs for various acid treatment times (2, 4, and 6 h). As shown in Fig. 1a, the untreated SWCNTs are in the range of 1-5 nm and include metal particles (black points) and amorphous carbon materials. With increasing acid treatment times, the metal catalyst was removed, the closed tube was opened and then the length of nanotubes was shortened [19-21]. In agreement with TEM study, EDX analysis of the functionalized samples showed a decrease in the metal catalyst (cobalt) with increasing treatment time.



(a)



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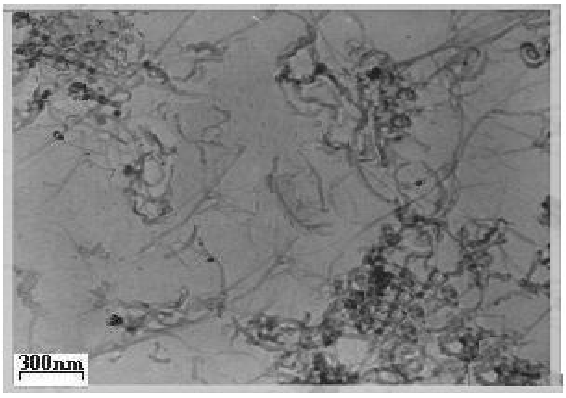

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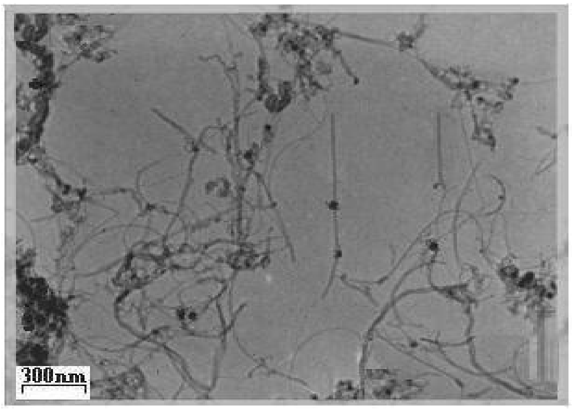


(d)

Fig. 1 TEM pictures of (a) untreated SWCNTs, (b) functionalized SWCNTs for 2h acid treatment times, (c) functionalized SWCNTs for 4h acid treatment times, (d) functionalized SWCNTs for 6h acid treatment times

The responses obtained for the runs according to experimental design mentioned in table II, are given in table III.

TABLE III
EXPERIMENTAL MATRIX, EXPERIMENTAL PLAN RELATED TO TABLE (1)

Exp. No.	**X_1**	**X_2**	SWCNT weight fraction	Acid treat time	Tensile Modulus (MPa)	Yield Stress (MPa)
1	-1	-1	0.5 %	2 hr	1023	38.67
2	-1	0	0.5 %	4 HR	1028	39.51
3	-1	+1	0.5 %	6 HR	978	38.07
4	0	-1	0.75 %	2 hr	1079	39.42
5	0	0	0.75 %	4 HR	1103	39.68
6	0	+1	0.75 %	6 HR	1010	38.14
7	+1	-1	1 %	2 hr	940	35.96
8	+1	0	1 %	4 HR	993	36.8
9	+1	+1	1 %	6 HR	865	35.7
10	0	0	0.75 %	4 HR	1103	39.68

IV. RESULT AND DISCUSSION

A.Tensile properties

The tensile modulus and yield stress of PP/ nanocomposites with different acid treatment times of and compatibilizer are listed in Tab. 3.

In particular, PP/PP-g-MA/a- nanocomposites (0.75 wt%) show large improvement, which is because of interfacial bonding between the PP matrix and functionalized and good dispersion of functionalized in the PP matrix, leading to a more effective stress transfer [22].

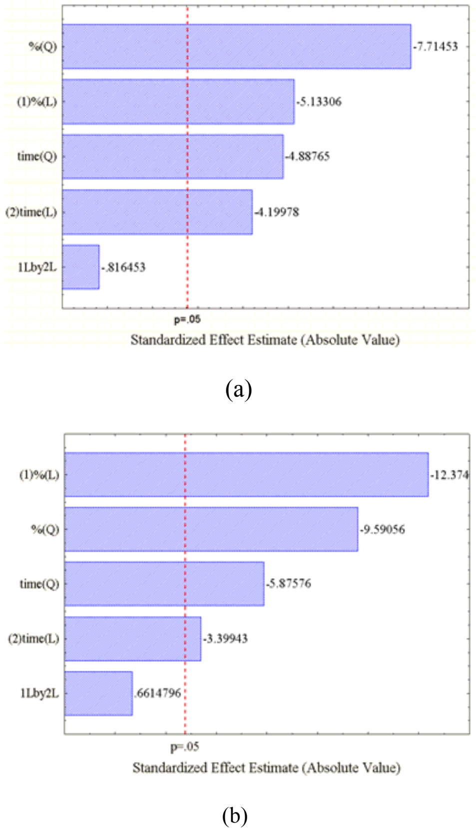
It is shown that all PP/PP-g-MA/a- (1 wt %) nanocomposites exhibit a lower tensile modulus than the other modified nanocomposites. This decrease in tensile modulus can be attributed to the low contribution of compatibilizer and a high content of defects in the functionalized in this matrix. In comparison with the PP/PP-g-MA/a- (0.5 wt %) nanocomposite, the tensile modulus of PP/PP-g-MA/a- (1 wt %) nanocomposite decreases from 1023 MPa to 940 MPa (2h acid treatment), 1028 MPa to 993 MPa (4h acid treatment), and 978 MPa to 865 MPa (6h acid treatment). It can also be clearly seen that the tensile properties of PP/PP-g-MA/a- nanocomposite with functionalized in acid mixture for 6h are lower than those of other PP/PP-g-MA/a- nanocomposites. These reductions are because of the high destruction of the sidewalls and shorter when the reaction time of the acid treatment increases to 6h.

B.Statistical analysis optimization

As shown in Table 2, a CCD was used, in which two independent variables were converted to dimensionless ones (x_1, x_2), with the coded values at 3 levels: (-1, 0, 1).The arrangement of CCD as shown in Table 2 was in such away that allows the development of the appropriate empirical equations ,Eq.(1) [16, 23, 24]. A polynomial regression response model shows the relationship of each factor towards the response as well as the interactions among the factors. Those factors can be optimized to give the maximum responses (tensile modulus and yield stress) with a relatively lower number of experiments. In this context, the corresponding interactions among the variables were studied and optimized using central composite design. Empirical model i.e., second order polynomial regression equations were developed by using Eq.(1) to predict the behavior of tensile modulus and yield stress on the various points of independent parameters. The quality of fit of the polynomial model equation was expressed by the coefficient of determination R^2 and Fisher's test value.Using the experimental results give in table (3), the regression model equation (second-order polynomial) by nonlinear effect relating tensile modulus, Y_1 and yield stress, Y_2 are given in Eq.(2) and Eq.(3) respectively.

$$\begin{aligned} Y_1 &= 1103.143 - 38.500\, x_1 \quad 31.500\, x_2 \\ &-7.500\, x_1 x_2 - 92.786\, x_1^2 \quad 58.786\, x_2^2 \end{aligned} \tag{2}$$

$$\begin{aligned} Y_2 &= 39.724 - 1.298\, x_1 \quad 0.357\, x_2 \\ &+0.085\, x_1 x_2 - 1.613\, x_1^2 \quad 0.989\, x_2^2 \end{aligned} \tag{3}$$



(a)

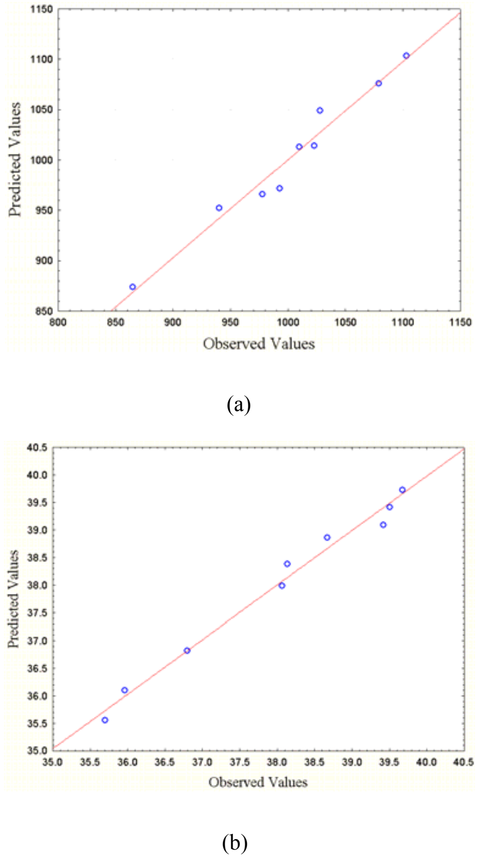
(b)

Fig. 2 Main effects and significance of parameters on the (a) Tensile Modulus and (b) Yield Stress

Confidence levels were accepted only when these where above $95\,\%$ ($P < 0.5$) and only terms found statistically significant were included in the model. According to Fig. (2), for both models, b_{12} as coefficient for showing the interaction between parameters x_1 and x_2 is not significant and should be dropped from these models.

Statistical significant of the model equation was determined by multiple coefficient of determination R^2 and this parameter for first model related to Tensile Modulus is $R^2 = 97\,\%$ and for second model related to Yield Stress is $R^2 = 98\,\%$.

The plot of predicted versus experimental values in Fig.(3) shows that for both models predicted values of central composite design model are located in close proximity to the experimental values.

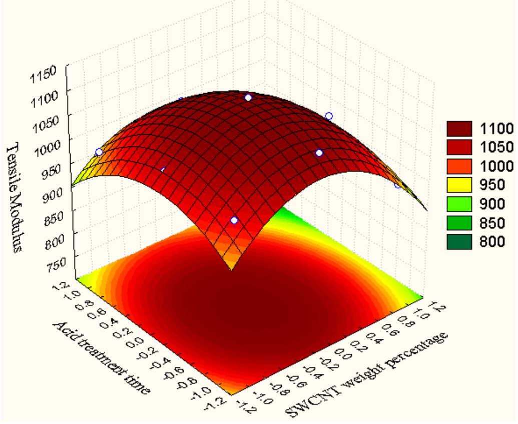


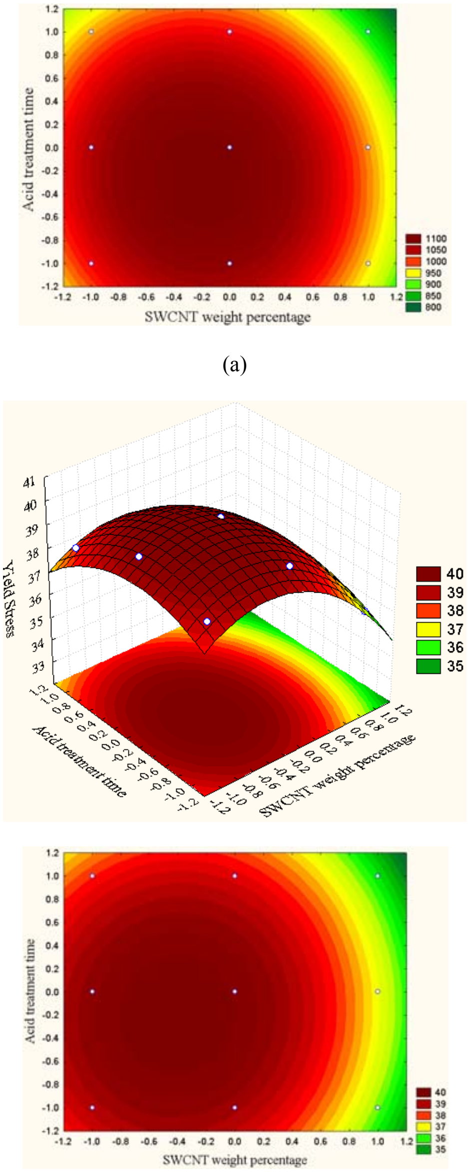
(a)

(b)

Fig. 3. Relationship between the observed and predicted values of (a) Tensile Modulus and (b) Yield Stress

For the graphical interpretation of the interactions, the use of three dimensional plots of the regression is highly recommended [23, 24]. Fig. 4 gives three-dimensional response surface curves were plotted to show nonlinear effects of parameters and to determine the optimum concentration.





(a)

(b)

Fig. 4 Second-order response surface plots of (a) Tensile Modulus, (b) Yield Stress.

C. Optimization

Although some studies on the effects of various parameters on mechanical properties have been reported, limited attend has been made to optimize the effective parameters using statistical optimization methods. But in this work by considering statistical models, Eq.(2) and Eq.(3) , using the grid search method to find the optimum conditions. The algorithm of this method is the dimension of each point in the grid frame work (in the form of coded value) was applied and the corresponding responses were obtained. All these values were compared with each other and the response with the highest value was considered as the optimum condition. All programming codes were done in Fortran 10. After finding the optimum condition we are tested these points by setting new experiment. The predicted and experimental responses and their optimum levels are shown in table. (IV).

TABLE IV
PREDICTED OPTIMUM AND EXPERIMENTAL RESPONSE AND THEIR OPTIMUM LEVELS

Mech. Prop	Predicted response	Exp. resp	SWCNT weight fraction (X_1)	Acid treatment time (X_2)
Tensile Modulus	1110.96 MPa	1112.75 MPa	-0.197_{coded} = 210 min	-0.255_{coded}= 0.7 %
Yield Stress	40.02 MPa	40.26 MPa	-0.407_{coded} = 216 min	-0.198_{coded}= 0.65 %

Comparing experimental value and calculated response from model for optimum point shows good agreement points.

V. CONCLUSION

In this research using SWCNTs as nano filler and also functionalize them by treatment with an acid mixture were successfully applied to improve mechanical properties, Tensile Modulus and yield Stress, of PP/SWCNT nanocomposite. Also central composite design as an experimental design model was successfully employed to study the linear, quadratic and interaction effects of each variables namely SWCNT weight fraction and acid treatment time and propose mathematically regression models. These regression models were used to optimize the effective variables for maximum tensile modulus and yield stress. After testing the predicted optimum points, we see good agreement between predicted points and points obtained from experiments.

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