

Modeling and Optimization of Carbon Fiber Processing: A RSM-FCCC Experimental Design Approach

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Abstract

In this study, low price carbon fibers have been produced by using cheap commercial polyacrylonitrile fibers through stabilization and carbonization in different conditions. To do this, a well-known design of experiments method, called the face-centered central composite, is implemented for the experimental plan, using two main process variables. The variables, including carbonization time and temperature, were investigated. Tensile strength and elastic modulus values of products samples were measured through standard procedures. Response surface method is then applied to interpret mechanical properties of carbon fibers as given experimentally functions of process variables. Optimization process revealed that optimum tensile strength and modulus elasticity of 1970 MPa and 226 GPa, respectively whilst precursor cost was reduced extensively.

Keywords: Carbon fibers, PAN fibers, Design of experiments, Face-centered central composite, Response surface method

1. Introduction

Carbon fibers are basically produced from precursor materials as well as polyacrylonitrile (PAN), rayon and pitch. PAN-based carbon fibers are the preferred reinforcement for structural composites due to their excellent specific strength and stiffness [1,2]. Special properties of carbon fibers make them attractive for many applications, but in this respect the main problem is their high price. High cost of carbon fibers is mainly due to the high cost of the relevant precursor i.e. special grade PAN fibers [3,4]. In order to let more popularity, carbon fibers price should definitely be lowered. Using cheap price commercial PAN fibers could be a feasible alternative. The commercial PAN fibers (textile grade of PAN fibers) are used in producing blanket, carpets and clothes [5].

Chemical structure and properties of PAN fibers have critical effects on the properties of fabricated carbon fibers. Some of the most critical characteristics of PAN fibers which make enormous variations in the carbon fiber properties are linear density, type and amount of comonomers, molecular weight and its distribution, preferred orientation, surface coating, crimps, size of the tow and the number of filaments in tow. There are obviously differences between the precursors used for high performance carbon fiber manufacture and textile grade fibers. The textile PAN fibers has higher cross sectional area and linear density, less molecular chain orientation and different type and amount of comonomers compared to special PAN fibers. In addition, the size of their tow is large. The textile PAN fibers tows are consist of 160,000–320,000 monofilaments as compared to 3000–12,000 monofilaments for special PAN fibers [6,7].

Properties of carbon fibers mainly depend on the composition and quality of the used precursor fibers but they can be improved through changing production process by applying modification on the stabilization and carbonization processes [2]. According to some research

reports, many kinds of textile PAN fibers had been used to produce low-priced carbon fibers [4,6]. Some of them focused on modifications of heating cycles of stabilization process [7-10]. The lack of comprehensive research on the effects of the carbonization process of PAN fibers is perceptible.

The main aim of this article is to examine the possibility of producing low cost carbon fibers from available economical commercial PAN fibers via focusing only on carbonization time and temperature. A set of process arrangements previously reported based on such cheap available fibers [11]. Because of his investigation the inexpensive textile grade PAN precursor is capable of generating high quality product characteristics, such as, tensile strength and elastic modulus, at a significantly reduced cost.

Using a collection of advanced statistical methods such as design of experiments, face-centered central composite; response surface method, analysis of variance, model validation methods besides utilizing economical low price precursor is the main contribution of the present paper which aids to follow process optimization systematically.

2. Experimental

In this investigation, a domestically low price commercial PAN fibers precursor was used. This precursor is composed of acrylonitrile (93 wt.%), methyl acrylate (6 wt.%) and sodium 2-methyl-2-acrylamidopropane sulfonate (1 wt.%).

During the following two stages, the PAN fibers were converted to carbon fibers:

- 1- Stabilization in a chamber furnace by applying air circulation system at temperatures ranging from 180 to 280°C in a few discrete working conditions based on the following cycles:
 - From 25 °C up to 180°C in 60 min and holding fibers for 1 hour in 180°C.

- From 180 °C up to 200°C in 30 min and holding fibers for 1 hour in 200°C.
- From 200 °C up to 240°C in 30 min and holding fibers for 1 hour in 240°C.
- From 240 °C up to 280°C in 30 min and holding fibers for 1 hour in 280°C.

2- Carbonization of the stabilized PAN fibers in a horizontal tubular furnace with a ceramic tube under a high purity nitrogen atmosphere (99.999%) at temperatures ranging from 1300 to 1400 °C for a period of 3-8 minutes. The stabilized PAN fibers passed from two holes in the sides' tubular furnace in such a way that a c-clamp fixed one tail and the other end positioned on a rubber roller under stretching force of a given hanging weight. The amount of stretching force for each monofilament was considered at 1.25 cN/tex. Nitrogen gas flow was injected into the furnace continuously through the other two holes to maintain positive nitrogen pressure in the furnace.

Tensile strength testing procedures followed the single fiber samples based on the ISO 11566 standard regulations. The test apparatus consisted of an Instron 5565 tensile tester equipped with a 2.5 N load cell and a cross head speed of 2 mm per minute. Gauge length was kept at 25 mm. At least 25 tensile tests were performed on each sample and the average of test results was reported.

In order to generate elementary samples, the design of experiments (DOE) was used. In this efficient scientific method, frequently random experimentation has been made to determine the effect of the independent process variables (factors) on the dependent variable (response) and their relationship is examined through a regression model. Nowadays DOE is a well-known experimental technique and has been applied in a wide range of industrial fields such as chemical, biological, drug and food processes to produce high quality products, to operate more economical process, to ensure more stable and reliable process [12]. The studies including application of DOE methods have been made for more than 40 years and

the advance of their applications has been assisted by the developments in the field of computer science.

There are a lot of DOE techniques and selection of them is made according to analysis objectives and also number of examined factors [14]. The objectives of the present experiment can be classified as screening, comparing and applying response surface method (RSM). Screening experiment is applied to determine the most effective factors on the process response. RSM is generally used to construct quadratic polynomial model and it is applied in consequence of a screening experiment. Screening experimentation aimed at finding the most important factors and it was planned according to a full two-level factorial experimental design method. In the present study carbon fibers tensile strength and elasticity modulus were selected as responses. All possible factors thought to have great effect on the responses and their levels were considered based on literature survey and authors backgrounds at the brainstorming stage of this study. We decided to examine the main interaction effects of the carbonization time, say later X_1 (in minutes) and carbonization temperature, X_2 (in degree of Centigrade) as the main affected independent variables and tensile strength, Y_1 (in MPa) and elasticity modulus; Y_2 (in GPa) as the response variables.

The two affected variables were studied at their maximum and minimum levels which are determined according to our experiences, technological limitations and also based on the literature survey. The number of experiments for two factors was determined as $2^2=4$ according to full two-level factorial experimental design method [15]. To simplify the calculations, variables were replaced by their codified values. The relation between codified variable (here in after mentioned by X_i ; and their natural values, U_i for $(i = 1,2)$ are given in Eqs. (1) to (3):

$$X_i = \frac{U_{i,natural} - U_{i,average}}{\Delta U} \quad (1)$$

$$U_{i,average} = \frac{U_{i,max} + U_{i,min}}{2} \quad (2)$$

$$\Delta U_i = \frac{U_{i,max} - U_{i,min}}{2} \quad (3)$$

The maximum, minimum and average (center or middle amount) values of the codified variables considered as (+1), (−1) and (0), correspondingly and defined in Table 1.

Table 1. Natural and codified values of factors

Key factors	Natural amounts			Relevant codified amounts		
	Max.	Center	Min.	Max.	Center	Min.
Carbonization temperature (°C); X_1	1400	1350	1300	+1	0	-1
Carbonization time (min); X_2	8	5	3	+1	0	-1

2.1. RSM-FCCC Experimental Design

One of the RSM designs called face-centered central composite (FCCC) design was used to identify the second-order polynomial model [16]. Design matrix given in Table 2 for two factors screening experiment was used to construct the FCCC design matrix by augmenting adding star points ($\pm \alpha^*$). The value of $\alpha^*=1.41$ is given ± 1 for FCCC design [13]. Here the centre point notify to the average value of a factor.

Experimental design matrix constructed according to standard order rule was given in Table 2 with the codified values of the factors. Experiments were executed randomly to provide protection against the extraneous factors, which could affect the measured response. Randomization of experiments may be used by using the Statistica 6 software (StatSoftTM Inc., USA). To estimate experimental errors and to detect the quadratic effects of two key factors, four runs were placed in the design matrix. In this Table the last two columns

represents the measured experimental data for tensile strength; Y_1 and elastic modulus; Y_2 .

For the 24 random designed experiments, average values of tensile strength in MPa and elastic modulus in GPa for carbon fiber are presented in the last two columns of this Table.

Table 2. FCCC experimental design matrix arrangement for two-level factorial design in four runs and consequences of measurements

Experiments	X_1	X_2	Y_1 (MPa)	Y_2 (GPa)
1	-1	-1	1842	183
2	-1	-1	1841	182
3	-1	-1	1842	183
4	-1	-1	1842	185
5	-1	1	1933	209
6	-1	1	1930	210
7	-1	1	1933	210
8	-1	1	1931	209
9	1	-1	1840	188
10	1	-1	1838	189
11	1	-1	1841	188
12	1	-1	1840	189
13	1	1	1943	210
14	1	1	1944	209
15	1	1	1944	209
16	1	1	1943	210
17	0	0	1900	198
18	0	0	1902	199
19	0	0	1900	199
20	0	0	1901	199
21	1.41	0	1917	197
22	0	1.41	1932	215
23	-1.41	0	1912	194
24	0	-1.41	1795	180

2.2. Statistical Analysis on the Experimental Results

The statistical method frequently used to compare the magnitude of estimated effects of factors with the magnitude of experimental error is called analysis of variance (ANOVA). If the magnitude of a factor effect is large when compared with experimental error, it is decided that the changes in the selected response cannot occur by chance and those changes in the response can be considered to be the effects of the factors. The factors causing a variation in the response are called significant. In this study, Fisher's F-test was used in the analysis of variance and given in Eqs. (4) to (6):

$$F = \frac{MSS_{effect}}{MSS_{error}} \quad (4)$$

$$MSS_{effect} = \frac{SS_{effect}}{d.f._1} \quad (5)$$

$$MSS_{error} = \frac{SS_{error}}{d.f._2} \quad (6)$$

In the above Eqs., SS_{effect} is called the sum of square of a factor effect and is calculated by using Yates' Algorithm. SS_{error} represents the sum of squares of error and it is calculated from the replicated center point experiments as given in Eq. (7):

$$SS_{error} = \sum_{\text{Center Point}} (y_{C,i} - \bar{y}_C)^2 \quad (7)$$

Also, center point data are used to investigate the existence of the curvature over the region of exploration [11]. For a single degree-of-freedom, sum of squares for curvature is given by Eq. (8):

$$SS_{Curvature} = \frac{n_F n_C (\bar{y}_F - \bar{y}_C)^2}{n_F + n_C} \quad (8)$$

3. Results and Discussion

3.1. ANOVA and RSM Results

By using the Yates' algorithm and the ANOVA method, estimates of the main and interaction effects and confidence bound of the factors illustrated in Tables 3 and 4 for two responses separately and respectively. These standard Tables consist of columns which sequentially point up to the amount of mean effect, named by "Effect", standard error of effects, "Std. Err.", t student statistic based on degree of freedom; here t(18), probability value (p-value), mean estimate of the regression model coefficients; "Coeff." and standard error of coefficients, "Std. Err. Coeff.".

Table 3. Application of ANOVA analysis to determine factors effects on carbon fibers tensile strength (Y_1)

	Effect	Std. Err.	t (18)	p-value	Coeff.	Std. Err. Coeff.
Mean/ Intercept	1900.75	0.496	3835.49	0.000	1900.75	0.496
X_1	4.61	0.444	10.40	0.000	2.31	0.222
X_1^2	14.04	0.738	19.04	0.000	7.02	0.369
X_2	96.93	0.444	218.55	0.000	48.47	0.222
X_2^2	-37.26	0.738	-50.53	0.000	-18.63	0.369
$X_1 * X_2$	6.87	0.496	13.87	0.000	3.44	0.248

Table 4. Application of ANOVA analysis to determine factors effects on
carbon fibers elastic modulus (Y_2)

	Effect	Std. Err.	t (18)	p-value	Coeff.	Std. Err. Coeff.
Mean/ Intercept	198.744	0.447	444.251	0.000	198.744	0.447
X_1	2.526	0.400	6.309	0.000	1.263	0.200
X_1^2	-2.301	0.666	-3.4555	0.003	-1.150	0.333
X_2	23.863	0.400	59.601	0.000	11.932	0.200
X_2^2	-0.289	0.666	-0.434	0.670*	-0.144	0.333
$X_1 * X_2$	-2.625	0.447	-5.868	0.000	-1.312	0.224

*The amount of p-value is too high and reveals no signification

All amounts of p-value in Table 3 are less than 0.05 and this value shows that both X_1 and X_2 are significant at 95% confidence level in linear, quadratic and interaction form and their effects should be taken part in the Y_1 regression curve. As can be seen from Table 4 the quadratic effect of the 2nd factor is not significant and should be pooled in errors term. Table 5 illustrates the results of the significant factors after polling process which demonstrates all amounts of p-values are less than 0.003.

Table 5. The results of the ANOVA to determine factors effects on carbon fibers elastic
modulus (Y_2) after pooling the insignificant effects in errors term

	Effect	Std. Err.	t (18)	p-value	Coeff.	Std. Err. Coeff.
Mean/ Intercept	198.614	0.324	613.280	0.000	198.614	0.324
X_1	2.526	0.392	6.448	0.000	1.263	0.196
X_1^2	-2.276	0.649	-3.507	0.002	-1.138	0.324
X_2	23.863	0.392	60.917	0.000	11.932	0.196
$X_1 * X_2$	-2.625	0.438	-5.998	0.000	-1.313	0.219

As can be seen from Tables 3 and 5, the main effects of carbonization time and carbonization temperature and the curvature over the studied region were found to be significant at the $\alpha = 0.05$ level. At this stage, it was decided to construct and identify a second-order polynomial model based on the coefficient estimations.

Based on the previously mentioned computer reports a second-order polynomial model between significant factors and responses were selected to illustrate the dependence of responses on the significant factors as given in Eqs. (9) and (10):

$$Y_1 = 1900.75 + 2.31X_1 + 7.02X_1^2 + 48.47X_2 - 18.63X_2^2 + 3.44X_1X_2 \quad (9)$$

$$Y_2 = 198.61 + 1.26X_1 - 1.14X_1^2 + 11.93X_2 - 1.31X_1X_2 \quad (10)$$

In the above Eqs., the amount of the 2nd order polynomial significant coefficient derived from the 6th column of Tables 3 and 5.

3.2. Model Validity

Graphical residual analysis is an important and efficient model confirmation test method and was used to check the adequacy of the constructed models [11]. The objective behind this method was to check the following assumptions which were made at the beginning stage of the experimental designs.

1. Residuals are normally distributed with mean zero and constant variance.
2. Residuals are random and distributed independently.

The residuals were calculated from the Eq. (11) as:

$$\text{Residuals} = \text{Observed } Y_i - \text{Model predicted } Y_i \quad (11)$$

Variance analysis of both Eqs. was found to be adequate to represent our data with calculated adjusted R square more than 0.9. The validation of Eqs. was checked by using graphical residual analysis on the Statistica package. In Figs. 1 and 2, normal probability plots of the residuals of Eqs. (1) and (2) were given correspondingly. As can be seen almost all residuals lie on near the straight lines which shows that residuals were distributed normally.

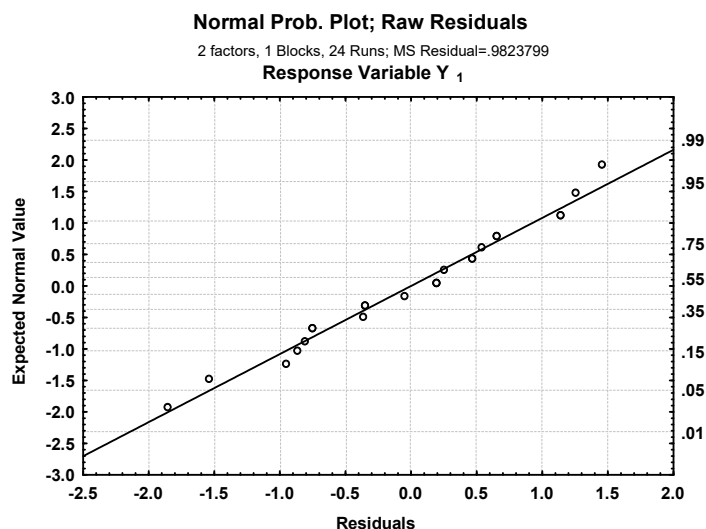


Figure 1. Normal graph of residuals for carbon fibers tensile strength model.

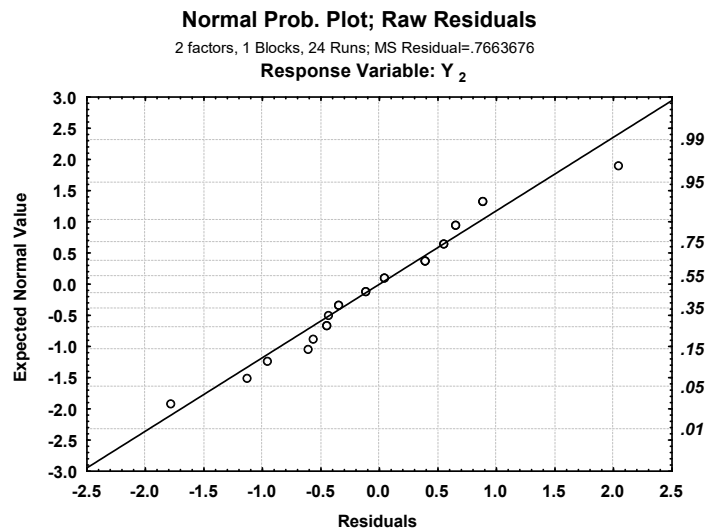


Figure 2. Normal graph of residuals for carbon fibers elastic modulus model.

In Figs. 3 and 4, the predicted responses were plotted versus residuals to check the assumption that the random errors are distributed with mean zero and constant variance. All residuals were randomly distributed between -1.5 and $+1.5$ without having any systematic structure.

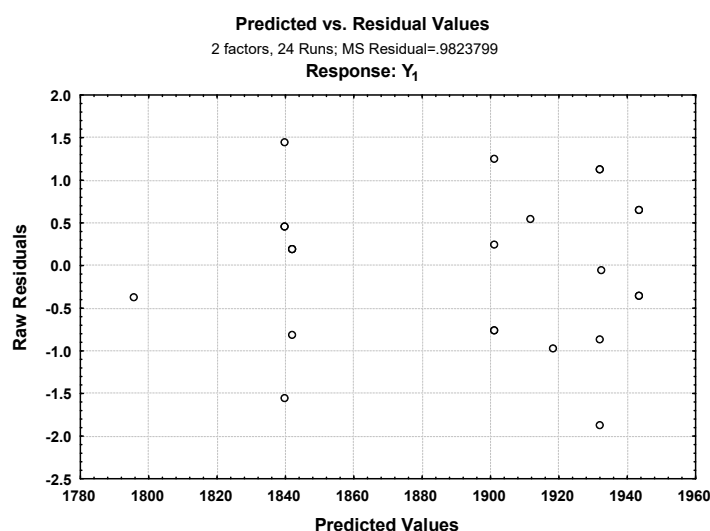


Figure 3. The predicted responses vs. residuals of carbon fibers tensile strength model.

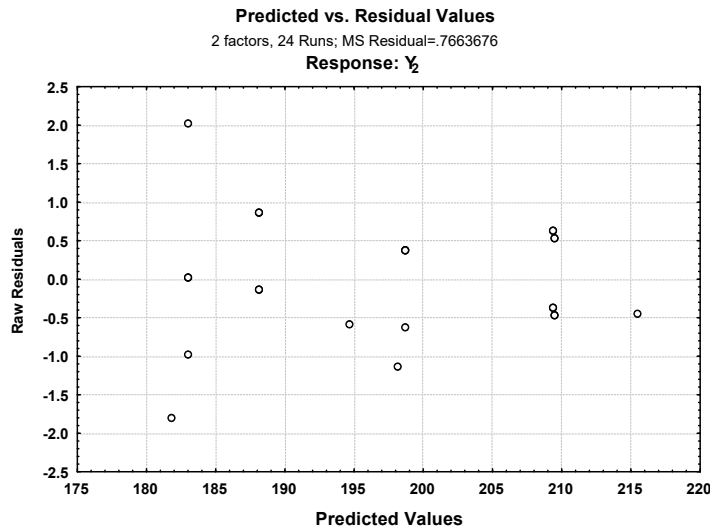


Figure 4. The predicted responses vs. residuals of carbon fibers elastic modulus model.

Since the residuals were distributed normally with constant variance, mean zero and independently, it was concluded that both models are good enough to fit the experimental data. In other words, the underlying assumptions about the errors were satisfied.

3.3. Optimization Process

Simultaneously, Fig. 5 illustrates the 3D surface beside contour plot of carbon fibers tensile strength as a function of carbonization temperature and carbonization time. As it shows, the maximum tensile strength will be achieved on maximum temperature setting.

Ordinary in real world for common usages, carbon fibers tensile strength has more attraction than elastic modulus. Based on Fig. 5 and also literature survey, carbonization time has direct positive relationship with tensile strength which means higher carbonization temperature could realize higher tensile strength. Due to the furnace type restriction, maximum practical adjustable temperature was 1450 degree of Centigrade ($X_1=2$ in codified value). Therefore, by substituting its equivalent amount in Eq. (9), the following object function achieves (Eq. 12):

$$Y_1 = 1933.45 + 55.35X_2 - 18.63X_2^2 \quad (12)$$

After differentiation, the optimum tensile strength will be $Y_1=1970$ whilst $X_1=2$ and $X_2=2$. In this case, theoretically optimum tensile strength will be 226 GPa after substitution of the optimum sets.

In order to reach carbon fibers with maximum elastic modulus, furnace temperature assigned to the maximum rate ($X_1=2$) based on the carried out experiments. In such case from Eq. (10), the amount of theoretically elastic modulus obtains as 226 GPa whilst X_2 is equal to 2. These sets of arrangement simultaneously maximize both tensile strength and elasticity modulus. Table 6 delivers optimization results in brief.

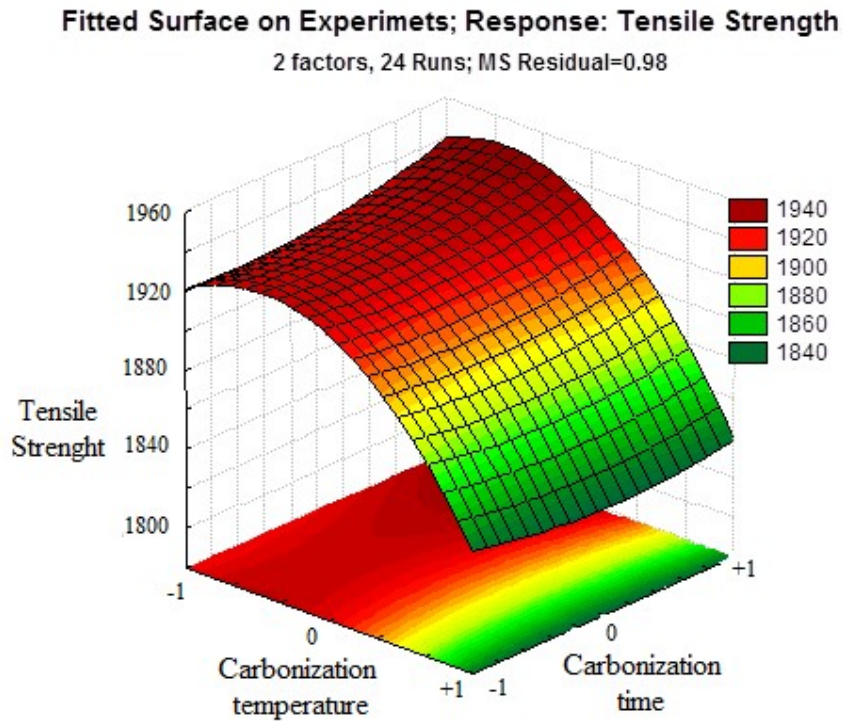


Figure 5. Variations of the carbon fibers tensile strength on the presence of two selected factors (carbonization temperature; X_1 in °C and carbonization time; X_2 in min.).

Table 6. Theoretical process setting to reach to maximum response variables

Process parameters		Attained response value	
Carbonization temperature (°C)	Carbonization time (min)	Tensile strength (MPa)	Elastic modulus (GPa)
1450	10	1970	226

The said theoretical arrangement was experimentally investigated and the observed values illustrated in Table 7. The optimization results shows the way to promote product quality characteristics from 1944 MPa and 215 GPa (the best previously observed values in elementary experiments) to 1970 MPa and 226 GPa which promote the end product quality 26 MPa in the first response and 11 GPa in the 2nd response variable. Such a result reasonably contains appropriate quality characteristic when raw material cost is near the ground.

Table 7. The observed versus predicted values of the models for tensile strength and modulus of elasticity of carbon fibers in further experiments

Process parameters		Calculated	Observed
Carbonization temperature (°C)	Carbonization time (min)	prediction amount	value
1450	10	1970	1986
1450	10	226	220

4. Conclusions

In this article, using available economical textile grade PAN fibers, which seems to be a suitable alternative for producing low price carbon fibers, was surveyed. In order to achieve a mathematical model for evaluating the effect of the affecting variables on tensile strength and

elastic modulus, a well-known experimental analysis method called ‘RSM-FCCC experimental design’ was used and a non-linear quadratic function attained. Through analyzing the valid models, an optimum set of process arrangements were obtained. According to the model, it is possible to predict the tensile strength of carbon fibers for different carbonization time and temperature. Based on the optimization procedure the most suitable process arrangement deduced whilst carbonization temperature sets on 1450 degree on Centigrade and carbonization time sets on 10 minutes. This set of arrangement could theoretically expect us for reaching the optimum set of arrangements to get the amount of 1970 MPa as carbon fibers tensile strength and 226 GPa as elastic modulus. These responses could contain good amount of contribution when raw material cost is near the ground.

The accuracy of such predictions tested experimentally after model validity test, which showed low amount of error in the two constructed mathematical models. Through using the delivered models, practitioners could accurately forecast the response values on any desired set of process parameters prior to carrying out any definite practical efforts. Also it is possible to find some efficient alternatives to set process parameters to reach to the desired responses.

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