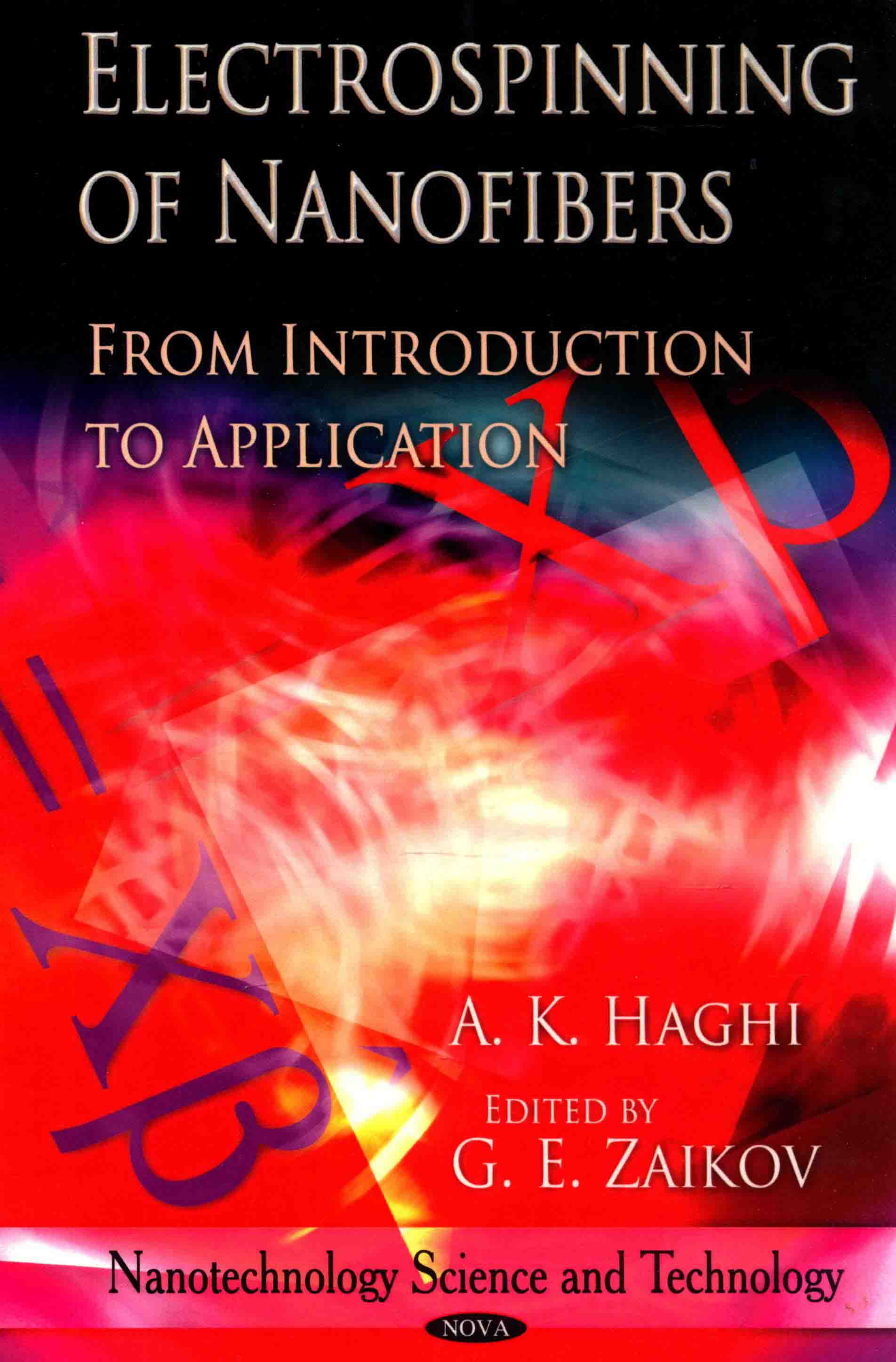
Electrospinning of Nanofibers

From Introduction to Application



A. K. Haghi

Edited by
G. E. Zaikov

Nanotechnology Science and Technology

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NANOTECHNOLOGY SCIENCE AND TECHNOLOGY

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FROM INTRODUCTION TO APPLICATION

A. K. HAGHI

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G. E. ZAIKOV

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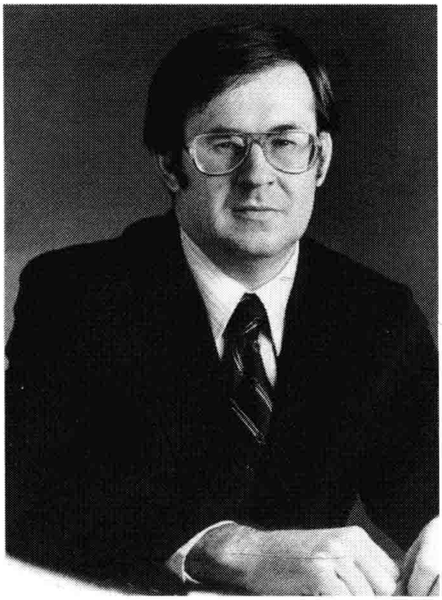

This volume is dedicated to the memory of Frank Columbus

On December 1st 2010, Frank H. Columbus Jr. (President and Editor-in-Chief of Nova Science Publishers, New York) passed away suddenly at his home in New York.

We lost our colleague, our good friend, a nearly perfect person who helped scientists from all over the world. Particularly Frank did much for the popularization of Russian and Georgian scientific research, publishing a few thousand books based on the research of Soviet (Russian, Georgian, Ukranian etc.) scientists.

Frank was born on February 26th 1941 in Pennsylvania. He joined the army upon graduation of high school and went on to complete his education at the University of Maryland and at George Washington University. In 1969, he became the Vice-President of Cambridge Scientific. In 1975, he was invited to work for Plenum Publishing where he was the Vice-President until 1985, when he founded Nova Science Publishers, Inc.

Frank Columbus did a lot for the prosperity of many Soviet (Russian, Georgian, Ukranian, Armenian, Kazakh, Kyrgiz, etc.) scientists publishing books with achievements of their research. He did the same for scientists from East Europe – Poland, Hungary, Czeckoslovakia (today it is Czeck republic and Slovakia), Romania and Bulgaria.

He was a unique person who enjoyed studying throughout the course of his life, who felt at home in his country which he loved and was proud of, as well as in Russia and Georgia.

There is a famous Russian proverb: "The man is alive if people remember him." In this case, Frank is alive and will always be in our memories while we are living. He will be remembered for his talent, professionalism, brilliant ideas and above all – for his heart.

PREFACE

Nanotechnology is revolutionizing the world of materials. The research and development of nanofibers has gained much prominence in recent years due to the heightened awareness of its potential applications in the medical, engineering and defense fields. Among the most successful methods for producing nanofibers is the electrospinning process. Electrospinning introduces a new level of versatility and broader range of materials into the micro/nanofiber range. An old technology, electrospinning has been rediscovered, refined, and expanded into non-textile applications.

Electrospinning has the unique ability to produce ultrathin fibers from a rich variety of materials that include polymers, inorganic or organic compounds and blends. With the enormous increase of research interest in electrospun nanofibers, there is a strong need for a comprehensive review of electrospinning in a systematic fashion. With the emergence of nanotechnology, researchers become more interested in studying the unique properties of nanoscale materials. Electrospinning, an electrostatic fiber fabrication technique has evinced more interest and attention in recent years due to its versatility and potential for applications in diverse fields. The notable applications include in tissue engineering, biosensors, filtration, wound dressings, drug delivery, and enzyme immobilization. The nanoscale fibers are generated by the application of strong electric field on polymer solution or melt. The non-wovens nanofibrous mats produced by this technique mimics extracellular matrix components much closely as compared to the conventional techniques. The sub-micron range spun fibers produced by this process, offer various advantages like high surface area to volume ratio, tunable porosity and the ability to manipulate nanofiber composition in order to get desired properties and function. Over the years, more than 200 polymers have been electrospun for various applications and the number is still increasing gradually with time.

The discovery and rapid evolution of electrospinning have led to a vastly improved understanding of nanotechnology, as well as dozens of possible applications for nanomaterials of different shapes and sizes ranging from composites to biology, medicine, energy, transportation, and electronic devices.

Electrospinning is a highly versatile method to process solutions or melts, mainly of polymers, into continuous fibers with diameters ranging from a few micrometers to a few nanometers. This technique is applicable to virtually every soluble or fusible polymer. The polymers can be chemically modified and can also be tailored with additives ranging from simple carbon-black particles to complex species such as enzymes, viruses, and bacteria.

Electrospinning appears to be straightforward, but is a rather intricate process that depends on a multitude of molecular, process, and technical parameters. The method provides access to entirely new materials, which may have complex chemical structures. Electrospinning is not only a focus of intense academic investigation; the technique is already being applied in many technological areas.

This book presents some fascinating phenomena associated with the remarkable features of nanofibers in electrospinning processes and new progress in applications of electrospun nanofibers.

This new book offers an overview of structure–property relationships, synthesis and purification, and potential applications of electrospun nanofibers. The collection of topics in this book aims to reflect the diversity of recent advances in *electrospun nanofibers* with a broad perspective which may be useful for scientists as well as for graduate students and engineers.

CONTENTS

Chapter 1

MECHANISM OF ELECTROSPINNING PROCESS

INTRODUCTION

Electrospinning is a novel and efficient method by which fibers with diameters in nanometer scale entitled as nanofibers, can be achieved. In electrospinning process, a strong electric field is applied on a droplet of polymer solution (or melt) held by its surface tension at the tip of a syringe's needle (or a capillary tube). As a result, the pendent drop will become highly electrified and the induced charges are distributed over its surface. Increasing the intensity of electric field, the surface of the liquid drop will be distorted to a conical shape known as the Taylor cone [1]. Once the electric field strength exceeds a threshold value, the repulsive electric force dominates the surface tension of the liquid and a stable jet emerges from the cone tip. The charged jet is then accelerated toward the target and rapidly thins and dries as a result of elongation and solvent evaporation. As the jet diameter decreases, the surface charge density increases and the resulting high repulsive forces split the jet to smaller jets. This phenomenon may take place several times leading to many small jets. Ultimately, solidification is carried out and fibers are deposited on the surface of the collector as a randomly oriented nonwoven mat [2]-[5]. Figure 1 shows a schematic illustration of electrospinning setup.

The objective of this paper is to use RSM to establish quantitative relationships between electrospinning parameters and mean and standard deviation of fiber diameter as well as to evaluate the effectiveness of the empirical models with a set of test data.

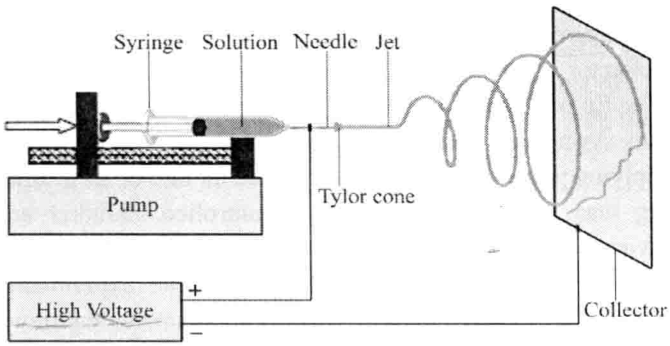

Figure 1. A typical image of Electrospinning process [6].

EXPERIMENTAL

Commercial Polyacrylonitrile (PAN) polymer containing 6% mathtlacrylate with molecular weight (Mw) of 100000 was supplied by Merk. N-methyl-2- pyrolidon (NMP) was from Riedel-de Haën. Aniline from Merck was vacuum distilled prior to use. The Polyaniline (PANI) used was synthesized in our laboratory.

Polyaniline was synthesized by the oxidative polymerization of aniline in acidic media. 3 ml of distilled aniline was dissolved in 150 ml of 1N HCl and kept at 0-5 °C. 7.325g of $(NH_4)_2S_2O_8$ was dissolved in 35 ml of 1N HCl and added drop wise under constant stirring to the aniline/HCl solution over a period of 20 minutes. The resulting dark green solution was maintained under constant stirring for 4 hrs. The prepared suspension was dialyzed in a cellulose tubular membrane (Dialysis Tubing D9527, molecular cutoff = 12,400, Sigma) against distilled water for 48 hours. Then it was filtered and washed with water and methanol. The synthesized Polyaniline was added to 150 mL of 1N (NH4) OH solution. After an additional 4 hrs the solution was filtered and a deep blue emeraldine base form of Polyaniline was obtained (PANIEB).The synthesized Polyaniline was dried and crushed into fine powder and then passed trough a 100 mesh. Intrinsic viscosity of the synthesized Polyaniline dissolved at sulfuric acid (98%) was 1.18 dl/g at 25 °C.

The PANI solution with concentration of 5 %(W/W) was prepared by dissolving exact amount of PANI in NMP. The PANI was slowly added to the NMP with constant stirring at room temperature. This solution was then allowed to stir for 1 hour in a sealed container. 20% (W/W) solution of PAN in NMP was prepared separately and was added drop wise to the well-stirred PANI solution. The blend solution was allowed to stir with a mechanical stirrer for an additional 1 hour.

Various polymer blends with PANI content ranging from 10 wt% to 30 wt% were prepared by mixing different amount of 5% PANI solution and 20% PAN solution. Total concentration of the blend solutions were kept as 12.5%.

Polymeric nanofibers can be made using the electrospinning process, which has been described in the literature and patent [20-21]. Electrospinning uses a high electric field to draw a polymer solution from tip of a capillary toward a collector. A voltage is applied to the polymer solution, which causes a jet of the solution to be drawn toward a grounded collector. The fine jets dry to form polymeric fibers, which can be collected as a web.

Our electrospinning equipment used a variable high voltage power supply from Gamma High Voltage Research (USA). The applied voltage can be varied from 1- 30 kV. A 5-ml syringe was used and positive potential was applied to the polymer blend solution by attaching the electrode directly to the outside of the hypodermic needle with internal diameter of 0.3 mm. The collector screen was a 20×20 cm aluminum foil, which was placed 10 cm horizontally from the tip of the needle. The electrode of opposite polarity was attached to the collector. A metering syringe pump from New Era pump systems Inc. (USA) was used. It was responsible for supplying polymer solution with a constant rate of 20 μl/min.

Electrospinning was done in a temperature-controlled chamber and temperature of electrospinning environment was adjusted on 25, 50 and 75 °C. Schematic diagram of the electrospinning apparatus was shown in Figure 2. Factorial experiment was designed to investigate and identify the effects of parameters on fiber diameter and morphology. (Table 1)

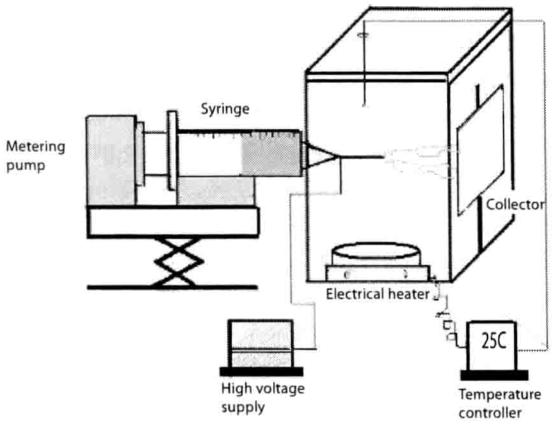

Figure 2. Schematic diagram of electrospinning apparatus.

Table 1. Factorial design of experiment

Factor	Factor level
PANI Content(wt%)	10,20,30
Electrospinning temperature(°C)	25,50,75
Applied voltage(kV)	20,25,30

Shear viscosities of the fluids were measured at shear rate of 500 sec^{-1} and 22 °C using a Brookfield viscometer (DVII+,USA).Fiber formation and morphology of the electrospun PANI/PAN fibers were determined using a scanning electron microscope (SEM) Philips XL-30A (Holland). Small section of the prepared samples was placed on SEM sample holder and then coated with gold by a BAL-TEC SCD 005 sputter coater. The diameter of electrospun fibers was measured with image analyzer software (manual microstructure distance measurement). For each experiment, average fiber diameter and distribution were determined from about 100 measurements of the random fibers. Electrical conductivity of the electrospun mats was measured by the standard four- probe method after doping with HCl vapor.

In this study, solution concentration (*C*), spinning distance (*d*), applied voltage (*V*), and volume flow rate (*Q*) were selected to be the most influential parameters. The next step is to choose the ranges over which these factors are varied. Process knowledge, which is a combination of practical experience and theoretical understanding, is required to fulfill this step. The aim is here to find an appropriate range for each parameter where dry, bead-free, stable, and continuous fibers without breaking up to droplets are obtained. This goal could be achieved by conducting a set of preliminary experiments while having the previous works in mind along with utilizing the reported relationships.

RESPONSE SURFACE METHODOLOGY

The mechanism of some scientific phenomena has been well understood and models depicting the physical behavior of the system have been drawn in the form of mathematical relationships. However, there are numerous processes at the moment which have not been sufficiently been understood to permit the theoretical approach. Response surface methodology (RSM) is a combination of mathematical and statistical techniques useful for empirical modeling and analysis of such systems. The application of RSM is in situations where several input variables are potentially influence some performance measure or quality characteristic of the process – often called responses. The relationship between the response (y) and k input variables ($\xi_1,\xi_2,...,\xi_k$) could be expressed in terms of mathematical notations as follows:

$$y = f(\xi_1, \xi_2, ..., \xi_k) \tag{3}$$

where the true response function f is unknown. It is often convenient to use coded variables ($x_1,x_2,..,x_k$) instead of natural (input) variables. The response function will then be:

$$y = f(x_1, x_2, ..., x_k) \tag{4}$$

Since the form of true response function f is unknown, it must be approximated. Therefore, the successful use of RSM is critically dependent upon the choice of appropriate function to approximate f. Low-order polynomials are widely used as approximating functions. First order (linear) models are unable to capture the interaction between parameters which is a form of curvature in the true response function. Second order (quadratic) models will be likely to perform well in these circumstances. In general, the quadratic model is in the form of:

$$y = \beta_0 + \sum_{j=1}^{k} \beta_j x_j + \sum_{j=1}^{k} \beta_{jj} x_j^2 + \sum_{i<j} \sum_{j=2}^{k} \beta_{ij} x_i x_j + \varepsilon \tag{5}$$

where ε is the error term in the model. The use of polynomials of higher order is also possible but infrequent. The βs are a set of unknown coefficients needed to be estimated. In order to do that, the first step is to make some observations on the system being studied. The model in Equation 5 may now be written in matrix notations as:

$$\mathbf{y} = \mathbf{X}\boldsymbol{\beta} + \boldsymbol{\varepsilon} \tag{6}$$

where $\mathbf{y}$ is the vector of observations, $\mathbf{X}$ is the matrix of levels of the variables, $\boldsymbol{\beta}$ is the vector of unknown coefficients, and $\boldsymbol{\varepsilon}$ is the vector of random errors. Afterwards, method of least squares, which minimizes the sum of squares of errors, is employed to find the estimators of the coefficients ($\hat{\boldsymbol{\beta}}$) through:

$$\hat{\boldsymbol{\beta}} = (\mathbf{X}'\mathbf{X})^{-1}\mathbf{X}'\mathbf{y} \tag{7}$$

The fitted model will then be written as:

$$\hat{\mathbf{y}} = \mathbf{X}\hat{\boldsymbol{\beta}} \tag{8}$$

Finally, response surfaces or contour plots are depicted to help visualize the relationship between the response and the variables and see the influence of the parameters [60], [61]. As you might notice, there is a close connection between RSM and linear regression analysis [62].

In this study RSM was employed to establish empirical relationships between four electrospinning parameters (solution concentration, spinning distance, applied voltage, and flow rate) and two responses (mean fiber diameter and standard deviation of fiber diameter). Coded variables were used to build the models. The choice of three levels for each factor in experimental design allowed us to take the advantage of quadratic models. Afterwards, the significance of terms in each model was investigated by testing hypotheses on individual coefficients and simpler yet more efficient models were obtained by eliminating statistically unimportant terms. Finally, the validity of the models was evaluated using the 15 test data. The analyses were carried out using statistical software Minitab 15.

RESULTS AND DISCUSSION

After the unknown coefficients (βs) were estimated by least squares method, the quadratic models for the mean fiber diameter (MFD) and standard deviation of fiber diameter (StdFD) in terms of coded variables are written as:

$$\begin{aligned} \text{MFD} = {} & 282.031 + 34.953x_1 + 5.622x_2 - 2.113x_3 + 9.013x_4 \\ & - 11.613x_1^2 - 4.304x_2^2 - 15.500x_3^2 \\ & - 0.414x_4^2 + 12.517x_1x_2 + 4.020x_1x_3 - 0.162x_1x_4 + 20.643x_2x_3 + 0.741x_2x_4 + 0.877x_3x_4 \end{aligned} \tag{9}$$

$$\begin{aligned} \text{StdFD} = {} & 36.1574 + 4.5788x_1 - 1.5536x_2 + 6.4012x_3 + 1.1531x_4 \\ & - 2.2937x_1^2 - 0.1115x_2^2 - 1.1891x_3^2 + 3.0980x_4^2 \\ & - 0.2088x_1x_2 + 1.0010x_1x_3 + 2.7978x_1x_4 + 0.1649x_2x_3 - 2.4876x_2x_4 + 1.5182x_3x_4 \end{aligned} \tag{10}$$

In the next step, a couple of very important hypothesis-testing procedures were carried out to measure the usefulness of the models presented here. First, the test for significance of the model was performed to determine whether there is a subset of variables which contributes significantly in representing the response variations. The appropriate hypotheses are:

$$\begin{aligned} & H_0 : \beta_1 = \beta_2 = \cdots = \beta_k \\ & H_1 : \beta_j \neq 0 \quad \text{for at least one } j \end{aligned} \tag{11}$$

The F statistics (the result of dividing the factor mean square by the error mean square) of this test along with the p-values (a measure of statistical significance, the smallest level of significance for which the null hypothesis is rejected) for both models are shown in Table 1.

Table 1. Summary of the results from statistical analysis of the models

	F	p-value	R^2	R^2_{adj}	R^2_{pred}
MFD	106.02	0.000	95.74%	94.84%	93.48%
StdFD	42.05	0.000	89.92%	87.78%	84.83%

The p-values of the models are very small (almost zero), therefore it could be concluded that the null hypothesis is rejected in both cases suggesting that there are some significant terms in each model. There are also included in Table 1, the values of R^2, R^2_{adj}, and R^2_{pred}. R^2 is a measure for the amount of response variation which is explained by variables and will always increase when a new term is added to the model regardless of whether the inclusion of the additional term is statistically significant or not. R^2_{adj} is the adjusted form of R^2 for the number of terms in the model; therefore it will increase only if the new terms improve the model and decreases if unnecessary terms are added. R^2_{pred} implies how well the model predicts the response for new observations, whereas R^2 and R^2_{adj} indicate how well the model fits the experimental data. The R^2 values demonstrate that 95.74% of MFD and 89.92% of StdFD are explained by the variables. The R^2_{adj} values are 94.84% and 87.78% for MFD and StdFD respectively, which account for the number of terms in the models. Both R^2 and R^2_{adj} values indicate that the models fit the data very well. The slight difference between the values of R^2 and R^2_{adj} suggests that there might be some insignificant terms in the models. Since the R^2_{pred} values are so close to the values of R^2 and R^2_{adj}, models does not appear to be overfit and have very good predictive ability.

The second testing hypothesis is evaluation of individual coefficients, which would be useful for determination of variables in the models. The hypotheses for testing of the significance of any individual coefficient are:

$$H_0 : \beta_j = 0 \qquad H_1 : \beta_j \neq 0 \tag{12}$$

Table 2. The test on individual coefficients for the model of mean fiber diameter (MFD)

Term (coded)	Coef	T	p-value
Constant	282.031	102.565	0.000
C	34.953	31.136	0.000
d	5.622	5.008	0.000
V	-2.113	-1.882	0.064
Q	9.013	8.028	0.000
C^2	-11.613	-5.973	0.000
d^2	-4.304	-2.214	0.030
V^2	-15.500	-7.972	0.000
Q^2	-0.414	-0.213	0.832
Cd	12.517	9.104	0.000
CV	4.020	2.924	0.005
CQ	-0.162	-0.118	0.906
dV	20.643	15.015	0.000
dQ	0.741	0.539	0.592
VQ	0.877	0.638	0.526

Table 3. The test on individual coefficients for the model of standard deviation of fiber diameter (StdFD)

Term (coded)	Coef	T	*p*-value
Constant	36.1574	39.381	0.000
C	4.5788	12.216	0.000
D	-1.5536	-4.145	0.000
V	6.4012	17.078	0.000
Q	1.1531	3.076	0.003
C^2	-2.2937	-3.533	0.001
d^2	-0.1115	-0.172	0.864
V^2	-1.1891	-1.832	0.072
Q^2	3.0980	4.772	0.000
Cd	-0.2088	-0.455	0.651
CV	1.0010	2.180	0.033
CQ	2.7978	6.095	0.000
dV	0.1649	0.359	0.721
dQ	-2.4876	-5.419	0.000
VQ	1.5182	3.307	0.002

The model might be more efficient with inclusion or perhaps exclusion of one or more variables. Therefore the value of each term in the model is evaluated using this test, and then eliminating the statistically insignificant terms, more efficient models could be obtained. The results of this test for the models of MFD and StdFD are summarized in Table 2 and Table 3 respectively. *T* statistic in these tables is a measure of the difference between an observed statistic and its hypothesized population value in units of standard error.

As depicted, the terms related to Q^2, CQ, dQ, and VQ in the model of MFD and related to d^2, Cd, and dV in the model of StdFD have very high *p*-values, therefore they do not contribute significantly in representing the variation of the corresponding response. Eliminating these terms will enhance the efficiency of the models. The new models are then given by recalculating the unknown coefficients in terms of coded variables in equations (13) and (14), and in terms of natural (uncoded) variables in equations (15), (16).

$$\begin{aligned} MFD &= 281.755 + 34.953x_1 + 5.622x_2 - 2.113x_3 + 9.013x_4 \\ &- 11.613x_1^2 - 4.304x_2^2 - 15.500x_3^2 \\ &+ 12.517x_1x_2 + 4.020x_1x_3 + 20.643x_2x_3 \end{aligned} \tag{13}$$

$$\begin{aligned} StdFD &= 36.083 + 4.579x_1 - 1.554x_2 + 6.401x_3 + 1.153x_4 \\ &- 2.294x_1^2 - 1.189x_3^2 + 3.098x_4^2 \\ &+ 1.001x_1x_3 + 2.798x_1x_4 - 2.488x_2x_4 + 1.518x_3x_4 \end{aligned} \tag{14}$$

$$\begin{aligned} MFD &= 10.3345 + 48.7288\,C - 22.7420\,d + 7.9713\,V + 90.1250\,Q \\ &- 2.9033\,C^2 - 0.1722\,d^2 - 0.6120\,V^2 \\ &+ 1.2517\,Cd + 0.4020\,CV + 0.8257\,dV \end{aligned} \tag{15}$$

$$\begin{aligned} StdFD &= -1.8823 + 7.5590\,C + 1.1818\,d + 1.2709\,V - 300.3410\,Q \\ &- 0.5734\,C^2 - 0.0476\,V^2 + 309.7999\,Q^2 \\ &+ 0.1001\,CV + 13.9892\,CQ - 4.9752\,dQ + 3.0364\,VQ \end{aligned} \tag{16}$$

The results of the test for significance as well as R^2, R^2_{adj}, and R^2_{pred} for the new models are given in Table 4. It is obvious that the *p*-values for the new models are close to zero indicating the existence of some significant terms in each model. Comparing the results of this table with Table 1, the *F* statistic increased for the new models, indicating the improvement of the models after eliminating the insignificant terms. Despite the slight decrease in R^2, the values of R^2_{adj}, and R^2_{pred} increased substantially for the new models. As it was mentioned earlier in the paper, R^2 will always increase with the number of terms in the model. Therefore, the smaller R^2 values were expected for the new models, due to the fewer terms. However, this does not necessarily suggest that the pervious models were more efficient. Looking at the tables, R^2_{adj}, which provides a more useful tool for comparing the explanatory power of models with different number of terms, increased after eliminating the unnecessary variables. Hence, the new models have the ability to better explain the experimental data. Due to higher R^2_{pred}, the new models also have higher prediction ability. In other words, eliminating the insignificant terms results in simpler models which not only present the experimental data in superior form, but also are more powerful in predicting new conditions. In the study conducted by Yördem et al. [36], despite high reported R^2 values, the presented models seem to be inefficient and uncertain. Some terms in the models had very high *p*-values. For instance, in modeling the mean fiber diameter, *p*-value as high as 0.975 was calculated for cubic concentration term at spinning distance of 16 *cm*, where half of the terms had *p*-values more than 0.8. This results in low R^2_{pred} values which were not reported in their study and after calculating by us, they were found to be almost zero in many cases suggesting the poor prediction ability of their models.

Table 4. Summary of the results from statistical analysis of the models after eliminating the insignificant terms

	F	*p*-value	R^2	R^2_{adj}	R^2_{pred}
MFD	155.56	0.000	95.69%	95.08%	94.18%
StdFD	55.61	0.000	89.86%	88.25%	86.02%

Table 5. The test on individual coefficients for the model of mean fiber diameter (MFD) after eliminating the insignificant terms

Term (coded)	Coef	T	*p*-value
Constant	281.755	118.973	0.000
C	34.953	31.884	0.000
d	5.622	5.128	0.000
V	-2.113	-1.927	0.058
Q	9.013	8.221	0.000
C^2	-11.613	-6.116	0.000
d^2	-4.304	-2.267	0.026
V^2	-15.500	-8.163	0.000
Cd	12.517	9.323	0.000
CV	4.020	2.994	0.004
dV	20.643	15.375	0.000