# **Abstract**

Since the fiber diameter determines the mechanical, electrical, and optical properties of electrospun nanofiber mats, the effect of material and process parameters on poly(ethylene oxide) (PEO) fiber diameter spun by Pressure coupled infusion gyration (PCIG) were studied.

Accordingly, the prediction and optimization of input parameters were performed using the response surface methodology (RSM) with the design of experiments technique and least square fitting. A central composite design of RSM was employed to develop a mathematical model as well as to define the optimum condition. Both linear and nonlinear fitting approaches were designed and used for the estimation of the equations of models. The goodness of the models were evaluated using Akaike Information Criterion (AIC), a lower AIC value indicates a better fitness of the model with the input data.

The parameters studied were polymer concentration (5 – 20 wt%), infusion flow rate (0.5 – 5 mL/min), working pressure (1×105 - 3×105 Pa), rotational speed (10000 – 36000 rpm). From the analysis of variance, the most significant factor that caused a remarkable impact on the experimental design response was identified.

# **Introduction**

**Nanofiber sub-paragraph**

**Nanofiber preparing method sub-paragraph**

**Electrospinning, pressurised gyration, infusion gyration, PCIG**

**PCIG** to feed the polymer solutions into the vessel simultaneously during rotation

Pressure coupled infusion gyration is able to bring materials to the nano-scale not only help to improve their properties and affords them new advanced characteristics beyond bulk materials, but also produce uniaxially aligned 3D fibrous bundles consistently and cost-effectively. During rotational spinning, pressure coupled infusion gyration effectively utilizes high speed rotation of the vessel to extrude several solution jets parallely jet out from orifices that are located on the vessel surface.

Compared with typical pressurised gyration [3] (**Table 4 and Figure 3a**) the fibre produced using pressure coupled infusion gyration was much thinner. This is because the dynamic fluid flow can be regulated by infusion rate of solution when flowing across orifice during spinning, hence the material input could be effectively used and obtaining the desired products morphology be obtained by balancing different combinations of processing parameters with solvent evaporation.

The diameter of nanofibers affects the surface area and pores. Therefore, the specific usage of nanofibers such as membranes or scaffolds requires a given diameter. But various parameters affect the PCIG process, such as the solution properties along with other parameters with the known and the unknown effects to each other, thus to achieve desired diameter, experiment level are very complex and the process of preparing fibers with desired diameters would be expensive and time-consuming. Researchers have tried to figure out scientific and predictive tools in variety of processes. Nowadays, there are several data mining and machine learning algorithms that are reliable to optimize the experiment process by predicting significant relationship between data using effective techniques such as Box–Benkhen design (BBD), response surface methodology (RSM), and ANN, with the latter more popular by now.

ANN and RSM are two widely used models of mathematical modelling and computer simulation for computational processes. ANN consist of input, hidden and output layer, which is inspired by the working principles/structures of biological neural networks of the human brain. There are different population of units (neurons) in each layer, and these units are interconnecting with each other to investigate their inter-relationships and predict the specific outputs that related with different input data and specific functions it used. ANN, more precisely, the three layers Back Propagation (BP) ANN has been used as a tool of modelling the electrospinning processes, as well as predicting the geometry and mechanical properties of spun fibers [references]. Due to the units in the hidden layer can be manipulated as requirements, hence any continuous functions can be represented at any precision. In addition, BP ANN is able to solve multivariate regression problems (linear/nonlinear) by training models through computing functions’ gradient, then adjust the weights and thresholds between neurons in each layer along the negative gradient direction, to optimum the functions (also known as gradient descent algorithm).

However, despite the aforementioned strengths of ANN, there are also several known limitations of ANN, including: the slow convergence when the estimated value is close to the target; sensitive to the noise of the training sample, i.e. relative poor training effect if intense changes in the sample; more notably, a tricky issue that is currently no general formula for the determination of the number of units (neurons) in hidden layer, when the network structure was designed. As the number of the units directly determines the ability of the network to dig linear/nonlinear information from data, insufficient quantity of selected units may lead information were expressed inadequately; an excessive quantity of units will increase the computational overhead exponentially, and also resulting in a decline in network generalization.

RSM is a convenient method that needs less number of experiments than ANN to construct an effective mode. It showed a good performance if the input and training data are well distributed statistically in the design of experiment [**find references**]. Based on the training data, RSM uses statistical methods, in the meanwhile, taking into account the combined effects of several parameters to estimate the relationships (e.g. functional relevance) and the response of the modelling process by fitting an empirical model (linear/nonlinear), then the resulted models can be evaluated and further used as a tool of predicting and optimizing the settings of the independent variables to reduce residuals. [Montgomery DC, Myers RH (1995) Response surface methodology: process and product optimization using designed experiments. Raymond H Meyers and Douglas C Montgomery A Wiley-Interscience Publications] According to its structural characteristics, in the aspect of obtaining results of the interaction between different components for whole system, sensitivity analysis, and other in-depth and advanced information, RSM has shown its better performance in comparison with ANN. In some previous studies, RSM has been used for optimizing process and material properties in different field, for instance poly(vinyl alcohol) hydrogel, thermoplastic elastomers, diamond-like carbon films.

In order to have an overview of the effect of the PCIG experimental parameter individually and a quantitative basis of the relationships between PCIG parameters and spun fiber diameter, the RSM employed in this work. To use a mathematical model to describe the effects of PCIG parameters allows us to represent the influencing parameter in a simple and systematic way and to predict the response of the experiments with different parameter combinations. In addition, owing to the benefit of RSM, the repeated experiments for testing the influences of all possible combinations of parameters on diameter could be lessened.

ParetoPlot ParetoDistribution

# **Materials and method (this part find the ‘good BP ANN’)**

**2.1 Materials and experiment preparation**

Poly (ethylene oxide) (PEO, molecular weight of 2×105 g mol−1) was purchased from Sigma-Aldrich (Poole, UK) was used as-received and deionised water was selected as the solvent. The pressure coupled infusion gyration used in this work as seen in the **Figure 1**, it consists of a cylinder rotational vessel with 40 mm height and 60 diameter. It equipped with 20 orifices that symmetrically and accordantly distributed on the vessel surface, and 0.5 mm in diameter for each orifice. A DC motor joint at the top of the vessel, which can work in the range of 4.5 V to 15 V of D.C. voltage to drive vessel rotation at various speeds that up to 36000 rpm. The injected polymer solution flow is controlled by a syringe pump (PHD Ultra 4400, Harvard Apparatus Ltd., Edenbridge, UK) with a 10-ml syringe and connected at the bottom of the vessel by a plastic tube. A Nitrogen cylinder connected to the vessel bottom using a T-junction to provide pressure (up to 3×105 Pa). The collector, a stationary copper mesh, was place around the vessel to collect the jetted fibers. The spun fibers were assessed by means of a JSM-6301F scanning electron microscopy (SEM), and the fiber diameters were determined by Image J software from the random fibers at different location per sample. A typical SEM image of spun fiber using PCIG process is shown in **Figure 2.**

**2.2 Design of Experiments**

In order to obtain a more systematic understanding of these process conditions and to establish a quantitative basis for the relationships between PCIG parameters and fiber diameter, response surface methodology (RSM) was employed. During this study, fiber diameters were prepared by varying four parameters: PEO solution concentrations, pressure, infusion flow rate and rotation speeds, and their relation to the fiber diameter was developed using RSM, all other parameters including humidity, and ambient temperature are considered as fixed during the experiment.

Based on previous work [**last paper**], it was found that the appropriate distance of collection (from orifices to collector) is determined by the duration of solvent evaporation and the diameter of the spiral trajectory required for the polymer jets. An insufficient collection distance will result in the formation of thicker or coarser fibers, which are without enough elongation before reaching collector. On the other hand, if the selective collection distance beyond its critical value that needed for evaporation of the particular solvent, the effect of the distance can be negligible. In this work the orifice – collector distance was fixed at 10 cm.

The infusion flow rate affect the hydrostatic pressure exists at the jetting orifices, and the volume and mass of polymer solution passed the orifice are also controlled by the infusion rate. A higher infusion rate will give to a relative shorter solvent evaporation/polymer jets stretching time, hence promote thicker and multiple polymer jets formed during the spinning, which were observed in the last work. Six levels of flow rate were chosen (0.5, 1, 2, 3, 4, 5 mL/min).

The polymer concentration is of the key factors in spinning process, it selectively affects the formation and morphology of spun fiber via adjusting solution’s fluid properties e.g. viscosity and chain entanglement degree, which is a pre-requisite for uniform fibres formation. A relative higher polymer concentration helps to stabilize the polymer jets in the fiber generation process, on the other hand causes a larger transfer rate of solution through the jetting orifices via hindering the solution’s evaporation, which is the crucial for the formation of thicker fiber. 5, 10, 15 and 21 wt% were used as the four levels of solution concentrations.

The influence of applied pressure was studied by performing the experiment at three levels of pressure (1×105 - 3×105 Pa). A high pressure would lead to a trend of reduction in fiber diameter at any fixed polymer concentration, this is attribute to the enhanced thinning effect introduced by gas blowing, and hence solvent evaporation that takes place in the radial direction of jets would be also facilitated by a higher applied pressure. In addition, the enhanced gas blowing would help to enhance the instability of polymer jets at the orifices, which would promote the formation of bead or defective fiber.

The combination of solution blowing and centrifugal force against with surface tension results in deformation of the polymer droplets, thereby enabling the formation of fibers from the vessel orifice. The higher rotational speed will enhance this deformation by increasing the centrifugal force. And the presence of non-Newtonian fluid shear stress against the normal stress, and lead to tension and deformation along the same direction as the plane effect [**references**]. Thus, the stretching in polymer jets will be further accelerated by the centrifugal force and gas blowing. The rotational speeds selected in this study are include 10000, 24000, 36000 rpm.

Various experiments have been carried out for different combinations of inputs and the production process parameters have been found. Seventy-five tests are taken to develop the back propagation neural network model, of which, sixty-four tests are used for training the back propagation neural network model and eleven tests are used for testin

**2.3 Response surface methodology implementation**

**2.3.1 Input and output preparation**

To avoid under-fitting, which is usually caused by too few input data for training, in this work, 120 experiments were carried out for different combination of parameters with different levels. To achieve a high fitting degree, the input data should be measured accurately and sensitive to the parameter of the experiment process. For each individual experiment, over 100 fiber diameters were obtained from the random fibers of each sample, and each diameter value was used as one input data to fit the **model**. However, there are 19 combinations gave us droplets or defective fibers, so the data of the left 101 experiments were used.

(Consequently, the XX was the output of the model. With the purpose of training models, XXX of the samples were randomly assigned to the training set and XXX of the samples are randomly assigned to the validation set. )

We used Mathematica to process the results of the experiments using multiple regression analysis. For that reason, both the linear and nonlinear models were applied, as we assumed a linear or nonlinear mapping exists between the parameters and fiber diameters. The goodness of the models that fit experimental data were compared using Akaike Information Criterion (AIC) test. A lower AIC value is more preferred as a smaller residuals existing between fitting curve and experimental data. Additionally, application of analysis of variance (ANOVA) was used to evaluate the quality of the fits, due to the mathematical model found after fitting the function to the data sometimes does not satisfactorily describe the experimental domain under study. The central idea of ANOVA is to compare the variations caused by changes of the levels of parameters with the variations by the random errors inherent in the measurements of the generated responses. Hence, it allows us to assess the source of experimental variance and the significance of the regression used to predict the responses.

**Sensitivity Analysis can be considered**

‘Sensitivity analysis Artificial neural network for modeling the elastic modulus’

Validation and test