J Mater Sci (2009) 44:647–654
DOI 10.1007/s10853-008-3050-y

Parametric study of manufacturing poly(lactic) acid nanofibrous mat by electrospinning

S. N. Patra · A. J. Easteal · D. Bhattacharyya

Received: 9 July 2008 / Accepted: 10 October 2008 / Published online: 27 November 2008

Abstract Electrospinning is a versatile method for manufacturing polymer-based multi-functional and high-performance nanofibrillar network. Two important characteristics, namely minimum diameter variation and bead area, render the nanofibre mats acceptable for many membrane type applications, but the relationship between processing parameters and microstructures is still not well understood. This article outlines a systematic study via the design of experiments in the context of selecting process control parameters while electrospinning nonwoven mats of nanofibres from poly(L-lactic acid). The goals are to obtain a robust set of parameters to reduce the variation in product quality by performing the minimum number of experiments. A desirable combination has been found to be low concentration of polymer solution, low feed rate, comparatively high applied voltage and a large distance between the collector and the needle. However, a low concentration of polymer solution may result in some bead formation if other factors are not changed accordingly.

Introduction

Electrospinning can be utilised to assemble polymer mats of nanofibres with diameters ranging from several microns to less than even 10 nm [1, 2]. Nonwoven textiles composed of electrospun fibres have large specific surface areas and small pore sizes compared to commercial textiles, making them excellent candidates for use in filtration and membrane applications. The electrospun fibres provide an interconnected porous network, which is desirable for drug gene/cell delivery and biomedical substrates (scaffolds) for tissue regeneration, immobilisation of enzymes and catalyst systems, wound dressings and artificial blood vessels [3, 4].

Control of the pore size in a fibre network is important for scaffold applications, particularly when relatively large-sized pores are required, e.g. in the range of a few hundred microns [5]. The scaffolds should be highly porous and the pore size must be controlled to allow cells to be seeded and to permit facile invasion of blood vessels for supply of nutrients to the cells [6, 7].

The experimental variables in electrospinning include the concentration and related properties (e.g. viscosity that depends on solute concentration) of the polymer solution from which the fibre networks are produced, and process parameters such as electric field, distance over which the electric field is applied and solution flow rate. The tensile force is generated by the interaction of the applied electrical field with the electrical charge carried by the polymer solution jet rather than by the spindles and reels used in conventional spinning [8]. As the solution jet travels, the solvent evaporates to form a charged polymer fibre, which is elongated by an electrical force and attracted to the collecting plate (Fig. 1) with opposite polarity [9]. While the electrospinning technique has been known for about 70 years [10], there has been a recent renewed interest in the technique since electrospun fibres have started finding applications in both nanotechnology and biotechnology. For the latter, nanofibres of biodegradable polymers are of particular interest [3, 4].

S. N. Patra · D. Bhattacharyya (✉)
Department of Mechanical Engineering, Centre for Advanced Composite Materials, The University of Auckland, Private Bag 92019, Auckland, New Zealand
e-mail: d.bhattacharyya@auckland.ac.nz

A. J. Easteal
Department of Chemistry, Centre for Advanced Composite Materials, The University of Auckland, Private Bag 92019, Auckland, New Zealand

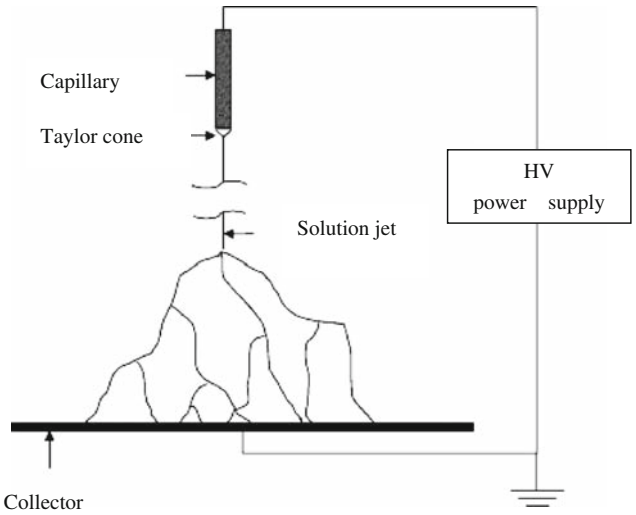

Fig. 1 Basic schematic diagram of electrospinning process [9]

For nanofibrous mats to be acceptable in many applications, the fibres should have a minimal variation in diameter and a very small number (preferably zero) of beads. If the field strength is too high, increased instability of the jet may lead to bead formation [3, 4]. On the other hand, if the distance between the needle tip and the collector is such that the field gradient is enough, there are fewer beads formed as the electric field provides sufficient stretching force to the jet. However, at a large distance the fibre diameter increases due to the decrease in the electric field gradient, resulting in less stretching of the fibres [5]. Another factor that may influence the diameter of the fibre is the flight time of the electrospinning jet—a longer flight time allows more time for the fibre to elongate before it is deposited on the collector plate [11]. Conversely shorter flight time makes less elongation generating coarse fibres. It must be acknowledged that the integration of nanofibres into useful devices requires fibres of well-controlled orientation, size and other target characteristics as well as reproducibility of locating them in specific positions and orientations. The ability to do so remains a major challenge [9], and effective parametric analyses are needed to achieve products with the required characteristics. Taguchi method of experimental design offers a scope for selecting the optimal levels of process parameters with minimum number of experiments carried out, thus significantly reducing the time required for experimental investigation. It is also effective in elucidating the effects of multiple factors individually and interactively, on product quality [12, 13]. The primary objective of the present study is to use the Taguchi method to establish the desirable set of four control parameters for making an electrospun nanofibre web from poly(L-lactic acid) (PLLA) with specific microstructural characteristics. The parameters used in this study are the concentration and feed rate of polymer solution, applied voltage and the distance between the collector and the needle. The target outcomes have been the minimal variation in nanofibre diameter and minimum mat area occupied by the beads.

Taguchi method

The Taguchi method [14] is aimed at finding a robust setting of control factors to make the product or process insensitive to the noise factors [15, 16] and to optimise them against the target outcomes. In order to execute a robust design, Taguchi employs two key tools, namely signal-to-noise (S/N) ratio to assess the quality and an orthogonal array (OA) to arrange the experiments that can accommodate many design factors simultaneously. Taguchi suggests S/N ratio as the objective function for matrix experiments as the ratio can reflect both the average and the variation of quality characteristics. The OA of experiments is to determine the optimum level for each factor and to establish the relative significance of an individual factor in terms of its main effects on the outcome. In order to achieve the 'lower is better' characteristics (i.e. small diameter and bead area), the S/N ratio is given by:

$$\mathrm{S/N} = -10 \log \frac{1}{n} \sum_{i=1}^{n} y^2, \tag{1}$$

where y represents the results of measurement, n the number of observations and subscript i indicates the number of simulation design parameters in the OA table. A greater S/N ratio always corresponds to more robust quality characteristics regardless of their category.

An analysis of variance (ANOVA) is performed as well to see which process parameters are statistically significant. Another tool, F-test [17], has been used to see which process parameters have significant effects on the performance characteristics. This is accomplished by separating the total variability of the S/N ratios, which is measured by the sum of the squared deviations from the total mean of the S/N ratio, into contributions by each of the process parameters and the error. First, the total sum of the squared deviations $\mathrm{SS_T}$ from the total mean of the S/N ratio, η, can be calculated as:

$$\mathrm{SS_T} = \sum_{i=1}^{m} (\eta_i - \overline{\eta})^2, \tag{2}$$

where m is the total number of experiments in OA and η_i indicates the S/N ratio for ith experiment [12, 18].

Experimental details

Design of experiment

The principal characteristics of robustness for electrospinning of PLLA considered in the present study include

Table 1 Factors and levels used in the experiments

Factors	Description	Level 1	Level 2
A	Concentration of polymer solution (%w/v)	4	7
B	Feed rate of polymer (mL/h)	1	2
C	Distance (mm)	80	100
D	Voltage (kV)	8	10

Table 2 Experimental layout plan using eight runs

Experiment number	Electrospinning parameter level			
	A Polymer concentration	B Feed rate	C Distance	D Voltage
1	1	1	1	1
2	1	1	2	2
3	1	2	1	2
4	1	2	2	1
5	2	1	1	2
6	2	1	2	1
7	2	2	1	1
8	2	2	2	2

making of fine nanofibres with least number of beads and a reduced sensitivity to external noise. Therefore, two performance indices have been considered: fibre diameter and number of beads. In the presented set of experiments, four factors (the concentration and feed rate of polymer solution, applied voltage and the distance between the collector and the needle) and two levels of each have been considered (Table 1). Instead of normal factorial design (2^4), 8-run OA is chosen due to its capability to check the interactions among various factors [14]. However, all 16 experiments have also been done to get a clearer idea of all the effects of both individual factors and their interactions at two different levels. Each process parameter is assigned to a column and each row of the matrix represents one trial. The sequence in which these trials are carried out has been randomised and the two levels of each factor have been represented by '1' or '2' in the matrix. Experimental layout plan for the electrospinning process parameters using L_8 OA is listed in Table 2, whereas Table 3 lists the actual data for fibre diameter and bead area along with their computed S/N ratios. Tables 4 and 5 list the ANOVA results of two characteristics separately.

Manufacturing of nanofibrous mat

Electrospinning of polylactic acid was accomplished using solutions of PLLA (using NatureWorks 3051D) with weight average molar mass about 1.044×10^5 g/mol (measured using gel permeation chromatography). Dichloromethane was used as the main solvent and dimethyl formamide was used for enhanced conductivity. Experiments were performed on a set-up that included a power supply, capable of generating high voltage, a syringe as capillary tube and a collector as target. A close cabinet was designed (Fig. 2) using transparent poly (methyl methacrylate) thick sheet for dust protection, reduced air blow and extra security of the operator.

Polymer solution was delivered to the top of a needle through a hypodermic glass syringe (Popper & Sons, Inc) as a capillary tube. The flow of the liquid spinnable polymer was controlled using a programmable syringe pump (Cole-Parmer Hz 50/60, cat# 789100C). The same type of hypodermic needle of 20G1TW (0.9 mm × 25 mm) from BD PrecisionGlide™ Needle was used throughout the experimental work. The power supply used was from Spellman DEL HVPS INST 230-30R that could make potential difference up to 30 kV. As the electric field increased beyond 7 kV, the hemispherical surface of the solution at the tip of the capillary tube extended to form a cone-like structure, commonly known as Taylor cone [19]. For collecting the nanofibres, commercial aluminium foil was used, which was kept at a distance so that solvent could evaporate and nanofibres could get enough flight time to dry. Aluminium stubs that had been well cleaned to create a smooth and glossy surface were used to collect the sample for visualisation under scanning electron microscope (SEM). The distance between the collector and the needle tip was maintained at 80–100 mm; white nanofibres adhered smoothly on the aluminium foil with a voltage in the range of 7 and 12 kV.

Selection of electrospinning parameters

The properties of the polymer solution have significant influences on the electrospinning process and the resultant fibre morphology. The viscosity and conductivity of the solution determine the extent of elongation of the solution [2, 20]. The viscosity of the polymer solution depends on both the molecular weight of the polymer and the concentration of the polymer solution [21]. In the current study, the molecular weight of the polymer was not varied. Furthermore, the conductivity of the polymer solution was also not considered as a parameter, because the relative proportions of the two solvents were kept constant (60:40 by volume). The feed rate of the polymer solution is an important parameter because it determines the amount of solution available for stretching to form nanofibres and plays a vital role in determining the fibre diameter and bead formation [3]. As recommended in reported studies [3, 4, 9], a concentration of 4–7% w/v and a feed rate of 1–2 mL/h were chosen for this study. It is to be noted that although a

Table 3 Experimental results for fibre diameter and bead area and their corresponding S/N ratios

Experiment number	Factors				Designation	Result		Calculated S/N ratio	
	A Polymer concentration	B Feed rate	C Distance	D Voltage		Fibre diameter (nm)	Bead area $(\mu m)^2$	S/N ratio for fibre diameter	S/N ratio for bead area
1	1	1	1	1	$A_1B_1C_1D_1$	88.31	192.72	−38.95	−45.73
2	1	1	2	2	$A_1B_1C_2D_2$	51.02	201.16	−34.18	−46.07
3	1	2	1	2	$A_1B_2C_1D_2$	75.08	184.10	−37.68	−45.31
4	1	2	2	1	$A_1B_2C_2D_1$	98.14	165.92	−40.06	−44.44
5	2	1	1	2	$A_2B_1C_1D_2$	146.03	94.27	−43.3	−39.56
6	2	1	2	1	$A_2B_1C_2D_1$	162.67	102.73	−44.35	−40.26
7	2	2	1	1	$A_2B_2C_1D_1$	144.16	104.14	−43.22	−40.37
8	2	2	2	2	$A_2B_2C_2D_2$	135.06	76.86	−42.67	−37.86

Table 4 Results of ANOVA technique for fibre diameter

Source of variation	Sum of squares	Degree of freedom	Mean square	*F*-ratio	Contribution (%)
A	4.02	1	4.02	143.57	76.5
B	0.06	1	0.06	2.14	1.1
D	0.55	1	0.55	19.64	10.5
AB	0.32	1	0.32	11.42	6.1
AC	0.06	1	0.06	2.14	1.1
BC	0.24	1	0.24	8.57	4.6
Error	0.028	1	0.028		
Total	5.278	7			

Table 5 Results of ANOVA technique for bead area

Source of variation	Sum of squares	Degree of freedom	Mean square	*F*-ratio	Contribution (%)
A	4.31	1	4.31	574.67	93.09
B	0.10	1	0.10	13.33	2.16
C	0.04	1	0.04	5.33	0.86
D	0.03	1	0.03	4.0	0.65
BC	0.15	1	0.15	20	3.24
Error	0.015	2	0.0075	–	
Total	4.645	7			

feed rate of 0.5 mL/h performed well at times, it had a tendency to clog the needle tip.

Higher electrical forces (i.e. larger applied voltage) provide extra stretch to elongate the fibres and thus make nanofibres with reduced diameter. The starting voltage in this study was 6 kV but as the spinning rate increased with increasing voltage, at voltages higher than 12 kV, the spinning rate became too fast to control and jet flow got diverged. Consequently, 8–10 kV was selected as an appropriate voltage range. As the distance between the collector and the needle tip was increased, electrospinning produced a nanofibre network with fewer beads. The 80–100 mm range of distance was found to be appropriate for this study. Other experimental variables were kept constant to isolate the effects of the four parameters that were varied. Experiments were performed in a closed chamber (Fig. 2) and attention was paid to maintain approximately the same relative humidity and ambient temperature for the duration of the experiments. Subsequently, the electrospun nanofibres were studied under a Philips XL30S SEM. Using an imagetool software (Uthansca), measurements of nanofibre diameter and bead area were made from the scanning micrographs. In order to ensure the accuracy of the results, experiments were replicated five times, requiring a total of 40 experiments to be performed. From each experimental SEM-micrograph, eight individual fibre strands were considered and therefore, from five repetitions, a total of 40 fibres were considered from the same set of experimental conditions to estimate the range of diameters and their variations.

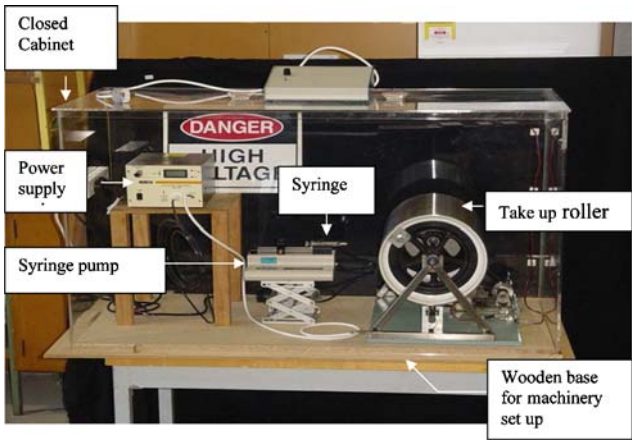

Fig. 2 Electrospinning set-up for this study

Results

S/N ratio approach

Two frequency distribution bar graphs are shown in Fig. 3a and b for two successive experiments (#1 and #2). The results are then substituted into Eq. 1 to obtain the corresponding S/N ratios (Table 3). Since the experimental design is orthogonal, it has been possible to separate out the effects of each spinning parameter at different levels with their interactions. In addition, the total mean S/N ratio for the eight experiments is calculated for two output characteristics. Figure 4 suggests that polymer concentration (factor A) and voltage (factor D) are more significant for achieving small fibre diameters. Feed rate (factor B) and distance between the needle and the collector (factor C) are of relatively low significance. It appears that the interactions between the factors affect the response very little. The low polymer concentration (A_1) and comparatively high voltage (D_2) appear to be the best choice to get fine fibre diameters. Although the other two factors are relatively insignificant on the average S/N responses, a low feed rate and a long distance have shown some positive impacts in making finer fibre diameters, which will be discussed later. Therefore, experiment #2 in Table 3 is the best for achieving small diameters (Fig. 5a) and an optimal parameter combination of $A_1B_1C_2D_2$ (among eight runs)

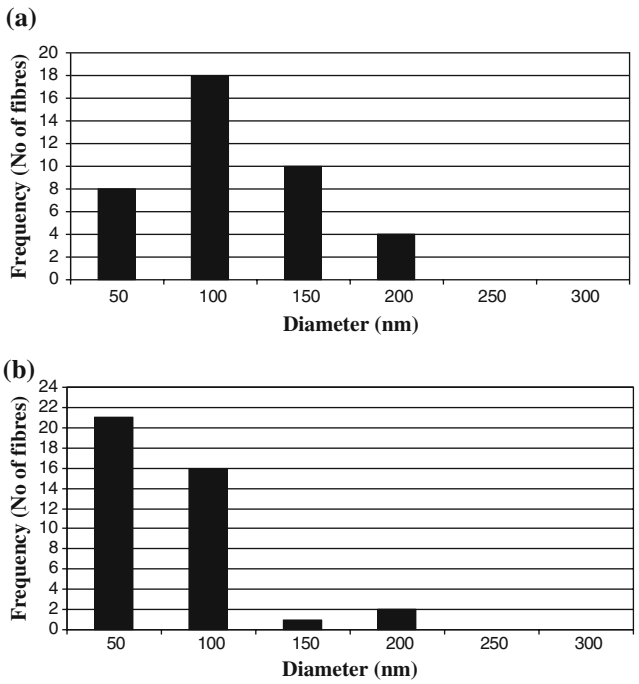

Fig. 3 Frequency distribution bar graphs of diameter range of nanofibres for two experiments **a** experiment #1, **b** experiment #2

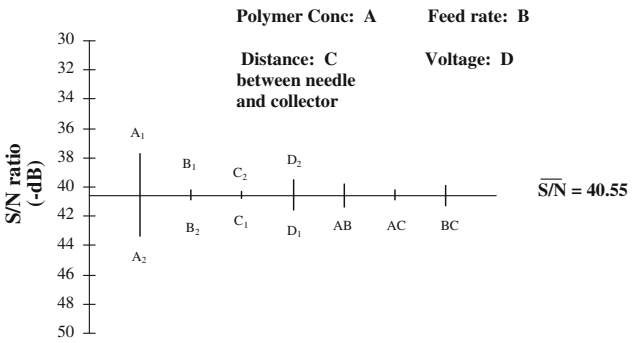

Fig. 4 Estimated factor effects for fibre diameter

has the maximum S/N value of −34.18 with the average nanofibril diameter of about 51 nm.

Figure 6, on the other hand, suggests that polymer concentration (factor A) is the most significant factor in controlling beads. In comparison, feed rate has a smaller but noticeable influence. It can also be suggested that factors C and D do not impact much in making beads if these are kept within the experimented range. However, the interaction between feed rate and needle-collector distance has a considerable influence on the average S/N response. Optimal combination for making minimum area occupied by beads (Fig. 7) turns out to be $A_2B_2C_2D_2$, which is experiment #8 in Table 3 with an S/N value of −37.86. The bead area calculated by using imagetool has been found to be 76.86 μm^2.

Analysis of variance

Table 4 lists the results of ANOVA by using Eq. 2 for fibre diameter. It can be said that the polymer concentration and applied voltage are the two significant electrospinning parameters that affect the fibre diameter, with contributions of 76.5 and 10.5%, respectively. The change of feed rate in the given range (Table 2) has no considerable effect on fibre diameter and has not shown any contribution from ANOVA analysis either. In Table 5, *F*-ratio and contribution (%) show that polymer concentration is the most dominating factor whose contribution goes up to 93% in making beads. In comparison, feed rate, applied voltage and distance between the needle tip and the collector have negligible contributions.

Discussion and validation

In this case study, both S/N ratio approach and ANOVA method draw similar conclusions. Polymer concentration contributes much in making fine fibre diameters. From Table 3, it is evident that in the first four experiments, S/N ratios for fibre diameter are higher as they have unchanged low polymer concentration. From experiments #2 and #3, it

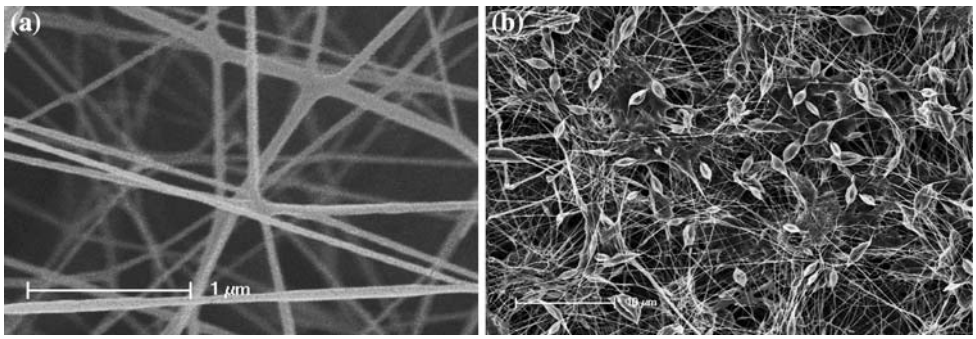

Fig. 5 SEM pictures of nanofibres from experiment #2: **a** nanofibres in higher magnification, **b** nanofibres with beads in lower magnification

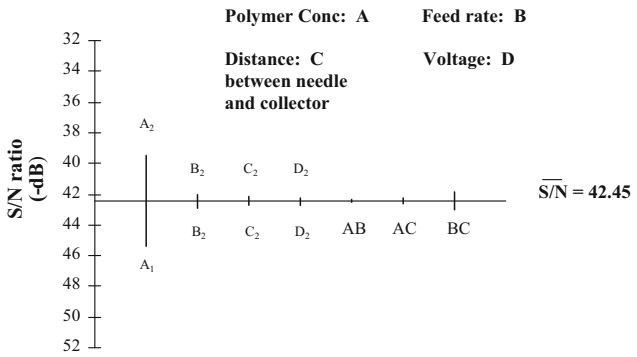

Fig. 6 Estimated factor effects for bead area

is clear that the S/N ratios are higher in comparison to those from experiments #1 and #4. This is due to level 2 of factor D, i.e. applied voltage of 10 kV. Always a higher electrical force makes a positive impact in providing extra stretch to elongate the fibre, thus producing reduced diameters. From both techniques of data analysis, it is clear that polymer concentration has an enormous influence on making bead-free nanofibre mats. An increase in the polymer concentration results in greater polymer chain entanglements within the solution, which is necessary to maintain the continuity of the jet during electrospinning. This polymer chain entanglement has been found to have a significant impact on whether the electrospinning jet breaks up into small droplets resulting in beads [20]. Other researchers [3, 4, 9] have suggested that for a given voltage, when feed rate is increased, there is a greater volume of solution that is drawn away from the needle tip. As a result, the solvent may not get sufficient time to dry and requires longer distance to evaporate the large quantity of solvent necessary for producing a considerable quantity of nanofibres. This is evident from the interaction effect of factors B and C, which is interestingly more than the individual effects of these two factors. According to Tan et al. [2], the morphology of the electrospun nanofibres is primarily affected by polymer concentration, its molecular weight and electrical conductivity of the solvent, followed by voltage and feed rate. The interaction effects between factors A and B and between A and C are also not that significant for bead area. Scanning micrographs of results from experiment #8 (Fig. 7) confirm nanofibres with the least number of beads although the diameters are found to be in the range of 100–200 nm (average $\sim$135 nm). This is obviously not very fine but shows less variation in diameters, which is still a very good result.

In order to determine the optimal conditions, and to compare the results with the expected performance, a set of 16 (2^4) confirmatory experiments, using full statistical analysis, were also performed. Taguchi analysis gives the best result for experiment #8 with the parametric combination of $A_2B_2C_2D_2$, keeping all the factors at high levels. However, in the full statistical analysis, experiment #12 (Table 6 in Appendix) with a parameter combination of $A_2B_1C_2D_2$ gives the superior results. It makes nanofibres almost bead-free (Fig. 8b), with fibrils looking almost uniform and diameters in the range of 325–425 nm (Fig. 8a). The bead area becomes 26.11 μm^2, with the maximum S/N

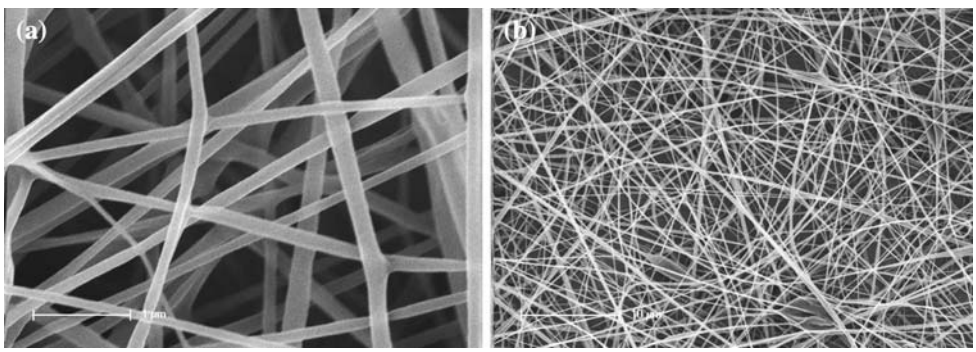

Fig. 7 SEM pictures of nanofibres of experiment #8: **a** nanofibres in higher magnification, **b** nanofibres with beads in lower magnification

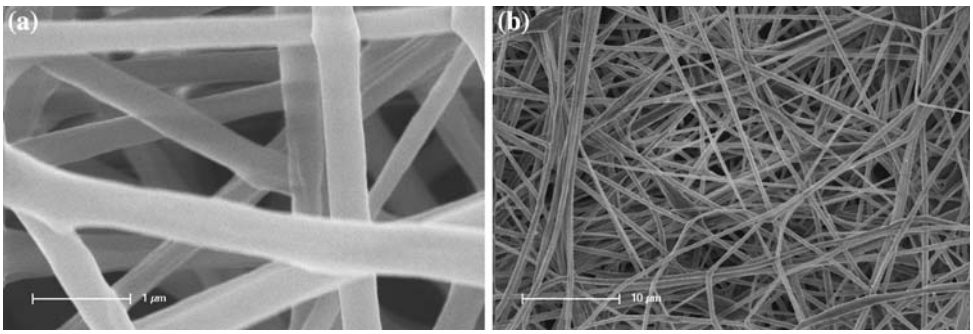

Fig. 8 SEM pictures of nanofibres from experiment #12: **a** nanofibres in higher magnification, **b** nanofibres with beads in lower magnification

value of −34.56. This can be treated as the best quality in the entire study because although this parametric combination makes relatively coarse fibres, the bead-free mat of uniform fibres could be very useful for biomedical or biotechnological purposes. These results are in agreement with those of Zong et al. [3] who have shown that a low solution feed rate, higher concentration and charge density of the solution create better conditions for minimum bead formation. However, it is worth mentioning here that this parameter combination $A_2B_1C_2D_2$ was not included in Taguchi's 8-run scheme although the result from the combination $A_2B_2C_2D_2$ was very close. Therefore, the decision on whether to use full statistical analysis or Taguchi's design of experiments should depend on the number of parameters, their levels and the availability of time and resources.

Conclusions

This paper has presented an application of Taguchi method for selecting the desirable process parameters in electrospinning operation of polylactic acid. The following conclusions can be made from the study:

(1) Taguchi's OA provides a simple, systematic and efficient methodology for finding a set of suitable spinning parameters. Although a full statistical analysis might produce a slightly different set of parameters with marginally improved results, Taguchi provides the advantage of saving time and avoiding too much tediousness.

(2) S/N ratio and ANOVA approaches have converged on the same type of parametric selection. Concentration of polymer solution plays a major role in making the fineness of the nanofibril, but when the beads are concerned, it influences in a reverse way. The ANOVA results indicate that polymer concentration contribute 93% in making beads. A lower polymer concentration with a low feed rate and relatively high voltage and distance between the needle tip and the collector appear to produce bead-like textures with fine fibres.

Acknowledgements The authors wish to acknowledge the financial support of the Foundation for Research, Science and Technology New Zealand. They would also like to acknowledge the experimental help received from Messrs Rex Halliwell, Callum Turnbull and Stephen Cawley.

Appendix

Table 6 Experimental results and S/N ratios for fibre diameters with replications

Experiment number	Factors				Results/replication					Average	S/N ratios
	A	B	C	D	Y1	Y2	Y3	Y4	Y5		
1	1	1	1	1	98.10	90.01	85.92	76.97	90.55	88.31	38.9466
2	1	1	1	2	56.52	51.07	54.31	46.17	47.04	56.07	35.0003
3	1	1	2	1	68.46	71.35	67.32	79	76.8	72.59	37.2344
4	1	1	2	2	48.66	58.12	60.40	59.40	53.76	51.02	34.1819
5	1	2	1	1	55.29	87.82	65.17	63.66	66.67	67.72	36.7236
6	1	2	1	2	98.83	75.13	80.73	67.76	52.93	75.08	37.6823
7	1	2	2	1	120.29	119.14	104.19	86.28	60.81	98.14	40.0571
8	1	2	2	2	73.43	58.15	65.52	54.74	56.36	61.64	35.8522

Table 6 continued

Experiment number	Factors				Results/replication					Average	S/N ratios
	A	B	C	D	Y1	Y2	Y3	Y4	Y5		
9	2	1	1	1	166.7	142.24	132.44	185.49	141.57	153.69	43.8025
10	2	1	1	2	135.76	159.31	144.33	152.62	138.11	146.03	43.3045
11	2	1	2	1	133.18	143.54	208.06	179.87	148.68	162.67	44.3485
12	2	1	2	2	366.95	362	328.81	437.64	434.68	386.02	51.7857
13	2	2	1	1	143.38	151.12	153.23	155.46	117.6	144.16	43.2169
14	2	2	1	2	277.44	252.32	260.47	231.37	232.08	250.74	48.0055
15	2	2	2	1	175.02	151.27	131.32	173.74	121.56	150.58	43.6445
16	2	2	2	2	135.29	108.67	147.67	153.67	129.95	135.06	42.668

References

1. Hou H, Jun Z, Reuning A, Schaper A, Wendorff JH, Greiner A (2002) Macromolecules 35:2429
2. Tan SH, Inai R, Kotaki M, Ramakrishna S (2005) Polymer 46:6128
3. Zong X, Kim K, Fang D, Ran S, Hsiao BS, Chu B (2002) Polymer 43:4403
4. Deitzel JM, Kleinmeyer J, Harris D, Beck Tan NC (2001) Polymer 42:261
5. Lee YH, Lee JH, An IG, Kim C, Lee DS, Lee YK, Nam JD (2005) Biomaterials 26:3165
6. Park JH, Park TG, Park HS, Lee DS, Lee YK, Yoon SC, Nam JD (2003) Biomaterials 24:2773
7. Nam YS, Park TG (1999) J Biomed Mater Res 47:8
8. Reneker DH, Chun I (1996) Nanotechnology 7:216
9. Frenot A, Chronakis IS (2003) Curr Opin Colloid Interface Sci 8:64
10. Formhals A (1934) US Patent 1975:504
11. Demir MM, Yilgor I, Yilgor E, Erman B (2002) Polymer 43:3303
12. Park SH (1996) Robust design and analysis for quality engineering. Chapman & Hall, London, UK
13. Roy VK, Nutek, Inc. http://www.vkroy.com/up-doe.html
14. Lochner RH, Matar JE (1990) Designing for quality: an introduction to the best of Taguchi and western methods of statistical experimental design. Quality Resources, New York
15. Phadke MS (1989) Quality engineering using robust design. Prentice Hall, Englewood Cliffs, NJ
16. Ross PJ (1996) Taguchi techniques for quality engineering. McGraw-Hill, New York
17. Fisher RA (1925) Statistical methods for research worker. Oliver & Boyd, London, UK
18. Nalbant M, Gokkaya H, Sur G (2007) Mater Des 28:1379
19. Inai R, Kotaki M, Ramakrishna S (2005) Nanotechnology 16:208
20. Ramakrishna S, Fujihara K, Teo WE, Lim TC, Ma Z (2005) Introduction to electrospinning and nanofibers. World Scientific Publishing Co. Pte Ltd, Singapore
21. Ghani JA, Choudhury IA, Hassan HH (2004) J Mater Process Technol 145:84