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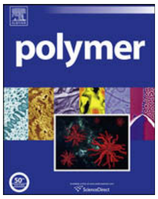

Effect of the addition of a fugitive salt on electrospinnability of poly(ε-caprolactone)

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ABSTRACT

Described in this paper is a novel study focused on producing bead-free ultrafine fibers, with narrow fiber diameter distribution, from Poly(ε-caprolactone) (PCL) via electrospinning. High quality product is achieved with the use of a new solvent system that involves an acid–base reaction to produce weak salt complexes, which serve to increase the conductivity of the polymer solution. Additionally, the salt formed dissociates easily and evaporates along with the solvent during the spinning process because its respective acid–base components are volatile at room temperature. This results into the formation of pure PCL nanofibers of ultrafine dimensions. Glacial acetic acid was used as the solvent for the polymer and the organic base pyridine was used to initiate the formation of salt complexes in the solution. Pyridine was added at six different levels to vary the conductivity and examine the latter's effect on fiber morphology. Along with the pyridine content, the polymer concentration was also varied to determine how the two interacted in influencing the size of the fiber and the quality of the structure obtained. It was found that bead-free fibers of sizes lying well within the nano range (140–340 nm) could be produced using the conducting solvent system. Two interesting effects were noted. For a given polymer concentration, the mean fiber diameter increased with increase in pyridine amount. And, lower the polymer concentration, higher was the amount of pyridine required to produce bead-free nanofibers. The combination of these effects along with the fact that the reproducibility of the results was high provided a means of producing fibers with predictable sizes.

1. Introduction

The suitability of using electrospun Poly(ε-caprolactone) (PCL) fibers as desirable scaffolds for tissue engineering has been reported in numerous studies [1–8]. The primary reasons for the wide acceptance of PCL in tissue engineering are its biocompatibility, non-toxicity, good mechanical properties, slow biodegradation rate conducive to supporting cell growth over longer period, and low cost.

In order to simulate physically, the extra cellular matrix (ECM) morphology, it is essential that the dimensions of the fibers match those of the elements of the latter. The diameters of the fibrils present in the ECM range from 50 to 500 nm [9]. This means that electrospinning of PCL for tissue engineering should result in fiber sizes falling in this range. Additionally, it has been shown recently that the smaller the average fiber diameter the better is the cell adhesion and proliferation onto the scaffold [10]. This is due to the increased specific surface area which results into more protein adsorption and hence more focal adhesion points for the cell attachment [10]. Many studies on electrospinning of PCL in the past, however, have failed to obtain bead-free fibers with diameters lying in the nano range [1–8,11–15].

In this study, we describe a method to improve the electrospinnability of PCL to produce uniform ultra fine nanofibers with narrow fiber diameter distribution. This is achieved by using a new solvent system that increases the conductivity of the solution, which has been shown to greatly affect the fiber morphology in electrospinning [16–19].

Literature shows that the conductivity of a polymeric solution can be enhanced by adding various compounds. These include organic salts, polyelectrolytes, and surfactants such as triethylbenzyl ammonium chloride (TEBAC) [20,21], hexamethylimidazolium chloride (HMIMCl) [20,21] and pyridinium formiate (PF) [22,23], polyallylamine hydrochloride (PAH) [24], polyacrylic acid sodium salt (PAA) [24], and inorganic salts such as NaCl [16,25–28], KH_2PO_4 [18], NaH_2PO_4 [18], $CaCl_2$ [26–28], $NaNO_3$ [27], LiCl [27,28], KCl [20,28] and $MgCl_2$ [28]. Although the use of such compounds result in smaller diameter fibers in electrospinning, many of these additives tend to remain in the final fibers, which in general will be undesirable for biomedical applications such as tissue engineering and drug

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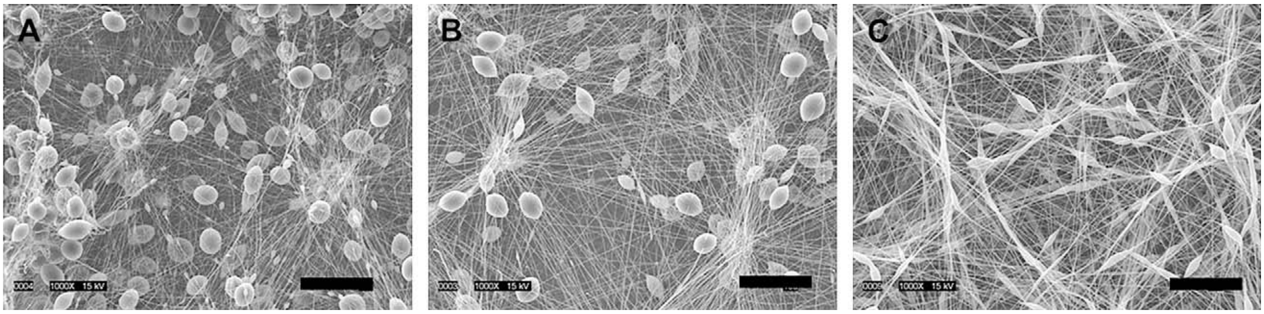

Fig. 1. SEM pictures depicting the effect of the solution concentration on the morphology of fibers electrospun from 15% (A), 17.5% (B), and 20% (C) PCL solutions in glacial acetic acid. (Magnification bar = 25 μm).

delivery. To cope up with this problem, our proposed solution for increasing the conductivity of a polymer solution is to use a fugitive salt that evaporates along with the solvent during electrospinning. Pyridine, an organic base compound, was used as an additive to accomplish this goal. When added to a PCL solution prepared with glacial acetic acid, pyridine is protonated and forms pyridinium acetate that evaporates during the electrospinning process. This results in pure polymeric nanofibers of smaller dimensions and superior uniformity than possible otherwise.

2. Materials and methods

2.1. Materials

Polycaprolactone (PCL) with a weight average molecular weight of 80,000 was obtained from Sigma–Aldrich, USA. ACS reagent grade glacial acetic acid (purity >99.7%) from Fisher Scientific, was used as the solvent for PCL. Pyridine, ACS reagent grade (purity >99.0%), obtained from Sigma–Aldrich, USA, was added in different amounts to the solution to increase the conductivity.

2.2. Methods

Solutions of PCL were prepared by dissolving the polymer in glacial acetic acid in five different concentrations: 10, 12.5, 15, 17.5, and 20% (wt/vol). The solutions were stirred gently overnight at 35 °C. In order to vary solution conductivity over a significantly wide range, pyridine was added to the solvent at six different levels: 0.1, 0.2, 0.5, 1, 2 and 5% (vol/vol).

A conventional electrospinning set up was used in the experiments. The solution was kept in a 5 ml plastic syringe (Becton-Dickinson, Research Triangle Park, NC) with a metal capillary needle (27 Gauge, 0.2 mm ID, 0.4 mm OD, 50 mm length, McMaster-Carr, Atlanta, GA). The flow rate of the solution was maintained constant at 300 μl/h using a syringe pump (NE-500, New Era Pump Systems, Inc., Farmingdale, NY). An aluminum plate of 15 cm diameter was used as the collector. A high voltage power supply (ES-30P, Gamma High Voltage Research, Ormond Beach, FL) was connected between the metal capillary and the collector plate. The distance between the end of capillary and the point of collection was kept constant at 15 cm. The electric field strength of 0.33 kV/cm was used in the trials in which pyridine was not used. This value of field strength was found adequate in overcoming the surface tension of the solution and generating a stable Taylor cone. On the other hand, when pyridine was added, the electric field strength required was higher, i.e. about 0.67 kV/cm. This value was maintained constant in all spinning experiments in which pyridine was used.

Table 1
Conductivity (in μS/cm) of acetic acid and PCL solution in acetic acid (12.5% (wt/vol)) with different amounts of pyridine added.

Pyridine concentration (%) (vol/vol)	Conductivity (μS/cm)
0	0.1
0.5	18
2	160
5	1368

The conductivity of the solutions was measured using Orion 162 Conductivity Benchtop Meter (Thermo Electron Corporation, Waltham, MA). The values reported are in μS/cm. The StressTech HR (ATS RheoSystems, Bordentown, NJ), a stress controlled rheometer, was used to measure the zero-shear rate viscosity (η_0). A 45 mm parallel plate and a stress sweep were used to collect the viscosity data. In the experiments, the gap used was 0.300 mm and the temperature used was 25 °C ± 0.1 °C. Surface Tensiometer 20 (Fisher Scientific, Pittsburgh, PA) was used to perform surface tension measurements of the solution.

To detect the presence of any residual solvent and pyridine in the final fibers, Fourier Transform Infrared Spectroscopy (FTIR) tests were conducted using Nicolet Nexus 470 Spectrophotometer with AVATAR Omni Sampler for Attenuated Total Reflectance (ATR) mode. The spectra of the PCL nanofibers, electrospun with and without pyridine, were compared. As a complimentary technique, CHN elemental analyzer (Perkin Elmer® 2400) was used to determine if any pyridinium acetate residue remained in the polymer after the evaporation of the solvent. This was accomplished by measuring the amount of nitrogen present in the sample, as that would confirm the presence of the salt. PCL films cast from 15% solution and 0, 0.5,1, 2 and 5% pyridine were used for this purpose. One sample per pyridine concentration was used for this analysis.

For examining the fiber morphology, all samples were sputter coated with Au–Pd (Anatech Hummer 6.2) and examined under SEM (JEOL JSM- 5900 LV). Fiber diameter and its distribution were

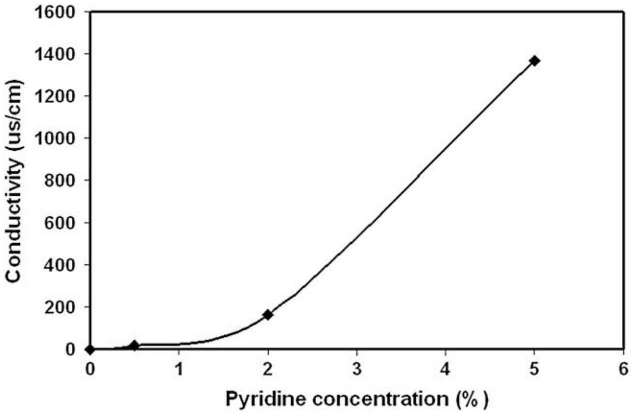

Fig. 2. Conductivity of polymer solution containing pyridine (12.5% PCL solution).

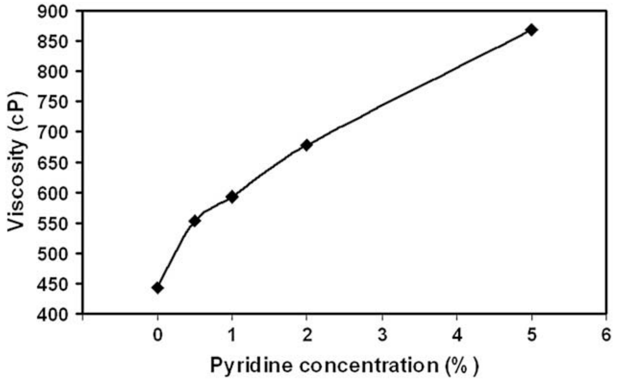

Fig. 3. Viscosity of polymer solution containing pyridine (12.5% PCL solution).

assessed using the image analysis software (Image J) developed by NIH. The analysis of variance (ANOVA) was used to identify significant factors controlling fiber diameter and the regression analysis was performed to generate predictive models.

3. Results

3.1. Effect of using pure solvent on morphology

In the first set of experiments, the concentration of PCL in pure glacial acetic acid was varied from 15 to 20%. PCL formed a clear solution with acetic acid, suggesting that the latter was a good solvent for the polymer. Electrospinning of these solutions, under identical conditions, described above, resulted in different fiber web morphologies (Fig. 1). At 15% concentration, mostly beads were noted. An increase in concentration to 17.5% gave a decrease in the number of beads as more and more of these appeared to have been drawn into fibers. At 20% concentration, a mixture of elongated beads, microfibers and nanofibers was obtained. If the concentration was increased beyond 20%, the high viscosity rendered the solution non-electrospinnable as, frequently, a discontinuous jet formed and the needle clogged.

3.2. Influence of addition of pyridine on the properties of polymer solution

Polymer solution containing different amounts of pyridine were tested for conductivity, viscosity and surface tension, as these solution properties were known to influence the processability of the solution.

The results given in Table 1 show that the addition of even a small amount of pyridine greatly increased the conductivity of the solution. This increase with pyridine was non-linear as seen in Fig. 2. The viscosity, on the other hand, after the first jump at 0.5% concentration, increased linearly with pyridine concentration (Fig. 3). The initial jump is thought to be due to the formation of large ionic complexes between the pyridine and acetic acid molecules and the increase thereafter due to the increase in the number of complexes formed in proportion to the pyridine amount. Addition of 0.5% pyridine to the solution gave an increase in the surface tension from 34 dynes/cm to 36 dynes/cm (Fig. 4). However, any further increase in the pyridine amount (up to even as large as 5%) did not show any significant effect on the property.

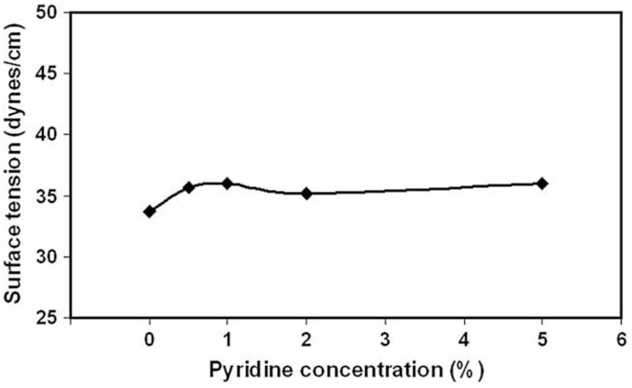

Fig. 4. Surface tension of polymer solution containing pyridine (12.5% PCL solution).

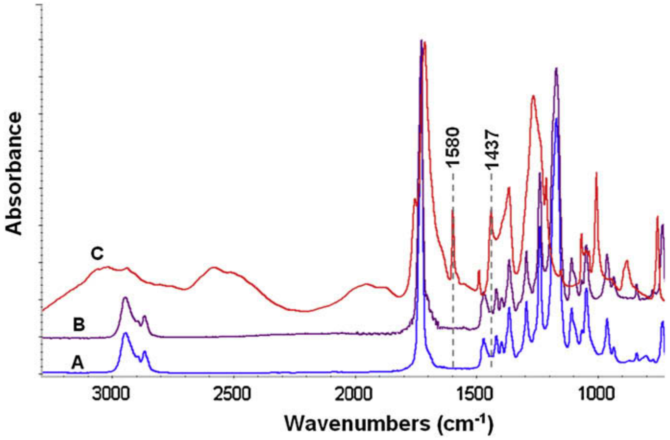

Fig. 5. Overlapped FTIR spectra of pure PCL (A) PCL nanofibers prepared using acetic acid as a solvent with 5% pyridine (B), and pyridinium acetate (C). Two wavenumbers (1580 and 1437 cm^{-1}) of interest are indicated for comparison purposes.

3.3. Fugitive nature of the salt and the solvent

Fig. 5 shows the overlapped FTIR spectra for pure PCL (A), electrospun PCL fibers (B) spun by adding 5% pyridine in acetic acid, and pyridinium acetate (C). Pyridinium acetate has two characteristic peaks at 1437 cm^{-1} and 1580 cm^{-1} representing, respectively, the C–N and C–C stretching vibrations in the plane of the pyridine ring [29]. The spectrum of electrospun PCL does not show any peaks at these frequencies (see Fig. 5). This suggests that no residual pyridinium salt was present in the fibers.

The amounts of nitrogen present in the PCL films were also measured using a highly sensitive CHN element analyzer. Since the only source of nitrogen was from pyridine molecule in the salt formed, the presence of the element would have shown the presence of the salt residue in the sample. Table 2 shows that a small amount of nitrogen was present in all samples, including control. However, the values did not show any correlation, whatsoever, with respect to the amount of pyridine added in the solvent, indicating that perhaps the small amount of nitrogen present was due to contaminants or from the air. Therefore, within the limits of these characterization techniques, it can be inferred that there was no residue of the pyridinium acetate present in the PCL fibers or films.

Table 2
Assessment of amount of nitrogen in PCL films using CHN elemental analyzer (15% PCL solution).

Sample ID	Solvent	% Nitrogen
Control	Glacial acetic acid (no pyridine)	0.03
PCL-0.5	Glacial acetic acid + 0.5% pyridine	0.08
PCL-1	Glacial acetic acid + 1% pyridine	0.12
PCL-2	Glacial acetic acid + 5% pyridine	0.10
PCL-5	Glacial acetic acid + 2% pyridine	0.08

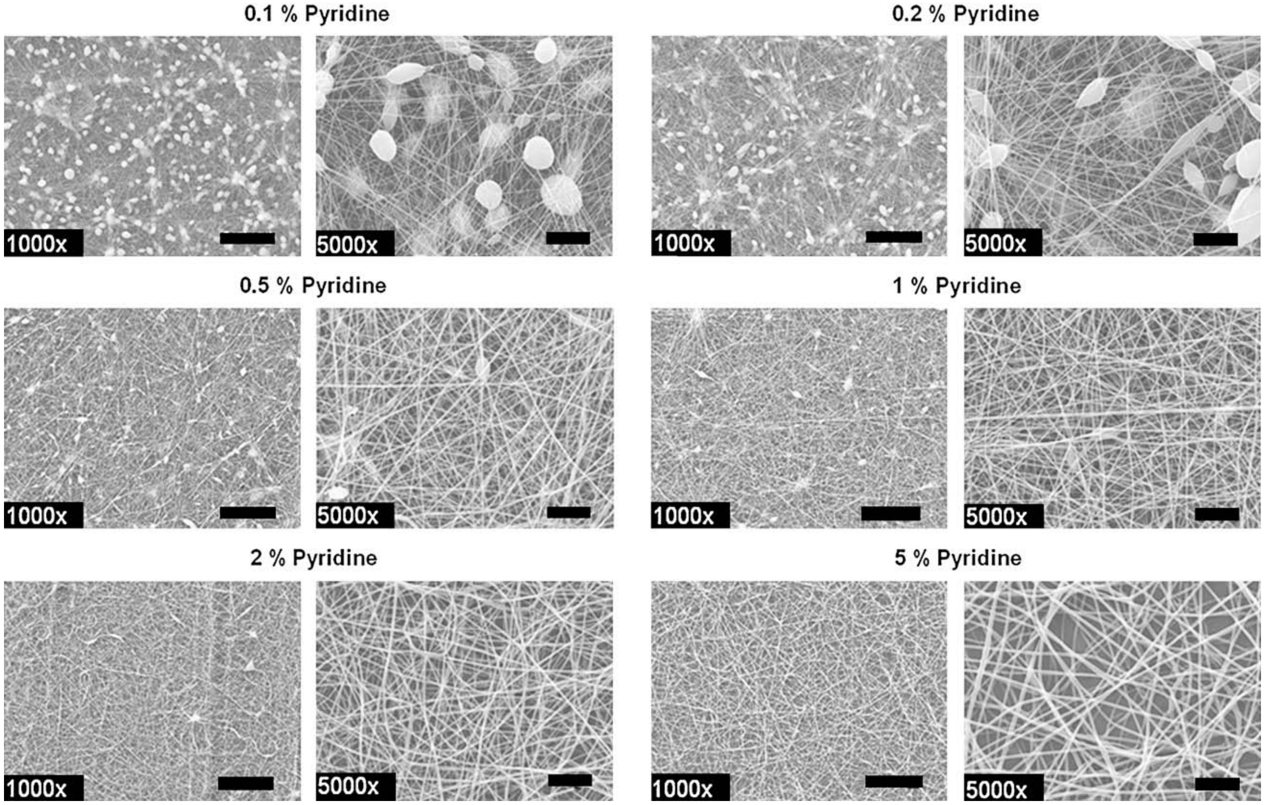

Fig. 6. Progression from beaded fibers to nanofibers with increasing pyridine concentration–10% PCL concentration (Magnification bar-25 μm for 1000× and 5 μm for 5000×).

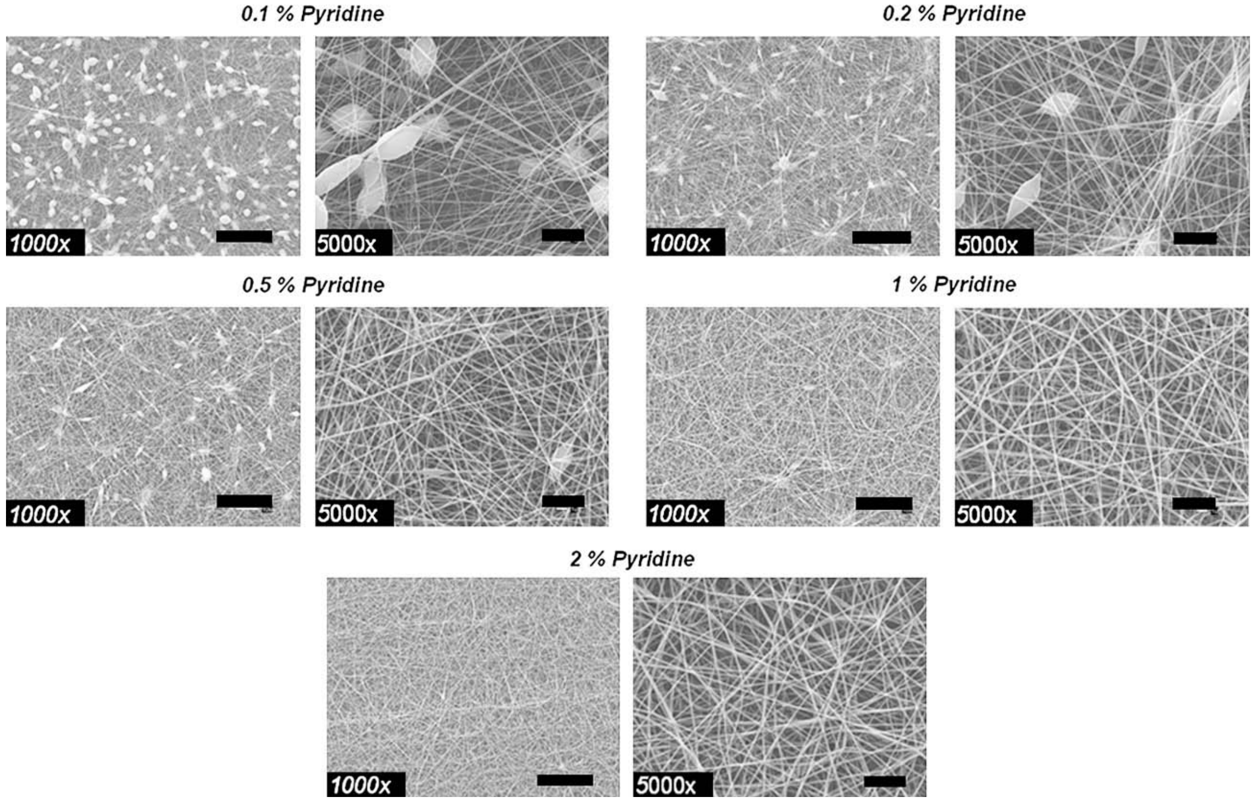

Fig. 7. Progression from beaded fibers to nanofibers with increasing pyridine concentration–12.5% PCL concentration. (Magnification bar-25 μm for 1000× and 5 μm for 5000×).

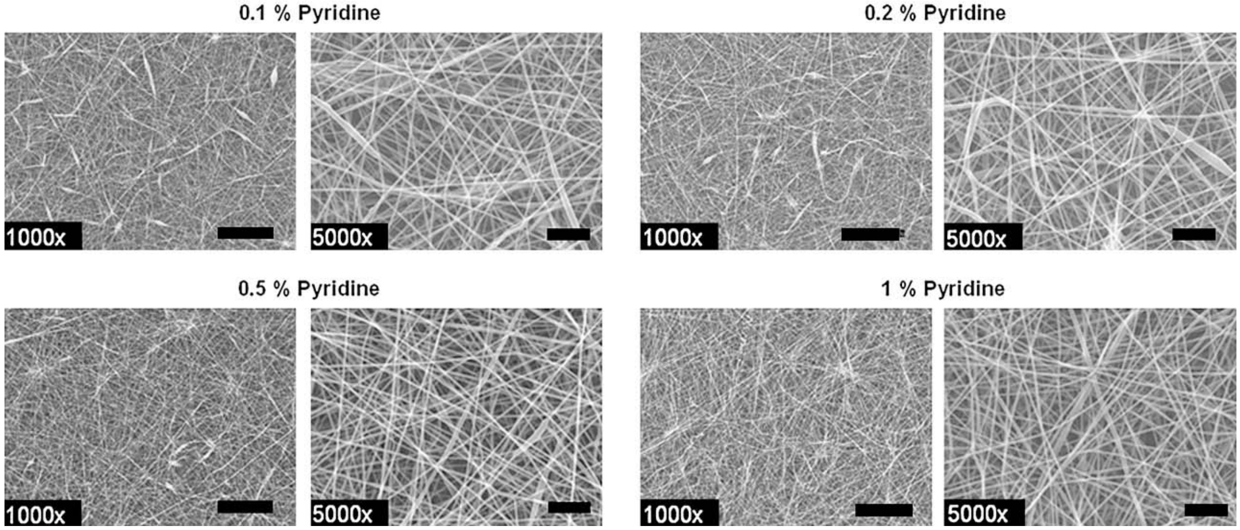

Fig. 8. Progression from beaded fibers to nanofibers with increasing pyridine concentration–15% PCL concentration. (Magnification bar-25 μm for 1000× and 5 μm for 5000×).

3.4. *Effect of pyridine on the morphology of electrospun webs*

Figs. 6–9 show the effect of adding different amounts of pyridine on the morphology of fibers electrospun using four different polymer concentrations. Two observations are made. Firstly, the addition of pyridine improved the quality of PCL fibers produced in electrospinning, by effectively suppressing bead formation to lead to finer sized uniform fibers. Secondly, and interestingly, for optimum results, the lower the PCL concentration, the higher the amount of pyridine needed. For example, to achieve bead-free nanosize fibers, 10% PCL solution required in excess of 2% pyridine, where as 17.5% PCL solution required less than 0.2% pyridine.

3.5. *Influence of pyridine addition on the fiber diameter*

The fiber diameters and the standard deviations obtained with various polymer and pyridine concentrations are listed in Table 3 and illustrated in Fig. 10. The italicized and bolded region in Table 3 indicates the results for the completely bead-free fibers. The values in this region show that, except for two cases, the fibers produced are of nanosize (<500 nm). This is in contrast to the results usually found in the electrospinning of PCL wherein the fiber diameters obtained are of sub-micron or micro size (>500 nm) [1–8,11–15]. It is clear from Fig. 10 that after the suppression of beads, the mean fiber diameter increased with pyridine amount for all polymer concentrations. The rate at which the diameter increased also increased with the polymer concentration. These results suggest that there exists a strong interaction between the effects of pyridine amount and the polymer concentration on fiber diameter, the possible reasons for which are given in Section 4.

The diameter values, obtained within the limitations of the experiments conducted (tests at 3 and 4% concentrations were not performed), were subjected to statistical analysis of variance (ANOVA) involved in the linear regression procedure. This was done to identify significant effects and to generate a predictive model. In this exercise, the diameter values of only the bead-free samples were included (values from the italicized and bolded region in Table 3). Table 4 shows the effects of pyridine amount, polymer concentration and the interaction between the two on fiber diameter. In the model, the square term of each of the parameters was also included in order to account for the presence of any non-linear effects. For the limited range of polymer concentrations used, effects of pyridine amount and polymer concentration on mean fiber diameter are positive at the 95% confidence level. The only insignificant term noted is the polymer concentration (C) square term, which was, nevertheless, retained in the model as its interaction with the square term of pyridine concentration (Py) was significant. Fig. 11 gives a comparison between the measured and predicted values of fiber diameters, which shows an excellent correlation.

The regression model obtained, with an R^2 value of 0.99, is as follows:

$$\begin{aligned}\text{Fiber diameter(nm)} = {} & 10.076 + (177.992{*}\text{Py}) - (23.625{*}\text{Py}^2) \\ & + (5.404{*}\text{C}) + (0.385{*}\text{C}^2) - (14.204 \\ & {*}\text{Py}{*}\text{C}) + (0.203{*}\text{Py}^2{*}\text{C}^2)\end{aligned}$$

This analysis, although somewhat limited in terms of the completeness of the data, mentioned earlier, shows that it should be possible to select conditions for producing electrospun nanofiber

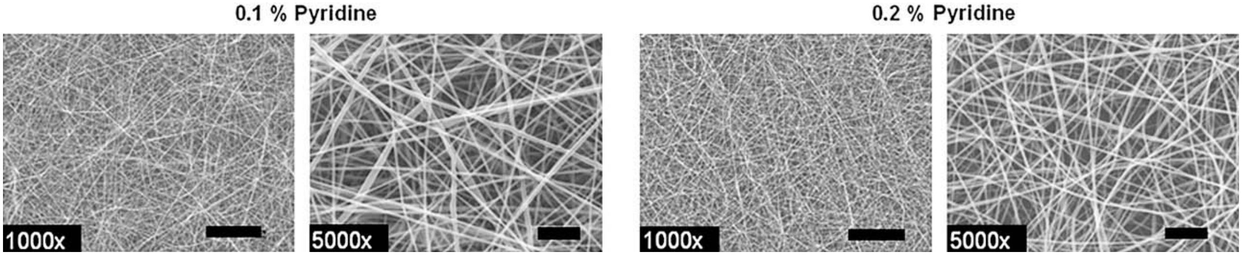

Fig. 9. Effect of pyridine concentration on the fiber morphology (17.5% PCL conc.) (Magnification bar-25 μm for 1000× and 5 μm for 5000×).

Table 3
Effect of pyridine amount on average fiber diameter and its distribution.

Polymer concentration (wt/vol)	Pyridine concentration (vol/vol)					
	0.1%	0.2%	0.5%	1%	2%	5%
10%	Mostly beads	Mostly beads	99 ± 21 (Few beads)	108 ± 17 (Few beads)	***141 ± 28***	***220 ± 31***
12.5%	Mostly beads	135 ± 22 (Few beads)	137 ± 20 (Few beads)	***155 ± 27***	***163 ± 30***	***338 ± 58***
15%	177 ± 32 (Few elongated beads)	179 ± 39 (Few elongated beads)	***171 ± 28***	***186 ± 32***	***213 ± 48***	***512 ± 88***
17.5%	215 ± 58 (Occasional elongated beads and thick fibers)	***188 ± 40***	***205 ± 50***	***186 ± 37***	***228 ± 57***	***857 ± 142***

structures from PCL that have the desired fiber size for a given application.

4. Discussion

Two instabilities, acting on the polymer solution jet, govern the electrospinning process: axisymmetric varicose instability (Rayleigh instability) and non-axisymmetric whipping instability [30–33]. The former results from the surface tension of the solution which tends to minimize the surface area by forming individual droplets, and the latter is produced by the electrostatic field, which causes bending and stretching of the jet through a rapidly spiraling motion. Which of these instabilities dominates depends on the factors related to solution properties and operating conditions: solution viscosity, conductivity, surface tension, and the strength of the applied electrostatic field.

The solution viscosity is controlled by the molecular weight and the solution concentration or, more fundamentally, by the extent of polymer chain entanglements [34,35] (see Fig. 12). If the density of chain entanglements in a given solution is appreciably less than a critical value, the jet formed breaks up into droplets, due to the set in off Rayleigh instability, and leads to beaded fibers. As seen in Fig. 12, after the on-set of chain entanglements, the viscosity curve takes on an upward turn [35,36]. Beyond this point fiber formation occurs. Homogenous fibers are, however, only formed after a critical chain entanglement density is achieved. In this region, the high resistance offered by the chain overlap to the jet break up suppresses the Rayleigh instability.

For a given molecular weight, chain entanglements increase with polymer concentration. With increase in the latter, therefore, the following progression in morphology can be expected: beads only (electrospraying), beads with incipient fibers, beaded fibers, nanofibers, and globular fibers or macrobeads [18,35,37]. The last result is due to the entanglements being so high that in some regions chains are not able to slip adequately apart to form uniform fibers.

Table 4
Factors affecting the mean fiber diameter as obtained with ANOVA.

Factors	*F* value	*p* value
Pyridine amount (Py)	340.39	<0.0001
Polymer concentration (*C*)	183.65	<0.0001
Py^2	38.47	0.0004
C^2	0.37	0.5630
$Py^{*}C$	155.11	<0.0001
$Py^{2*}C^2$	7.53	0.0288

The second key parameter that affects the morphology of the fibers is the solution conductivity [16,19]. Fluids with high conductivity have high surface charge density. Under a given electric field, this results in an increase in the elongational force on the jet, which is caused by the self-repulsion of the excess charges on the surface. This inhibits the Rayleigh instability, enhances whipping and leads to finer fibers [33]. It has been shown that, for given material and processing parameters, the relative dominance of the two instabilities is a function of the surface charge density [33,38] and, therefore, lack of the latter can result into beaded fiber morphology [16].

In this work, glacial acetic acid was used as a solvent for PCL. In the initial trials using this solvent a wide range of polymer concentrations was used. However, by varying the polymer concentration alone, uniform fibers could not be obtained (see Fig. 1). Therefore, this phenomenon was considered to be due to the lack of conductivity of the solution, as glacial acetic acid (Dielectric constant: 6.2 at 20 °C) and PCL are both poorly conductive.

Therefore, in an effort to enhance the conductivity of the PCL–acetic acid solutions, we used an organic base 'pyridine' as an additive. Pyridine is a clear liquid that is protonated by reaction with acids. The ring structure of pyridine has nitrogen with a pair of non-bonding electrons. Therefore pyridine is a Bronsted type base. It accepts a proton from an acid, thus forming a positively charged aromatic polyatomic ion called pyridinium cation in a reversible

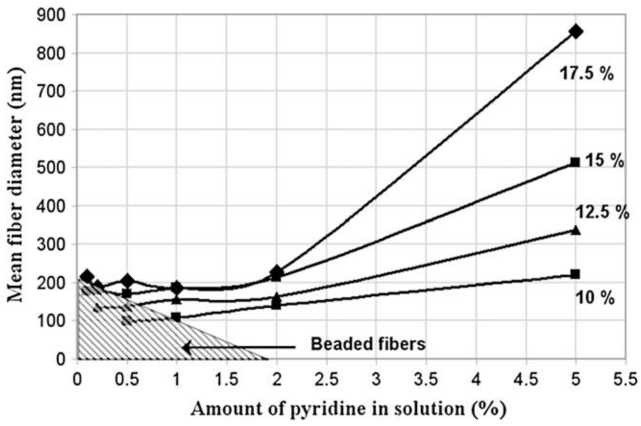

Fig. 10. Effect of the amount of pyridine in the solution on the mean fiber diameter.

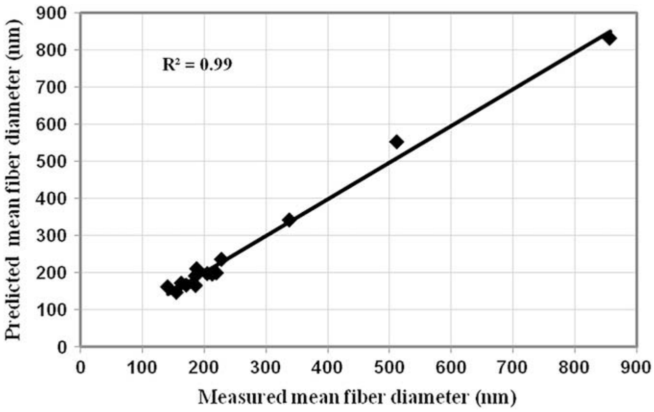

Fig. 11. Correlation between the measured and predicted values of the mean fiber diameter.

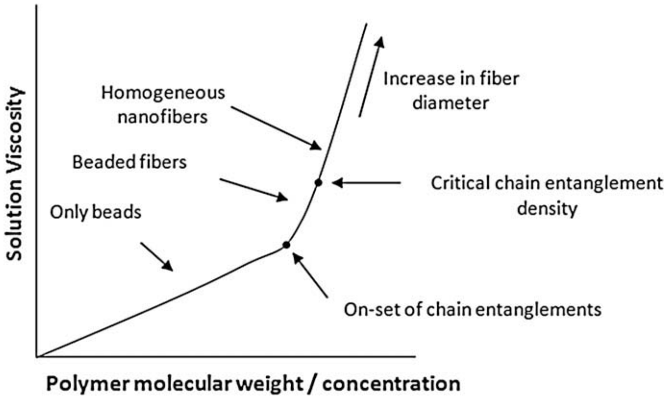

Fig. 12. Illustration of dependence of fiber morphology on the extent of chain entanglements.

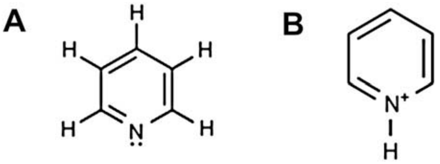

Fig. 13. Chemical structure of pyridine (A), and the pyridinium cation (B) that forms by reaction with acids.

reaction (Fig. 13). This increases the conductivity of the solution (see Table 1 and Fig. 2).

Per this mechanism, pyridine forms 'pyridinium acetate' by reacting with acetic acid. The salt pyridinium acetate easily disassociates, as its respective components are volatile at room temperature. The advantage of using this approach is that the salt vaporizes off together with the solvent during the electrospinning process [24,39] and offers a structure composed of pure polymer. The evaporation of the salt pyridinium acetate was confirmed using the infrared spectroscopy (FTIR) (see Fig. 5) and the CHN elemental analyzer (see Table 2), as described in Section 3.3.

It is clear from Figs. 6–9 that the addition of pyridine improved the quality of the PCL fibers produced in electrospinning; the tendency of the bead formation was suppressed and the fibers produced were of nanosize. Additionally, we found that the lower the PCL concentration in the solution, the higher the amount of pyridine needed in order to obtain bead-free fine fibers. For example, 10% PCL solution required in excess of 2% pyridine, whereas 17.5% PCL solution required less than 0.2% pyridine to lead to bead-free fibers. This second observation reflects that the requirement of high charge density decreases with increase in polymer concentration. It is suggested that this is due to an increase in viscosity with increase in polymer concentration (higher polymer chain entanglement density). The increased cohesiveness among the polymer chains further acts against the surface tension and dampens the Rayleigh instability.

The third important observation made was the effect of pyridine addition on the solution viscosity. The viscosity of the polymer solution, for any given PCL concentration, increased linearly with the increase in pyridine amount (see Fig. 3). This is primarily due to the presence of more salt complexes between acetic acid and pyridine molecules that involve ring structures of pyridine. This amplifies the flow resistance of the solution and hence increases the viscosity.

The continued increase in the conductivity and the viscosity initially results in an effective suppression of beads. However, after the formation of homogenous fibers, the increase in the fiber diameter could only be attributed to the relative dominance of the effect of viscosity. It has been shown in the literature that higher solution viscosity leads to higher visco-elastic force acting on the jet. This counteracts the fiber stretching Coulombic force generated by the applied electric field and leads to an increase in fiber diameter [35,40–43] (see Fig. 12). Also, an increase in solution viscosity causes an increase in the bending rigidity of the jet. This further limits the extent of the spiraling motion during whipping and reduces the drawing of the jet causing the diameter to be larger [33,44,45]. Therefore, it is noted that the fiber diameter remained relatively unaffected with increase in conductivity up to a certain value (Fig. 10); after this, the increase in viscosity produced a predominant effect and caused the mean fiber diameter to increase. A consistent increase in the fiber diameter with increase in pyridine concentration beyond about 1% (especially for 15 and 17.5% PCL concentrations) could be attributed to an increase in visco-elastic force resulting from an increase in chain entanglements.

5. Summary and conclusions

In this work, a study was conducted to improve the electrospinnability of PCL in order to produce bead-free uniform ultrafine diameter fibers with narrow fiber diameter distribution. This was achieved by increasing the conductivity of the PCL solution in acetic acid. Addition of pyridine in the acetic acid produced a volatile salt in the solvent that increased the ionic concentration of the solution and, consequently, the surface charge density required for enhanced whipping action during electrospinning. Additionally, the salt being volatile ensured that pure polymeric fibers were formed.

This work has served two important purposes. It has demonstrated that uniform and ultrafine or nano diameter fibers can be produced from PCL using a new solvent system involving acid–base reaction. It has also shown reasonably well that, by using various combinations of polymer concentration and pyridine amount, it should be possible to engineer structures with desired fiber diameters for different applications.

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References

[1] Fujihara K, Kotaki M, Ramakrishna S. Biomaterials 2005;26:4139–47.
[2] Khil MS, Bhattarai SR, Kim HY, Kim SZ, Lee KH. J Biomed Mater Res Part B Appl Biomater 2005;72B:117–24.
[3] Li WJ, Danielson KG, Alexander PG, Tuan RS. J Biomed Mater Res 2003;67A:1105–14.
[4] Li WJ, Tuli R, Huang X, Laquerriere P, Tuan RS. Biomaterials 2005;26:5158–66.
[5] Li WJ, Tuli R, Okafor C, Derfoul A, Danielson KG, Hall DJ, et al. Biomaterials 2005;26:599–609.
[6] Ma Z, He W, Yong T, Ramakrishna S. Tissue Eng 2005;11(7/8):1149–58.
[7] Venugopal J, Ma LL, Yong T, Ramakrishna S. Cell Biol Int 2005;29:861–7.
[8] Yoshimoto H, Shin YM, Terai H, Vacanti JP. Biomaterials 2003;24:2077–82.
[9] Smith LA, Ma PX. Colloids Surf B Biointerfaces 2004;39:125–31.
[10] Chen M, Patra PK, Warner SB, Bhowmick S. Tissue Eng 2007;13(3):579–87.
[11] Dalton PD, Klee D, Möller M. Polymer 2005;46:611–4.
[12] Fridrikh SV, Yu JH, Brenner MP, Rutledge GC. Phys Rev Lett 2003;90(14):1445021–4.
[13] Lee KH, Kim HY, Khil MS, Rab YM, Lee DR. Polymer 2003;44:1287–94.
[14] Tan EPS, Ng SY, Lim CT. Biomaterials 2005;26:1453–6.
[15] Zeng J, Chen X, Liang Q, Xu X, Jing X. Macromol Biosci 2004;4:1118–25.
[16] Fong H, Chun I, Reneker DH. Polymer 1999;40:4585–92.
[17] Huang L, Nagapudi K, Apkarian RP, Chaikof EL. J Biomater Sci Polym Ed 2001;12(9):979–93.
[18] Zong X, Kim K, Fang D, Ran S, Hsiao BS, Chu B. Polymer 2002;43:4403–12.
[19] Zuo W, Zhu M, Yang W, Yu H, Chen Y, Zhang Y. Polym Eng Sci 2005;45:704–9.
[20] Arumugam GK, Khan S, Heiden PA. Macromol Mater Eng 2009;294:45–53.
[21] Seo JM, Arumugam GK, Khan S, Heiden PA. Macromol Mater Eng 2009;294:35–44.

[22] Zeng J, Hou H, Schaper A, Wendorff JH, Greiner A. e-Polymer 2003;9:1–9.
[23] Wutticharoenmongkol P, Supaphol P, Srikhirin T, Kerdcharoen T, Osotchan T. J Polym Sci Polym Phys Ed 2005;43:1881–91.
[24] Son WK, Youk JH, Lee TS, Park WH. Polymer 2004;45:2959–66.
[25] Mckee MG, Hunley MT, Layman JM, Long TE. Macromolecules 2006;39:575.
[26] Kim SJ, Lee CK, Kim SI. J Appl Polym Sci 2005;96:1388.
[27] Qin XH, Yang EL, Li N, Wang SY. J Appl Polym Sci 2007;103:3865.
[28] Arayanarakul K, Choktaweesap N, Aht-ong D, Meechaisue C, Supaphol P. Macromol Mater Eng 2006;291:581–91.
[29] Tarasevich Y, Telichkun V, Ovcharenko F. Theor Expert Chem 1973;6:658–62.
[30] Fong H, Reneker DH. In: Salem DR, editor. Structure formation in polymeric fibers. Cincinnati: Hanser Gardner; 2001 [chapter 6].
[31] Dzenis Y. Science 2004;304:1917–9.
[32] Shin YM, Hohman MM, Brenner MP, Rutledge GC. Appl Phys Lett 2001; 78(8):1149–51.
[33] Hohman MM, Shin YM, Rutledge G, Brenner MP. Phys Fluids 2001;13(8):2221–36.
[34] McKee MG, Wilkes GL, Colby RH, Long TE. Macromolecules 2004;37:1760–7.
[35] Shenoy SL, Bates WD, Frisch HL, Wnek GE. Polymer 2005;46:3372–84.
[36] Ferry J. Viscoelastic properties of polymers. New York: Wiley; 1980.
[37] Gupta P, Elkins C, Long TE, Wilkes GL. Polymer 2005;46:4799–810.
[38] Hohman MM, Shin M, Rutledge G, Brenner MP. Phys Fluids 2001;13:2201–20.
[39] Dersch R, Steinhart M, Boudriot U, Greiner A, Wendorff JH. Polym Adv Technol 2005;16:276–82.
[40] Lyons J, Li C, Ko F. Polymer 2004;45:7597–603.
[41] Kenawy E, Layman J, Watkins J, Bowlin G, Matthews J, Simpson D, et al. Biomaterials 2003;24:907–13.
[42] Koski A, Yim K, Shivkumar S. Mater Lett 2004;58:493–7.
[43] Jarusuwannapoom T, Hongrojjanawiwat W, Jitjaicham S, Wannatong L, Nithitanakul M, Pattamaprom C, et al. Eur Polym J 2005;41:409–21.
[44] Yarin AL, Koombhongse S, Reneker DH. J Appl Phys 2001;89:3018–26.
[45] Reneker DH, Yarin AL, Fong H, Koombhongse S. J Appl Phys 2000;87: 4531–47.