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Electrospinning of polycarbonate nanofibers with solvent mixtures THF and DMF

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The current work demonstrates the electrospinning of polycarbonate dissolved in solvent mixtures of tetrahydrofuran (THF) and dimethylformamide (DMF) to obtain fibers on a nanoscale. The solvent mixtures played a significant role on the morphology of the fibers. The spun fibers showed the characteristics of strong networking with each other as the THF ratio was increased in the solvent mixtures (like 60:40, 70:30 of THF:DMF). The electrostatic voltage, viscosity and surface tension also showed major effects on the fiber morphology and formation of beads. At lower THF and DMF ratios and lower spinning voltages, the bead revealed a globular mushroom shape, while at higher ratios and higher voltages, the beads formed the shape of spindle. The microstructures of the electrospun polycarbonate fibers were quantitively investigated by Scanning Electron Microscope (SEM) and Transmission Electron Microscope as a function of processing variables.

1. Introduction

Since the last few decades, polymers have received a greater attention over metals in various applications and are now being widely used in many applications ranging from insulating plastics grocery bags to highly sophisticated electronic devices like transistors and diodes. In the twentieth century, the flexibility and lighter weight of polymers encouraged scientists to apply electrostatic voltage to draw fibers from polymer solution or polymer melts [1]. Since that period, the electrospinning process has received tremendous attention because of its ability to generate consistent polymer fibers ranging from 5 to 500 nm in diameter [1]. The small diameter polymer fibers with small pore size and large surface areas have spread their applications range from textile industry to medical science, optics and electronics field [1].

Electrospinning process is simple to implement, but complicated to understand. In the beginning of the twentieth century, it was proved that an electrostatic field was able to form and accelerate liquid jets from the tip of a capillary [2]. The introduction of the electric field was able to distort the hemispherical liquid drop suspended in equilibrium at the end of a capillary tube into a conical shape. By introducing the electric field, a number of charges are produced on the surface of the polymer solution and the electric potential becomes in balance with the surface tension of the polymer solution [2], the force balance between the electric field and the surface tension is not enough to form the jet at the capillary tube. At lower viscosity, the solution does not exist as a stable jet for a long time and will break up into droplets. On the other hand, high viscosity solutions will exist as jets all the way to the target along with the force balance between the repulsive force and the surface tension [2]. Therefore, electrospinning process can produce submicron to nanoscale fibers by selecting a proper solvent and polymer concentration as well as controlling the intrinsic conductivity, the viscosity and the surface tension of the solution [3].

The above advantage of the electrospinning process over the conventional spinning process has increased its interest in the recent years. A number of studies of electrospinning of various polymers have been explored in the last few years. Most of the studies focused on the type of the polymer-solvent system, which produced fibers consistently on the nanoscale [1, 3, 4, 8, 9]. Though several literatures have reported the effect of processing variables on the fiber shape and distribution [2, 9], to our knowledge, it has not been reported to show the significance of solvent evaporation on the fiber morphology.

Polycarbonate is a promising thermoplastic material and has been widely used as an injection molded material. Very little research on electrospinning of polycarbonate has been performed that has just been focused on the fiber formation by selecting the proper polymer solvent system. Therefore our research work focused on the morphology and structure changes of polycarbonate fibers with different solvent mixture ratios (THF:DMF as 60:40; 70:30 to neat THF by vol%) at different

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spinning voltages (from 10 to 30 kV) and different polymer concentrations (13, 13.5, 14 and 15% by weight).

The purpose of this research is to study the effect of the spinning processing variables on the fiber morphology and find out an optimum condition required to generate nanometer polycarbonate fibers. We have found significant changes in fiber diameter and morphology such as fiber networking with various processing parameters including solvent evaporation. The fiber morphology under different solvent mixture ratios has been observed and the choice of solvent mixtures and the evaporation of the solvents have shown splaying or splitting of the fibers during electrospinning. The solution viscosity or the concentration of the polymer solution has shown a great influence on the fiber diameter as well as on bead density and has been demonstrated elaborately in the current work. Electrostatic voltage has a great impact on the fiber diameter as it gradually decreases with increasing electrostatic voltage. The current research also showed a significant effect of electric field on the bead shape.

The effect of the various process parameters investigated at our laboratory, shows that viscosity, surface tension and electric potential can change the structure and morphology of the electrospun fibers. Therefore, the present work reveals the changes in fiber structure and morphology of the polycarbonate with solvent mixtures THF and DMF and discusses the effect of the major processing variables in a systematic way.

2. Experimental

2.1. Materials

Polycarbonate pellets with average molecular weight of 27,000 was used. The solvents tetrahydrofuran and N, N dimethylformamide were purchased from Aldrich and used as received. Solutions of polycarbonate at various

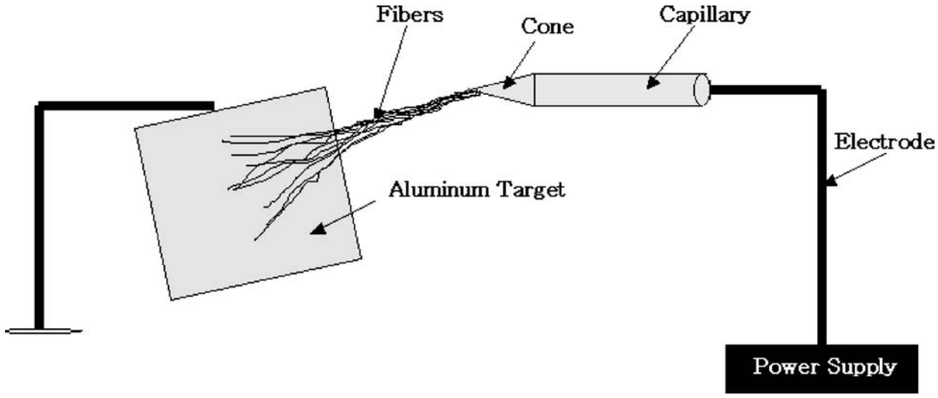

Figure 1 Schematic diagram of the electrospinning set-up.

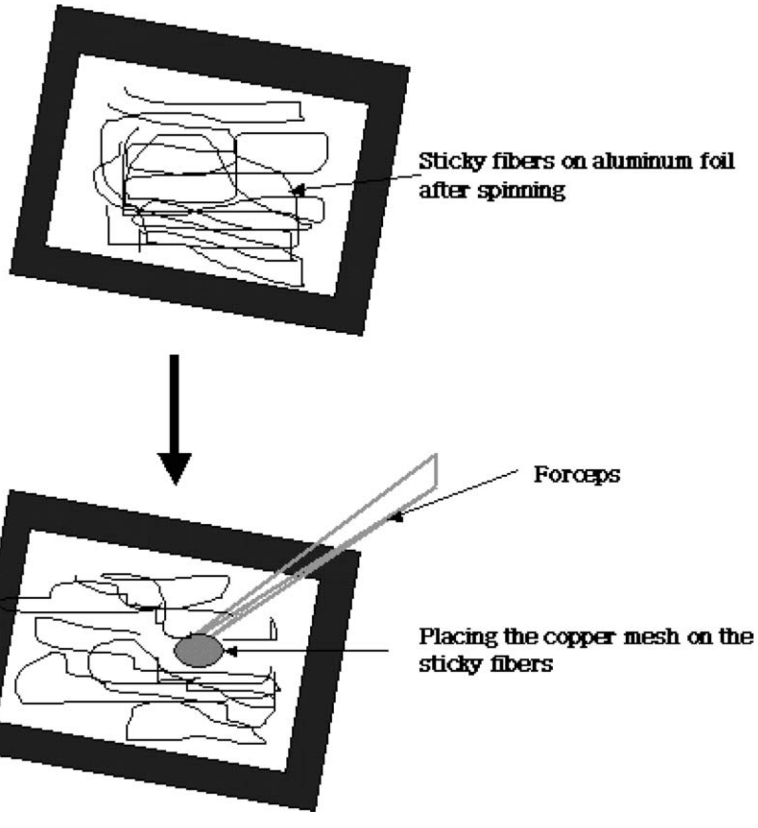

Figure 2 Schematic diagram of the Transmission Electron Microscopy Sample Preparation (TEM) for electrospun PC fibers.

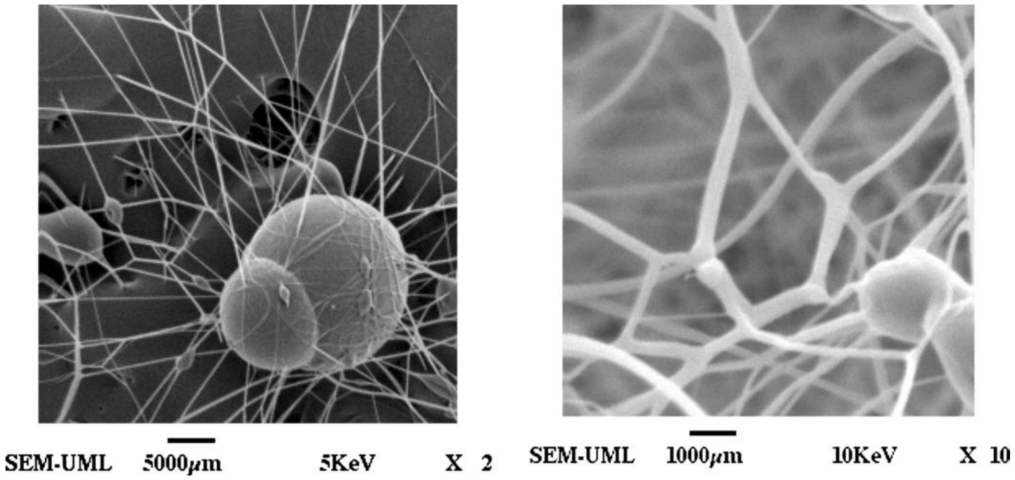

Figure 3 SEM images of spider web structure created by splitting of fibers (left and right) produced by spinning of a 14% PC with solvent mixtures THF:DMF at 70:30 at a voltage of 25.0 kV.

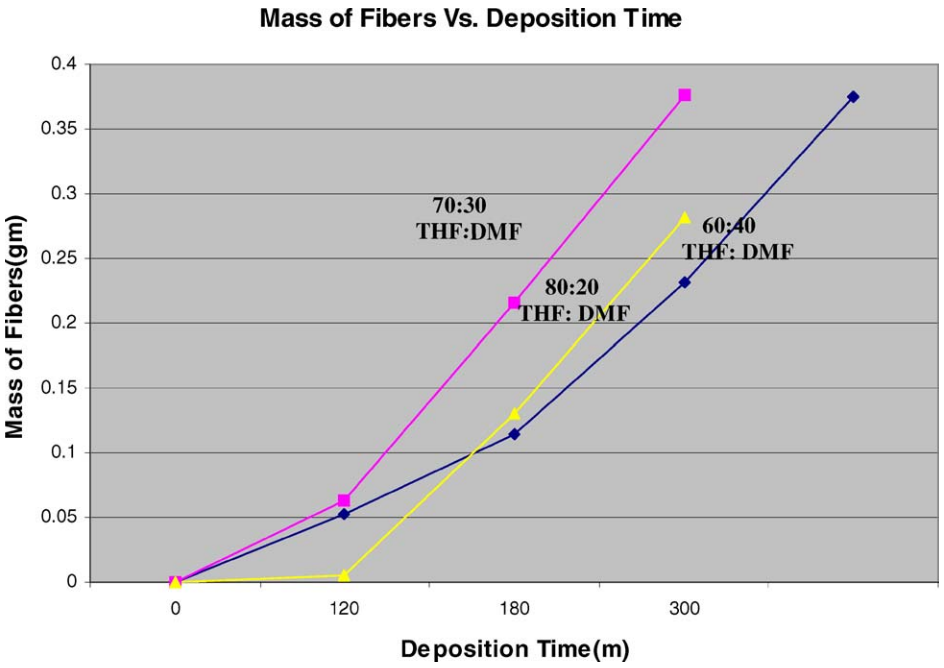

Figure 4 Mass deposition of electrospun fibers as a function of deposition time from 14% PC solution with 60:40, 70:30 and 80:20 THF:DMF ratios.

concentrations (13, 14 and 15% by weight) and different ratios of THF and DMF (THF:DMF at 60:40, 70:30, 80:20, 90:10 ratios and neat THF by vol%) were prepared and electrospun.

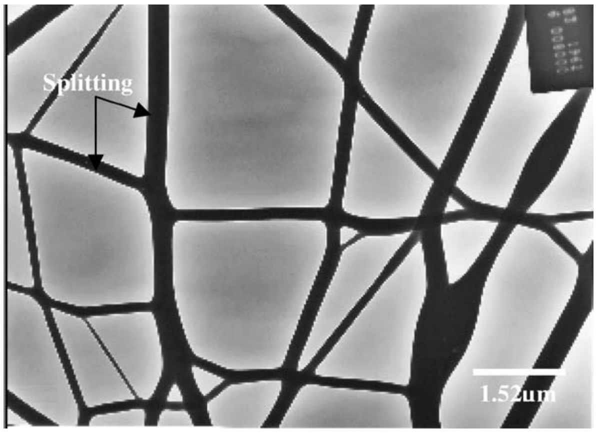

Figure 5 Transmission electron micrograph of spider web structure of PC fibers by splitting.

2.2. Electrospinning

The electrospinning apparatus consisted of a DC power source (Gamma High Voltage Research, Inc. Model HV ES 30P/100), where the charged electrode wires were immersed in a polymer solution held by a glass pipette. Fibers were collected on an electrically grounded target of copper mesh (for TEM observation) or aluminum stub (for SEM observation). Spinning potentials ranged from 10 to 30 kV. A schematic diagram of the electrospinning process is shown in Fig. 1.

2.3. TEM and SEM sample preparation

The sample preparation for SEM is relatively easier than for TEM. The target used for SEM observation was a simple aluminum stub. The stub was simply clamped in the alligator clip and used as a target. The TEM sample holder was a 3 mm diameter copper grid. The copper mesh with a carbon film was attached to aluminum foil, which was already deposited with spun sticky polycarbonate fibers followed by the spinning of PC fibers in

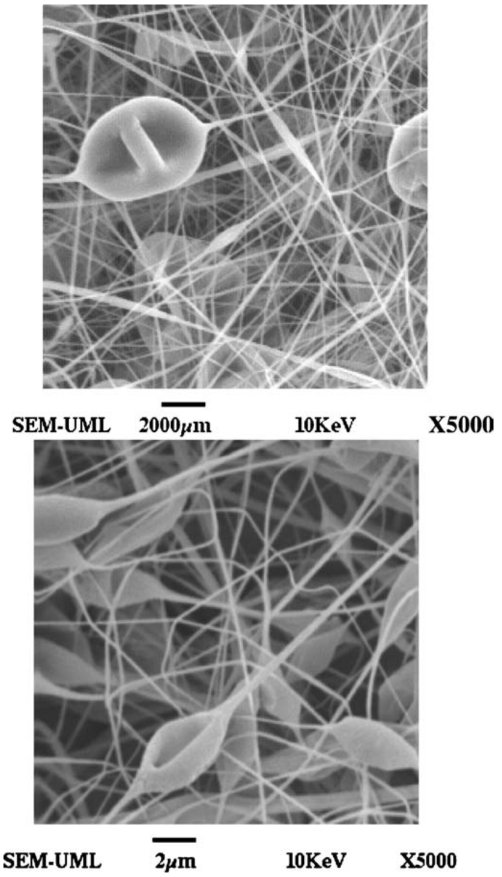

Figure 6 Scanning electron micrographs of bead defects.

the middle of the copper mesh for several seconds. After spinning, the copper mesh was carefully removed from the aluminum foil with forceps and placed in TEM for microstructure observation. A schematic diagram of TEM sample preparation is shown in Fig. 2.

2.4. Electron microscopy analysis

Scanning electron microscope (SEM) images were obtained using an AMRAY 1400 and Transmission electron microscope (TEM) images were obtained using a Philips EM400T at 120 keV. All fiber images were statistically measured and analyzed by GAIA Blue image processing software.

3. Results and discussion

3.1. Effect of solvent mixtures THF and DMF

THF:DMF at various volume ratios such as 60:40, 70:30, 80:20, 90:10 and neat THF significantly changed the fiber morphology provided other experimental parameters remained constant. The effect of the solvent on the fiber morphology has not been studied before and this phenomenon is still uncertain to understand. In the current work, increasing THF to DMF ratios revealed that polycarbonate pellets were more easily dissolved in THF compared to DMF.

The effect of solvent mixtures ratios on the fiber morphology and structure revealed the spider web structure of the fibers (Fig. 3). The scanning electron micrographs of the electrospun polycarbonate fibers with solvent mixtures THF and DMF at 70:30 ratios, clearly showed that the solvent mixtures, especially higher ratios of THF and DMF were major cause to form the "spider web" of the fibers. It was predicted that during the electrospinning experiment, fiber diameter decreased due to the evaporation of the solvent that led the increase in the forces from the surface charge density [4]. In the present electrospinning experiment with polycarbonate solution at higher ratios of THF and DMF solvent mixtures, more solvent evaporation occurred due to the higher vapor pressure of THF and was predicted to evaporate right from the tip of the capillary. On the other hand, since DMF has lower vapor pressure, it was expected to evaporate slowly especially likely after deposition of fibers on the target. Therefore at higher THF/DMF ratios, rate of the solvent evaporation from the fiber surface increased due to large volume of THF in the polymer solution and caused the fibers to carry more charges per unit mass.

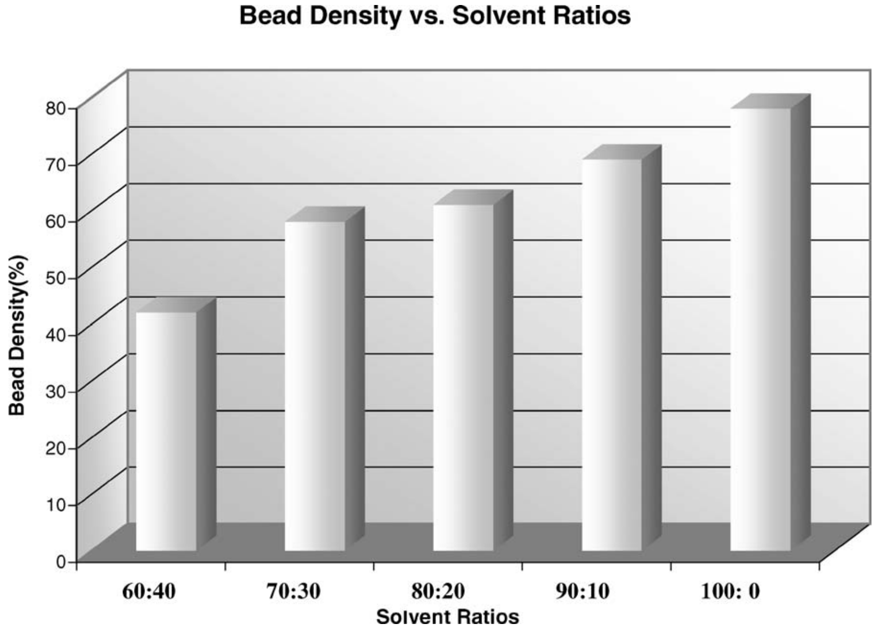

Figure 7 Bead density as a function of solvent ratios THF and DMF produced by 14% PC solution at a voltage 30 kV.

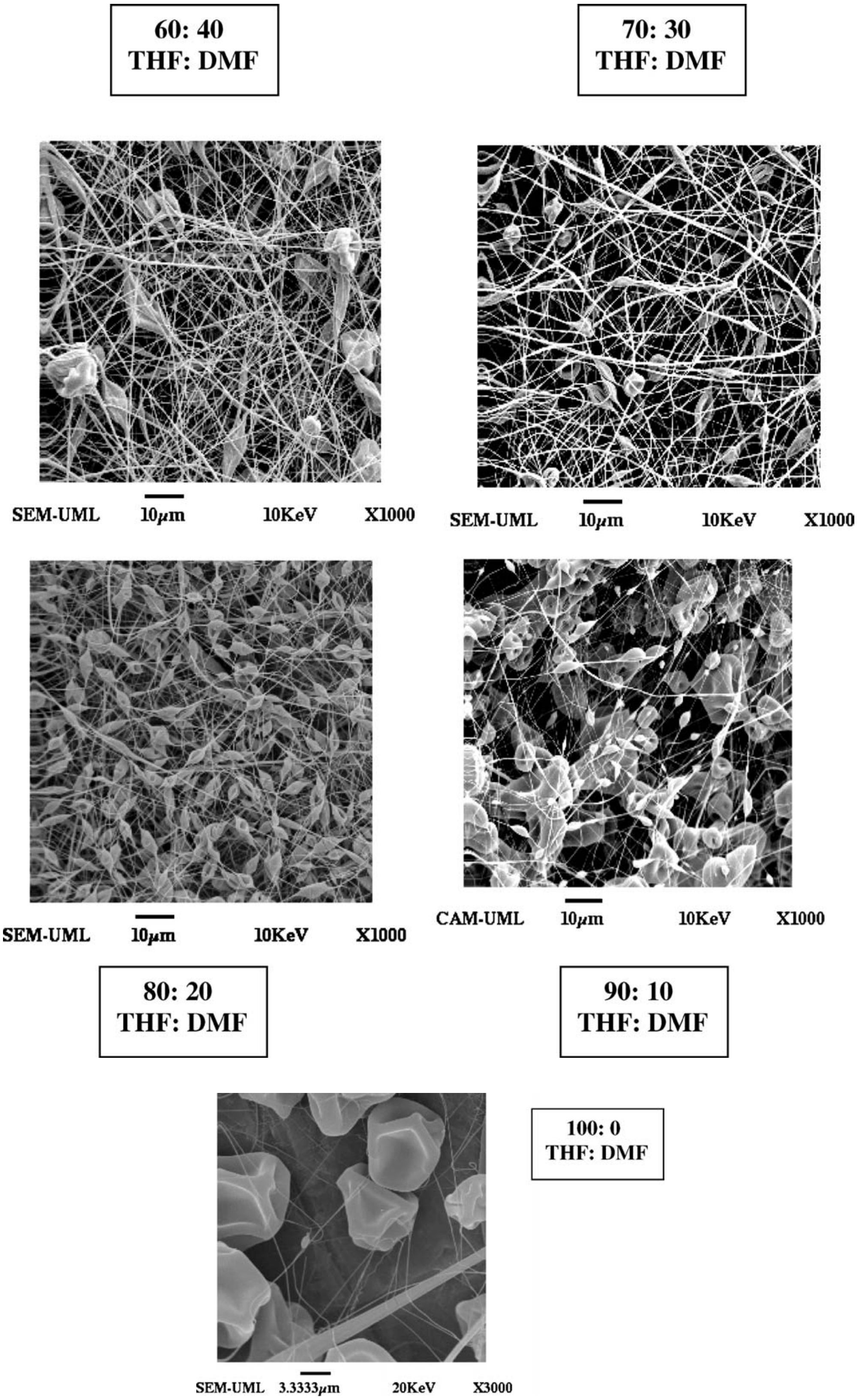

Figure 8 Scanning electron micrographs of bead formations as a function of increasing ratios of THF and DMF produced by 14% PC solution at a voltage 30 kV.

A measurement of charges per mass of fibers with increased ratios of THF/DMF polymer solution was performed in order to investigate the effect of the solvent evaporation rate on the charge of mass of fiber. The charge per mass of fiber was measured from electrospinning current. But the electrospinning current was negligible for its lower value [2] and assumed to increase with an increase in the mass flow rate from the capillary tip to the grounded target at fixed processing variables [1]. A quantitative analysis was employed in order to measure the charge per mass of fibers by measuring the mass deposition of fibers at different duration of time when other parameters were held constant (Fig. 4). It was observed that with increased ratios of THF and DMF, the charge per mass of fibers increased while the electrospinning current was held at

TABLE I Charge per mass of fibers as a function of solvent mixtures ratios at a voltage 25 kV

Current flow during spinning (μamps)	Solvent mixtures ratios (THF:DMF)	Charge per mass of fibers (μC/gm)
0.01	60:40	4.55
0.01	70:30	7.47
0.01	80:20	7.96

the same value (Table I). It was predicted that overcharged fibers were unable to stay longer and therefore repelled each other during the travel of the fibers towards the grounded target. The repulsion of the same charges caused the bigger fiber to split into smaller ones. The continuous "splitting" of the fibers during electrospinning generated the fiber distribution like a "network" (Fig. 5).

The solvent mixture THF and DMF affected the bead formation (defects or byproduct of electrospinning) (Fig. 6). In this experiment, fiber morphology was studied from 60:40 (THF:DMF) ratio to 100:0 (THF:DMF) ratios. With increasing THF:DMF ratios, the bead formation as well as the bead density increased (Fig. 7). It was known that the formation of beads and beaded fibers was driven by the surface tension and the surface tension coefficient depended on the polymer and solvent [5]. During the electrospinning of polycarbonate with increased THF and DMF ratios, the solution was noticed to lose the capability to form more fibers than bead due to higher THF evaporation rate. It was expected that surface tension of the higher THF/DMF solutions gradually increased and therefore the solution lost the capability to form more fibers against the relatively higher surface tension. The scanning electron micrographs showed that at lower ratios of solvent mixtures (THF:DMF at 60:40), a fewer number of bead defects was generated, but as the ratios were gradually increased (such as 70:30, 80:20, 90:10 and neat THF), formation of bead became prominent over fibers. As a result, electrospinning process finally generated only beads with few fibers at 100:0 THF:DMF ratios (Fig. 8).

3.2. Effect of spinning voltage

The spinning voltage played a significant role on the fiber structure and size. The ultimate goal of the current electrospinning experiment was to create nanofibers (less than 10 nm) from polycarbonate pellets dissolved in solvent mixtures THF and DMF. In the current work, it was observed that high electrostatic potential suppressed the surface tension by stretching the fibers into thinner diameter [5]. An electric potential lower than 10 kV did not form uniform fibers since 10 kV potential was not high enough to overcome the surface tension. Therefore electrospinning at 10 kV resulted in more mushroom shape bead defects (Fig. 9) than fibers. As the electric potential increased to 25 kV or 30 kV, surface tension behavior was no longer dominant over the fiber shape. As a result, the distance between the beads increased and changed into a spindle shape (Fig. 10). At higher electric potential, the bead defects were affected by the stretching of the jet and then revealed the spindle shape from a globule mushroom. At higher voltages such as 30 kV, the fiber diameter decreased due to the simultaneous stretching effect of charged fibers [4]. During the travel of the fibers towards the target, the higher voltage achieved the opportunity to stretch the fibers more and resulted in thin (nano) fibers (Fig. 11). The stretching effect of the electrostatic voltage on the fiber thickness was systematically investigated by electrospinning of polymers at 10, 17 and 25 kV (Fig. 12). At lower voltage (10 kV), the force balance between the repulsive force and surface tension was not able to stretch the fibers to a great degree, but as the electric potential increased, fibers became more stretched and thinner. Therefore, nanometer polycarbonate fibers were produced by increasing the electric voltage, while the other parameters were held at a suitable condition.

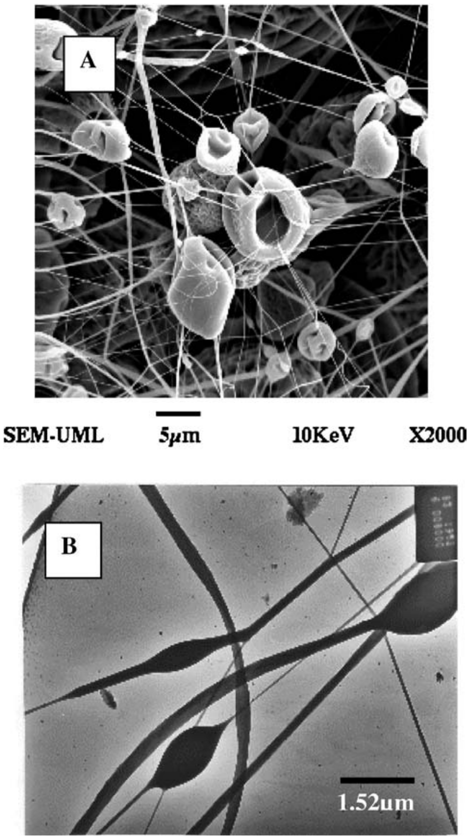

Figure 9 Scanning and transmission electron micrographs of globule beads (A & B at 10 kV) of electrospun 14%PC with solvent mixture ratios (THF:DMF 70:30).

3.3. Effect of polymer concentration

Viscosity or the polymer concentration showed an important role in the fiber morphology changes. Highly viscous solution was likely to overcome surface tension and then formed the droplets into jet along with the voltage. The effect of spinning voltage on the fiber thickness showed that higher spinning voltage was desirable to produce thinner fibers by simultaneous stretching. Therefore the force balances between the higher viscosity and lower voltage created thicker fibers since viscosity or the polymer concentration was a positive

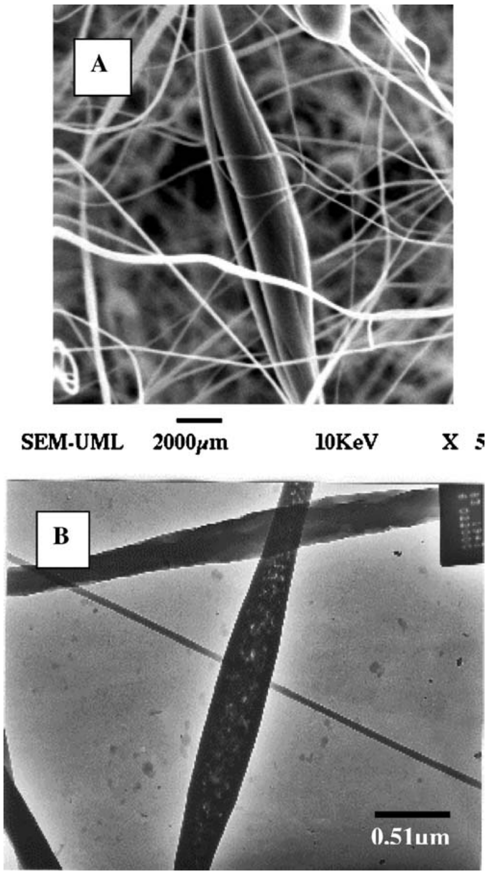

Figure 10 Scanning and transmission electron micrographs of spindle shape beads (A & B at 25 kV) of electrospun 14%PC with solvent mixture ratios (THF:DMF 70:30).

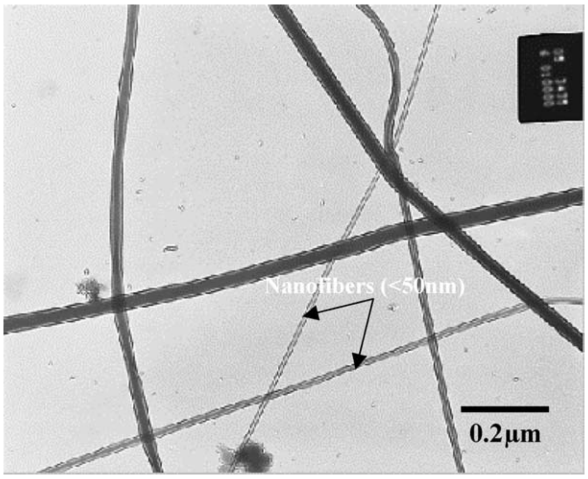

Figure 11 Transmission electron micrographs of electrospun PC fibers on a nanoscale.

force to form thicker fibers. Therefore higher spinning voltage (30 kV) was chosen to understand the effect of polymer concentration on the fiber size and structure at the same concentration (14% Polycarbonate) solution. The higher voltage potentials such as 25–30 kV tended to stretch the fibers into thinner diameter, while the higher concentration of the polymer solution tried to form thicker fibers by preventing the stretching of fibers. The force balances between the higher concentrated solutions and higher electrostatic potential transformed the fiber shape into a curly and wavy structure

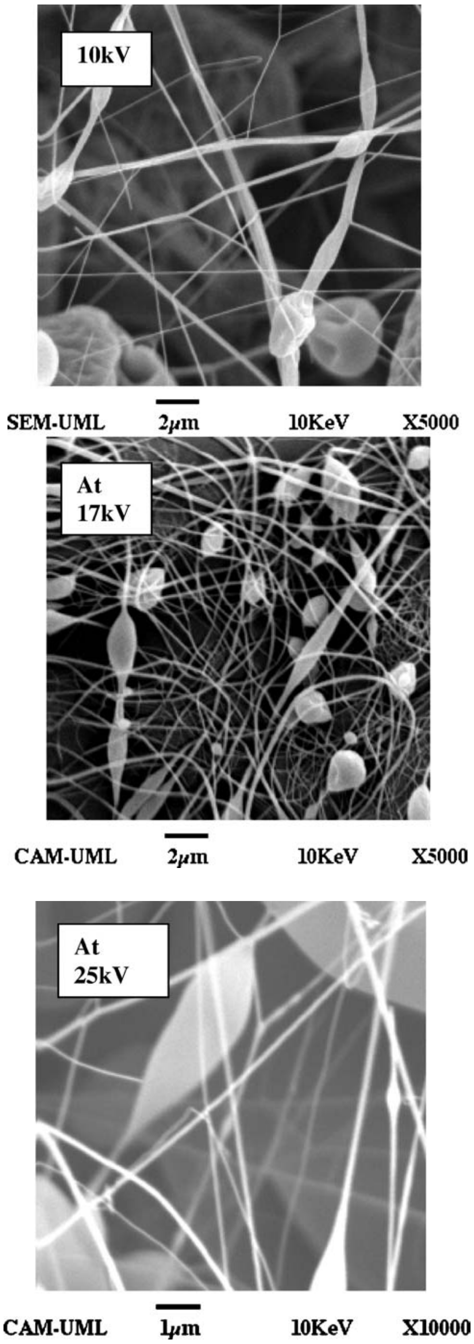

Figure 12 Effect of spinning voltage on polycarbonate nanofibers electrospun from 14%PC solutions with 90:10 THF:DMF ratios.

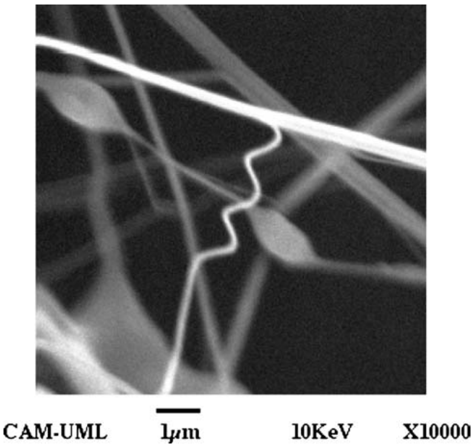

Figure 13 Scanning electron micrograph of curled shape fiber produced from electrospun 14%PC with solvent mixtures THF:DMF at 80:20 at a voltage 25 kV.

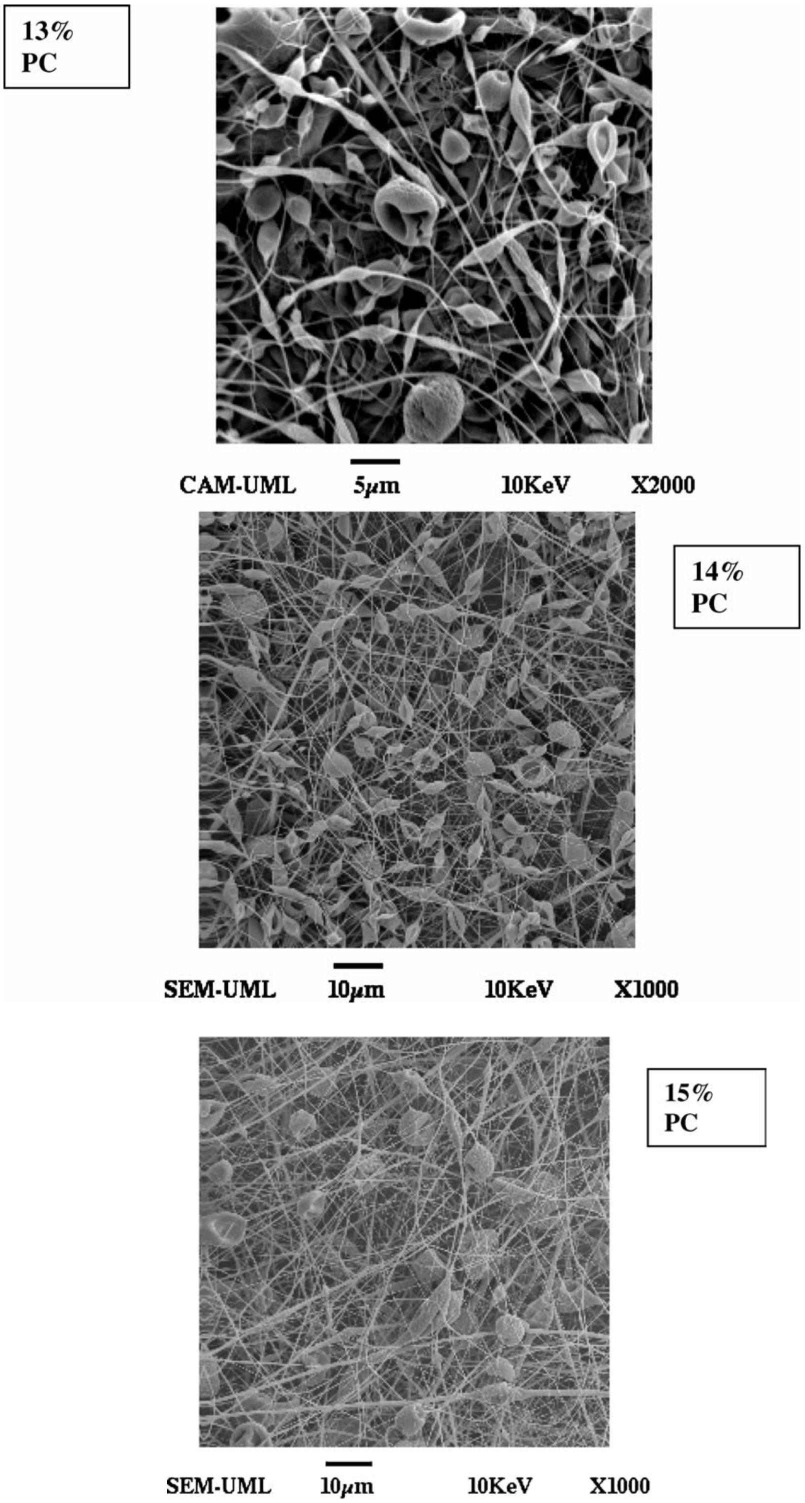

Figure 14 Scanning electron micrographs of electrospun 14%PC with solvent mixtures THF:DMF at 80:20 at a voltage 25 kV to show the effect of polymer concentration on the bead defect.

(Fig. 13). Under this extreme condition, the applied higher voltage could not stretch fibers anymore at a certain point since the fibers lost their stretching property and elasticity property. As a result, resulted force balance ended up with weaker and curly structured fibers.

Polymer concentration also had an effect on bead formation and bead density. Fibers produced from lower concentrated solution exhibited more beads while other parameters (voltage, distance from the capillary to the target, solvent ratios) remained constant. Highly concentrated polymer solutions produced fewer beads while lower concentrated polymer solutions produced large number of beads. For instance, 13% concentrated polymer solution produced more bead defects than at 14% concentrated polymer solution (Fig. 14). Since highly viscous solution is desirable to form fibers, surface tension became dominant over viscosity at lower concentration and formed more beads. But as the viscosity increased in the solution, surface tension became dominated by viscosity and resulted in less number of beads, while the other variables were maintained constant.

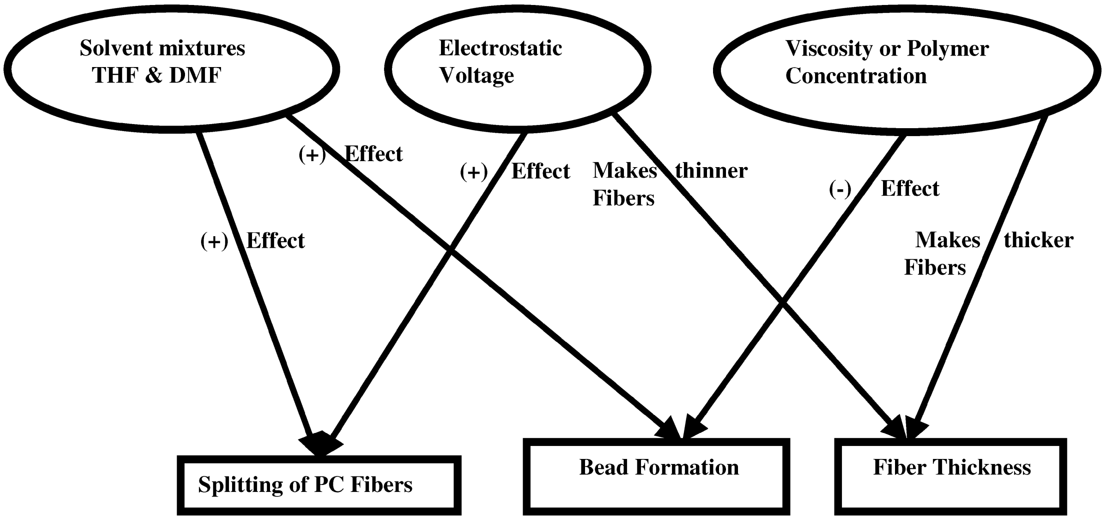

Figure 15 Flow diagram of the effect of various process variables on the morphology and structure of the PC fibers.

The effects of all electrospinning parameters on the fiber morphologies are shown by a flow diagram in Fig. 15.

4. Conclusions

In this work, the effects of major process parameters on the morphology of electrospun PC nanofibers were explored. The morphology of the nanofibers was strongly influenced by solvent evaporation, voltage and viscosity. It was found that solvent evaporation played a major role in the fiber morphology changes. Increasing the THF/DMF ratios and the spinning voltages the fiber mat transformed into the spider web. The bead formation and bead density also appeared to be influenced by the solvent mixtures and viscosity. The force balance between the higher spinning voltage and viscosity showed the large effect of the force balance on the fiber thickness. The optimum conditions of the solvent evaporation, viscosity and spinning voltage resulted in nanometer scale polycarbonate fibers. The 14% PC solution with solvent mixtures THF and DMF at 60:40 ratios at a voltage 25 to 30 kV produced excellent polycarbonate fibers on a nanometer scale. The current experimental conditions did not produce uniform nanofibers, but provided a set of process guidelines for forming polycarbonate nanofibers.

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