THE DIAMETER SIZE REDUCTION OF COMPOSITED POLY Ɛ-CAPROLACTONE-CO-LACTIDE (PLCL) NANOFIBERS USING MULTI-WALLED CARBON NANOTUBES (MWCNTs) AS THE NANOFILLER

F.FADIL[a], N. A.BUANG[a,b*], M. P.PRABHAKARAN[c,d], S.RAMAKRISHNA[c,d]
[a]*Department of Chemistry, Faculty of Science, UniversitiTeknologi Malaysia, 81310 Johor, Malaysia*
[b]*Ibnusina Institute for Fundamental Science Studies, UniversitiTeknologi Malaysia, 81310, Johor, Malaysia*
[c]*Centre for Nanofibers and Nanotechnology, E3-05-14, Nanoscience and Nanotechnology Initiative, Faculty of Engineering, National University of Singapore, 2 Engineering Drive 3, Singapore 117576*
[d]*Department of Mechanical Engineering, National University of Singapore, 9 Engineering Drive 1, Singapore 117576*

Electrospinning process is the widely used technique in the fabrication of nanofibers. It is involves jet initiation of polymer solution and its conversion into nanofibrous polymer formation under high voltage electric field. The electrospinning control process over the polymer nanofibers diameter formation is quite challenging. The spinning polymer solution property is one of the most significant factors that determine the polymer jet stability during the electrospinning process. To control over this factor, nanofiller was introduced. Fabrication of composite polymer nanofibers using poly ε-caprolactone co-lactide (PLCL) with the presence of multi-walled carbon nanotubes (MWCNTs) as the nanofiller at 0.1 to 1.0 wt% loading was performed and the fabricated electrospun MWCNTs/PLCL nanofibers diameter were determine using scanning electron microscope (SEM) to discover their morphological characteristic changes upon the introduction of MWCNTs. Transmission electron microscope (TEM) analysis revealed the distribution of MWCNTs inside the electrospun nanofibers. The beadless, smooth surface of electrospun MWCNTs/PLCL nanofibers were produced from the spinning solution of 11 wt% (w/v) of PLCL containing MWCNTs in DCM/DMF (70:30) at an applied voltage of 10-15 kV with spinning solution flow rate of 1.0 mL/hr. The diameter size reduction of MWCNTs/PLCL nanofibers were observed over the increment of the MWCNTs percentage loading.

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1. Introduction

Electrospinning is one of the nanofibers making technique which is reliable to produce various type nanofibers such as porous, hollow or dense nanofibers. The versatility and feasibility of electrospinning system in transforming natural and synthetic polymer into fibrous formhas seized the attention of researchers to fabricate novel nanofibrous materials for diverse applications.The basic of electrospinning system consists of three important parts which are source of high voltage, syringe pump and grounded collector. At some stage in electrospinning process, a charged polymer droplet was held by its surface tension at the end of the spinneret and then slowly elongated to take a filament form due to the applied electric field [1]. As the intensity of the

*Corresponding author: noraziah@kimia.fs.utm.my

electric field is increased, the hemispherical surface of the polymer liquid at the tip of spinneret elongates to form a conical shape known as the "Taylor cone"and then travel through the way to the grounded collector [2].

The stability of the jet current and "Taylor cone"shape produced during electrospinning process is very important in the nanofibers formation. For instance, Ying *et al.*, (2005) studied the changes of Taylor cone of the polymer droplet at different electric filed applied. The finding showed that at low electrical field, it give less stable cone shape while too high electrical field would diminish the cone shape [3].On the other hand, parameter such as surface tension of the spinning solution might as well affect the electrospinning processing as reported by Fong*et al.* (1999). They described that electrical forces altered the capillary breaking of the electrospun jets by surface tension [4]. Recent study by Nitanan *et al.* (2012) has introduced salt into the polymer solution, showing the decrement in the poly styrene (PS) nanofibers diameter size. They found that by adding salt, it has increased charge density of the spinning solution [5]. In this study, we were incorporated multi-walled carbon nanotubes (MWCNTs) at different percentage loading into PLCL solution and investigate the effect of adding MWCNTs on the electrospun nanofibers diameter formation by having proper control of spinning solution mixture surface tension.

2. Materials and method

Materials

Multi-walled carbon nanotubes (MWCNTs) used in this study was produced directly by catalytic chemical vapor deposition (CCVD) reactor system, under nitrogen atmosphere with the continuous flow of acetylene gas as the carbon source at 700 ℃. The residual of metal catalyst and carbonaceous material was removed via purification process through acid digestion using 5M of hydrochloric acid (HCl) as the oxidant. The diameter of MWCNTs is in the range of 10-50 nm with carbon purity of 90% carbon decomposition [6].

The polymer used in this study is poly ($_L$-lactide)-co- ε-caprolactone) PLCL (70:30, molecular weight 150kDa) which was purchased from Boehringer Ingelheim Pharma (Ingelheim, Germany). Dichloromethane (DCM) and N,N-dimethyl formamide (DMF) were purchased from Merck (Germany) and Sigma Aldrich (USA), respectively and were used without further purification.

Spinning solution preparation

Six different concentration of MWCNTs solution were prepared starting from 0.1 until 1.0 wt% of MWCNTs loading. MWCNTs in DCM/DMF mixture solution (70:30 v/v) were sonicated for 20 minutes and then stirred for two days. 11 wt% (w/v) of PLCL was added to the each of MWCNTs solution prepared and further stirred overnight before undergo electrospinning process.

Surface tension analysis preparation

Surface tension of the MWCNTs/PLCLmixture solution was checked via Du Nuoy ring technique using interfacial tensiometer DST 30 (SEO, Korea).30 ml of solution in 100 ml beaker was used foreach test. The distance between the immersed ring and liquid surface was fixed at 4.5 mm to insure a clean break of the meniscus on the immersed platinum–iridiumring. The circumference (R) of the ring and the ring dimensions ratio (R/R0) were givenby the manufacturer as 0.5960 cm and 53.3906, respectively. The calculation was made by the pre-programmed software in the tensiometer. The surface tension of the sample was recorded as shown from the machine display.

Electrospinning process

The MWCNTs/PLCL mixture solution was loaded into plastic syringes equipped with blunt 25-gauge needles. The syringe then was attached to the vacuum pump (KDS 100, KD Scientific, Holliston, MA). During electrospinning, high voltage power (Gamma High Voltage Research Inc., US) was applied through the metallic clip attached to the needle end tip of the plastic syringe containing MWCNTs/PLCL solution. The current voltage was adjusted between 10-15 kV, with electrospinning solution flow rate at 1.0 mL/hr. The nanofibers formed were collectedon an electrically grounded aluminum foil attached to the jet collector. The distance between jet and end tip needle is approximately 8 cm. As for control, PLCL solution at 11 wt% (w/v) was prepared and the electrospinning process was conducted at flow rate of 1.0 mL/hr with 10 kV current voltage applied.

Characterization of electrospun nanofibers

Scanning electron microscope (SEM)

The morphology characterization of the electrospun PLCL and MWCNTs/PLCL composite nanofibers were conducted by scanning electron microscope (FEI-QUANTA 200F) after gold coated with Auto-sampler coater (JEOL JFC-1200 fine coater, Japan) with an accelerating voltage of 10kV. For quantification of electrospun nanofibers diameters, measurements were made on 20 random locations of the nanofibers using image analysis software (Image J, National Institutes of Health, USA).Method for nanofibers diameter measurement was followed as described by Kanani and Bahrami (2011). The diameter mean value ± standard deviation (SD) was calculated by the software. The average diameter of these 20 measurements was used as the nanofibers average diameter [7].

Transmission electron microscope (TEM)

High-resolutiontransmission electron microscopy (HRTEM) model JEOL EM-2100 was used to get the insight observation of the MWCNTs incorporation inside the nanofibers. Briefly, PLCL and MWCNTs/PLCL nanofibers were mounted onto the copper sample grid during the electrospinning process. The nanofibers stick onto thegrid membrane was bombarded with high electric beam and nanofibers images were collected.

Electrical conductivity

Electrochemical Impedance Spectroscopy (EIS) (HIOKI 3532-50 LCR HiTESTER) was used for measuring electrical conductivity of PLCL and MWCNTs/PLCL nanofibers composite. Nanofibers sample was sandwiched in between of the two stainless steel electrodes of a conductivity holder. The frequency range was set between 50 Hz to 5 MHz. The conductivity was calculated using the following equation:

Conductivity = Sample thickness/ Rb*Area

Where Rb is the bulk resistance (in Ohm) and Area is the electrode-sample contact area (in cm^2).

3. Results and discussion

The SEM micrographs of the electrospun PLCL and MWCNTs/PLCL nanofibers are shown in Figure 1, where we observed the quality of dense type nanofibers in term of their homogeneity, small range nanofibers size and beadles fibrous structure formation.

Optimizing the solution concentration and electrospinning conditions for MWCNTs embedded into PLCL was the major step towards the preparation of composited nanofibers via electrospinning. The 11% (w/v) of PLCL solution produced uniform fibers at anapplied voltage of 11kV, with fiber diameter of 490 ± 70 nm as obtained from Image J software analysis. The SEM images of electrospun composite MWCNTs/PLCL fibers depicted the randomly mat arranged beadless fibers with fibers average diameter of 390 ± 78, 384 ± 69, 379 ± 83, 326 ± 77, 299 ± 85, 258 ± 70, accordingly to the MWCNTs percentage loading starting from 0.1, 0.2, 0.3, 0.4, 0.5 and 1.0 wt%, respectively. The MWCNTs/PLCL nanofibers was produced at applied voltage in the

range of 13-15kV, slightly higher electric field applied to overcome clogging effect at the spinneret tip.

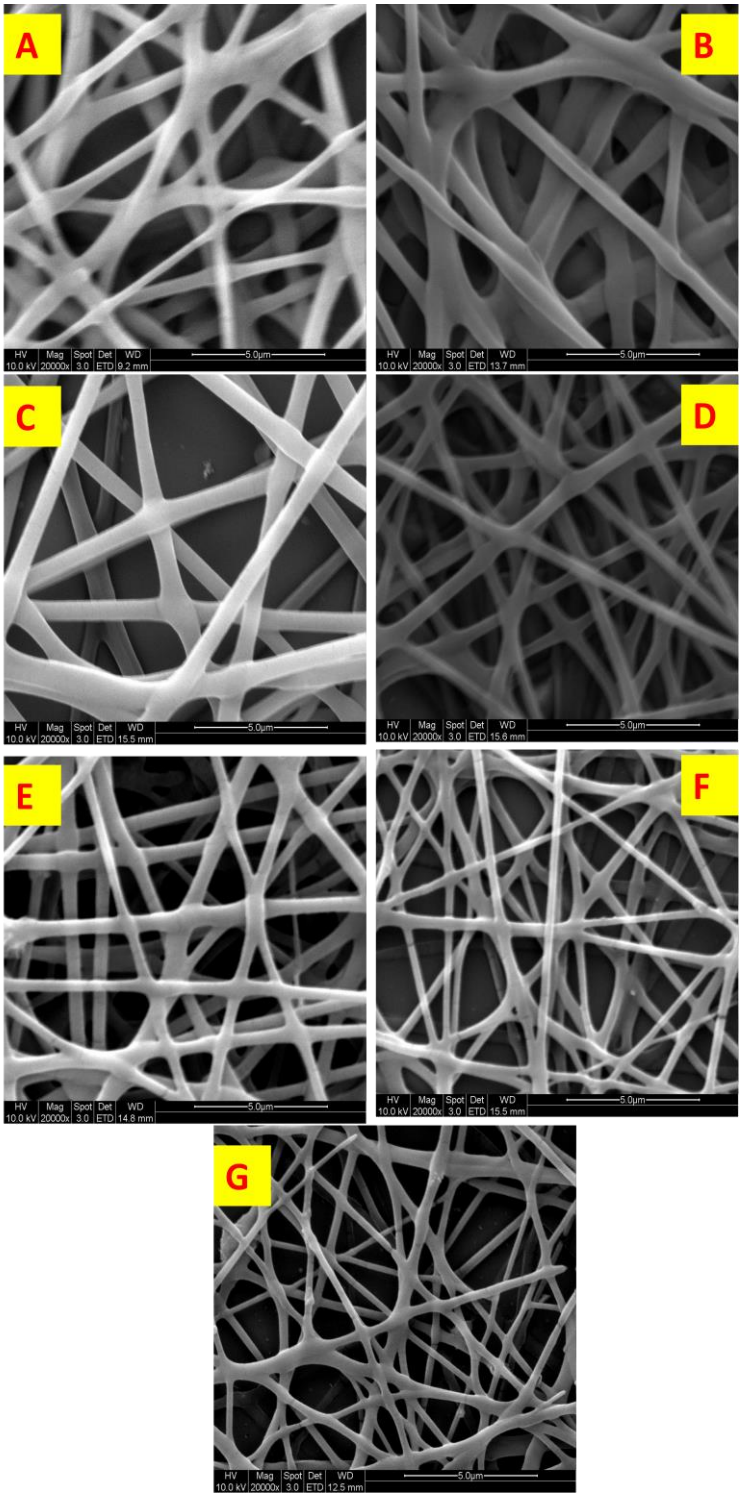

Fig. 1: SEM micrograph of electrospun (A) PLCL (B) MWCNTs/PLCL (0.1 wt%) (C) MWCNTs/PLCL (0.2 wt%) (D) MWCNTs/PLCL (0.3 wt%) (E) MWCNTs/PLCL (0.4 wt%) (F) MWCNTs/PLCL (0.5 wt%) (G) MWCNTs/PLCL (1.0 wt%) nanofibers

The fibrous structure of the electrospun composite MWCNTs/PLCL nanofibers was shown to have a certain trend in the fiber diameter sizes formation accordingly to the different percentage loading of MWCNTs. SEM images depicted the gradual decrement of the fibers

diameter size upon the increasing of MWCNTs loading. In this study, we would like to highlight the surface tension characteristic of the spinning solution upon with MWCNTs embedment. Surface tension values of each of the MWCNTs/PLCL solution were tabulated in Table 1. Data has revealed that the surface tension of the spinning solution mixture was gradually decreased with the increasing of the MWCNTs loading in the polymer matrix. The decreasing of the surface tension of spinning solution has lowered down the spinning solution interfacial bonding. It is also gives higher solvent evaporation rate during spinning process, thus producing finer diameter of electrospun nanofibers [8].

Other than that, the conductivity of the spinning solution mixture would also affect the Taylor cone stability [9]. Electrical conductivity characteristic of MWCNTs/PLCL nanofibers was shown in Table 1. Considering that MWCNTs is an electrical conductive material, adding MWCNTs into the polymer solution has allow large current flow during electrospinning and induced large charge accumulation in the solution jet, resulting in strong electrostatic repulsion among the jet sprays during spinning process.

Table 1: Electrical conductivity and surface tension values of PLCL and MWCNTs/PLCL nanofibers

Nanofibers scaffold	**Electrical conductivity (S/m)**	**Surface tension (Dyne/cm)**
PLCL	1.32 E-10	58.6
MWCNTs/PLCL (0.1 wt%)	1.86 E-10	57.7
MWCNTs/PLCL (0.2 wt%)	2.53 E-10	56.4
MWCNTs/PLCL (0.3 wt%)	3.59 E-10	55.9
MWCNTs/PLCL (0.4 wt%)	4.57 E-10	54.5
MWCNTs/PLCL (0.5 wt%)	4.91 E-10	53.8
MWCNTs/PLCL (1.0 wt%)	5.18 E-10	53.2

The composite PLCL/MWCNTs nanofibers show good conductivity performance by several orders of magnitude at very low percolation threshold (< 0.1wt %) of MWCNTs. The observation on the enhancement of the composite PLCL/MWCNTs electrical conductivity values showed a good indication of MWCNTs distribution in the composite nanofibrous scaffold. MWCNTs do have slightly low electrical conductivity value compared to SWCNTs and graphene[10, 11]. However, MWCNTs can consistently conduct electric when the tubules floss of MWCNTs has form interconnected network among them and performed as transfer agent[12]. The electrical conductivity performance of MWCNTs/PLCL gradually showed a consistent increment, suggesting that upon higher loading of MWCNTs,they were well distributed in the nanofibers, allowing for the electric current to flow.

The dispersion of MWCNTs in the composited electrospun PLCL nanofibers also was supported by the TEM micrograph in Figure 2. TEM analysis done was further provides crucial identification of MWCNTs embedment within the composite nanofibers. TEM micrograph has depicted the randomly distributed MWCNTs inside of nanofibers in a well dispersed state rather than in an aggregated form. The embedded MWCNTs within nanofibers observed were between 10-50 nm in diameter.

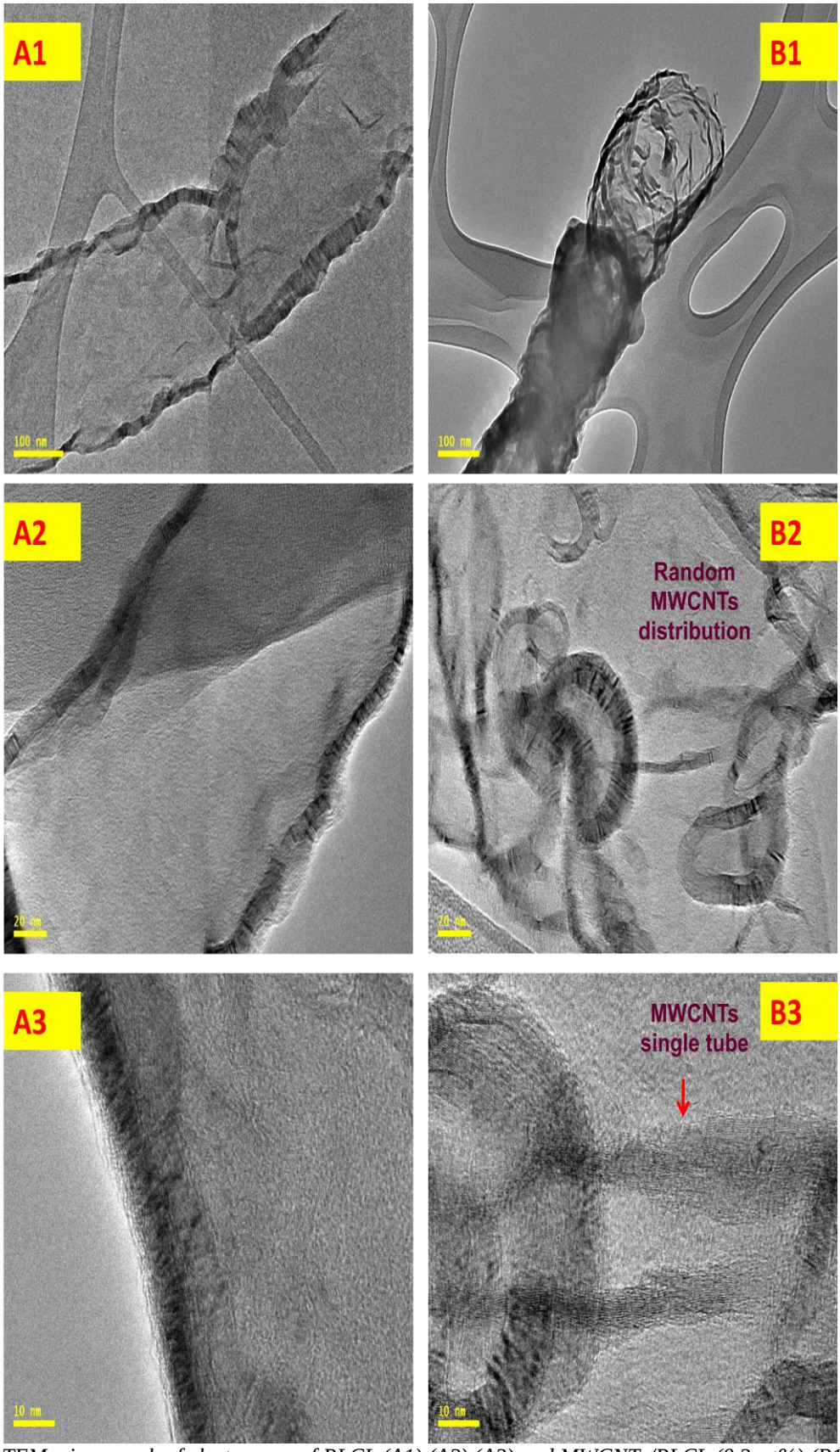

Fig. 2. TEM micrograph of electrospun of PLCL (A1) (A2) (A3) and MWCNTs/PLCL (0.3 wt%) (B1) (B2) (B3) nanofibers at magnification of 100 nm, 20 nm and 10 nm, respectively

4. Conclusion

The underlying principle of electrospinning is the major part to be well optimized in producing small diameters nanofibers. In this study, we revealed the importance of nanofiller (MWCNTs) loading in the contribution to the spinning solution surface tension properties. By having lower value of spinning solution surface tension upon the gradually increased MWCNTs loading, jet initiation of the spinning droplet solution become more stable thus producing smooth and beadless fibrous structure of smaller diameter composite MWCNTs/PLCL nanofibers.

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