

Effects of Temperature and Carbon Nanocapsules (CNCs) on the Production of Poly(D,L-lactic acid) (PLA) Nonwoven Nanofibre Mat

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Abstract

Solution viscosity can be regarded as the most important factor in determining the morphology of the product obtained in electrospinning. Viscosity can be adjusted for a given solution by tuning the solution temperature or by adding fillers to the solution prepared. The electrospinning of PLA solution was performed at a temperature ranging from 25 to 100 °C to determine the effects of temperature on fiber morphology. For the solution of sufficiently high entanglement density (i.e., 20 wt%), the as-spun fiber diameter was in the range of 330 ± 20 nm because the electrospinning was conducted at elevated temperatures. In contrast, for the solution without sufficient entanglement density (i.e., 13 wt%), the solution entanglement density was enhanced by the addition of fillers, which caused the as-spun fibers to become smooth. The fiber diameter obtained was in the range of 90 ± 10 nm. By varying the solution temperature, the chain entanglement status existing in the solution remained intact. In contrast, the chain entanglement density could be enhanced by the addition of fillers. However, both temperature and fillers significantly altered the solution viscosity. Therefore a complete understanding of the temperature and filler effect on the solution and electrospinning gave rise to a feasible route for manipulating the as-spun fiber diameter.

Key words: PLA, nonwovens, nanofibres, carbon nanocapsules.

Introduction

Poly(D,L-lactic acid) (PLA) has been widely used in various biomedical applications due to its biodegradability and biocompatibility. PLA is a compostable polymer derived from renewable sources and is mainly used as implant devices, tissue scaffolds, and internal sutures [1 - 3]. Commercial PLA is composed of copolymers of poly(L-Lactic acid) (PLLA) and poly(D-Lactic acid) (PDLA) with different ratios. One hundred percent PLLA and PDLA are crystallised polymers, and PLA is usually an amorphous copolymer. The degradation rate depends upon the PLA products morphology, that is, the

thinner the PLA fibre the higher the degradation rate. Thus, obtaining a thinner PLA fibre with a large specific surface area is an important task for its end application [4 - 6]. Typically, PLA fibres can be obtained from the melt spinning process. The diameter of as-spun fibres is limited to micrometers, and the properties of PLA are damaged because of the high melting temperature. Therefore electrospinning is a powerful technique for producing polymer nanofibres with a diameter ranging from micro- to nanometers, depending upon the solution properties (viscosity, conductivity and surface tension) and processing parameters (flow-rate, applied voltage and working distance) [7 - 10]. Solution electrospinning yields thin fibres by carefully controlling the solution properties and working parameters. It is a preferred process because fibres can be readily obtained without damaging the nature of PLA polymers [11 - 13].

Since the polymer is dissolved in the solvent, the solution viscosity could be regarded as an entanglement density; the higher the solution viscosity, the higher the entanglement density. A sufficient entanglement density existing in a given solution is an important requirement for successful electrospinning; otherwise electrospinning could degenerate into electrospraying. Viscosity is well documented to be the most important solution

property in determining fibre diameter since the lower the solution viscosity, the thinner the fibres [14 - 20]. Moreover a higher solution conductivity is required to acquire thinner fibres. On the basis of these two aforementioned facts, two approaches are proposed to further reduce the as-spun fibre diameter. The first is aimed at increasing solution conductivity by adding a soluble salt or more conductive solvent [21 - 23]. However, adding a third-party material such as salt or solvent into the solution renders solution electrospinning more complicated and requires that the fibre mats obtained be purified further to remove the salt.

The second approach is aimed at reducing solution viscosity by increasing the solution temperature [24 - 26]. Therefore to obtain a fibre with the diameter desired, a heating apparatus was designed for electrospinning at elevated temperatures in our lab [26]. By varying the solution temperature, the chain entanglement status existing in the solution (a prerequisite condition for preparing uniform fibres) remained intact. When the solution viscosity was reduced, a feasible route to manipulate the as-spun fibre diameter was formed. Using this concept could facilitate a larger degree of freedom to further reduce the electrospun fibre diameter in sizes desired.

Since solution viscosity is a crucial factor in the determination of electrospun fibre morphology for a semi-dilute solution, the solution viscosity could be enhanced by increasing the polymer concentration or by including an insoluble filler such as carbon nanocapsules (CNCs), which were used in this study. CNCs are polyhedral nano-scaled particles that consist of a concentric graphene-layered structure with a cavity in the center and can be considered as materials with properties in-between fullerene and carbon nanotubes (CNTs) [27, 28]. Due to their good rigidity and conductivity, CNCs are considered as excellent fillers added to the PLA solution prepared. The solution entanglement density and solution conductivity were both enhanced by the addition of CNCs. Compared with CNTs, CNCs possess a much lower aspect ratio, leading to good dispersion in the solution. Compared with single-phase fibres, the formation of composite fibres allowed additional design freedom to tailor the physical properties of fibres required for specific applications.

This work aims to obtain a complete understanding of the effects of temperature and filler on solution viscosity, and of the morphologies of the cone/jet/fibre developed during the electrospinning of PLA solutions. The results illustrate a close relationship between the solution rheology and electrospun products. As compared to room-temperature electrospinning, the high-temperature process provided a feasible route for further diameter reduction. The effects of CNC on the solution viscoelasticity and morphology of the electrospun PLA fibres were also investigated.

Experimental

PLA pellets with a molecular weight of 1.78×10^5 g/mol (code number: 8300D) were obtained from Nature Work Co. Dimethyl formamide (DMF) purchased from J.T. Baker (HPLC grade) was used as a solvent to prepare polymer solutions with different concentrations for electrospinning. The surface tension (γ), conductivity (κ) and viscosity (η_0) of the solutions prepared were measured using a Face surface tension meter (CBVP-A3), Consort conductivity meter (C832), and Brookfield viscometer (LV DV-I+, spindle 18, and cup 13R), respectively. The linear viscoelastic properties of the solutions were measured in a Rheometrics

(ARES) using the cup-and-bar feature at various temperatures. The morphology of the fibres was observed under a scanning electron microscope (SEM, Hitachi S4100), and the fibre diameters were measured for a collection of ~ 500 fibres, from which the average fibre diameter (d_f) was determined. A transmission electron microscope (TEM, Joel JEM-1200EX) was used to determine the locations of CNC particles in the nanofibres.

PLA solution electrospinning at elevated temperatures

A jacket-type heating device was used to maintain the PLA solution at the desired temperature (25 - 100 °C) in electrospinning. A significant temperature gradient was found along the needle due to its 'one-dimensional fin' geometry. Therefore an apparent temperature difference between the solutions and electrified Taylor cone was found. To resolve this problem, an IR emitter was used to maintain the environmental temperature and reduce the temperature difference. An as-prepared solution was delivered through a syringe pump (Cole-Parmer) at a controlled flow rate (Q , ranging from 0.1 to 5 mL/h) to the needle ($D_i/D_o/\text{length} = 0.69/1.07/4.0$ mm, unless otherwise indicated), where a high electrical voltage (V , ranging from 6 to 25 kV) was applied using a high-voltage source (Bertan, 205B).

PLA solution with CNC filler electrospinning at room temperature

Surface-modified CNCs produced by the pulse plasma arc-discharge method [27, 28] were kindly provided by the Industrial Technology Research Institute (ITRI). For solutions (i.e., 10, 13 and 15 wt% solutions) without sufficient

concentration, 1 wt% of the CNCs was added to the solution prepared. The solution viscosity and conductivity could be enhanced by including CNC fillers. Different amounts of surface-modified CNCs were added to the 13 wt% PLA solution, after sonication. All the solutions prepared were then subjected to room temperature electrospinning (needle size: $D_i/D_o/\text{length} = 1.07/1.47/40.0$ mm). Afterwards composite fibres were prepared by electrospinning PLA solutions with various amounts of CNCs.

In this study, two different types of electrospinning apparatus were created to conduct nanofibre production. The general scheme of the electrospinning apparatus is shown in *Figure 1*.

Result and discussion

In our previous study [29] it was shown that for PLA solution electrospinning, the minimum solution concentration required for obtaining smooth fibre is 20 wt% (data now shown). The fibre diameter obtained is limited to 500 nm by carefully controlling electrospinning working parameters. As the solution concentration was below 20 wt% (without sufficiently high entanglement density), only beaded fibres were obtained. Therefore, to investigate the effects of temperature, 20 wt% PLA solution was used. In contrast, to investigate the effects of the filler, 10, 13 and 15 wt% PLA solutions were used.

Effects of temperature on solution properties and electrospinning

Shear experiments were carried out at temperatures ranging from 25 to 100 °C. As expected, η_0 was reduced at high tem-

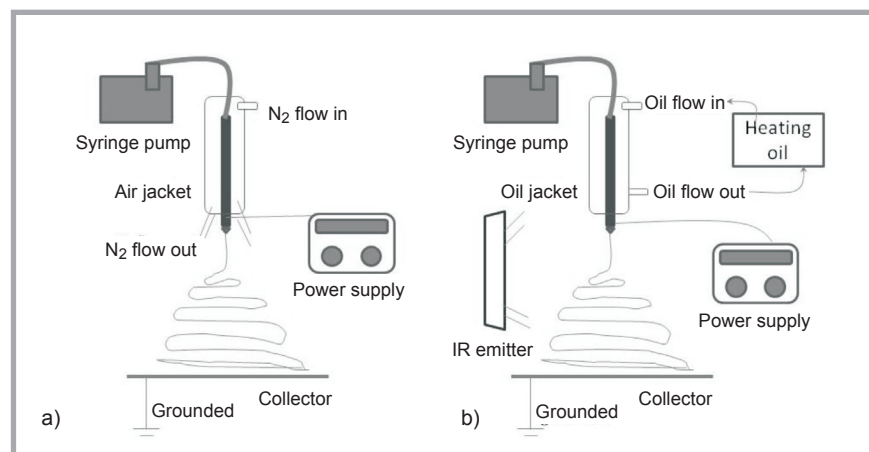


Figure 1. General scheme of electrospinning apparatus; a) room-temperature and b) high-temperature electrospinning equipment.

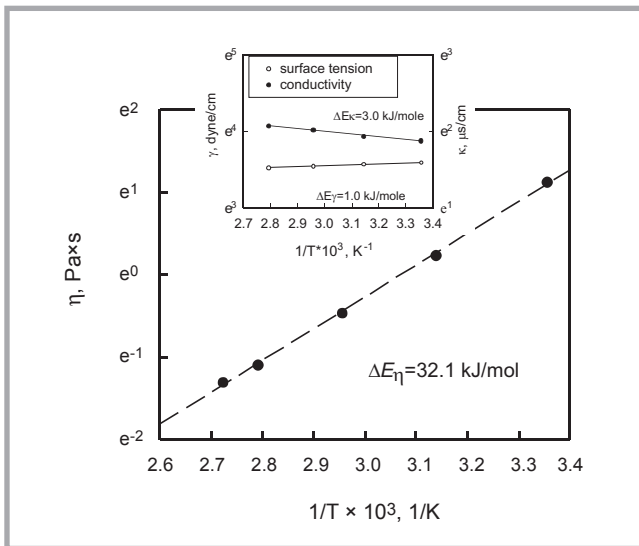


Figure 2. Temperature effects on the 20 wt% PLA solution viscosity in the range of 25–100 °C. (The inset shows the effects of temperature on the solution surface tension and conductivity).

peratures. The temperature (T) dependence of η_0 was assumed to be governed by the Arrhenius-type activation energy **Equation 1**, where T_0 is the reference temperature, and R is the gas constant. **Figure 2** shows the log η_0 versus $1/T$ plot for the 20 wt% solution, from which the activation energy for the flow (ΔE_η) was determined from the slope.

$$\eta_0(T) = \eta_0(T_0) \exp\left[\frac{\Delta E}{R} \left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \quad (1)$$

A flow activation energy (ΔE_η) of 33.9 kJ/mol was obtained. Accordingly the viscosity of the 20 wt % solution was decreased markedly from 3090 to 270 cP when the temperature was raised from 25 to 100 °C. Similarly ΔE_η and ΔE_η were found to be 3.0 and 1.0 kJ/mol, as shown

in **Figure 2**, indicating that γ and κ did not vary significantly when the solution temperature was changed.

For a given solution, the solution viscosity can be adjusted to a different level by tuning the operating temperature. Using this concept gives a greater degree of freedom to produce the electrospun fibre diameter in different sizes. A heating unit was used to maintain the solutions and the ambient at high temperature conditions. A jacket-type heating device maintained the solution temperature up to 150 °C. On the other hand, an IR emitter was situated at a distance of 10 cm away from the needle. The IR emitter was used to maintain the environmental temperature up to 120 °C and sustain that of the pendant drop (or Taylor cone) at the needle end.

Table 1. Effects of temperature on the cone/jets/fibre morphologies; 20 wt%, $H = 14$ cm, $Q = 1$ mL/h, 12.5 kV.

Temp., °C	η_0 , cP	κ , $\mu\text{S}/\text{cm}$	γ , dyne/cm	d_f , nm
25	3096	36.1	6.5	503±118
37	1971	35.8	6.7	352±102
45	1267	35.4	6.9	318±85
56	789	34.5	7.5	308±79
68	588	33.8	7.9	309±61

Table 2. Effect of CNC contents on the solution properties and electrospun fibre morphology.

PLA, wt%	CNC, wt%	η_0 , cP	κ , $\mu\text{S}/\text{cm}$	γ , dyne/cm	d_f , nm
10	0	100	6.5	35.9	beaded fiber
10	1	302	99.1	35.5	60 ± 10
13	0	525	6.4	36.3	beaded fiber
13	1	511	97.2	35.9	80 ± 10
13	3	564	101.4	36.2	83 ± 13
13	5	772	115.4	35.4	90 ± 15
15	0	763	6.5	36.1	beaded fiber
15	1	821	105.6	35.9	200 ± 40

With the controlled solution and ambient temperatures, investigating the T effects on the cone/jet/fibre morphologies was possible. High-temperature electrospinning was performed at a given flow-rate ($Q = 1$ ml/h), working distance ($H = 14$ cm), and applied voltage ($V = 11.5$ kV) using the 20 wt% solution at various temperatures, ranging from 25 – 100 °C.

For the electrospinning process, a minimum voltage was required to maintain a stable cone-jet mode. When the voltage applied was increased to a certain level, the stable cone-jet became unstable. At this stage the experimental data obtained cannot be compared fairly. Therefore the lower bound voltage (V_s) and upper bound voltages (V_{us}) were defined to obtain a ‘functioning domain’. The functioning domain shows the range of

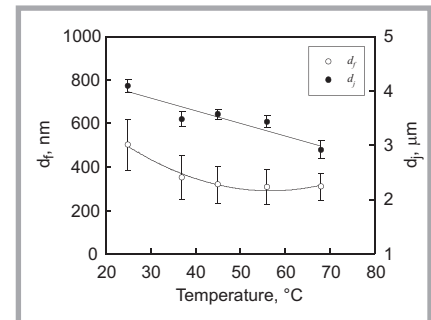


Figure 3. Effects of solution electrospinning temperature on the electrified jet diameter, d_j , and electrospun fibre diameter, d_f ; 20 wt%, $H = 14$ cm, $Q = 1$ mL/h, 12.5 kV.

operating voltages required for stable cone-jet mode electrospinning. When the applied voltage was in the range of ($V_{us} - V_s$), the electrospinning could be operated in a stable status. As compared to room temperature electrospinning, a larger processing domain ($V_{us} - V_s$) was obtained to conduct electrospinning at elevated temperatures (data not shown). The minimum diameter of electrospun fibre was around 500 nm, no matter how the working parameters (Q , V , H) were manipulated in room temperature electrospinning. However, the as-spun fibre diameter dramatically decreased when the working temperature was higher than the room temperature. The fibre diameters obtained were around 500 and 320 nm for solution temperatures of 25 and 45 °C, respectively.

As the temperature of the electrospinning solution was increased from 25 to 68 °C, a bigger cone with a shorter and thinner

straight jet was observed, as shown in **Table 1**, which may indicate a higher electric field working in the jet (E_j), derived from enhanced jet whipping [26]. These findings imply that d_f would be reduced with an increasing solution temperature. As shown in **Figure 3**, a slight increase in the solution temperature to 37 °C leads to a pronounced reduction in d_f ; however, the effect becomes less distinct for temperatures higher than 56 °C. As the working temperature was further increased, the as-spun fibre diameter did not change significantly, indicating that when a high viscous solution was electrospun at elevated temperatures, the solvent easily evaporated, and the solution jet became more concentrated. Without the solvent, the charged jet could no longer be extended, becoming solid; even the electric repulsion force working in the area of bending instability. Therefore a suitable ambient temperature has to be carefully controlled by the IR emitter.

The effects of temperature on the solution viscosity (η_0) and morphologies of the cone/jet/fibre developed during the electrospinning of the PLA solutions are listed in **Table 1**.

Effects of the CNC filler on solution properties

When the solution concentration was higher than the critical concentration (i.e., 20 wt%), which has a sufficiently high entanglement density, the solution could be electrospun into smooth fibre shapes [17]. The requisite viscosity could be obtained either by increasing the polymer concentration or introducing insoluble fillers. Compared with single-phase fibres, the formation of composite fibres allowed more design freedom to tailor the physical properties of the fibres required for specific applications. This section focused on the CNC fillers' effect on the PLA solution properties and as-spun fibre morphologies, which had various amounts of CNCs. Different amounts of surface-modified CNCs were added to the PLA solution after sonication. The solution prepared was then electrospun to form PLA/CNC composite fibres.

For solutions without sufficient concentration (i.e., 10, 13, and 15 wt% PLA solutions), 1 wt% CNCs were added; the properties of the solutions are shown in **Table 2**. By adding 1 wt% CNCs into the 10 wt% solutions, κ was significantly increased to 10 times larger than that with-

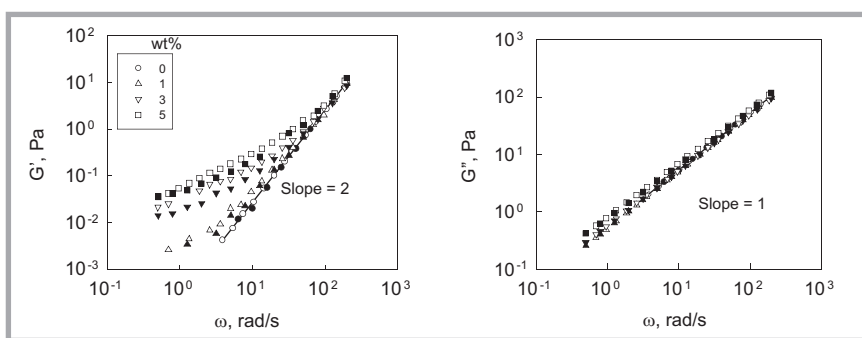


Figure 4. Dependence of G' and G'' of the 13 wt% PLA solutions with various CNC loadings.

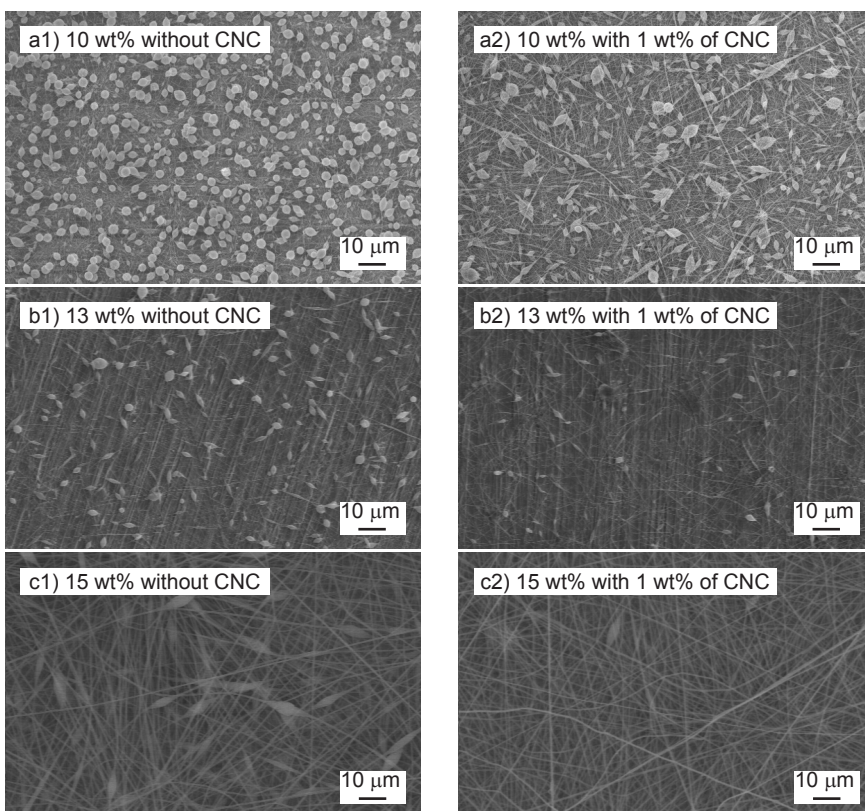


Figure 5. SEM images of PLA fibre electrospun from: a) 10, b) 13 & c) 15 wt% PLA solution without (left) and with 1 wt% of CNCs (right); $H = 7$ cm, $Q = 0.3$ mL/h, 6.0 ~ 9.0 kV.

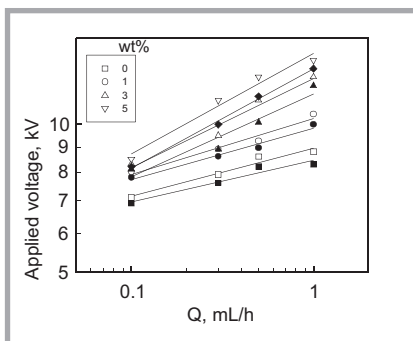


Figure 6. Functioning domain for electrospinning of the 13 wt% PLA solutions with various CNC loadings showing the range of operating voltages required for stable cone-jet mode electrospinning; $H = 7$ cm, V_s , and open symbols for the upper bound voltages, V_{us} .

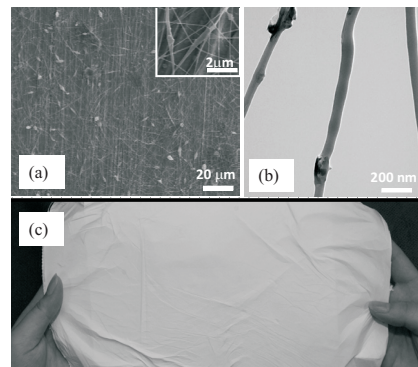


Figure 7. Electron microscope images of the electrospun fibre mat: a) SEM, b) TEM images and c) electrospun nonwoven fibre mat from PLA solution with 1 wt% of CNCs loadings; CNCs were added to the 13 wt% PLA solution, $H = 7$ cm, $Q = 0.3$ mL/h, 7.5 ~ 11.0 kV.

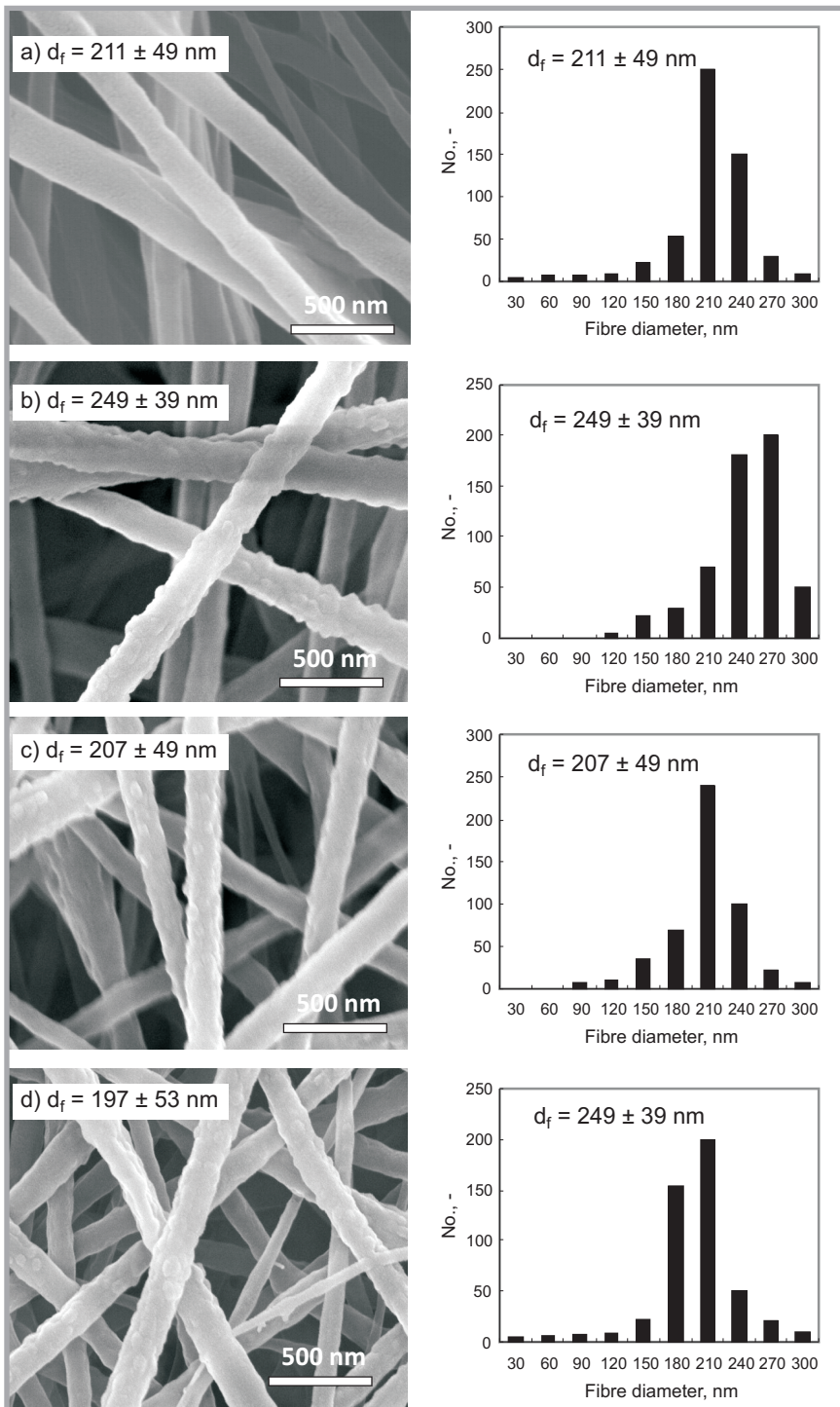


Figure 8. Morphology of fibre electrospun from 15wt% PLA solution, and fibre diameter distribution: a) 1.0 mL/h, 9.3 kV, b) 1.0 mL/h, 12.5 kV, c) 0.3 mL/h, 8.8 kV, d) 0.3 mL/h, 9.0 kV, a) without CNCs, b) - d) with 1 wt% of CNCs; H is fixed at 7 cm.

out CNCs and η_0 was also dramatically enhanced. A similar trend was found in the 13 and 15 wt% solutions. To further investigate the CNC effects on solution properties, various amounts of CNCs, ranging from 0 ~ 5 wt%, were added to the 13 wt% PLA solution. When 1 wt% of CNCs was added to the solution, the solution viscosity was slightly decreased. When the amounts of CNCs were further increased up to 3 and 5 wt%, the solu-

tion's η_0 and κ slightly increased, while γ showed no significant difference.

Figure 4 shows a log-log plot of G' together with G'' versus ω . It indicates that as a result of CNCs (1, 3, and 5 wt%) being added to the 13 wt% PLA solution, the value of G' increased at low frequencies in the oscillatory shear mode rheology experiment. At a slope of 1.98, the unfilled solution exhibited a homogenised

status. When 1 wt% of CNCs was added to the solution, a rising G' was detected in the low frequency regime. A modulus plateau was virtually observed for a CNC content of up to 3 wt%. The plateau modulus was then further increased with an increase in the CNC content. The formation of the modulus plateau was attributed to the plausible formation of a new network involved in the interaction between the PLA chains and CNC particles. The effect of CNC addition on the viscoelastic properties of the PLA solution is shown in **Table 2**, indicating that κ was significantly enhanced, and solution viscosity (η_0) was also enhanced when CNCs were added to PLA solution; in contrast, γ remained intact.

Effects of the CNC filler on the electrospinning process

Figure 5 demonstrates that the PLA fibres were electrospun from 10, 13 and 15 wt% solutions with and without 1 wt% of CNCs at $Q = 0.3$ mL/h, $H = 7$ cm. For a given solution, the addition of CNC fillers was a way to produce more entanglements between the polymer chains and CNCs in the solutions. When electrospinning the 10 wt% PLA solution, only beaded fibres were produced; this meant that the polymer chain entangled network was not strong enough to prevent the formation of beads. It is interesting to discover that the addition of CNCs to the PLA solution resulted in a relatively uniform fibre shape and fewer beads. This filler effect could also be observed when electrospinning 13 and 15 wt% solutions with 1 wt% of CNCs inside. This could be attributed to a new network that was formed between the PLA chains and CNC particles. Thus the formation of beaded fibres was eliminated because η_0 and κ were dramatically enhanced. The fibre diameter obtained was in the range of 80 – 100 nm.

Effects of the CNC filler on electrospun fibre morphologies

The experimental data shows that the addition of 1 wt% of CNCs resulted in the formation of bead-less fibres since the formation of beads was first eliminated by introducing 1 wt% of CNCs into 13 wt% solution electrospinning. To further examine the CNC filler effects on electrospun fibre morphology, more CNCs were added to 13 wt% solutions. **Figure 6** shows the functioning domain for electrospinning 13 wt% PLA solutions with various CNCs loadings,

indicating that a higher electrospinning voltage was required to maintain a stable cone-jet mode for a solution with higher conductivity. This phenomenon was also observed in electrospinning PS/DMF solutions with the addition of salt [17]. The figure also indicates that in studying the filler effects of CNC, it seemed impossible to fix a given voltage for a fair comparison. Therefore the V required for each solution with various amounts of CNCs was chosen as $1/2 (V_{HS} - V_S)$.

In this work, electrospun PLA fibres containing more CNCs were prepared by electrospinning 13 wt% solutions and increasing CNC amounts up to 5 wt%. The experimental result shows that the number of beads was decreased by electrospinning 13 wt% solutions with 1 wt% of CNCs, which was followed by a slight increase as 5 wt% of CNCs was added. Upon further inspection using TEM, the beads observed were formed by the aggregation of CNC particles, as shown in **Figure 7**. We also obtained electrospun fibres forming the nonwoven mat, as shown in **Figure 7.c**, via this useful method.

Finally when the 15 wt% solution with 1 wt% of CNCs was electrospun into fibres, as shown by the SEM image in **Figure 8**, the CNC particles were uniformly distributed on the fibre surface (b), in contrast with the pure PLA fibres (a). Moreover the as-spun fibre diameters of the PLA/CNC composite nano-fibres were also slightly larger than those of the pure PLA fibres, which were 248 ± 38 and 211 ± 48 nm, respectively. On the other hand, in different conditions we can obtain thinner fibres than those from PLA solution, as shown in **Figure 8.c, 8.d**.

With the addition of CNCs to the PLA solutions, the PLA/CNC solution's viscosity and conductivity were increased with an increase in the amounts of CNCs. The solution entanglement density was significantly enhanced by adding CNCs to lower-concentration solutions. This phenomenon was also confirmed by the value of $G'(\omega)$ of the 13 wt% PLA solution with various amounts of CNCs, which was enhanced using the ARES rheometer. Thus the viscosity desired can be obtained by adding CNC filler material to the solutions. This indicates that the solution's concentration was enhanced by the fillers because an entanglement was created between the polymer chain and CNC fillers. This finding can open areas for further

exploration in the field of electrospinning in a semi-dilute region by introducing a filler into polymer solutions.

Conclusion

For a given solution with a sufficiently high concentration, the solution viscosity can be adjusted to a different level by tuning the operating temperature. The solution viscosity was significantly reduced at elevated temperatures, giving rise to a reduction in the electrospun fibre diameter. The as-spun fibre diameter was dramatically decreased to 330 ± 20 nm for the solution electrospun at elevated temperatures.

For a solution with insufficient entanglement density, it can be enhanced with the addition of fillers. As CNC fillers were added to the 10, 13, and 15 wt% PLA solutions, the number of beaded fibres was decreased during electrospinning. When more than 1 wt% of CNC was added to the solution prepared, the formation of beaded fibres was eliminated, while the solution viscosity and conductivity were dramatically enhanced. Therefore electrospun fibres with a relatively smooth fibre shape were obtained, and the as-spun fibre diameter could be further reduced to 90 ± 10 nm. This work was motivated by the lack of studies reporting on fibrous mats containing nanosize conducting particles, such as CNCs. Due to their conductive nature being similar to carbon nanotubes (CNTs), the polymer/CNC electrospun composite fibres obtained in this study are good examples for comparison with previous studies. The further investigation will focus on the physical properties of PLA/CNC composite fibres and experimental results will be reported in the coming article.

We have successfully demonstrated the temperature and filler affect the morphology of electrospun fibres. A complete understanding of the factors which affect solution electrospinning could provide a feasible route for manipulating the as-spun PLA fibre diameter.

References

1. Murugan R, Ramakrishna S. *Tissue Eng* 2007; 13: 1845-1866.
2. Lim LT, Auras R, Rubino M. *Progress in Polymer Science* 2008; 33: 820-852.
3. Sill TJ, Recum HA. *Biomaterials* 2008; 29: 1989-2006.
4. Kim K, Yu M, Zong X, Chiu J, Fang D, Seo YS, Hsiao BS, Chu B, Hadjiargyrou M. *Biomaterials* 2003; 24: 4977-4985.
5. Li D, Fery MW, Baeumer AJ. *J Membr Sci* 2006; 279: 354-363.
6. Bhattarai SR, Bhattarai N, Yi HK, Hwang PH, Cha DI and Kim HY. *Biomaterials* 2004; 25: 2595-2602.
7. Huang ZM, Zhang YZ, Kotaki M, Ramakrishna S. *Compos Sci Technol* 2003; 63: 2223-2253.
8. Zong X, Kim K, Fang D, Ran S, Hsiao BS, Chu B. *Polymer* 2002; 43: 4403-4412.
9. Deitzel JM, Kleinmeyer J, Harris D and Tan NCB. *Polymer* 2001; 42: 261-272.
10. Doshi J, Reneker DH. *J Electrostatics* 1995; 35: 151-160.
11. Agarwal S, Wendorff JH, Greiner A. *Polymer* 2008; 49: 5603-5621.
12. Gupta D, Venugopal J, Mitra S, Giri Dev VR, Ramakrishna S. *Biomaterials* 2009; 30: 2085-2094.
13. Zhang L, Webster TJ. *Nano Today* 2009; 4: 66-80.
14. Mckee MG, Wilkes GL, Colby RH, Long TE. *Macromolecules* 2004; 37: 1760-1767.
15. Shenoy SL, Bates WD, Frisch HL, Wnek GE. *Polymer* 2005; 46: 3372-3384.
16. Yu JH, Fridrikh SV, Rutledge GC. *Polymer* 2006; 47: 4789-4797.
17. Wang C, Hsu CH, Lin JH. *Macromolecules* 2006; 39: 7662-7672.
18. uang C, Chen S, Lai C, Reneker DH, Qiu H, Ye Y, Hou H. *Nanotechnology* 2006; 17: 1558-1563.
19. Zhang L, Hsieh YL. *Nanotechnology* 2006; 17: 4416-4423.
20. Wang C, Hsu C H, Hwang ich. *Polymer* 2008; 49: 4188-4195.
21. Reneker DH, Chun I. *Nanotechnology* 1996; 7: 216-223.
22. Zong X, Kim K, Fang D, Ran S, Hsiao BS and Chu B. *Polymer* 2002; 43: 4403-4412.
23. Lin K, Chua KN, Christopherson GT, Lim S and Mao HQ. *Polymer* 2007; 48: 6384-6394.
24. Zhou H, Green TB and Joo YL. *Polymer* 2006; 47: 7497-7505.
25. Givens SR, Gardner KH, Rabolt JF and Chase DB. *Macromolecules* 2007; 40: 608-610.
26. Wang C, Chien HS, Hsu CH, Wang YC, Wang CT and Lu HA. *Macromolecules* 2007; 40: 7973-7983.
27. Iijima S. *Nature* 1991; 354: 56-58.
28. Iijima S and Ichihashi T. *Nature* 1993; 363: 603-605.
29. Wang C, Chien HS, Yan KW, Hung CL, Hung KL, Tsai SJ and Jhang HJ. *Polymer* 2009; 50: 6100-6110.

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