Title	Preliminary study on solvent effect in fiber fabrication in near-field electrospinning
Author(s)	Sudipta Bain; Pisut Koomsap
Citation	Sudipta Bain, & Pisut Koomsap. (2016). Preliminary study on solvent effect in fiber fabrication in near-field electrospinning. Proceedings of the 2nd International Conference on Progress in Additive Manufacturing (Pro-AM 2016), 415-420.
Date	2016
URL	http://hdl.handle.net/10220/41764
Rights	© 2016 by Pro-AM 2016 Organizers. Published by Research Publishing, Singapore

PRELIMINARY STUDY ON SOLVENT EFFECT IN FIBER FABRICATION IN NEAR-FIELD ELECTROSPINNING

SUDIPTA BAIN, PISUT KOOMSAP*

Industrial and Manufacturing Engineering, Asian Institute of Technology
Pathumthani, Thailand

ABSTRACT: Recently, near-field electrospinning (NFES) has been applied in additive manufacturing (AM) for the creation of scaffolds with controllable patterns from a polymer solution. Although the patterns can be achieved, fibers are deposited in liquid form due to insufficient solidification time. The buildup of the third dimension remains a challenge for this technique using a short standoff distance. This paper presents a preliminary study concerning the influence of solvents on the solidification of the fibers formed. Dimethylformamide (DMF) and Dichloromethane (DCM) having much different boiling points were two solvents used in this investigation. Results shows that the boiling temperature of the solvent had influence on the solidification of the fibers leading to different obtained diameters. DCM having much lower boiling temperature delivered the thinner fibers than DMF.

KEYWORDS: Near-field electrospinning, ESRP, PCL, DMF, DCM

INTRODUCTION

Electrospinning, a conventional process that applies electrical charge to draw a fiber from a polymer solution, has gained popularity during the last few decades when research has advanced towards microscale and nanoscale applications. In tissue engineering, electrospinning has been applied to produce scaffolds that are porous support structures for cell attachment, proliferation and differentiation. Its fiber morphology tunability can be used to control scaffold mechanical properties, degradation rate and cell behavior (Nezarati et al., 2013). However, a random fiber deposition limits an ability to control the construction of internal channels inside the scaffolds (Lam et al., 2002). Consequently, cells tend to grow on the surface instead of penetrating inside the scaffolds (Li et al., 2014).

The ability to control the pattern of fiber deposition has been an interest of researchers because it will help improve the performance of electrospinning, and near-field electrospinning (NFES) has been one approach for keeping the jet straight during the deposition by shortening a standoff distance between a needle tip and a collector to be within the straight part of a trajectory (Sun et al., 2006). NFES was investigated for a layer-by-layer fabrication (Auyson et al., 2013) and a result has led to the development of an in-house AM technique, called electrospinning-based rapid prototyping (ESRP), for the fabrication of a scaffold with a controllable pattern of fine fibers from a polymer solution (Chanthakulchan et al., 2015a). Similar technique, called E-jetting, is also available for the fiber creation but from a liquid melt instead of the solution (Li et al., 2014).

According to Chanthakulchan et al., (2015a), the creation of patterns was controllable; repeatable and reproducible, but because the distance was shorten, large amount of a solvent remained in the

Proc. of the 2nd Intl. Conf. on Progress in Additive Manufacturing
Edited by Chee Kai Chua, Wai Yee Yeong, Ming Jen Tan, Erjia Liu and Shu Beng Tor

Published by Research Publishing, Singapore
ISSN: 2424-8967

jet and the majority of solidification process happened on the collector. Consequently, the fibers were ribbon-like, and the fibers laid along y-axis were larger than those laid along x-axis because of vibration. Additional investigation indicated that the fiber diameter reduced when the standoff distance increased, that airflow had slight effect on the fiber diameter and on the deposition precision, and that the influence of relative humidity was unclear (Chanthakulchan et al., 2015b). To obtain the deposition of a cylindrical fine fiber, the polymer jet should be solidified by the time it reaches the collector. Increasing a solidification time can be done to certain extent because the jet trajectory become random for the long standoff distance. Besides, the solidification also depends upon the evaporation of the solvent contained in the jet. Therefore, presented in this paper is the investigation on the influence of solvents on the ESRP-based fabricated fibers. Two solvents having much different boiling temperatures along with their mixed solvents at different compositions were studied.

INVSTIGATING INFLUENCE OF SOLVENT

In traditional far-field electrospinning (FFES), the diameter of a created fiber decreases with the increase of the boiling point of a solvent (Wannatong et al., 2004). This might be because the slow evaporation of a high boiling point solvent allows the polymer jet to solidify slowly and to experience whipping effect when an unsolidified fiber is stretched significantly. On the other hand, a low boiling point solvent evaporates quickly and expedites the solidification of the fiber. The solidified fiber cannot be stretched much when whipping effect occurs.

However, whipping effect does not occur in case of NFES, and the influence of the solvents may be opposite. As aforementioned, the fibers that were fabricated by ESRP from previous study were in liquid form when they reached the collector. The solvent used in the study was Dimethylformamide (DMF) that has high boiling point (152-154 ^{0}C). It was foreseen that the fiber would be solidified quicker if a low boiling point solvent was used instead. Majority or all of solvent would evaporate during the polymer jet traveled. The fiber was expected to be dry and be able to maintain its shape when it reached the collector.

Therefore, experiments have been conducted to investigate the influence of the evaporation of solvent on the ability to produce a controllable pattern of cylindrical fine fibers. Dichloromethane (DCM) that its boiling point is between 39-42^{0}C was selected for the low boiling point solvent and DMF was selected for the high boiling point solvent. Their mixed solvents were also investigated. Since DCM and DMF have much different boiling points, all DCM will evaporate first from the mixed solvent prior to the evaporation of DMF. The composition of DCM and DMF in the mixed solvents could also play a role in the fiber solidification.

Material preparation

In this study, polymer material was Polycaprolactone (PCL) with molecular weight 45000 g/mol obtained from Sigma Aldrich Chemistry, and solvents were N, N-Dimethylformamide (DMF) with Mn 73.10 g/mol from QReC and Dichloromethane (DCM) with Mn 84.93 g/mol from eMerck KGaA EMSURE. Five compositions of DMF/DCM were used in this study: 100/0, 75/25, 50/50, 25/75, and 0/100. The solutions of 70% weight ratio of PCL in these mixed solvents were prepared. For the solutions contained high amount of DMF (i.e., 100/0 and 75/25), the substances were mixed together and placed on a stirring machine at 80^{0}C for 15 minutes and then cooled down to room temperature. For others, the mixtures were stirred for 3-4 hours at room temperature.

Sample

Single layers along y-axis were created for all samples initially. The dimension of all samples was 15mm x 20mm with 500 µm gap size. In case that the fiber deposited randomly, the second layers along x-axis were created also for comparison.

Machine setup

For the fabrication of each sample, an aluminum foil was placed on a collector platform and connected to a ground line while a positive line of a power supply was connected to the tip of a needle that was set 11 mm above the collector. Three sizes of needles were used in this study: 22G, 24G and 26G. Their inner diameters are 413, 311 and 260 µm, and their outer diameters are 717, 565 and 463 µm respectively. The collector's speed was set at 200 mm/s with acceleration and deceleration of 50mm/s^2. A syringe pump was used to feed the solutions.

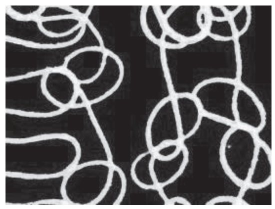
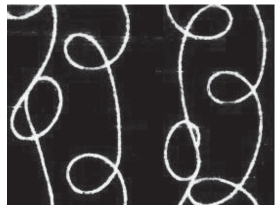
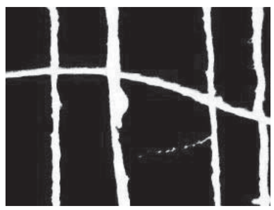
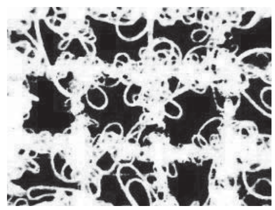
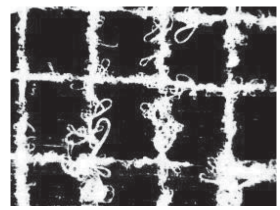
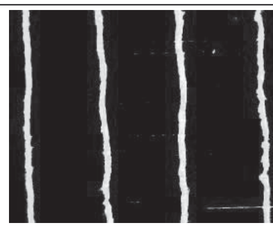
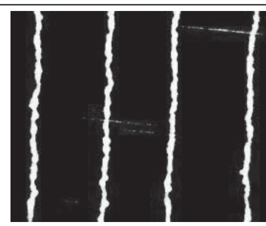
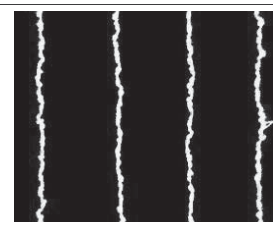
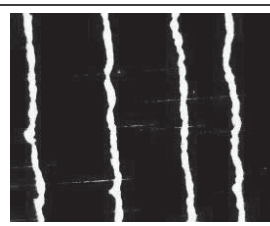
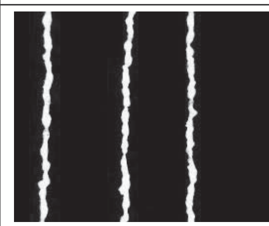
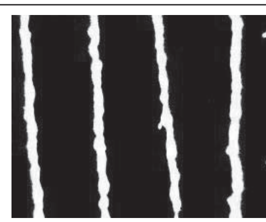
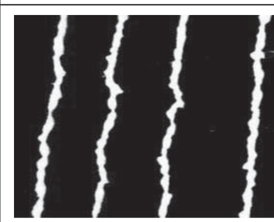
Evaluation method

An USB digital microscope with digital microscope software was used to take the images of fabricated fiber patterns. The resolution of the magnified images varied from 2.77µm to 2.94µm per pixel. The diameter of the fiber was averaged from the measurements at three positions, head, middle and tail of the fiber and for each sample, an average fiber diameter was calculated from the averages of three randomly picked fibers.

RESULTS AND DISCUSSION

Fifteen combinations of five composition levels of mixed solvents of DMF/DCM and three needle sizes were experimented. Three samples were made for each combination. Examples of the fabricated patterns are shown in Table 1. It can be seen that the straight fibers were obtained when the polymer jets contained high amount of DMF. The introduction of DCM into the solutions helped reduce the fiber size. However, the fibers were randomly deposited when the polymer jets contained high amount of DCM. The fiber diameter was also influenced by the needle size. The smaller the needle was, the smaller the fiber would be. However, the influence of the solution composition decreased as the needle size decreased. The influences of the two factors are illustrated in Figure 1. The results from two-way ANOVA, as shown in Figure 2, confirm that the solution composition, needle size and their interaction have significant effect on the fiber diameter (i.e., their p-values were less than 0.05). The obtained results were different from those reported for the traditional FFES. The fibers were large for 100% DMF because of the expansion of the liquid jet after landed on the collector. DMF has high boiling point; therefore, much higher voltage and longer standoff distance are required to create a fiber (Son et al., 2004). The created fiber is small for FFES because DMF has high dielectric constant that has an influence on fiber stretching during whipping effect occurs. The reduction in diameter when the mixed solvents were used indicates that the slow evaporation of DMF caused the large fiber. The random deposition of the fibers was a surprise for the solutions with high amount of DCM because DCM has low dielectric constant and the solutions have much higher viscosity than the solutions with 100% DMF. In fact, a solution with high viscosity has better resistant to whipping effect, and low dielectric constant of a solvent limits the availability of free charge in the solution which is necessary for initiating the bending instability (Sun et al., 2012). The presence of whipping effect might be because the high evaporation rate of DCM increased surface tension on a droplet and large amount of charge was required to overcome the surface tension. This large amount of charge also created repulsive forces and initiated whipping effect quickly. According to the results, mixed solvent is recommended for achieving the fabrication of a controllable pattern of cylindrical fine fibers.

Table 1. Obtained fibers from different compositions of mixed solvent and needle sizes

DMF/DCM Ratio	Needle Gauge		
	22G	24G	26G
0/100			
25/75			
50/50			
75/25			
100/0			

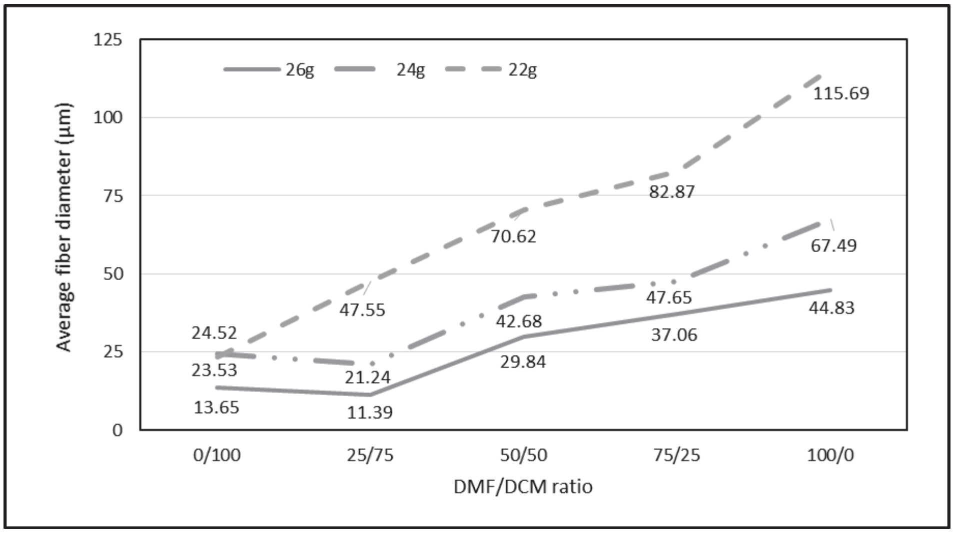


Figure 1. The influence of mixed solvent and needle size on fiber diameter

Two-way ANOVA: Diameter versus Needle, Composition

```
Source       DF       SS       MS      F      P
Needle        2  12924.8  6462.39  65.74  0.000
Composition   4  18159.3  4539.83  46.19  0.000
Interaction   8   3323.1   415.39   4.23  0.002
Error        30   2948.9    98.30
Total        44  37356.0

S = 9.914   R-Sq = 92.11%   R-Sq(adj) = 88.42%

                  Individual 95% CIs For Mean Based on
                  Pooled StDev
Needle     Mean  -----+---------+---------+---------+----
22g     68.0740                           (--*---)
24g     40.7193           (--*---)
26g     27.3547  (--*---)
                 -----+---------+---------+---------+----
                     30        45        60        75

                       Individual 95% CIs For Mean Based on
                       Pooled StDev
Composition     Mean  ---+---------+---------+---------+------
0/100        20.5778  (--*---)
25/75        26.7289     (--*---)
50/50        47.7156               (---*--)
75/25        55.8622                    (--*--)
100/0        76.0289                              (--*--)
                      ---+---------+---------+---------+------
                        20        40        60        80
```

Figure 2. Two-way ANOVA on diameter versus needle size and solution composition

CONCLUSIONS

The experiments were conducted to investigate the effects of solvents in fiber fabrication. The results show that the boiling point of a solvent has an effect on the fiber formation and on the pattern creation, and the mixed solvent is recommended. To achieve a controllable pattern of small fibers with a needle smaller than 26G will require a solution with high portion of a high boiling point solvent but the fiber will not be much smaller because the fiber reduction rate decreased as the needle size decreased.

REFERENCES

Auyson, K., et al. (2013). "Investigation of applying electrospinning in fused deposition modeling for scaffold fabrication", *In: High Value Manufacturing: Advanced Research in Virtual and Rapid Prototyping: Proceedings of the 6th International Conference on Advanced Research in Virtual and Rapid Prototyping*, Leiria, Portugal, October, 2013, 149 -154.

Chanthakulchan, A., Koomsap, P., Auyson, K., & Supaphol, P. (2015a). "Development of an electrospinning-based rapid prototyping for scaffold fabrication", *Rapid Prototyping Journal*, 21(3), 329-339.

Chanthakulchan, A., Koomsap, P., Parkhi, A.A., & Supaphol, P. (2015b) "Environmental effects in fibre fabrication using electrispinning-based rapid prototyping", *Visual and Physical Prototyping*, 10(4), 227-237.

Lam, C.X.F., Mo, X.M., Teoh, S.H., & Hutmacher, D.W. (2002). "Scaffold development using 3D printing with a starch-based polymer", *Material Science and Engineering C*, 20(1-2), 49-56.

Li, J.L., Cai, Y.L., Guo, Y. L., Fuh, J.Y.H., Sun, J., Hong, G.S., Lam, R.N., Wong, Y.S., Wang, W., Tay, B.Y., & Thian, E.S. (2014). "Fabrication of three-dimensional porous scaffolds with controlled filament orientation and large pore size via an improved E-jetting technique", *Journal of Biomedical Materials Research B: Appplied Biomaterials,* 102B(4), 651-658.

Nezarati, R.M., Eifert, M.B. & Hernandez, E.C. (2013). "Effects of humidity and solution viscosity on electrospun fiber morphology", *Tissue Engineering: Part C*, 19(10), 810-819.

Son, W. K., Youk, J. H., Lee, T. S., and Park, W.H. (2004), "The effects of solution properties and polyelectrolyte on electrospinning of ultrafine poly(ethylene oxide) fibers", *Polymer*, 45, 2959-2966.

Sun, D.H., Chang, C., Li, S., & Lin, L.W. (2006), "Near-field electrospinning", *Nano Letters*, 6, 839-842.

Sun, Z., Deitzel, J. M., Knopf, J., Chen, X., and Gillespie, Jr., J.W. (2012). "The effect of solvent dielectric properties on the collection of oriented electrospun fibers", *Journal of Applied Polymer Science*, 125, 2585-2594.

Wannatong, L., Sirivat, A. & Supaphol, P. (2004). "Effects of solvents on electrospun polymeric fibers: preliminary study on polystyrene", *Polymer International*, 53(11), 1851–1859.