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3D PRINTING OF POLYCAPROLACTONE MEMBRANE

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ABSTRACT: This paper presents a feasibility study of using 3D printing (or additive manufacturing) technique to fabricate polycaprolactone films and membranes. Polycaprolactone is a biocompatible and biodegradable polymer found in many medical applications. In this research, a desktop plotter is used to print polycaprolactone solution line by line. It has been demonstrated that the 3D printing process is able to print a film/membrane with anisotropic structure and pre-definable porosity. This process is different from solvent casting or electrospinning which has limited control over the structure of the film/membrane. This work offers an alternative approach for film/membrane fabrication, and the findings in this preliminary study are potentially useful for developing new medical devices.

INTRODUCTION

Films and membranes are widely used in many applications. Biodegradable films and membranes, whose thickness typically ranges from a few micrometers to a few hundred micrometers, are especially important in environmental and medical applications, such as environment-friendly packaging, wound dressing, and tissue engineering scaffolds. However, methods to make biodegradable films and membranes are currently limited. Solvent casting is the most common method to fabricate thin films [1, 2]. In this method, an organic solvent is used to dissolve a polymer, and then as the solvent evaporates, the dissolved polymer precipitates and forms a thin film. Electrospinning is a high voltage-based process for making fiber meshes [3, 4]. The high voltage causes jetting behavior of polymer solution at the nozzle tip. Slowly, fibers build up on the collector and form a porous membrane. Biaxial-drawing is a method to make thin films by stretching a polymer pre-form [1, 5, 6]. Though these methods can be used to produce films or membranes as final products, they have limited control over the structure of the films and membranes during the fabrication process, meaning that the films/membranes fabricated by these methods are generally isotropic and the porosity can hardly be pre-defined.

3D printing, also known as additive manufacturing or rapid prototyping, is a group of technologies that fabricates freeform object in a layer by layer manner [7]. Due to the advantages of automation, free-form fabrication, customization and very high controllability over external shape and internal porous structure, 3D printing is well suited for tissue engineering and regenerative medicine applications [8-10], including indirect fabrication [11-13]. It is even believed that 3DP printing will help create three dimensional organized tissues or organs in future [14]. Polycaprolactone is a biocompatible and biodegradable synthetic polymer. It can be easily processed into 3D structures, for example, it can be 3D printed into porous scaffolds [15-17], 3D laser sintered into drug delivery devices [18, 19], and melt spun into 3D aligned microfibers [20-22]. However, it is unclear if polycaprolactone could be 3D printed into a thin film or membrane. In addition, in 3D printing, a user is able to decide the way an object is built. For example, a cylinder can be built in two ways (shown in Figure 1), which could result in two structures of different properties [7]. This triggers the question if 3D printing could print film/membranes of

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different properties by simply changing the way of building it. This motivates us to propose an alternative approach for fabricating biodegradable films and membranes. Therefore, the objective of this preliminary study is to examine the feasibility of 3D printing polycaprolactone films and membranes.

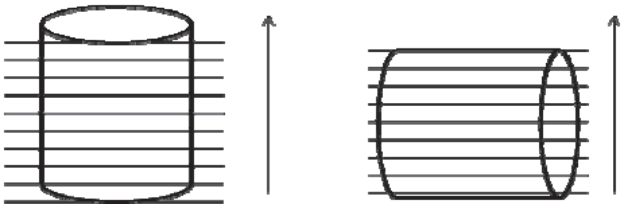

Figure 1: A cylinder is layer-by-layer built in different directions.

MATERIALS & METHOD

Briefly, 0.5 gram of polycaprolactone powder (CAPA 6501, Perstorp) was dissolved in 10 ml of chloroform and then the solution was poured into a 5 cc syringe. The barrel of the syringe was closed with a plunger and connected to a nozzle tip (Gauge: 25G). After that, it was amounted to a 3D liquid dispenser (Model: DR3331T, Technodigm, Singapore). A glass slide was fixed on the stage as substrate to be printed on. A simple point program (shown in Figure 2) was edited in the control panel to print a solid polycaprolactone film. Similarly, the program was modified to print a polycaprolactone grid. A PDP 1000 High Precision Controller (Technodigm, Singapore) was used to control the dispensing process. The extrusion speed was set at 0.0001 mm/s, retract speed 0.001 mm/s and retract distance 0.001 mm.

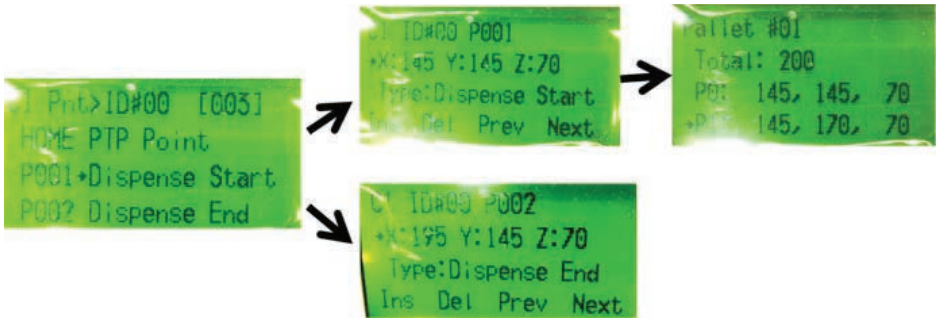

Figure 2: An example code of for printing a solid polycaprolactone film. The printing area (X x Y mm) is 50 x 25 mm. The number of lines or tracks is 200.

Figure 3 shows the printing process. Initially, the polycaprolactone solution was extruded as droplet, but it spread quickly once in contact with substrate surface. As the extruded flow continued, the nozzle tip moved along defined path, generating a solution track. Then a solute track was left on the substrate following the immediate evaporation of the solvent. A solid film

was printed by dispensing overlapping tracks in one layer. A grid pattern was printed by dispensing discrete tracks in two layers.

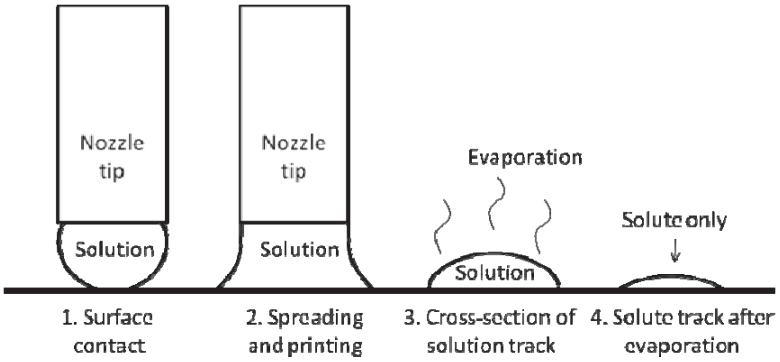

Figure 3: A schematic of printing one track.

RESULTS AND DISCUSSION

Solvent casting and electrospinning are common methods to fabricate thin films and membranes. The film made by solvent casting is an isotropic solid and does not have any porosity. The membrane fabricated by electrospinning is generally porous but usually have no anisotropic structure, unless in some cases the fibers are aligned. However, the porosity of electrospun membranes can hardly be pre-defined. Instead, the porosity is usually measured after the membrane is fabricated. In other words, both processes have limited control over the structure of the membrane.

Different from solvent casting and electrospinning, 3D printing offer the possibility of controlling the structure of films/membranes and printing both isotropic and anisotropic films as well as membranes with pre-defined porosity. Figure 4 shows a printed polycaprolactone film. The film is 25 mm x 50 mm and consists of 200 overlapping tracks. On the whole, it is a transparent film, but when broken down, it is 200 lines. The line-by-line principle is analogous to the layer-by-layer principle in additive manufacturing. Apparently, the film looks no difference from solvent casted films, but because of the distinct structure, it is hypothesized that this film is anisotropic and has distinct optical and mechanical properties. However, systematic characterization of the films is beyond the scope of this feasibility study, and will be completed in future. Another point to note is that with proper handling, the film can be easily removed from the glass surface and remain intact, as shown in figure on the right.

Figure 5 shows a printed polycaprolactone mesh. The grid is 15 mm x 15 mm and consists of two layers. The size of the pore can be represented by the spacing between parallel polycaprolactone tracks. The spacing depends on the total number of tracks set in the program. Therefore, pore size and porosity is not random, but controlled with order. This is distinct from electrospun meshes.

Due to dripping effect, the start and end of each track will always have more materials than the track line. The accumulated solution drops coalesce and become larger and larger, forming solid edges. This phenomenon can be easily observed in both Figure 4 and Figure 5 and is difficult to be completely avoided. Therefore, it is suggested to increase the size of printed film/ membrane so as to rendering the solid edges insignificant when compared to the inner region.

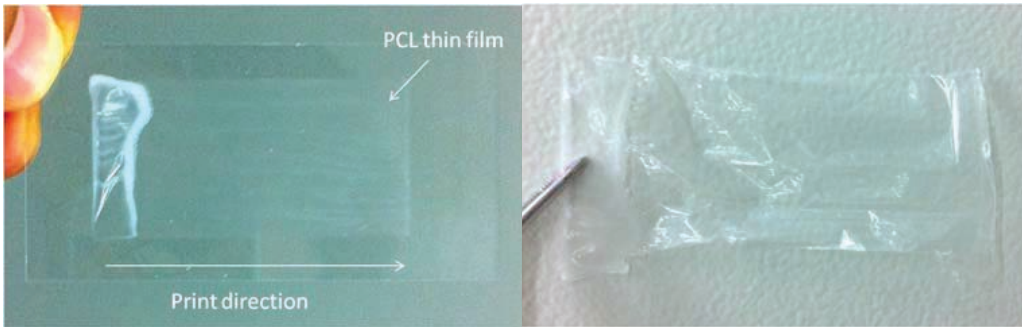

Figure 4: Printed polycaprolactone thin film with anisotropic structure.

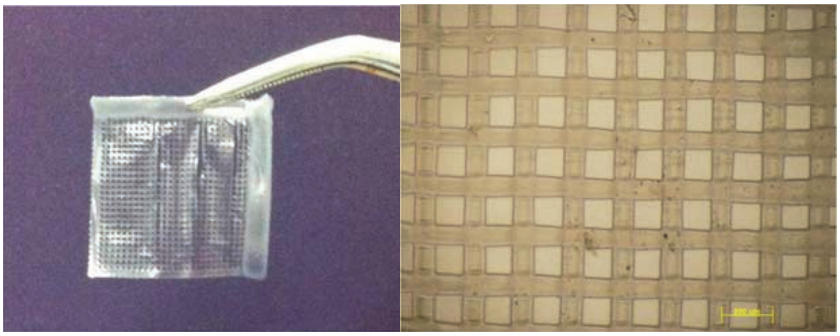

Figure 5: Printed polycaprolactone mesh. Scale bar: 500 μm.

Although current work is limited to printing polycaprolactone alone, it is possible to generalize this approach and print other polymer solutions to serve different purposes and applications. It is also possible to add additional chemicals such as drugs into the solution for incorporation. Therefore, this film printing technique is versatile and promising to be used for a variety of applications.

CONCLUSION

This paper describes a preliminary study of using 3D dispenser to print a thin polycaprolactone thin film/membrane. The goal of this study is to examine the feasibility and identify potential research directions. It has been demonstrated that a thin film/membrane can be successfully printed by a 3D liquid dispenser. The process is controllable, simple and fast. More importantly, it enables the possibility of printing anisotropic films and membranes with pre-definable porosity (from zero to highly porous). The printed film/membrane is potentially useful for developing new medical devices. Future works of this research include process optimization, fabrication and characterization, and applications in biomedical field such as tissue engineering and drug delivery.

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REFERENCES

1. Yang, J., et al., *Fabrication and surface modification of macroporous poly(L-lactic acid) and poly(L-lactic-co-glycolic acid) (70/30) cell scaffolds for human skin fibroblast cell culture.* Journal of Biomedical Materials Research, 2002. **62**(3): p. 438-446.
2. Tiaw, K.S., et al., *Processing methods of ultrathin poly(ε-caprolactone) films for tissue engineering applications.* Biomacromolecules, 2007. **8**(3): p. 807-816.
3. Li, D. and Y. Xia, *Electrospinning of nanofibers: Reinventing the wheel?* Advanced Materials, 2004. **16**(14): p. 1151-1170.
4. Reneker, D.H. and I. Chun, *Nanometre diameter fibres of polymer, produced by electrospinning.* Nanotechnology, 1996. **7**(3): p. 216-223.
5. Kee Woei, N., et al., *Evaluation of ultra-thin poly(ε-caprolactone) films for tissue-engineered skin.* Tissue Engineering, 2001. **7**(4): p. 441-455.
6. Cheng, Z. and S.H. Teoh, *Surface modification of ultra thin poly (ε-caprolactone) films using acrylic acid and collagen.* Biomaterials, 2004. **25**(11): p. 1991-2001.
7. Chua, C.K., K.F. Leong, and C.S. Lim, *Rapid Prototyping: Principles and Applications (3rd edition)*2010: World Scientific.
8. Bártolo, P.J., et al., *Biomanufacturing for tissue engineering: Present and future trends.* Virtual and Physical Prototyping, 2009. **4**(4): p. 203-216.
9. Derby, B., *Printing and prototyping of tissues and scaffolds.* Science, 2012. **338**(6109): p. 921-926.
10. Chua, C.K., M.J.J. Liu, and S.M. Chou. *Additive manufacturing-assisted scaffold-based tissue engineering*. in *Innovative Developments in Virtual and Physical Prototyping - Proceedings of the 5th International Conference on Advanced Research and Rapid Prototyping*. 2012.
11. Tan, J.Y., C.K. Chua, and K.F. Leong, *Indirect fabrication of gelatin scaffolds using rapid prototyping technology.* Virtual and Physical Prototyping, 2010. **5**(1): p. 45-53.
12. Liu, M.J.J., et al., *The development of silk fibroin scaffolds using an indirect rapid prototyping approach: Morphological analysis and cell growth monitoring by spectral-domain optical coherence tomography.* Medical Engineering and Physics, 2013. **35**(2): p. 253-262.
13. Tan, J.Y., C.K. Chua, and K.F. Leong, *Fabrication of channeled scaffolds with ordered array of micro-pores through microsphere leaching and indirect Rapid Prototyping technique.* Biomedical Microdevices, 2013. **15**(1): p. 83-96.
14. An, J., et al., *Advanced nanobiomaterial strategies for the development of organized tissue engineering constructs.* Nanomedicine, 2013. **8**(4): p. 591-602.
15. Yeong, W.Y., et al., *Porous polycaprolactone scaffold for cardiac tissue engineering fabricated by selective laser sintering.* Acta Biomaterialia, 2010. **6**(6): p. 2028-2034.
16. Liao, H.T., et al., *Fabrication of tissue engineered PCL scaffold by selective laser-sintered machine for osteogeneisis of adipose-derived stem cells: The research has proven that a bone tissue-engineered scaffold can be made using the selective laser sintering method.* Virtual and Physical Prototyping, 2011. **6**(1): p. 57-60.
17. Sudarmadji, N., et al., *Investigation of the mechanical properties and porosity relationships in selective laser-sintered polyhedral for functionally graded scaffolds.* Acta Biomaterialia, 2011. **7**(2): p. 530-537.
18. Leong, K.F., et al., *Building porous biopolymeric microstructures for controlled drug delivery devices using selective laser sintering.* International Journal of Advanced Manufacturing Technology, 2006. **31**(5-6): p. 483-489.

19. Leong, K.F., et al., *Characterization of a poly-ε-caprolactone polymeric drug delivery device built by selective laser sintering.* Bio-Medical Materials and Engineering, 2007. **17**(3): p. 147-157.
20. Liu, A., et al., *A portable device for fabricating biomaterial microfiber bundles.* Key Engneering Materials, 2010. **447 448**: p. 750-754.
21. An, J., et al., *Solvent-free fabrication of three dimensionally aligned polycaprolactone microfibers for engineering of anisotropic tissues.* Biomedical Microdevices, 2012. **14**(5): p. 863-872.
22. Sun, G., et al., *Clothing polymer fibers with well-aligned and high-aspect ratio carbon nanotubes.* Nanoscale, 2013. **5**(7): p. 2870-2874.