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SYNTHETIC VASCULAR MATERIALS VIA A VAPORIZATION OF SACRIFICIAL
COMPONENT (VaSC) APPROACH

BY

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DISSERTATION

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ABSTRACT

The introduction of microchannels into traditional composites has numerous applications ranging from self-healing to autonomous cooling materials. However, current approaches for microvascularization are hindered by scalability and lack of compatibility with the composite manufacturing process. Herein, we present the development of a new procedure for incorporating microchannels into composites that overcome these limitations. Namely, the vaporization of sacrificial component (VaSC). The chosen sacrificial material, poly(lactic acid) (PLA), can be easily incorporated into composites and undergoes a solid-to-gas transition at ca. 280 °C, which allows for the extraction of the gaseous product from the composite leaving hollow spaces in the matrix. The fabrication of a microvascular composite by this method necessitated the development of PLA sacrificial fibers, and three distinct production techniques for producing the desired PLA fibers were explored (chemical modification of commercial PLA fibers, homespun PLA fibers, and micro-structuring of a PLA film). The dissertation also discusses the coated sacrificial fibers (CSFs) as a building block for biomimetic vascular structures.

In addition, the fabrication of a microporous battery separator *via* a similar VaSC approach was developed. In order to improve the safety of automobile battery systems, we sought to apply produce a thermally stable battery separator that prevents cell shortage by establishing a high-temperature fabrication route. A solution containing PLA and polyimide (PI) was cast into form a biphasic film; thermal removal of the PLA phase left a microporous PI film. Experimental evidence showed that the microporous PI film that was fabricated using the PLA sacrificial component had superior thermal properties and could potentially replace current commercial separators.

To Mom and Dad

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CHAPTER 1

INTRODUCTION

1.1 Self-Healing Materials

1.1.1 Design and Development of Self-Healing Materials

Natural materials have evolved fascinating self-healing mechanisms to sustain themselves. In the case of superficial injuries in mammal organisms, a vascular network (e.g., the circulatory system) helps to restore and heal mechanical damage *via* a blood-clotting cascade and subsequent tissue regeneration. A similar natural autonomic self-healing system that functions without any external stimulus occurs when the different organs of a latex-bearing plant are injured. In this example, latex oozes out and very efficiently seals the lesion through coagulation. More specifically, this plant species stores latex is under high pressure (7–15 bar) in the laticifer such that upon injury, the pressure in the laticifer drops from 7 bar to ambient pressure (ca. 1 bar) causing the luteoids to burst and the protein Hevein to be released, ultimately healing the injury.¹⁻³ These self-healing approaches in mammals and plants, as well as other living systems, offer a vast array of inspiration for developing biomimetic synthetic materials and structures with self-healing properties.

A number of methods have been developed to achieve self-healing in synthetic materials. Introducing reversible cross-linking reactions (such as Diels-Alder and retro DA reaction,⁴⁻⁶ ionomers,⁷⁻⁹ and supermolecular polymers¹⁰⁻¹²) in polymeric systems often enables the material with self-healing properties; however, the reported systems do not

show autonomic self-healing ability and an external trigger such as thermal, photo, or chemical stimulus is needed to achieve reversibility, and thereby the self-healing ability.

Shape memory materials can also exhibit self-healing abilities under given circumstances.¹³⁻¹⁴ Shape memory alloys (SMAs), such as Nitinol (nickel–titanium), exhibit self-healing when heated.¹⁵ For instance, if these alloys are permanently deformed and heated above certain temperatures, they will return to their original shape. Unfortunately, the need for external intervention (such as heat) limits the applications of these materials.

One large area of self-healing materials is based on the underlying concept of healing through the compartmentalization of reactive phases. In order to impart a synthetic material with entirely “autonomous” healing functionality, the materials are designed to store a latent self-healing agent that is released only when triggered. The technical scope of compartmentalization includes two different types of materials systems: 1) capsule-based technologies and 2) microvascular systems (**Figure 1.1**). Briefly, the capsule-based systems incorporate a healing agent in discrete spherical shells, which can be ruptured by mechanical damage. Similarly, vascular systems carry healing agents in a network of channels such that when damage ruptures the vasculature the healing agent can be delivered to the wound site.

1.1.2 Microcapsule-Based Self-Healing Materials

The general scheme for a capsule-based self-healing system is shown in **Figure 1.2**. In this example, damage causes a crack to form in the material, which eventually propagates until it ruptures the microcapsules that contain a healing agent. The healing agent then

flows into the crack plane driven by capillary forces, and undergoes polymerization, rebonding the crack faces. The entire process is triggered by damage, and recovery occurs under ambient conditions requiring no human intervention.

White and co-workers¹⁶⁻²¹ originally developed a self-healing epoxy based on a ring-opening metathesis polymerization (ROMP) reaction between microencapsulated dicyclopentadiene (DCPD) and Grubbs catalyst that is dispersed throughout the epoxy matrix. Cracks caused by mechanical damage rupture the microcapsules and release the liquid DCPD into the crack plane through capillary action. When DCPD comes in contact with the embedded Grubbs catalyst, the ROMP reaction occurs and results in the formation of cross-linked polyDCPD.

Other modified routes that employ the microcapsule/catalyst systems to achieve self-healing were later reported.^{20,22,23} Rule et al. incorporated Grubbs' catalyst into wax microspheres to protect the Grubbs' catalyst from premature degradation, showing ca. 100% healing efficiency.²⁰ Jones et al. examined the role of the crystal morphology and dissolution kinetics of Grubbs' catalyst on the materials self-healing capability.²⁴ The use of an alternative metathesis catalyst or healing chemistry has also been extensively explored. Second generation Grubbs' catalyst,²⁵ Hoveyda Grubbs' catalyst,^{25,26} and tungsten hexachloride (WCl_6) catalyst^{27,28} have all shown moderate levels of healing in fracture testing. More recently, Coope et al. demonstrated self-healing using encapsulated epoxy resin and scandium(III) triflate catalyst particles.²⁹

Polydimethylsiloxane (PDMS) has also been exploited for self-healing materials. In one demonstration, the component PDMS and polydiethoxysiloxane (PDES) were phase-

separated as droplets suspended in an epoxy vinyl ester matrix. This matrix also contained microcapsules of the catalyst, dibutyltin dilaurate (DBTL), dissolved in chlorobenzene.³⁰ Upon mechanical damage, the microcapsules ruptured, releasing the catalyst into the crack plane, thus initiating the formation of PDMS. Later studies involved a two-capsule PDMS system in which a platinum-based catalyst and PDMS precursor were encapsulated in one capsule while the hydrosiloxane initiator was encapsulated in another.³¹ When the contents of both capsules were transported into the crack plane, hydrosilylation occurred, resulting in a cross-linked PDMS network. Based on tear strength recovery 48 h after the initial damage had occurred, healing efficiencies of 70–100% were reported.³¹ The same PDMS chemistry was also used in a self-healing flexible laminate composite in which puncture holes were sealed upon the polymerization of the encapsulated PDMS and catalyst components.³² The effectiveness of this self-healing elastomer was defined by its ability to prevent gas leakage through a punctured composite using a pressure test cell.

Caruso and co-workers^{33,34} developed a self-healing approach that is based on solvent encapsulation. Solvent-filled microcapsules were incorporated into thermoset matrices and thermoplastic materials such as poly(methyl methacrylate) and the healing performance was demonstrated. When microcapsules with solvent cores were incorporated into an epoxy thermoset, the release of the solvent upon damage promoted the mobility of any residual functional groups in the material to entangle and react across the crack plane, which rendered the material autonomically self-healing.³³ Full recovery of fracture toughness was achieved for a thermoset matrix that incorporated microcapsules containing unreacted epoxy monomer dissolved in the solvent.³⁴ Upon

crack damage, the embedded capsules ruptured to release their components; the unreacted epoxy reacted with the residual amines in the matrix, healing the matrix with up to 100% efficiency. More environmentally friendly solvents (e.g., ethyl phenylacetate and phenylacetate) were employed as healing agents, showing promise for a commercial system.³⁴

1.1.3 Microvascular Self-Healing Materials

Although self-healing materials based on a capsule system showed significant mechanical recovery, these materials are limited to autonomous repair of a single damage event in a given location. Once the capsules are depleted of healing agent, no further healing events can happen. For enhanced lifetime and extended usability in structural applications, a system capable of multiple healing events is desirable.

Materials systems with microvascular networks were created to mimic biological circulatory systems.³⁵ In these systems, the healing agent is continuously replenished to the site of damage. For example, Toohey and co-workers³⁶ designed a microvascular system that allows the self-healing species to be continuously circulated within a vascular network inside the material, enabling multiple healing events. Briefly, they formed a three-dimensional microvascular network in a substrate and DCPD was stored in the embedded network. Later, Toohey and coworkers³⁷ reported an increase in the number of healing cycles by designing the microvascular substrates with two separated liquid components of two-part epoxy chemistry. Upon damage, the two-component epoxy resin and hardener were both released into the damaged region, where they mixed and cured. Hansen et al.³⁸ improved upon this approach by creating interpenetrating microvascular

networks capable of segregating a two-part epoxy healing chemistry while minimizing the separation between the two healing agents to facilitate mixing in the damaged region.

Toohey and Hansen's approaches were based on a direct-write assembly technique, in which a vascular pattern was written using fugitive wax as ink. Unfortunately this method is not suitable for creating networks in continuous fiber composites due to the high pressures and temperatures required for processing these materials. The method is also limited in scale and speed, making it impractical for commercial composite manufacturing.

Another method to create microchannels is to use hollow glass fibers. Self-healing using hollow fibers embedded within an engineering structure, similar to the arteries in a natural system, has been investigated at different length scales in different engineering materials by various authors, for example: bulk concrete,³⁹⁻⁴³ bulk polymers,⁴⁴ and polymeric composites at both a millimeter lengthscale⁴⁵ and micrometer length scale.⁴⁶⁻⁴⁸ The use of hollow glass fibers embedded in a composite laminate was pioneered by Bleay et al..⁴⁶ In their work, commercial hollow fibers were consolidated into lamina and then manufactured into composite laminates (the self-healing material acts as the structural fibers). The key advantage of the hollow fiber self-healing concept is that the fibers can be located to match the orientation of the surrounding reinforcing fibers thereby minimizing the Poisson's ratio effect and the mismatch of properties between the self-healing network and the host structural fibers. Using this method, the fibers can be placed at any location within the stacking sequence to address specific failure threats. Moreover, different healing resins can be used depending upon the operational requirements of the

structure, different activation methods can be used to cure the resin and crucially, a significant volume of healing agent can be made available.

Hollow glass fibers provide building blocks for introducing microchannels to structural composites. Bond and co-workers⁴⁸⁻⁵¹ have explored a two part epoxy chemistry stored within hollow glass fibers to heal a structural, fiber-reinforced epoxy composite. Their work has shown that a hollow-fiber self-healing approach can be used for the repair of advanced composite structures. It has also been shown that hollow glass fibers containing a two-part healing resin can be manufactured and incorporated within a standard autoclave processing technique, indicating that this healing approach could be readily applied to existing composite manufacturing techniques. Through the specific placement of four self-healing plies to match the critical damage threat, it has been shown that a standard commercial available two-part epoxy resin system (Cycom 823) can be used for the repair of internal matrix cracking and delaminations through the thickness of a 16-ply laminate.

The hollow glass fiber approach suffers from several challenges, including the relatively large diameter of the fibers compared to the reinforcement, the need for fiber fracture and low viscosity resin systems to facilitate fiber and damage infusion and the requisite extra processing stage for fiber infusion. More importantly, this approach is limited to one-dimensional vascular features only; it is nearly impossible to fabricate a two or three-dimensional interconnected microvascular network using hollow glass fibers.

In yet another approach to creating microvascular structures, electrohydrodynamic viscous fingering (EHVF), a low viscosity, electrically conductive fluid at high voltage is

injected into a viscous dielectric fluid.⁵² The combination of electrostatic and viscous stresses drives the injecting fluid to form a hierarchical, branched structure. However, controlling the 3D microstructure and incorporating EHVF technique into traditional composite manufacturing methods limits the use of this method.

Other fabrication approaches such as laser micromachining,⁵³⁻⁵⁵ soft lithography⁵⁶⁻⁵⁹ and sugar and polyethylene fibers^{60,61} all produce microvascular structures, but none of these are suitable for rapid, large-scale production of fiber-reinforced composites with complex vasculatures due to either incompatibility with existing composites manufacturing methods and materials or lack of scalability and vascular complexity of the fabrication approach. Thus, to extend the reach of microvascular structures for large scale commercial applications,⁶² scalable microvascular fabrication methods are needed.

1.1.4 Introduction to Vaporization of Sacrificial Component (VaSC)

The integration of microchannels into a structural composite requires a fabrication route that is both scalable and robust. This dissertation presents a new method that is based on sacrificial fibers. Ideally the sacrificial fibers can be handled simultaneously with reinforcing fibers, and they will decompose under a defined external trigger, such as a critical processing temperature. Removal of the sacrificial fibers from the composite will yield an interconnected 3D microvascular network. The process is expected to be scalable, rapid, and easily integrated into existing composite manufacturing.

Microvascular composite fabrication begins with the mechanized weaving of sacrificial fibers into 3D woven glass preforms (**Figure1.3a**). The position, length, diameter, and curvature of fibers are varied to meet the desired design criteria. The interstitial pore

space between fibers is infiltrated with a low-viscosity thermosetting resin (e.g., epoxy) and cured at elevated temperature (**Figure 1.3b**). After curing, the sample is trimmed to expose the ends of the sacrificial fiber. The fiber is then removed by heating the sample above 200 °C to vaporize the fiber, yielding empty channels and a 3D vascular network throughout the composite (**Figure 1.3c**). This process is known as vaporization of sacrificial components (VaSC). After fiber removal, the microvascular composite can be filled with a fluid having the desired physical properties to create a multifunctional material (**Figure 1.3d**).

The sacrificial fibers used in the VaSC process must satisfy several criteria. First, the fiber must be strong enough to survive the mechanical weaving and vacuum infiltration process. Second, for the creation of complex geometries and large length-to-diameter aspect ratios, the fiber must remain solid during matrix curing (e.g., the polymer must be stable up to 180 °C) but then be easily removed *via* depolymerization to monomer vapor at higher temperatures. Finally, the depolymerization and gas production temperature must exist in a narrow range between the highest resin cure temperatures and lowest thermal degradation temperatures (200–240 °C).⁶⁸ When selecting materials, all these criteria should be met with the additional consideration of choosing a fiber that is industrial scalable and commercially available.

1.2 Poly(lactic acid) (PLA) as a Sacrificial Component

Poly(lactic acid) (PLA) is a thermoplastic that spontaneously depolymerizes into gaseous lactide monomers at temperatures above 280 °C. The degradation behavior of PLA has attracted widespread interest because of its bioabsorbable and environmentally-benign

depolymerization products.⁶³⁻⁶⁵ For example, Pitet and coworkers utilized PLA as a sacrificial component in copolymers to create porous membranes for battery separators.⁶⁶ Herein we explore the possibility of constructing high-aspect ratio microchannels by embedding sacrificial PLA fibers⁶⁷ in an epoxy thermoset and then triggering thermal depolymerization. The uncatalyzed depolymerization of PLA is realized by heating the polymer above 280 °C which results in the formation of lactide, a gaseous monomer at this temperature. However, existing epoxy processing protocols⁶⁸ demand milder processing conditions (i.e., a lower fiber depolymerization temperature to prevent thermal damage of the thermoset matrix). We demonstrated that minimal matrix damage can be realized by using a catalyst to lower the PLA depolymerization temperature.

Previously, Fan et al. found that poly(L-lactide) (PLLA) depolymerization temperature could be reduced by 90 °C when the PLLA was blended with calcium oxide and magnesium oxide.⁶⁹ They found that metal oxides both lowered the degradation temperature of PLLA and completely suppressed the production of oligomeric species as opposed to small molecule lactides. Similar results were reported by Mori et al. regarding the pyrolysis of PLLA containing tin reagents.⁷⁰ They reported a depolymerization process composed of backbiting and transesterification reactions caused by Sn-alkoxide chain ends. The tin catalyst promoted the cleavage of ester bonds in the polymer backbone, facilitating the fragmented polymer ends in chain backbiting and thus, depolymerization (**Figure 1.4**).⁶⁹⁻⁷¹

As noted by Otera in a review article,⁷² there are hundreds of other promoters that can be used to accelerate transesterification reactions and these various catalysts (from several

chemical categories) were screened to determine the optimum ones for sacrificial fiber development.

1.3 Development of Microporous Films for Battery Separators

1.3.1 The Importance of Battery Separators

An ideal energy storage system should possess high energy density, the ability to release power at a constant rate and a long life span, but foremost, it must be safe to operate. Recently, lithium-ion batteries⁷³⁻⁷⁵ have expanded into hybrid electric vehicle applications; thus, the safety issues of lithium-ion batteries are no longer slight lab-scale dissatisfactions, but rather, battery malfunctions could have a serious industrial and economic impact. Over the years researchers have been actively looking to address these safety issues from the view of novel functional materials. Among the many components of a lithium-ion battery that could lead to malfunctions, the battery separator is a crucial module that has direct influence on the battery's life, safety, and performance. The battery separator is a thin membrane encased in a lithium ion battery that is placed between cathode and anode in order to prevent physical contact between the two electrodes, but is porous so that the lithium ions can be transported between electrodes.⁷⁶⁻
⁷⁸ Commercially available battery separators – the most famous example being Celgard – are used widely in lithium-ion battery applications for their proper mechanical properties and electrochemical stability; however, they do not have a high thermal stability. Celgard shrinks at high temperature due to residual stress induced during the stretching and collapsing of pores, thus it causes an internal shortage between electrodes during battery operation.⁷⁹ This internal shortage will lead to accelerated electrochemical reactions that

could cause thermal runaway to take place, eventually resulting in safety hazard.⁸⁰ For high-density energy storage system, it would be beneficial to use a high temperature resistant battery separator in order to improve the safety, abuse tolerance and life span of the battery.

1.3.2 Previous Methods for Battery Separator Preparation

Recently, researchers have been actively pursuing solutions to the thermal shrinkage of commercial lithium-ion battery separators and there are several reported approaches aimed at diminishing thermal shrinkage of the separator. Song et al.⁸¹ coated a thin layer of polyimide on top of a commercial Celgard membrane and demonstrated enhanced thermal stability for the new material. Unfortunately, their strategy not only requires an extra step in separator manufacturing but also has issues in producing uniform coatings that adhere well to their substrates.

Another alternative material for high temperature lithium-ion battery separators are nonwoven fabrics. Several different approaches such as paper-making, wet-laid, melt-blowing, and electrospinning have been implemented in the successful fabrication of nonwoven films that have superior thermal stability compared to Celgard.⁸²⁻⁸⁹ For example, Jeong et al.⁸⁸ synthesized a PVDF-HFP/PET nonwoven fabric and demonstrated good porosity control and electrochemical performance. Choi further improved this approach⁸⁹ by coating the non-woven fabric with a layer of silicon nanoparticles to better control the porosity and pore sizes. However, nonwoven materials made with the wet-laid and melt-blowing methods tend to have unsatisfactorily large pore

sizes, and nonwovens made with electrospinning are limited by the high cost coating step and low throughput.

1.3.3 Fabrication of Microporous Films Using VaSC

Herein we explore an alternative, high temperature route to overcome the shortcomings of commercial separators. Our approach was based on a membrane material that utilizes a high melting point, chemically stable and electrochemically inert polymer. Polyimide (PI) was chosen due to its excellent thermal, chemical and mechanical properties. For the past few decades, the supreme properties of polyimide have enabled its applications in many research fields, such as nanofiltration membranes and high-temperature coatings. A second polymer, a thermal porogenic material, is introduced to form a biphasic membrane with the polyimide. The second phase, poly(lactic acid) (PLA), can be thermally depolymerized into gaseous products and result in a porous structure in the polyimide (**Figure 1.5**). The thermal degradation temperatures of polyimide and poly(lactic acid) are 480 °C and 280 °C, respectively. The 200 °C temperature difference allows for an operation window in which PLA can be removed to form pores while the polyimide remains unaffected.

There are a few previous reports in which a sacrificial component is used to fabricate a porous structure. Hillmyer and co-workers^{66,90,91} fabricated a porous film using a block copolymer consisting of polyethylene and poly(lactic acid), however, multiple synthesis steps and high cost limits its commercial application. In this work, both components, polyimide and poly(lactic acid), are commercially available at low cost, making the VaSC approach feasible for large-scale commercial production.

1.4 Overview of the Dissertation

Two categories of synthetic vascular materials are reported in this dissertation: microvascular materials for self-healing applications (Chapters 2, 3, 4 and 5) and microporous film for battery separator (Chapter 6). The fabrications of these materials rely on a PLA sacrificial component and the novel technique developed in this dissertation: Vaporization of Sacrificial Component (VaSC).

In Chapter 2, the process of treating a commercial PLA fiber using a catalyst is discussed. Various catalyst systems are screened and the best catalyst is chosen according to their performances. A solvent impregnation technique is used to incorporate the catalyst in the PLA fibers. Parameters significantly affect the incorporation and these parameters are studied in order to obtain the optimal procedure for fiber treatment. In addition, the depolymerization mechanism of PLA fiber degradation is studied.

Fibers produced using the method in Chapter 2 can be readily applied to microvascular composites manufacturing, however, since catalyst particles are limited on the fiber surface, the fibers would take long time to be removed. In Chapter 3, this limitation is solved by using a new fiber production method –fiber spinning to produce fibers with homogeneously distributed catalyst particles. Studies show that the homespun fibers greatly shorten the time needed to fully remove the fibers from the matrix, accelerating the manufacture process.

The microvasculature produced by using PLA fiber is limited in single channel geometry. However, biological systems are abundant in two (or three) dimensional and interconnected microvascular networks. In order to produce similar synthetic structure, a

fabrication route for a two-dimensional microvascular network is introduced in Chapter 4. In this chapter, a two-dimensional PLA film is fabricated from a solvent-casting procedure, and then the PLA film is micro-structured by using a punch and die tool set fabricated using Micro-Electric Discharge Machining (μ EDM). Two-dimensional microchannels with a wide range of hydraulic diameters and aspect ratios can be fabricated using this method, which unleashes the possibility to create authentic biomimetic structures in a synthetic microvascular material.

Chapter 5 aims at developing the next generation of microvascular composite that has independent and intermingled microchannel networks and is capable of energy and mass transport by adding a coating material to the PLA fiber. After VaSC, the coating remains in between channels providing a barrier between microchannels and a pathway for interchannel communication. This chapter discusses the preliminary steps of developing a non-permeable elastomer coating material. The ongoing research in the area of porous coating material will introduce mass transport properties to microvascular composites.

In Chapter 6, a microporous film is fabricated by using the VaSC procedure. A biphasic film containing PLA and PI is produced and thermal removal of PLA from the biphasic film introduces porous structure in the polyimide film. The porous film is shown to be a potential candidate to replace the current lithium-ion battery separator, possessing the advantage of no shrinkage at elevated temperatures. The phase separation behavior of the polymer blends and the morphologies of the porous film are discussed in great detail. In addition, electrochemical performances of the porous film are evaluated and compared to commercial separators.

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1.6 Figures

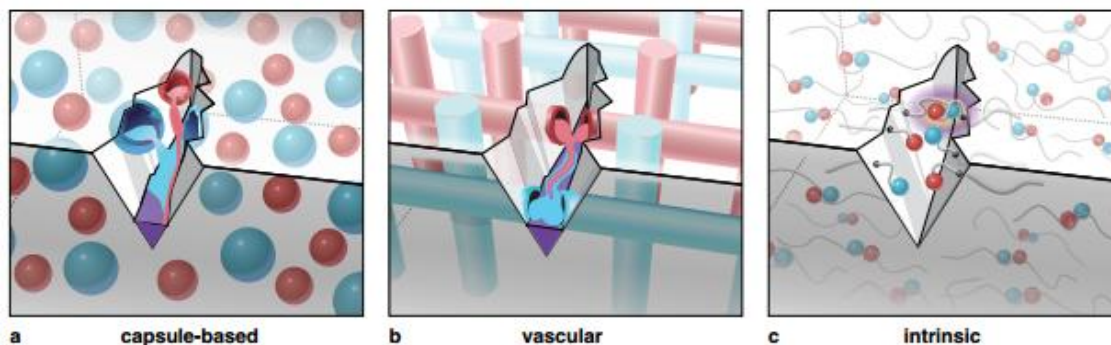


Figure 1.1 Autonomous self-healing systems are divided into three major categories. Capsule-based systems (a) sequester healing agents (blue), and polymerizers (red), in shells throughout the material. Vascular systems (b) use a network of refillable channels to deliver both healing agent and polymerizer. Intrinsic systems (c) utilize the reversible nature of certain chemical bonds to incorporate healing abilities directly into the material, which is not within the scope of this dissertation. Reprinted with permission from B. J. Blaiszik, S. L. B. Kramer, S. C. Olugebefola, J. S. Moore, N. R. Sottos, and S. R. White, *Annu. Rev. Mater. Res.* **2010**, *40*, 179. Copyright 2010, Annual Reviews.

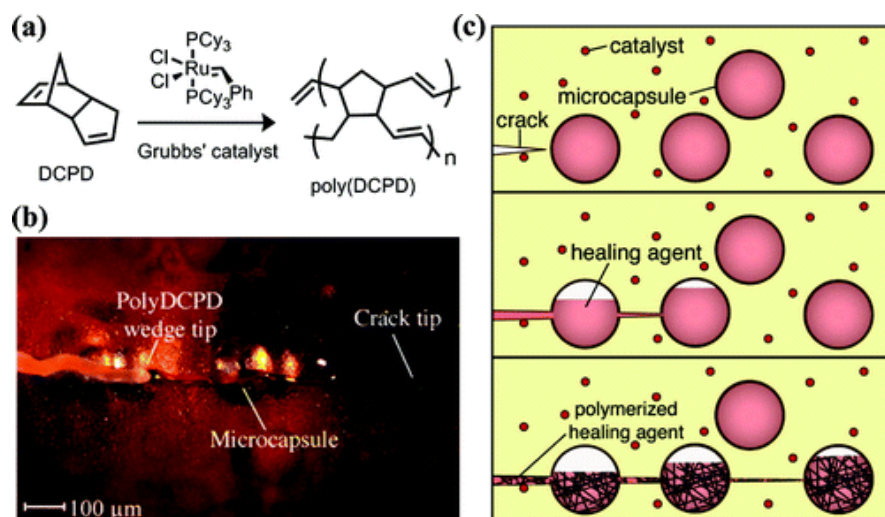


Figure 1.2 (a) Ring-opening metathesis polymerization of DCPD forming poly(DCPD); (b) Optical micrograph of an in situ fatigue specimen showing poly(DCPD) formed in the crack plane behind the crack tip; (c) Schematic drawing of the autonomic self-healing system showing crack initiation, rupture of microcapsules, release of healing agent, and the resulting polymer formed in the crack plane. Reprinted with permission from M. M. Caruso, D. A. Davis, Q. Shen, S. A. Odom, N. R. Sottos, S. R. White, and J. S. Moore, *Chem. Rev.* 2009, 109, 5755. Copyright 2009 American Chemical Society.

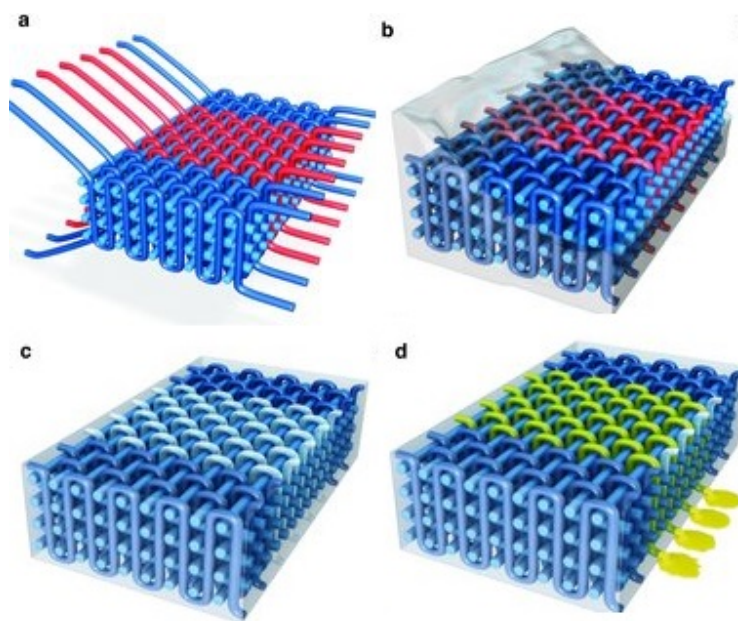


Figure 1.3 VaSC fabrication procedure. Schematic diagrams of a) straight warp and weft yarns (light blue) with interwoven Z -fiber tows (dark blue) and sacrificial fibers (red) to form an orthogonal 3D structure; b) epoxy resin infuses the preform; c) thermal depolymerization and monomer vaporization results in a 3D microvascular network integrated into a structural composite; d) fluid (yellow) fills the microvascular channels. Reprinted with permission from A. P. Esser-Kahn, P. R. Thakre, H. Dong, J. F. Patrick, V. K. Vlasko-Vlasov, N. R. Sottos, J. S. Moore, and S. R. White, *Adv. Mater.*, **2011**, 23, 3654. Copyright 2011 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

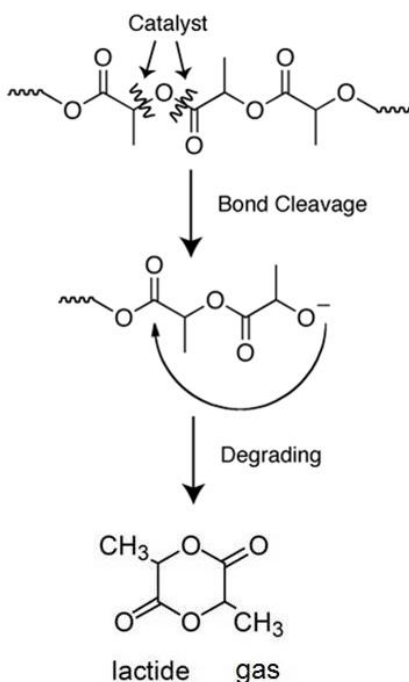


Figure 1.4 Scheme for cascade degradation of PLA into gaseous lactide monomer by the addition of a chemical catalyst. Adapted from Reference 70. Copyright 2004 Elsevier.

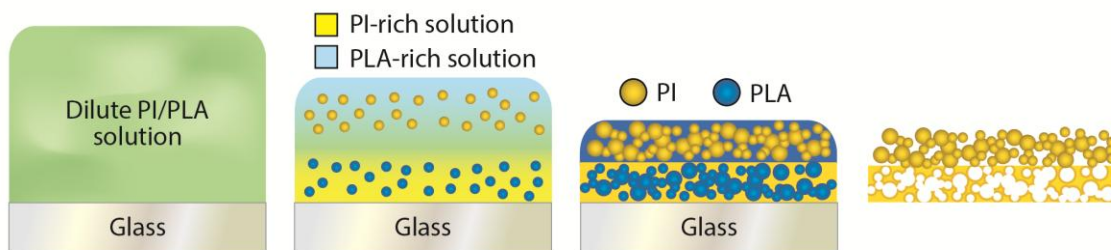


Figure 1.5 Schematics of phase separation during the porous polyimide separator fabrication process. From left to right: dilute PI/PLA solution cast on glass slide; PI and PLA begin to crash out of solution as solvent evaporates; full solvent evaporation leaves behind a biphasic solid film; finally, treatment of the biphasic film at $280\text{ }^{\circ}\text{C}$ removes the PLA, leaving a porous PI film. (Image courtesy of Stephen J. Pety)

CHAPTER 2*

CHEMICAL TREATMENT OF POLY(LACTIC ACID) FIBERS TO ENHANCE THE RATE OF THERMAL DEPOLYMERIZATION

2.1 Introduction

2.1.1 Microvascular Materials

Microvascular-based self-healing systems have attracted attention for their ability to achieve multiple healing cycles in response to mechanical damage.¹⁻⁴ Previously, a number of techniques for introducing microchannels in polymer resins and polymeric composites have been reported.^{2,3,5-8} For example, the direct-write assembly technique provides a way to inscribe a vascular pattern using fugitive wax as ink. Unfortunately, this technique is limited to low curing temperature polymers and small scale material systems/composites.^{3,4} Similarly, hollow glass fibers^{2,6} provide building blocks for introducing microchannels to structural composites; yet, this approach is constrained to one dimensional vascular features. In another approach⁷, electrohydrodynamic viscous fingering (EHVF), a low viscosity, electrically conductive fluid at high voltage is injected into a viscous dielectric fluid. The combination of electrostatic and viscous stresses drives the injecting fluid to form a hierarchical, branched structure. However, controlling the 3D microstructure and incorporating EHVF technique into traditional composite manufacturing methods limits the practical applications of this method. All of these approaches face challenges before they can be used to integrate three dimensional

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microvascular networks into conventional large-scale structural composite materials. Thus, to extend the reach of microvascular structures for large scale commercial applications,⁹ scalable microvascular fabrication methods are critically needed. Herein we report initial progress toward the development of a vascularization technique employing sacrificial fibers,⁸ which is compatible with commercial composite manufacturing techniques. The reported method takes advantage of thermally degradable polymer fibers¹⁰ embedded in a matrix material (i.e., the “holomatrix”). The ideal sacrificial fiber depolymerizes completely when heated,¹⁰ and the application of a vacuum allows controlled removal of the depolymerized, volatile monomer from the matrix, ultimately leaving behind empty channels in the “apomatrix” (**Figure 2.1**). The major challenge in this process is to access a sacrificial fiber that depolymerizes at temperatures below the degradation temperature of the matrix material. Preferably, the sacrificial fiber will be removed from the epoxy matrix during a post-curing stage, wherein the temperature for fiber removal is higher than the initial curing temperature but lower than the matrix degradation temperature.¹¹

2.1.2 PLA Fibers and Their Limitations

The degradation behavior of poly(lactic acid) (PLA) has attracted widespread interest because of its bioabsorbability and environmentally-benign depolymerization products.^{12–14} Recently, Pitet and coworkers utilized PLA as a sacrificial component in copolymers to create porous membranes for battery separators.¹⁵ We posited that high-aspect ratio microchannels could be constructed by embedding sacrificial PLA fibers¹⁶ in an epoxy thermoset and then triggering thermal depolymerization. The thermal depolymerization of PLA occurs above 280 °C and results in the formation of lactide, a gaseous monomer

at this temperature (**Figure 2.2**).¹⁶ However, existing epoxy processing protocols¹⁷ demand milder processing conditions (i.e., a lower fiber depolymerization temperature) to prevent thermal damage to the thermoset matrix. Herein we show that minimal matrix damage can be realized by using a catalyst to lower the temperature required for PLA depolymerization. Previously, Fan et al. found that the depolymerization temperature of poly(L-lactide) was reduced by up to 90 °C when the polymer was blended with calcium oxide.¹⁸ Similar results were reported by Mori et al. when poly(L-lactide) was mixed with tin reagents.¹⁹ The catalysts in these examples promote the cleavage of ester bonds in the polymer backbone, facilitating chain backbiting, and thus, depolymerization.^{18–20} Since we ultimately hope to achieve large-scale sacrificial fiber production, our efforts aimed to find an economical and stable catalyst that would not significantly erode the mechanical integrity of the PLA fibers under conventional composite processing conditions. As such, various catalysts²¹ and catalyst deposition processes were screened to determine the optimum catalyst for sacrificial fiber development.

2.2 Catalytic Depolymerization of PLA

2.2.1 Catalyst Screening

Following a reported literature procedure,¹⁸ catalysts that had previously been used to decrease the depolymerization temperature of PLA were screened and divided into three main categories: 1) earth metal oxides, 2) tin-containing compounds, and 3) rare metal triflates. Dynamic TGA curves of PLA films blended with each of the various catalysts are shown in **Figure 2.3** and **Figure 2.4**. Among the catalysts screened, strontium oxide and tin(II) octoate were found to have the greatest effect on the PLA depolymerization

onset temperature, decreasing it to approximately 180 °C, which was ca. 100 °C lower than unmodified PLA (**Figure 2.3 and Figure 2.4**). The significant decrease in depolymerization temperature was deemed sufficient for fibers to be removed prior to thermal damage of conventional epoxy thermosets.¹⁷

2.2.2 Catalyst Evaluation

In order to survive conventional composite fabrication,²⁻⁴ the catalyst should not significantly change the mechanical properties of the PLA fibers. Typical weaving requires a fiber strength of ca. 23 MPa.²⁶ Unfortunately, that both strontium oxide and tin(II) octoate degraded PLA fiber properties. Strontium oxide, as well as other earth metal oxides, formed a strongly basic hydroxide upon contact with water which deteriorated the PLA fiber. Surface damage was evident upon visual inspection (**Figure 2.5**) where the oxide caused either a reduction of the fiber's cross-sectional area or splintering of the fiber. Tin(II) octoate, an oily liquid, had poor dispersibility in the solvent mixture and resulted in greasy fibers.²⁷ PLA blended with tin(II) oxalate began to depolymerize at temperatures ca. 80 °C lower than unmodified PLA (**Figure 2.4**). The dispersibility of tin(II) oxalate in TFE/water mixture guaranteed good catalyst incorporation into the fiber. Moreover, DSC analysis revealed the tin(II) oxalate was stable at temperatures up to the PLA depolymerization (**Figure 2.6**). As a result, tin(II) oxalate was selected for modifying PLA fibers.

2.3 Incorporation of Catalyst into PLA Fibers

2.3.1 Methods

Incorporation of catalysts into PLA fibers requires either surface treatment or impregnation of the fiber.^{22–24} Previously Quirk et al. developed a PLA fiber modification method to immobilize bio-molecules on the fiber surface.²⁴ Through a process that involved reversible swelling of the polymer surface regions, they showed that guest molecules were effectively entrapped in the fiber. Building on this fiber modification procedure, we employed a solvent/non-solvent mixture to controllably swell the PLA fiber and allow the depolymerization catalyst to infiltrate the fiber. The solvent was then removed by evaporation, immobilizing the catalysts (**Figure 2.7**). Solvent composition and fiber-solvent soaking time were optimized in order to produce sacrificial fibers that could be efficiently removed from an epoxy thermoset. The thermal depolymerization behavior of the chemically treated fibers was also compared to that of untreated PLA fibers under the same experimental conditions, in order to demonstrate the effect of catalyst impregnation.

2.3.2 Optimization of Fiber Processing Parameters

The PLA fiber was soaked in a trifluoroethanol (TFE)/water mixture, which caused rapid polymer swelling at the surface,²⁴ allowing for infiltration of catalysts into the fiber. The effects of solvent composition, fiber-solvent soaking time, and post-soak treatment were evaluated by isothermal TGA and the data were correlated with observations of fiber removal.

2.3.2.1 Solvent Composition

Solvent composition (the ratio of TFE to water) was investigated so that maximum catalyst incorporation was achieved without dissolving the fiber. Control experiments demonstrated the TFE/water treatments lacking a catalyst had no effect compared to untreated fibers (**Figure 2.8**). When catalyst was present in the soaking bath, TGA (**Figure 2.9**) showed faster PLA mass loss with an increasing amount of TFE in the mixture. At 240 °C, the rate of PLA fiber weight loss increased significantly as the TFE/water ratio was increased up to 60:40, above which, the PLA fibers were dissolved. From these results, we concluded that TFE facilitated fiber swelling, which allowed more catalysts to diffuse in, and in turn caused a faster depolymerization reaction upon heating. The amount of catalyst entrapped in the fiber determined the efficiency of sacrificial fiber removal, which was manifested in the subsequent fiber removal measurements (**Figure 2.10**). When other processing parameters were held constant, fibers treated with more TFE had a larger fiber removal fraction under the same thermal conditions.

2.3.2.2 Solvent Soaking Time

The fiber soaking time also affected the catalyst adsorption efficiency, presumably because the longer the fiber was treated, the more catalyst was able to diffuse into the fiber. PLA fibers were soaked in the TFE/water/tin(II) oxalate mixture for varying amounts of time (2–24 h), and the depolymerization was subsequently analyzed. Isothermal TGA showed a significant increase in the rate of PLA fiber weight loss with increased soaking time (**Figure 2.11**). Fiber removal data was consistent with TGA

observations, and showed that the fiber treated for the longest time yielded the fastest rate of removal (**Figure 2.12**).

2.3.2.3 Choosing a Drying Method

In the previously reported literature procedure,²⁴ polymer swelling was reversed by the addition of a large excess of nonsolvent (water). Our system responded to large increases of water with a decrease in the rate and extent of the thermal depolymerization compared to simple solvent evaporation. Under otherwise identical processing conditions, fibers that were dried in air had a significantly larger fraction of thermal depolymerization than those that were treated with water (**Figure 2.13**). Thus, the best method to quench catalyst impregnation was found to be simple air-drying. After soaking the fiber in a solvent/catalyst mixture, the fiber was removed and dried in the air which allowed the solvent to evaporate and the catalyst particles to become immobilized.

2.3.2.4 Optimized Processing Parameters

For PLA fibers (diameter: 500 μm), the optimum processing procedure involved soaking PLA fiber in a solvent mixture containing 60 % TFE and 40 % H_2O dispersed with 10 wt% tin(II) oxalate for 24 h and air-drying the fiber afterwards.

2.3.2.5 Processing Parameters for Fibers with Different Diameters

For PLA fibers of different diameters (20 μm and 200 μm), the optimum processing procedures involved the same steps, however the solvent composition and fiber soaking time were varied to achieve optimal fiber removal (see **Table 2.1**).

2.3.3 Effect of Catalyst Incorporation

The thermal depolymerization behavior of the chemically treated PLA fibers in an epoxy thermoset was compared to that of an untreated fiber under the same thermal conditions. A 5 cm long 200 μm diameter PLA fiber treated with tin(II) oxalate using the optimized fiber treatment protocol was completely removed after heating in vacuo at 180 $^{\circ}\text{C}$ for 20 h, yielding an empty microchannel; in contrast, a large portion of solid fiber remained in the epoxy for the untreated PLA fiber (**Figure 2.14**).

2.4 Study of Catalytic Depolymerization Mechanism

2.4.1 Analysis of Depolymerization Product

The product of catalyst treated fiber heated at 240 $^{\circ}\text{C}$ for 4 h was analyzed by ESI-MS (**Figure 2.15**) and ^1H NMR (**Figure 2.16**). Both results indicated that lactide monomer was the predominant product.

2.4.2 Mechanistic Study

PLA fiber molecular weight change was monitored by GPC analysis during the tin(II) oxalate assisted catalytic depolymerization process. **Figure 2.17** shows the GPC traces of depolymerization products at various reaction times: 0 min, 30 min and 120 min. Number average molecular weight (M_n) and weight average molecular weight (M_w) were calibrated and plotted as a function of reaction time in **Figure 2.18**.

Average molecular weight data was fit to a random chain scission model (**Figure 2.19**). Using the approach developed by Murray et al, the number average chain length (N) of a polymer during the course of random chain scission was given by

$$N_t = \frac{N_0}{B+1} \quad (2.1)$$

where N_0 is the initial number average chain length and N_t is the number after an average of B bonds have been broken per original molecule. The degree of degradation,

α , is defined by $\alpha = \frac{B}{N_0 - 1}$ which reduced to

$$\alpha = \frac{B}{N_0} \quad (2.2)$$

for large number of N_0 .

Assuming the chain scission rate (the ester hydrolysis rate) remains constant during the entire degradation process, that is

$$\alpha = kt \quad (2.3)$$

Combining equations 2.1, 2.2 and 2.3, gives equation 2.4:

$$N_t = \frac{1}{\frac{1}{N_0} + kt} \quad (2.4)$$

which is the governing equation of N_t as a function of t .

Fitting the experimental data with function 2.5, **Figure 2.19** was obtained.

$$y = \frac{1}{a + bx} \quad (2.5)$$

Qualitative agreement between the experimentally determined molecular weight and the model's predictions support the proposed mechanism of random chain scission for PLA during catalytic depolymerization.

2.5 Conclusion

Sacrificial fibers based on catalyst-impregnated poly(lactic acid) (PLA) were useful components for the fabrication of microvascular networks in polymeric composites. Exploring various catalysts and impregnation techniques, PLA fibers that depolymerize at lower temperatures and thus minimize thermal damage to the matrix were obtained. Based on a series of numerous screening experiments, tin(II) oxalate was determined to be the ideal catalyst and was incorporated into PLA fibers by an impregnation procedure using a solvent mixture of TFE and water. Thus we have established a practical processing procedure for 500 μm diameter PLA fibers that involved soaking the fibers in a solvent mixture containing 60 % TFE and 40 % H_2O dispersed with 10 wt% tin(II) oxalate for 24 h and air-drying the fiber. This fiber treatment procedure provided a reliable method to prepare sacrificial PLA materials that were suitable for fabrication of microvascular networks. Catalyst-infused PLA fibers embedded in an epoxy thermoset were completely removed at 180 $^{\circ}\text{C}$ after 20 h *in vacuo* with lactide monomer as the removed sacrificial product. Studies involving the time evolution of PLA molecular weight suggested a catalytic depolymerization mechanism based on random chain scission. The fiber-treatment method reported here together with the commercial availability of PLA fibers should allow for both scalability and processability that can be applied to a wide variety of composite materials.

2.6 Experimental Section

2.6.1 Materials

PLA fibers (diameters: 20 μm , 200 μm , and 500 μm) were obtained from Teijin Monofilament Germany GmbH and used as received. PLA pellets (P1566, $M_w=85,000$ – $160,000$) for catalyst screening were used as received from Sigma-Aldrich. Screened catalysts (magnesium oxide (MgO), calcium oxide (CaO), barium oxide (BaO), strontium oxide (SrO), scandium triflate ($\text{Sc}(\text{OTf})_3$), tin(II) acetate, tin(II) oxalate, tin(II) octoate) were all obtained from Sigma-Aldrich unless otherwise noted. Diglycidyl ether of bisphenol A resin (DGEBA or EPON 828) was used as received from Miller-Stephenson with the curing agent EPIKURE 3300 received from Hexion. Epoxy samples were prepared using a mass ratio of 22.7 parts per hundred (pph) EPIKURE 3300 to EPON 828. Other chemicals were all obtained from Sigma-Aldrich unless otherwise noted.

2.6.2 Characterization

2.6.2.1 TGA

Thermogravimetric analysis (TGA) was performed on a Mettler-Toledo TGA851^e, calibrated with indium, aluminum, and zinc standards. For each experiment, the sample (ca. 10 mg) was weighed (± 0.02 mg) in an alumina crucible. For dynamic measurements, the mass loss was recorded during a heating cycle over the temperature range of 25 to 650 $^{\circ}\text{C}$ at a heating rate of 10 $^{\circ}\text{C}\cdot\text{min}^{-1}$. For isothermal experiments, the temperature was ramped from 25 to 240 $^{\circ}\text{C}$ at a rate of 50 $^{\circ}\text{C}\cdot\text{min}^{-1}$ and subsequently held at 240 $^{\circ}\text{C}$ for 2 h.

2.6.2.2 DSC

Differential scanning calorimetry (DSC) was performed on a Mettler-Toledo DSC821^e instrument calibrated to indium and zinc standards. Dynamic experiments were performed under nitrogen atmosphere to measure heat flow (positive exothermal) from 25 to 450 °C at a heating rate of 10 °C·min⁻¹, and all DSC experiments were performed in 40 µL aluminum pans that were hermetically sealed.

2.6.2.3 Microscopy

Fiber surface morphology and fiber removal in epoxy thermosets were imaged using a Leica DMR Optical Microscope at various magnifications, and ImageJ software was used to measure the fraction of PLA fiber removed.

2.6.2.4 GPC

Analytical gel permeation chromatography (GPC) was performed on a Waters 515 HPLC pump, a Viscotek TDA Model 300 triple detector array, a Thermoseparations Trace series AS100 autosampler, and a series of 3 Waters HR Styragel columns (7.8 X 300mm, HR3, HR4, and HR5) in THF at 30 °C. The GPC was calibrated using monodisperse polystyrene standards, and all molecular weight data were reported as polystyrene equivalents.

2.6.2.5 ESEM

Environmental Scanning Electron Microscopy (ESEM, Philips XL30ESEM-FEG) was used to image cross-sections of the holomatrix. SEM images were acquired after sputter-coating the sample surface with carbon. Selected area elemental analysis was performed

by EDS (Energy Dispersive X-ray Spectroscopy, attached to the SEM) with a 20 kV electron source and spot size of 3.0 nm.

2.6.2.6 ESI-MS

Mass spectra were recorded on a 70-VSE C in ES+ mode through the University of Illinois Mass Spectrometry Laboratory, SCS.

2.6.2.7 NMR

¹H-NMR spectra were obtained using a Varian 400 spectrometer in the VOICE NMR laboratory at University of Illinois. Spectra were referenced to the residual proton solvent (CDCl₃) peak.

2.6.2.8 MicroCT

An Xradia BioCT (MicroXCT-400) was used to image the apomatrix at 40 keV (8 W power and 200 μA current) at a 4X objective for 5 s exposure times. Rotation intervals were 0.25 ° for a complete 360 ° scan. Images were visualized in 3D with XM3Dviewer and reconstructed in 3D using XMReconstructor.

2.6.3 Catalyst Screening

Chemicals listed above were screened by the reported literature procedure¹⁸ except commercial PLA pellets were used in place of synthesized material. Commercial PLA pellets were dissolved in chloroform (1 g/mL) and the test catalysts were blended into the viscous solution (ca. 10 wt% to PLA). The mixture was vigorously stirred for 1 h to disperse the catalysts uniformly. The dispersed mixture was cast on a petri dish and allowed to dry before rinsing with methanol. A thin film was obtained on the petri dish

and was dried under vacuum (0.2 torr) for 24 h. The vacuum-dried films were then removed from the petri dish and manually cut into pieces for TGA experiments.

2.6.4 Fiber Treatment

Catalysts were incorporated into PLA sacrificial fibers by a modified literature procedure.²⁴ Catalysts were evenly dispersed (10 wt%) in a miscible mixture of trifluoroethanol (TFE, a PLA solvent) and water (a PLA nonsolvent). The PLA fibers were soaked in the stirred solvent/catalyst mixture at 37 °C for a set period of time (2–24 h), removed and subsequently air-dried. For improved visualization during macroscopic imaging, rhodamine 6G (0.5 wt%) was incorporated into PLA fibers using a similar fiber treatment procedure.

2.6.5 Sacrificial Fiber Removal

Chemically treated PLA fibers were embedded in an EPON 828: EPIKURE 3300 matrix that was cured in a silicone rubber mold using the standard protocol of curing at room temperature for 24 hours followed by 1.5 h at 80 °C and 1.5 h at 150 °C.²⁵ Holomatrices were carefully polished before thermal treatment so that fiber ends were exposed. The holomatrices were heated in a sealed vacuum oven (Fisher Isotemp 283) at a constant temperature (ranging from 180 to 220 °C) under vacuum (1 torr). The fraction of fiber removed (defined as the ratio of empty channel length over the full fiber length) was measured for each sample after heating for 2 h.

2.6.6 Time Evolution of Catalytic Depolymerization

PLA fibers (diameter 500 μm) treated with catalyst were placed in a vial and heated at 240 $^{\circ}\text{C}$ in a sealed oven. Thermal depolymerization products at each designated time point were extracted and analyzed using GPC. The vapor condensation collected from heated fibers was analyzed by ESI-MS and ^1H NMR.

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2.8 Figures and Tables

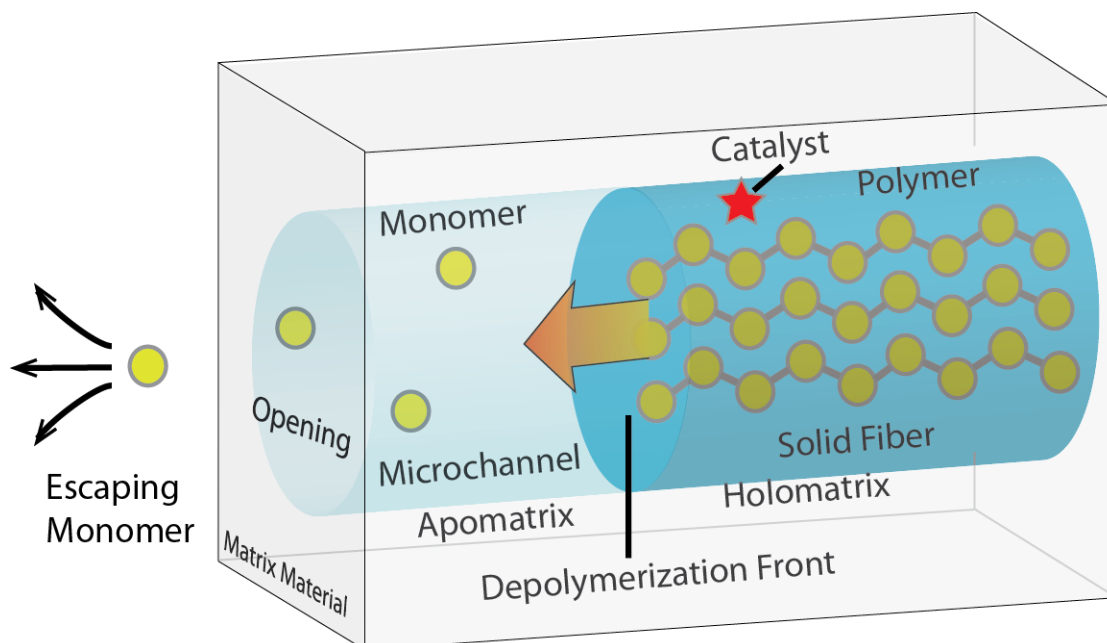


Figure 2.1 Illustration showing the holomatrix (fiber embedded matrix) to apomatrix (microchannel embedded matrix) transformation by vaporization of a sacrificial fiber. Reprinted with permission from H. Dong, A. P. Esser-Kahn, P. R. Thakre, J. F. Patrick, N. R. Sottos, J. S. Moore, S. R. White, *ACS Appl. Mater. Interfaces*. **2012**, 4, 503. Copyright 2012 American Chemical Society.

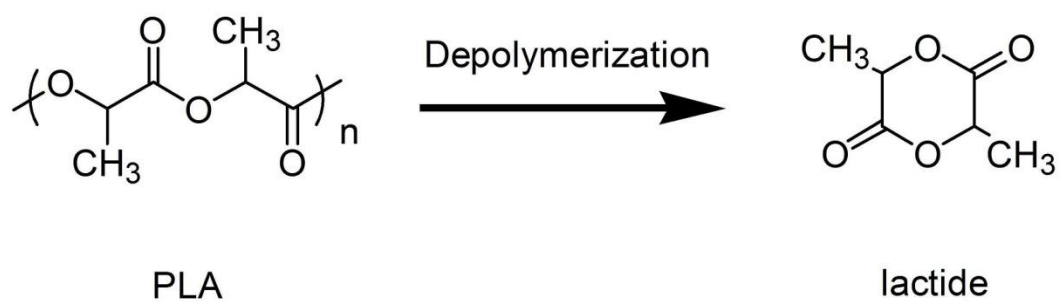


Figure 2.2 Thermal depolymerization reaction of poly(lactic acid) (PLA) to lactide. Reprinted with permission from H. Dong, A. P. Esser-Kahn, P. R. Thakre, J. F. Patrick, N. R. Sottos, J. S. Moore, S. R. White, *ACS Appl. Mater. Interfaces*. **2012**, 4, 503. Copyright 2012 American Chemical Society.

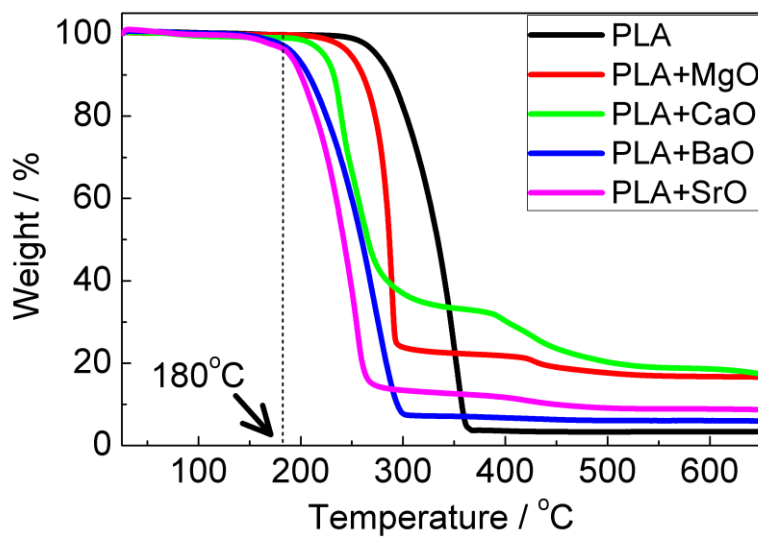


Figure 2.3 Dynamic TGA curves for PLA films showing the catalytic effect of earth metal oxides. In those experiments, the alumina crucible was loaded with chopped PLA films. Reprinted with permission from H. Dong, A. P. Esser-Kahn, P. R. Thakre, J. F. Patrick, N. R. Sottos, J. S. Moore, S. R. White, *ACS Appl. Mater. Interfaces*. **2012**, 4, 503. Copyright 2012 American Chemical Society.

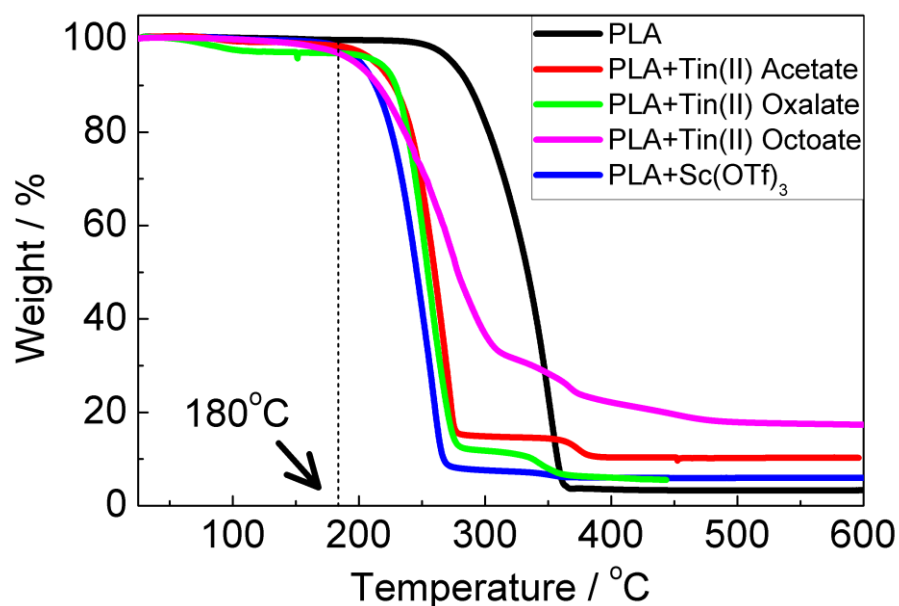


Figure 2.4 Dynamic TGA curves for PLA films showing the catalytic effect of tin-containing compounds and metal triflates. In those experiments, the alumina crucible was loaded with chopped PLA films. Reprinted with permission from H. Dong, A. P. Esser-Kahn, P. R. Thakre, J. F. Patrick, N. R. Sottos, J. S. Moore, S. R. White, *ACS Appl. Mater. Interfaces*. **2012**, 4, 503. Copyright 2012 American Chemical Society.

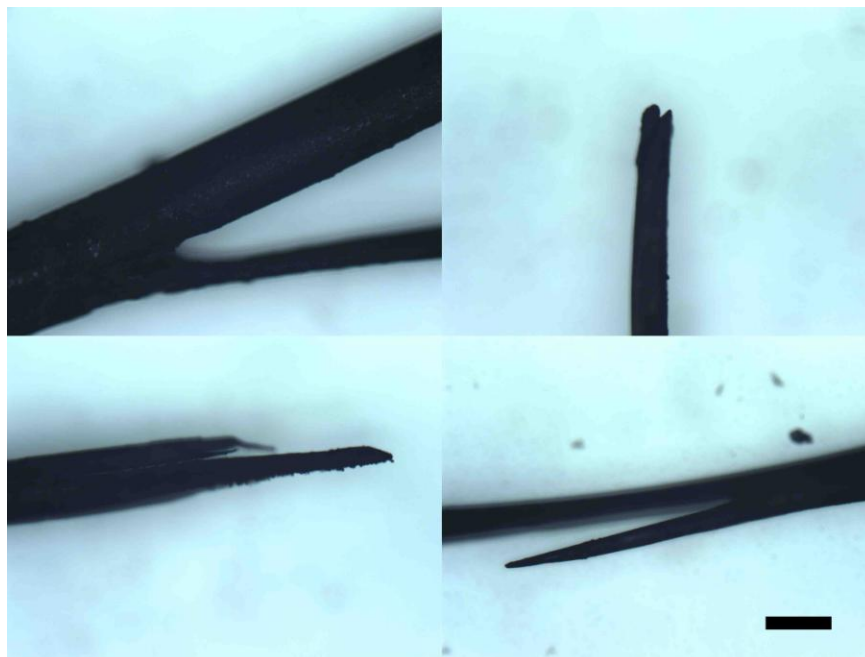


Figure 2.5 Optical images showing the deterioration of PLA fiber (500 μm) after treatment with SrO (Scale bar: 250 μm). Reprinted with permission from H. Dong, A. P. Esser-Kahn, P. R. Thakre, J. F. Patrick, N. R. Sottos, J. S. Moore, S. R. White, *ACS Appl. Mater. Interfaces*. **2012**, 4, 503. Copyright 2012 American Chemical Society.

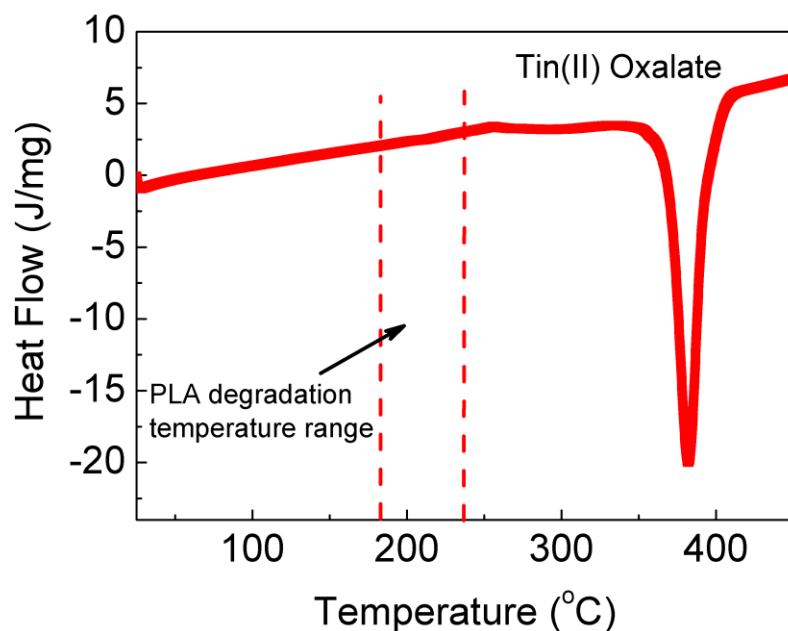


Figure 2.6 DSC curve for tin(II) oxalate showing its thermal stability up to PLA depolymerization temperature range (180 °C – 240 °C). Reprinted with permission from H. Dong, A. P. Esser-Kahn, P. R. Thakre, J. F. Patrick, N. R. Sottos, J. S. Moore, S. R. White, *ACS Appl. Mater. Interfaces*. **2012**, 4, 503. Copyright 2012 American Chemical Society.

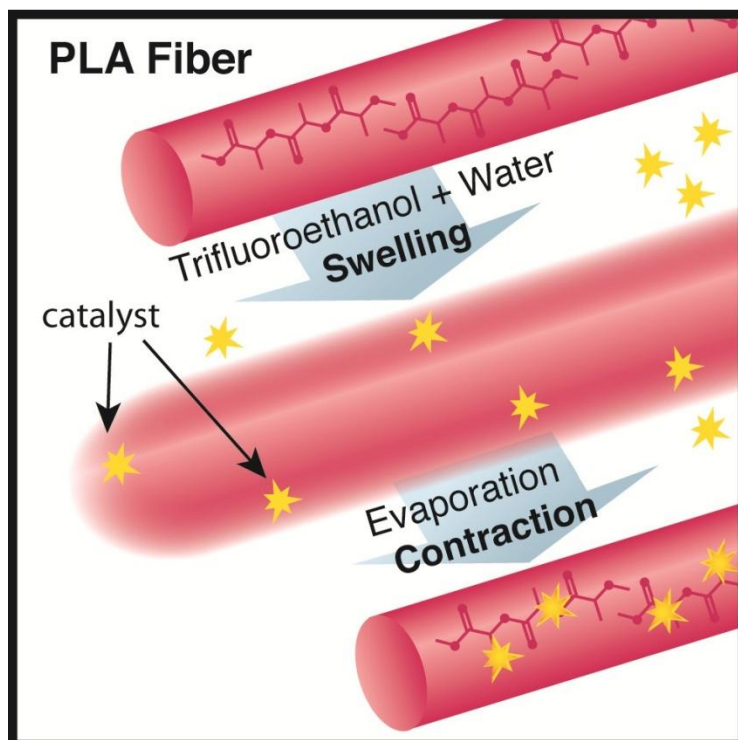


Figure 2.7 Illustration showing the treatment of a PLA fiber with the depolymerization catalyst by a procedure that reversibly swells the fiber. Reprinted with permission from H. Dong, A. P. Esser-Kahn, P. R. Thakre, J. F. Patrick, N. R. Sottos, J. S. Moore, S. R. White, *ACS Appl. Mater. Interfaces*. **2012**, 4, 503. Copyright 2012 American Chemical Society.

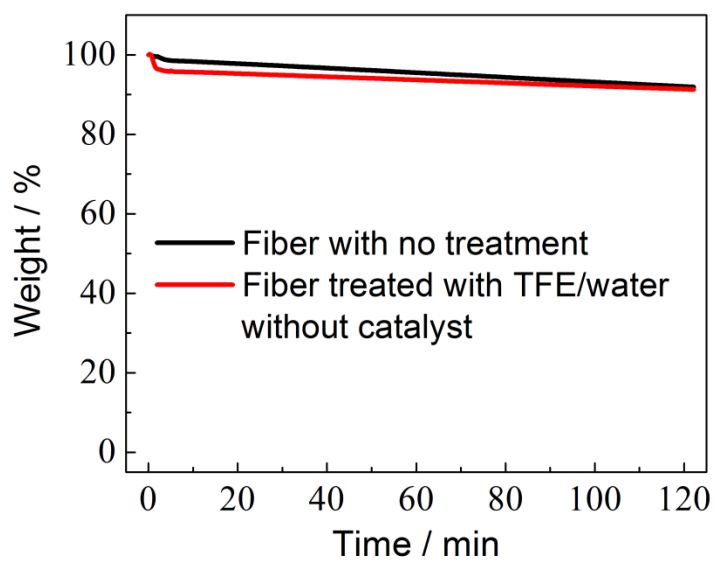


Figure 2.8 Dynamic TGA curves for PLA fibers with no chemical treatment and fibers treated with TFE/water without any catalyst.

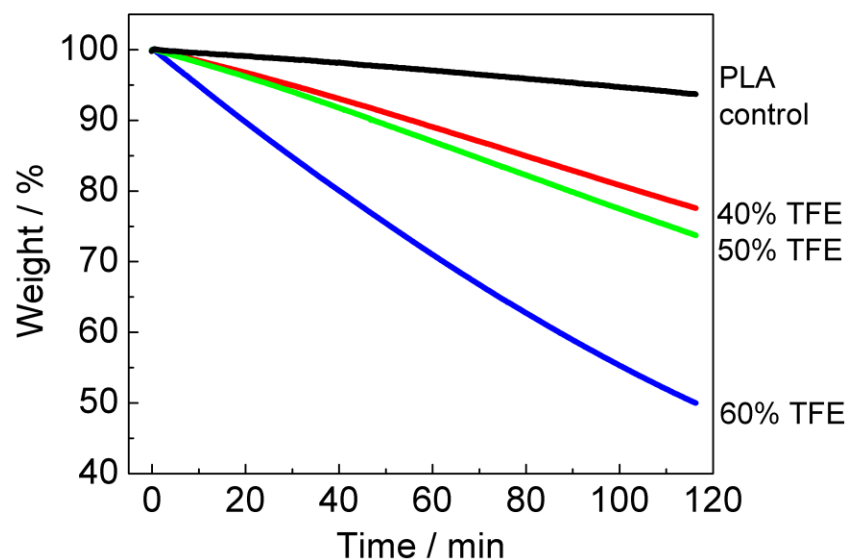


Figure 2.9 Isothermal TGA curves (240 °C) showing the effect of solvent composition (soaking time: 12 h); the uppermost black line is for a PLA fiber treated with 100 % H₂O with 10 wt% tin(II) oxalate as control; each of the other traces include 10 wt% tin(II) oxalate with the indicated quantity of TFE. All these experiments were performed using PLA fibers with a diameter of 500 μm. Reprinted with permission from H. Dong, A. P. Esser-Kahn, P. R. Thakre, J. F. Patrick, N. R. Sottos, J. S. Moore, S. R. White, *ACS Appl. Mater. Interfaces*. **2012**, 4, 503. Copyright 2012 American Chemical Society.

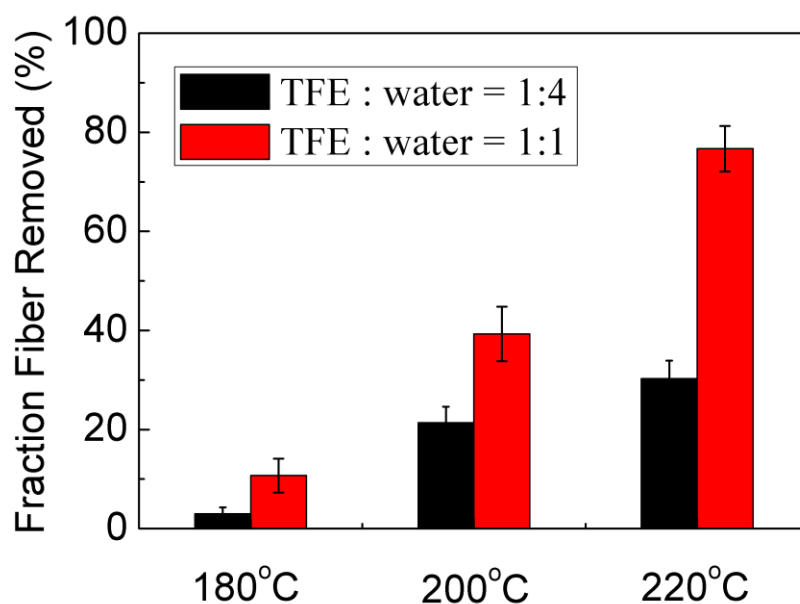


Figure 2.10 Fiber removal data at different temperatures varying solvent composition with 10 wt% tin(II) oxalate (fiber length: 5 cm, thermal treatment time: 2 h). All these experiments were performed using PLA fibers with a diameter of 500 μm . Reprinted with permission from H. Dong, A. P. Esser-Kahn, P. R. Thakre, J. F. Patrick, N. R. Sottos, J. S. Moore, S. R. White, *ACS Appl. Mater. Interfaces*. **2012**, 4, 503. Copyright 2012 American Chemical Society.

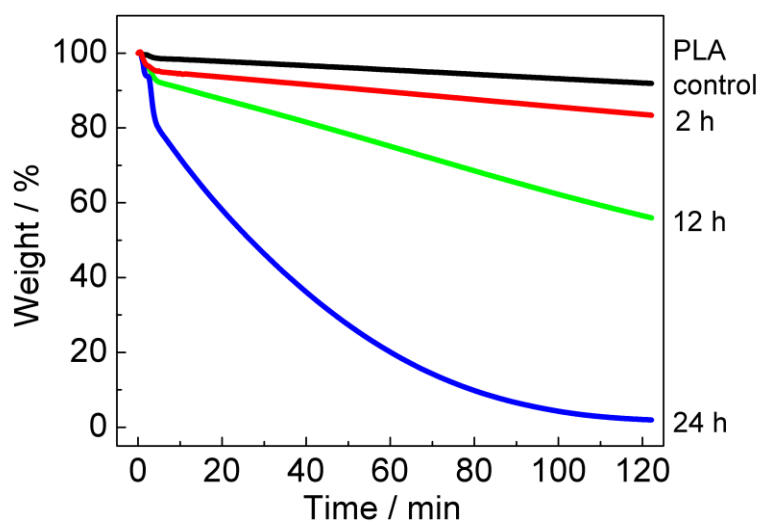


Figure 2.11 Isothermal TGA curves (240 °C) showing the effect of different soaking times (solvent composition: 60 % TFE; catalyst concentration: 10 wt% tin(II) oxalate); the uppermost black line is for a PLA fiber with no treatment as control. All these experiments were performed using PLA fibers with a diameter of 500 μm . Reprinted with permission from H. Dong, A. P. Esser-Kahn, P. R. Thakre, J. F. Patrick, N. R. Sottos, J. S. Moore, S. R. White, *ACS Appl. Mater. Interfaces*. **2012**, 4, 503. Copyright 2012 American Chemical Society.

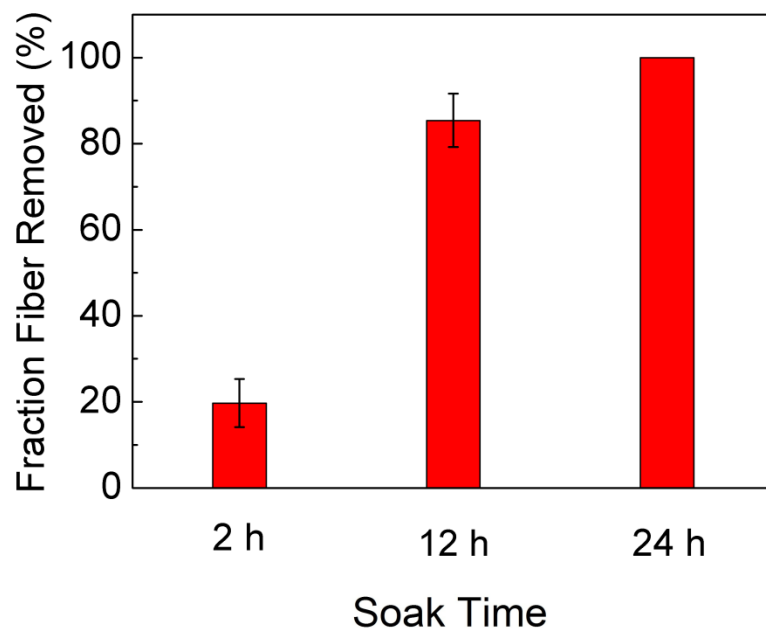


Figure 2.12 Fraction of fiber removed by varying soaking time (fiber length: 5 cm, solvent composition: 60 % TFE, thermal treatment temperature: 200 °C, thermal treatment time: 2 h; catalyst concentration: 10 wt%). All these experiments were performed using PLA fibers with a diameter of 500 μm . Reprinted with permission from H. Dong, A. P. Esser-Kahn, P. R. Thakre, J. F. Patrick, N. R. Sottos, J. S. Moore, S. R. White, *ACS Appl. Mater. Interfaces*. **2012**, 4, 503. Copyright 2012 American Chemical Society.

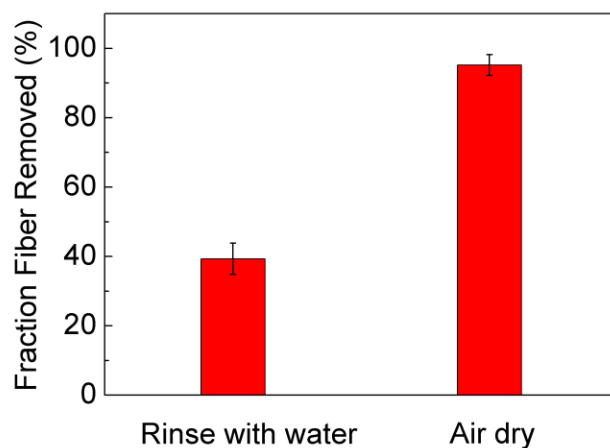


Figure 2.13 Fiber removal fraction data using different post-exposure treatments (fiber diameter: 500 μm , solvent composition: 60 % TFE, tin(II) oxalate concentration: 2 wt%, soak time: 12 h, thermal treatment temperature: 200 $^{\circ}\text{C}$, thermal treatment time: 2 h). Reprinted with permission from H. Dong, A. P. Esser-Kahn, P. R. Thakre, J. F. Patrick, N. R. Sottos, J. S. Moore, S. R. White, *ACS Appl. Mater. Interfaces*. **2012**, 4, 503. Copyright 2012 American Chemical Society.

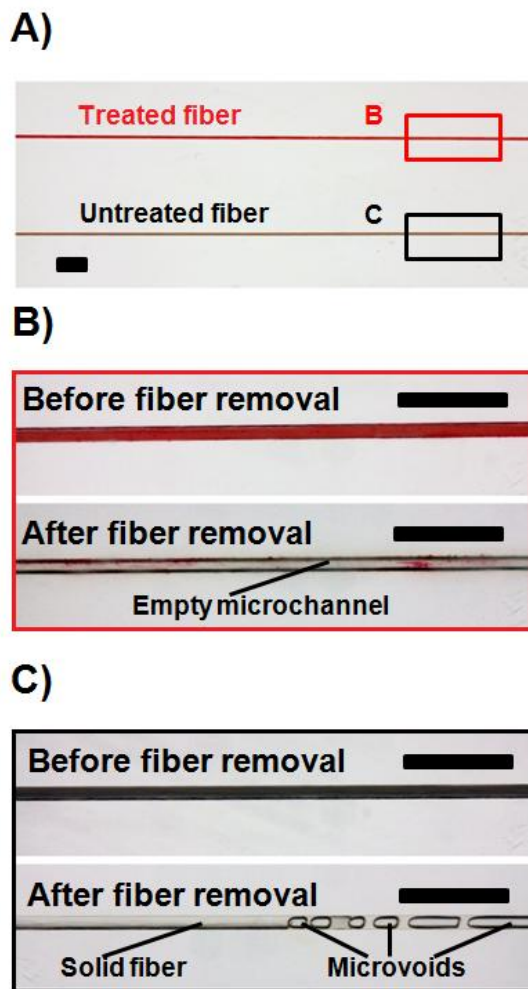


Figure 2.14 A) Optical images of test sample of epoxy matrix containing both PLA fiber treated with tin(II) oxalate (top) and untreated PLA fiber (bottom) and zoomed-in images of holomatrices (before fiber removal) and apomatrices (after fiber removal) for PLA fiber treated with tin(II) oxalate B) and untreated PLA fiber C). Rhodamine 6G (0.5 wt%) was incorporated into PLA fiber together with tin(II) oxalate. Heat treatment was conducted at 180 °C *in vacuo* for 20 h. (Scale bar: 2 mm) Reprinted with permission from H. Dong, A. P. Esser-Kahn, P. R. Thakre, J. F. Patrick, N. R. Sottos, J. S. Moore, S. R. White, *ACS Appl. Mater. Interfaces*. **2012**, 4, 503. Copyright 2012 American Chemical Society.

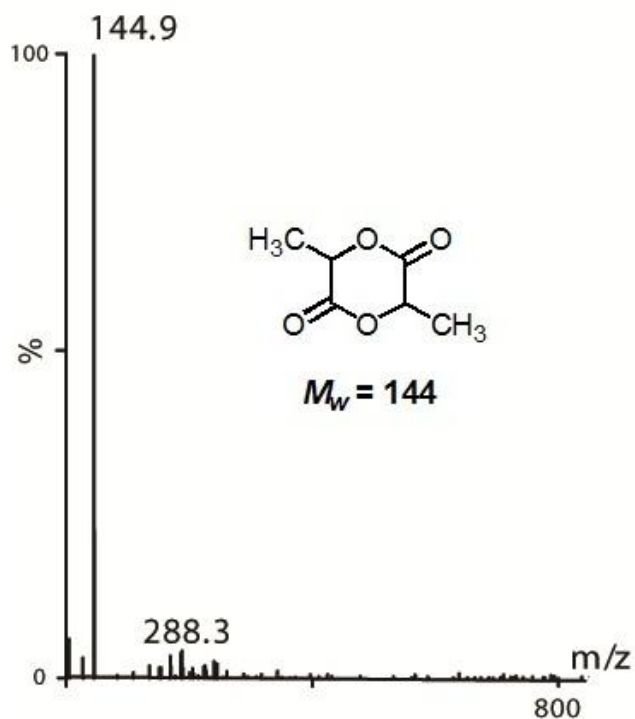


Figure 2.15 ESI-MS spectrum of PLA catalytic depolymerization product after 4 h. Reprinted with permission from H. Dong, A. P. Esser-Kahn, P. R. Thakre, J. F. Patrick, N. R. Sottos, J. S. Moore, S. R. White, *ACS Appl. Mater. Interfaces*. **2012**, 4, 503. Copyright 2012 American Chemical Society.

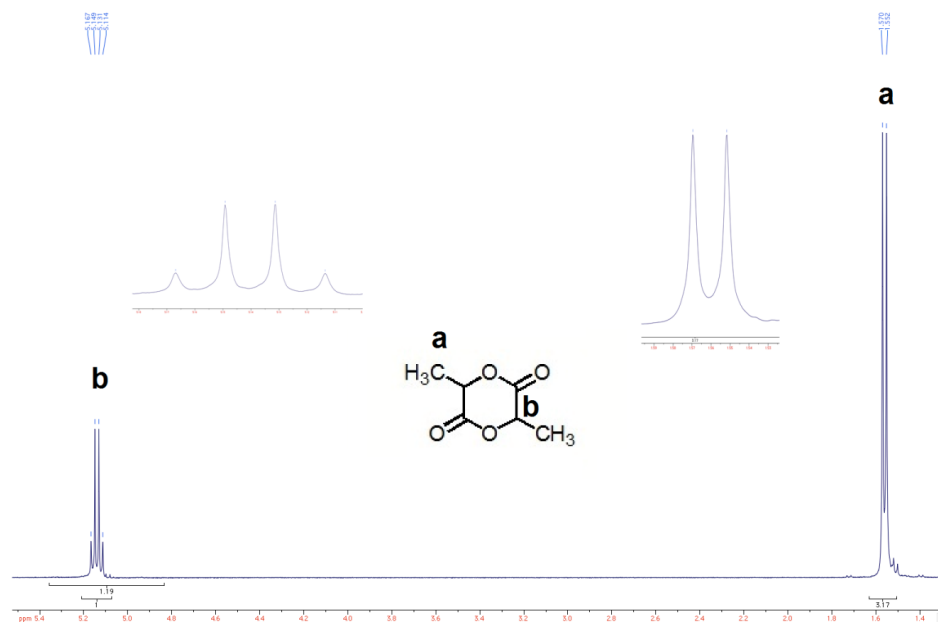


Figure 2.16 ^1H NMR (Solvent: CDCl_3) spectrum and splitting patterns for product of tin(II) oxalate treated PLA fiber (500 μm) heated at 240 $^\circ\text{C}$ for 4 h (Cropped to show the alkyl region only). Reprinted with permission from H. Dong, A. P. Esser-Kahn, P. R. Thakre, J. F. Patrick, N. R. Sottos, J. S. Moore, S. R. White, *ACS Appl. Mater. Interfaces*. **2012**, 4, 503. Copyright 2012 American Chemical Society.

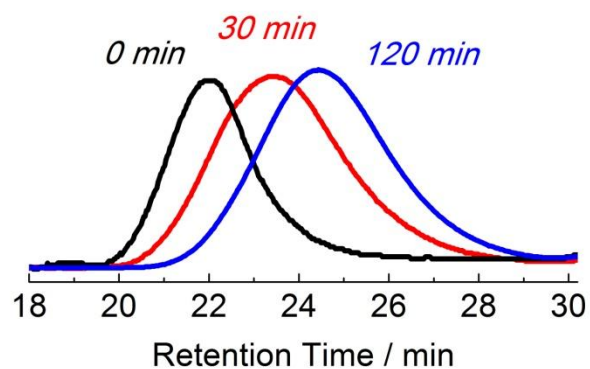


Figure 2.17 GPC traces of the PLA catalytic depolymerization product at different reaction times. Reprinted with permission from H. Dong, A. P. Esser-Kahn, P. R. Thakre, J. F. Patrick, N. R. Sottos, J. S. Moore, S. R. White, *ACS Appl. Mater. Interfaces*. **2012**, 4, 503. Copyright 2012 American Chemical Society.

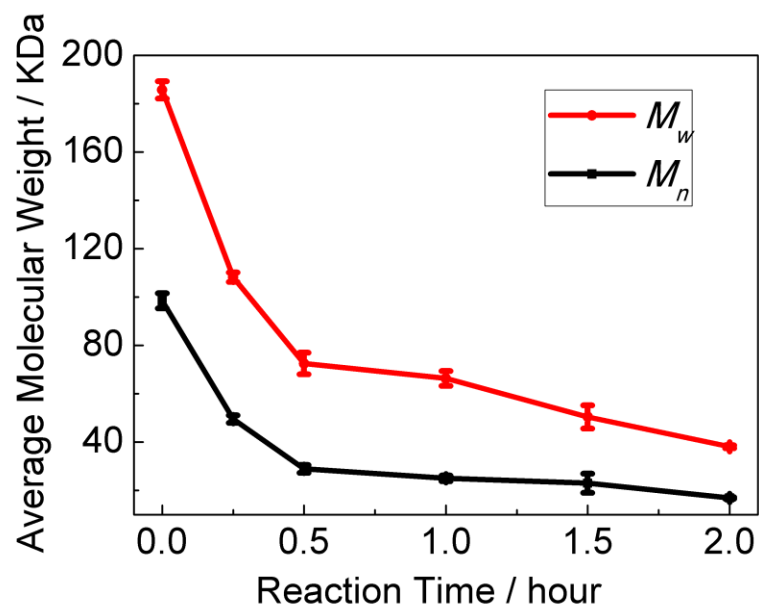


Figure 2.18 Average molecular weight plotted as a function of reaction time. Reprinted with permission from H. Dong, A. P. Esser-Kahn, P. R. Thakre, J. F. Patrick, N. R. Sottos, J. S. Moore, S. R. White, *ACS Appl. Mater. Interfaces*. **2012**, 4, 503. Copyright 2012 American Chemical Society.

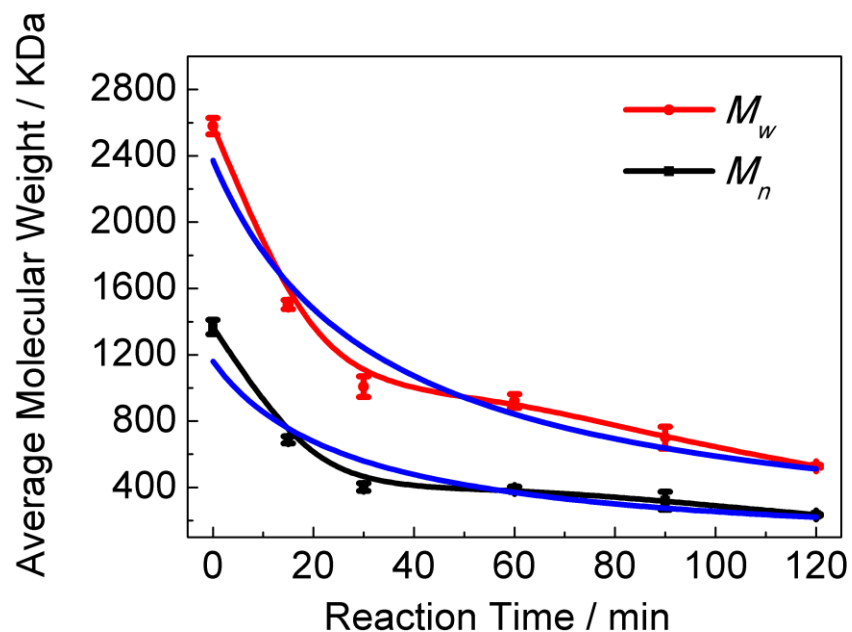


Figure 2.19 Average molecular weight plotted as a function of reaction time and fitting curves (blue) assuming a chain random scission model. Reprinted with permission from H. Dong, A. P. Esser-Kahn, P. R. Thakre, J. F. Patrick, N. R. Sottos, J. S. Moore, S. R. White, *ACS Appl. Mater. Interfaces*. **2012**, 4, 503. Copyright 2012 American Chemical Society.

Table 2.1 Optimum fiber processing parameters for PLA fibers of different diameters.

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Fiber diameter (μm)	Solvent composition	Fiber soaking time	Tin(II) oxalate amount
20	20% TFE, 80% water	12 h	10 wt%
200	50% TFE, 50% water	24 h	10 wt%
500	60% TFE, 40% water	24 h	10 wt%

CHAPTER 3[†]

SOLUTION SPUN SACRIFICIAL PLA FIBERS THAT UNDERGO RAPID AND EFFICIENT THERMAL DEPOLYMERIZATION

3.1 Introduction

3.1.1 Preparation of Microvascular Materials

Synthetic microvascular materials mimicking natural systems have allowed the development of biomimetic technologies such as self-healing, active cooling, mass/energy transport, and bio-sensing systems.¹⁻¹⁰ Practical three dimensional microvascular materials, especially composites, require rapid, reliable and scalable fabrication routes. Existing approaches such as direct-write assembly,^{4,5} hollow glass fibers,^{6,7} electrostatic discharge,⁸ and sugar and polyethylene fibers⁹ have demonstrated the introduction of microchannels in polymeric matrices; however, they lack the ability to integrate complex, deterministic microvascular networks into conventional fiber reinforced structural composites. The VaSC method¹⁰ described previously was a reliable and scalable route for microvascular composites with significantly improved materials compatibility. The method was based on the thermal depolymerization of catalyst-impregnated poly(lactic acid) (PLA) fibers.^{10,11} Under high temperatures, PLA fibers depolymerized to their gaseous monomer lactide^{11,12} leaving behind hollow microchannels after vacuum evacuation. Catalysts impregnated into the PLA fibers lowered the depolymerization temperature by promoting the cleavage of ester bonds.¹³ The incorporation of various catalysts *via* the solvent-impregnating technique^{11,14}

[†] Catherine M. Possanza and Dr. Piyush R. Thakre contributed to some of the content presented in this chapter.

lowered PLA depolymerization to temperatures at which the matrix materials are stable, making the fabrication route compatible with traditional matrix composite materials were stable, ultimately making the fabrication route compatible with traditional matrix manufacturing protocols.¹⁵ The screening of several catalysts revealed that tin(II) oxalate (SnOx) was the most successful at decreasing the PLA depolymerization temperature.¹¹

3.1.2 Limitations of Treated Commercial PLA Fibers

The VaSC method is robust, scalable and works at temperatures below the degradation temperatures of typical thermoset matrices; however, the process has prolonged manufacturing time. Typically, the VaSC process included a lengthy catalyst impregnation time of 24 h followed by another 24 h heat treatment to remove the fiber from the matrix.¹¹ To accelerate manufacturing and reduce potential thermal damage to the matrix material, it is very important to reduce the time needed to fully remove the sacrificial fibers.

Catalyst loading and homogeneity are crucial parameters for efficient fiber removal. Based on a standard test protocols from the prior work,¹⁰ fiber removal reached as much as 95% in the first 6 h of the VaSC procedure; however, 24 to 48 h were needed for complete fiber removal. For the commercial PLA fibers treated with catalyst, SEM images were obtained on a cross-section of the holomatrix with an embedded sacrificial fiber (**Figure 3.1**). As shown in **Figure 3.2**, tin(II) oxalate was visible only along the edges of the interface. Elemental analysis (EDS, **Figure 3.2**) revealed the presence of tin-rich regions (white spots) at the fiber interface, compared to the area of epoxy matrix. Imaging of the apomatrix with MicroCT (**Figure 3.3**) revealed residual tin on the

microchannel surface. Based on the imaging results, it was concluded that the catalyst was predominantly located on or near the surface of the PLA fiber.¹¹ Insufficient catalyst and its inhomogeneous distribution throughout the fiber resulted in the polymer melting instead of depolymerizing into its gaseous monomers. The molten polymer clogged the channels, impeding removal of monomer vapors. Thus, the development of a fiber spinning method is imperative so as to achieve uniform distribution of controlled catalyst amounts in the fiber for rapid and efficient thermal depolymerization, expediting fiber removal process.

3.1.3 Fiber Spinning Method

Spinning has been widely studied and established as an industrial process for fiber production.¹⁶⁻¹⁸ Both melt and solution spinning processes have been explored for PLA,¹⁸⁻²⁰ but spinning of catalyst/PLA mixtures has not been reported to the best of our knowledge. Although melt spinning produces stronger fibers,¹⁹ the operating temperature is limited to the narrow window between the PLA melting point (ca. 170 °C) and the onset depolymerization temperature in the presence of catalyst (ca. 180 °C).¹¹ To avoid fiber degradation during processing, a new spinning procedure (**Figure 3.4, Figure 3.5, Scheme 3.1**) was employed in which catalysts are premixed with a PLA solution. The final fibers have homogeneously dispersed catalyst and perform significantly better in the VaSC removal process than the catalyst-impregnated commercial fibers.

Herein the production and characterization of solution spun PLA fibers of varying diameters is described. Scanning electron microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS) are used to study the catalyst distribution. Depolymerization

behavior of spun fibers is studied by thermogravimetric analysis (TGA) and compared to catalyst-impregnated commercial fibers. Finally, single fiber tension tests are performed to measure tensile strength of the spun fibers.

3.2 Fiber Spinning Procedure

The fiber spinning procedure began by dissolving commercial PLA pellets in an appropriate solvent (demonstrated with dichloromethane (DCM) in this work¹⁹). After the pellets were fully dissolved, a solid or liquid catalyst was added and stirred until a homogeneous mixture was observed. The PLA/catalyst blend was conditioned at elevated temperature to remove excess solvent, and then extruded through a spinneret. The extruded fiber was collected on a Teflon winder and dried. (**Scheme 3.1**, see experimental section for details).

3.3 Characterization of Homespun PLA Fiber

3.3.1 Diameter Control

Microvascular networks with controlled channel diameters allow for the fabrication of multi-dimensional vascularized materials, which are common in nature (e.g., leaves, blood vessels, etc.). In order to fabricate such networks, the diameter of the spun filament needs to be regulated. In the fiber spinning procedure, PLA fibers with different diameters were obtained by using varied size spinnerets (**Figure 3.6**, **Table 3.1**). A continuous PLA fiber strand produced using a 0.5 mm spinneret is shown in **Figure 3.7**.

3.3.2 Catalyst Distribution

The distribution of catalyst in spun fibers is critical for improving the depolymerization process and removal behavior of sacrificial PLA. Cross-sectional SEM images of catalyst-loaded fibers prepared by the previous solvent-impregnating procedure showed the existence of catalyst particles predominantly on the fiber surface (**Figure 3.2**).¹¹ Longitudinal cross-sections of spun fiber produced by solution spinning were characterized using the same method (**Figure 3.8 – 3.10**). Homogeneously distributed SnOx particles were clearly observed as bright spots in the spun PLA fiber with SnOx; Energy Dispersive X-ray Spectroscopy (EDS) confirmed these regions are rich in tin catalyst (**Figure 3.8**). In addition, MicroCT image (**Figure 3.9**) revealed that the spun fiber produced by solution spinning method significantly improved the catalyst distribution, compared to commercial fiber treated with SnOx. For spun fibers with tin(II) octoate (SnOc, a liquid catalyst), the catalyst was more uniform than spun fibers with SnOx. A SnOc modified fiber was compared to a blank PLA fiber in **Figure 3.10**, and EDS confirmed the presence of tin throughout the fiber. It was observed that the liquid SnOc catalyst was more uniformly dispersed in contrast to discrete phases of SnOx catalyst particles. The uniform distribution of SnOc throughout a spun PLA fiber was considered favorable for efficient depolymerization upon heating to facilitate clearing the channel.

3.3.3 Depolymerization Profile of Spun Fibers

The depolymerization behavior of spun and commercial fibers was studied by examining depolymerization onset temperatures using TGA at a heating rate of 10 °C ·min⁻¹ (**Figure**

3.11). While unmodified PLA fiber showed an onset depolymerization temperature at ca. 330 °C, solvent-impregnation of SnOx catalyst reduced the temperature to ca. 255 °C.¹¹ The onset was further decreased with spun SnOx fibers (ca. 210 °C). Moreover, as observed in the TGA profile, the amount of residue remaining at the end of the heating cycle was approximately two times higher in the spun fiber (ca 10 wt%) compared to the impregnated fibers (ca. 5 wt%). The increased amount of residue indicates an improved catalyst loading in the spun fiber, considering the same concentration of catalyst was used for each process. The results suggest that in the solvent-impregnation method, significant quantities of the catalyst were not absorbed due to the limited fiber-swelling region; however, in the fiber spinning approach a more complete catalyst loading was achieved. In addition to better catalyst incorporation, the spinning method offers the possibility of incorporating a variety of catalyst. As described in prior work,¹¹ liquid catalyst tin(II) octoate (SnOc) did not perform well in the solvent-impregnating procedure as SnOc simply adsorbs on the surface of a PLA fiber instead of absorbing into the fiber.¹¹ However, since SnOc was completely miscible in the PLA solution, PLA fibers with uniform distribution of SnOc were obtained by the spinning method (**Figure 3.10**). Due to the catalyst homogeneity in the fibers as discussed above, the depolymerization profile of spun fibers with SnOc showed an even lower depolymerization temperature, with onset at ca. 180 °C.

3.3.4 Rate of Fiber Removal

Subsequent studies on fiber removal were conducted using samples embedded in an epoxy matrix. Time dependency of the fiber depolymerization inside epoxy matrix was studied by measuring the empty channel length using an optical microscope. Spun fiber

containing a SnOc catalyst started to vaporize in the epoxy matrix almost instantly when exposed to 200 °C (**Figure 3.12**). These fibers were completely removed within 2 hours, outperforming all other fiber variations. Spun fibers with SnOx catalyst displayed 87% removal after 2 h and reached complete removal after 8 h. The homogeneity of SnOc liquid in the fiber spinning process as demonstrated above most likely accounts for a quicker and more efficient removal during the VaSC procedure when compared to SnOx doped, spun fibers (for a more thorough discussion please refer to Section 3.7). Commercial PLA fiber impregnated with SnOx exhibited slower fiber removal with an average removal fraction of 87% after 8 h.²¹ The control sample of unmodified PLA fibers showed only ca. 23% fiber removal after full 8 h of heating at 200 °C.

3.3.5 Mechanical Properties

Weaving of sacrificial fibers into three-dimensional structural preforms provides the potential for scalable 3D microvascular composites.¹⁰ The fibers must have sufficient tensile strength to survive the weaving process. Cold-drawing is a common procedure employed to increase the mechanical strength of a single fiber.²²⁻²³ It is believed that during the drawing process, the individual polymer chains tend to align in the fiber, thus increasing the strength of the overall material.²³ By measuring the drawn fiber length, the draw ratios (defined as the drawn fiber length over the as-spun fiber length) can be calculated and therefore fibers with different draw ratios can be made. Spun PLA fibers with different draw ratios were prepared and their tensile strengths were studied by single fiber tension tests. A plot of tensile strength versus draw ratio is shown in **Figure 3.13**. As expected, drawing significantly increased fiber failure strength. The use of a catalyst (result shown with SnOc) did not significantly impact fiber failure strength. Even with

minimal drawing, all studied fibers exceeded the ca. 23 MPa threshold strength required for industrial weaving processes.²⁴

Degree of orientation is a parameter reflecting the crystallite alignment in a single polymer fiber which is generally examined by Wide Angle X-Ray Scattering (WAXS).^{25,26} In this work, calculations from WAXS patterns (**Figure 3.14**) show that after drawing, the degree of orientation of pure spun PLA fiber increased from 0 to 23%, while crystallinity of the fiber remained unchanged. It is believed that during the cold-drawing process, crystallites in the fiber were aligned in the drawing direction so as to increase the degree of orientation and the tensile strength.

3.3.6 Effect of Catalysts on Glass Transition Temperature

Using Dynamic Mechanical Analysis (DMA), the glass transition temperatures (T_g) of unmodified spun fiber, spun fiber with SnOx and spun fiber with SnOc were measured. The $\tan \delta$ plots of the three fibers are shown in **Figure 3.14**. Unmodified spun PLA fiber showed a T_g around 60 °C, and this temperature was increased to ca. 68 °C when the fiber was doped with SnOx. It is speculated that the SnOx particles hinder the movement of polymer chains, increasing the glass transition temperature. Interestingly, for spun fiber doped with SnOc, the T_g also showed an increase to ca. 67 °C.

3.3.7 Discussion of SnOc-Doped PLA Fiber

Several factors can be considered as the possible cause of a faster depolymerization for SnOc doped PLA fiber:

- 1) the liquid catalyst changes the morphology (i.e. the crystallinity) of the fiber;
- 2) the liquid catalyst plasticizes the polymer;

3) the liquid catalyst completely wets the fiber, improving the catalyst distribution.

Using the knowledge obtained from the experimental data, the first two factors were excluded as 1) the crystallinity of spun fiber with SnOc was measured to be 23.2 %, which is very similar to that of unmodified spun fiber (23.6%); and 2) according to the T_g measurements (**Figure 3.14**), the addition of SnOc overall increased the T_g . Even if SnOc does plasticizes PLA, the plasticizing effect is overshadowed by the the fact that the catalyst hinders the chain movement so as to increase the glass transition temperature. As a result, the improved catalyst distribution is the sole and predominant factor for faster depolymerization.

3.4 Conclusion

In this chapter, a fiber spinning method, which produces sacrificial PLA fibers that have a high loading of homogenously dispersed depolymerization catalyst was developed. The fibers were able to rapidly depolymerize at temperatures compatible with thermoset resins in polymer composites to yield microvascular materials. Fibers produced by solution spinning outperformed commercial fibers that were treated using a solvent-impregnation approach by exhibiting a lower depolymerization temperature and requiring less time for complete fiber removal. This new fiber spinning approach, when combined with the microvascular composite manufacturing technique (VaSC), could lead to a considerably shorter manufacturing cycle (3h, compared to the previous 48 h) and reduces potential damage to the composite matrix from thermal degradation (VaSC temperature reduced to 180 °C) (**Scheme 3.2**). These improvements open up a new avenue to produce sacrificial building blocks for synthetic microvascular materials, enabling rapid, reliable and large-scale microvascular composites fabrication.

3.5 Experimental Section

3.5.1 Materials

Poly(lactic acid) (PLA) pellets (Molecular weight: 340 kDa) were obtained from Purac Biomaterials and used as received. Depolymerization catalysts tin(II) oxalate (SnOx) and tin(II) octoate (SnOc) were obtained from Sigma-Aldrich. Diglycidyl ether of bisphenol A resin (EPON 828) was used as received from Miller-Stephenson with the curing agent EPIKURE 3300 received from Hexion. Epoxy samples were prepared using a mass ratio of 22.7 parts per hundred (pph) of EPIKURE 3300 to EPON 828. All other chemicals were obtained from Sigma-Aldrich unless otherwise noted.

3.5.2 Characterization

3.5.2.1 TGA

Thermogravimetric analysis (TGA) was performed on a Mettler-Toledo TGA851^e, calibrated with indium, aluminum and zinc standards. For each experiment, the sample (ca. 10 mg) was weighed (± 0.02 mg) in an alumina crucible. For dynamic measurements, the mass loss was recorded during a heating cycle over the temperature range of 25 to 650 °C at a heating rate of 10 °C·min⁻¹.

3.5.2.2 Microscopy

Fiber removal in epoxy matrix was imaged using a Leica DMR Optical Microscope at various magnifications and ImageJ software was used to measure the fiber removal fraction. Spun fiber diameters were measured using the same microscope.

3.5.2.3 ESEM

Environmental Scanning Electron Microscopy (ESEM, Philips XL30ESEM-FEG) was used to image cross-sections of spun fibers. SEM images were acquired after sputter-coating the sample surface with carbon and were collected using backscattering electrons. Elemental analysis for selected area and elemental mapping were performed by EDS (Energy Dispersive X-ray Spectroscopy, attached to the SEM) with a 20 kV electron source and spot size of 3.0 nm.

3.5.2.4 Fiber Tension Test

The tensile strength of spun fibers was measured at room temperature on an Instron Machine (Instron Mini-44). For each test sample, a fiber with the gauge length of 30 mm was clamped between pneumatic grips and the test was performed in a displacement-controlled mode at a rate of 10 mm/min. The corresponding tension load was measured using a 500 N load cell. Engineering stress and strain were calculated from the load-displacement data and tensile strength was determined as the load obtained at failure.

3.5.2.5 Wide angle X-ray scattering (WAXS)

WAXS experiment was conducted through the Materials Chemistry Laboratory at the University of Illinois. WAXS data was collected on a Bruker General Area Detector Diffraction System (GADDS) equipped with a P4 four-circle diffractometer and HiStar multiwire area detector. A Bruker M18XHF22 rotating anode generator operating at 50 kV and 40 mA supplied the Cu K α graphite monochromatized incident beam. Several fibers were mounted parallel to each other on an aluminum mount. The sample to detector distance was 8.5 cm. Two frame series were collected at 2 θ settings of (-10, 0,

and 10 degrees). The first frame series was collected with the fibers aligned vertically and the second series was collected with the fibers in horizontal alignment. The combined 2D images were then integrated and combined into 1D patterns.

3.5.2.6 DMA

Dynamic Mechanical Analysis (DMA) was performed on TA Instruments RSA3. Different fiber specimens were tested in oscillating tension and compression over a range of temperatures, using the DMA environmental chamber to control the temperature. A 0.1 N tensile load was applied to the fiber at an oscillating rate of $5 \mu\text{m}\cdot\text{s}^{-1}$. The temperature ramp was $3 \text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ from $20 \text{ }^{\circ}\text{C}$ to $120 \text{ }^{\circ}\text{C}$. Storage and loss moduli were measured and $\tan \delta$ was calculated from the moduli data and plotted against temperature.

3.5.3 Preparation of PLA Solution

Commercial PLA pellets (6 g) were dissolved in a beaker filled with excessive amount of DCM (150 mL) at room temperature and the solution was concentrated by boiling off extra solvent until solution volume reached 35 mL. Catalysts (SnOx particles or SnOc liquid) were blended into the viscous solution (10 wt% tin equivalence to PLA). The solution was stirred for 30 min in order to disperse the catalyst well.

3.5.4 Fiber Spinning Process

In the fiber spinning setup (**Figure 3.5**), the solution chamber was pre-heated to $55 \text{ }^{\circ}\text{C}$. Concentrated PLA solution (10 mL, contains dispersed catalysts) was carefully transferred to the chamber. The chamber was conditioned in the heater for 5 min then on a benchtop for additional 5 min before extrusion, allowing the solution to further

concentrate. PLA solution was extruded at 55 °C at an extrusion speed of 8 cm/hr. The solution passed through the spinneret (diameter ranging from 0.25 mm to 1 mm) and formed a single fiber. Two heaters below the spinneret provided extra heat to further evaporate the solvent. Extruded fiber was collected on a Teflon bobbin without applying additional stress and was air-dried at 50 °C.

3.5.5 Fiber Removal Study

Spun fibers (along with unmodified PLA fiber and catalyst-impregnated commercial PLA fiber) were embedded in an EPON 828: EPIKURE 3300 epoxy thermoset that was cured in a silicone rubber mold using the standard protocol. Cured epoxy thermoset was carefully trimmed before heating in order to expose fiber ends. Epoxies containing sacrificial fibers were heated in a sealed vacuum oven (Fisher Isotemp 283) at 200 °C under vacuum (1 torr). The fiber removal fraction (the ratio of empty channel length over the full fiber length) was measured for each sample at different time intervals 1, 2, 4 and 8 hours. Fiber removal data were averaged over 25 one-inch fiber samples.

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3.7 Figures, Tables and Schemes

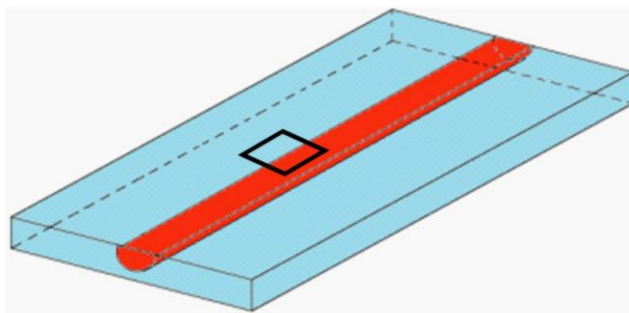


Figure 3.1 Illustration of holomatrix in which a sacrificial fiber is embedded in an epoxy thermoset. The rectangular perimeter defines the cross-sectional area where the SEM image (**Figure 3.2**) was obtained. Reprinted with permission from Reference 11. Copyright 2012 American Chemical Society.

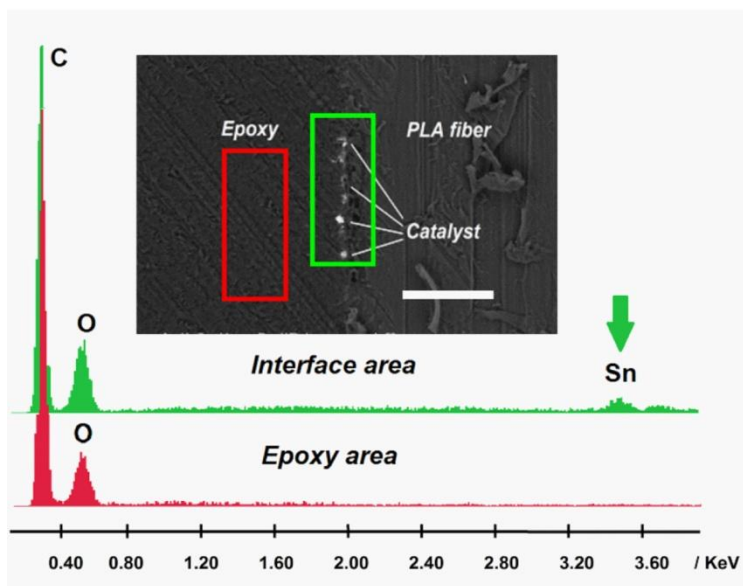


Figure 3.2 SEM image of cross-sectional area and elemental information for highlighted surface areas (Scale bar: 50 μm). Reprinted with permission from Reference 11. Copyright 2012 American Chemical Society.

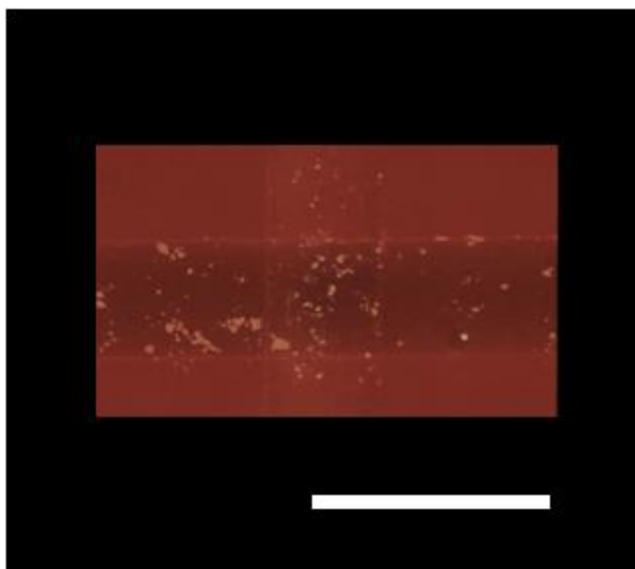


Figure 3.3 MicroCT 3D reconstruction of an apomatrix showing empty microchannels as a result of sacrificial fiber removal (Scale bar: 1000 μm , white spots were assigned as tin since heavier elements provide the most contrast). Reprinted with permission from Reference 11. Copyright 2012 American Chemical Society.

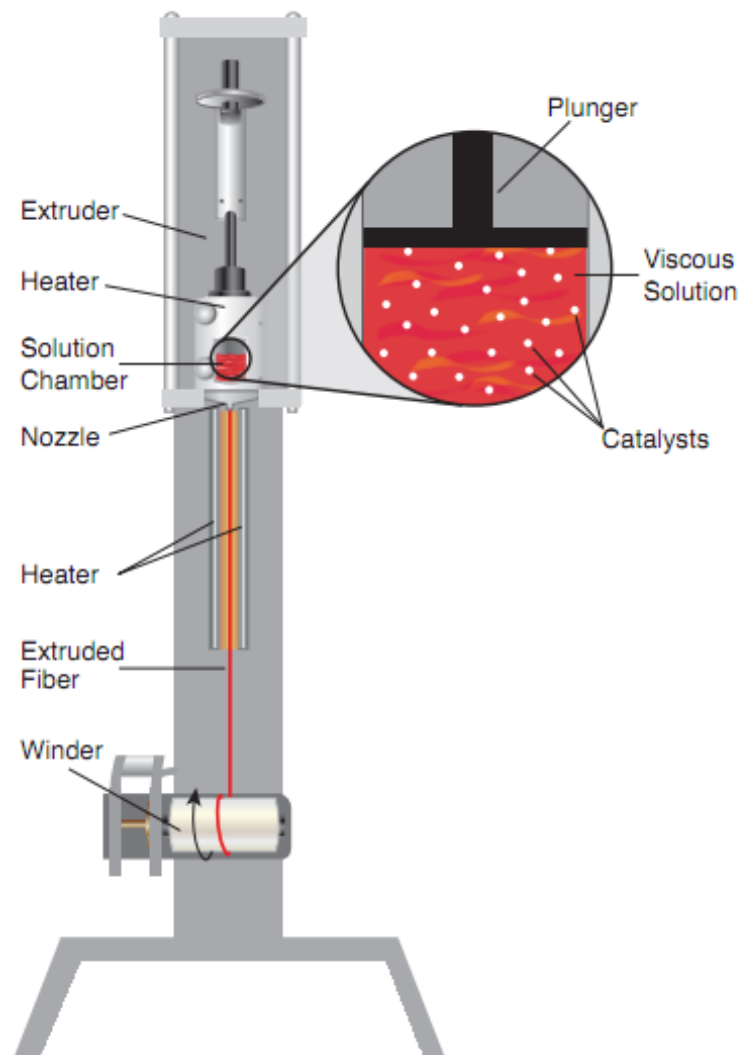


Figure 3.4 Schematic illustration of the solution spinning setup (solution chamber with feeding material magnified).



Figure 3.5 Photograph of the solution spinning setup. The PLA solution (dispersed with catalysts) is placed in the heated chamber. Using a motor-driven extruder, the PLA solution is extruded through the nozzle and excess solvent is evaporated as the extruded fiber passes through additional heating chambers. Extruded fiber is collected on a Teflon winder and dried.

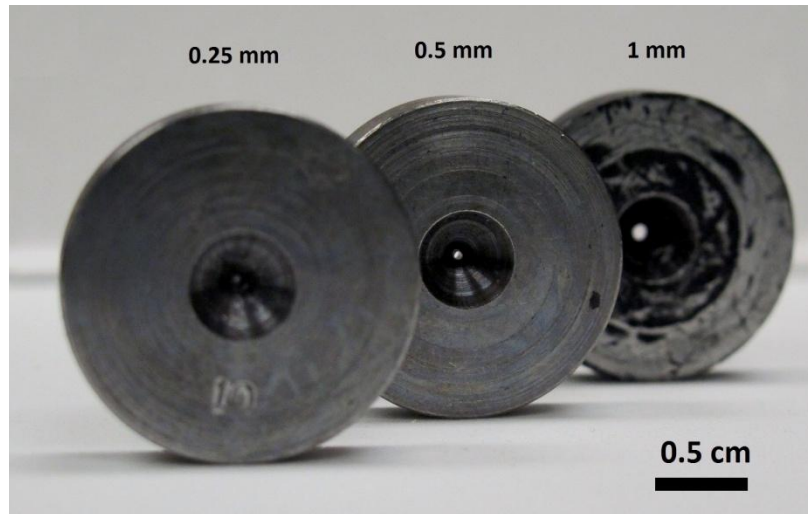


Figure 3.6 Photograph of three spinnerets of different sizes.

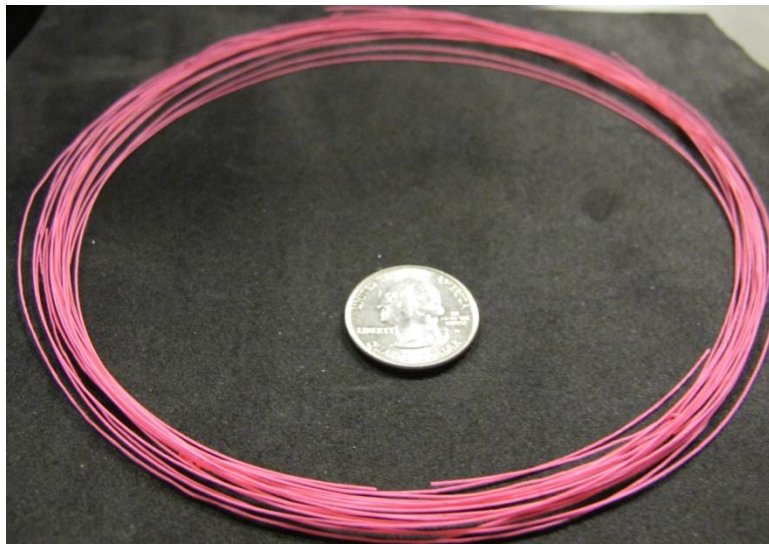


Figure 3.7 Photograph of a continuous PLA fiber strand produced using a 0.5 mm spinneret. (Image courtesy of Catherine M. Possanza)

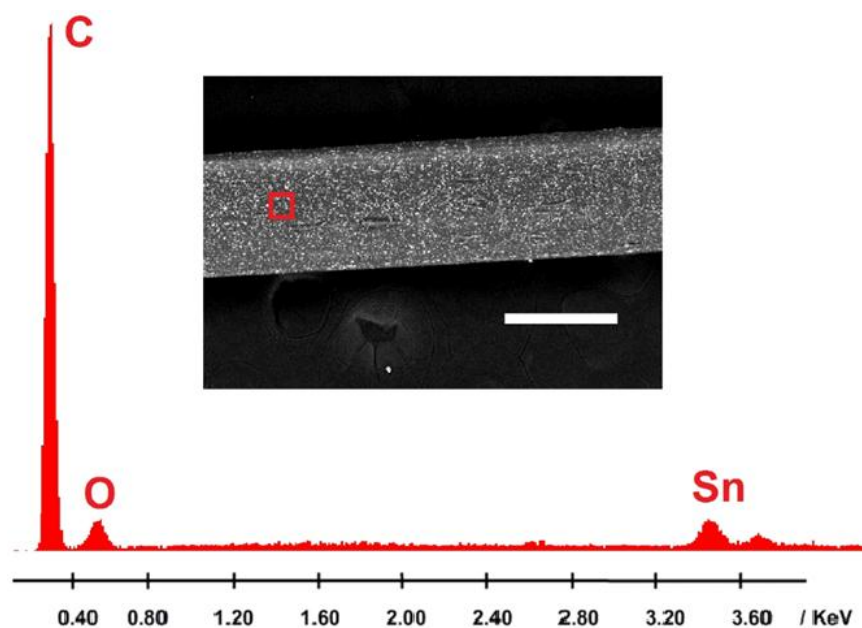


Figure 3.8 SEM image of spun PLA fiber with tin(II) oxalate and EDS data collected within the red rectangular area. (Scale bar = 400 μm)

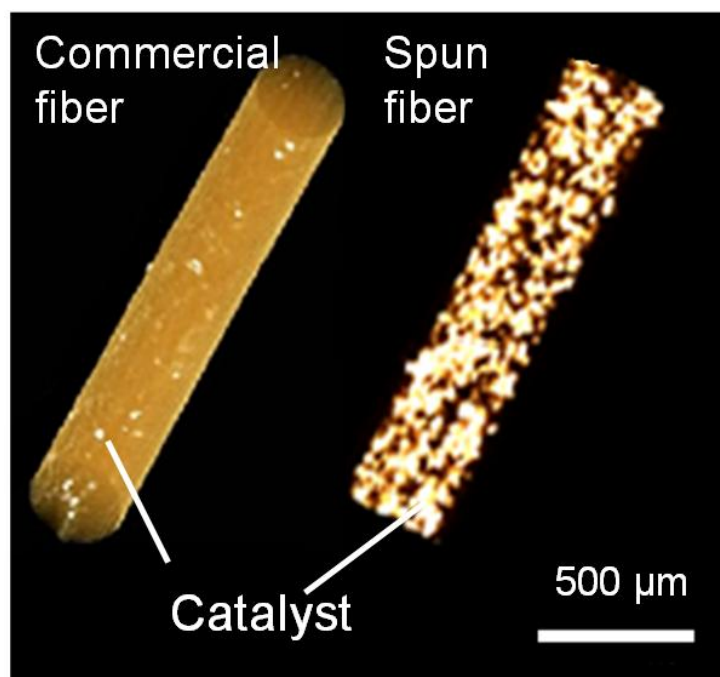


Figure 3.9 MicroCT image of PLA fiber with tin(II) oxalate produced by chemical treatment of commercial fiber (left) and solution spinning method (right).

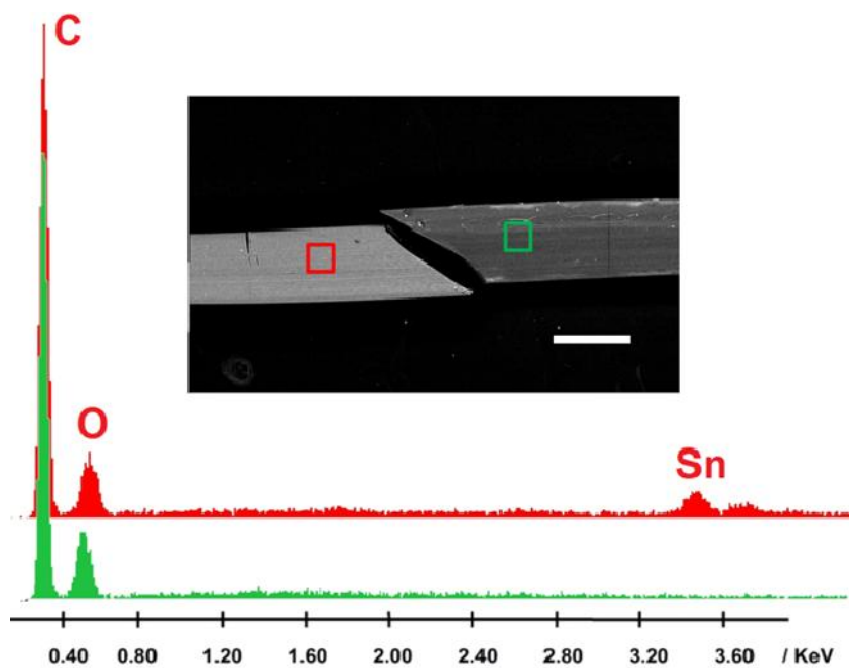


Figure 3.10 SEM images of spun PLA fiber with tin(II) octoate (left) and unmodified PLA fiber (right) and EDS data collected within the corresponding areas. (Scale bar = 400 μm)

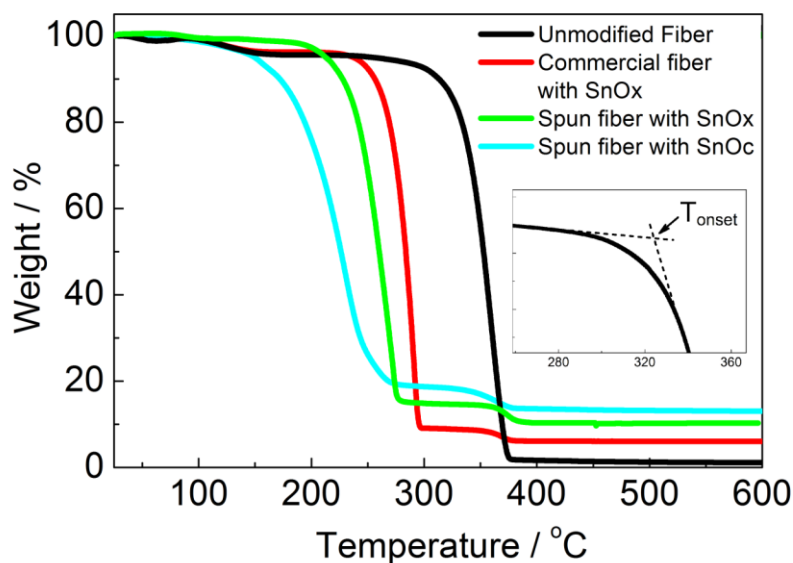


Figure 3.11 Dynamic TGA curves (at a heating rate of $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$) for unmodified PLA fiber, SnOx-impregnated commercial PLA fiber, spun fiber with SnOx and spun fiber with SnOc. For all TGA profiles, fiber onset depolymerization temperature is determined as the temperature that corresponds to the intersection of two tangent lines in the TGA curve (example shown as an inset TGA profile of the unmodified fiber). In those experiments, the alumina crucible was loaded with chopped $400\text{ }\mu\text{m}$ PLA fibers.

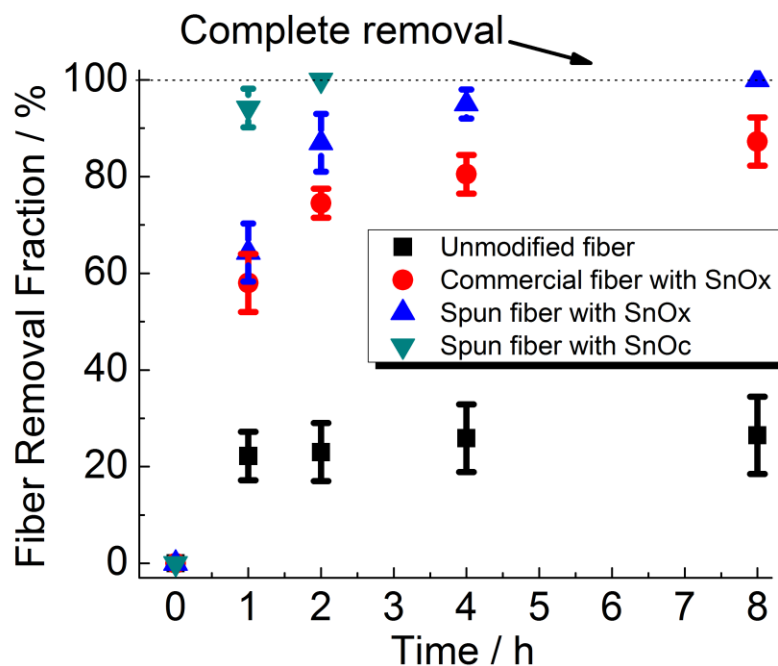


Figure 3.12 Fiber depolymerization data for various PLA fibers at each time interval. Sacrificial fibers embedded in epoxy matrix were heated in a sealed vacuum oven at 200 °C under vacuum. Fiber removal fraction was defined as the ratio of empty channel length over the full fiber length. Fiber removal data were averaged over 25 fiber samples of 1 inch length.

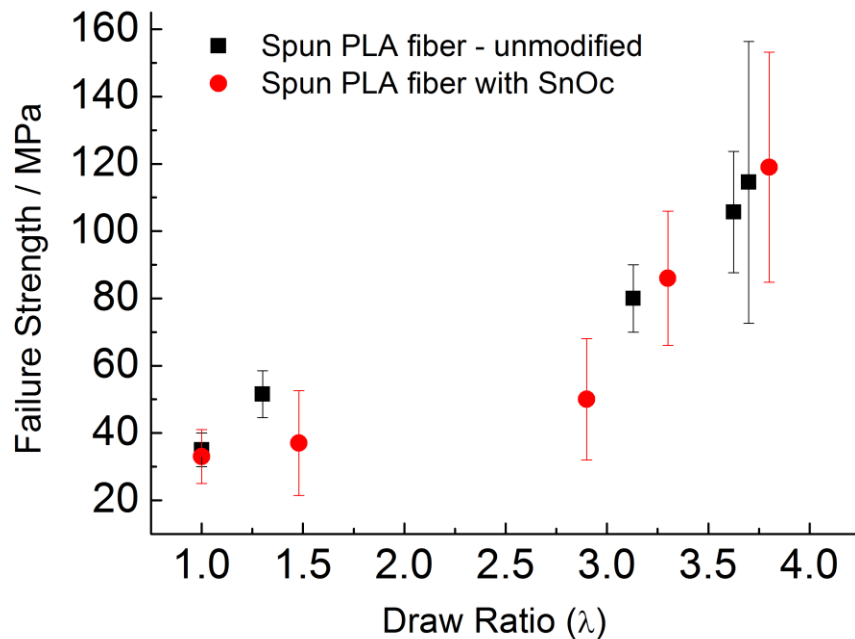


Figure 3.13 Failure strengths of unmodified PLA fiber (black) and spun PLA fiber with SnOc (red). Draw ratio is defined as the drawn fiber length over as-spun fiber length. Failure strength was calculated from the load-displacement data, which is measured at room temperature on a mini-instron frame. For each data point, failure strength was averaged over 5 to 10 fiber samples.

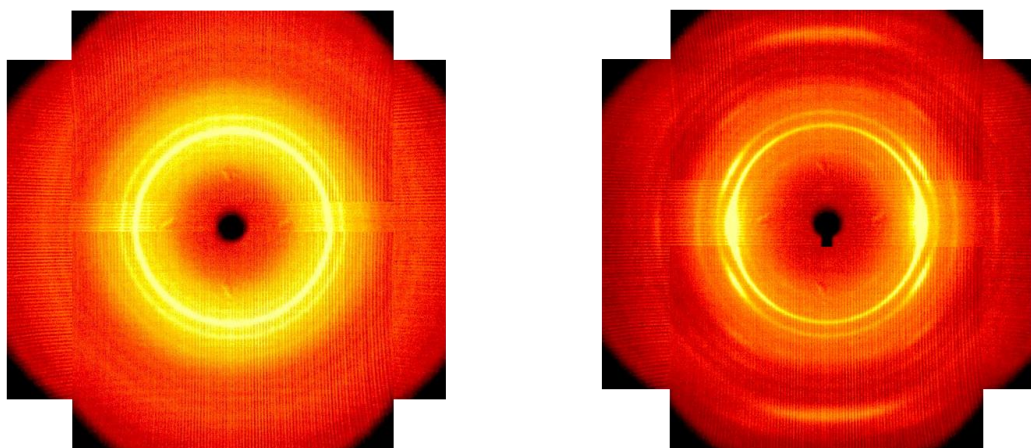


Figure 3.14 Wide Angle X-Ray Scattering (WAXS) patterns of as-spun pure PLA fiber (left) and drawn (60%) pure PLA fiber (right).

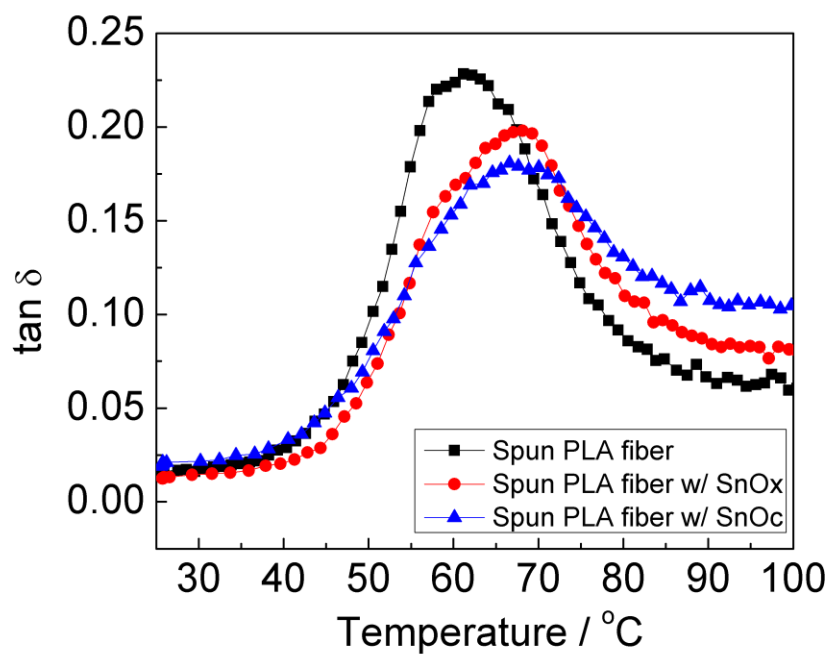
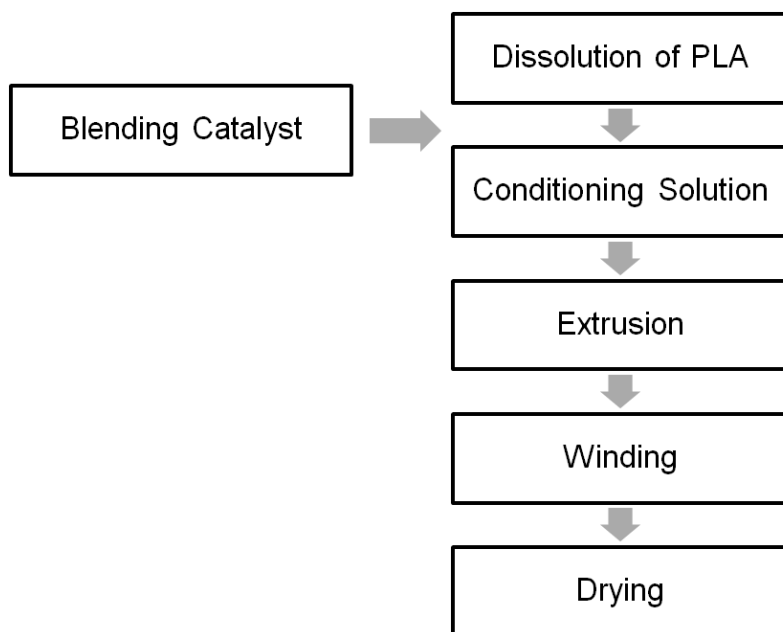


Figure 3.15 DMA data ($\tan \delta$) of spun PLA fiber and spun fiber with different catalysts.

The peak of $\tan \delta$ curve corresponds to the glass transition temperature of the polymer.

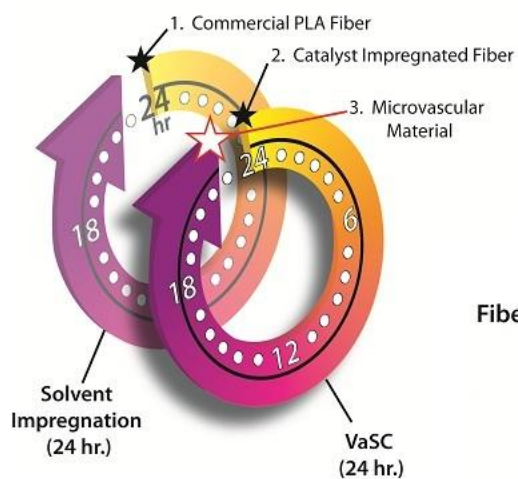
Table 3.1 Different sized spinnerets and obtained fiber diameters. Spun fiber diameters were measured by optical microscope, averaged over 5 to 10 fiber samples.

Spinneret Diameter (mm)	0.25	0.50	1.00
Spun Fiber Diameter (mm)	0.14 ± 0.02	0.42 ± 0.03	0.75 ± 0.05

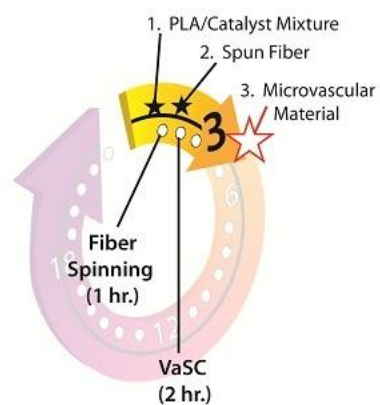


Scheme 3.1 Flow chart of solution spinning procedure.

Solvent Impregnation Approach (48 hr.)



Fiber Spinning Approach (3 hr.)



Scheme 3.2 Time lines for microvascular material fabrication using solvent-impregnating approach (left) and fiber spinning approach (right).

CHAPTER 4[‡]

MICRO-STRUCTURING OF POLY(LACTIC ACID) FILM FOR TWO-DIMENSIONAL MICROVASCULAR MATERIAL

4.1 Introduction

4.1.1 Flexible Microvascular Materials

Rigid polymeric materials such as thermosetting polymers,¹ epoxy resins,² fiber/polymer composites³ provide non-deformable structural support and are broadly utilized in construction,⁴ transportation,⁵ and other civil engineering infrastructures.⁵ In contrast, flexible polymer materials⁶⁻¹¹ that undergo tensional and shear deformation upon external stimuli are capable of mimicking biological materials found in nature, such as tissues, cell membranes, skins, etc.. These characteristics are essential when material performance relies on deformation or when surface conformity is required, such as in packaging materials,⁶ bio-integratable clinical devices,⁷⁻¹¹ membrane technology¹² and soft robotics.¹³⁻¹⁶

Materials with internal cavities allow circulation of gases,¹⁵⁻¹⁶ fluids,¹⁷⁻¹⁸ or solids¹⁹ inside them which provide a variety of new functions. Many technological inventions have been developed to control fluid behavior in small channels, for example, microvascular materials^{17-18, 20-23} are a category of materials that have interconnected microchannels with high-aspect ratios embedded in a matrix; when injected with a fluid, the contents and properties of the fluid imparts additional functions to the matrix.²³ In a flexible matrix, the incorporation of microchannels and the substance inside those microchannels

[‡] Nicholas I. Maniscalco contributed to some of the content presented in this chapter.

are apt to change the color, property, and even the shape of the matrix. Whitesides demonstrated that a silicone matrix with a colored fluid circulating inside could be used as a camouflage material for soft machines.²⁴ In another system, a metal grating inside a flexible matrix that significantly increased electrical conductivity was demonstrated to be useful as a soldering material.²⁵ In other reports,^{19, 25, 26} the so-called self-shaping materials relied on an intrinsic deformable matrix in cooperation with an endoskeleton that was responsive to external stimuli, changing the mechanical, chemical, electrical and magnetic properties of the entire composite.

There are a number of ways to fabricate flexible microvascular materials and reported fabrication routes are predominantly based on soft lithography techniques^{7-11, 13-16, 19, 24-25} and direct ink writing technology.^{17, 18} Both techniques are successful in creating useful materials with microchannel structures, however, they have significant disadvantages that limit them from being broadly utilized. Soft lithography not only requires multiple lithography steps, but is also slow, low throughput and costly; direct ink writing is difficult to scale up to commercial production. In contrast, Vaporization of Sacrificial Component (VaSC)²³ presents a novel method in which a sacrificial polymer fiber is embedded in a polymer matrix; subsequent vaporization of this polymer fiber leaves empty channels inside the matrix. VaSC is advantageous over previous fabrication methods because it is scalable, inexpensive, robust, and allows more complex geometries to be incorporated into a wider range of matrix materials.

4.1.2 Limitations of Current VaSC Technology

All VaSC demonstrations to date have focused on a simple fiber geometry, lacking complexity and tunability in the sacrificial component. Incorporation of a two-dimensional and three-dimensional sacrificial polymer structures in the resin matrix will lead to two-dimensional and three-dimensional interpenetrated channels in a matrix, revealing the possibility of fabricating more complex structures and biomimetic patterns akin to leaves, circulatory systems, or helices. For a higher dimensional microchannel system, it is desirable to maintain a larger reservoir and obtain better resistance to channel blockage without greatly impacting the mechanical properties.^{27, 28} A new and facile method to create a two-dimensional sacrificial structure was designed to overcome the obstacle where simply connecting nodes of fibers in order to create a two-dimensional microchannel proves to be tedious and low throughput. Materials having internal vascularized structures with controlled, optimized geometries may impart new functionality by providing energy and mass exchange, structural support, and shape transformation to a flexible matrix.

4.1.3 Micro-Structuring of Sacrificial PLA Film

A number of ways for creating two-dimensional polymer structures have been reported previously. Microfluidics on foil has gained momentum due to advantages in employing thin films with cost-effective manufacturing of devices using hot embossing of a silicon microfabricated mold into a PMMA membrane.²⁹ While using silicon molds could reduce the mold material expense, issues remain with fabrication expense, large area scalability, and silicon die failure due to the brittle nature of silicon. Microfluidics has emerged as a

distinct field demonstrating broad influence over our basic understanding of science and technological development, however, the need for making microfluidic devices widely and inexpensively available remains an important challenge. Commercial tools and techniques must be developed for high-volume large-area microstructuring of materials containing complex architectures.^{30,31} The use of such a material as a microvascular component requires a fabrication route that is readily accessible, industrial scalable, as well as economical.

Herein, a two-dimensional PLA film is micro-structured into a PLA grid using a tool set that is produced by Micro-Electric Discharge Machining (μ EDM). The use of μ EDM for electrode-making and punch-making processes was first proposed by Masuzawa.³² μ EDM selectively removes a conductive material by plasma discharge. The tool and parts are separated by a small gap of dielectric liquid. Plasma discharge consumes a portion of the tool and part electrodes as an electrical current pulse is driven across the gap in the dielectric liquid.³³ The tools used in this research are fabricated by wire μ EDM from A4 tool steel. The stripper hole and die hole are fabricated by sinker EDM simultaneously.

4.1.4 Procedure Overview

The creation of two-dimensional sacrificial polymer grids to be used in fabricating a flexible material with interconnected channels inside was developed. The procedure starts with the production of a poly(lactic acid) (PLA) film, which is then perforated to create a polymer grid. This grid is then embedded in a silicone liquid precursor followed by curing of the silicone into a solid material that locks the 2D grid inside. Afterwards, the silicone is subjected to high temperatures, whereupon the PLA grid depolymerizes into a gas and leaves behind interconnected two-dimensional microchannels inside the flexible

silicone. The final structure is similar to the microfluidic devices that were previously reported, but this approach has the advantages of improved reproducibility and scalability. The self-shaping ability of the flexible material is demonstrated by infiltrating liquid metal (galium) inside the 2D channels and shaping the matrix, then lowering the temperature to solidify the metal. The “endoskeleton” formed by the ductile metallic grating provides structure support and electrical conductivity to the composite. Applications such as soft electronics,⁷⁻¹¹ soft robotics,¹³⁻¹⁶ electronic soldering,²⁵ and three-dimensional antennas³⁴ will greatly benefit from such a design.

4.2 Fabrication Route

Figure 4.1 illustrates and summarizes the procedure used to produce the flexible microvascular material. The technology comprises six steps: 1) preparing PLA solution for film fabrication; 2) fabrication of PLA film by solvent casting or spin coating; 3) micro-structuring of PLA film to create PLA grid; 4) incorporation of PLA grid into a matrix material precursor; 5) curing of the matrix to form a solid structure; and 6) removal of PLA grid to create two-dimensional microchannels inside the matrix. The following sections will discuss these fabrication steps in greater detail.

4.2.1 PLA Film Fabrication

The procedure began with the fabrication of a sacrificial PLA film. Commercial PLA pellets were dissolved in chloroform and then a depolymerization catalyst, tin octoate, was added to the solution. The PLA solution is similar to the solution that was used to produce the aforementioned solvent-spun PLA fibers. The addition of a catalyst is known to lower the depolymerization temperature of PLA material from 280 °C to 200 °C, so

that the PLA can be removed at a temperature that does not considerably degrade the surrounding matrix.²³ In this case, the silicone matrix remains unaffected at 280 °C, however, the addition of the catalyst reduces film removal time.³⁸ The PLA solution was either spin coated on a glass slide to get thin films or solvent-cast on a glass plate using a doctor blade to yield thicker films. Film thickness was controlled within $\pm 10\ \mu\text{m}$ from 10 to 63 μm by varying the spin coater speed from 500 to 3000 RPM for a polymer concentration of 15% (W/V) (**Figure 4.2**). The doctor blade could be adjusted to get conformal films from 20 to 250 μm within 5 % of thickness variation.

4.2.2 Hand-Cut PLA Film

The dried PLA films were hand-cut into specific two-dimensional geometries. **Figure 4.3** and **Figure 4.4** show a branched network and a grid structure cut by a razor blade. These structures were embedded in a matrix and subsequently removed to form empty channel networks; however, well-controlled and reproducible fabrication of microchannels calls for a more precise micro-structuring method.

4.2.3 Micro-Structuring of PLA Film

The micro-structuring of the PLA film was accomplished by the mechanical punch and die tool set using a benchtop arbor press (**Figure 4.5**). The tool set consists of a die, punch, stripper plate, support block, and base block. The components were vertically aligned with the use of guide pins to prevent interference and ensure appropriate clearances were maintained. The diamond shaped punch tool consists of 86 teeth arrayed in a honeycomb lattice with a web spacing of 250 μm (**Figure 4.6**). The rectangular shaped punch tool consists of 70 teeth arrayed with a vertical spacing of 400 μm and a horizontal spacing of

200 μm as shown in (**Figure 4.7**). The tool set was assembled as shown in **Figure 4.5**. The punch movement and precision stripper were aligned to the die and base block with four alignment pins which constrained the motion of the components to eliminate interference and decreased tool wear rates.

The PLA film was carefully aligned into the die, taped into place and the punch was transmitted through the material with the benchtop arbor press. The punched chads fell into the hollowed support block and the punch and die were manually separated. Ejection pins were inserted into the top of the punch and the arbor press was used to transmit a force from the pins to the stripper plate which removes the PLA film from the punch teeth. The PLA film was realigned onto the die and the process is repeated as necessary. This process may be repeated continually to produce 1.4 cm wide films of any desired length. **Figure 4.8** depicts the PLA films punched using the arbor press tool. SEM images (**Figure 4.9**) show the microstructures of these films. For each geometry, the arbor press tool can process PLA films with a wide range of thicknesses (**Figure 4.10**). Using this method, PLA grids that are 10 cm in length and 1.4 cm in width can be produced (**Figure 4.11**). The production of such a lattice structure using our method is extremely simple and scalable. The fabrication of a bigger grid is only a matter of repetitive machine runs, instead of being limited by the technology itself, such as the lithography method. Plus, this process lends itself well to be scaled up for roll-to-roll processing with a progressive die tool set.

In addition, the capability of aligning multiple strips adjacent to one another at the nodes was demonstrated. As seen in **Figure 4.12**, two strips of PLA film (10 cm long and 1.4 cm wide) were connected using a “welding solution” (15 wt% PLA/chloroform solution

with 10 wt% tin octoate) at the nodes and a 2.8 cm wide film was produced. Thus, this micro-machining technique is capable of being scaled to different geometric cross sections and it is conceivable that conjoining matrices with advanced architectures using polymer bonding at nodal intersections would be viable for customizable, very large area production of two and three dimensional flexible microvascular structures.

4.3 Controlled Geometries, Dimensions, and Aspect Ratios

Controlling microchannel dimension is critical in the design of microvascular material. In nature, the various, hierarchical sizes of channels (artery, vein and capillaries; phloem and xylem) are commensurately scaled with their functions to guarantee efficient energy/mass transport throughout the entire organism.^{35,36} In a vascularized material designed for self-healing or autonomous cooling, it is important to implement the optimized vascular dimension so that good healing/cooling takes place without greatly sacrificing the integrity of the material.^{27,28} The choice of microchannel diameters has to account for a number of parameters, such as spatial distribution, pumping scheme, and structural integrity. For example, for a multiscale microvascular material mimicking a branched circulatory system, in order to achieve an efficient fluid transport, the dimensions of microchannels in each generation are defined by Murray's law.^{18,37} It is thus important to fabricate microchannels with a wide variety of channel diameters, lengths, and also aspect ratios.

This micro-structuring technique is capable of creating two geometries: diamond and square. In the diamond geometry, the dimension of the grid is 234 μm in both directions. Since the thickness of the film that can be processed with the diamond punch ranges from 10 μm to 100 μm , the hydraulic diameter of the resulting square channel ranges from 20

to 140 μm . For the 10 cm long PLA grid (**Figure 4.11**), when embedded in a matrix and thermally removed, it creates microchannels with aspect ratios ranging from 70 to as high as 5200, although this is by no means a limitation. Similarly, the square structure has different dimensions in two perpendicular directions, 288 μm in the horizontal direction and 590 μm in the vertical direction. The 10 cm long PLA grid with a square geometry is capable of producing microchannels with an aspect ratio between 400 and 5200 in the horizontal direction, and 30 to 500 in the vertical direction. **Table 4.1** summarizes the microchannel dimensions for the two geometries. In summary, microchannels with hydraulic diameters ranging from 20 to 350 μm , aspect ratios ranging from 30 to 5200 were fabricated using the PLA grids produced by punch and die tool. This demonstrates the ability to use a single tool geometry to produce a multitude of hydraulic diameters and aspect ratios which may be required for multi-scale processing.

4.4 Flexible Microvascular Material from 2D PLA Grid

4.4.1 Incorporating PLA Grid into a Flexible Substrate

The micro-structured PLA grid was cast in a super soft silicone material – Ecoflex. Ecoflex has a very low Young's modulus (18MPa), thus it is easily deformed and responds quickly to pressure. Whitesides et al. fabricated soft robots using Ecoflex that can pick up objects when pneumatically actuated.¹³⁻¹⁶ They also designed a camouflage material for such a soft robot;²⁵ the desirable properties of Ecoflex greatly benefit these applications where flexibility and conformity are required. When made very thin, an Ecoflex film can even be used as an accessory for clinical devices. Rogers et al. exploited Ecoflex film as a support for their flexible electronics and other tattoo-like bio-

intergratable therapeutic and diagnostic devices.^{10,11} In this chapter, Ecoflex was chosen because the fabrication process is very easy to control, and its high deformability allows itself to be twisted, bent, and morphed into arbitrary geometries with a metal “endoskeleton” inside, thus the self-shaping effects of such a composite material can be demonstrated.

The PLA grid was incorporated into the Ecoflex substrate *via* a “layer-by-layer” assembly technique. First, a thin layer of Ecoflex was cured into a solid film from a two-component precursor. The PLA grid was then carefully transferred onto the solid film. Another layer of Ecoflex precursor was poured on top of the grid and cured into a solid flexible film (**Figure 4.13**). After the matrix was fully cured and PLA grid was completely locked inside, the composite was subjected to high temperature for PLA removal.^{23,38} At 200 °C (with the presence of catalyst) PLA started to depolymerize into a gaseous monomer which was subtracted from the matrix with the assistance of vacuum. The matrix was trimmed to expose the ends of the grid before putting in a vacuum oven so that the gaseous product could escape during evacuation. **Figure 4.14A** shows that after 6 h of heat treatment at 200 °C, evacuation was complete revealing empty channels embedded in the matrix. The full evacuation of the PLA grid was demonstrated by filling the entire microchannels with red-dyed water (**Figure 4.14B**). **Figure 4.15** shows the MicroCT image of an Ecoflex matrix with empty 2D microchannels inside (diamond geometry).

In addition, the joint film (10 cm by 2.8 cm, **Figure 4.10**) was also able to be fully removed inside a matrix (**Figure 4.16**) and allowed liquid circulation.

4.4.2 Demonstration of Self-Shaping Ability

The creation of microchannel structure in a soft matrix material enables the formation of an endoskeleton that acts as a structural support. An endoskeleton in biology either functions as pure support, or serves as an attachment site for muscle and a mechanism for transmitting muscular forces. A few previous articles reported the creation of such microstructured endoskeleton in a matrix material. These endoskeleton materials were usually based on a UV-curable liquid epoxy precursor,¹⁹ a liquid metal that solidifies at proper temperatures,²⁵ or a stress-responsive fiber-like material that is mechanically distinct from the hydrogel matrix.²⁶ Herein, the formation of an endoskeleton inside the microvascularized Ecoflex was demonstrated by filling the entire microchannels with a liquid metal, and subsequently cooling the material below the melting point of the liquid metal. Owing to the high deformability of the Ecoflex, the composite can be morphed into various shapes while the metal is still liquid and when the metal solidifies into a rigid structure inside the matrix, the composite acquires a specific shape. Gallium was chosen for this work due to its extremely low melting point (30 °C), which provided an uncomplicated experimental procedure to achieve a liquid-solid transformation near room temperature. Despite the small fraction of gallium in the entire matrix (2%), gallium functions as an effective endoskeleton that holds the Ecoflex in shape due to its exceptionally high Young's modulus (9.8 Gpa). The self-shaping ability of such a composite material was demonstrated by being twisted into a helix (**Figure 4.17A**), into a jellyroll (**Figure 4.17B**), and into roman letters spelling out "UIUC" (**Figure 4.17C**, four letters are made with the same sample; the dot in the letter "i" is aluminum foil).

This example extends possibilities for the matrix to be filled with other fluids that may be responsive to electrical, magnetic, chemical, optical, thermal, or other external stimuli. With the ability to impart additional phenomena into the flexible matrix, such a material could be useful in flexible/soft electronics, electronic soldering, soft robotics, self-healing materials, “microsolidics” and MEMS. In addition, this research also provides some insight to the polymer/metal composite research field.

4.5 Conclusion

Thus we have achieved a new fabrication route to produce a flexible material utilizing recent advancements in VaSC with high throughput micro-structuring of a PLA film. Taking advantage of economies of scale in manufacturing production, this method can also be scaled to produce various feature sizes at a myriad of geometries. The ability to polymer weld multiple strips at overlapping nodes was demonstrated and provides for an additional degree of freedom in manufacturing capacity. A sacrificial PLA film was fabricated and micro-structured using a simple μ EDM manufactured micro-punch-and-die tool prototype to manufacture two-dimensional microchannels in a flexible Ecoflex matrix. Microstructures with hydraulic diameters ranging from 20 to 350 μm were created, unleashing the possibility of creating multi-scale microvascular materials. The self-shaping ability of the flexible microvascular material embedded with an endoskeleton was demonstrated by filling the microchannels with liquid metal and allowing it to solidify to hold the matrix shape. The described method produces novel materials using scalable manufacturing techniques and has the potential to benefit the fields of microfluidics, soft robotics, flexible electronics, and MEMS.

4.6 Experimental Section

4.6.1 Materials

Poly(lactic acid) (PLA) pellets (Molecular weight: 340 KDa) were obtained from Purac Biomaterials and used as received. Depolymerization catalyst tin(II) octoate (SnOc) was obtained from Sigma-Aldrich. Ecoflex® Supersoft Silicone (Ecoflex® 00-30, both part A and part B) was used as received from Smooth-on Inc. Ecoflex samples were prepared using a mass ratio of 1:1 part A to part B. All other chemicals were obtained from Sigma-Aldrich unless otherwise noted.

4.6.2 Characterization

4.6.2.1 MicroCT

An Xradia BioCT (MicroXCT-400) was used to image the apomatrix at 40 keV (8 W power and 200 μ A current) at a 4X objective for 5 s exposure times. Rotation intervals were 0.25 ° for a complete 360 ° scan. Images were visualized in 3D with XM3Dviewer and reconstructed in 3D using XMReconstructor.

4.6.2.2 ESEM

Environmental Scanning Electron Microscopy (ESEM, Philips XL30ESEM-FEG) was used to image the punch, die, surface of PLA grids and cross-sections of PLA grids. SEM images were acquired after sputter-coating the sample surface with gold/palladium and were collected using secondary electrons.

4.6.3 Preparation of PLA Solution

Commercial PLA pellets (6 g) were dissolved in a beaker filled with 35 mL of chloroform at room temperature. SnOc liquid was physically blended into the viscous solution (10 wt% tin equivalence to PLA). The solution was stirred for 30 min in order to disperse the catalyst well.

4.6.4 Film Casting Process

PLA solution was either spin coated on a glass slide using a spin coater (Specialty Coating Systems Model 6808) or cast on a glass plate using a doctor blade. In the spin coating setup, the solution was applied on the center of a glass slide that sat on top of the spin stub. The glass slide was then rotated at high speed (500 – 3000 RPM) in order to spread the PLA solution evenly on the glass slide and allow simultaneous solvent evaporation. Each spin coating experiment last 2 min. In the doctor blading set up, the PLA solution was applied on the edge of a glass plate and a doctor blade (Micrometer Adjustable Film Applicator: MTI EQ-Se-KTQ-150) set to an appropriate height (300 μ m to 1.5 mm) was drawn across the solution to yield thicker PLA films.

4.6.5 Micro-Structuring of PLA Film

The PLA film was carefully aligned into the die, taped into place and the punch was transmitted through the material with the benchtop arbor press. The punched chads fell into the hollowed support block and the punch and die were manually separated. Ejection pins were inserted into the top of the punch and the arbor press was used to transmit a force from the pins to the stripper plate which removes the PLA film from the punch teeth. The PLA film was realigned onto the die and the process is repeated as necessary.

This process may be repeated continually to produce 1.4 cm wide films of any desired length.

4.6.6 Composite Fabrication Process

A straight single PLA fiber was attached to the PLA grid using a solution containing 15 wt% PLA and 2 wt% SnOc in chloroform. The jointing of PLA fiber onto the PLA grid aims at easing the later liquid infiltration process since a circular syringe tip only fits into a circular orifice. The PLA grid was incorporated into the Ecoflex substrate *via* a “layer-by-layer” assembly technique. First, a thin layer of Ecoflex material (mixed with 1:1 ratio of part A to part B) was poured into a mold and cured into a solid at 80 °C for 2 h according to manufacture specifications. The PLA grid was then carefully transferred onto the solid film. Another layer of Ecoflex precursor was poured on top of the grid and cured into a solid flexible film.

4.6.7 VaSC Process

Cured Ecoflex was carefully trimmed before heating in order to expose the ends of PLA grid. Ecoflex was heated in a sealed vacuum oven (Fisher Isotemp 283) at 200 °C under vacuum (1 torr) for 6 h for complete PLA material evacuation.

4.6.8 Microchannel Infiltration Process

Water with red food coloring was manually injected into the empty channels using a syringe to visualize the channel inside the Ecoflex. Liquid gallium metal was injected into the Ecoflex in the same fashion on a slightly heated hot plate (40 °C). After gallium injection, the Ecoflex was taken away from the hot plate and manually morphed into

desirable shapes. The composite was then allowed to cool down to room temperature (23 °C) while maintaining the specific shape.

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4.8 Figures and Tables

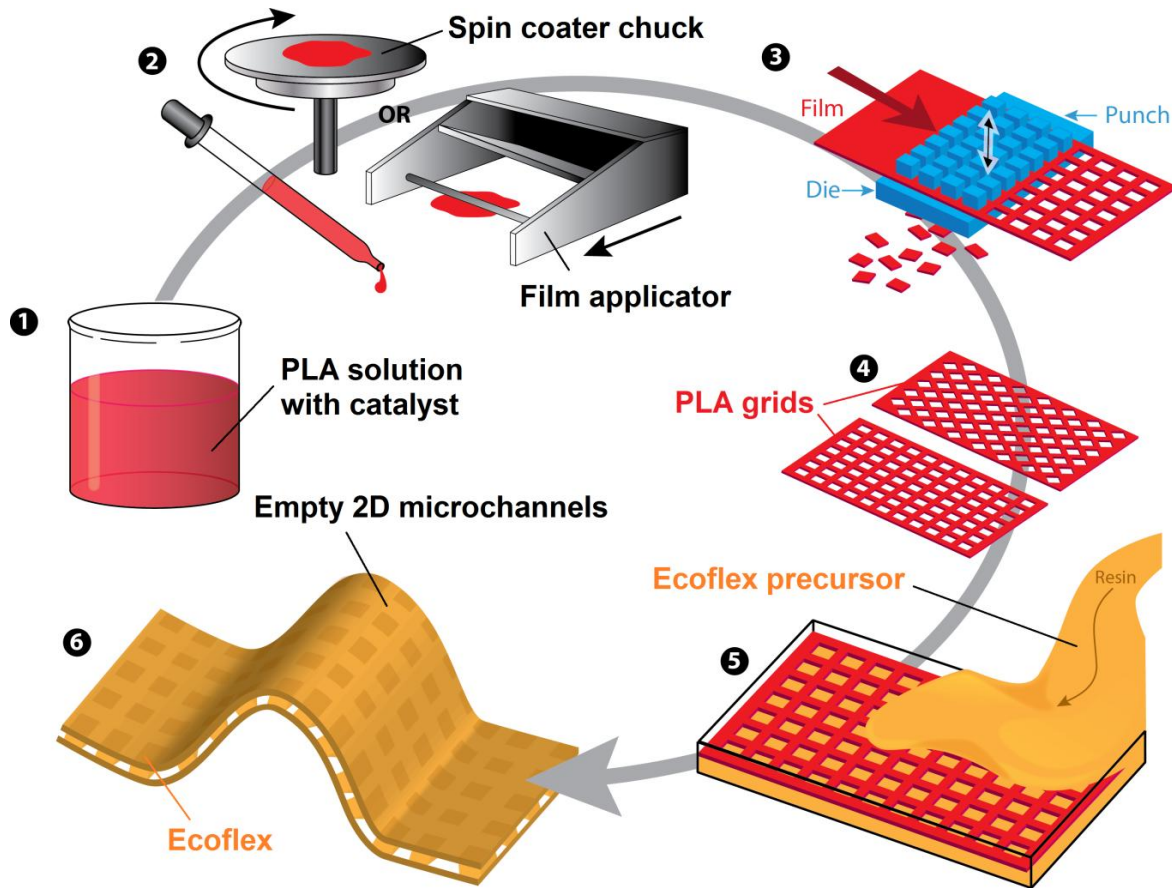


Figure 4.1 Fabrication steps for making a two-dimensional flexible microvascular composite. 1) preparation of PLA solution; 2) fabrication of PLA film; 3) microstructuring of the PLA film; 4) PLA grid produced after step 3); 5) incorporation of the PLA grid into the matrix; 6) removal of the PLA grid.

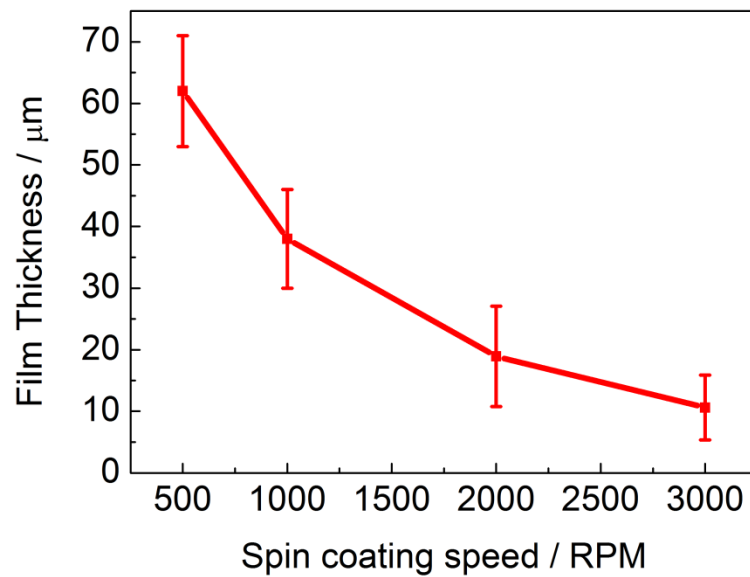


Figure 4.2 Relationship between film thickness and spin coating speed for a polymer concentration of 15% (W/V).

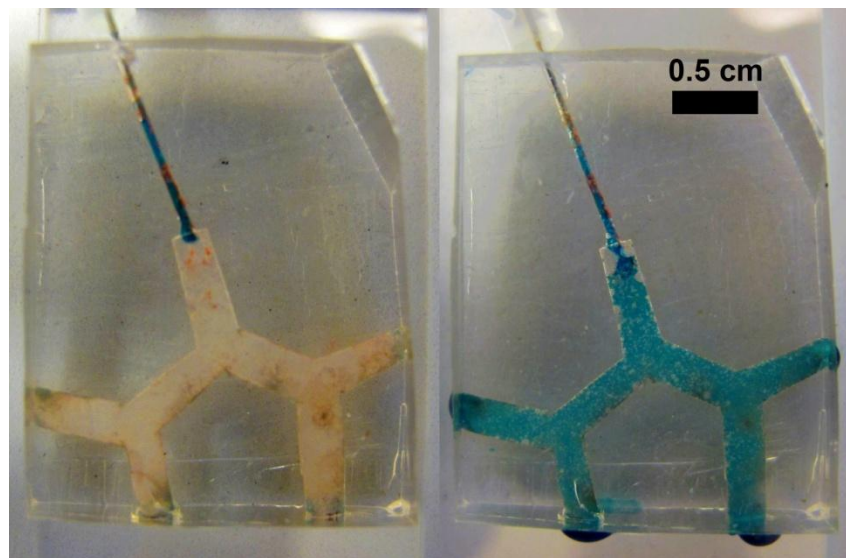


Figure 4.3 Photograph of a PDMS matrix with a branched channel network (left) and network filled with dyed water (right). The channel is fabricated by using a PLA film hand-cut into a branched structure.

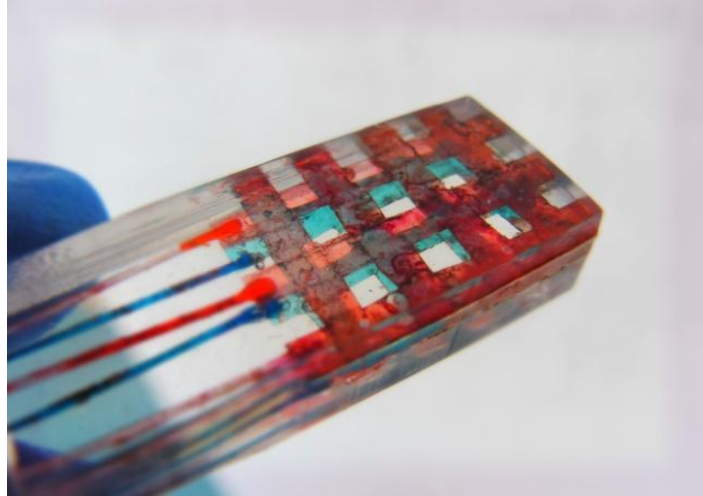


Figure 4.4 Photograph of a PDMS matrix with two separate grid networks (filled with dyed water with different colors). The networks are fabricated by using two PLA films hand-cut into grids.

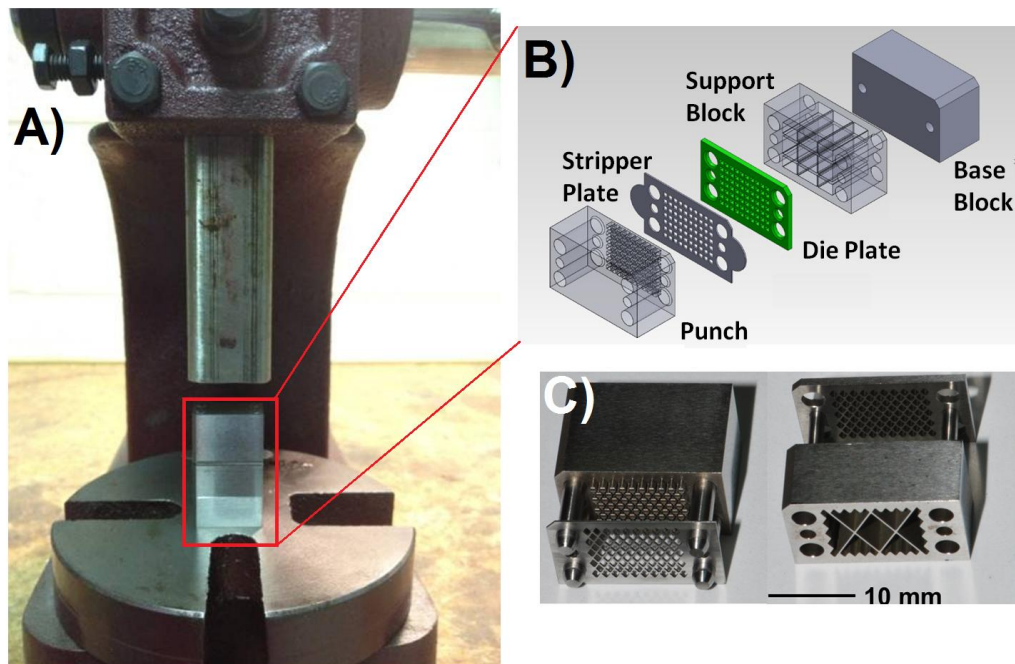


Figure 4.5 A) Front view of the Arbor press tool; B) Illustrations of punch and die fabricated using μ EDM technique; C) Front and back view of the diamond punch used in this work. (Image courtesy of Nick Maniscalco)

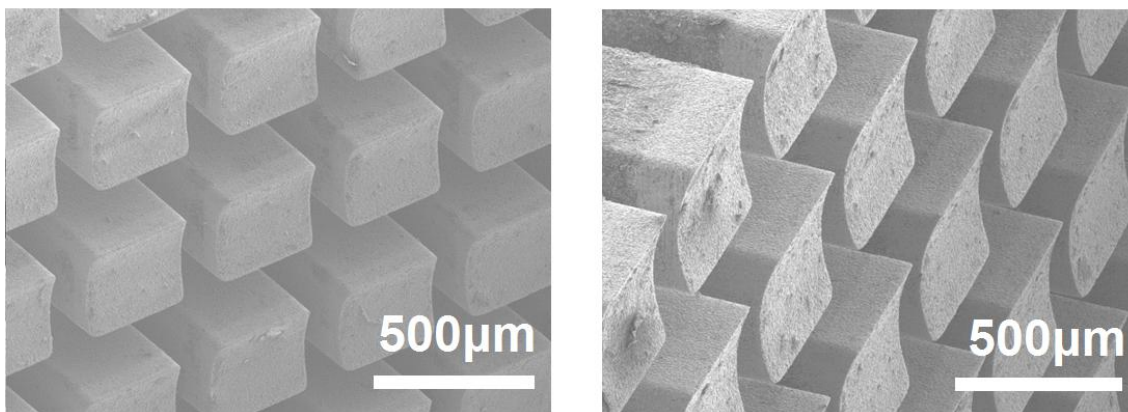


Figure 4.6 SEM images of the punch (left) and die (right) that has a square geometry.

(Image courtesy of Nick Maniscalco)

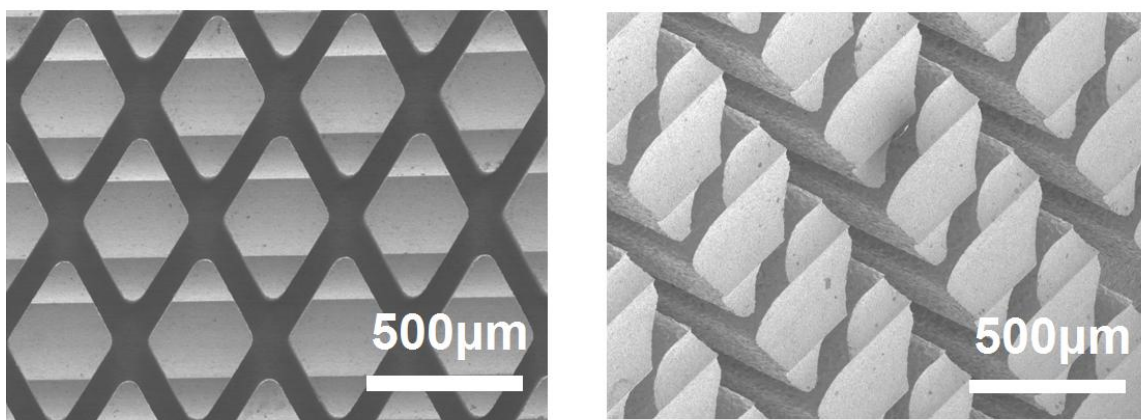


Figure 4.7 SEM images of the punch (left) and die (right) that has a diamond geometry.

(Image courtesy of Nick Maniscalco)

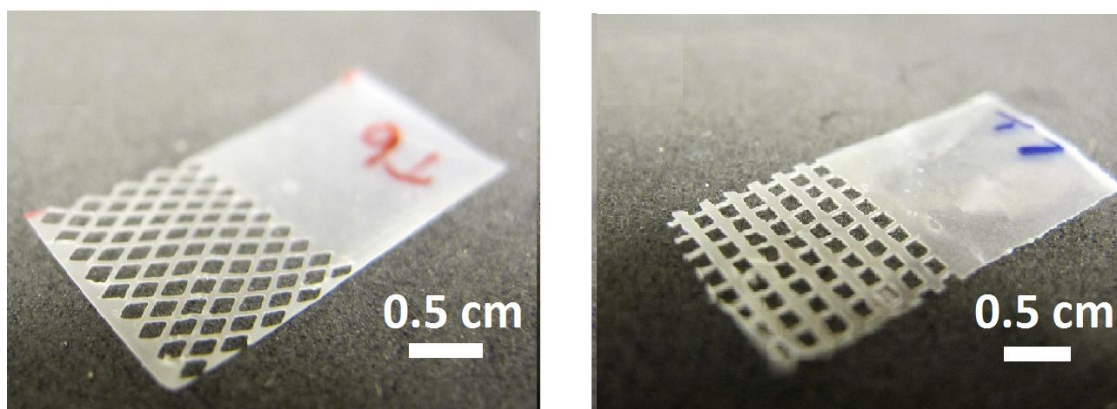


Figure 4.8 Images of PLA films processed using the punch tool.

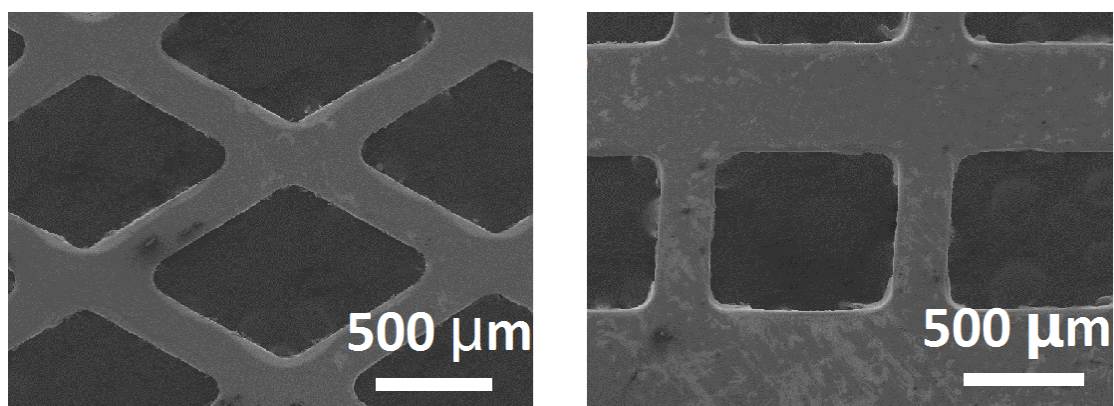


Figure 4.9 SEM images showing the microscopic structures of the punched PLA film.

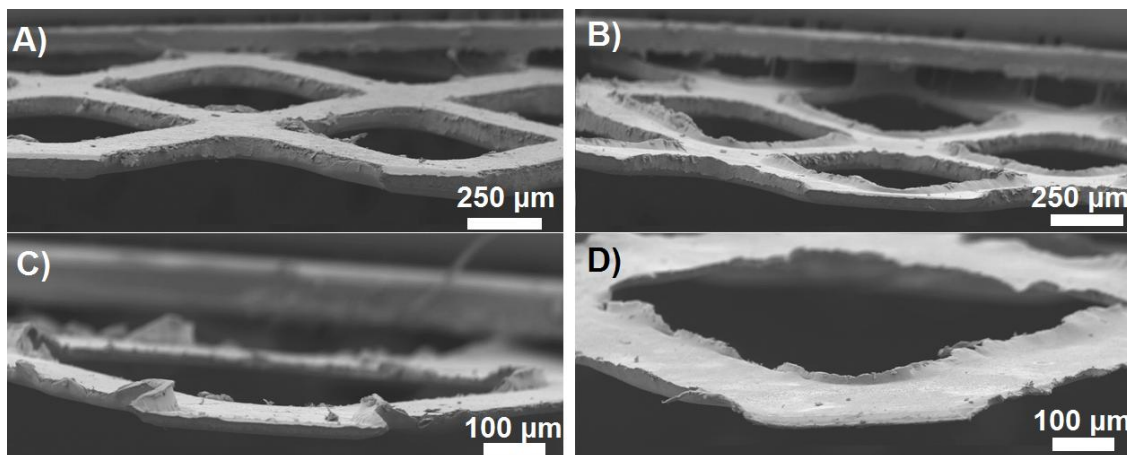


Figure 4.10 Cross-sectional SEM images of stamped PLA films with different thicknesses: A) 67 μm ; B) 47 μm ; C) 24 μm ; D) 18 μm .

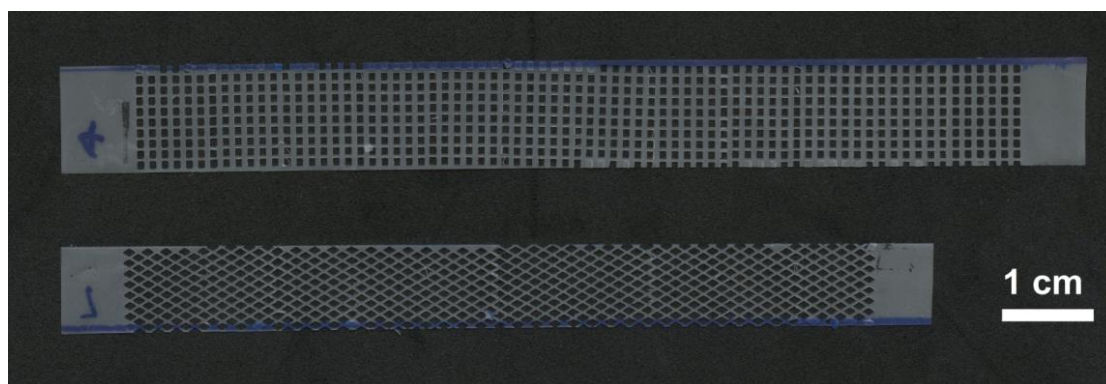


Figure 4.11 Image of PLA grids created by the micro-machining tools. Two geometries (square and diamond) are shown.

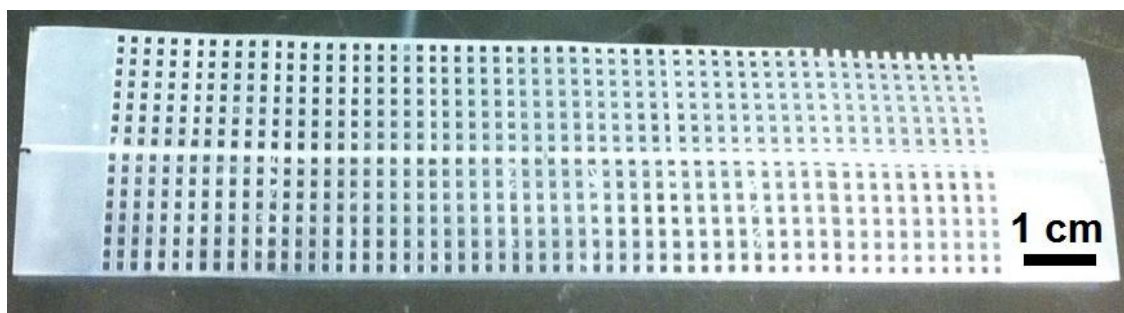


Figure 4.12 PLA grids joint at the nodes using a welding solution to create a wider PLA grid.

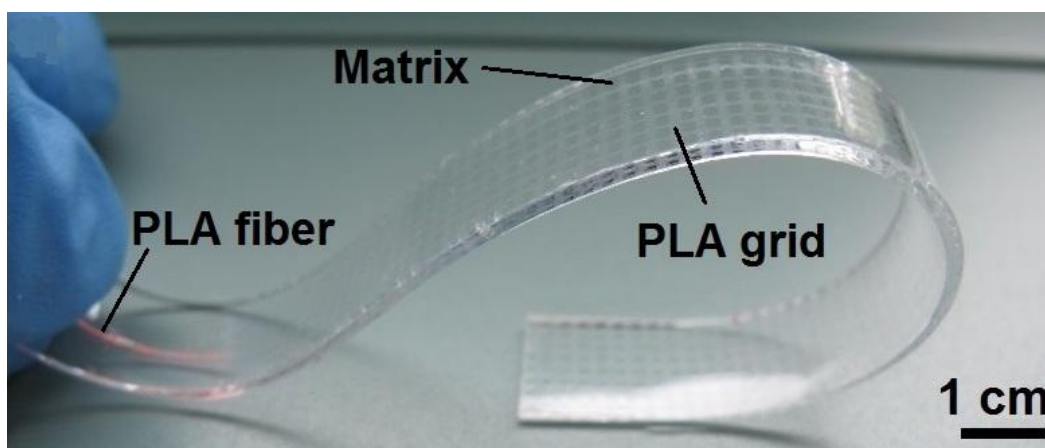


Figure 4.13 Image of a square PLA grid incorporated into Ecoflex matrix.

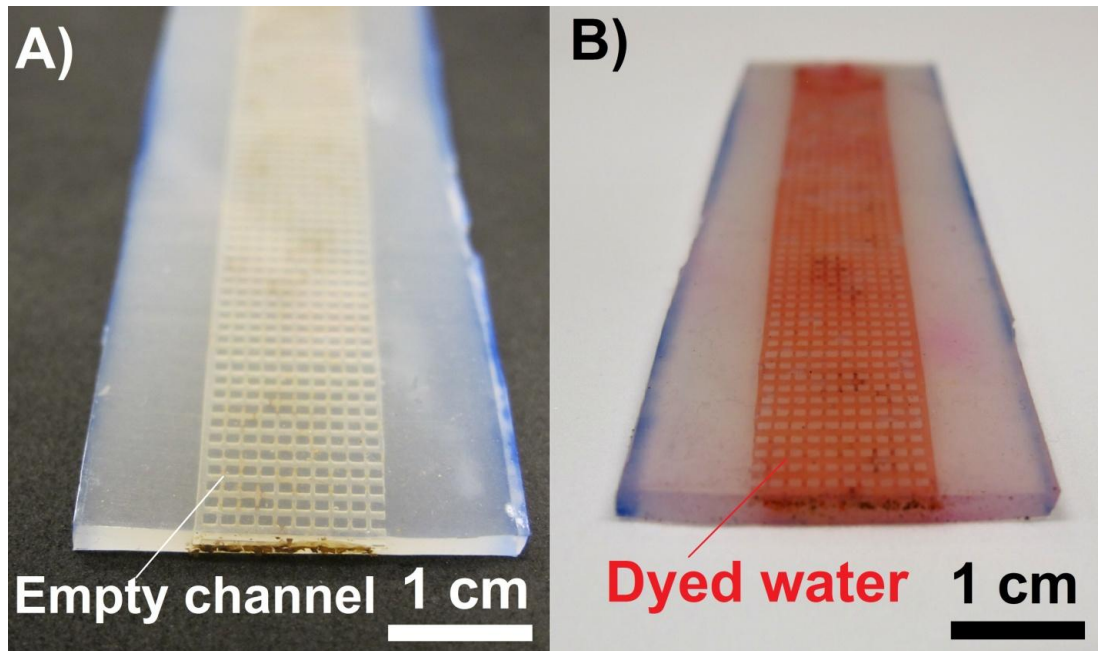


Figure 4.14 Image showing the empty two-dimensional microchannels inside Ecoflex after VaSC process (A) and the channels filled with dyed water (B).



Figure 4.15 MicroCT Image showing the empty two-dimensional microchannels (diamond geometry) inside Ecoflex after VaSC process.

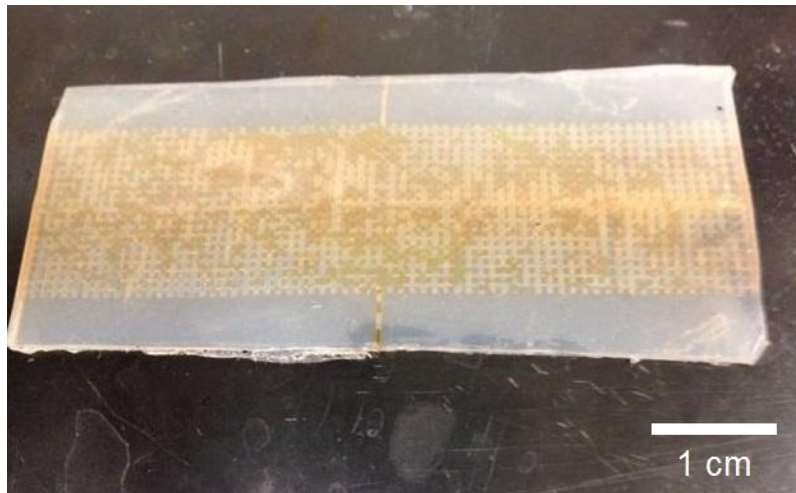


Figure 4.16 Image of a joint PLA grid incorporated into Ecoflex matrix and removed.

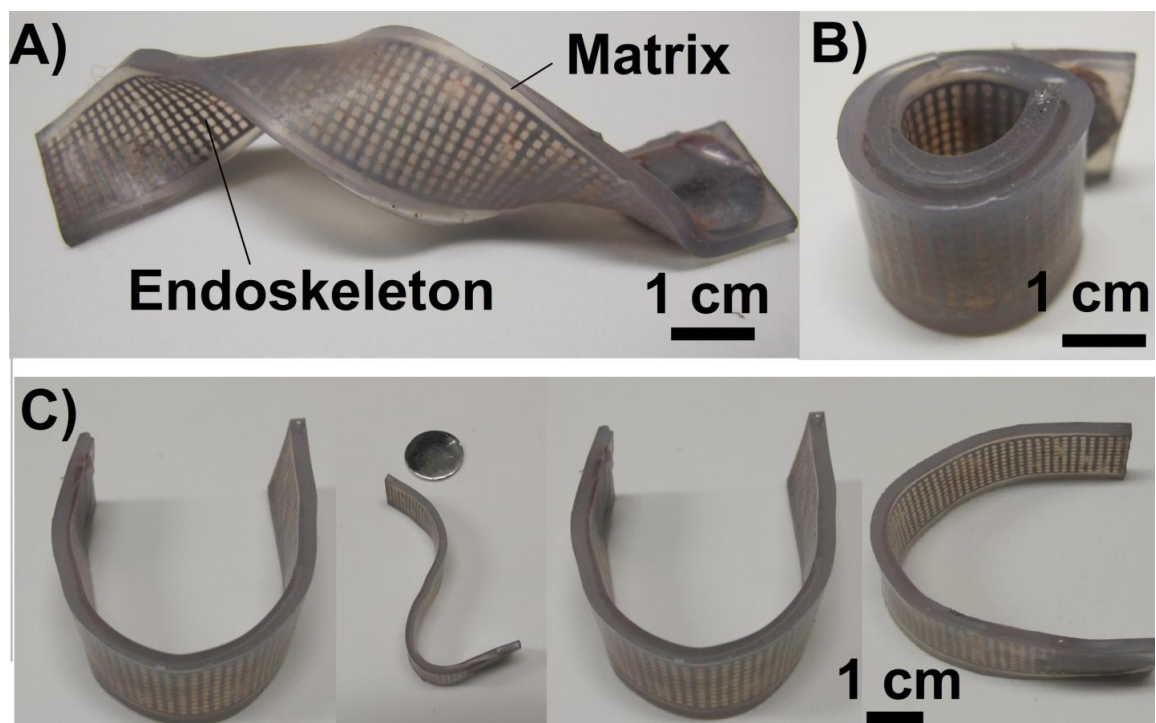
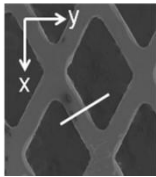
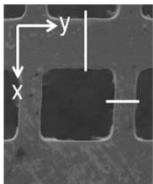


Figure 4.17 Photographs of Ecoflex with embedded liquid metal endoskeleton. After the injection of liquid metal inside the microchannels in the matrix and liquid metal cooled to a solid material, the Ecoflex composite acquires defined shapes, such as A) helix; B) jelly-roll; C) letters spelling out “UIUC”.

Table 4.1 Dimensions of the PLA grids micro-structured with the arbor press tool and the calculations of hydraulic diameters and aspect ratios of the microchannels.

Geometry	Image depiction	Dimensions (all in μm unless otherwise noted)	Hydraulic diameter of resulting channel (μm)	Aspect ratio of resulting channel
Diamond		Film thickness: 10 – 100 Length in x direction: 10 cm Length in y direction: 1 cm PLA grid width: 234 in both directions	19.2 – 140.1 in both directions	720 – 5200 in x direction 70 – 520 in y direction
Square		Film thickness: 10 – 250 Length in x direction: 10 cm Length in y direction: 1 cm PLA grid width: 288 in x direction 590 in y direction	19.3 – 267.7 in x direction 19.7 – 351.2 in y direction	370 – 5200 in x direction 30 – 500 in y direction

CHAPTER 5

COATED SACRIFICIAL PLA FIBERS FOR INDEPENDENT, INTERMINGLED MICROVASCULAR NETWORKS

5.1 Introduction

5.1.1 Current Technology and Its Limitation

Fiber-reinforced polymer composites make up a new class of lightweight materials with high strengths. Since their emergence, they have found applications in a wide variety of fields, ranging from dentistry¹ to sporting goods to aerospace engineering.² While the reinforcing fibers woven throughout the materials provide mechanical strength and stiffness, the performance and lifetimes of these composites can be improved through the incorporation of dynamic functionalities. Natural composites, such as those found in tree trunks, not only offer high-strength but also integrate a vascular system capable of energy and mass transport, allowing for the delivery of vital nutrients required for growth and metabolism. Integrating the dynamic functionality of energy and mass transport to a synthetic composite requires a similar microvascular network. In previous work, vascular networks were constructed within a fiber-reinforced composite by vaporization of sacrificial fibers, and these systems demonstrated the ability to move various liquids throughout the composite. However, this method is limited to a single vascular network because of the need to control channel spacing. Herein we provides a general solution to this limitation by adding a coating onto the sacrificial fibers that enables the manipulation of spacing and transport properties between the microchannels.

In order to develop a new generation of composites with independent, intermingled microvascular networks, we were inspired by natural composite structures found in living organisms, and desired that the synthetic analogs would exhibit the desirable dynamic functionalities of energy and mass transport by controlling vascular spacing and interchannel communication. We aimed to advance the VaSC procedure by coating the fiber with a solid polymer (**Figure 5.1**). The variable properties of the coating, such as conductivity, permeability, etc., will add new functionality to allow for controlled tuning of transport properties between channels. Coated sacrificial fibers (CSFs) are thus envisioned as a building block for fabricating the next-generation of advanced composites. The availability of these CSF building blocks will enable the manufacture of synthetic composites that emulate the circulatory, respiratory and possibly even nervous systems of living organisms, creating new vistas in multifunctional microvascular materials.

5.1.2 Biological Motivations

5.1.2.1 Independent, Intermingled Channels

Natural microvascular composites transport different liquids by keeping them in their separate, yet very closely spaced vacuoles. In a tree vascular bundle, xylem and phloem cells function as carriers of water and carbohydrate solutions respectively. The xylem and phloem cells in tree body are separated by lignin found in the tree's cell walls (**Figure 5.2**).³ Synthetic composites which resemble a vascular bundle would be able to carry different liquids or transport the same liquid but in opposite directions (**Figure 5.2**). With the current VaSC method, it is difficult to fabricate such a composite because the

resulting channels will fuse upon contact between fibers (**Figure 5.3**). Experimentally, fusion between channels can be observed in two parallel fibers in close proximity (**Figure 5.4**) and in two perpendicular fibers that came into contact (**Figure 5.5**). As a result, cross-flow occurs when liquid is injected from one channel and flows into the other (**Figure 5.6**). We hypothesized that the application of a protective fiber coating could prevent the channels from fusing together, producing independent channels that allow the composite to carry two or more liquids without mixing (**Figure 5.2**). The fabrication of integrated but independent vascular networks has potential to be used to test a two-part self-healing system⁴ in which healing components (e.g. epoxy resin and hardener) flow in two separate channels together with a third channel carrying heated substrates to facilitate the reaction of two healing components upon cracking.

5.1.2.2 Countercurrent Exchange Systems

Flowing two or more liquids through the microvascular channels requires a system with efficient energy and mass transport. Nature uses countercurrent exchange systems for optimal mass and energy transfer. In the human circulatory system, blood in arteries and veins flows in the opposite directions, during which a large amount of heat exchange takes place (**Figure 5.7**).⁵ In a microvascular composite fabricated from CSFs, the fiber coatings will provide a membrane through which heat can be transported (**Figure 5.7**). Controlled by the thickness of the coating material, spacing between two channels is critical to microvascular composite design because coating thickness must be above a certain threshold in order to function as a protective layer and, at the same time, below a certain value so that heat can be efficiently exchanged between channels. Another example of a countercurrent exchange system is the piscine respiration system. Fish use

countercurrent flow to transfer oxygen into their blood from surrounding water (**Figure 5.8**).⁵ By applying a selectively permeable coating to the fiber, the microvascular composite will then possess the ability to allow for the transfer of selected substances from one microchannel to the other *via* the semipermeable fiber coating. Composites with controlled vascular spacing and transport properties between microchannels will find potential applications in thermal management (**Figure 5.7**), gas exchange (**Figure 5.8**), water purification units, and flow batteries (**Figure 5.26**).

5.1.3 Benefits of Fiber Coating

There are three main purposes for the coating work. First, the coating will be applied to sacrificial fibers to fabricate independent microvascular networks. After sacrificial fibers are removed from the matrix material, the coating will act as a barrier that isolates two adjacent microchannels. This separation could potentially benefit self-healing applications where isolated networks are desirable. Second, the channel surface properties can be explored through tailoring and modification of the coating materials to achieve the desired hydrophilicity and wetting properties. Microchannels can be further reinforced with a coating that has high modulus. Third, desirable interchannel transport abilities can be achieved with selectively permeable coatings. In the previous work, the spacing between microchannels is filled with matrix material that lacks selective permeability. With the porous coating, the transport properties between channels may be controlled. In summary, the application of functional coating on sacrificial fibers allows for the integration of new features and functionalities into microvascular composites fabricated from CSFs.

5.2 Non-Permeable Polymer Coating on PLA Fibers

5.2.1 Material Selection

A non-permeable coating material must satisfy several criteria. First, the coating must be compatible with both the fiber and the matrix without damaging their properties. Second, the coating material must be able to solidify (cure) within a short period of time. Third, the coating must survive the heat that is needed to thermally remove the sacrificial fiber. Here we explore one material that satisfies all these criteria with the additional, practical consideration of being scalable and easily processable.

Poly(epoxycyclohexylmethylsiloxane-*co*-dimethylsiloxane) (Poly(ECMS-*co*-DMS))⁶ (**Figure 5.9**) was initially selected as the coating material because it has similar properties to the polydimethylsiloxane (PDMS) matrix material and can be readily applied to a ultra-violet (UV) cure apparatus.⁷ Poly(ECMS-*co*-DMS) is a liquid elastomer precursor that undergoes a cationic polymerization upon UV exposure (wavelength 235 nm) and cross-links itself into a solid elastomeric material (**Figure 5.10**).

The thermal stability of the coating material should guarantee that after VaSC process, the sacrificial fibers can be removed without affecting the coating. Experimentally, the thermal stability of cross-linked poly(ECMS-*co*-DMS) was demonstrated by heating it at 240 °C for 4 h, with the polymer remaining intact (**Figure 5.11**).

5.2.2 Coating Setup

The coating apparatus was a modified version of a dip coating setup (**Figure 5.12**). In the experiment setup, commercial PLA fiber was pulled out from a syringe filled with

poly(ECMS-*co*-DMS) liquid precursor mixed with a UV initiator⁶ (100:1 wt%). UV source (4000 mW/cm²) was applied right below the syringe tip which cured the liquid material into a solid coating around the fiber.

In order to continuously produce coated sacrificial fibers in an industrial scale, an automated and scalable coating apparatus was desired. As seen in **Figure 5.13**, a fiber coating setup that is capable of continuous production will be designed. In this setup, the movement of sacrificial fibers would be controlled by a motor. The PLA fibers will be coated with the liquid coating precursor from an agent bath, exposed to UV irradiation that cures the coating material, and then collected by the drum. In a similar version of the setup (**Figure 5.14**), the fibers are exposed to heat which cures the coating material. This fiber coating setup could be useful for coating materials whose solidification is triggered by heat (such as a concentrated polymer solution).

5.2.3 Coating Characterizations

Figure 5.15 shows a photograph of the poly(ECMS-*co*-DMS) coated PLA fiber. Cross-sectional SEM image of a coated PLA fiber embedded in an epoxy matrix (**Figure 5.16**) and measurement of the coated fiber diameter (**Figure 5.17**) proved that the coating is relatively even throughout the entire length of the fiber. From the SEM images and fiber diameter measurements, the thickness of the coating was ca. 100 μm . Furthermore, CSFs with different coating thicknesses were produced by using PLA fibers and syringe tips of different sizes (**Table 5.1**).

When a CSF is embedded in a matrix, the VaSC process will remove the fiber but the coating will remain around the empty channel. MicroCT image (**Figure 5.18**) showed a

microchannel produced by fiber removal, and the coating material around the channel survives because of its high thermal stability.

5.3 Fabrication of Independent Channel Networks Using CSFs

Fabrication of independent microchannels using coated sacrificial fibers as the building block was explored. Two coated PLA fibers produced using the modified dip coating setup were placed perpendicular to each other in an epoxy matrix. After the PLA fibers were removed using the VaSC method, the coating material protected the two channels from fusing together. MicroCT image of two perpendicular, interconnecting CSFs (**Figure 5.19**) shows that the coating overlaps after the fibers are removed, but the channels remain independent and show no interconnection. Furthermore, two close-packed perpendicular channels could be infused with liquids of different colors without mixing (**Figure 5.20**). In another example, two interwoven coated PLA fibers were placed in a PDMS matrix. Subsequent removal of the fibers resulted in two independent channels as demonstrated by two different color liquids circulating in the two channels without mixing. (**Figure 5.21**) These results demonstrate the feasibility of fabricating independent, intermingled microvascular networks.

5.4 Composites Capable of Heat Exchange

Coated sacrificial fibers provide a tool to reliably create biomimetic material systems capable of reproducing and extending many of the transport functions performed by microvascular systems in nature. One of the various functions is heat exchange. In human circulatory system, blood in arteries and veins flows in the opposite directions during which a large amount of heat exchange occurs (**Figure 5.7**).⁵ Mimicking heat exchange

in a synthetic microvascular composite requires the fabrication of adjacent independent microchannels with a membrane in between that is capable of conducting heat. In a composite fabricated from coated sacrificial fibers (CSFs), the fiber coating provides a heat-conductive layer through which heat is transported (**Figure 5.7**).

Two current flow modes exist in a flow system.⁸ In cocurrent flow, the streams in two channels flow in the same direction, whereas in countercurrent flow, the streams flow in opposite directions. In a countercurrent flow system, the driving force of heat exchange (i.e., temperature difference of the flow system (ΔT)) is larger than that of cocurrent flow because countercurrent maintains a temperature difference along the course of exchange.⁸

When studying heat transfer in a flow system, the temperature difference of the flow system (ΔT) is often referred to as log mean temperature difference (LMTD).⁸ LMTD is defined as following:

$$\Delta T = LMTD = \frac{\int_A^B \Delta T(z) dz}{\int_A^B dz} \quad (5.1)$$

assuming that heat transfer occurs in a heat exchanger along the z axis, from generic coordinate A to B . $\Delta T(z)$ is the temperature difference along the axis at position z .

Applying Newton's law of cooling and other assumptions (See Appendix), the expression of ΔT is derived to be:

$$\Delta T = LMTD = \frac{\Delta T(B) - \Delta T(A)}{\ln \frac{\Delta T(B)}{\Delta T(A)}} \quad (5.2)$$

where the temperature differences are $\Delta T(A)$ at point *A* and $\Delta T(B)$ at point *B*. Based on equation 5.2, LMTD can be calculated from experimental data.

Based on the aforementioned concept, a successful fabrication route was developed for independent, interwoven channels that are capable of heat exchange. The specimen in **Figure 5.21** was used to demonstrate heat exchange capability in a microvascular composite. In the heat-exchange experiment set up (**Figure 5.22**), boiling water (100 °C) and iced water (0 °C) were pumped into the two microchannels (1 mL/min) from the same direction in cocurrent flow mode (**Figure 5.23**) and from opposite directions in countercurrent flow mode (**Figure 5.24**). An infrared (IR) camera was used to monitor the temperature profile on PDMS matrix surface (**Figure 5.25**). Sensitive thermal couples were used to detect the temperature change at each channel inlet and outlet. After heat exchange reached equilibrium, LMTD was calculated from temperature readings of four inlets/outlets (**Table 5.2**). Experimental data show that in countercurrent flow, LMTD is larger than cocurrent flow, indicative of a more efficient thermal exchange action taking place. Based on this preliminary experimental result, it was concluded that, with other parameters constant, countercurrent flow allows for a more efficient energy exchange.

This preliminary study demonstrated that the fabrication of independent channels enables systematic study of biomimetic heat exchange. The exploration of coated sacrificial fibers will create new vistas for multifunctional microvascular composites.

5.5 Development of Porous Coating Material

Selectively permeable, porous polymer coating can be generated between microchannels by coating sacrificial fibers with a two-polymer mixture of sacrificial PLA and a

thermally stable polymer such as polyimide (PI). When these coated fibers are incorporated into a composite and PLA degradation is induced, the PLA phase in the coating will be removed to leave behind a porous coating. In one preliminary example, a polyimide/poly(lactic acid) coating was prepared by dipping PLA fiber in a mixture of PI and PLA (1.3 wt% PI, 2.0 wt% PLA) in chloroform. PLA was then removed from the coating using the VaSC procedure. As a result, two empty channels with a porous membrane in between them that was capable of selective mass transport was obtained. The technology of applying a porous coating precursor onto a PLA fiber is still under development.

The exchange abilities between adjacent networks *via* a semipermeable coating may enable this new technology to be readily applied to a wide variety of research areas from gas exchange^{9,10} to water purification¹¹ to flow batteries¹² (**Figure 5.26**). Coated sacrificial fiber technology will provide an established formula in applications where transport properties are needed.

5.6 Conclusion

Therefore, a new generation of microvascular composites building upon the fiber vascularization technique with a supplementary coating on sacrificial fibers was achieved. Initial studies focused on a non-permeable poly(ECMS-co-DMS) coating material. The sacrificial PLA fibers were successfully coated using a modified version of a dip coating apparatus and the successful fabrication of evenly coated fibers was demonstrated. The coating material around the sacrificial fiber functions to prevent the channels from fusing with each other, thereby enabling the fabrication of independent,

intermingled microchannels. Composites fabricated from CSFs have the ability to mimic biological countercurrent heat exchange, which is a desirable functionality in synthetic microvascular materials. Porous coating technology is currently under development to enable mass transport between microchannels. Composites with controlled vascular spacing and transport properties between microchannels demonstrate potential use in a wide spectrum of applications such as CO₂ sequestration, dialysis, water purification, and flow batteries.

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5.8 Figures and Tables

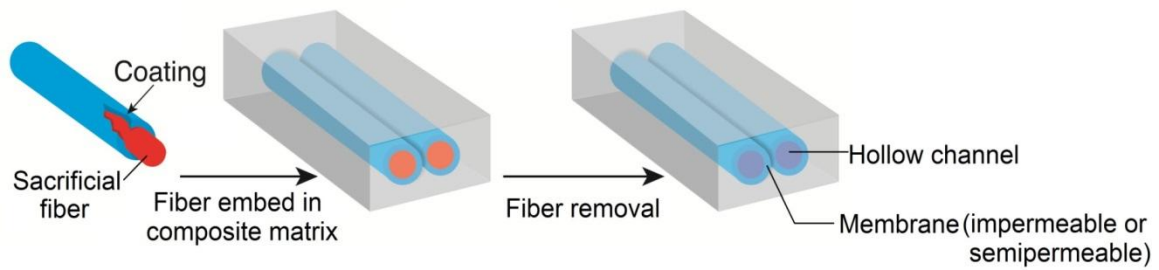


Figure 5.1 Schematic representation of coated sacrificial fibers (CSFs) in microvascular composite fabrication.

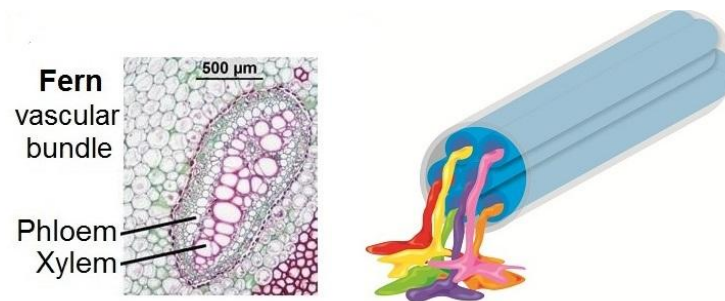


Figure 5.2 Tree vascular bundle microstructure and conceptual image of microvascular composite fabricated from CSFs with integrated, independent channels.

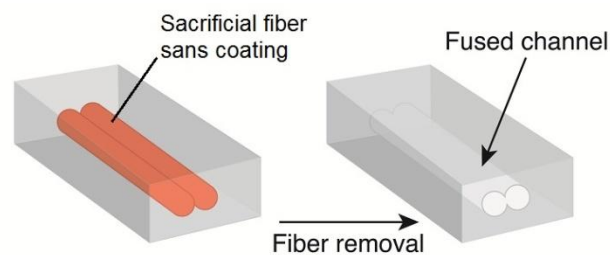


Figure 5.3 Schematic illustration of fused channels that result from uncoated sacrificial fibers.

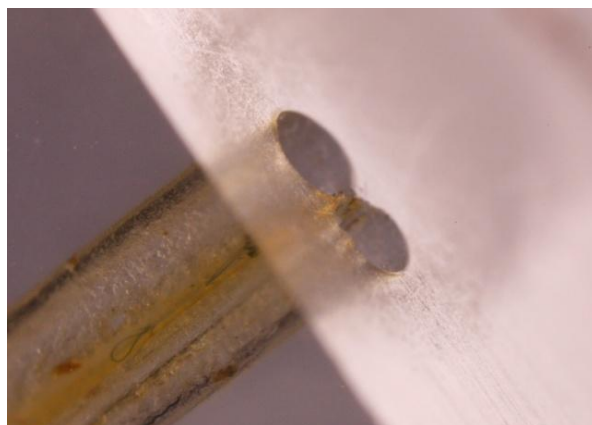


Figure 5.4 Optical image of fused channels resulting from two parallel, uncoated sacrificial fibers. (Fiber diameter: 500 μm)

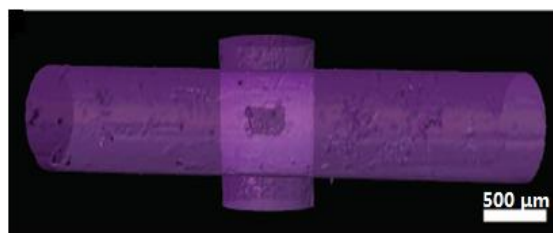


Figure 5.5 MicroCT image of fused channels that result from two perpendicular, uncoated sacrificial fibers. (Fiber diameter: 500 μm) Reprinted with permission from A. P. Esser-Kahn, P. R. Thakre, H. Dong, J. F. Patrick, V. K. Vlasko-Vlasov, N. R. Sottos, J. S. Moore, and S. R. White, *Adv. Mater.*, **2011**, 23, 3654. Copyright 2011 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

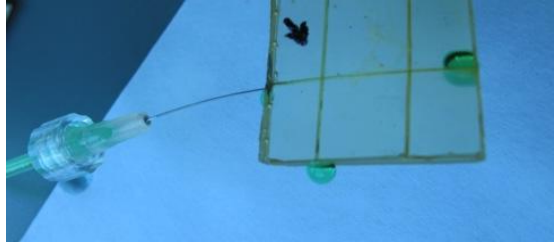


Figure 5.6 Photograph showing the cross-flow of two fused channels resulted from two perpendicular, uncoated sacrificial fibers. The black arrow indicates where the fusion takes place. (Fiber diameter: 200 μm)

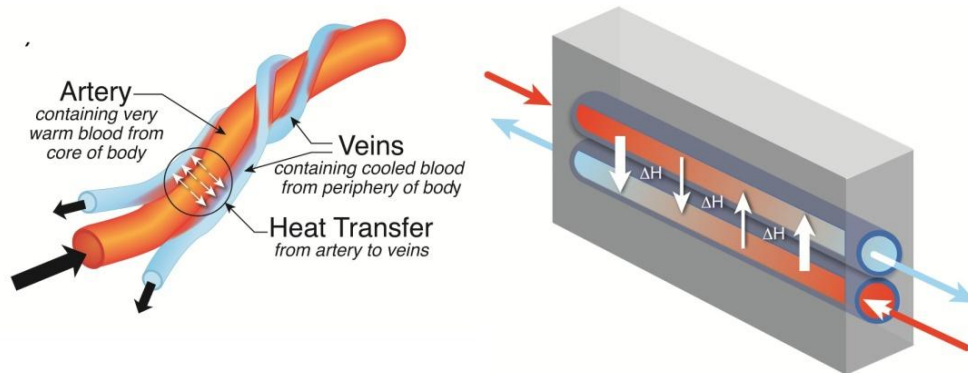


Figure 5.7 Natural countercurrent systems and conceptual images of synthetic composites: countercurrent heat exchange between blood in arteries and veins in human circulatory system (left); composite capable of heat exchange when heat is transported through the fiber coating (right)

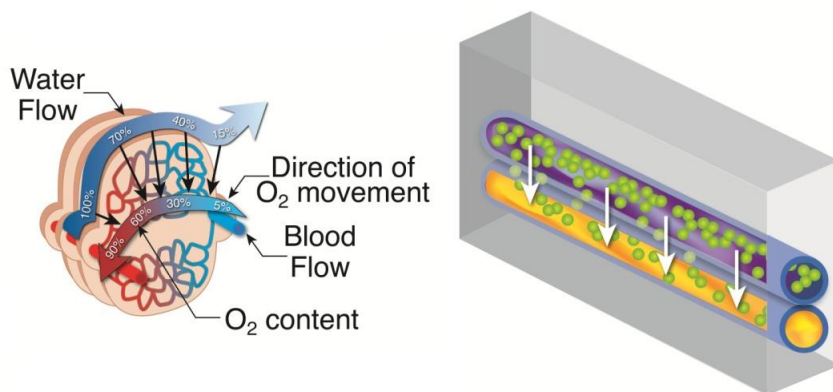


Figure 5.8 Natural countercurrent systems and conceptual images of synthetic composites: oxygen is exchanged via countercurrent flow from water to blood in fish respiratory system (left); composite that is capable of mass exchange when mass is transported through the semipermeable fiber coating (right).

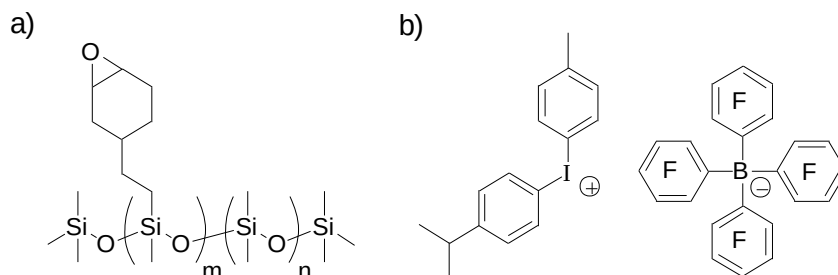


Figure 5.9 Structure of poly(ECMS-co-DMS) elastomeric liquid precursor (a) and cationic polymerization initiator (*p*-isopropylphenyl) (*p*-methylphenyl) iodonium tetrakis(pentafluorophenyl) borate (b).

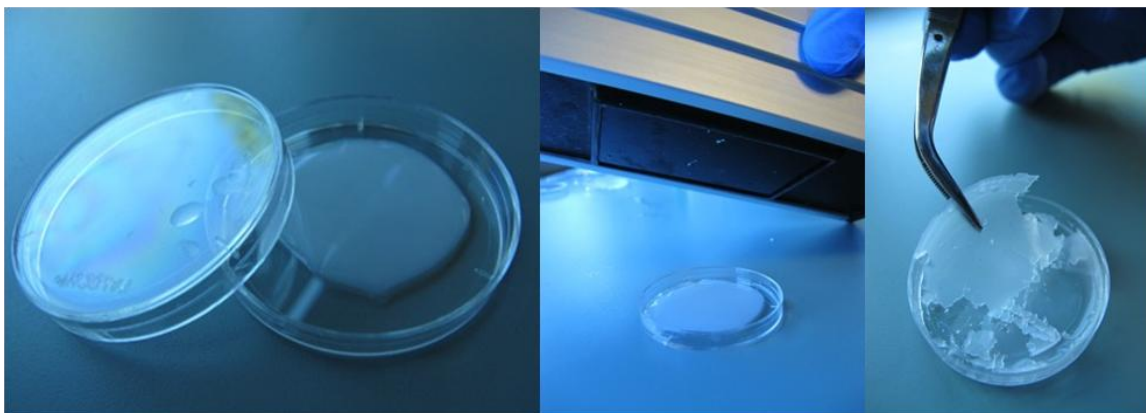


Figure 5.10 Curing stages of poly(ECMS-co-DMS): liquid precursor (left); curing initiated by UV light (middle); and cured solid polymer (right).

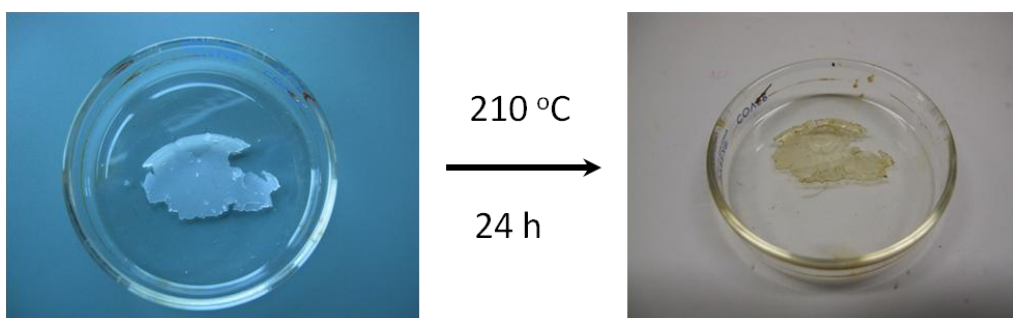


Figure 5.11 Thermal stability demonstration of cured poly(ECMS-co-DMS) polymer.

The cured polymer is heated at 210 °C for 4 h and remains intact.

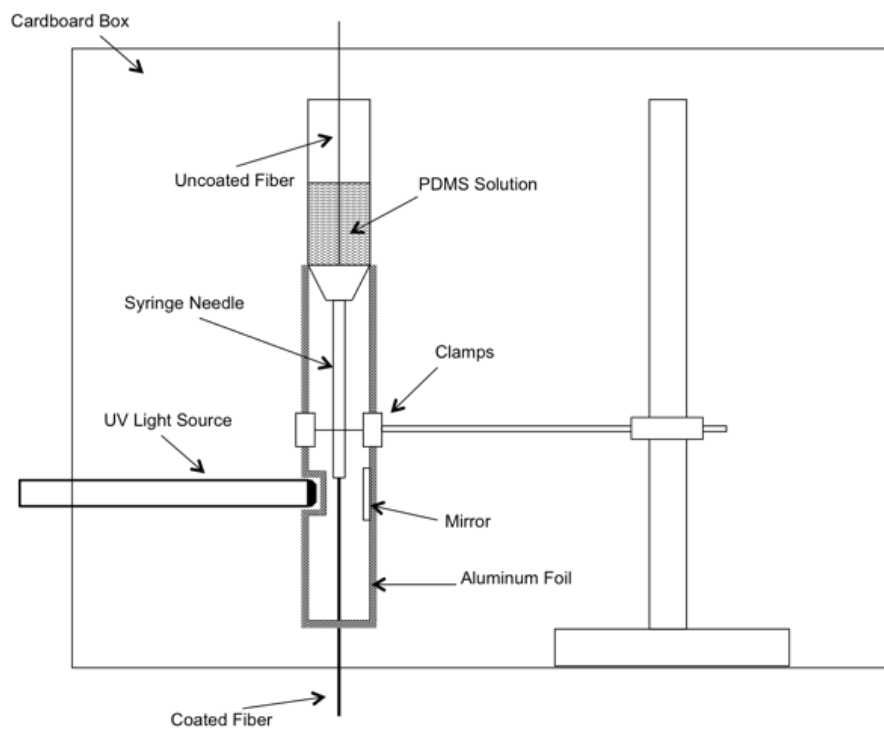


Figure 5.12 Lab scale experimental setup for producing PLA fibers coated with cross-linked poly(ECMS-co-DMS).

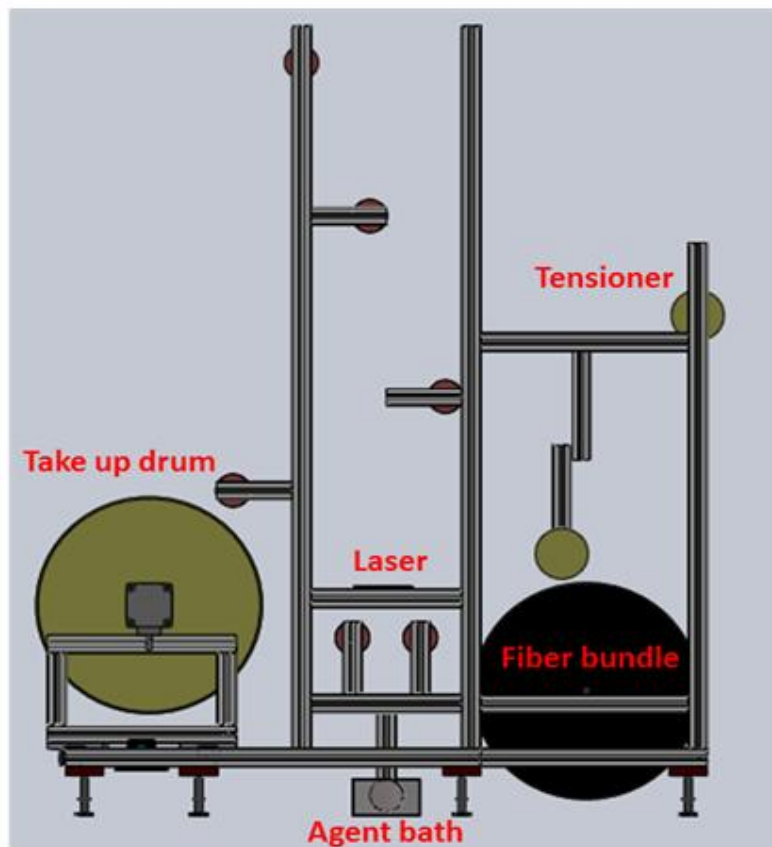


Figure 5.13 Schematic illustration of an industrial-scale coating apparatus. The apparatus could be used for the cross-linking reaction initiated by a laser. (Image courtesy of Sang Yup Kim)

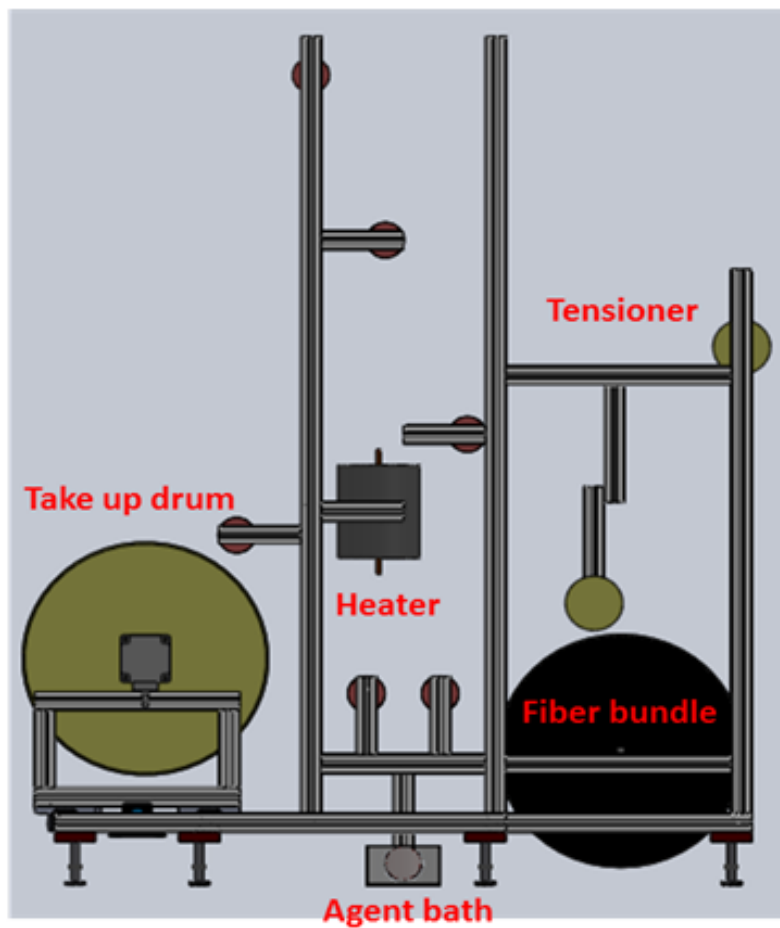


Figure 5.14 Schematic illustration of an industrial-scale coating apparatus. This apparatus could be used for thermal initiated cross-linking reaction. (Image courtesy of Sang Yup Kim)



Figure 5.15 Optical microscope image of cross-linked poly(ECMS-*co*-DMS) coating on sacrificial PLA fiber.

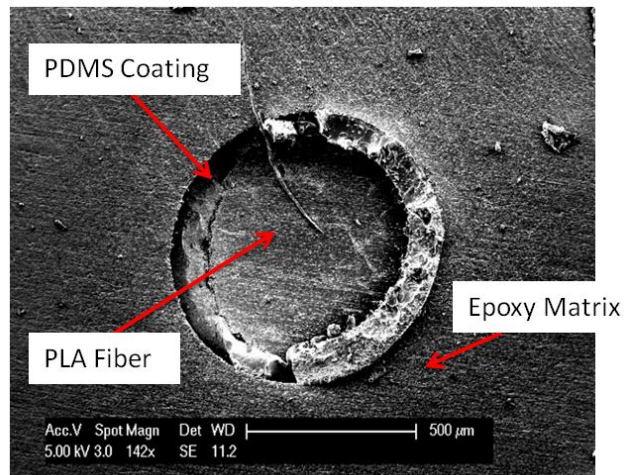


Figure 5.16 Cross-sectional SEM image of coated PLA fiber (diameter: 500 μm) embedded in an epoxy matrix.

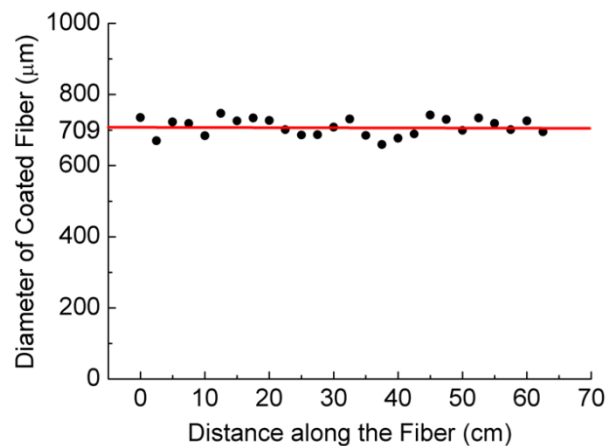


Figure 5.17 Diameter of coated PLA fiber along the fiber length measured by optical microscopy.

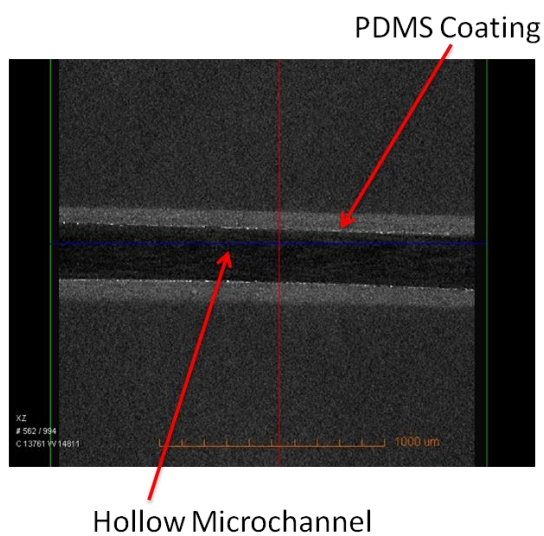


Figure 5.18 MicroCT image of an empty microchannel surrounded by cross-linked poly(ECMS-*co*-DMS) coating material embedded in an epoxy matrix.



Figure 5.19 MicroCT image of two perpendicular, independent channels resulted from removing coated sacrificial PLA fibers.

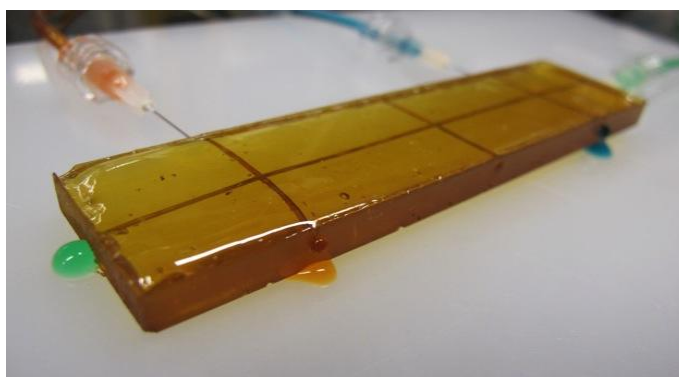


Figure 5.20 Photograph showing there is no cross-flow between adjacent channels even the channels are in close proximity. This specimen is prepared by using poly(ECMS-co-DMS) coated sacrificial fibers. (Fiber diameter: 200 μm)

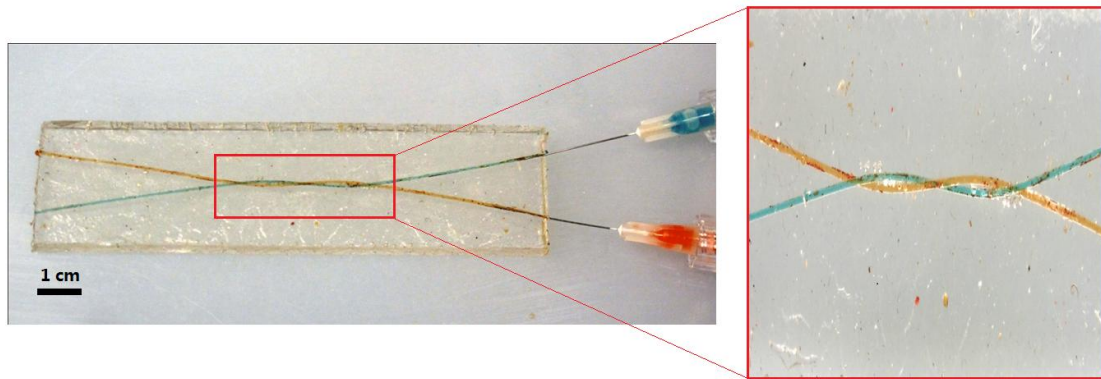


Figure 5.21 Image of a PDMS matrix with two independent, interwoven channels filled with blue and orange liquid respectively and zoomed-in area showing the interwoven fibers.

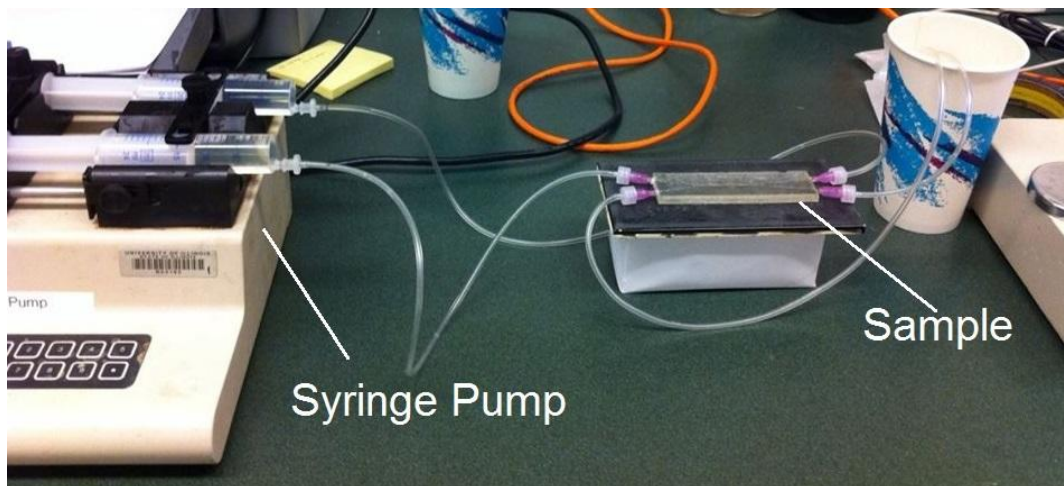


Figure 5.22 Experimental setup for measuring the LMTD of a flow system. The pumping of the fluids is controlled by the syringe pump. An IR camera (above the sample, not shown in this figure) monitors the surface temperature change of the sample.

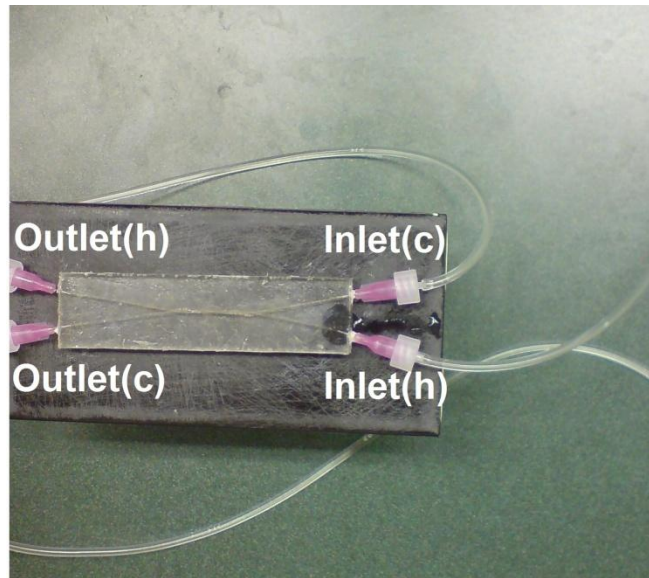


Figure 5.23 The representation of inlets and outlets for a cocurrent flow system. (c) stands for cold fluid (ice water) and (h) stands for hot fluid (boiling water).

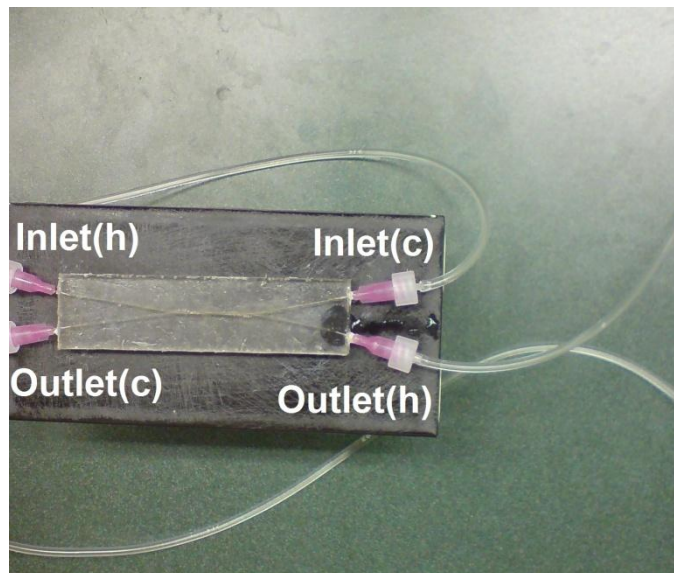


Figure 5.24 The representation of inlets and outlets for a countercurrent flow system. (c) stands for cold fluid (ice water) and (h) stands for hot fluid (boiling water).

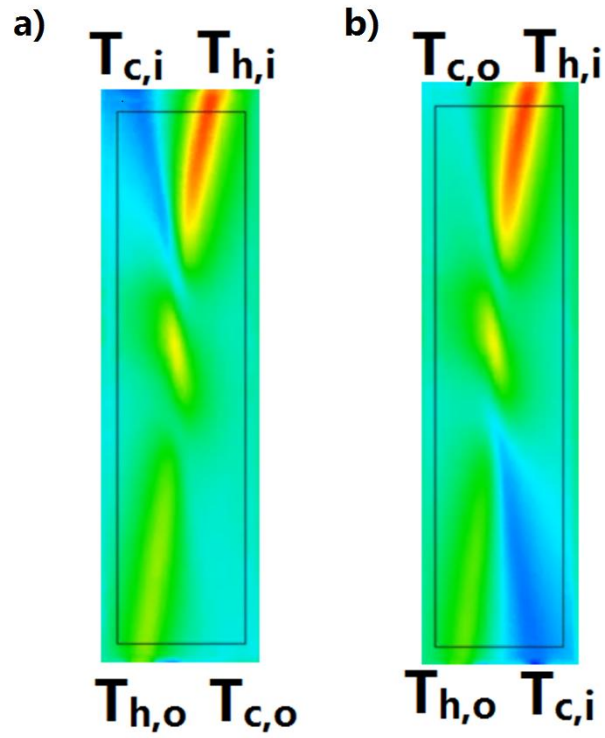


Figure 5.25 Infrared (IR) images showing the temperature profiles of PDMS matrix surface after heat exchange reaches equilibrium. Boiling water and iced water flow in the same direction in cocurrent flow mode (a) and in opposite directions in countercurrent flow mode (b). Temperatures of each inlet/outlet are shown in **Table 6.2**.

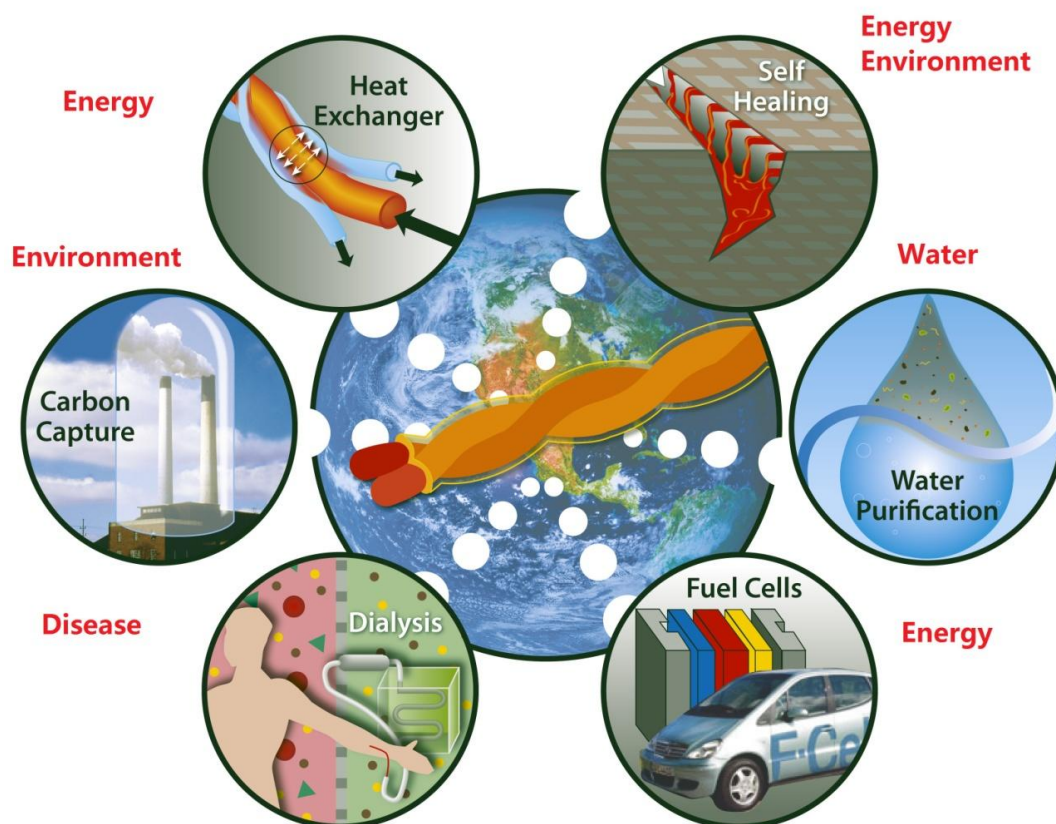


Figure 5.26 Envisioned application areas accessible by CSF technique.

Table 5.1 Thicknesses of coated sacrificial PLA fibers prepared using syringe tips of different sizes.

PLA Fiber diameter (μm)	Syringe tip inner diameter (μm)	Coated PLA fiber diameter (μm)
200	250	230
200	330	270
300	410	350
300	510	400
500	610	700

Table 5.2 Temperatures of four inlets/outlets in cocurrent and countercurrent flow modes.

LMTD is calculated for each flow mode.

Flow Mode	$T_{h,i}$ / °C	$T_{c,i}$ / °C	$T_{h,o}$ / °C	$T_{c,o}$ / °C	$\Delta T(B)$ / °C	$\Delta T(A)$ / °C	$LMTD = \frac{\Delta T(B) - \Delta T(A)}{\ln \frac{\Delta T(B)}{\Delta T(A)}}$
Cocurrent	32.6	20.7	27.0	23.2	$T_{h,i} - T_{c,i}$ 11.9	$T_{h,o} - T_{c,o}$ 3.8	7.10
Countercurrent	35.7	19.3	27.7	22.5	$T_{h,i} - T_{c,o}$ 13.2	$T_{h,o} - T_{c,i}$ 8.4	10.60

CHAPTER 6[§]

MICROPOROUS BATTERY SEPARATOR FABRICATED FROM A POLYIMIDE/POLY(LACTIC ACID) BLEND

6.1 Motivation

6.1.1 Safety Concerns for Lithium-Ion Battery

Lithium-ion batteries are rapidly expanding in importance in fields such as portable electronics, power tools, and electric vehicles due to their high energy density.¹⁻³ However, with higher energy density comes greater safety risks. An important component for the safety of Li-ion batteries is the separator, a film responsible for preventing contact between the anode and cathode in a battery that still allows sufficient ion flow between the two components.⁴⁻⁶ It is crucial that the anode and cathode stay separated at all times since contact can lead to short circuits, overheating, and eventually thermal runaway and fire.⁷ The most common commercial separators are made of low-cost polyolefin materials; however, these separators shrink at elevated temperatures, which ultimately leads to thermal runaway and battery failure.⁸

6.1.2 Previous Methods for Separator Manufacture

Several approaches have been taken to improve the thermal stability of separators. Thermal stability of polyolefin separators can be improved by coating them with ceramic particles^{9,10} or high-temperature polymers.^{11,12} Unfortunately, this requires an extra step

[§] Stephen J. Pety contributed to some of the content presented in this chapter.

in separator manufacturing, and producing uniform coatings that adhere well to their substrates remains an existing challenge.

Separators made with high-temperature polymers instead of polyolefins offer another approach to improved thermal stability. The most common approach to making high-temperature polymer separators is to create nonwovens through the melt-blowing or electrospinning methods; polymers used to make nonwoven separators include cellulose,^{13,14} polyamide,^{15,16} and polyester.^{17–19} However, nonwovens made with the wet-laid and melt-blowing methods tend to have unsatisfactorily large pore sizes, and nonwovens made with electrospinning are challenged by high cost and low throughput, limiting the use of these technologies.

6.1.3 Porous Film Using PLA as a Sacrificial Component

Here we demonstrate the development of a polyimide (PI) microporous separator that overcomes many of the disadvantages of current separators discussed above. PI (**Figure 6.1**) is a promising high-temperature material for Li-ion battery applications and has seen recent success in separators both as a coating material^{11,20} and as a material for electrospinning nonwovens.^{21–23} We created a PI separator by solution casting a blend of PI and a porogen and then removing the porogen through heat treatment. The porogen we chose was polylactide (PLA, **Figure 6.2**), which can be removed *via* thermal depolymerization at ca. 280 °C (**Figure 6.3**). Existing uses of PLA as a sacrificial material include, the creation of nanoporous films from block copolymers^{24,25} and the formation of microvascular channel networks in polymer composites.^{26,27}

Herein, we demonstrate control over the morphology of the PI separators by changing various parameters in the solution casting process. Changes in morphology were observed to correlate with the electrochemical performance of the separator in Li-ion coin cells. Separators made with the optimized morphology had similar electrochemical performance to commercial polyolefin separators, while possessing significantly improved thermal stability.

6.2 Fabrication of Biphasic Polymer Film and Porous Separator

6.2.1 Fabrication Route

Our route started with the fabrication of a biphasic polymeric film (**Scheme 6.1**). Polyimide and poly(lactic acid) were dissolved in a communal solvent (chloroform) and the solution was cast on a glass substrate. The film was then peeled off from the substrate and subjected to 280 °C to remove the poly(lactic acid) phase (**Figure 6.2**).

6.2.2 Miscibility of Polymer Blend

In a system consisting of polymer blends, the maximum amount of each polymer that can be dissolved in the solvent is limited. Our efforts explored this limitation by plotting a two-dimensional miscibility diagram (**Figure 6.4**), whose axes are the concentrations of each individual polymer. In the diagram, the purple line indicates the separation of the miscible and immiscible regions, below which polyimide and poly(lactic acid) form a miscible, clear solution in chloroform. Above this line, the two polymers are immiscible and phase separate into a cloudy mixture. In this work, all the films were prepared in the miscible region at varying PI:PLA ratios, while keeping the total concentration of the two polymers constant (3 – 4 wt%).

6.3 Characterization of Biphasic Film Precursor and Porous Separator

6.3.1 Film Morphology Study

Using scanning electron microscopy (SEM), we examined the morphologies of the biphasic film, both before and after poly(lactic acid) phase is removed. In each case, we examined the top, bottom surface and the cross-section of the film. The results are summarized in **Figure 6.5**. Before PLA removal, we observed two distinct layers across the thickness of the film. Both layers consist of spherical structures surrounded by solid polymer, but the two layers show very distinct structures. (**Figures 6.5A, 6.5B and 6.5C**). This unique phase separation behavior is further elucidated by examining the polyimide film after PLA is removed. According to **Figures 6.5D, 6.5E, and 6.5F**, the polyimide separator exhibits a “bilayer” asymmetric structure where the top layer consists of solid, sintered polyimide spheres and the bottom layer is made of a “sponge-like” polyimide material. In both layers, the polyimide phase is surrounded by percolated pores generated from the thermal removal of PLA phase.

We hypothesize this bilayer structure was the result of two different phase separation processes that occur during the film casting process. A proposed schematic of phase separation during solvent casting is shown in **Figure 6.6**. As solvent evaporates during casting, PLA begins to precipitate from solution in the bottom half of the film while PI begins to precipitate from solution in the top half. We attribute this phenomenon to the differences in surface energy between the glass substrate and the surrounding air. When all of the solvent has left the film, the result is a bilayer film where the top layer consists of a PLA phase surrounding PI spheres and the bottom layer consists of a PI layer

surrounding PLA spheres. When the film is treated at high temperature to remove PLA, the result is a porous bilayer film.

6.3.2 Processing Conditions vs. Film Morphology

Film processing conditions affect the morphology of the polyimide separator to a great extent. Among the many parameters we studied, PI:PLA ratio has the biggest influence on the phase separation behavior. We studied different film morphologies by observing the cross-sections of the polyimide separators under SEM, varying the PI:PLA ratio. **Figure 6.7** reveals an interesting trend regarding to the thicknesses of the spherical layer and the “sponge-like” layer: the thickness of the spherical layer/“sponge-like” layer decreases/increases as PI:PLA ratio increases, possibly because higher amounts of polyimide forms thicker continuous polyimide phase. These different morphologies have a strong influence on the battery behavior when assembled into a coin cell, which will be discussed in the next section.

The PI:PLA ratio in the biphasic film also affects the porosity of the separator film, which is an important characteristic that directly controls the electrochemical performance. We investigated five different PI:PLA ratios and measured the porosity by measuring the solvent uptake per unit volume. **Figure 6.8** demonstrates the relationship between the measured porosity and the percentage of PLA in biphasic film. We noticed that the biphasic film consisting 60% poly(lactic acid) material only yields *c.a.* 48% porosity, and similar porosity loss is observed for other ratios as well. We hypothesize that the collapsing of polyimide material during the PLA removal procedure is the cause of the disparity between measured porosity and projected porosity (about 12% in

average). In general, it is a clear trend that polyimide separator made from a solution consisting more poly(lactic acid) material presents higher solvent uptake per volume, and this trend will be accounted for when evaluating electrochemical performances.

6.4 Electrochemical Properties of the Separator

6.4.1 Electrochemical Stability

The separator must be electrochemically stable against the electrolyte and electrodes in the working voltage ranges when a battery operates. Herein, the electrochemical stability window of the polyimide separator was observed from the linear sweep voltammograms (LSV). **Figure 6.9** shows that the electrochemical stability of the polyimide separator is comparable to that of a commercialized Celgard separator and no decomposition of any components between 5 mV to 5.0 V vs. Li⁺/Li takes place. This indicates that the polyimide has the potential of being a good alternative to a Celgard separator.

6.4.2 Film Processing Conditions vs. Ionic Conductivity

Film processing parameters were carefully studied in order to obtain the optimal separator for lithium-ion battery application. As mentioned before, the ratio of two polymer components has the most direct influence on the morphology of the separator, and consequently, the performance of the coin cell assembled with the separator. Herein, separators were prepared by varying the PI:PLA ratio, encased in coin cells and electrochemically tested. We summarize the impedance and discharge capacity values with different processing parameters in **Figure 6.10**.

We observed a clear trend that the impedance of the coin cell decreases as the poly(lactic acid) component in the biphasic film increases (**Figure 6.10**). Combining the aforementioned morphology study and the impedance data, we propose two distinct phase separation behaviors and two different ionic transportation mechanisms. As shown in the schematic illustration (**Figure 6.11**), the spherical polyimide structure is shown to be more ionic conductive than the “sponge-like” structure, providing a shorter, less tortuous pathway for ionic movement. In contrast, the “sponge-like” structure shows a longer and more tortuous pathway; in addition, the formation of dead-ends and closed pores hinders ionic movement. This explains for films that are prepared with a lower PI:PLA ratio (which has a thinner “sponge-like” layer (**Figure 6.7**)), impedances are lower. Besides, the films prepared with a lower PI:PLA ratio are also measured to be more porous (**Figure 6.8**), which also assists ionic transport through the separator.

Also recognized in **Figure 6.10** is a negative correlation between the impedance versus the discharge capacity of the cells. When a separator with higher impedance is assembled into the coin cell, the coin cell will experience more hindered ionic transport, thus it shows decreased discharge capacity due to a higher ohmic polarization. In the best case we experimented, separator processed with a PI:PLA ratio of 40:60 exhibits impedance and discharge capacity value very close to those of a coin cell assembled with a commercial Celgard separator. This represents the optimal PI film reported herein.

6.4.3 Competitive Electrochemical Performance

To demonstrate the competitive performance of the PI separators, galvanostatic cycling results were compared for cells made with other PI separators as well as a commercial

separator. **Figure 6.12** depicts the charge and discharge curves (at C/10 cycling rate) of coin cell using a polyimide separator, showing specific capacity about 194 mAh/g with a capacity retention ratio of 96 %, nearly the same as of a coin cell assembled with a commercial Celgard separator (193 mAh/g, 95 %). **Figure 6.13** shows stable cycling behavior at C/10 rate at room temperature; no abnormal or unstable charge/discharge profiles were observed in the polyimide separators after 10 cycles. Notice that in **Figure 6.13** we also included films prepared with other ratios (PI:PLA= 50:50, 60:40) as a comparison. **Figure 6.14** summarizes the charge and discharge capacities of the polyimide separators as a function of the discharge current density (i.e., discharge C-rate). Noticeably the discharge capacities drop at higher discharge current densities, where the influence of ionic transport on the ohmic polarization (IR drop) is more significant. The best-case PI separator performed similarly to Celgard at C/3 and C/2 but performed notably worse at 1C, with a discharge capacity of only 61 mAh/g vs. 140 mAh/g for Celgard. Considering this fall off, we hypothesize that the PI separator still possessed too tortuous of a morphology to allow effective ion transport at high discharge rates. Further optimization of morphology is expected to overcome this limitation. However, the current PI separator may still find use in low rate applications.

6.5 Thermal Stability of the Separator

The thermal shrinkage of the polyimide separator was observed by measuring the dimensional change (length-based) after the separator was subjected to heat treatment at various temperatures for 0.5 h. **Figure 6.15** exhibits that, whereas the conventional Celgard separator continues to shrink with increasing temperature, the polyimide separator is hardly changed over a wider range of temperature. This difference in the

thermal shrinkage between the two separators becomes more significant as the temperature is increased to 140 °C. **Figure 6.16** shows photographs of the polyimide separator and the Celgard separator after being exposed to 140 °C for 0.5 h. The Celgard separator is highly shrunk and its thermal shrinkage is observed to be 32%. In contrast, the polyimide separator shows little change in the thermal shrinkage. The polyimide is thermally stable, because it has a high depolymerization temperature of more than 460 °C; therefore, it is believed that the superior thermal stability of the polyimide plays a critical role in preventing the thermal shrinkage of separator. Thus, the polyimide separator is expected to be a highly safe separator for lithium ion battery with desired thermal stability.

6.6 Conclusion

In this chapter, a porous polyimide film was fabricated for high temperature battery separator applications. Polyimide was chosen because of its superior mechanical, chemical and thermal properties. A biphasic poly(lactic acid)/polyimide membrane was fabricated and the poly(lactic acid) phase was thermally removed to create microporous polyimide film. Phase separation, film morphology and ionic conductivity of the resulting film were studied. Different processing conditions caused the polyimide to exhibit two distinct phase separation behaviors: 1) sintered polyimide particles with interstitial pores and 2) “sponge-like” polyimide with percolating pores. Hypothetically the sintered particles are more conductive to ions because they provide a less tortuous pathway for ionic movement. Smaller PI:PLA ratio created more porosity in the film, which is more advantageous for battery separator applications. The best separator had comparable electrochemical performance to a commercial separator when assembled in a coin cell

and tested. The high temperature stability of the polyimide separator makes it potentially useful in lithium-ion batteries, where coin cell shortage can be totally eliminated.

6.7 Experimental Section

6.7.1 Materials

Matrimid 5218 polyimide (PI) was purchased from Alfa Aesar and was used as received. The molecular weight of the polyimide measured by gel permeation chromatography (GPC) is as follows: $M_n=38,000$, $M_w=73,000$. Poly(lactic acid) 3251-D (PLA) was purchased from NatureWorks and was used as received. Bulk mesocarbon microbead (MCMB) anode material (Enerland), $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ (Li333) cathode material (Enerland), and a commercial polyolefin separator material were obtained from Argonne National Laboratory. All other chemicals were purchased from Sigma-Aldrich if not specified. Cathodes and anodes were cut to the appropriate size using a 1.27 cm punch purchased from McMaster-Carr. Separators were cut to the appropriate size using a 1.59 cm punch. C2032-type coin cell hardware components and the coin cell crimper were purchased from MTI Corporation.

6.7.2 ESEM

Environmental scanning electron microscopy (ESEM, Philips XL30ESEM-FEG) was used to image top surface, bottom surface and cross-sections of the polyimide separators. Cross-section samples were prepared by freeze-fracturing pre-notched films in liquid nitrogen. SEM images were acquired after sputter-coating the sample surfaces with gold-palladium.

6.7.3 Film Casting and PLA Removal

The biphasic PI/PLA film was cast *via* a modified solvent-casting technique. PI/PLA solution (1.5 mL) was spread out on one 1 inch by 3 inch glass slide using a pipette, and then the slide was sealed in an airtight container for a controlled amount time. The container seal was then opened and the film was allowed to dry at room temperature for 2 h followed by 6 h drying at 70 °C. After drying, the glass slide was submerged into a water bath allowing for the biphasic film to detach from the glass slide. The film was then removed by tweezers, surface water was wiped off, and then the film was heated in a sealed vacuum oven (Fisher Isotemp 283) at 280 °C under vacuum for 4 h for complete PLA removal.

6.7.4 Porosity Measurement

Porosities of separators were measured using a solvent uptake method. The masses of the porous films were measured on a scale, and then the porous films were soaked in hexadecane for 6 h and taken out. The residual solvent on the surface of the films was carefully wiped off using a kimwipe. The masses of the films with the solvent filling the pores were measured again. The porosities of the films were calculated based on the volume fractions of the solid film and the pore-filling solvent.

6.7.5 Coin Cell Cycling

The coin cells were assembled using $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ (Li333) cathode, mesocarbon microbead (MCMB) anode and either a PI separator or a commercial polyolefin separator with 1 M LiClO_4 -EC/DMC (1:1 in volume) as electrolyte in the argon-filled glove box. The sequence of the coin cell consisted of the anode cap, spring, spacer, anode disk,

polyimide separator, electrolyte (120 μ L), cathode disk, spacer, and top cap (**Figure 6.17**). After assembly, cells were removed from the glove box and mounted in the cycler for testing at different C-rates at room temperature.

Galvanostatic cycling was performed on coin cells using an Arbin BT2000 cycler. At least three cells were tested per case and at least 10 cycles were run per cell.

6.7.6 Linear Sweep Voltammetry (LSV)

The electrochemical stability window of the separators was evaluated by a linear sweep voltammetry (LSV) experiment performed on coin cells with a working electrode of aluminum and a counter electrode of lithium metal. Scans were run from 5 mV to 5.0 V at a scan rate of 1.0 mV/s.

6.7.7 Ionic Conductivity Measurement

The ionic conductivity of the coin cells was evaluated using the electrochemical impedance spectroscopy (EIS) measurement by applying an AC voltage of 20 mV amplitude in the frequency range of 0.001 Hz – 300 KHz using a CH Instruments Model 660 Electrochemical Workstation. Impedance data at 1 KHz were selected to represent comparative impedance values for the coin cells. At least five cells were tested per test case.

6.7.8 Thermal Stability Demonstration

The thermal stability of the separators was evaluated by measuring the length change after the separators were subjected to heat treatment at various temperatures for 0.5 h.

The lengths of the separators were measured using a caliper. The thermal shrinkage of the separators was calculated using the formula below:

$$\text{Shrinkage}(\%) = \frac{L_i - L_f}{L_i} \times 100\%$$

where L_i and L_f are the lengths of the separator before and after heat treatment, respectively.

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6.9 Figures and Schemes

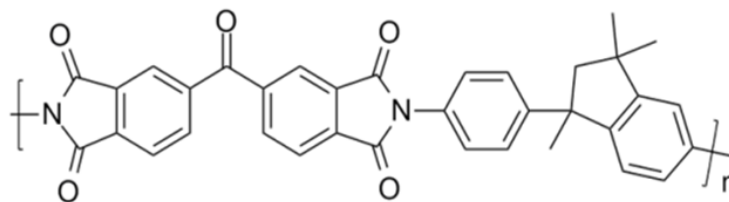


Figure 6.1 Chemical structure of polyimide (Matrimid 5218).

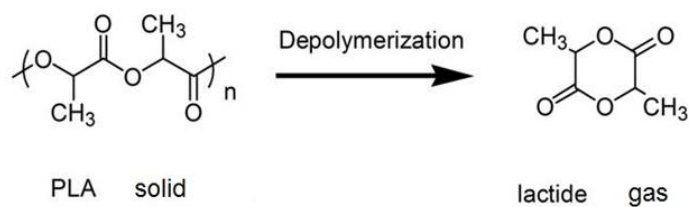


Figure 6.2 Chemical structure and thermal depolymerization of poly(lactic acid) (PLA).

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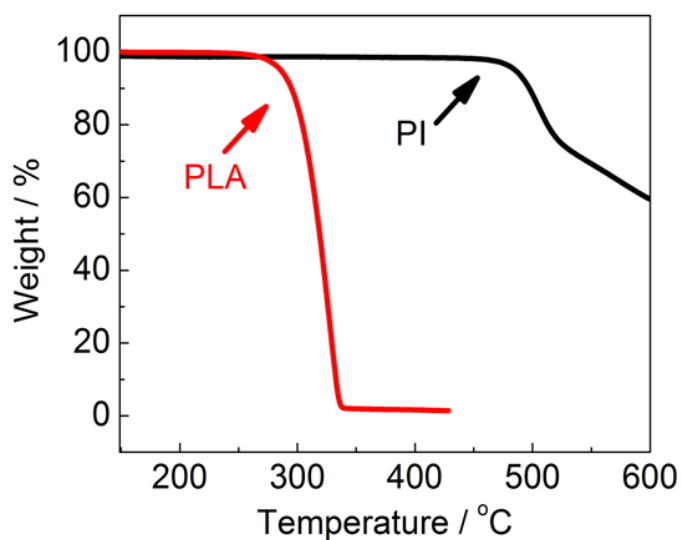


Figure 6.3 Dynamic TGA curves for polyimide and poly(lactic acid), arrows indicate the depolymerization temperatures.

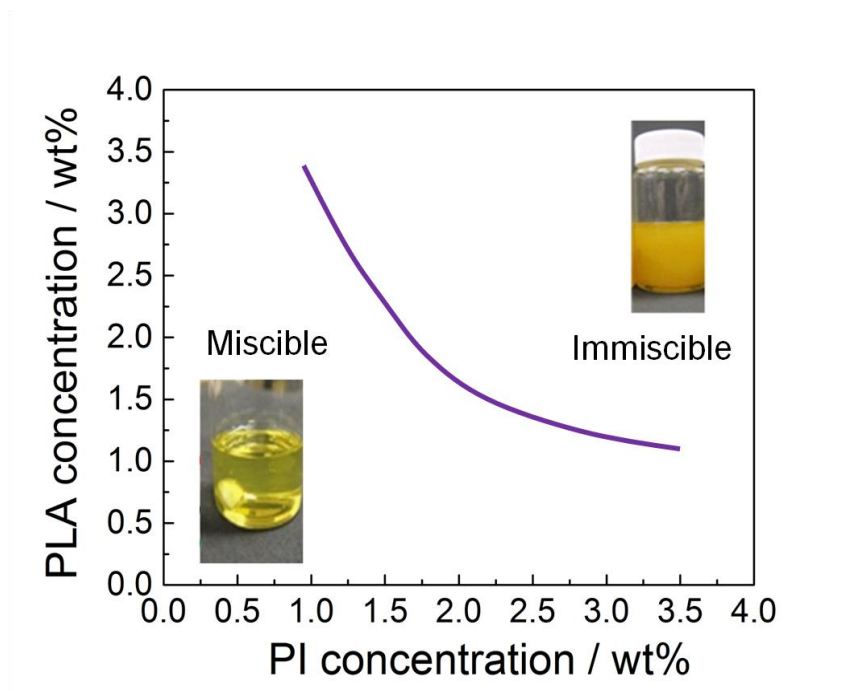


Figure 6.4 Two-dimensional phase separation diagram between polyimide and poly(lactic acid). The purple line separates the miscible (below) and immiscible (above) regions. Picture insets show representative miscible and immiscible solutions.

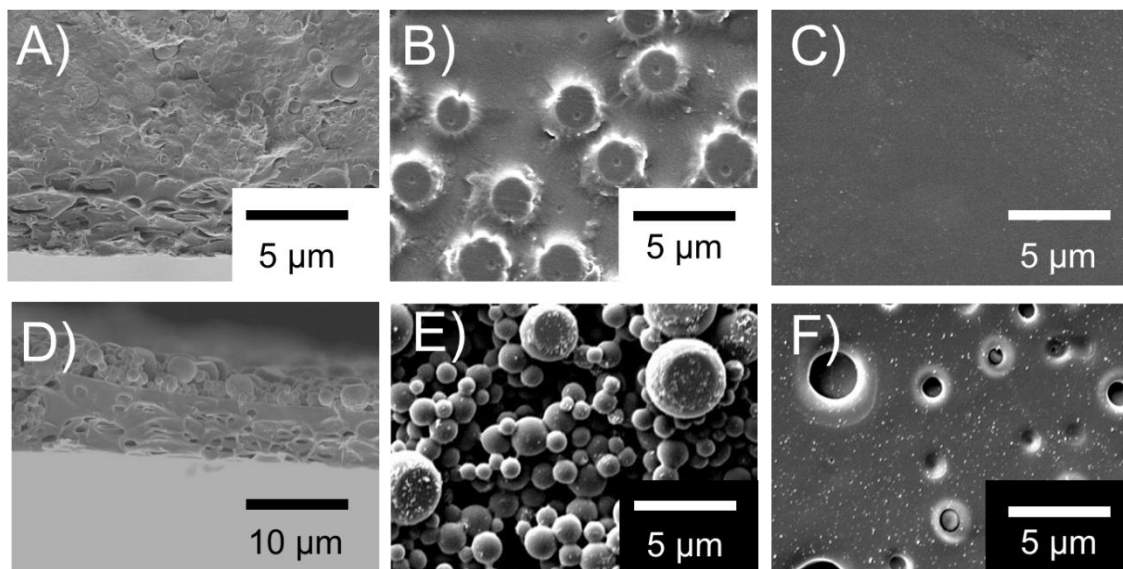


Figure 6.5 SEM images of a biphasic film (A – C) and of a porous separator formed after treatment of a biphasic film at 280 °C (D – F). Images are of the cross-section (A and D), top (B and E), and bottom (C and F) of the film. (Image 6.5F courtesy of Stephen J. Pety)

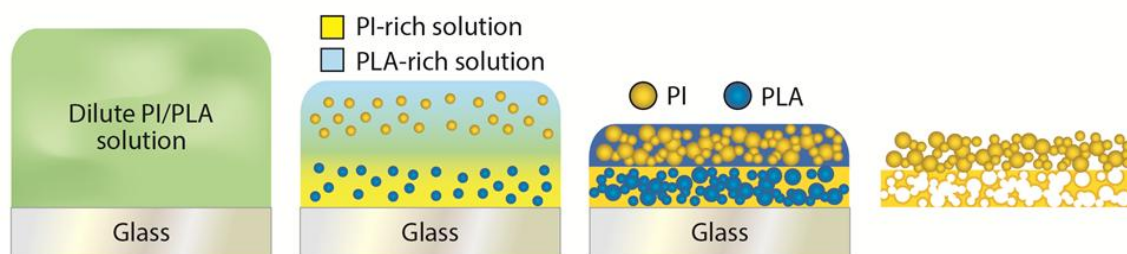


Figure 6.6 Schematic of the solution casting process to create PI separators. From left to right: a dilute PI/PLA solution is cast on a glass substrate; PI and PLA begin to crash out of solution as solvent evaporates; full solvent evaporation leaves a biphasic solid film and treatment of the biphasic film at 280 °C removes the PLA, leaving a porous separator. (Image courtesy of Stephen J. Pety)

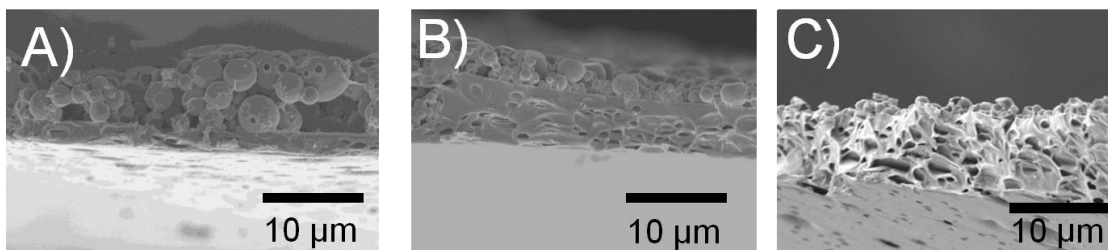


Figure 6.7 SEM images of cross-sections of separators prepared with different PI/PLA ratios and annealed for 10 min. The ratios are A) 40/60, B) 50/50, and C) 70/30.

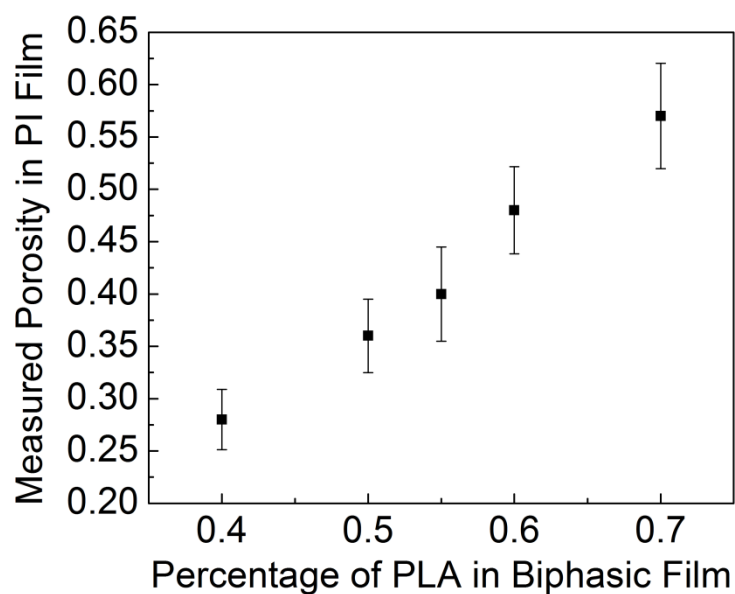


Figure 6.8 Measured porosity of separators made with biphasic films possessing different PI/PLA ratios.

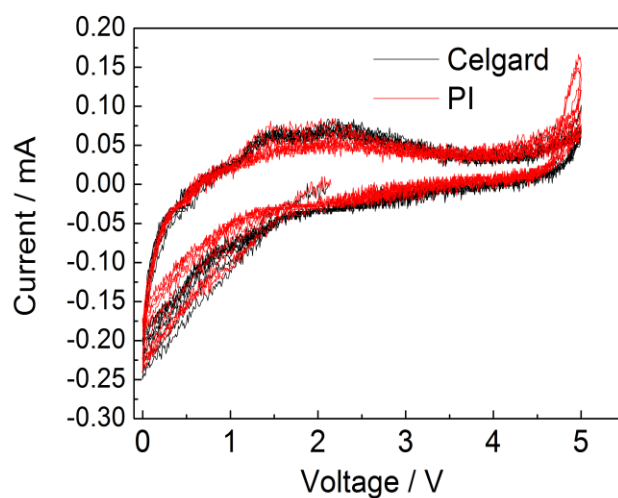


Figure 6.9 Linear Sweep Voltammetry (LSV) curves obtained for newly synthesized PI film and a commercial separator (Celgard). Eight scans from 0 to 5 V are shown at a scan rate of 1.0 mV/s.

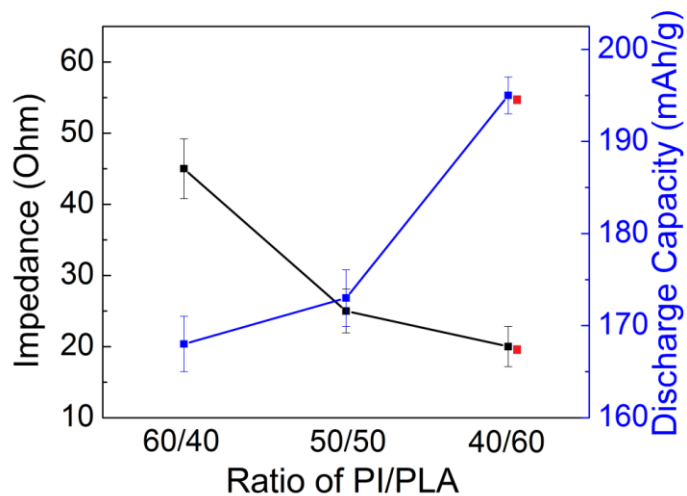


Figure 6.10 Impedance and discharge capacity at C/10 rate of coin cells made with different separators. Error bars represent the standard deviation between cells. The red dots represent the impedance and discharge capacity values measured for coin cell assembled with commercial Celgard separator.

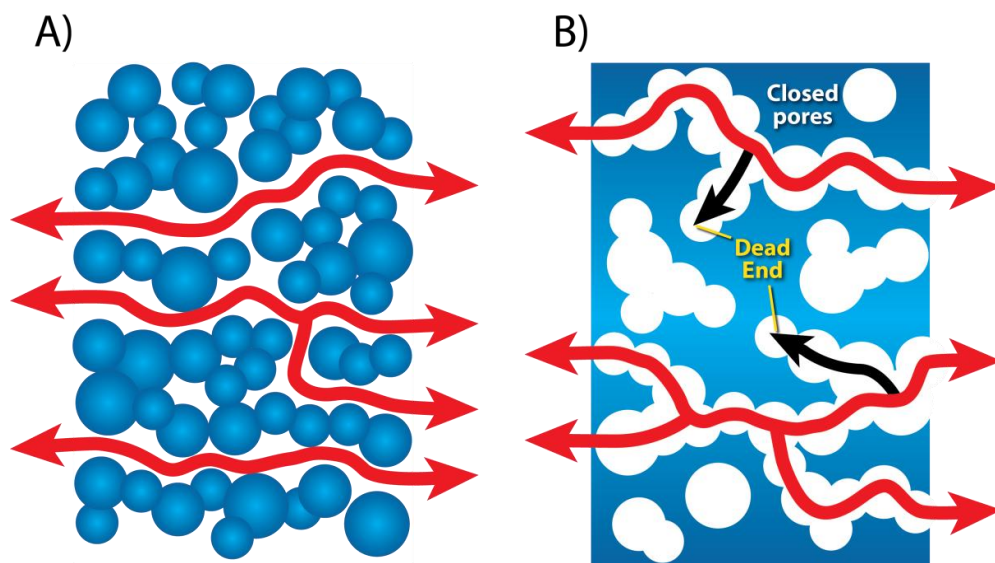


Figure 6.11 Schematic illustrations of different ion transport mechanisms present in the two layers of the separator. A) depicts an “open-cell” porous structure which is developed during the early solvent annealing process, this morphology produces a less tortuous pathway and a shorter travel length for ionic movement; B) depicts a “closed-cell” porous structure which is developed during the late solvent annealing process; this morphology produces a more tortuous pathway and a longer travel length for ionic movement.

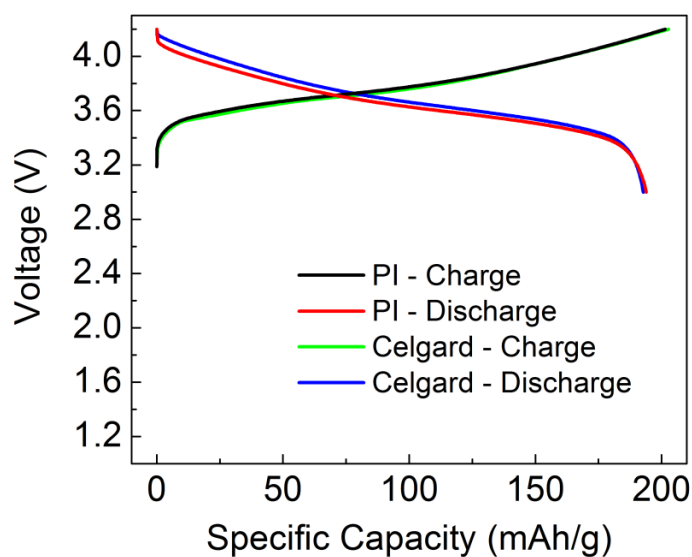


Figure 6.12 Galvanostatic cycling curve for coin cells assembled with polyimide separator (40:60=PI:PLA, 10 mins annealing) and commercial separator Celgard, as a control. The plot shows one charge-discharge cycle at C/10.

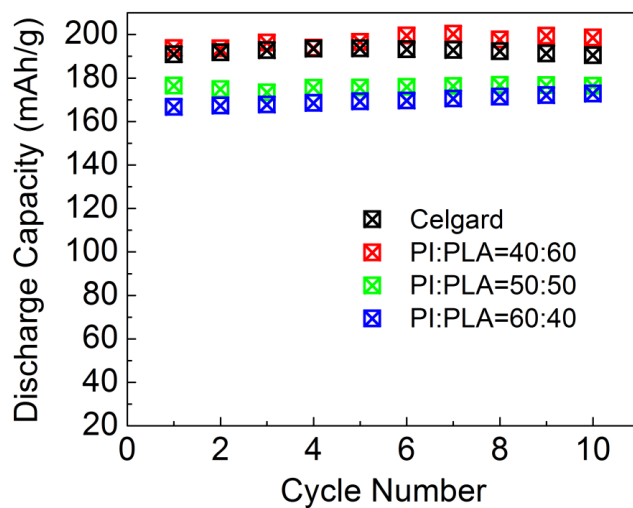


Figure 6.13 Discharge capacity vs. cycle number for coin cell assembled with polyimide separators with different PI:PLA composition (10 mins annealing time) and Celgard as a control. Data is shown for 10 cycles at C/10.

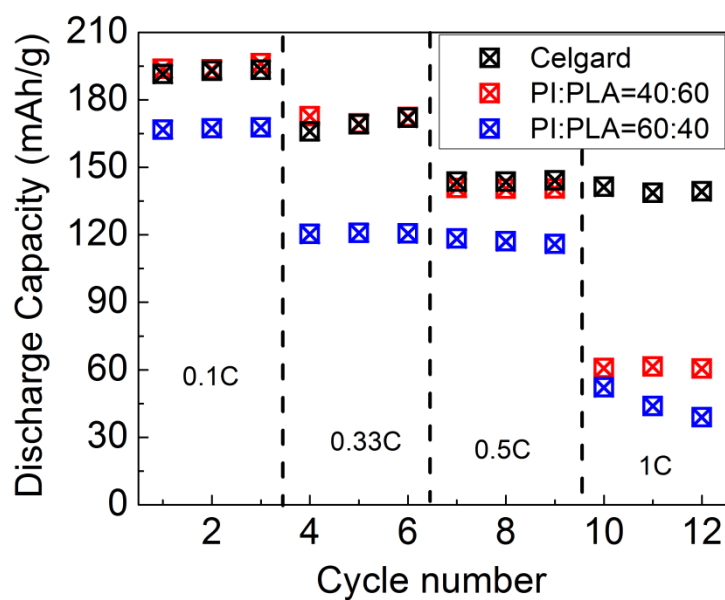


Figure 6.14 Discharge capacity vs. cycle number for polyimide separator and commercial separator, Celgard at different C-rates: C/10, C/3, C/2 and C/1.

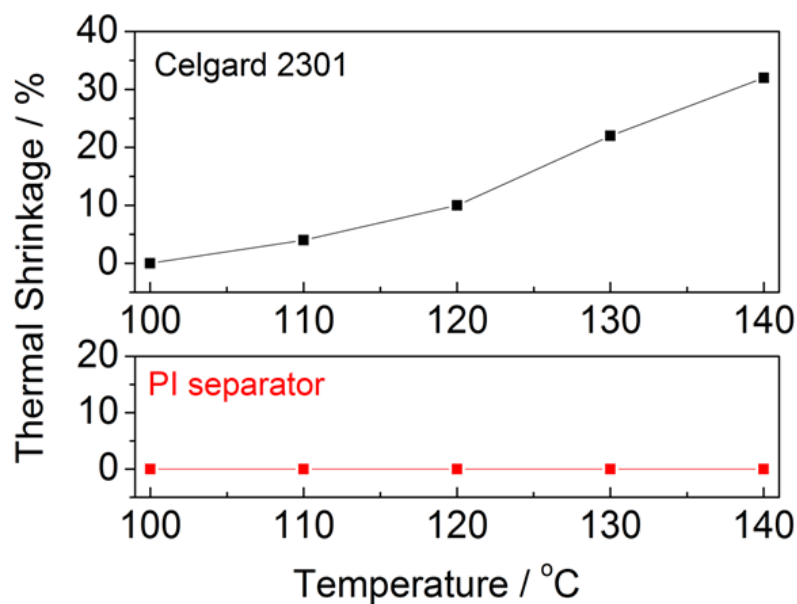


Figure 6.15 Thermal shrinkage calculations at increasing temperatures for polyimide separator and Celgard.

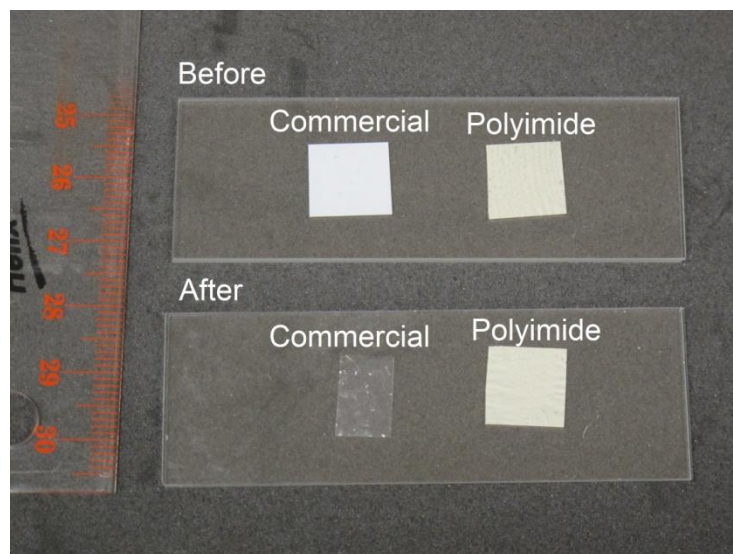
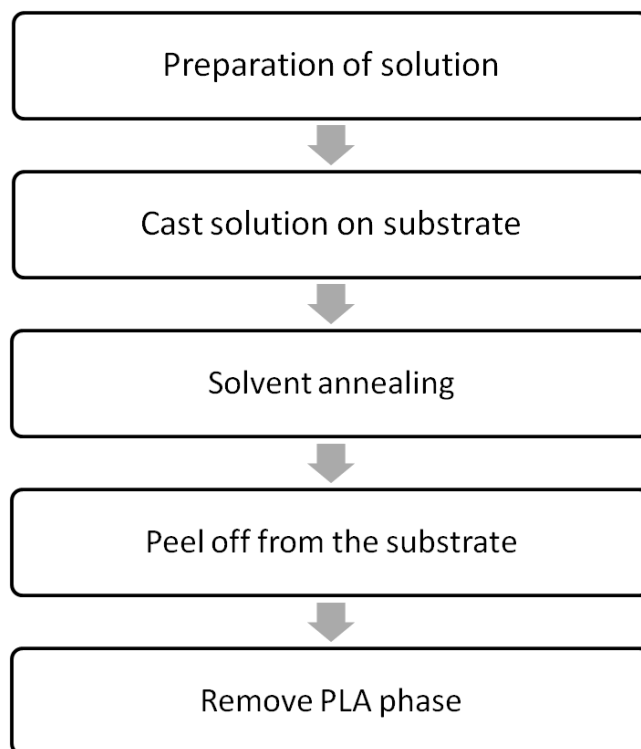


Figure 6.16 Photograph of polyimide and commercial separator, Celgard, before and after exposure to 140 °C for 0.5 h.



Figure 6.17 Assembling sequence of a lithium-ion coin cell battery. (Image courtesy of Marta Baginska)



Scheme 6.1 Flow chart for the fabrication of microporous polyimide battery separator.

CHAPTER 7

SUMMARY AND OUTLOOK

In summary, we have developed a novel fabrication route - Vaporization of Sacrificial Component (VaSC) that allows access to a variety of different synthetic vascular materials. VaSC used sacrificial fibers incorporated into a glass-fiber reinforced composite with subsequent thermal removal to create microchannels inside the composite. Depending on the geometries of the poly(lactic acid) (PLA) sacrificial material (single fiber, two-dimensional sheet, or phase separated polymer blend), the vascular materials exhibited corresponding structures (single microchannel, two-dimensional interconnected microchannels, or microporous structure). The developed VaSC fabrication of microvascular composites for self-healing and autonomous cooling applications is both scalable and compatible with the traditional composites fabrication, a feature that had not been achieved with previous approaches to microvascularization.

Firstly, we have introduced a production technique based on chemical treatment of commercial PLA fiber. Initial difficulties of using a PLA material lay in its high depolymerization temperature (ca. 280 °C) that also caused thermal degradation of the epoxy matrix. This challenge was overcome by finding a catalyst (tin (II) oxalate, SnOx) that efficiently lowered the depolymerization temperature to 200 °C. As such, SnOx was incorporated into the commercial PLA fiber by using a surface impregnation technique in which the use of a solvent swelled fiber surface allowed the catalyst to diffuse into the fiber, and subsequent de-swelling entrapped the catalyst on fiber surface. Different processing parameters (THE/water ratio, solvent soaking time) were studied in order to

produce catalyst-impregnated fibers that could be efficiently removed from the matrix. In addition, the study of catalytic depolymerization mechanism suggested the depolymerization reaction occurred *via* random chain scission.

Chemical treatment of commercial fibers produced PLA fibers that were readily used to fabricate microvascular composites; however, they were limited by the time needed for full fiber removal (24 h). The limitation originates from the heterogeneously distributed catalyst particles that predominately locate on the fiber's surface. As a result, PLA fibers created by this technique did not fully convert into a gas during heat treatment but largely turned into a molten liquid. Thus, a solvent spinning technique was introduced to overcome these limitations. In the solvent spinning technique, commercial PLA pellets were dissolved in a solvent and catalyst was mixed into the solution. This mixture was then extruded into a fiber by using a home-made, lab-scale fiber spinning setup. The solvent-spun PLA fibers showed a significant improvement in catalyst distribution, thus when they were embedded in a matrix, considerably shorter time (2 h) was needed in order to fully remove the fibers. In addition, drawing experiments were performed on the spun fibers to show that the fibers are robust enough for industrial weaving processes.

Unfortunately, the microvasculature produced by using the above PLA fibers was limited to single channel geometry. Biological systems, however, are abundant in two (or three) dimensional and interconnected microvascular networks. In order to produce similar synthetic structures, a fabrication route for a two-dimensional microvascular network is explored. Two-dimensional PLA films were fabricated from a solvent-casting procedure, and then the PLA films were micro-structured by using a punch and die tool set fabricated using μ EDM. Two-dimensional microchannels with a wide range of hydraulic

diameters and aspect ratios were fabricated using this method, which unleashed the possibility to create authentic biomimetic structures in a synthetic microvascular material. Additionally, the incorporation of two-dimensional microvascular networks into a flexible matrix introduced novel self-shaping functionality to the material.

Further efforts were aimed at developing the next generation of microvascular composites that had independent and intermingled microchannel networks and were capable of energy and mass transport by adding a coating material to the PLA fiber. After the fibers were removed, the coating remained in between channels and provided a barrier between microchannels and a pathway for interchannel communication. The initial steps of developing a non-permeable elastomer coating material were reported. The coating material acted as a barrier between two adjacent channels and independent microchannels could be fabricated in this way. A composite that was capable of countercurrent heat exchange was also fabricated using CSFs and preliminary results showed that countercurrent heat exchange was more efficient than cocurrent exchange. Further efforts in this area are focused on using a porous coating material that can introduce mass transport properties into microvascular composites.

The aforementioned work dealt with bulk PLA as the sacrificial component and showed that when the PLA material was embedded in a matrix, removal of the PLA created either 1D or 2D microchannels. If the PLA material exists in a polymer blend together with a surviving material, the removal PLA will create microporous structures. Further efforts showed that when PLA could be co-dissolved in a solvent with polyimide and a biphasic film could be cast from the solution. Thermal removal of PLA from the biphasic film introduced pores and the porous polyimide was shown to be useful as a high temperature

lithium-ion battery separator. The phase separation behavior, morphology of the polyimide separator, and the ionic conductivity of the separator depended heavily on the processing parameters (solvent annealing time, PI/PLA ratio), and these parameters were studied in order to produce the optimal separator for battery applications. Two distinct phase separation mechanism were observed in the separator and their differences were accounted for when designing the processing parameters. When assembled in a coin cell, the microporous polyimide separator showed very competitive electrochemical performance compared to commercial separators. The advantage of this new separator is that it does not shrink at elevated temperatures (which happens to commercial separators) due to the high thermal stability of polyimide, improving the safety and life span of a lithium-ion battery system.

Collectively, the development of both battery separators and vascularized materials showed that Vaporization of Sacrificial Component (VaSC) is a valuable technique for accessing functional materials with complex architectures. Moreover, the use of commercially available and bio-friendly PLA as the sacrificial component makes these processes not only elegantly simple, but industrially viable. The potential applications for the techniques discussed herein are broad and far reaching, including: self-healing materials, autonomous cooling composites, structural remodeling scaffolds, water purification units, carbon capture systems and flow batteries.

APPENDIX

Derivation of “log mean temperature difference” (LMTD)

When studying heat transfer in a flow system, the temperature difference (ΔT) is often referred to as “log mean temperature difference” (LMTD), defined as following:

$$\Delta T = LMTD = \frac{\int_A^B \Delta T(z) dz}{\int_A^B dz}$$

assuming that heat transfer is occurring in a heat exchanger along an axis z , from generic coordinate A to B , between two fluids, identified as 1 and 2, whose temperatures along z are $T_1(z)$ and $T_2(z)$. $\Delta T(z)$ is the temperature difference between $T_1(z)$ and $T_2(z)$. Besides, the temperature differences are $\Delta T(A)$ at point A and $\Delta T(B)$ at point B , having defined $\Delta T(z) = T_2(z) - T_1(z)$.

In this expression, the direction of fluid flow does not need to be considered. It is also unimportant which stream is the hot and which is the cold one, as a change of role will be represented by negative numbers.

Applying Newton’s law of cooling: the rate of change of the temperature of the two fluids is proportional to the temperature difference between them, we have:

$$\begin{aligned} \frac{dT_1}{dz} &= k_a (T_1(z) - T_2(z)) = -k_a \Delta T(z) \\ \frac{dT_2}{dz} &= k_b (T_2(z) - T_1(z)) = k_b \Delta T(z) \end{aligned}$$

That gives:

$$\frac{d\Delta T}{dz} = \frac{d(T_2 - T_1)}{dz} = \frac{dT_2}{dz} - \frac{dT_1}{dz} = K \Delta T(z)$$

where $K = k_a + k_b$.

Now dz can be expressed as a function of ΔT :

$$dz = \frac{1}{K} \frac{d\Delta T}{\Delta T}$$

Substituting this expression back into the formula for LMTD, dz can be removed:

$$LMTD = \frac{\int_A^B \Delta T(z) dz}{\int_A^B dz} = \frac{\int_{\Delta T(A)}^{\Delta T(B)} \frac{1}{K} d\Delta T}{\int_{\Delta T(A)}^{\Delta T(B)} \frac{1}{K} \frac{d\Delta T}{\Delta T}}$$

K is constant and can be cancelled out. After integration, equation 5.2 can be finally obtained:

$$LMTD = \frac{\int_{\Delta T(A)}^{\Delta T(B)} d\Delta T}{\int_{\Delta T(A)}^{\Delta T(B)} \frac{d\Delta T}{\Delta T}} = \frac{[\Delta T]_{\Delta T(A)}^{\Delta T(B)}}{[\ln \Delta T]_{\Delta T(A)}^{\Delta T(B)}} = \frac{\Delta T(B) - \Delta T(A)}{\ln \frac{\Delta T(B)}{\Delta T(A)}} .$$