

Chemical Treatment of Poly(lactic acid) Fibers to Enhance the Rate of Thermal Depolymerization

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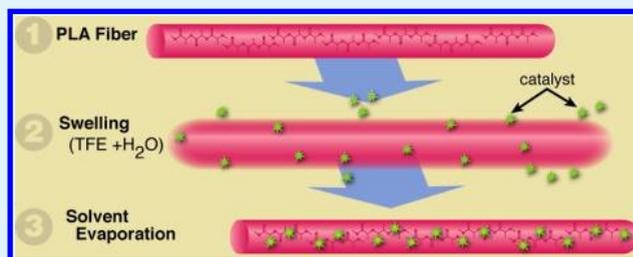
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S Supporting Information

ABSTRACT: When heated, poly(lactic acid) (PLA) fibers depolymerize in a controlled manner, making them potentially useful as sacrificial fibers for microchannel fabrication. Catalysts that increase PLA depolymerization rates are explored and methods to incorporate them into commercially available PLA fibers by a solvent mixture impregnating technique are tested. In the present study, the most active catalysts are identified that are capable of lowering the depolymerization temperature of modified PLA fibers by ca. 100 °C as compared to unmodified ones.

Lower depolymerization temperatures allow PLA fibers to be removed from a fully cured epoxy thermoset resin without causing significant thermal damage to the epoxy. For 500 μm diameter PLA fibers, the optimized treatment involves soaking the fibers for 24 h in a solvent mixture containing 60% trifluoroethanol (TFE) and 40% H₂O dispersed with 10 wt % tin(II) oxalate and subsequent air-drying of the fibers. PLA fibers treated with this procedure are completely removed when heated to 180 °C in vacuo for 20 h. The time evolution of catalytic depolymerization of PLA fiber is investigated by gel permeation chromatography (GPC). Channels fabricated by vaporization of sacrificial components (VaSC) are subsequently characterized by scanning electron microscopy (SEM) and X-ray microtomography (Micro CT) to show the presence of residual catalysts.

KEYWORDS: poly(lactic acid) (PLA), sacrificial fiber, microvascular network, thermal depolymerization, composites



INTRODUCTION

Microvascular materials systems have attracted attention for their ability to achieve multiple healing cycles in response to mechanical damage.^{1–4} Previously, a number of techniques have been reported to introduce microchannels in polymer resins and polymeric composites.^{2,3,5–8} The direct-write assembly technique provides a way to write a vascular pattern using fugitive wax as ink, however, is limited to low-curing-temperature polymers and small-scale material systems/composites.^{3,4} Hollow glass fibers^{2,6} provide building blocks for introducing microchannels to structural composites; however, this approach is limited to 1D vascular features only. In another approach,⁷ 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, EVHF is limited by the inability to control the 3D microstructure and the difficulty of integrating it with commercial composite manufacturing methods. In the present work, we report our initial progress toward the development of a scalable approach based on the use of sacrificial fibers,⁸ which is

compatible with commercial composite manufacturing techniques.⁹ The method takes advantage of thermally degradable polymer fibers¹⁰ embedded in a matrix material (the “holomatrix”). The ideal sacrificial fiber depolymerizes when heated,¹⁰ whereas the application of a vacuum allows controlled removal of the depolymerized monomer from the matrix, leaving behind empty channels in the “apomatrix” (Figure 1). The major challenge in this particular method is achieving the sacrificial fiber depolymerization at temperatures below the degradation temperatures of the embedding matrix material, i.e., the holomatrix. Ideally, the sacrificial fiber depolymerization should take place during a high-temperature postcuring stage for an epoxy matrix that is higher than the cure temperature but lower than the matrix degradation temperature.¹¹

The degradation behavior of poly(lactic acid) (PLA) has attracted widespread interest because of its bioabsorbable and environmentally benign depolymerization products.^{12–14} Recently, Pitet and co-workers utilized PLA as a sacrificial

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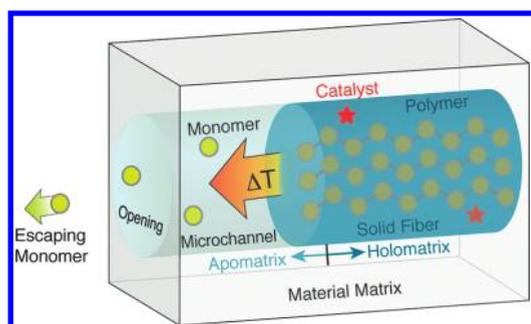


Figure 1. Schematic showing the holomatrix (fiber embedded matrix) to apomatrix (microchannel embedded matrix) transformation by vaporization of sacrificial fiber.

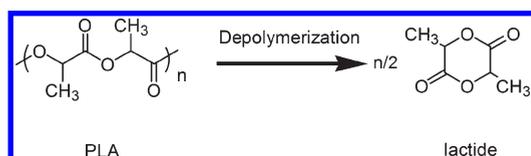


Figure 2. Thermal depolymerization reaction of poly(lactic acid) (PLA).

component in copolymers to create porous membranes for battery separators.¹⁵ Here, we explore the possibility of constructing high-aspect-ratio microchannels by embedding sacrificial PLA fibers¹⁶ in an epoxy thermoset and then triggering thermal depolymerization. The uncatalyzed depolymerization of PLA is realized by heating above 280 °C, which results in the formation of lactide, a gaseous monomer at this temperature (Figure 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. Here we show that minimal matrix damage is realized by using a catalyst to lower the PLA depolymerization temperature. Previously, Fan and co-workers found that poly(L-lactide) depolymerizes at a temperature 90 °C lower when blended with calcium oxide.¹⁸ Similar results were reported by Mori and co-workers regarding the pyrolysis of poly(L-lactide) containing tin reagents.¹⁹ These catalysts promote the cleavage of ester bonds in the polymer backbone, facilitating the fragmented polymer ends to undergo chain backbiting and thus depolymerization.^{18–20} With an eye toward the development of large-scale sacrificial fiber production, we have sought an economical and stable catalyst that does not significantly erode the properties of the PLA fibers under conventional composite processing conditions. We screened various catalysts²¹ and catalyst deposition processes to determine the optimum systems for sacrificial fiber development.

Incorporation of catalysts into PLA fibers requires either a surface treatment or impregnation process.^{22–24} Previously, Quirk and co-workers developed a PLA fiber modification method to immobilize biomolecules 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. Here, we build on this modification procedure by employing a solvent/nonsolvent mixture to controllably swell the fiber and allow a depolymerization catalyst to infiltrate the fiber. The solvent is then removed by evaporation, immobilizing the catalyst (Figure 3). Solvent composition and fiber-solvent soaking time

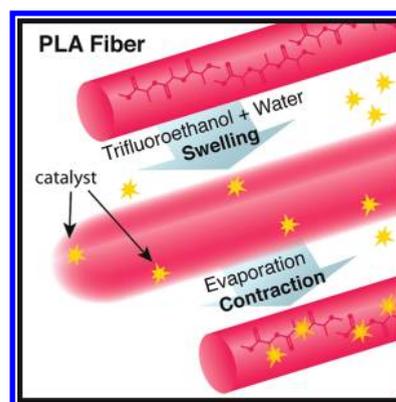


Figure 3. Illustration showing the treatment of a PLA fiber with the depolymerization catalyst by a procedure that reversibly swells the fiber.

are optimized for producing sacrificial fibers that are efficiently removed from an epoxy thermoset. The thermal depolymerization behavior of the chemically treated fibers is compared to that of the untreated fibers under the same experimental conditions to demonstrate the effect of catalyst impregnation.

The increased demand for compact, lightweight functional structures in aerospace applications could be met, in part, by microvascular composites. The embedded vascular network provides energy and mass transport in a structural solid—enabling new, autonomous functionality in structural composite materials. Autonomous functionality like self-healing is especially crucial for applications in which there is no means for human intervention, situations that are common in both manned and unmanned space vehicles. By circulating liquid healing agents within the vascular network, autonomous repair of composite damage due to fatigue or impact from debris is achieved. Self-healing functionality improves safety and increases the longevity of aerospace structures. By circulating gas or liquid phase coolants, these structural composites can be used in high-temperature applications like those encountered by hypersonic air vehicles. Circulating other functional fluids like magnetic or electrically conductive colloids could enable electromagnetic modulation of the host composites with applications in stealth operation of aerospace vehicles, reconfigurable antennas, and embedded communication buses.

This new microvascular fabrication method is facile, robust, scalable, and provides a material architecture for integrating multiple functionalities in aerospace structures.

EXPERIMENTAL SECTION

Materials. PLA fibers (diameters 20, 200, 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, and 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.

Characterization. Thermogravimetric analysis (TGA) was performed on a Mettler-Toledo TGA851^c, 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. For isothermal experiments, the temperature was ramped from 25 to 240 °C at a rate of 50 °C min⁻¹ and subsequently held at 240 °C for 2 h. Differential scanning calorimetry (DSC) was performed on a Mettler-Toledo DSC821^e calibrated with indium and zinc standards. Dynamic experiments were performed under a 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 μ L aluminum pans that were hermetically sealed. 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. Analytical gel permeation chromatography (GPC) was performed on a Waters 515 HPLC pump, Viscotek TDA model 300 triple detector array, a Thermostations Trace series AS100 autosampler, and a series of 3 Waters HR Styragel columns (7.8 \times 300 mm, 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. 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. ESI-MS - Mass spectra were recorded on a 70-VSE C in ES+ mode through the University of Illinois Mass Spectrometry Laboratory, SCS. 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. An Xradia BioCT (MicroXCT-400) was used to image the apomatrix at 40 keV (8 W power and 200 μ A current) at a 4 \times objective for 5 s exposure times. Rotation intervals were 0.25° for a complete 360° scan. Images were visualized in 3D with XM3Dviewer and 3D reconstruction was achieved using XMReconstructor software.

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.

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 the same fiber treatment procedure.

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 h 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

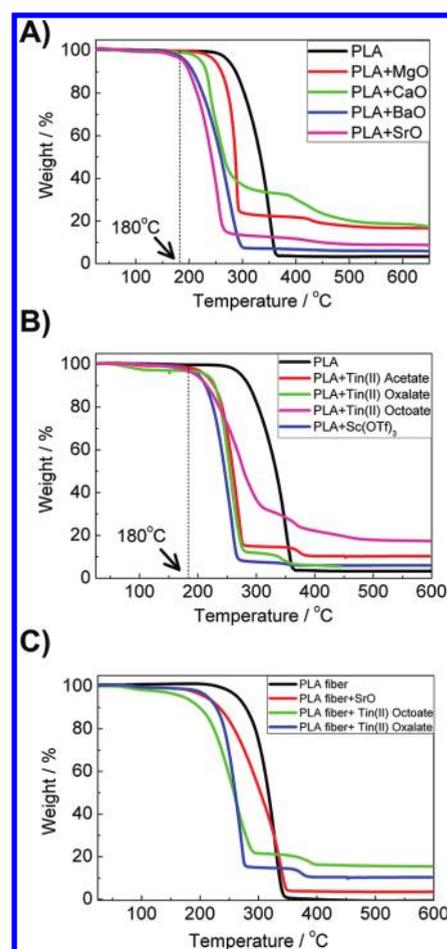


Figure 4. Dynamic TGA curves for PLA films showing the catalytic effect of (A) earth metal oxides, and (B) tin-containing compounds and metal triflates; (C) Dynamic TGA curves of untreated PLA fiber (diameter 20 μ m) and catalyst-treated PLA fibers (diameter 20 μ m).

removed (defined as the ratio of empty channel length over the full fiber length) was measured for each sample after heating for 2 h.

Time Evolution of Catalytic Depolymerization. PLA fibers (diameter 500 μ m) treated with catalyst were placed in a vial and heated at 240 °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.

RESULTS AND DISCUSSION

Catalyst Screening and Fiber Incorporation. Following the reported literature procedure,¹⁸ we screened catalysts that have previously been used to decrease the depolymerization temperature of PLA, dividing them into the following categories: (1) earth metal oxides, (2) tin-containing compounds, and (3) rare metal triflates. Dynamic TGA curves of PLA films blended with various catalysts are shown in panels A and B in Figure 4. Among the catalysts screened, strontium oxide and tin(II) octoate had the greatest effect on the PLA depolymerization onset temperature, decreasing it to nearly 180 °C, which is ca. 100 °C lower than unmodified PLA (Figure 4A,B). Fortunately, these catalysts proved compatible with the fiber treatment protocol and lowered the depolymerization temperature of PLA fibers as seen in Figure 4C.

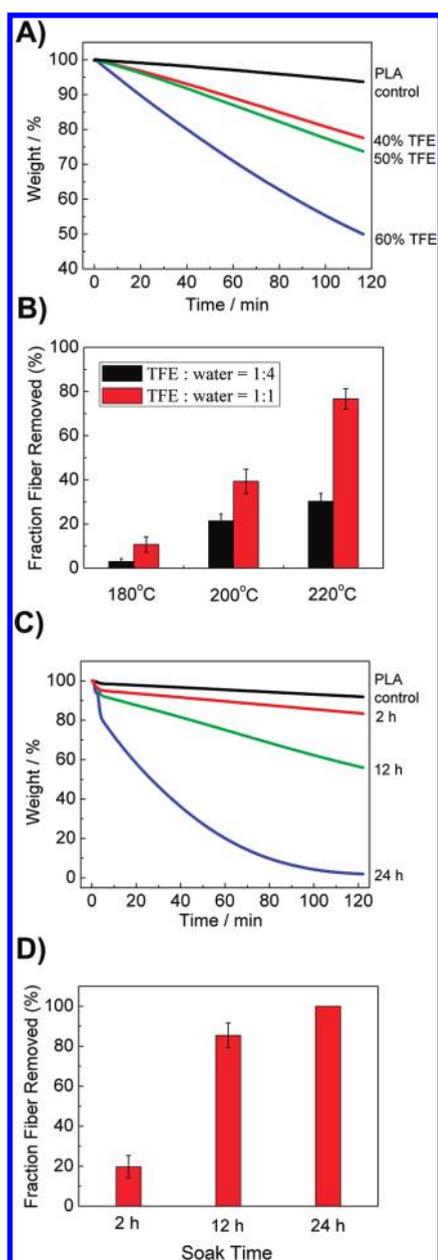


Figure 5. (A) Isothermal TGA curves (240 °C) showing the effect of solvent composition (soaking time: 12 h), the uppermost black line is for a PLA fiber treated with 100% H₂O with 10 wt % tin(II) oxalate as control; each of the other traces include 10 wt % tin(II) oxalate with the indicated quantity of TFE. (B) Fiber removal data at different temperatures varying solvent composition with 10 wt % tin(II) oxalate (fiber length: 5 cm, thermal treatment time: 2 h); (C) 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; (D) 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.

The significant decrease in depolymerization temperature was deemed low enough for fibers to be removed prior to thermal damage of conventional epoxy thermostets.¹⁷

To survive conventional composite fabrication,^{2–4} the catalyst should not significantly change the mechanical properties of the fibers. Typical weaving requires a fiber strength of ca. 23 MPa.²⁶ Both strontium oxide and tin(II) octoate degraded PLA fiber properties. Strontium oxide, as well as other earth metal oxides, form a strongly basic hydroxide upon contact with water, which deteriorated the fiber. Surface damage was evident from visual inspection (see the Supporting Information) 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 a temperature ca. 80 °C lower than unmodified PLA (Figure 4B). The dispersibility of tin(II) oxalate in TFE/water mixture guaranteed good catalyst incorporation into the fiber. Moreover, DSC analysis revealed the thermal stability of tin(II) oxalate up to the PLA catalytic depolymerization temperature range (see the Supporting Information). As a result, tin(II) oxalate was selected for modifying PLA fibers.

Fiber Processing Parameters. The PLA fiber was soaked in the TFE/water mixture, which caused rapid polymer swelling at the surface,²⁴ allowing for infiltration of catalysts into the fiber. We evaluated the effects of solvent composition, fiber-solvent soaking time, and postsoak treatment by isothermal TGA and correlated these data with observations of fiber removal.

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 (data not shown). When catalyst was present in the soaking bath, TGA (Figure 5A) 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 increased up to 60:40, above which the fibers were dissolved. TFE facilitated swelling, presumably allowing more catalysts to diffuse in, which 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 fiber removal measurements (Figure 5B). When other processing parameters were held constant, fibers treated with more TFE had a larger fiber removal fraction under the same thermal conditions.

The fiber soaking time also affected the treatment efficiency, presumably because a longer time allowed more catalyst to diffuse into the fiber. We soaked PLA fibers in the solvent/tin(II) oxalate mixture for varying amounts of time (2–24 h), and subsequently analyzed the depolymerization reaction. Isothermal TGA showed a significant increase in the rate of PLA fiber weight loss with increased soaking time (Figure 5C). Fiber removal data were consistent with TGA observations, showing that the fiber treated for the longest time yielded the fastest rate of removal (Figure 5D).

In the previously reported literature procedure,²⁴ polymer swelling was reversed by the addition of a large excess of nonsolvent (water). In our hands, adding a large amount of water resulted in a decrease in the rate and extent of the thermal depolymerization compared to a simple solvent evaporation. Thus, 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. Under otherwise identical processing conditions, fibers that were dried in the air had a significantly larger fraction of thermal depolymerization than those

Table 1. Optimum Fiber Processing Procedures for PLA Fibers of Different Diameters

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

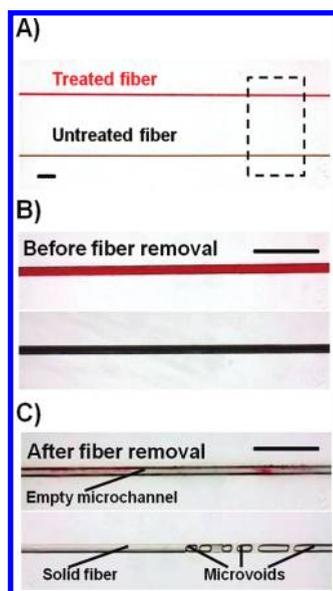


Figure 6. (A) Optical image of epoxy matrix test sample containing both PLA fiber treated with tin(II) oxalate (top) and untreated PLA fiber (bottom) and (B, C) zoomed-in images of (B) holomatrix (before fiber removal) and (C) apomatrix (after fiber removal). The dashed rectangular perimeter defines the zoomed-in area. 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).

treated with water (see the Supporting Information). Thus, the best method to quench catalyst impregnation is simple air-drying.

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 afterward. For PLA fibers of different diameters (20 and 200 μm), the optimum processing procedures involved the same steps with different solvent composition and fiber soaking time (Table 1). The thermal depolymerization behavior of these chemically treated PLA fibers in an epoxy thermoset was compared to that of the untreated one 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 °C for 20 h, yielding an empty microchannel; in contrast, a large portion of solid fiber remained for the untreated PLA fiber (Figure 6).

Time Evolution of Catalytic Depolymerization. We monitored the PLA fiber molecular weight change during the tin(II) oxalate assisted catalytic depolymerization process by GPC analysis. Figure 7A shows the GPC traces of depolymerization products at various reaction times: 0 min, 30 and 120 min. Number average molecular weight (M_n) and weight average molecular

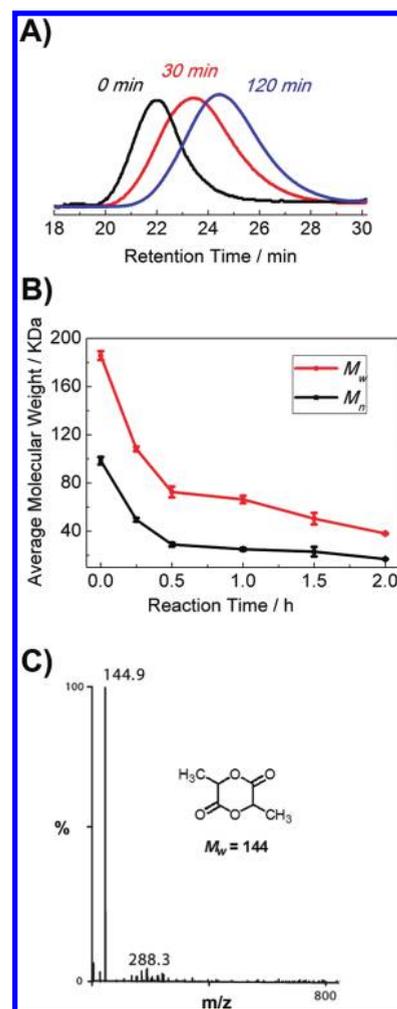


Figure 7. Experimental evidence for PLA catalytic depolymerization to lactide monomer: (A) GPC traces of the PLA catalytic depolymerization product at different reaction times; (B) average molecular weight plotted as a function of reaction time; (C) ESI-MS spectrum of PLA catalytic depolymerization product after 4 h.

weight (M_w) were calibrated and plotted as a function of reaction time in Figure 7B. Average molecular weight data fit to a random chain scission model (see the Supporting Information). Qualitative agreement between the experimentally determined molecular weight and the model's predictions support the mechanism of random chain scission for PLA catalytic depolymerization. The product of catalyst treated fiber heated at 240 °C for 4 h was analyzed by ESI-MS (Figure 7C) and ^1H NMR (see the Supporting Information). Both results indicated lactide monomer as the predominant product.

Characterization of Holomatrix and Apomatrix. To study the catalyst distribution on the fiber, we obtained SEM images on a cross-section of the holomatrix where the sacrificial fiber was embedded (Figure 8A). As shown in Figure 8B, tin(II) oxalate was visible along the edges of the interface. Elemental information (Figure 8B) revealed the presence of tin-rich regions (white spots) at the fiber interface, compared to the area of epoxy matrix. The apomatrix was further imaged by MicroCT (Figure 8C) and revealed tin on the microchannel surface. Although catalyst residue remains on the microchannel surface after fiber removal, it is easily removed by flushing water or chloroform through the channel.

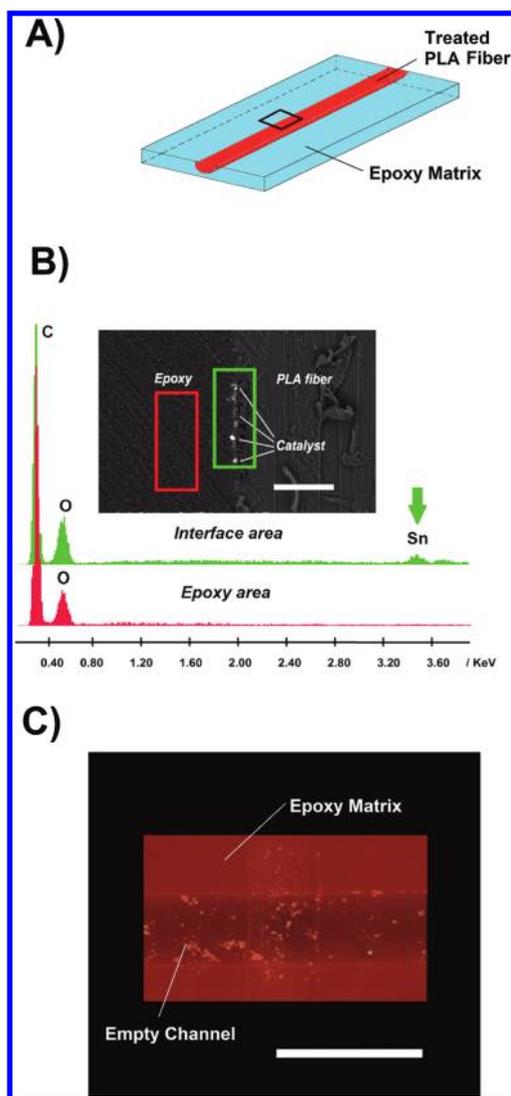


Figure 8. (A) Illustration of holomatrix in which a sacrificial fiber is embedded in an epoxy thermoset. The rectangular perimeter defines the cross-sectional area where SEM image B was obtained; (B) SEM image of cross-sectional area and elemental information for highlighted surface areas (scale bar, 50 μm); (C) MicroCT 3D reconstruction of an apomatrix showing empty microchannels as a result of sacrificial fiber removal (scale bar, 1000 μm ; white spots were designated as tin since heavier elements provide higher contrast).

The exact diffusion depth of the catalyst and the precise quantity of tin(II) oxalate on the surface are presently unknown.

CONCLUSION

Sacrificial fibers based on catalyst-impregnated poly(lactic acid) (PLA) are useful components for the fabrication of microvascular networks in polymeric composites. We explored various catalysts and impregnation techniques to formulate PLA fibers that depolymerize at lower temperatures and thus minimize thermal damage to the matrix. On the basis of a series of screening experiments, tin(II) oxalate performed the best and was incorporated in PLA fibers by an impregnation procedure using a solvent mixture of trifluoroethanol (TFE) and water. We found 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 afterward. This fiber treatment procedure provides a reliable method to prepare sacrificial PLA materials that are 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 final product. Characterization of the fiber/epoxy interface in the holomatrix and the microchannel surface of the apomatrix showed the presence of tin(II) oxalate on those surfaces. Studies on 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 ready availability of PLA fiber should allow for both scalability and processability that can be applied to a wide variety of composite materials. Further research on the fabrication of vascular networks will be reported in due course.

ASSOCIATED CONTENT

S Supporting Information. Additional microscope image, DSC curve, fiber removal fraction data, ^1H NMR spectrum, and study of depolymerization mechanism. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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