Composites: Part A 100 (2017) 361–370

Contents lists available at ScienceDirect

Composites: Part A

journal homepage: www.elsevier.com/locate/compositesa

Robust sacrificial polymer templates for 3D interconnected microvasculature in fiber-reinforced composites

J.F. Patrick [a], B.P. Krull [a,b], M. Garg [a,b], C.L. Mangun [c], J.S. Moore [a,d], N.R. Sottos [a,b,*], S.R. White [a,e,*]

[a] Beckman Institute for Advanced Science and Technology, University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA
[b] Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA
[c] CU Aerospace LLC, Champaign, IL 61820, USA
[d] Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA
[e] Department of Aerospace Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA

ARTICLE INFO

Article history:
Received 20 January 2017
Received in revised form 10 May 2017
Accepted 18 May 2017
Available online 30 May 2017

Keywords:
A. Multifunctional composites
B. Microstructures
E. 3-D printing
Weaving

ABSTRACT

A promising pathway for multifunctionality in fiber-composites is to mimic biological vasculature that enables living organisms with concerted homeostatic functions. In this paper, newfound material and processing advancements in vaporization of sacrificial components (VaSC), a technique for creating inverse replica architectures via thermal depolymerization of a sacrificial template, are established for enhanced vascular composites manufacturing. Sacrificial poly(lactic acid) with improved distribution of catalytic micro-particles is extruded into fibers for automated weaving and filament feedstock for 3-D printing. Fiber drawing after extrusion improves mechanical robustness for high-fidelity, composite preform weaving. Joining one-dimensional (1D) interwoven fibers with printed sacrificial (2D) templates affords three-dimensional (3D) interconnected networks in a fiber-composite laminate that inherits damage-tolerant features found in natural vasculatures. In addition to providing a conduit for enhanced functionality, the sacrificial templating techniques are compatible with current composites manufacturing processes, materials, and equipment.

1. Introduction

In biological systems, fluid transport through internal vasculature enables a variety of metabolic and homeostatic functions including respiration, circulation, thermal regulation, and self-repair. Natural, load-bearing materials such as bone and wood rely on nutrient exchange through vascular networks to achieve cellular proliferation (growth) and tissue regeneration (repair). Fiber-reinforced composites (FRC) possess comparable structural characteristics to natural counterparts, but lack the dynamic functionality enabled by hierarchical vasculature. The fabrication of vascular architectures (Fig. 1) with sacrificial precursors that can also survive the stringent manufacturing requirements of the host material has been a long standing challenge.

Direct-write assembly (DWA) [1,2] of wax-based fugitive inks produces intricate, 3D interconnected vascular templates that can be melted and removed from solid polymer after liquid monomer infusion and solidification [3–7]. These sacrificial scaffolds however, are too delicate to survive FRC manufacturing under elevated temperatures and/or compaction pressure during cure. Several research groups have created 1D microchannels (Fig. 1a) within FRC for self-healing and sensing applications by embedding hollow glass fibers [8–12], manual extraction of silicone tubes [13,14] or steel wires coated with chemical release agent [15–20], or “lost-wax” removal of melted solder wires via heat and vacuum [21–23]. Yet, these approaches lack the capability to create three-dimensional, interconnected networks - a critical requirement for replicating biologically inspired architectures and functions.

The vaporization of sacrificial components (VaSC) process [24–28] has proven to be a robust method for creating multi-dimensional microvascular networks within FRC. Early VaSC demonstrations [24,25] relied on solvent swelling of poly(lactic acid) (PLA) fibers to locally incorporate tin (II) oxalate (SnOx) catalyst particles that facilitate lower temperature depolymerization through bond cleavage in the polymer backbone. More recent studies [28,29] have incorporated catalysts by solvent- or melt-blending techniques to improve homogeneity within the sacrificial

* Corresponding authors at: 3365, Beckman Institute, 405 North Mathews Avenue, Urbana, IL 61801, USA (N.R. Sottos). 3361, Beckman Institute, 405 North Mathews Avenue, Urbana, IL 61801, USA (S.R. White).

E-mail addresses: n-sottos@illinois.edu (N.R. Sottos), swhite@illinois.edu (S.R. White).

http://dx.doi.org/10.1016/j.compositesa.2017.05.022
1359-835X/

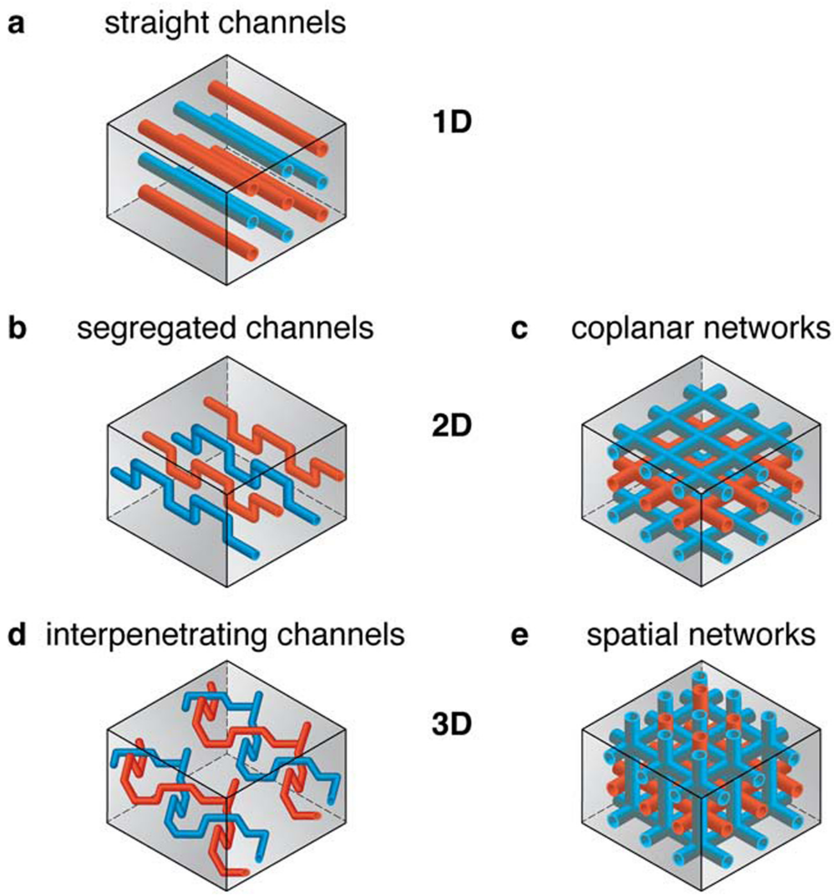

Fig. 1. Vascular hierarchy. (a) One-dimensional (1D) straight channels; (b) Two-dimensional (2D) segregated channels; (c) 2D coplanar interconnected networks; (d) Three-dimensional (3D) interpenetrating channels; (e) 3D spatial interconnected networks.

polymer. DWA has been used to print sacrificial PLA scaffolds via solvent-casting which were subsequently removed from cured epoxy to reveal isolated, spiral microchannels [29]. Fused deposition modeling (FDM) has also been adapted to create multi-dimensional sacrificial PLA templates that were subsequently evacuated from neat epoxy [28]. Three-dimensional, interpenetrating vasculature (Fig. 1d) has been constructed in FRC laminates by VaSC of interwoven sacrificial PLA fibers, and were shown to improve *in situ* mixing of liquid healing agents [30]. However, the resulting microchannels lacked interconnectivity and pathway redundancy, rendering them prone to blockages in fluid pathways as a result of damage to the network. Despite recent advances in printing soft, biomimetic materials [31], the creation of multi-dimensional, interconnected and redundant microvascular networks like those found in natural materials [32] has remained an unmet challenge in fiber-composites.

This paper describes, for the first time, the fabrication of 3D interconnected (Fig. 1e) microvascular networks within a fiber-reinforced polymer composite. These vascular architectures are realized through advancements in catalyst dispersion, melt-spinning of sacrificial fibers with post-processing to improve their mechanical properties, and melt-extrusion of sacrifical filament for 3-D printing. Tuning the sacrificial PLA degradation kinetics and fiber mechanical properties enables seamless composite textile preform integration, survival during FRC processing, and consistent *in situ* evacuation within cured composites. Two types of complex microvascular architectures are constructed in FRC prototypes to demonstrate the versatility and scope of advanced VaSC processing methods.

2. Materials and methods

2.1. Sacrificial material preparation

Sacrificial poly(lactic acid) (PLA) was prepared by combining commercial PLA with varying concentrations of tin (II) oxalate (SnOx) catalyst. Both solution and melt-blending [33] techniques were explored to produce a uniform dispersion of catalyst within PLA for improved evacuation (VaSC) characteristics.

2.1.1. SnOx catalyst particle sizing

Since the sacrificial PLA/SnOx material is used to create vascular precursors with features on the micro-scale (typically between 100–500 μm), the as received SnOx (Sigma-Aldrich) particulates are either sieved (U.S. Std. No. 500) or further ground in a high-speed rotary mixer (Col-Int Tech, FW-100) in 100 g batches for several minutes to ensure particle sizes less than 25 μm. Catalyst powder was stored in an atmospheric desiccator to prevent clumping.

2.1.2. Solvent blending SnOx and PLA

Solvent blending was performed by combining 20 g of PLA (4043D [34], Natureworks LLC, $M_w \approx 150$ kDa [35]) in a glass container with 200 mL of dichloromethane (DCM) and sealed until the PLA was fully dissolved; typically 24 h with intermittent manual agitation. The desired proportion of SnOx (per wt% of PLA) was then added to the solution and shaken until uniformly dispersed. Immediately after agitation (before particle settlement), the