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Energy-Efficient Manufacturing of Multifunctional Vascularized Composites

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Abstract

The retention and transport of different fluids inside synthetic microvascular fiber-reinforced polymer (FRP) composites enable environmentally adaptive functions, including thermal regulation, self-healing, and electromagnetic modulation. However, manufacturing of vascularized components involves an energy- and time-intensive multistep process to cure the host matrix (several hours at elevated temperature) and then evacuate the embedded sacrificial template (12–24 hours at 200 °C under vacuum). Here, we demonstrate rapid (minutes), energy-efficient, and scalable fabrication of vascularized FRP composites at room temperature using the exothermic frontal polymerization of a dicyclopentadiene host matrix. The chemical energy released during frontal curing of the host resin facilitates the endothermic depolymerization of an embedded sacrificial thermoplastic to create structures with high-fidelity microchannels, reducing the thermal energy for fabrication by nearly four orders of magnitude compared to previous methods. The presence of fiber reinforcement in this tandem curing and vascularization strategy presents several challenges related to successful frontal curing and microchannel formation. Increasing the volume fraction of fiber reinforcement (V_f) decreases the volume of the host resin matrix, generating less energy for sustaining the curing and vascularization processes. Heat retention for several minutes after completion of frontal curing using thermally insulating tooling is crucial for obtaining clear microchannels in composite specimens with $V_\mathrm{f} = 60\%$. Simulation of the vascularization process confirms the slower depolymerization of the sacrificial templates in high-V_f composites. A nominal decrease in channel circularity also occurs with an increase in the compaction pressure required for high V_f of composite panels. We leverage this rapid manufacturing strategy to fabricate hybrid composites with vascular networks that span the bulk of the composite and a surface coating for potential self-healing applications.

Keywords

Frontal polymerization, fiber-reinforced polymer composites, vascular composites, vascularization, depolymerization

Introduction

Surface and internal damage reduce the service life of structural fiber-reinforced polymer (FRP) composites.[1,2] To address this challenge, self-healing strategies have emerged to improve the performance lifetime and reliability of composite parts. Strategies include thermally reversible cross-links in polymer matrices,[3,4,5] dispersed thermoplastic agents within the polymer matrix,[6,7,8] encapsulated polymerizable healing agents embedded in the polymer matrix,[9,10,11,12] and reactive fluids delivered to damage locations via embedded microvascular networks.[13,14,15] Of these strategies, the microvascular approach is appealing for its ability to repeatedly heal large-scale internal damage, such as delamination and transverse cracking, and recover mechanical properties.[13,14,15] Microvascular networks also enable healing of large-scale surface damage in coated systems. Gergely et al.[16] designed a regenerative coating system by fabricating a vascular network that bridged a thermoset coating and an underlying polymer substrate. Upon abrasive damage to the coating, the network delivered a photocurable, one-part healing agent to the damage site to recover the mass lost and the functionality of the coating. In addition to healing, microvascular materials enable other functions such as autonomous cooling where circulating a coolant within the embedded network regulates the temperature of the composite to enable operation at elevated temperatures without structural degradation.[17,18,19]

Previous studies on vascularized composites demonstrated that branching 2D and 3D channel networks facilitate interspersion of the functional fluid throughout the composite volume for improved self-healing performance.[14] Of the manufacturing strategies published, the Vaporization of Sacrificial Components (VaSC) technique was the first to enable fabrication of complex and scalable vascular architectures in FRP composites.[14,15,20,21] As shown in Figure 1a, VaSC requires a sacrificial polymer template that is embedded within a liquid resin matrix. The template must withstand the curing of the host resin (several hours at elevated temperature) without depolymerizing. Then, the cured part is heated above the depolymerization temperature of the sacrificial polymer (12–24 hours at 200 °C under vacuum) to facilitate its evacuation and yield a hollow replica of the starting template. As shown in Figure 1c, curing a centimeter-long vascular composite within a 1 m^3 oven consumes 10^8 J of energy over 20 hours. Cure of larger-scale vascular composites requires an oven or autoclave that scales in size with the part to be produced, thereby consuming commensurately more energy to achieve the cure conditions required.[22] Thus, VaSC is a time and energy-intensive, multistep process.[20,23]

Garg et al.[24] recently reported the rapid manufacturing of vascular thermosets at room temperature by harnessing the surplus chemical enthalpy during the frontal polymerization (FP) of a host resin[25,26] to concurrently achieve vascularization. The exothermic energy released during the frontal curing of the resin matrix facilitates the coordinated depolymerization of the embedded sacrificial polymer (Figure 1b), eliminating the need for a separate VaSC step. This tandem curing and vascularization technique reduces the fabrication energy by six orders of magnitude and expedites the manufacturing time by three orders of magnitude compared to bulk-cure manufacturing a vascular composite of the same dimensions (Figure 1c).

[insert Figure 1]

Sustaining frontal polymerization in composites is challenging due to increased energy dissipation and reduced availability of exothermic energy as the volume fraction of resin decreases with increasing fiber volume fraction.[27,28] Frontal curing of vascular composites is even more challenging because a successful vascularization requires excess exothermic energy generation in the resin matrix to achieve the endothermic depolymerization of the embedded sacrificial material.

In this work, we examine the impact of the volume fraction of fiber reinforcement on successful vascularization in FRP composites through this tandem manufacturing strategy. We first investigate the effect of the fiber reinforcement loading (up to 60 vol. %) on the depolymerization of an embedded 1D sacrificial fiber. We measure the temperature evolution of the resin matrix during frontal curing and compare the channel fidelity with the starting template. A computational model simulates this thermo-chemical process and provides insight into the effect of the fiber reinforcement on the temporal lag between the matrix polymerization and sacrificial polymer depolymerization reactions. Finally, we demonstrate the versatility of this method by fabricating a hybrid composite with a 2D undulating channel connecting the bulk composite to a surface coating as a potential design for healing both internal and surface damage.

Materials and Methods

Sacrificial Fiber Template

The selected sacrificial material is UV-activated polypropylene carbonate (PPC) blended with 3 wt. % photoacid generator (PAG) that undergoes acid-catalyzed depolymerization into propylene carbonate (PC) monomer.[29] The PPC pellets were generously provided by Novomer Inc. and 4-Methylphenyl[4-(1-methylethyl)phenyl]iodonium tetrakis(pentafluorophenyl)borate photoacid generator (PAG) was gifted by Bluestar Silicones. Target sacrificial fiber diameters are 400 μm to minimize distortion of the reinforcement and subsequent degradation of cured composite properties.[30] Detailed descriptions of the sacrificial polymer processing, characterization, and UV irradiation are presented in publications by Garg et al.[24,31] All references to the sacrificial fibers or templates used in this work refer to PPC blended with 3 wt. % PAG, unless otherwise noted.

Thermal depolymerization via mass loss of sacrificial templates (3 mg samples) in a nitrogen environment is measured on a thermogravimetric analyzer (TGA) equipped with an evolved gas analysis furnace (Q500, TA instruments). For dynamic tests, the mass loss is recorded during a heating cycle over the temperature range from 40 °C to 250 °C at a linear ramp rate of 2-10 °C min^{-1}. For isothermal tests, the temperature is ramped from 40 °C to 10 °C below the desired temperature at a linear ramp rate of 10 °C min^{-1}, then subsequently ramped to the desired temperature at a linear ramp rate of 5 °C min^{-1} to minimize temperature overshoot. The ultimate tensile strength and modulus of sacrificial fibers are measured in quasi-static uniaxial tension experiments at room temperature on a TA Instruments RSA G2 dynamic mechanical analyzer

(DMA). The ends of each fiber are glued to cardstock paper tabs using a commercial epoxy resin (J-B weld^{TM}) and cured at room temperature for 48 hours in a dark room. A gauge length of 25 mm and a linear strain rate of 5 μm s^{-1} is maintained in each experiment.

Wet Layups for Vascular Composites

All vascular composites are fabricated using a wet layup technique. The resin matrix is comprised of dicyclopentadiene (DCPD), 5-ethylidene-2-norbornene (ENB), second-generation Grubbs' catalyst (GC2), and tributyl phosphite inhibitor (TBP), all purchased from Sigma-Aldrich and used as received without further purification. The DCPD-based resin is prepared by mixing 52 mg of GC2 directly with 5 μL of TBP (0.3 molar equivalent with respect to GC2) and 81 g of 95/5 DCPD/ENB solution (10,000 molar equivalents with respect to GC2) in a glass container. The container is placed in a cooled (12 – 15 °C) sonication bath for 40 mins to dissolve the GC2 while mitigating any background polymerization. The resin is used to prepare the wet layup immediately after complete dissolution of GC2. The brief application of a thermal trigger initiates the frontal ring-opening metathesis polymerization of the DCPD-based resin into polydicyclopentadiene (pDCPD) thermoset.[32,33] The composite reinforcement is 10×13 cm^2 Toray T300 2 × 2 twill weave carbon fiber (CF) fabric.

The CF/DCPD laminate is assembled within a 4 mm thick polyurethane gasket to control the cured composite thickness (t) and on top of a surface heater (OMEGALUX®) secured on a thermally insulated polyisocyanurate tool plate (448-D, Fibre Glast Developments Corp., 25.4 mm thick) (Figure 2a). A target CF volume fraction (V_f) is achieved by varying the number of CF plies (n) used in the laminate according to the equation $V_{\mathrm{f}} = \frac{f_{\mathrm{A}} n}{\rho_{\mathrm{f}} t}$, where f_{A} and ρ_{f} are CF fabric properties (areal weight and fiber density, respectively) and t is kept constant. A micropipette is used to infuse each CF ply with resin before stacking the next ply. Vascular composites with straight channels are manufactured by positioning a sacrificial fiber in the midplane of the laminate. For example, for a composite with target V_f = 30 % (n = 10 plies), the sacrificial fiber is placed between the 5th and 6th CF plies. Once the plies are stacked and infused with resin, a second polyisocyanurate tool plate is placed on top of the assembled laminate. The layup is then moved into a hydraulic press (G15H-15-CPX, Wabash) and compacted at room temperature to achieve the target V_f, evacuate air bubbles, and suppress void formation during curing. Once the hydraulic press reaches the desired compaction pressure (P), the surface heater is powered for 35 s to initiate polymerization of the resin matrix (Figure 2b). Robertson et al.[28] showed that powering a surface heater can initiate a polymerization front to propagate (bottom to top) through the laminate thickness and cure the laminate. Through-thickness curing requires more energy input into the laminate (200 W over 35 s) compared to in-plane curing (50 W over 35 s) for the same dimensions. The additional energy input achieves a hotter maximum temperature in the resin matrix during through-thickness curing compared to in-plane curing, which becomes very attractive for simultaneous vascularization. Furthermore, the surface heater acts as a heated boundary to achieve a slow cool-down in the cured composite after frontal curing. The layups are allowed to cool for 1 hour before removing from the hydraulic press.

[insert Figure 2]

A composite with a serpentine vascular network and surface coating is manufactured as shown in Figure 3. The CF/DCPD laminate is comprised of 16 plies of CF fabric (target V_f = 50 %) and assembled within a square gasket 5 mm thick to achieve a target composite thickness and coating thickness of 4 mm and 1 mm, respectively. A sacrificial fiber is hand-stitched through a stack of 8 CF plies. The remaining 8 plies are stacked directly on the surface heater (secured on polyisocyanurate tooling), followed by the woven stack, and thoroughly infused with resin. A thin sheet (ca. 1 mm thick) of partially cured DCPD gel is carefully laid on top of the CF/DCPD laminate, then a second polyisocyanurate tool plate is placed on the rigid gel. The assembled layup is compacted in a room-temperature hydraulic press (P = 340 kPa) before powering the surface heater for 35 s to initiate through-thickness curing.

[insert Figure 3]

Characterization of Front Characteristics and Channel Fidelity in Single Channel Vascular Composites

T-type thermocouples (TMQSS, Omega, 508 μm diameter) are embedded in the wet layup along the laminate thickness to measure *in-situ* temperature evolution. Thermocouple T1 is placed at the heater-laminate interface, T2 at the laminate midplane, T3 at the laminate-top tool plate interface. Figure 4 shows representative thermal profiles at thermocouples T1 and T3 for an experiment with tandem frontal curing and VaSC compared to a control case without frontal curing (GC2 excluded from the resin formulation). For both experiments, V_f = 30 %. The two tests initially show similar temperature profiles after the heater is powered on at ca. 116 s. The temperature then increases rapidly once the polymerization front is initiated (T_initiate) at ca. 145 s and the heater is powered off shortly after at ca. 151 s. Representative thermal profiles at thermocouple T3 show that the front propagates to the laminate surface seconds after T_initiate. The front temperature (T_front) is defined as the peak temperature measured at each thermocouple. The cure time (t_cure) is defined as the time between powering the heater and the front reaching the laminate surface (i.e., time corresponding to T_front at thermocouple T3). Therefore, the t_cure accounts for the energy input by the heater and its contribution to the depolymerization of the embedded sacrificial fiber.

[insert Figure 4]

Panels with successful vascularization exhibit sustained through-thickness curing and complete depolymerization of the embedded sacrificial fiber. Complete depolymerization is qualitatively assessed by inserting a steel wire (280 μm diameter) through the straight channel in the cured composite. An ethanol solution containing trace amounts of Nile Red dye is then flushed through each channel to confirm channel clearance. For the serpentine channel composite, vascularization is assessed by injecting the dyed fluid into the channel and imaging the fluid transport with an optical camera focused on the transparent pDCPD coating surface. The optical video is converted to greyscale followed by changing the color of pixels associated with the dyed fluid (from white to pink) to enhance the color contrast with the surrounding black composite.

Circularity and aspect ratio of the resulting channels are measured by polishing cross-sections of 2 × 1 cm^2 samples taken from the center of the cured vascular composite, then imaging the surfaces with an optical digital microscope (VHX-5000, Keyence). ImageJ software is used to measure the circularity ($C = 4\pi \frac{Area}{Perimeter^2}$) and aspect ratio ($AR = \frac{Major\ axis}{Minor\ axis}$) of the channel for each polished sample. A value of 1.00 indicates a perfect circle for both C and AR measurements.[34] Lower C values are measured for noncircular shapes, such as an ellipse (AR = 2.00, C = 0.77)[34] and square (AR = 1.00, C = 0.79).

Modeling of Frontal Polymerization and Depolymerization of Single Channel Composites

The frontal curing of composites and the depolymerization of sacrificial fibers are coupled thermo-chemical processes, which are simulated by a multiphysics model to gain further insights into this manufacturing strategy. This model builds on our previous computational modeling of synchronized FP and VaSC in neat DCPD along the PPC fiber direction, considers a through-thickness curing and VaSC process, and further accounts for composite specimens at different volume fractions of the CF reinforcement. For computational efficiency, we consider a rectangular area of the wet layup cross section in the *y-z* plane (Figure 7a). The thickness and width of this area are 4.0 mm and 1.0 mm, respectively. We account for the sacrificial fiber, CF/DCPD laminate, and polyisocyanurate rigid foam tool plates above and below the laminate in these simulations. The choice of simulation dimensions eliminates boundary effects and only half of the domain is considered in the simulation due to symmetry. In the CF/DCPD laminate domain, the thermo-chemical model is expressed in terms of the temperature, T (in K), and degree-of-cure, α (non-dimensional), and takes the form:

$$\begin{cases} \nabla \cdot (\bar{\kappa} \nabla T) + \left(1 - V_{\mathrm{f}}\right) \rho_{1} H_{r1} \dfrac{\partial \alpha}{\partial t} = \overline{\rho C_{p}} \dfrac{\partial T}{\partial t} \\ \dfrac{\partial \alpha}{\partial t} = A_{1} \exp\left(-\dfrac{E_{1}}{RT}\right) (1-\alpha)^{n_{1}} \alpha^{m_{1}} \dfrac{1}{1 + \exp\left[C_{1}\left(\alpha - \alpha_{c1} - \alpha_{0}\right)\right]} \end{cases} \tag{1}$$

where the first equation is a diffusion equation with a source term from the heat of reaction, which links to the curing rate as described by the cure kinetics in the second equation. κ (in W m^{-1} K^{-1}) is the thermal conductivity, ρ (in kg m^{-3}) the density, C_p (in J kg^{-1} K^{-1}) the specific heat, and H_r (in J kg^{-1}) the total enthalpy of reaction. The subscript '1' indicates quantities associated with DCPD, and the overbar indicates the homogenized properties of the CF/DCPD laminate. The cure kinetics takes a typical Arrhenius equation form, characterized by the Arrhenius constant *A* (in s^{-1}), the activation energy *E* in (kJ mol^{-1}), the universal gas constant *R* (in J mol^{-1} K^{-1}), and the constants n_1, m_1, C_1, and α_{c1}. α_0 represents the initial degree of cure of the CF/DCPD matrix. A similar form of this model was used for modeling FP in unidirectional composites,[27,35,36] where the rules of mixtures (i.e., $\overline{f} = \left(1 - V_{\mathrm{f}}\right) f_{1} + V_{\mathrm{f}} f_{f}$, the subscript '*f*' indicates fiber quantities) works very well for those homogenized properties. In the case of woven composites, we use the same method for all homogenized quantities except for the thermal conductivity. Specifically, we adopt a homogenization model for the thermal conductivity of woven composites in the transverse direction,[37,38] which accounts for the fiber volume fraction, fiber size, and arrangements. Thermal conductivities of the CF/DCPD composite at 30%, 40%, 50%, and 60% CF volume fractions are computed to be 0.25, 0.28, 0.3, and 0.32, respectively (in W m^{-1} K^{-1}). The thermal conductivities of DCPD, CF and PPC used in the model are provided in Table 1.

The depolymerization process of the PPC fiber is described similarly in terms of the thermal field and the degree of depolymerization, β, with $\beta = 0$ corresponding to the intact sacrificial fiber and $\beta = 1$ to the fully depolymerized state:

$$\begin{cases} \nabla \cdot \left(\kappa_2 \nabla T \right) - \rho_2 H_{r2} \dfrac{\partial \beta}{\partial t} = \rho_2 C_{p2} \dfrac{\partial T}{\partial t} \\ \dfrac{\partial \beta}{\partial t} = A_2 \exp\left(- \dfrac{E_2}{RT} \right) (1 - \beta)^{n_2} \beta^{m_2} \end{cases} \tag{2}$$

where the subscript ‘2’ indicates quantities associated with PPC, and H_{r2} the total heat absorbed per unit mass by the depolymerization of the sacrificial material. For the rigid foam above and below the laminate, only the diffusion equation similar to that in equations (1-2) is considered without the heat of reaction term. A convective boundary condition with convection heat transfer coefficient $h = 25$ W m^{-2} K^{-1} is applied to the outer surface of the top rigid foam tool plate.

The parameters associated with physical and thermal properties and cure kinetics of DCPD have been well established in previous studies,[24] so we focus on obtaining depolymerization kinetics parameters of the PPC fiber used in the current study. An unconstrained multivariable optimization process using a derivative-free method[39] is adopted to optimize the depolymerization parameters against the dynamic TGA data in Figure 5a, using initial values and ranges from our previous study.[24] The final depolymerization kinetics capture the mass loss history at three different ramping rates (2, 5, and 10 °C min^{-1}) reasonably well as shown in Figure 5a. The depolymerization kinetics modeling parameters of PPC, as well as the physical and thermal properties of the DCPD, CF, PPC fiber and foam tool plates are provided in Table 1 and Table 2.

Table 1. Physical and thermal properties of the sacrificial fiber (PPC 3 wt.% PAG), neat DCPD, composite reinforcement (Toray T300 2 × 2 twill weave CF), and layup tool plates (polyisocyanurate rigid foam) used in the thermo-chemical computational model.

Material	κ (W m^{-1}K^{-1})	ρ (kg m^{-3})	C_p (J kg^{-1} K^{-1})	H_r (J g^{-1})
PPC	0.25	1313	1800	20
DCPD	0.15	980	1600	400
CF	9.36	1772	758	N/A
Foam	0.03	95.8	1453	N/A

Table 2. Kinetic parameters for simulating the degree of degradation of the sacrificial fiber (PPC 3 wt.% PAG) in the computational model.

Material	E_2 (kJ mol^{-1})	A_2 (s^{-1})	m_2	n_2
PPC	108.0	6.18×10^{12}	0.30	0.98

To conduct a through-thickness curing and VaSC simulation, the temperature history measured from the bottom heater (i.e., T1 for the no FP case in Figure 4) when the heater is powered on (35 s) is prescribed at the bottom of the laminate. Only the fiber volume fraction as well as the homogenized property corresponding to the volume fraction of reinforcement is updated for each type of specimen. Successful depolymerization is denoted by $\beta = 0.9$ or higher.

Results and Discussion

Sacrificial Fiber Compatibility with Frontal Curing of Composites

The ideal sacrificial templates for frontal curing of vascular composites should satisfy two major criteria – survive deformation during compaction of the composite layup and then depolymerize rapidly with the enthalpy released during FP. Sacrificial PPC meets these seemingly contradictory requirements due to the orthogonal nature of the latent PAG catalyst. Dynamic TGA experiments at three different ramp rates (2, 5, and 10 °C min^{-1}) show that UV-activated PPC (3% PAG) fibers have a depolymerization onset temperature (T_d, defined by 5% mass loss) between 90 – 100 °C (Figure 5a), which is significantly below the peak temperature achieved during frontal curing. Isothermal TGA experiments reveal that the mass loss kinetics of the sacrificial fibers is heavily influenced by the depolymerization temperature. Complete mass loss occurs within 15 mins at 100 °C, but this process takes 2 hours at 60 °C (Figure 5b). By comparison, frontal curing of the host resin matrix occurs on the order of minutes to seconds with varied cool down rates depending on the sample size, trigger configuration, and layup boundary conditions. The as-extruded PPC (3 % PAG) fibers have a yield strength of 29 MPa and UV irradiation only causes a small decrease in strength to 27 MPa (Figure 5c). A similar drop in tensile modulus from 2.6 GPa to 2.3 GPa occurs after catalyst activation. This insignificant reduction in mechanical properties may have been caused by slight depolymerization of PPC due to the heat generated by the UV source during exposure. The yield strength of the UV-activated sacrificial fibers is greater than typical normal stresses experienced during automated weaving (23 MPa).[40] The UV-activated fibers do not break when bent repeatedly around tight radii of curvature (< 5 mm), which is also a good indicator of their survival during stitching into the reinforcement fabric[41] for obtaining vascular composites with complex networks.

[insert Figure 5]

Effect of V_f on Straight Channel Formation

We use through thickness curing in composites containing a single sacrificial fiber as a model system for evaluating vascularization success experimentally and numerically. The measured T_front and t_cure of frontal-cured vascular composites with varying a single straight channel along the midplane are summarized in Figure 6 and Table 3. The highest V_f achieved experimentally is ca. 60 %, which approaches the theoretical maximum packing for the CF reinforcement used in this study (63 vol. %).[42,43] The average T_{front} (measured at T2) decreases from 194 °C to 136 °C with an increase in V_{f} from 30 % to 60 %. A similar trend for predicted T_{front} is captured by the thermo-chemical model (Figure 6a). Simulation results are also in close agreement with the experimentally measured increase in t_{cure} from 31.2 s to 38.3 s with increasing V_{f} (Figure 6b). According to our homogenized thermo-chemical model, heat diffusion in the laminate is dependent on the thermal conductivity of the CF reinforcement in the transverse direction. Experimentally measured transverse thermal conductivity for laminates with comparable reinforcement (Brochier T300 2 × 2 twill weave CF fabric) showed low thermal conductivity values and small changes with V_{f} in the range of 30 % to 60 %,[37] which is consistent with our model calculations.[37] Therefore, we predict that the small transverse thermal conductivity results in a small heat diffusion term that minimally changes with increasing V_{f} and has little impact on the through-thickness front propagation, resulting in nearly constant composite cure times.

[insert Figure 6]

Table 3. Summary of front characteristics and channel fidelity in frontal-cured composites with straight channels[a].

			T_{front} (°C)[b]					
n	*P* (kPa)	V_{f} (%)	T1	T2	T3	t_{cure} (s)	*C*	*AR*
10	200	30 ± 1.5	169 ± 3.8	194 ± 4.2	176 ± 9.7	31.2 ± 3.7	0.93 ± 0.01	1.12 ± 0.08
14	340	42 ± 1.2	157 ± 20	175 ± 10	163 ± 11	30.4 ± 2.6	0.91 ± 0.02	1.27 ± 0.10
16	480	49 ± 0.7	143 ± 7.3	150 ± 5.0	150 ± 2.4	31.9 ± 2.1	0.91 ± 0.01	1.24 ± 0.01
20	680	60 ± 1.1	126 ± 2.7	136 ± 7.5	137 ± 0.7	38.3 ± 0.6	0.80 ± 0.04	1.89 ± 0.16

[a] The sacrificial fibers used in composite experiments measure $C = 0.93 \pm 0.01$ and $AR = 1.02 \pm 0.02$.

[b] Data for all three thermocouple locations in Figure 2.

Complete depolymerization of embedded sacrificial fibers is achieved in all panels with V_f ranging from 30 % to 60 %. Successful vascularization is partly attributed to the T_{front} values that exceed the T_d of the sacrificial fiber (90 – 100 °C) in all specimens (Figure 6a) due to the additional energy input to the laminate by the underlying surface heater. As shown in Figure 4, the heater also acts as a heated boundary and keeps the composite above 90 °C for 8 – 20 mins and above 60 °C for 42 – 55 mins to enable the continued depolymerization of the embedded sacrificial fiber.

Our thermo-chemical model predicts that the slow cool down in the cured composite after frontal curing is crucial for ensuring successful vascularization, especially for specimens with higher V_f. As shown in Figure 7b-c, the depolymerization profile of the embedded sacrificial fiber closely follows the polymerization profile of the resin matrix for a composite with $V_f = 30$ %. At 30.6 s after the heater is powered on, the polymerization front cures the composite matrix surrounding the sacrificial fiber ($\beta \sim 0$). A short time later at 32.2 s, the sacrificial fiber rapidly depolymerizes to $\beta \sim 0.60$. By the time the heater is powered off at 35 s, the fiber is almost fully depolymerized ($\beta \sim 1$). As indicated in Figure 7c, the sacrificial fiber eventually achieves full depolymerization while the surrounding matrix achieves a maximum degree of cure of ca. 0.90 (maximum value achieved for DCPD resin system[28,44]). The model also predicts that the sacrificial template depolymerizes at a slower rate as the V_f increases (Figure 7d). For example, the sacrificial fibers in $V_f = 40$ % and 50 % simulations only achieve $\beta = 0.18$ and $\beta = 0.01$, respectively, after 35 s from the start of the simulation. The contribution from the cool down stage becomes more critical at higher V_f to achieve full depolymerization of the sacrificial fiber and thus clear channels. For example, the sacrificial fiber in the $V_f = 60$ % simulation is predicted to achieve $\beta \sim 0.95$ at 1,000 s after the start of the simulation or 16 min after the composite t_{cure}. This continued depolymerization post-curing could potentially facilitate the vascularization of higher sacrificial fiber loadings (i.e, denser vascular networks) and more complex network geometries.

[insert Figure 7]

We also evaluate the fidelity (*C* and *AR*) of the resulting microchannels through image analysis. Optical micrographs of channel cross-sections from all single channel composites are shown in Figure 8 and the measured *C* and *AR* values are summarized in Table 3. Optical micrographs of specimens with V_f = 30 % (Figure 8a), V_f = 40 % (Figure 8b), and V_f = 50 % (Figure 8c) panels reveal that the resulting channels are less circular (*AR* = 1.12, *AR* = 1.27, and *AR* = 1.24, respectively) than the sacrificial fiber template (*AR* = 1.02). A decrease in *C* from 0.93 to 0.91 is observed when V_f is increased from 30 % to 50 %. These minor channel deformations are comparable to the prior reports on the bulk-cure manufacturing of vascularized multifunctional composites.[45] Panels with V_f = 60 % (Figure 8d) have the most significant channel deformation, with *C* = 0.80 and *AR* = 1.89. Comparable channel deformation was observed in bulk-cured vascularized composites with high-V_f and attributed to the high compaction pressures applied on layup surfaces (*P* = 640 – 700 kPa).[46,47] In our V_f = 60 % experiments, the sacrificial fiber is similarly embedded in a laminate that is under a relatively high compaction pressure (*P* = 680 kPa) and additionally experiences a rapid temperature evolution. Therefore, we hypothesize that the sacrificial fiber (T_g ~ 35 °C)[24] deformed during front initiation (ca. 75 °C) and subsequent curing (maximum average ca. 133 °C) under compaction pressure.

[insert Figure 8]

Remarkably, all vascular composites are cured within 38 s with 7 kJ energy input (200 W over 35 s to power the surface heater). In comparison, bulk curing vascular composites with the same dimensions in an oven consumes 10^5 kJ energy over several hrs.[24] Through-thickness curing of larger-scale components will require scaling up the heater dimensions to initiate polymerization in the laminate. However, the heater only needs to be powered for several seconds compared to bulk curing in an oven for several hours. Tandem VaSC and frontal curing thereby offers several orders of magnitude fabrication time and energy savings compared to lengthy, multi-stage, conventional oven-cure manufacturing.

Serpentine Vascular Network for Self-Healing

We extend the VaSC and frontal curing strategy to demonstrate the fabrication of a serpentine vascular composite with potential for self-healing of both surface and internal damage. Similar to the coating system reported by Gergely et al.,[16] our specimen is prepared by layering a partially cured DCPD gel on a CF/DCPD laminate with an embedded undulating vascular network that connects the two layers.

Following through-thickness curing, a rigid pDCPD coating layer (ca. 1 mm thick) is formed on the surface of the CF/pDCPD composite layer (ca. 4 mm, V_f ~ 50 %) and the embedded 2D sacrificial fiber is fully depolymerized (Figure 9a). The resulting channel is visualized by injecting an ethanol solution with Nile Red dye into the 2D channel (Figure 9b). The thermocouple data measured at the composite-coating interface indicates that the composite surface achieves a hotter T_{front} (ca. 170 °C) compared to a 1D vascular panel with no coating (ca. 150 °C, Table 3), suggesting that the partially cured DCPD gel also underwent frontal curing. We also hypothesize that the DCPD gel bonded well to the CF/DCPD laminate during the curing process because optical micrographs of the panel cross-section do not show an observable demarcation between the coating and composite layers. We attribute the successful vascularization of the undulating sacrificial fiber to the additional energy input by the surface heater as well as the exothermic polymerization of the gel layer.

[insert Figure 9]

The composite in Figure 9 is the first demonstration of frontal curing of a composite with coating and the first demonstration of frontal curing and VaSC of a fiber-reinforced composite with a complex vascular structure. This one-step processing eliminates potentially complex and expensive multistep processing to adhere functional coatings onto substrates.[48]

Conclusions

A synchronous vascularization and frontal curing strategy was used to rapidly manufacture CF/pDCPD composites with straight and serpentine channels. Use of through-thickness curing enabled the concurrent exothermic polymerization of the composite matrix and depolymerization of the embedded sacrificial fiber with 7 kJ of energy input over 35 s, offering several orders of magnitude fabrication time and energy savings compared to bulk curing vascular components.

We first examined a range of CF volume fractions to explore the window for successful vascularization of straight 1D fibers. Complete channel clearance was achieved for panels with V_f from 30 % up to 60 %. Computational modeling shows the importance of the cool down stage for the continued depolymerization of the embedded sacrificial fiber, especially at higher volume fractions. Channel cross-sectional geometries were comparable to the initial sacrificial fiber template for composites with V_f from 30 % to 50 %.

Next, we demonstrated the frontal curing of a composite system with a serpentine channel network and surface coating with potential for self-healing functionality. The thermo-chemical model utilized in the single straight channel study can be modified to guide more complex vascular network designs and explore new architectures to optimize transport of healing fluid in response to given damage mode.

Declaration of conflicting interests

The author(s) declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

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