

Experimental Details

Materials: Fugitive wax ink was made from mixtures of mineral oil (Fisher Scientific), microcrystalline wax (Strahl & Pitsch Inc.) and stearic acid (Sigma-Aldrich) in either a 43:57:5 or a 43:57:10 w/w/w ratio. Epoxy was composed of EPON 828:Epikure 3274 (Miller-Stephenson) combined in a 5:2 w/w ratio. Poly(diallyldimethyl ammonium chloride) and halloysite nanoclay were received from Aldrich. Z-6040 glycidoxysilane was received from Dow Corning.

Scaffold preparation: Fugitive scaffolds were assembled by the direct-write process as detailed by Therriault et al.¹ Ink loaded into pressurized syringes was pattern-deposited onto substrates using a robotic positioning platform (Aerotech) building a planar line pattern, then building a second layer above that and repeating to yield a three-dimensional scaffold. Multilayers were assembled onto scaffolds by alternating immersion in aqueous solutions/dispersions of 10^{-2} M PDADMAC and 1 mg/mL halloysite with three intermediate Milli-Q pure rinse baths in a Stratosequence6 (Nanostrata, Inc.) dipper. Halloysite dispersions were pH adjusted to 8.5 or higher to insure negative particle surface charge and ultrasonicated for 5 minutes prior to deposition.

Epoxy sample preparation: Scaffolds were immersed in a 0.5 v/v% aqueous solution of Z-6040 at pH 4.5 for 15 minutes to promote adhesion to epoxy precursors, then infiltrated with mixed epoxy pre-polymer and allowed to solidify overnight at room temperature, followed by a 3-day cure at 30° C. Finished polymer parts were heated above the wax melting temperature in order to wick out scaffold materials, followed by room temperature immersion in petroleum ether to remove any hydrocarbon residue. MicroCT samples were imaged after curing with no modification. Samples examined by SEM were fractured to obtain axial cross-sections then sputter-coated with gold-palladium to enhance imaging quality. Samples measured by FDIC were cut to reveal radial cross-sections with an Isomet 1000 saw (Buehler), then surface polished using a Buehler Ecomet 3 in several stages down to 4000 grit to obtain a flat surface and coated with ~300 nm diameter silica particles containing the fluorescent dye rhodamine B to generate a correlation pattern.

Characterization: Light-scattering measurements of halloysite dispersions $< 0.1 \text{ g L}^{-1}$ were carried out using a NICOMP 380 ZLS particle sizer (Particle Sizing Systems). SEM images and EDS spectra were obtained with a Philips XL30 ESEM-FEG with EDAX attachment. MicroCT was performed using an Xradia MicroXCT-200.

FDIC: Samples were imaged using a Leica DM-R fluorescence microscope with a 10x objective lens and 1280 x 1024 pixel resolution Qimaging Retiga 1300 digital camera. Image resolution was determined to be 534 nm per pixel. Correlations were performed with custom DIC code where a course-fine search is used to obtain an initial guess for a Newton-Raphson scheme.² Subset sizes were 16.5 by 16.5 μm and correlations were performed every 5.3 μm . Samples were imaged, then loaded in uniaxial tension using a load frame (Ernest F. Fullam, Inc.) and imaged a second time under load. Applied load was measured using a 445 N capacity load cell (Entran) and loading rate was kept constant at 1 $\mu\text{m/s}$. After unloading, samples were allowed to relax for 30 minutes between measurements.

¹ D. Therriault, S.R. White and J.A. Lewis, Nat. Mater., 2003, 2, 265.

² H.A. Bruck, S.R. McNeill, M.A. Sutton and W.H. Peters, Exp. Mech., 1989, 29, 261.

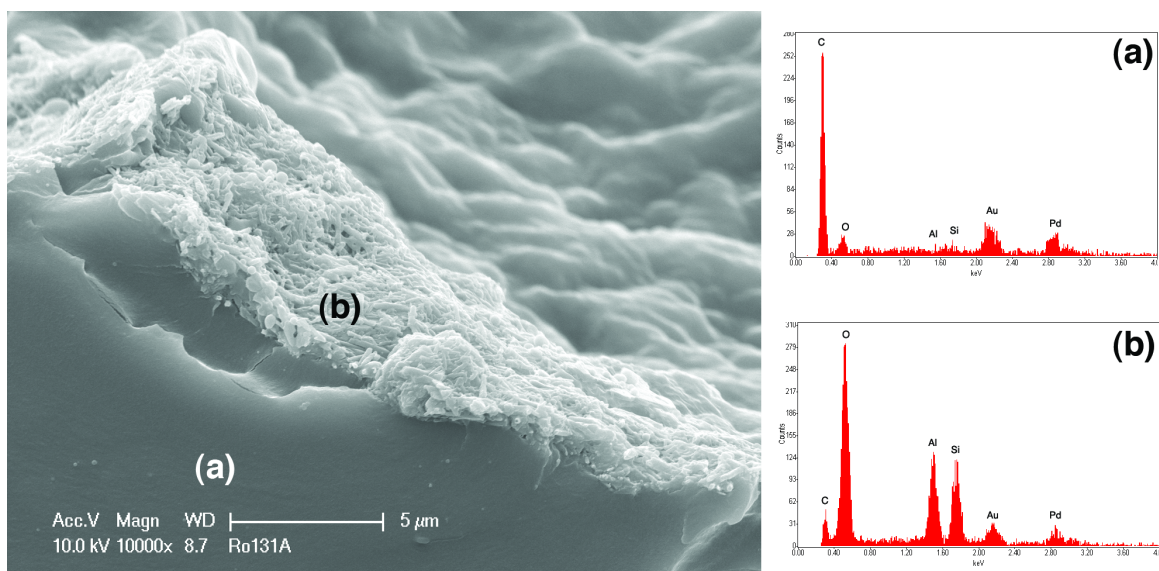


Fig. S1 SEM image of microvascular channel edge with deposited PDADMAC/halloysite multilayer. EDAX spectra of (a) the epoxy surface and the (b) multilayer show the presence of silicon and aluminium in the multilayer, but not in the epoxy.

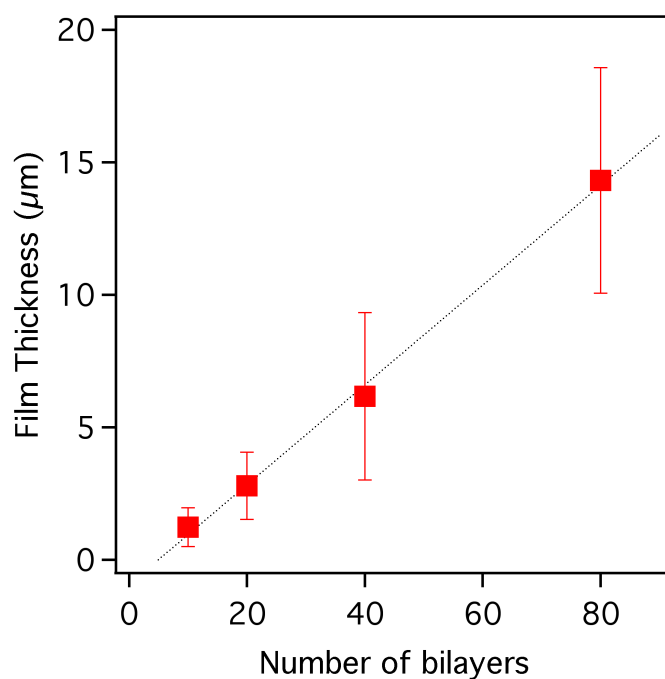


Fig. S2 Graph of number of deposited PDADMAC/halloysite multilayers vs. multilayer thickness as measured by SEM. Error bars show one standard deviation from the mean. A linear fit to the data yields a value of 188 ± 7 nm per bilayer with a chi-square value of 0.229.

S-Movie1 Rotating MicroCT reconstruction of a section of microvascular network within an epoxy matrix containing a deposited (PDADMAC/halloysite)₈₀ multilayer. Increasing brightness indicates increasing X-ray contrast.

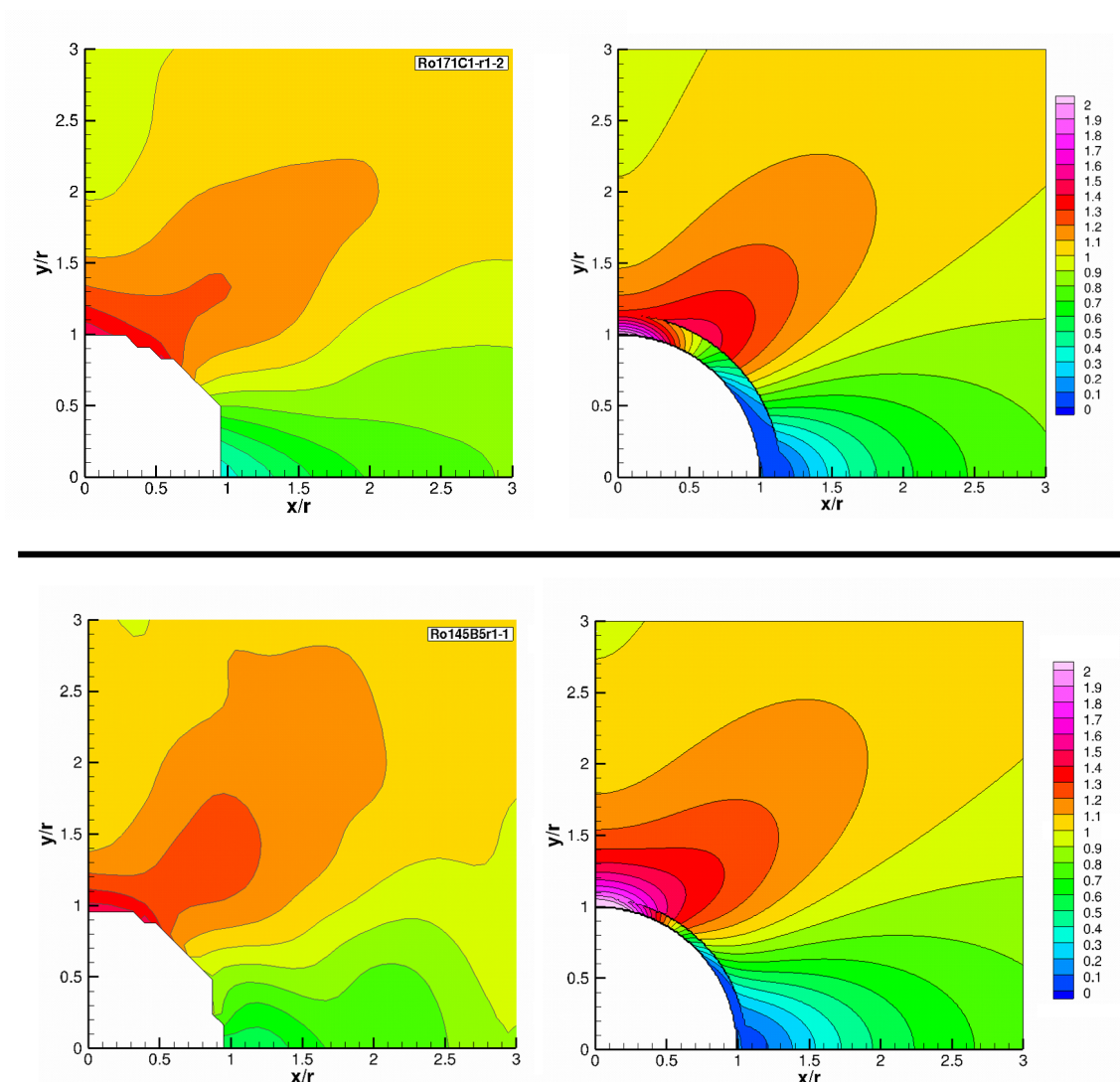


Fig. S3 FDIC measurements (left side) and analytical solutions (right side) of strain fields for channels with 80-bilayer (top) and 40-bilayer (bottom) deposited (PDADMAC/halloysite) films. The film thicknesses used as input for the analytical solutions was taken from SEM measurements, and the modulus used to match FDIC was roughly estimated by direct visual comparison. Note that the analytical solutions show a distinct ring region attributed to the reinforcing film, but this was not visible in the experimental data, perhaps due to the resolution of the technique. Note: $r = 100 \mu\text{m}$.