

Supplementary Information

Fiber with butterfly wings: creating colored carbon fibers with increased strength, adhesion, and reversible malleability

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1.1. Materials

Carbon fiber samples were supplied by Carbon Nexus at Deakin University, Australia. All chemicals, reagents and solvents were purchased from Sigma-Aldrich Chemical Company and used as received.

1.2. Functionalization of carbon fibers

A 12k tow of pristine, unsized carbon fiber (Carbon Nexus) was submerged in an electrochemical cell as the working electrode, along with a platinum mesh counter electrode and a Ag/AgCl reference electrode. The carbon fiber tow was affixed with copper tape to improve contact with the electrode clips. The solution consisted of 4-nitrobenzenediazonium tetrafluoroborate salt (0.0237 g, 2 mM) and acrylic acid monomer (3.43 mL, 1 M) in 0.01 M H₂SO₄ (aq). Cyclic voltammetry was applied to the system, sweeping from -1 V to +1 V at a rate of 0.01 V s⁻¹ for 10 sweeps. The fiber tow was then removed and thoroughly washed with dichloromethane, chloroform, ethanol and acetone (200 mL each), before allowing to dry in air. The fibers appear blue under white light and exhibit stiffness, maintaining the shape they were manipulated into while wet.

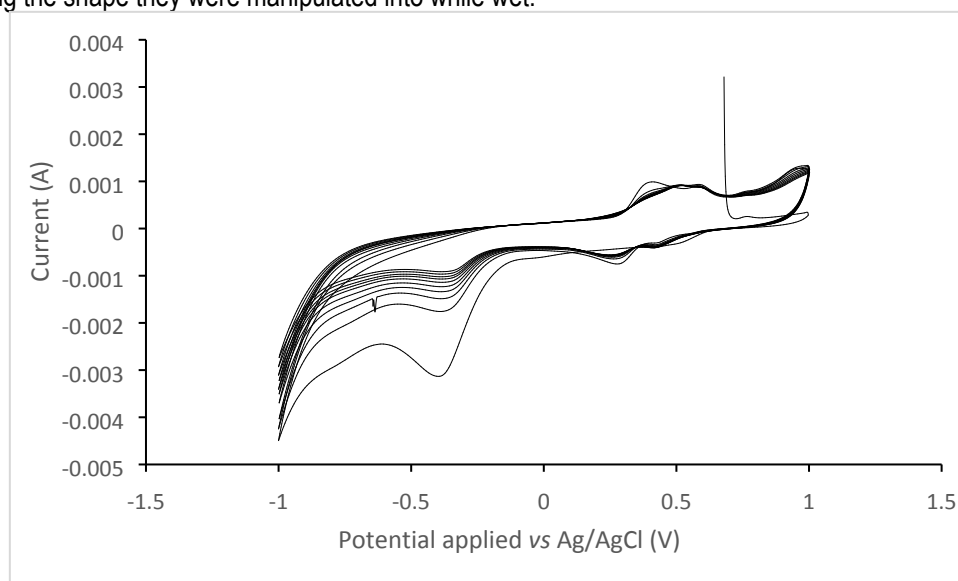


Figure S1. Typical CV of the SEEP process on carbon fibers.

1.2.1 Initiating color change in treated fibers

A treated carbon fiber tow was subjected to low volumes (0.5-1.0 mL) of volatile solvent (acetone). This caused the blue color to disappear, and then, as the solvent evaporated, the color of the fibers reappears and cascades through the visible light spectrum (red, orange, yellow/green, blue). With the complete evaporation of solvent, the fibers retain the initial blue color.

1.2.2 Molding and remolding

A treated carbon fiber tow maybe cast into a desired geometric shape (rod, circle, spiral, etc.) by softening in acetone, holding the fiber in the desired shape and allowing it to dry through evaporation. This drying may be accelerated through heating with no detriment to the fibers.

1.3 Evaluation of interfacial shear strength

Samples were tested on a Favimat + Robot 2 single fiber tester (Textechno H. Stein) which automatically records linear density and force extension data for individual fibers loaded into a magazine (25 samples) with a pretension weight of (~100-150 mg) attached to the bottom of each carbon fiber. Linear density was recorded using a gauge length of 25 mm, a minimum of 75 single filaments were used to determine tensile strength and Young's modulus of control and treated samples. These values are reported in units of GPa. Tensile load-extension curves were collected at 1 mm min⁻¹ using a gauge length of 25 mm. Load data was normalized by dividing by the linear density to give specific stress strain curves from which tensile strength (ultimate specific stress or tenacity) and specific modulus could be determined. The mean values of tenacity and modulus were determined and since the statistical distribution of carbon fiber strengths is usually described by a weakest link model, the strengths were also analyzed by the two-parameter Weibull probability (*P*) equation:

$$P = 1 - \exp \left[- \left(\frac{\sigma}{\sigma_0} \right)^m \right] \quad (1)$$

where P is the cumulative probability of failure of a carbon fiber at applied tensile strength σ , m is the Weibull modulus or shape parameter of the carbon fiber and σ_0 is the Weibull scale parameter or characteristic stress. P is determined for each point using the median rank method:

$$P = \frac{i - 0.3}{n + 0.4} \quad (2)$$

where n = no. of sample points and i is the rank. Rearrangement of the probability expression to a straight line form allows m and σ_0 to be obtained by linear regression.

1.4. Statistical analysis

A two-sample t-test, assuming equal variance, was used to test whether data was significantly different or not; a P-value less than 0.05 was considered statistically significant.

1.5. Single filament fragmentation sample preparation and analysis

Five individual fibers were prepared (for each different sample) by placing the fiber along the center of a dog-bone shaped mold, and adding 350 mg pretension weight to both ends of the fiber which were allowed to hang either side of the mold. This ensured the fiber would remain straight and centralized within the composite. Epoxy resin RIM935 was prepared along with hardener RIM937 (in a 10:4 w/w ratio as recommended by manufacturer), by stirring together at room temperature for 30 minutes to ensure even distribution, followed by storage under vacuum for 15 minutes to remove large bubbles from the solution. The resin mixture was then poured into the molds to ensure complete immersion of the fiber, and cured at room temperature for two days, followed by post-curing at 100°C for 12 hours. The samples were finally ground and polished to yield the final test coupon with the dimensions 25 mm × 5 mm × 1.5 mm. The samples were extended to failure to ensure maximum fragmentation within the sample, using a tensile tester (Instron 5967, Instron Pty Ltd, USA) fitted with a 30 kN load cell. Each fragmentation test was monitored in real time using a digital microscope/camera (AD-4113ZT Dino-Lite, AnMo Electronics Co. Taiwan), and the fragments measured using a calibrated optical microscope (Olympus BX51M (Japan) equipped with Olympus DP70, images were processed using Olympus Stream image software). These data, along with values collected from Weibull analysis (experimental section 2.4) were then processed according to the Kelly-Tyson model, where l is the average fragment length, and l_c is the critical length.

$$l_c = \frac{4}{3} l \quad (3)$$

Using the Weibull modulus m and the characteristic strength σ_0 at gauge length L_0 , the characteristic strength at critical length $\sigma_f(l_c)$ can be calculated.

$$\sigma_f(l_c) = \sigma_0(L_0) \left(\frac{L_0}{l_c} \right)^{\frac{1}{m}} \quad (4)$$

Finally, using the average fiber diameter d (determined to be 7 μm), the apparent interfacial shear strength τ can be calculated using the following equation:

$$\tau = \frac{\sigma_f(l_c)d}{2 l_c} \quad (5)$$

2.0 Atomic Force Microscopy

Surface roughness of fibers was determined using contact mode Atomic Force Microscopy (AFM). A Bruker Dimension SPM 3000 atomic force microscope was used with a scan rate of $0.5 \mu\text{m min}^{-1}$. The proportional, integral and derivative control conditions during surface analysis were maintained at 1.62 V, 1.34 V and 0.15 V, respectively. A cantilever with a spring constant of 0.12 N m^{-1} and silicon nitride probe tip was used. Single fibers were extracted from fiber tows and mounted to a glass microscope slide. A scalpel tip was then used on a small section of the fiber to attempt to scrape of any polymer from the surface. Images of the fiber were then taken at 9 different locations across the fiber length at a $3 \times 3 \mu\text{m}$ scale. Images were then imported into NanoScope Analysis 1.4 software and the linear surface roughness tool used to map polymer thickness. The height of the polymeric deposit was determined using the section tool in NanoScope 1.4. The height trace was cut along the longitudinal axis of the fiber to minimize erroneous values due to the innate curvature of the fiber.

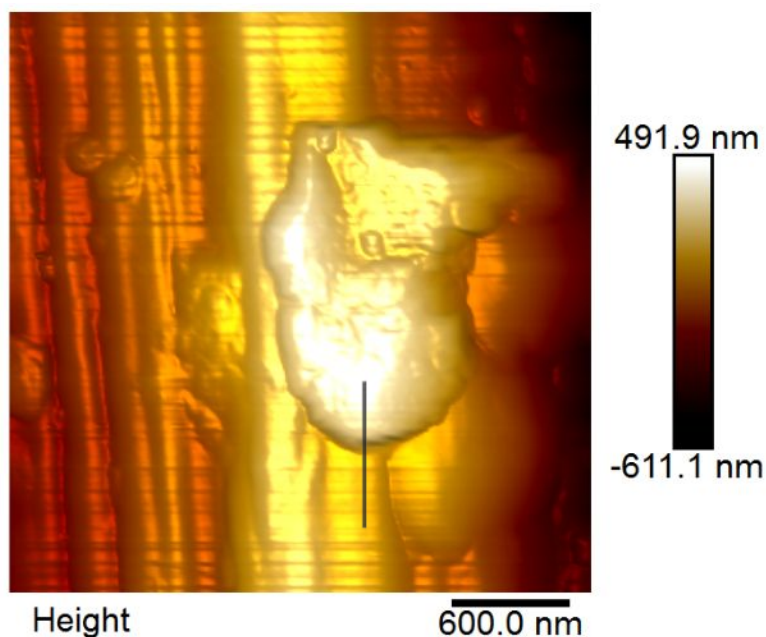


Figure S2. Two dimensional AFM used to get film thickness with section used highlighted.

3.0 Generation of CIE plots and image analysis processes.

Video footage of the color changing fiber was processed using Tracker software (<https://physlets.org/tracker/>). Videos were imported to the software and the location of interest on the fiber surface was analyzed using the 'RGB Region' function, to determine the mean Red, Green and Blue channel values of the selected point. The video was then played and the RGB values for each frame were collected. These RGB values were then exported to Microsoft Excel for further processing. The RGB values from the video analysis were graphed to form an RGB plot (Figure 2), displaying the change in RGB value over time, corresponding to a change in color of the fiber. To generate the CIE plots (Figures 2) the mean RGB values were converted to XY coordinates and plotted on a CIE 1931 2-degree observer chromaticity diagram (www.efg2.com/lab). Images and video were captured using a Nikon D850 camera with a 24-85 mm lens. The colored fiber images (Figure 1) were mildly enhanced using Adobe Photoshop, the original images are found in (ESI Figure S3). The image set was imported into Photoshop, then the following adjustments were made. The shadow, vibrance and saturation were set to 1%, 25% and 5% respectively.

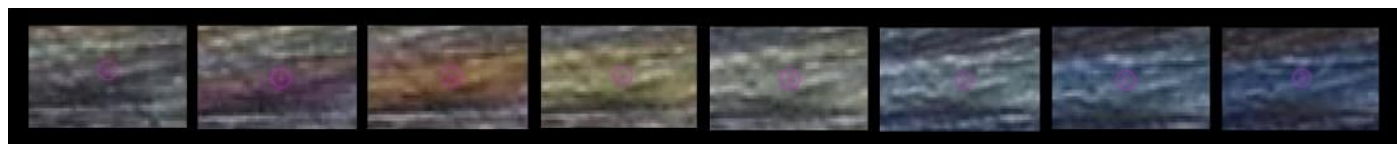


Figure S3. Original image used to track the color change of fibers during solvent evaporation.

4.0 Injection molding

The polymer COC 5013L-10 (Amtrade International Pty Ltd, Adelaide, Australia) was heated in a three stage 25 mm diameter nitrided screw with a length to diameter ratio of 20:1 followed by a two stage parallel nozzle in a Demag Systec 100/420-200°C injection molded (PBE Roboplas Sales & Service Pty Ltd, Sydney, Australia). The hopper block was cooled to 85°C to prevent polymer melting in the hopper during use. The feed portion of the screw was heated to 235°C before increasing the temperature to 245°C during compression and again to 265°C during metering. Finally, in the nozzles two heating zones are set to 265°C dropping to 260°C at

the orifice to reduce drooling between shots, the resulting material maintained a melt temperature between 265°C and 270°C depending on cycle time consistency.



Figure S4. Injection molding conditions used for COC polymer.

The screw was filled at 100 RPM with 5 bar of back pressure with the first 3 mm filled with the remaining material from the melt cushion of the previous shot and the final 8 mm were sucked back to further reduce drool and freezing between shots. The material was injected in 98 mm shots in to the tool cavity which was heated to 125°C using oil heated by a tool temp TT-181 (PBE Roboplas Sales & Service Pty Ltd, Sydney, Australia). The injection was performed in 3 stages, the first 15 mm of the screw was injected with a max pressure and speed of 100 bar and 75 mm s⁻¹ allowing the cold slug at the start of the flow to be seated in a well opposite the sprue. The next 73 mm was injected at 150 mm s⁻¹, filling the part before the pressure is reduced to the holding pressure for the last 10 mm of material at 20 mm s⁻¹ and 51 bar. Once injected, the holding pressure is maintained for a further 15 s, reducing sink marks, improving the polymers adhesion to the fibers and reducing the impact of knit lines. Before the tool opens and the part is ejected, the component was given a further 25 s to cool without injection pressure reducing residual stresses within the part.

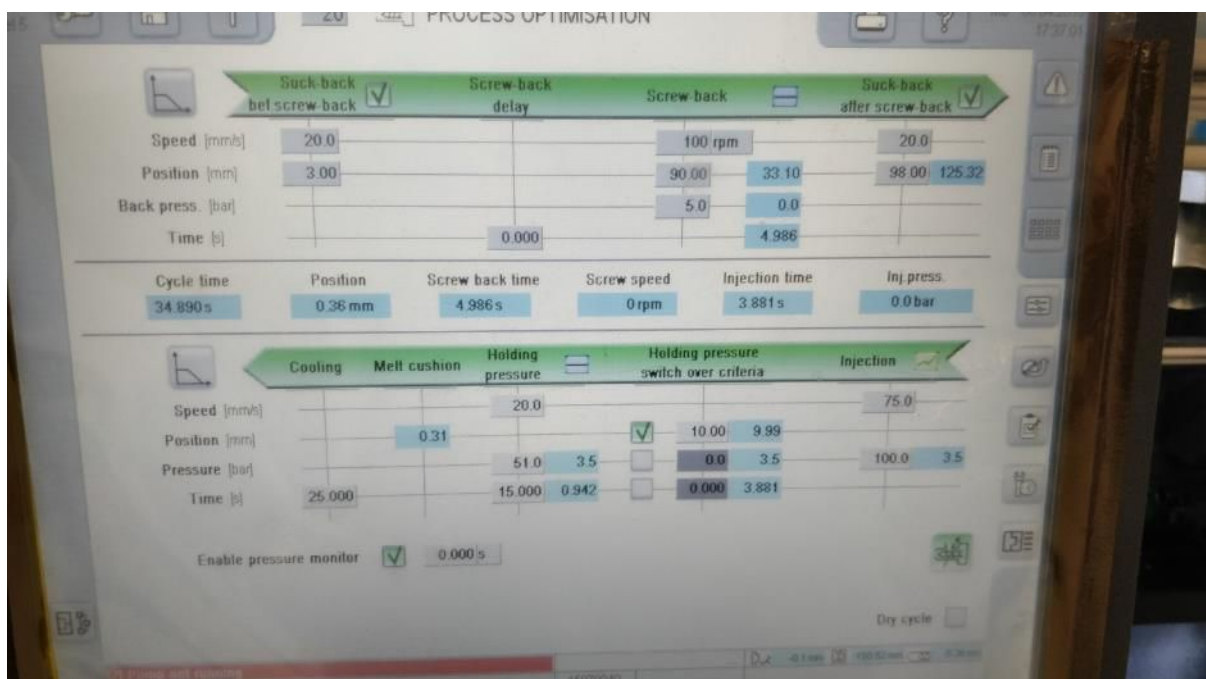


Figure S5. Screw conditions for injection molding.

For sample preparation an about 3 cm long functionalized tow was placed with blue tag in the cavity of the aluminum mold in the injection molder. Then the mold was closed and the injection process, which is explained above, begun. After the process was finished, the injection molder opened and the sample was demolded. Subsequently the sample was placed under a microscope. The used microscope was an Olympus SZ 61 fitted with an Olympus DP 22 camera. It uses visible light and a system of lenses to magnify samples up to 4.5x magnification. Several pictures were taken using the DP software, which comes with the camera, at different magnifications. When taking the pictures indirect sunlight was illuminating the room as well as the standard room lighting. The light source of the microscope was the only direct light source on the sample. The thickness of the sample was 5 mm. The functionalized carbon fiber tow was on the bottom of the sample due to the placement in the mold. Hence, to get the images one had to look through the whole sample to see the tow embedded in the resin. The thickness of the sample is not a disadvantage since the used material (COC) has excellent optical properties and has optimal properties in transmit light in the visible region (wavelength).

5.0 SEM Images of functionalized fibers

Scanning electron microscope images of the treated fibers were taken to see if any evidence of a diffraction grating was observed. Samples were prepared by cutting and then mounting on carbon tape. Microscope is a JEOL JSM-7800F Field Emission SEM. Imaged at 3kV using secondary electron detector, the samples were not required to be gold coated before imaging. This revealed only the typical longitudinal striations which have been observed for bare and unfunctionalized fibers, as reported previously by our group.¹ These images at various magnifications are provided below.

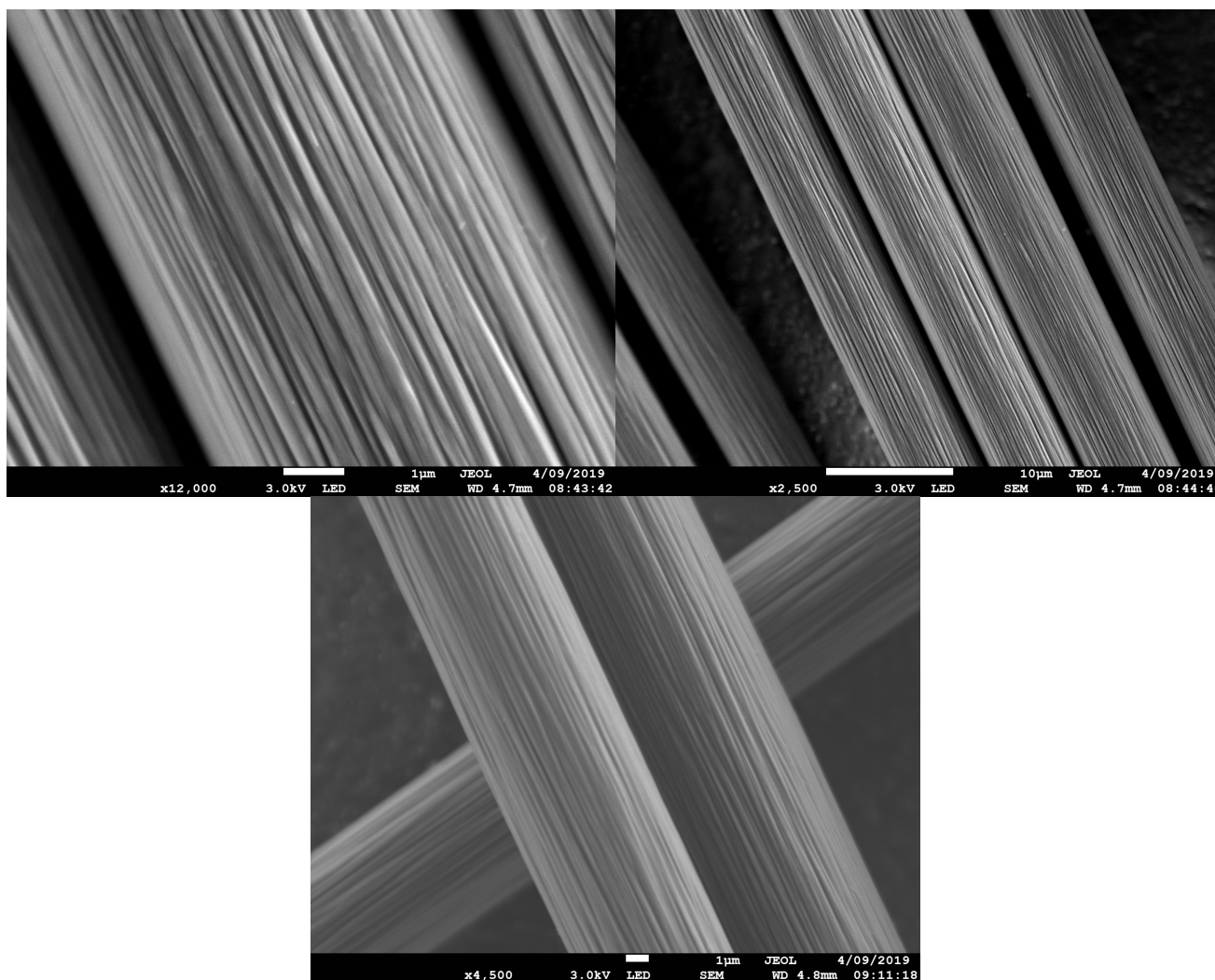


Figure S6. SEM images of the functionalized fiber showing typical striations associated with the wet spinning process for precursor fabrication and no sign of a diffraction grating.

(1) Servinis, L.; Beggs, K. M.; Scheffler, C.; Wölfel, E.; Randall, J. D.; Gengenbach, T. R.; Demir, B.; Walsh, T. R.; Doeven, E. H.; Francis, P. S.; Henderson, L. C. Electrochemical surface modification of carbon fibres by grafting of amine, carboxylic and lipophilic amide groups. *Carbon* **2017**, *118*, 393-403, DOI: <https://doi.org/10.1016/j.carbon.2017.03.064>.