

Supporting Information
for

Carbon fibre surface modification facilitated by silver-catalysed radical decarboxylation

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I. Experimental procedures

General

Starting materials and reagents were purchased from Sigma-Aldrich or Oakwood and were used as supplied. Unless otherwise stated, all reactions were conducted under an atmosphere of nitrogen. Methyl acrylate was dried over MgSO_4 and distilled under reduced pressure.

Analytical methods

Proton (^1H) and carbon (^{13}C) NMR spectra were recorded on a Bruker DRX400 spectrometer operating at 400 MHz for proton and 100 MHz for carbon nuclei

Number-average molecular weight (M_n) and dispersity (M_w/M_n) of polymers were determined using an EcoSEC TOSOH gel permeation chromatography (GPC), calibrated against polystyrene standards. Samples were run using TOSOH alpha 4000 and 2000 columns and the instrument was equipped with both a refractive-index (IR) and ultraviolet (UV) detectors (UV detection, $\lambda = 280$ nm). DMF (with 10 mM LiBr) was used as mobile phase with a flow rate of 1.0 mL/min.

Thermal gravimetric analysis (TGA) was performed on a Mettler-Toledo instrument between 25-600 °C, with a heating rate of 20 °C/min.

X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Scientific Nexsa Surface Analysis System equipped with a hemispherical analyzer. The incident radiation was monochromatic Al $K\alpha$ X-rays (1486.6 eV) at 72 W (6 mA and 12 kV, $400 \times 800 \mu\text{m}^2$ spot). Survey (wide) and high-resolution C 1s (narrow) scans were recorded at analyzer pass energies of 150 and 50 eV and step sizes of 1.0 and 0.1 eV, respectively. The base pressure in the analysis chamber was less than 5.0×10^{-9} mbar. A low-energy dual-beam (ion and electron) flood gun was used to compensate for surface charging. Data processing was carried out using Avantage software, and the energy calibration was referenced to the main line of C 1s at 284.8 eV.

SEM imaging was performed on a Zeiss Supra 55-VP at an electron accelerating voltage (electron high tension) of 5 kV. CF samples were mounted to an aluminium pin stub using double sided carbon tape. Samples were sputter coated with Pt (4 nm) using a Leica EM ACE600 High Vacuum Sputter Coater prior to imaging to enhance the visualization.

Synthesis of PMA-co-PAA

A mixture of 2-cyanobutanyl-2-yl 3,5-dimethyl-1H-pyrazole-1-carbodithioate (175 mg, 0.7 mmol), methyl acrylate (5 mL, 55.2 mmol), acrylic acid (0.95 mL, 13.8 mmol) and anhydrous DMSO (2 mL) was degassed by freeze-pump-thaw method 3 times. To this was added AIBN solution, (0.2 M solution in toluene, 0.70 mL, 0.14 mmol) and the mixture was heated to 70 °C overnight. The resulting mixture was diluted with MeOH (2 mL) and precipitated by addition to an excess of Et_2O . The resulting polymer was further precipitated from DCM/ Et_2O twice.

$M_n = 5234$, $D = 1.60$

Functionalisation of carbon fibre

To a flask containing milled carbon fibre (13.0 g), PMA-co-PAA (3.0 g), sodium persulfate (4.27 g) and AgNO₃ (0.60 g) under a nitrogen atmosphere was added a degassed mixture of water (250 mL) and acetonitrile (250 mL). The resulting mixture was heated to 60 °C and stirred for 16 h. After cooling to room temperature, the fibres was isolated by filtration and washed with acetonitrile (250 mL), tetrahydrofuran (250 mL), water (500 mL) and methanol (250 mL) and dried under vacuum.

Mn	Mw	Mz	Mw/Mn	Mz/Mw
5234	8388	11504	1.603	1.372

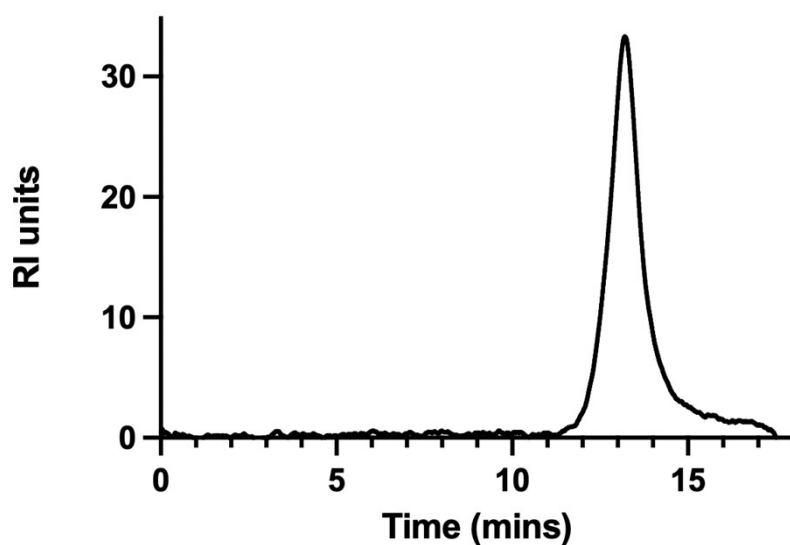


Figure S1 – GPC trace of PMA-co-PAA polymer

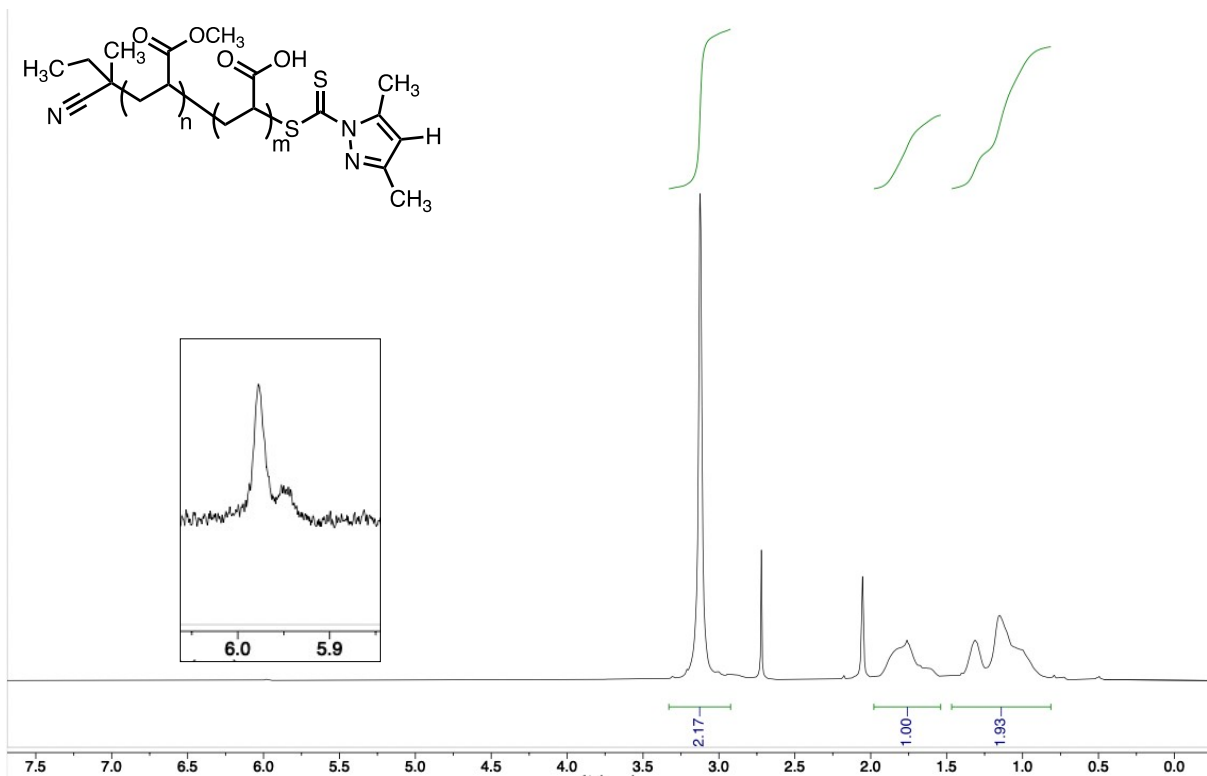


Figure S2 - ¹H NMR of PMA-co-PAA polymer (400 MHz, acetone-*d*₆)

Sample preparation and mechanical testing

Fibre was loaded at 10 wt% in RIM 935/RIMH 936 epoxy resin (100:29 by mass, respectively). The fibre-loaded resin was poured into silicon moulds to form dog-bone specimens for tensile testing (4 mm thick, 45 mm in effective elongation length, 7 mm, and clamping areas of 25 mm by 20 mm in respective length and width) and rectangular specimens for flexural testing (4 mm thick, 12 mm wide, and 35 mm long). A total of six specimens were tested for each variant (control and modified fibre) using an Instron load frame following ASTM D638 (tensile) and ASTM D2344 (flexural). For tensile testing, wedge action tensile grips held the samples for controlled elongation using Bluehill 3 software at a rate of 2 mm/min. Load, displacement, and stress and strain curves were recorded to calculate yield strength (via 0.2% offset rule), ultimate tensile strength, and Young's Modulus (Eq S1). For flexural testing, samples were placed into a 3-point bend fixture with an effective span of 30 mm between the two support pins. A central roller of 10 mm diameter was used to apply a bending force across the flexural specimen at a displacement-controlled rate of 2 mm/min. Applied compressive load and displacement were recorded to calculate flexural strength and modulus (Eq S2).

$$E = \frac{\sigma}{\varepsilon}$$

Equation S1: where σ = stress; ε = strain

$$E_{flex} = \frac{L^3 F}{4wh^3 d}$$

Equation S2: where L = distance between supports; d = deflection due to load; F = applied load