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A novel approach to the functionalization of pristine carbon fibre using an azomethine 1, 3-dipolar cycloaddition approach

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SUPPLEMENTARY MATERIAL

S1- S2- Synthesis experimental of glycine adduct

S3 – Young' Modulus

S4 – SPM 3x3 um images for treatment 1

S5 – SPM 3x3 um images for treatment 2

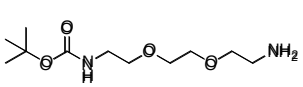
4.8 Synthesis of novel compounds

General chemical experimental

All ^{1}H and ^{13}C Nuclear Magnetic Resonance (NMR) spectra were recorded on a Jeol JNM-EX 270 MHz as indicated. Samples were dissolved in deuterated chloroform ($CDCl_3$) with the residual solvent peak used as an internal reference ($CDCl_3$ – δH 7.26 ppm). Proton spectra are reported as follows: chemical shift δ (ppm), (integral, multiplicity (s = singlet, br s = broad singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, m = multiplet), coupling constant J (Hz), assignment). Purity of the synthesised compounds was determined by ^{1}H NMR.

Chemical experimental

Synthesis of *tert*-butyl [2-[2-(2-aminoethoxy)ethoxyethyl]carbamate (14)



A solution of di-*tert*-butyl dicarbonate (3.0 g, 13.75 mmol) in CH_2Cl_2 (100 mL) was

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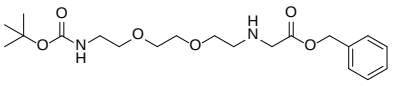
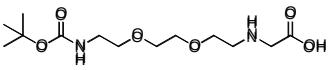
added dropwise over 2 hours to a stirring solution of 2,2-(Ethylenedioxy)bis(ethylamine) (6.021 mL, 41.24 mmol) and CH_2Cl_2 (150 mL) at 0°C for 2 hours. The reaction was then stirred a further 18 hours at room temperature, and the resulting mixture transferred to a separating funnel where it was washed with saturated aqueous NaCl (5 × 50mL). The organic phase was dried over $MgSO_4$, filtered and concentrated *in vacuo* to afford a viscous colourless off-white oil in >95% purity (3.312 g, 97%). ^{1}H NMR (270 MHz, $CDCl_3$): δ = 3.59 (s, 4H, (C*H*$_2$O)$_2$), 3.51 (m, 4H, (C*H*$_2$O)$_2$), 3.29 (q, $^3J_{HH}$ = 5.4, 5.13, 2H, C*H*$_2$NH), 2.85 (t, $^3J_{HH}$ = 5.4, 4.86, 2H, C*H*$_2$NH$_2$), 1.42 (s, 9H, C(C*H*$_3$)$_3$) [1]

Synthesis of 5,8-Dioxa-2,11-diazatridecanoic acid, 1-(1,1-dimethylethyl) 13-(phenylmethyl) ester (15)



To a solution of **14** (2.180g, 8.78 mmol) and anhydrous tertrahydrofuran (15mL), triethyl amine (1.835mL, 13.17 mmol) was added and the mixture allowed to stir and heat to 70°C. Benzyl bromoacetate (2.086mL, 13.17 mmol) was added to the mixture, a reflux condenser attached and the reaction was then stirred for 18 hours. The resulting mixture was then transferred to a separating funnel and diluted with ethylacetate. This was then washed with saturated NaCl solution (5 × 20mL), the organic phase separated and dried ($MgSO_4$). The solvent was then removed *in vacuo*. This was followed by column chromatography using 40% ethyl acetate 60% petroleum spirit solution, and the resulting pale yellow oil was confirmed to be the desired phenylmethyl ester (2.601g, 75%). ^{1}H NMR(270 MHz, $CDCl_3$): δ= 7.32 (m, 5H, Ph), 5.11 (s, 2H, PHC*H*$_2$), 5.04 (br.s. 1H, N*H*), 3.67 (s, 2H, C*H*$_2$O), 3.58 (m, 2H, C*H*$_2$O), 3.49 (m, 2H, C*H*$_2$O), 3.44 (m, 2H, C*H*$_2$O), 3.25 (m, 2H, C*H*$_2$NH), 2.96 (t, 2H, $^3J_{HH}$ = 5.40, C*H*$_2$NH), 1.42 (s, 9H, C(C*H*$_3$)$_3$) [2].

Synthesis of 5, 8-Dioxa-2,11-diazatridecanedioic acid, 1-(1,1-dimethylethyl) ester (16)



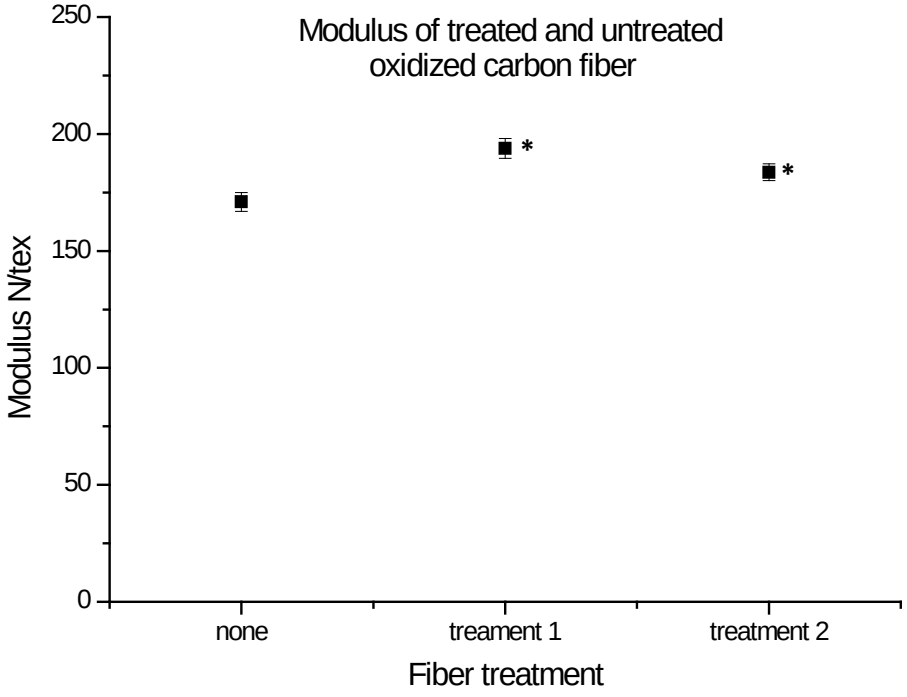
A 150 mL round bottom flask was equipped with a vacuum line and N_2 balloon. The flask was evacuated and charged with nitrogen, followed by addition of palladium on activated carbon (0.43 g. 10% wt/wt). The flask was then refilled with nitrogen and a solution of **15** (4.25 g, 10.73 mmol) in methanol (160mL) was added. A hydrogen balloon was then fitted, followed by evacuation and filling (x 3) to ensure sufficient pressure, the reaction was then stirred for 16 hours at room temperature. The palladium was removed through a celite plug under vacuum filtration and the solvent removed *in vacuo* to afford the pure off-white solid **16** (2.31 g, 70%), confirmed to be the desired acid by ^{1}H NMR (g,mmol,%). ^{1}H NMR(400MHz, DMSO-*d*6): δ= 3.46 (m, 6H, (C*H*$_2$O)$_3$), 3.36 (m, 2H, C*H*$_2$O), 3.05 (m, 2H, C*H*$_2$NH), 2.82 (m, 2H, C*H*$_2$NH), 2.50 (br.s. 1H, N*H*), 1.37 (s, 9H, C(C*H*$_3$)$_3$). ^{13}C NMR(400MHz, DMSO-*d*6): δ= 173.16, 156.19, 78.15, 69.96, 55.86, 53.67, 40.06, 28.78ppm [3].

[1] S. Fixon-Owoo, F. Levasseur, K. Williams, T.N. Sabado, M. Lowe, M. Klose, A. Joffre Mercier, P. Fields, J. Atkinson, Phytochemistry, 63 (2003) 315-334.
[2] K. Kordatos, T. Da Ros, S. Bosi, E. Vázquez, M. Bergamin, C. Cusan, F. Pellarini, V. Tomberli, B. Baiti, D. Pantarotto, V. Georgakilas, G. Spalluto, M. Prato, The Journal of Organic Chemistry, 66 (2001) 4915-4920.

[3] T. Schröder, K. Schmitz, N. Niemeier, T.S. Balaban, H.F. Krug, U. Schepers, S. Bräse, Bioconjugate Chemistry, 18 (2007) 342-354.

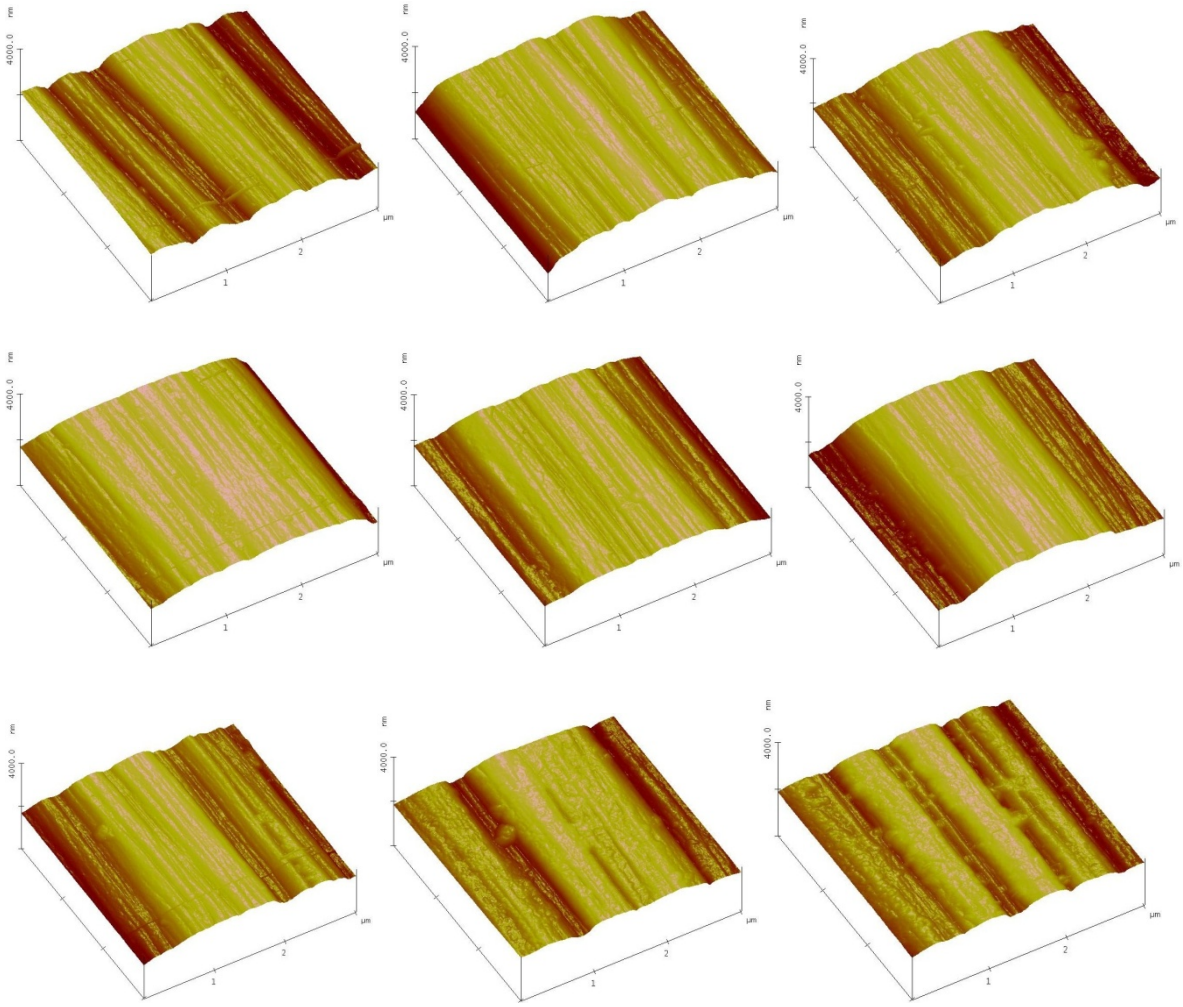
Young's Modulus

The second physical property to be analysed was modulus; the youngs modulus or stiffness of individual carbon fibers can have a large influence over the properties of a final composite, with many of the high grade aerospace composites having the highest modulus carbon fiber to maximise strength. As such, it was considered very important that the treatments employed did not degrade the stiffness properties of the sample. Analysis of the untreated fibers gave an average modulus of 170.96 N/tex, but surprisingly, after treatment 1, the sample modulus showed a statistically significant increase to an average value of 193.87 N/tex. After treatment 2, this value then decreased slightly to 183.66 N/tex which was again, statistically higher than the untreated sample.



Average modulus of treated and untreated carbon fibers (statistically significant figures denoted *)

1,3 – dipolar cycloaddition 3 x 3um images



1,3 – dipolar cycloaddition - deprotected 3 x 3um images