Rapid surface functionalization of carbon fibres using microwave irradiation in an ionic liquid.

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SUPPLEMENTARY INFORMATION

S1 **Fibre Washing Procedure**

S2 **X-ray photoelectron Spectroscopy**

S3 – S5 **IR and Raman Spectra**

S6 **Single fibre analysis**

S7 **Weibull analysis**

S8 – S9 **IFSS analysis**

S9 **PFG-NMR Diffusion**

Fibre Washing Procedure

After reaction the fibres were removed from the microwave reaction vessel and placed on a Buchner Funnel. They were then sequentially washed with 250 mL of each of acetone and deionized water. The fibres were then transferred to a desiccator equipped with high vacuum, and dried at reduced pressure (1-5 mm Hg) and room temperature for 24 hours.

X-ray Photoelectron Spectroscopy

XPS analysis was performed using an AXIS Ultra-DLD spectrometer (Kratos Analytical Inc., Manchester, UK) with a monochromated Al K_α source (hν = 1486.6 eV) at a power of 150 W (15 kV × 10 mA), a hemispherical analyzer operating in the fixed analyzer transmission mode and the standard aperture (analysis area: 0.3 mm × 0.7 mm). The total pressure in the main vacuum chamber during analysis was typically below 10^{-8} mbar.

Bundles of fibres were suspended across a custom-designed frame attached to standard sample bars. This ensured that only the sample to be analysed was exposed to the X-ray beam and that any signal other than that originating from carbon fibres was excluded. Each specimen was analysed at two different locations at a photoelectron emission angle of 0° as measured from the surface normal (corresponding to a take-off angle of 90° as measured from the sample surface). Since the microscopic emission angle is ill-defined for fibres the XPS analysis depth may vary between 0 nm and approx. 10 nm (maximum sampling depth).

Data processing was performed using CasaXPS processing software version 2.3.15 (Casa Software Ltd., Teignmouth, UK). All elements present were identified from survey spectra (acquired at a pass energy of 160 eV). To obtain more detailed information about chemical structure, C 1s, O 1s and N 1s high resolution spectra were recorded at 20 eV pass energy (yielding a typical peak width for polymers of 1.0 eV). If required these data were quantified using a Simplex algorithm in order to calculate optimised curve fits and thus to determine the contributions from specific functional groups.

The atomic concentrations of the detected elements were calculated using integral peak intensities and the sensitivity factors supplied by the manufacturer. Atomic concentrations are given relative to the total concentration of carbon as follows: the concentration of a given element X was divided by the total concentration of carbon and is presented here as the atom number ratio (or atomic ratio) X/C. This value is more robust than concentrations when comparing different samples. Binding energies were referenced to the aliphatic hydrocarbon peak at 285.0 eV. The accuracy associated with quantitative XPS is ca. 10% - 15%.

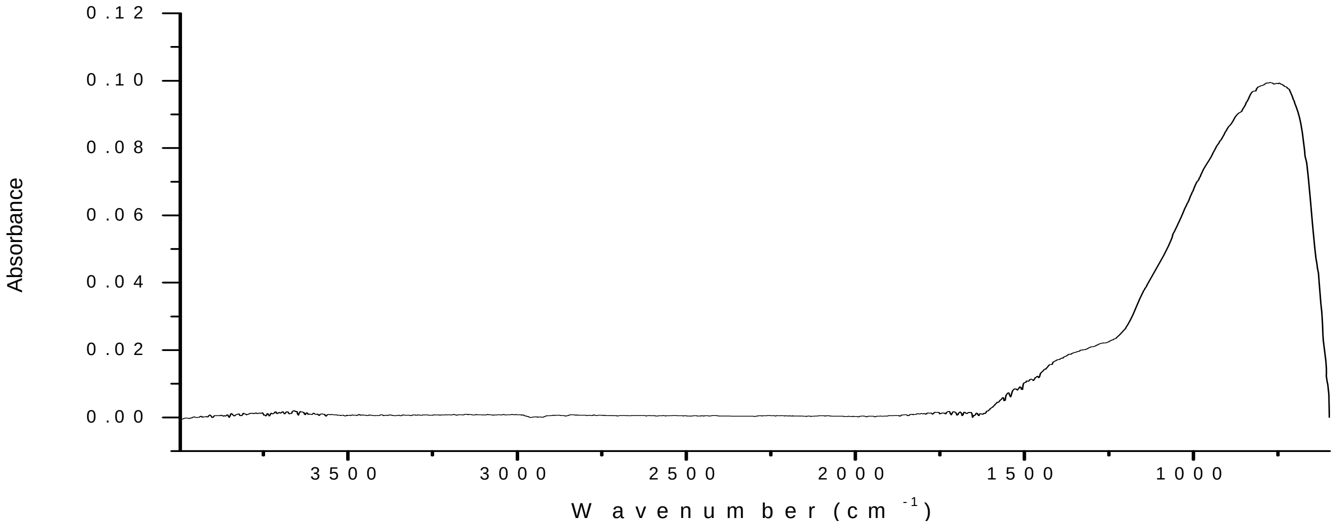
Precision (i.e. reproducibility) depends on the signal/noise ratio but is usually much better than 5%. The latter is relevant when comparing similar samples.

IR and Raman Spectroscopy

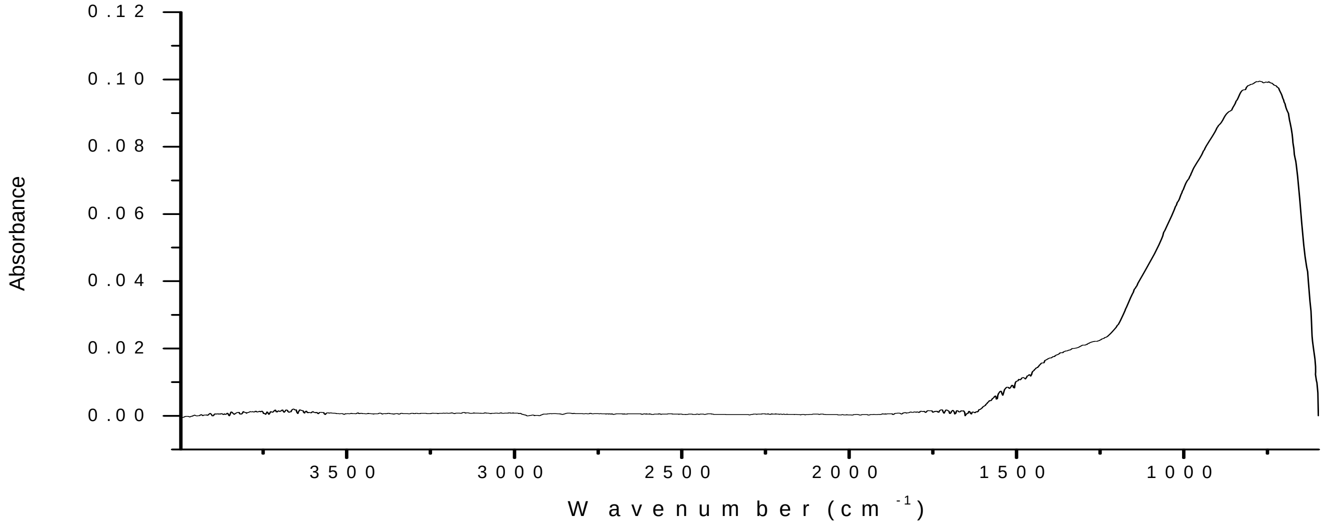
Infrared spectra were obtained on a Bruker Lumos, using ATR mode with a germanium crystal. For each sample 64 scans at 4 cm^{-1} resolution were acquired in absorbance mode. Raman spectra were recorded on a Renishaw InVia, using 514 nm excitation, 50 % laser (25mW) and a 10 second exposure time using 50 x objective.

IR Spectra

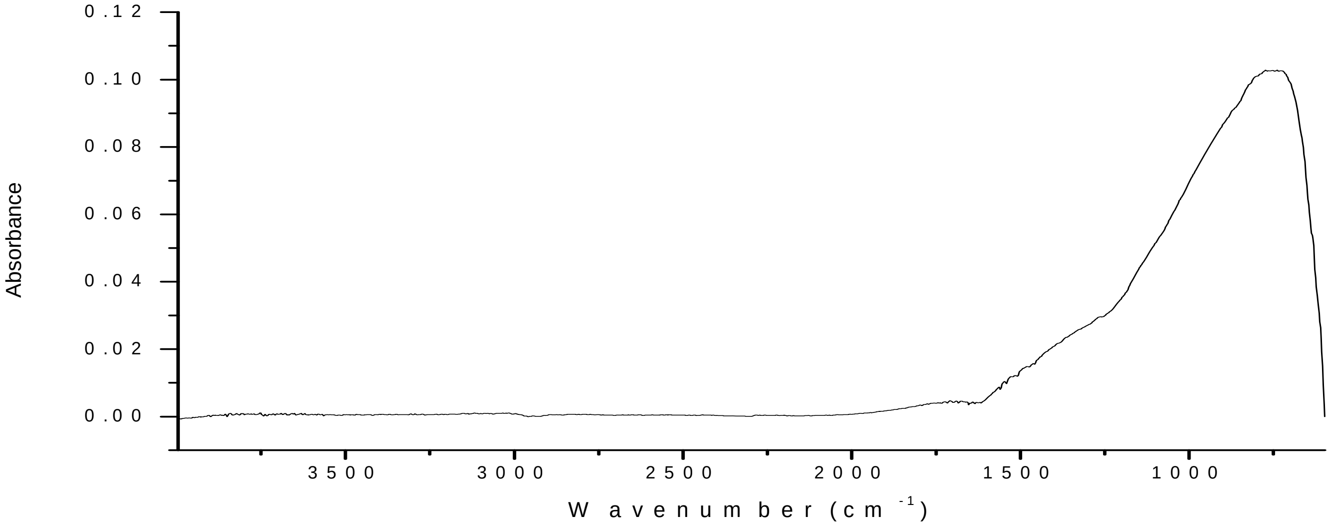
Control



EmimTFSI

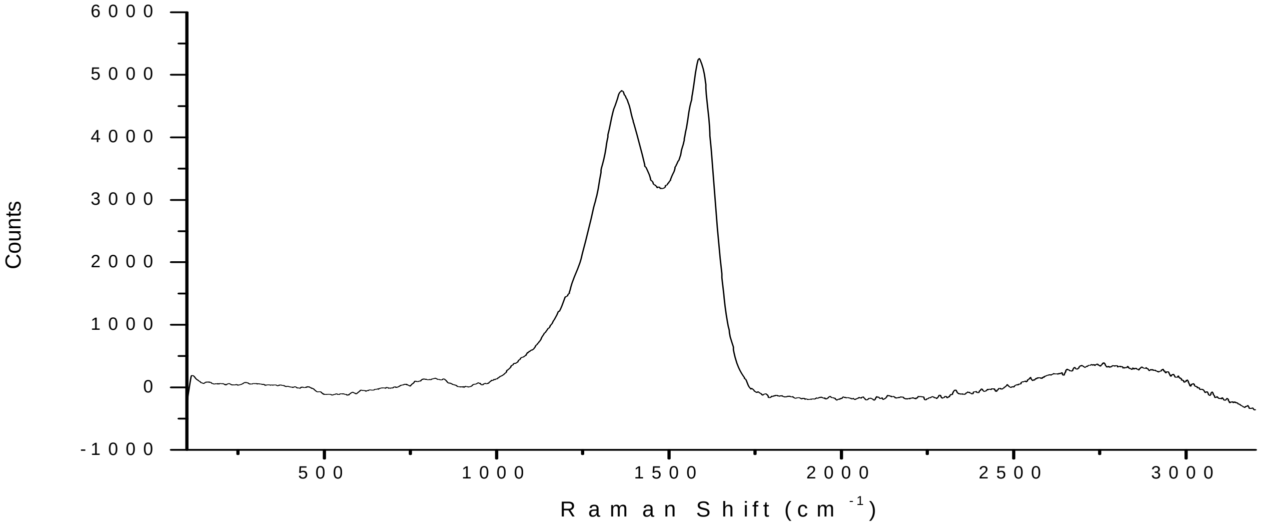


1,2-DCB



Raman Spectra

Control



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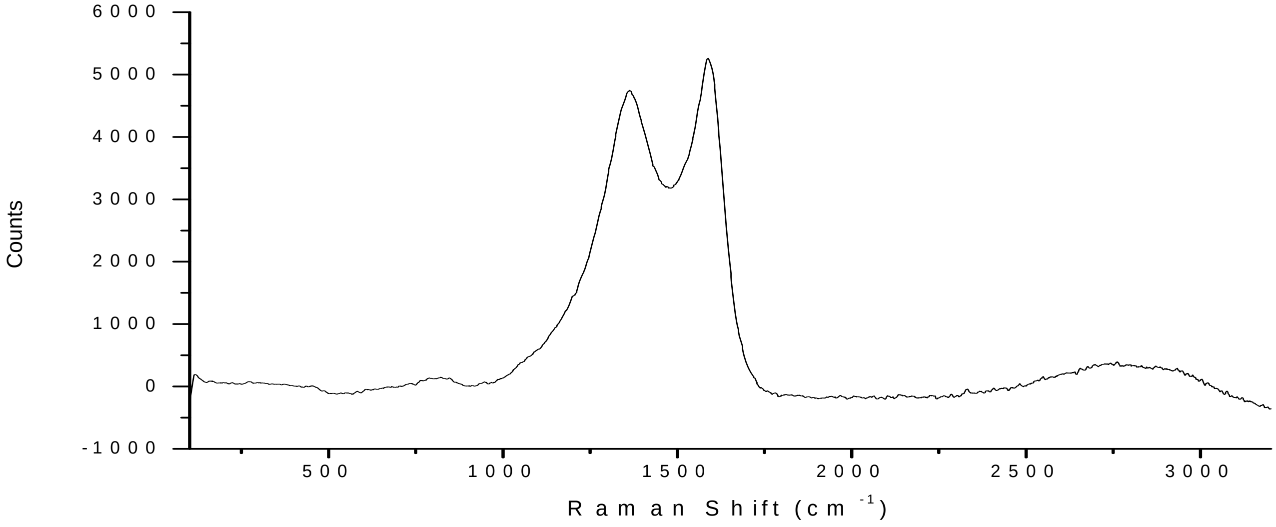
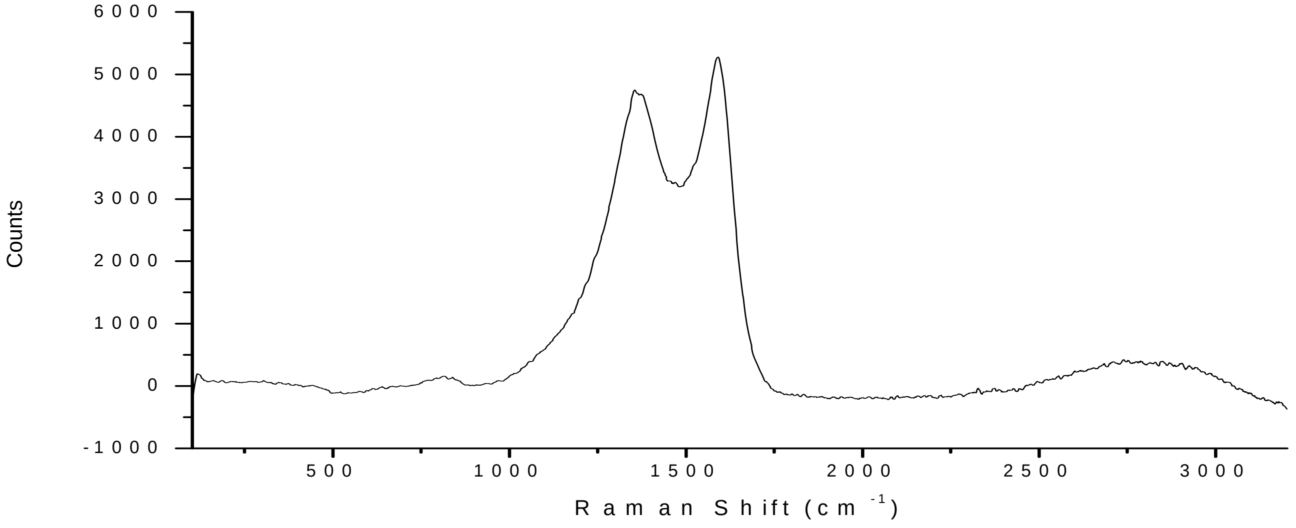
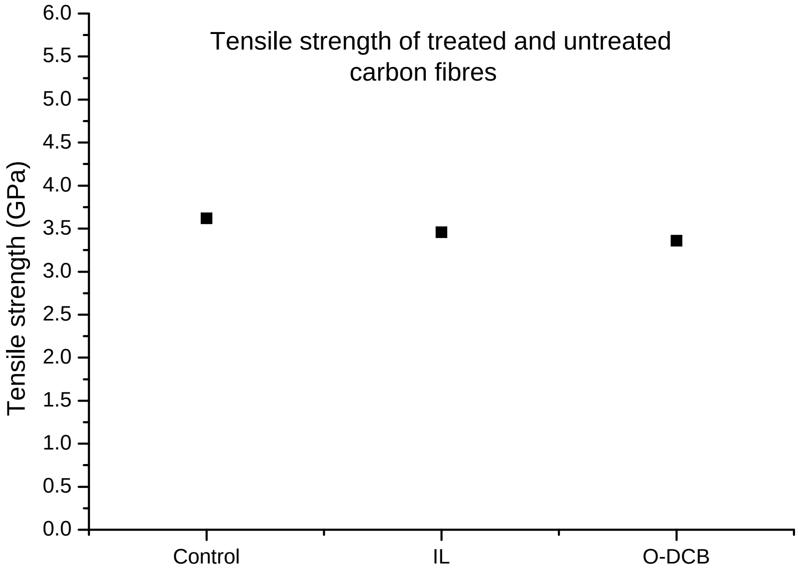


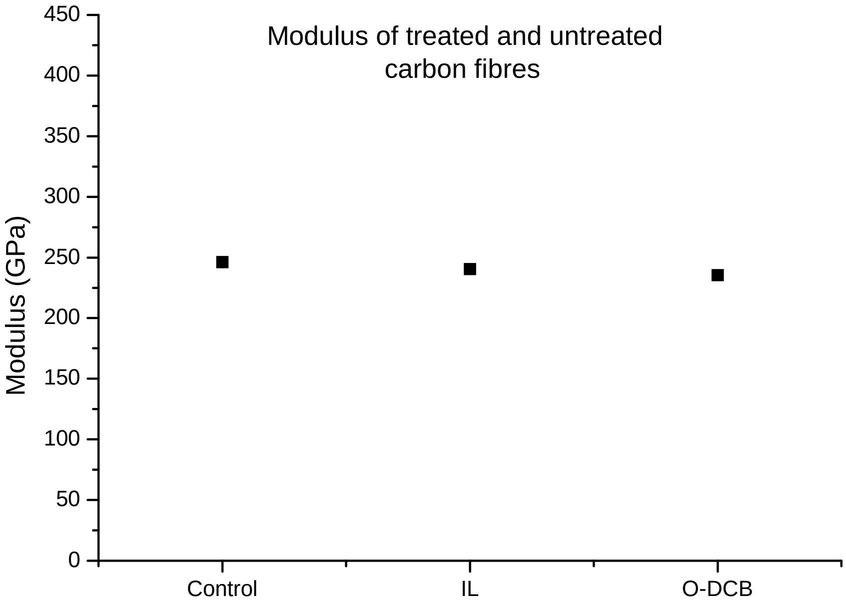
1,2-DCB



Single fibre analysis

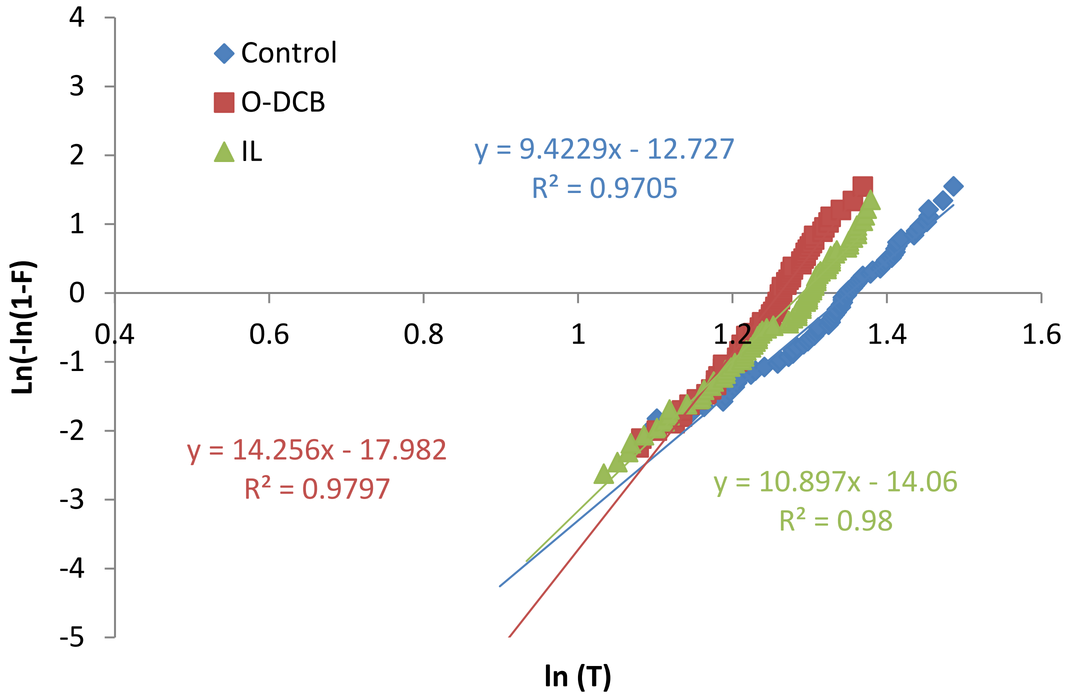


It was important to determine the single-fibre physical properties of both the untreated fibres and functionalised fibres. The tensile strength of carbon fibers is a crucial property which contributes to their outstanding performance in composite materials. As such, it is important that any proposed surface treatments do not significantly alter the tensile strength of individual fibers (indicating degradation). The results of the study show only negligible decreases in performance.

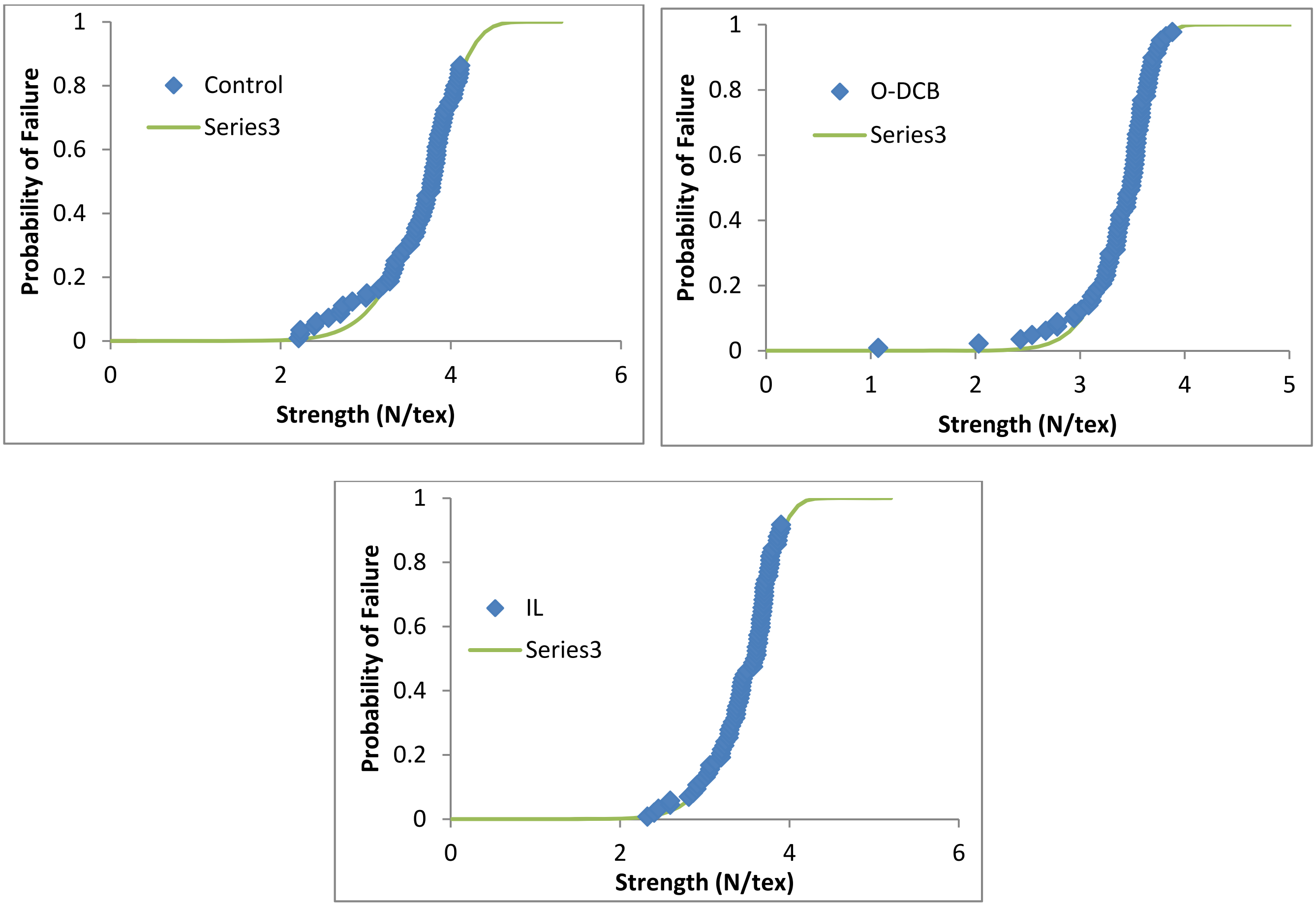


The elastic modulus (a measure of stiffness) is also an important performance characteristic of carbon fiber. Again, after treatment very small decreases were detected, although it was considered that the treatments maintained crucial fibre properties.

Weibull analysis



Weibull analysis was conducted, and the data plotted to determine Weibull modulus (shape parameter) and specific strength. Obvious outliers were removed, and the resulting data sets are presented above.



Weibull distributions of control fibres, O-DCB and IL treated fibres. The results highlight that each data set fits a Weibull distribution and as such, it can be assumed that Weibull analysis is appropriate for this fibre type.

IFSS analysis

Six individual fibres from each sample were prepared by placing each fibre down the centre of a dog-bone shaped mould, with each end of the fibre pre-tensioned using 450 mg weights to ensure it was kept straight and centred within the mould. Epoxy resin RIM935 was then mixed with hardener RIM937 in a 5:2 w/w ratio, and air bubbles removed under reduced pressure to remove voids. The resin mixture was then poured carefully into each of the six moulds, taking care to immerse the fibres fully, before allowing the samples to cure at room temperature for 48 hours, and further post-cured at 100 °C for 12 hours. The cured samples were then ground to approximately 1.5 mm thickness, followed by polishing with 9 µm and 3 µm diamond microbeads respectively to ensure maximum uniformity and transparency. The approximate dimensions of the final test coupon are 25 mm × 5 mm × 1.5 mm.

Each coupon was then strained parallel to fibre direction using a tensile tester (Instron 5967, Instron Pty Ltd, USA), up to 8% of the total gauge length to ensure crack saturation. The samples were tested at a crosshead speed of 0.05 mm/min until matrix failure occurred. The test rig was equipped with a digital microscope (AD-4113ZT Dino-Lite, AnMo Electronics Co. Taiwan), and the fibre fragmentation and saturation were monitored *in situ*, followed by fragment measurements using an optical microscope (High Resolution Olympus DP70, Olympus Melville NY).

Combined data for each sample: average fragment length for each single fibre composite, fibre critical length(l_c), gauge length at which tensile strength was measured (L0), specific strength (σ0), Weibull modulus (m), specific strength at critical length (σ0 (l_c), fibre diameter (d), interfacial shear strength (τ).

Control	average	l_c (mm)	L0 (mm)	σ0	m	σ0 (l_c)	*d* (mm)	τ (IFSS)
1	448.4364	0.598	25	3.86	9.42	5.737199	0.007	0.033584
2	492.5385	0.657	25	3.86	9.42	5.68035	0.007	0.030274
3	454.6275	0.606	25	3.86	9.42	5.728854	0.007	0.033078
4	409.2364	0.546	25	3.86	9.42	5.793182	0.007	0.03716
5	401.0189	0.535	25	3.86	9.42	5.80567	0.007	0.038003

av	0.0323
std.dev	0.0018
Std.err	0.0008

O-DCB	average	l_c (mm)	L0 (mm)	σ0	m	σ0 (l_c)	*d* (mm)	τ (IFSS)
1	318.0156	0.424	25	3.53	14.25	4.699201	0.007	0.038789
2	329.6935	0.440	25	3.53	14.25	4.687324	0.007	0.03732

3	334.5517	0.446	25	3.53	14.25	4.682514	0.007	0.036741
4	351.7091	0.469	25	3.53	14.25	4.666109	0.007	0.034826
5	409.0714	0.545	25	3.53	14.25	4.616898	0.007	0.029627

av	0.0376
std.dev	0.0011
Std.err	0.0006

IL	average	l_c (mm)	L0 (mm)	σ0	m	σ0 (l_c)	*d* (mm)	τ (IFSS)
1	375.629	0.501	25	3.63	10.9	5.196473	0.007	0.036314
2	332.6143	0.443	25	3.63	10.9	5.254778	0.007	0.041471
3	347.2794	0.463	25	3.63	10.9	5.234019	0.007	0.039563
4	351.9077	0.469	25	3.63	10.9	5.227665	0.007	0.038995
5	299.0351	0.399	25	3.63	10.9	5.306334	0.007	0.04658

av	0.0406
std.dev	0.0026
Std.err	0.0015

PFG-NMR Diffusion

^{1}H and ^{19}F pulsed field gradient diffusion measurements were carried out at 7.05 T on a Bruker Avance III 300 MHz (^{1}H frequency) wide-bore spectrometer and using a Bruker 5mm Diff50 gradient probe. Samples were packed into standard 5 mm silica NMR tubes and the measurements were carried out at a stabilised temperature of 20 °C. The pulsed field gradient stimulated echo (PFG-STE) pulse sequence was used with a 90° pulse length of 5 and 7 µs for ^{1}H and ^{19}F respectively. The gradient pulse lengths were set to 5 ms and the diffusion times to 20 ms. Gradient strengths were incremented in 16 steps between 0 and 400 G cm−1 depending on the diffusion coefficient of the species studied. A 5 s recycle delay was used. The resulting data sets were processed and fitted using the Skejskal-Tanner equation using the Bruker Topspin software:

$$I = I_0 \exp(-D\,\gamma^2\, g^2 \delta^2 (\Delta - \frac{\delta}{3}))$$

where I is the observed signal intensity, I0 is the maximum signal intensity, D is the diffusion coefficient, γ is the gyromagnetic ratio of the nucleus observed, δ is the gradient pulse length and Δ is the diffusion time.