

## Supplementary Material for

### **Carbon fibre reinforced cellulose-based polymers: intensifying interfacial adhesion between the fibre and the matrix**

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## 1. Carbon fibre characterization techniques

**Thermogravimetric analysis.** TGA measurement was performed with a Shimadzu DTG-60AH equipment (Kyoto, Japan). Samples were heated under N<sub>2</sub> atmosphere from room temperature to 900 °C with a heating rate of 20 °C/min.

**X-ray photoelectron spectroscopy.** XPS analysis was carried out using a Thermo Scientific K-Alpha X-ray Photoelectron Spectrometer System with an Al K<sub>α</sub> monochromated X-ray source (1486.6 eV) at a power of 36 W (12 kV × 3 mA) (Waltham, MA, USA). The analysis spot size was 400 μm. Carbon fibre samples were mounted on the sample holder (60 × 60 mm, 9 sample bars) at each end using a carbon tape and the analyzing area was chosen to cover only carbon fibres. Survey spectrum was recorded with a resolution of 1 eV to obtain elemental composition. High-resolution C1s, N1s, O1s and F1s spectra were recorded with a pass energy of 20 eV and a resolution of 0.1 eV in order to acquire more information about the chemical bonds on the surface. Binding energy scale was calibrated to the hydrocarbon C1s peak at 285.0 eV. Peak fitting was performed using Thermo Scientific Avantage Software version 5.89 (Waltham, MA, USA). The software allows the user to change peak width and peak position, background correction was performed with built-in Smart algorithm and peak fitting was executed with Powell method using Gauss-Lorentz Mix algorithm.

**Raman spectroscopy.** Raman spectroscopy was performed with a Thermo Scientific DXR Raman Microscope (Waltham, MA, USA) at an excitation wavelength of 780 nm.

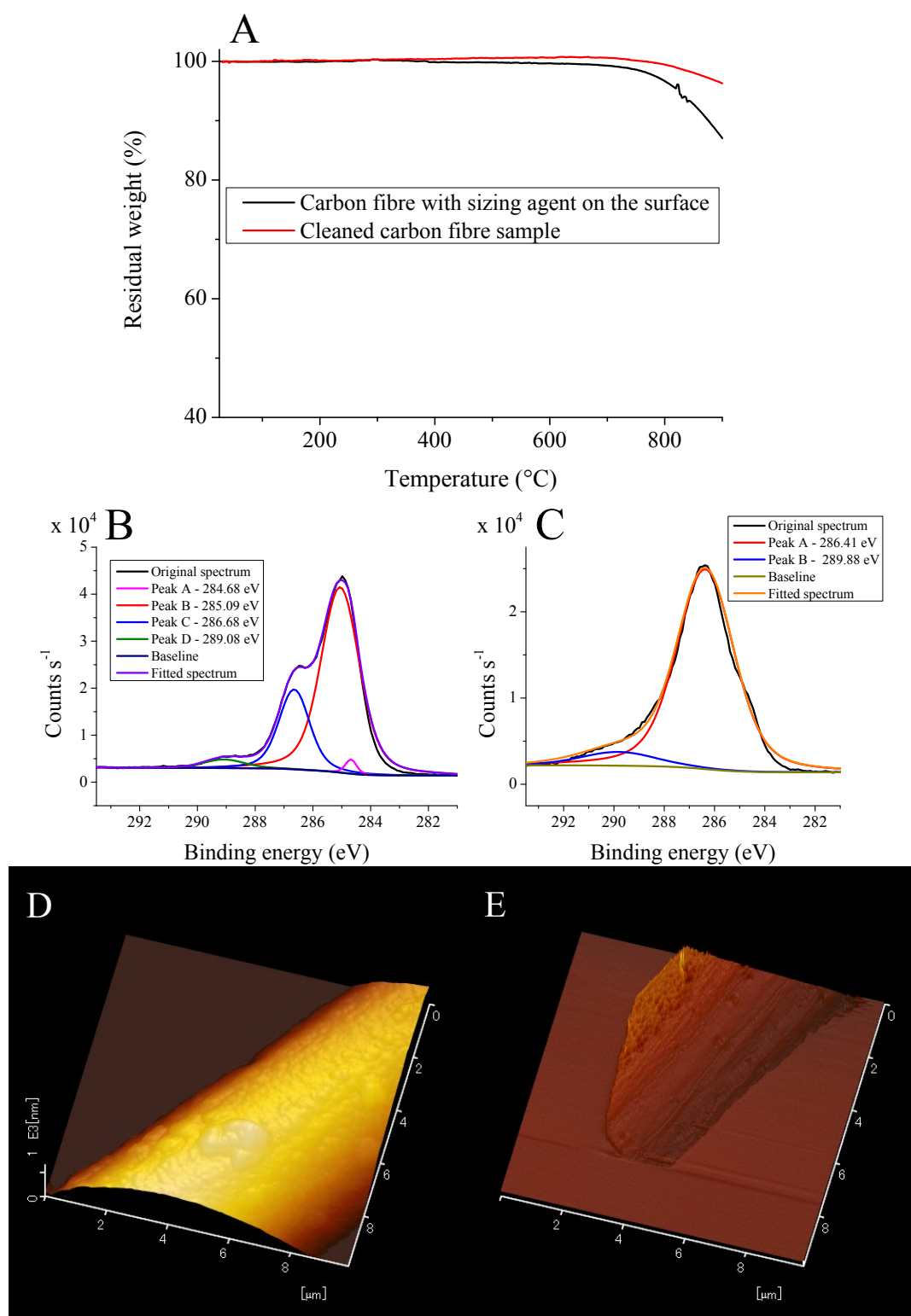
**Optical microscopy.** The mechanism of micromechanical failure at the saturation in the fragmentation test was investigated using an Olympus BX50 microscope (Tokyo, Japan) equipped with polarizing lens.

**Surface topography.** Carbon fibre images were recorded on a JSM-7610F Field Emission Scanning Electron Microscope (FE-SEM) using an accelerating voltage of 15 kV and a working distance of 8 mm (JEOL, Tokyo, Japan). The FE-SEM system was equipped with a JEOL EX-230\*\*BU EX-37001 Energy Dispersive X-Ray Analyzer to obtain EDS spectrum and perform chemical mapping (JEOL, Tokyo, Japan).

Fracture surfaces were analyzed using a Hitachi S4500 scanning electron microscope with an accelerating voltage of 10 kV. Samples were coated with Au-Pd in a Hitachi E1030 ion sputter for 60 s (Hitachi, Ltd., Tokyo, Japan).

AFM images were recorded on SII NanoTechnology Nanocute (Hitachi, Ltd., Tokyo, Japan) machine.

## 2. Removal of the sizing agent



**Figure S1.** (A) TGA analysis of carbon fibre samples with sizing agent on the surface and after removal of the sizing agent (cleaned). (B) XPS spectrum of carbon fibre T700 with sizing agent on the surface and after cleaning (C). (D) and (E) show AFM images of carbon fibre T700 with sizing agent on the surface and after cleaning, respectively.

### 3. Synthetic procedures

**Synthesis of XPS-tagged cellulose propionate (CP).** 5 g CP (30.8 mmol anhydroglucose unit) was dissolved in dichloromethane and 0.430 mL triethylamine (3.08 mmol) was added to the system. 0.456 mL 4-(trifluoromethyl)benzoyl chloride (3.08 mmol) was slowly added to the dichloromethane solution while the system was cooled using an ice bath. Thereafter, the reaction mixture was warmed to room temperature and allowed to react for 12~16 hours (overnight reaction). The solution was precipitated in large amount of water/methanol mixture (1:1 ratio, 500 mL) and the product was collected using vacuum filtration. The precipitated products were further reprecipitated in water/methanol mixture (1:1 ratio, 500 mL) using acetone as a good solvent, filtrated, and dried in a vacuum oven at 50 °C for 24 h. The resulting product has a DS value of 0.034 in respect to the XPS-tag (Figure S7). FTIR spectrum is shown in Figure S6.

**Tosylation of XPS-tagged cellulose propionate.** 2 g XPS-tagged CP (12.34 mmol anhydroglucose unit, DS: 2.79, 0.86 mmol free OH) was dissolved in 100 mL pyridine. Subsequently, 7 g tosyl chloride (36 mmol) dissolved in 20 mL pyridine was added dropwise to the system within 30 min. The reaction mixture was stirred for 24 h at 8 °C and the product was precipitated in ice water, and washed with ethanol under vacuum filtration. The product was reprecipitated in distilled water using acetone as a solvent and dried in a vacuum oven at 50 °C for 24 h. The product has a DS of 0.147 in respect to the tosyl group (<sup>1</sup>H- and <sup>13</sup>C-NMR spectra are shown in Figure S8 and S9). FTIR spectrum is shown in Figure S6.

**Functionalization of the carbon fibre surface via diazonium species.** The diazotization and *in situ* grafting have been carried out according to previously reported procedure that had been derived from a synthetic route elaborated for carbon nanotubes.<sup>1,2</sup> It has been proven that the reaction does not affect detrimentally key single fibre physical parameters.<sup>1</sup> The reaction medium was gently stirred with small stirring bar to avoid harsh impact with the fibre. A brief example of the applied method is given as follows. 30 mL *ortho*-dichlorobenzene, 15 mL acetonitrile and 162.6 mg 4-[(*N*-Boc)aminomethyl]aniline (0.73 mmol) was bubbled with nitrogen for 10 min (degassing process). 25 mg carbon fibre was then immersed in the solution under nitrogen atmosphere. To this solution, 170 µL isoamyl nitrite (1.46 mmol) was added and the reaction vessel was heated to 50 °C. After 24 h reaction time the solvent was decanted and the fibres were washed with dichloromethane until yielding a clear solution. Thereafter, the fibres were filtered and rinsed with 200 mL dichloromethane, deionized water

and acetone using a Buchner funnel. The fibres were then placed in a vacuum oven at 50 °C for 24 h.

**Deprotection of Boc-protected amine after the grafting procedure.** Deprotection step has been performed according to previously reported procedure with functionalized carbon fibre samples, which had been proven not to affect detrimentally key physical parameters of single fibres.<sup>1</sup> The fibres were immersed in 20 mL 2 M anhydrous HCl - 1,4-dioxane solution for 24 h at room temperature. Thereafter, the reaction medium was decanted and the fibres washed with 3 × 150 mL water. To obtain the free amine, the fibres were immersed in NaOH solution (2 M, three times 20 mL for 10 min). After that, to remove the base, the fibres were washed with 100 mL water five times and rinsed with 150 mL acetone using a Buchner funnel, and dried in a vacuum oven at 50 °C for 24 h.

**Nucleophilic replacement reaction on the carbon fibre surface.** 25 mg carbon fibre was immersed in 40 mL DMSO and 0.1 mL triethylamine (0.73 mmol) was added to the system. Afterwards, 1 g XPS-tagged tosylated CP dissolved in 20 mL DMSO was measured into the vessel. The system was kept at 100 °C for 24 h. The functionalized fibres were filtered and washed with 200 mL dichloromethane, deionized water and acetone, respectively. After that, the fibres were placed in a vacuum oven at 50 °C for 24 h.

**Alkylation of benzoic acid grafted onto the carbon fibre surface.** 25 mg functionalized fibre was immersed in NaOH solution (2 M, three times 20 mL for 10 min). After that, to remove the base the fibres were washed with 50 mL water five times followed by thorough washing with acetone and dichloromethane. Thereafter, the fibres were immersed in 20 mL toluene and 100 µL benzyl chloride (0.87 mmol) and 2 µL trimethylamine (catalytic amount) were added to the system. The reaction vessel was heated to 100 °C. After 24 h reaction time, the fibres were vacuum filtered and rinsed with 200 mL dichloromethane, deionized water and acetone. The fibres were then placed in a vacuum oven for 24 h. The same procedure has been performed with 4-(trifluoromethyl)benzyl chloride.

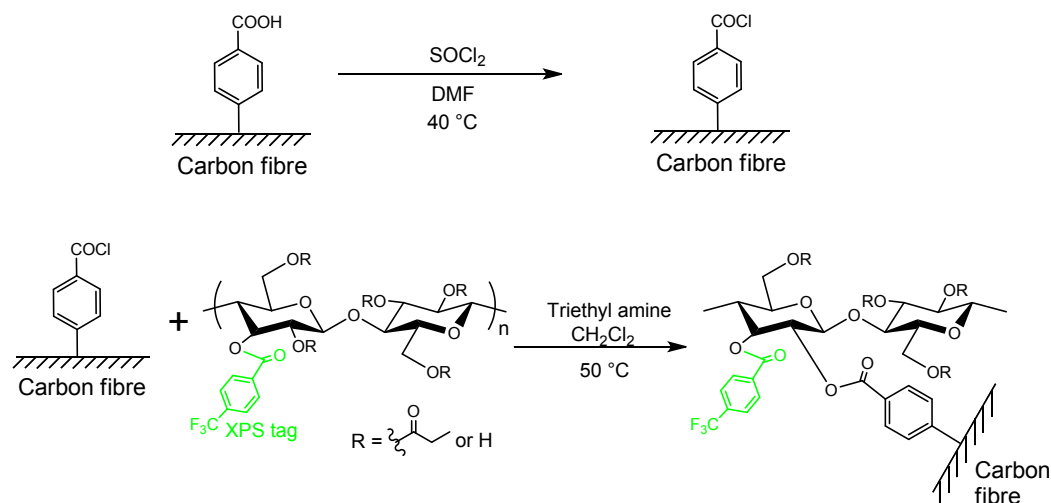
**Acylation of 4-(aminomethyl)benzene grafted onto the carbon fibre surface.** 25 mg functionalized fibre was immersed in 40 mL dichloromethane. To this solution 117.6 µL pyridine (1.46 mmol) and then 169.6 µL benzoyl chloride (1.46 mmol) were added. After 24 h reaction time, the fibres were vacuum filtered and rinsed with 200 mL dichloromethane, deionized water and acetone. The fibres were then placed in a vacuum drying oven for 24 h.

The same acylation process was performed with 4-(trifluoromethyl)benzoyl chloride, propionyl chloride and decanoyl chloride as acylating agents.

**Electrochemical grafting – synthesis of the diazonium salt.** Synthesis of the diazonium salt for electrochemical grafting experiment was performed according to Kosynkin et al.<sup>3</sup> 0.2336 g  $\text{NOBF}_4$  (2 mmol) was measured in a reaction vessel under argon atmosphere. Dry acetonitrile (10 mL) was then injected through a rubber septum and the vessel was cooled down in an acetonitrile/liquid nitrogen bath ( $-41\text{ }^\circ\text{C}$ ). Thereafter, 0.44456 g 4-[(*N*-Boc)aminomethyl]aniline (2 mmol) dissolved in 10 mL acetonitrile was added over 30 min using a syringe. The solution was stirred for 2 hours at  $-30\text{ }^\circ\text{C}$  and then directly used for the electrochemical experiments due to the instability of the diazonium species.

**Electrochemical grafting – cyclic voltammetry experiment.** Cyclic voltammetry experiments were performed using a 3-electrode system with an ALS/CHInstruments Electrochemical Analyzer Model 1200A and a SVC3 voltammetry cell (ALS Co., Ltd, Tokyo, Japan).  $\text{Ag}/\text{Ag}^+$  non-aqueous reference electrode (RE-7, ALS Co., Ltd, Tokyo, Japan) and a platinum counter electrode were applied. 25 mg carbon fibre with a length of  $\sim 20$  cm was employed as working electrode. One end of the fibre tow was fixed to the terminal using a copper tape. The supporting electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile. The working electrode was cycled between 1 and  $-1$  V vs.  $\text{Ag}/\text{AgNO}_3$ . According to our preliminary optimization experiments,  $0.2\text{ V s}^{-1}$  scan rate and 10 mM diazonium salt concentration was applied. Following electrochemical experiments the fibres were cleaned thoroughly with 200 mL dichloromethane, deionized water and acetone, and placed in a vacuum oven at  $50\text{ }^\circ\text{C}$  for 24 h.

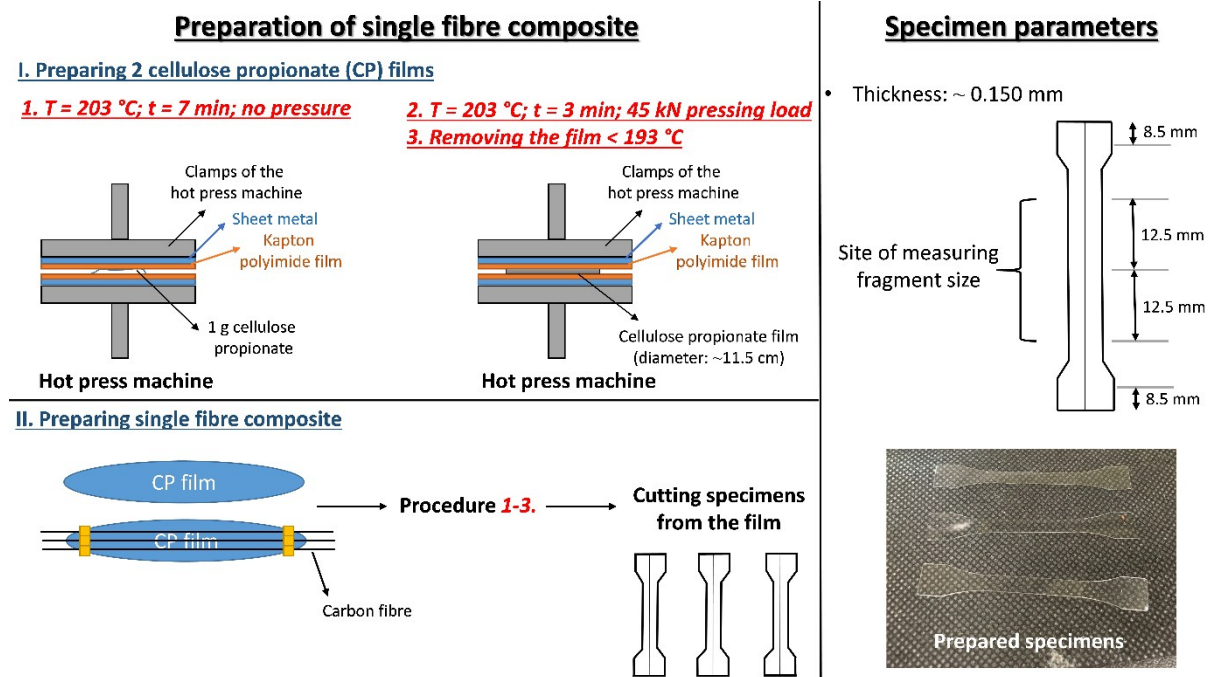
### Experimental procedure for carbon fibre functionalization via acylation reaction



20 mL thionyl chloride, 1 mL DMF (catalyst) and 25 mg functionalized carbon fibre were reacted at 40 °C under argon atmosphere for 6 h. Thereafter, the solvent was decanted and the fibres were washed with dichloromethane several times (100 mL). The fibres were then immersed in 40 mL dichloromethane and 0.1 mL triethylamine (0.73 mmol) was added to the system. Afterwards, 1 g XPS-tagged cellulose propionate dissolved in 40 mL dichloromethane was measured into the vessel. The system was kept at 50 °C under argon atmosphere for 24 h. The functionalized fibres were filtered and washed with dichloromethane, deionized water and acetone, respectively, using a Buchner funnel. After that, the fibres were placed in a vacuum oven for 24 h at 50 °C.

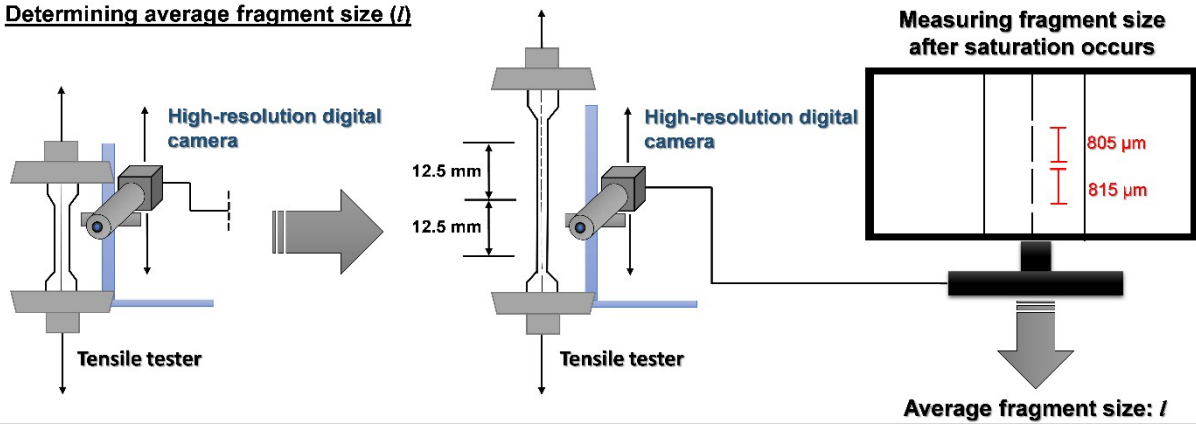


## 4. Single fibre fragmentation test



**Figure S2.** Preparation of single fibre composites for the fragmentation test.

**Preparation of single fibre composite.** The pressing temperature was set to  $203\text{ }^{\circ}\text{C}$ , which had been determined by observing the flow characteristics of CP with a Shimadzu CFT-500EX Flowtester (Kyoto, Japan); pressing temperature was chosen to be  $10\text{ }^{\circ}\text{C}$  above the offset temperature corresponding to a point when the piston moved 5 mm. Two films were made first from 1 g CP according to the following procedure. CP sample was placed between the clamps of the hot press machine at  $203\text{ }^{\circ}\text{C}$  for 7 min using two sheet metals and Kapton polyimide films (for obtaining smooth surface of the film), then it was compressed for 3 min (45 kN pressing load was applied) and the heating was turned off afterwards. The films were removed after the temperature dropped below  $193\text{ }^{\circ}\text{C}$ . 3 single carbon fibre filaments were fixed on one film with tapes to ensure that they remain straight during processing. The film containing single fibres was covered with another one and the same pressing procedure was then applied as shown above. Dog-bone shaped specimens (75 mm long) containing one fibre in the middle were cut from the composite film.

**Determining average fragment size ( $l$ )****Calculating interfacial shear strength (IFSS)**

1. Critical fragment size ( $l_c$ ) from the average fragment size ( $l$ ):

$$l_c = \frac{4}{5} l$$

2. Apparent interfacial shear strength ( $\tau$ )

$$\tau = \frac{\sigma_{fu} d}{2l_c}$$

3. Fibre strength at critical length ( $\sigma_{fu}$ ):

$$\sigma_{fu} = \sigma_l \left( \frac{l_l}{l_c} \right)^{\frac{1}{m}}$$

$d$  – carbon fibre T700SC diameter (7  $\mu\text{m}$ )

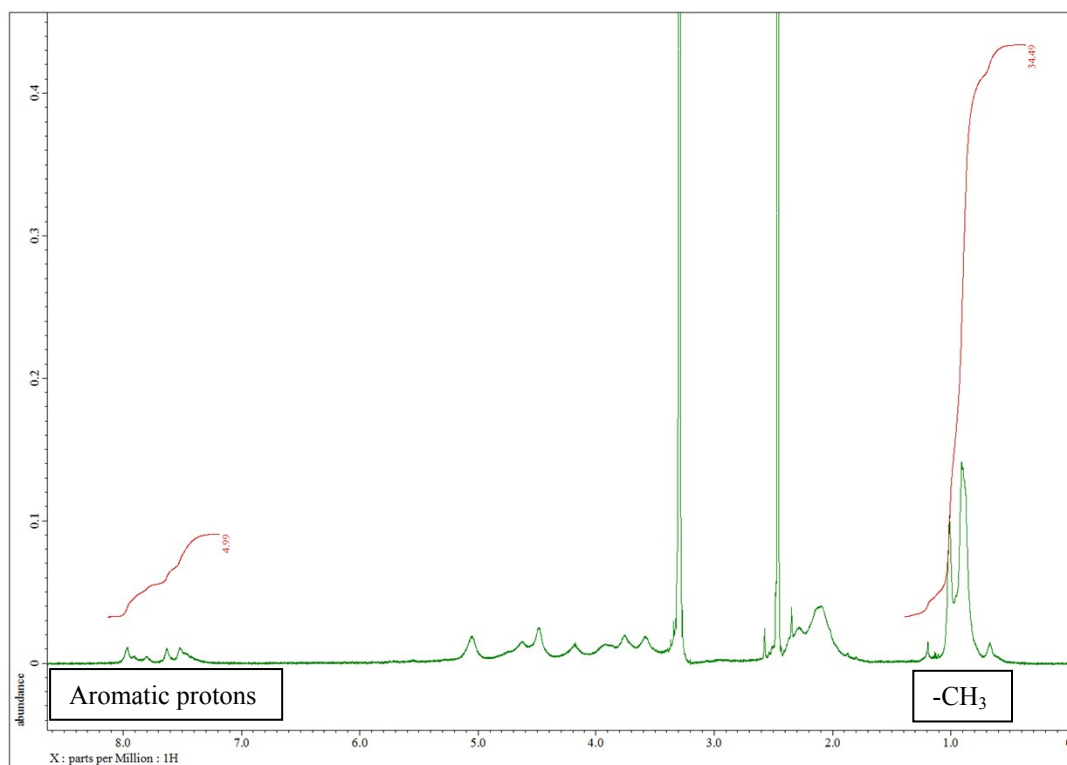
$\sigma_l$  – carbon fibre tensile strength at  $l_l$  gauge length

$l_l$  – gauge length during single fibre tensile test

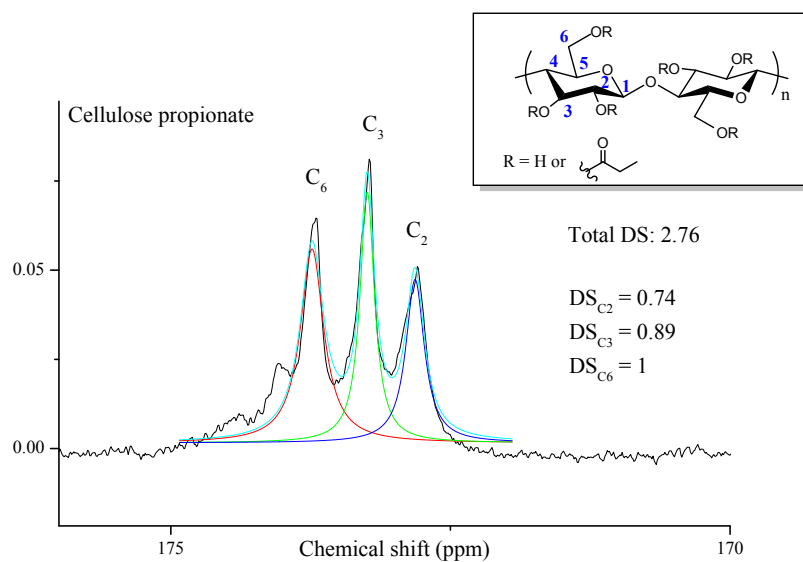
$m$  – Weibull modulus calculated from single fibre tensile test data

**Figure S3.** Determination of the interfacial shear strength of single fibre composites.

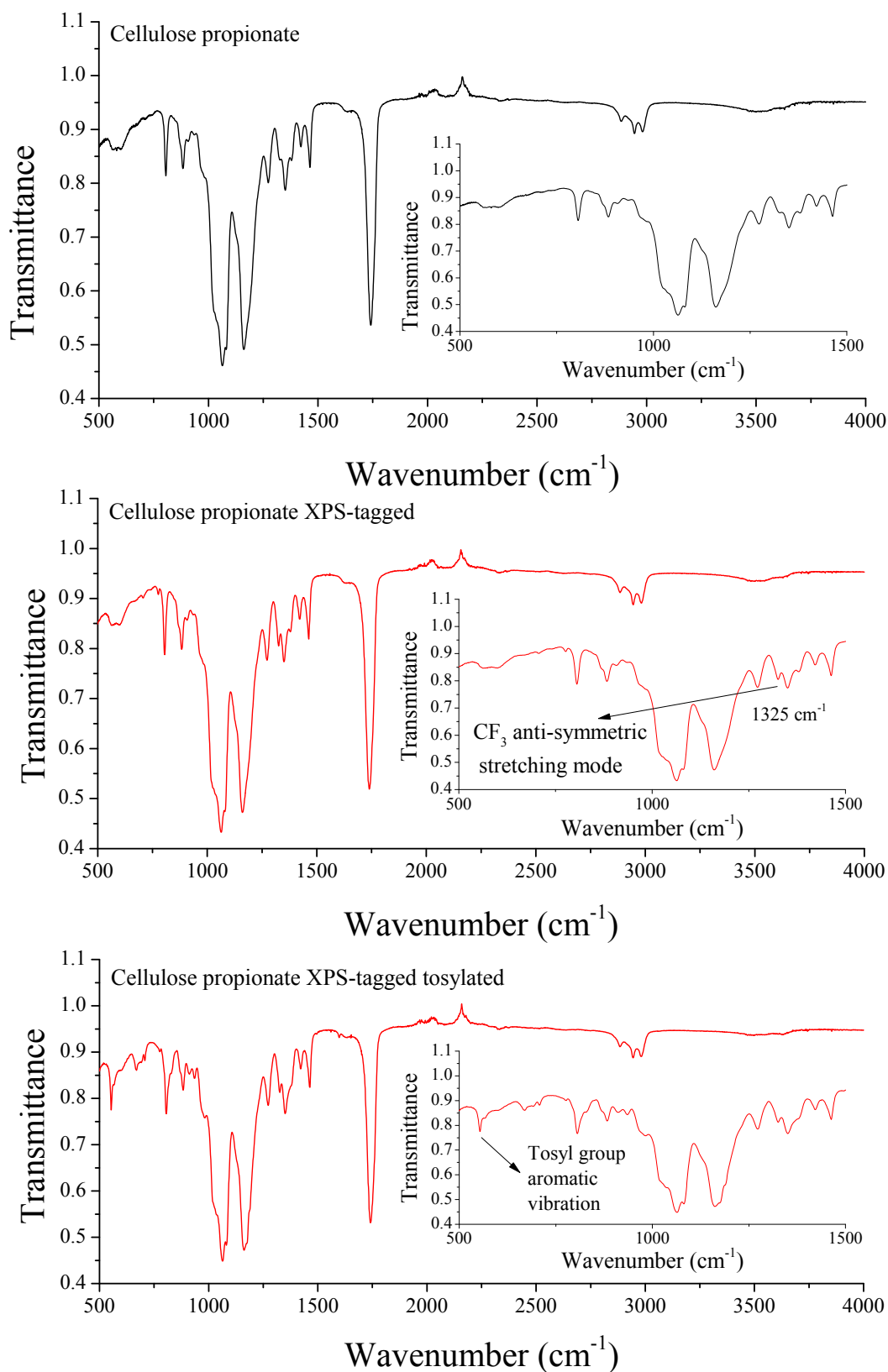
## 5. Characterization of cellulose derivatives



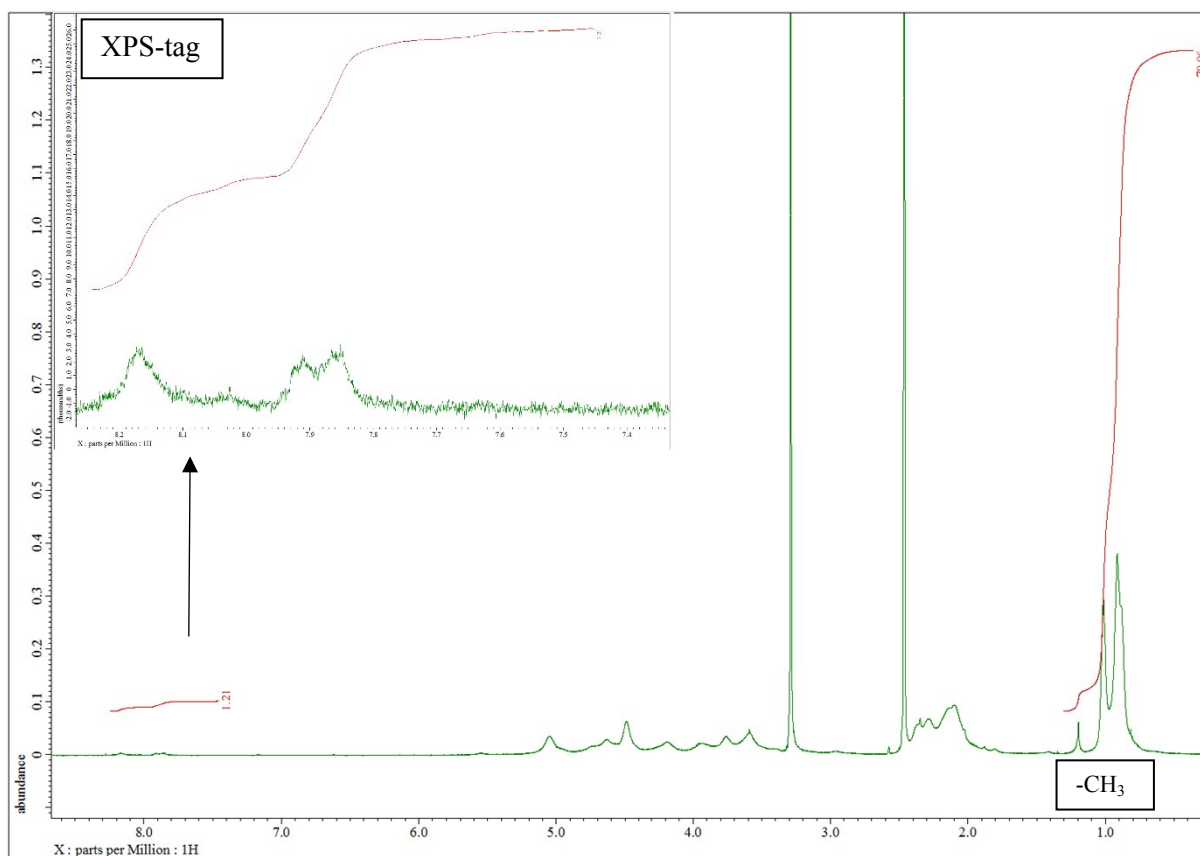
**Figure S4.**  $^1\text{H}$ -NMR spectrum of benzoylated cellulose propionate for DS value determination.



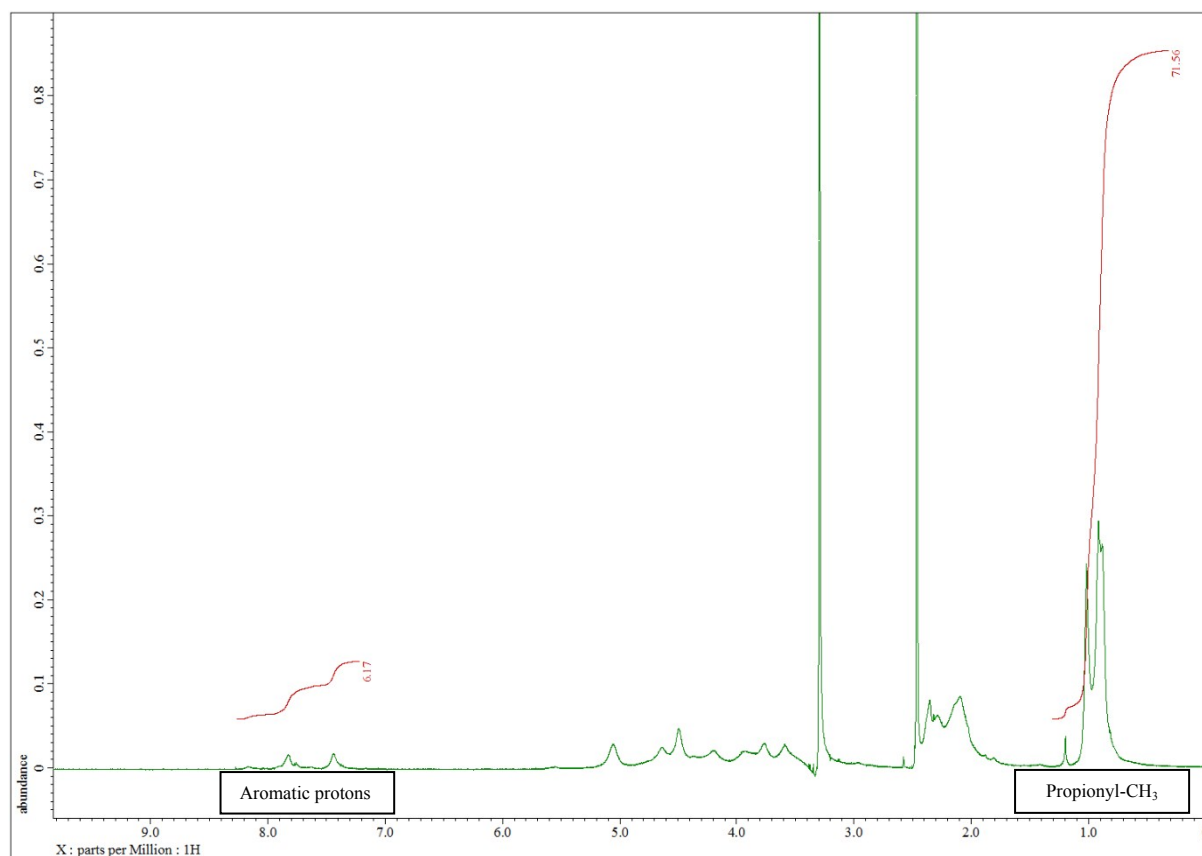
**Figure S5.** Curve fitting to the carbonyl carbon peaks in quantitative  $^{13}\text{C}$ -NMR spectrum of cellulose propionate sample prepared in  $\text{CDCl}_3$ .



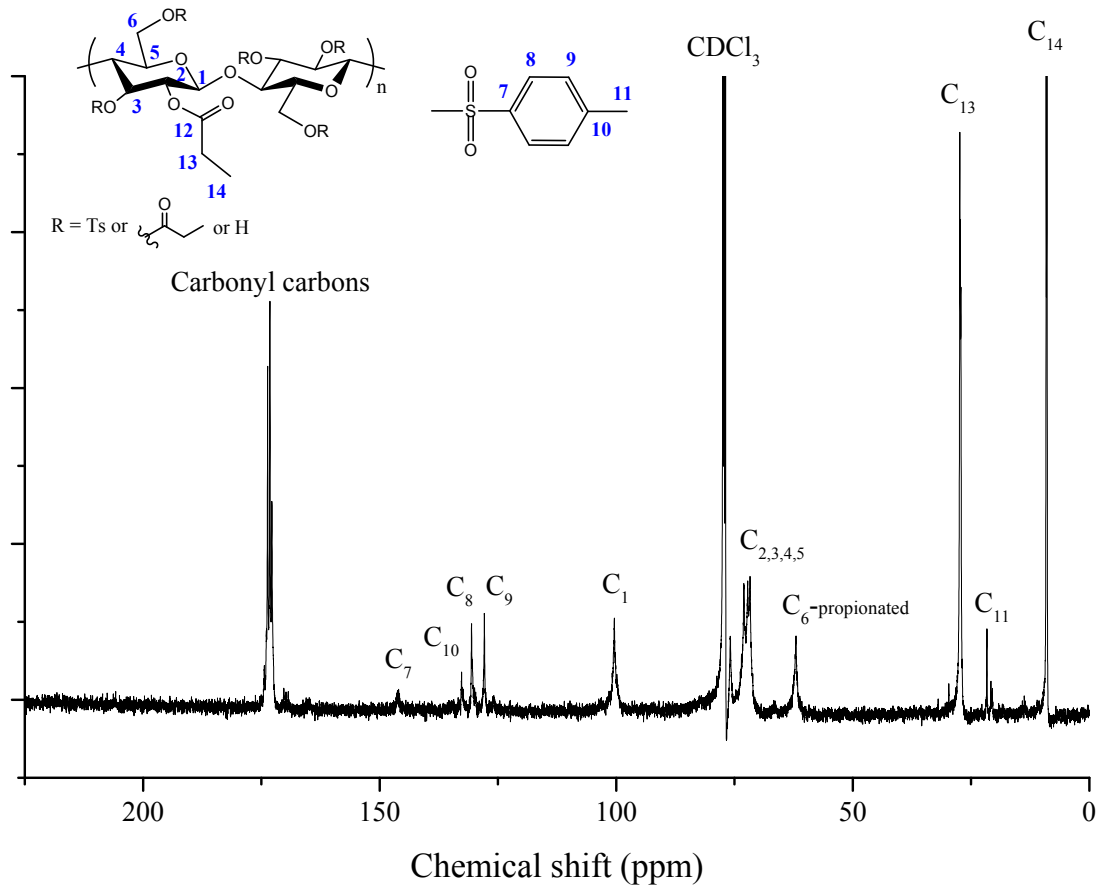
**Figure S6.** FTIR spectra of synthesized cellulose derivatives with insets showing magnified spectral regions of special importance.



**Figure S7.**  $^1\text{H-NMR}$  spectrum of XPS-tagged cellulose propionate.

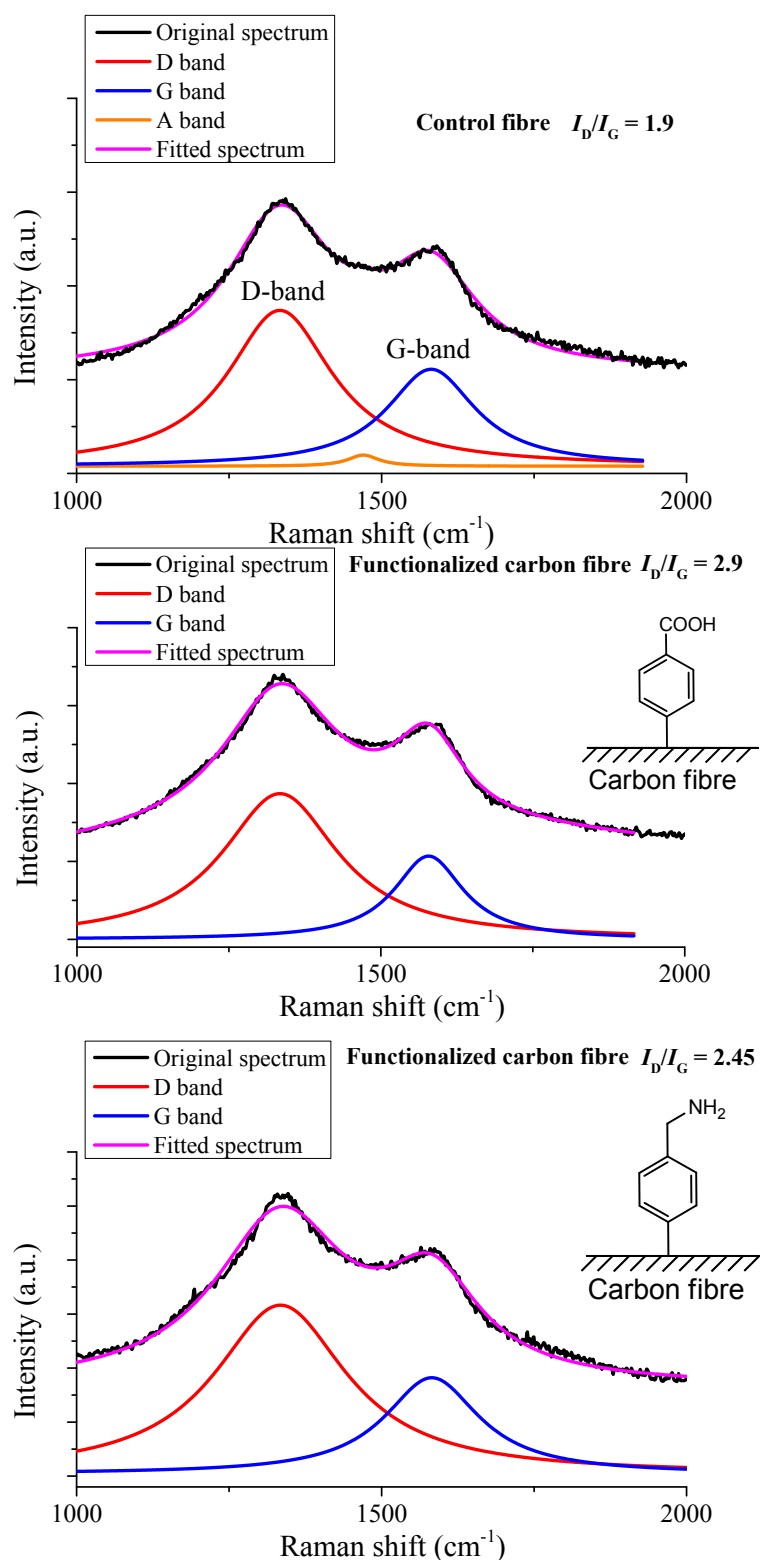


**Figure S8.**  $^1\text{H-NMR}$  spectrum of tosylated XPS-tagged cellulose propionate.



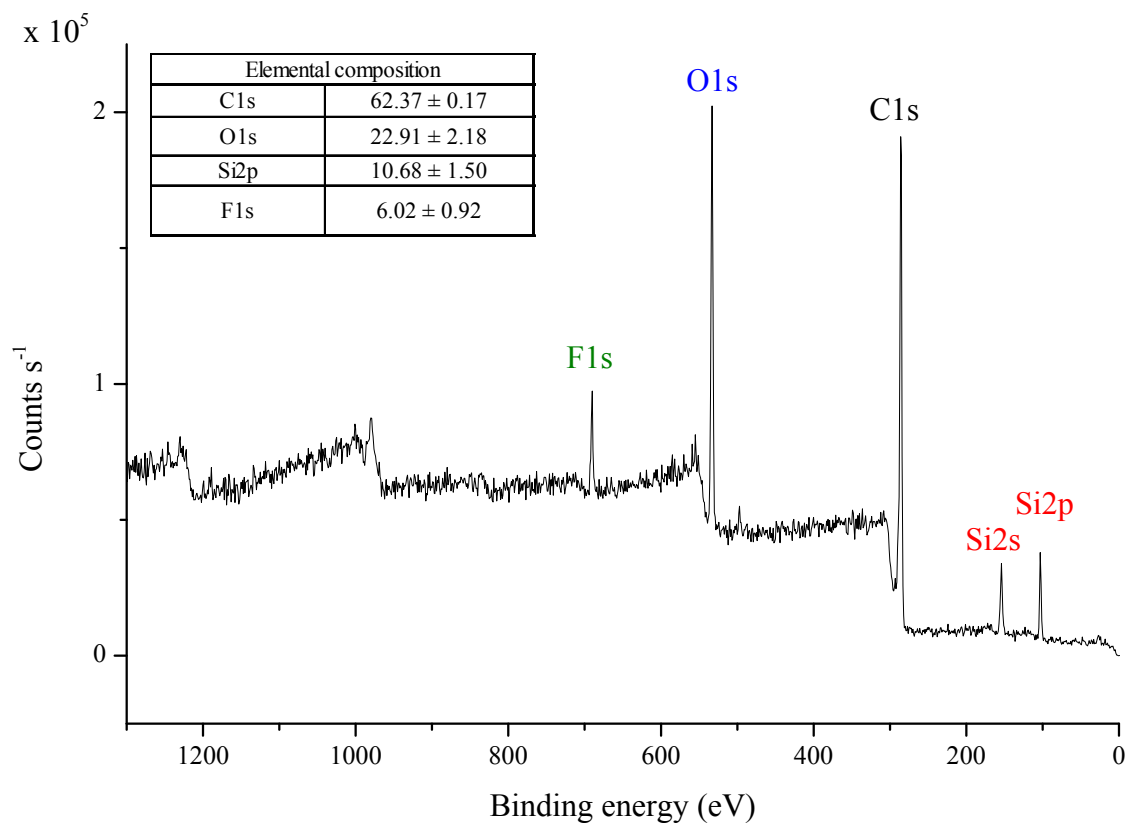
**Figure S9.**  $^{13}\text{C-NMR}$  spectrum of tosylated XPS-tagged cellulose propionate.

## 6. Raman spectra



**Figure S10.** Raman spectra with fitting to the D and G band recorded on control and functionalized fibres. For the control sample a small A band was also included in the fitting referring to amorphous carbon.<sup>4</sup>

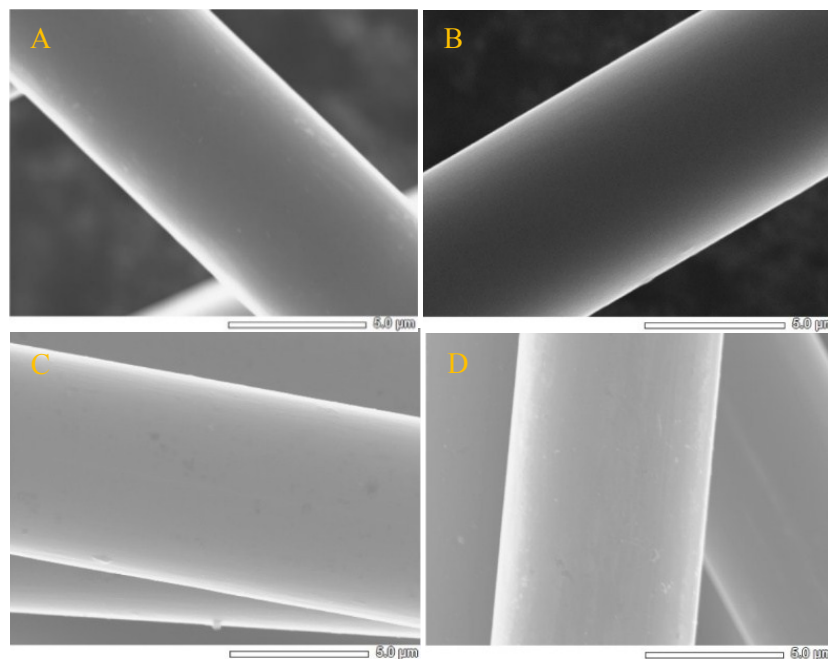
## 7. XPS spectrum



**Figure S11.** Survey spectrum of carbon fibre sample functionalized with tosylated cellulose propionate (deviations are calculated from 3 measurements on different spots of the carbon fibre surface).

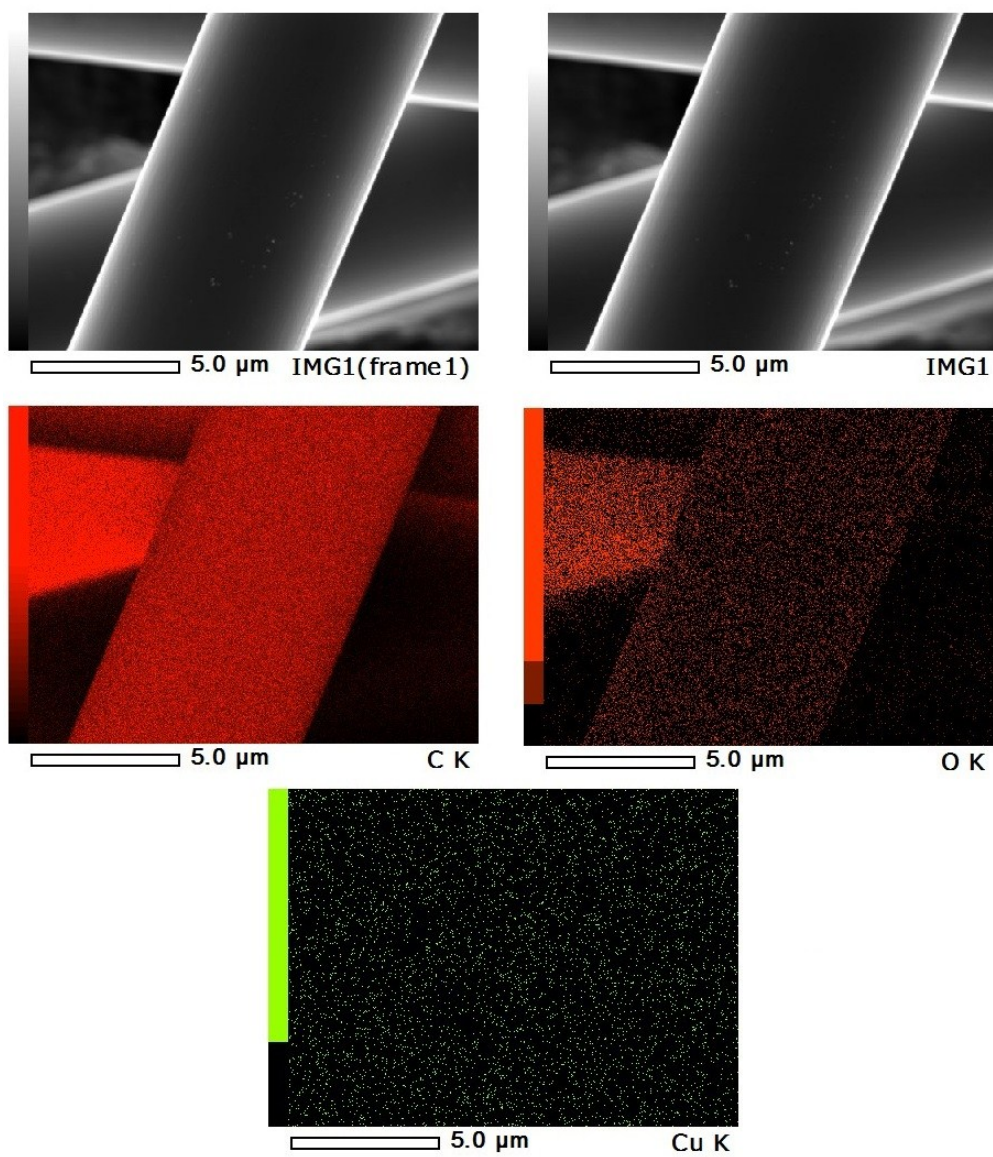


## 8. Scanning electron microscopy images of carbon fibre samples

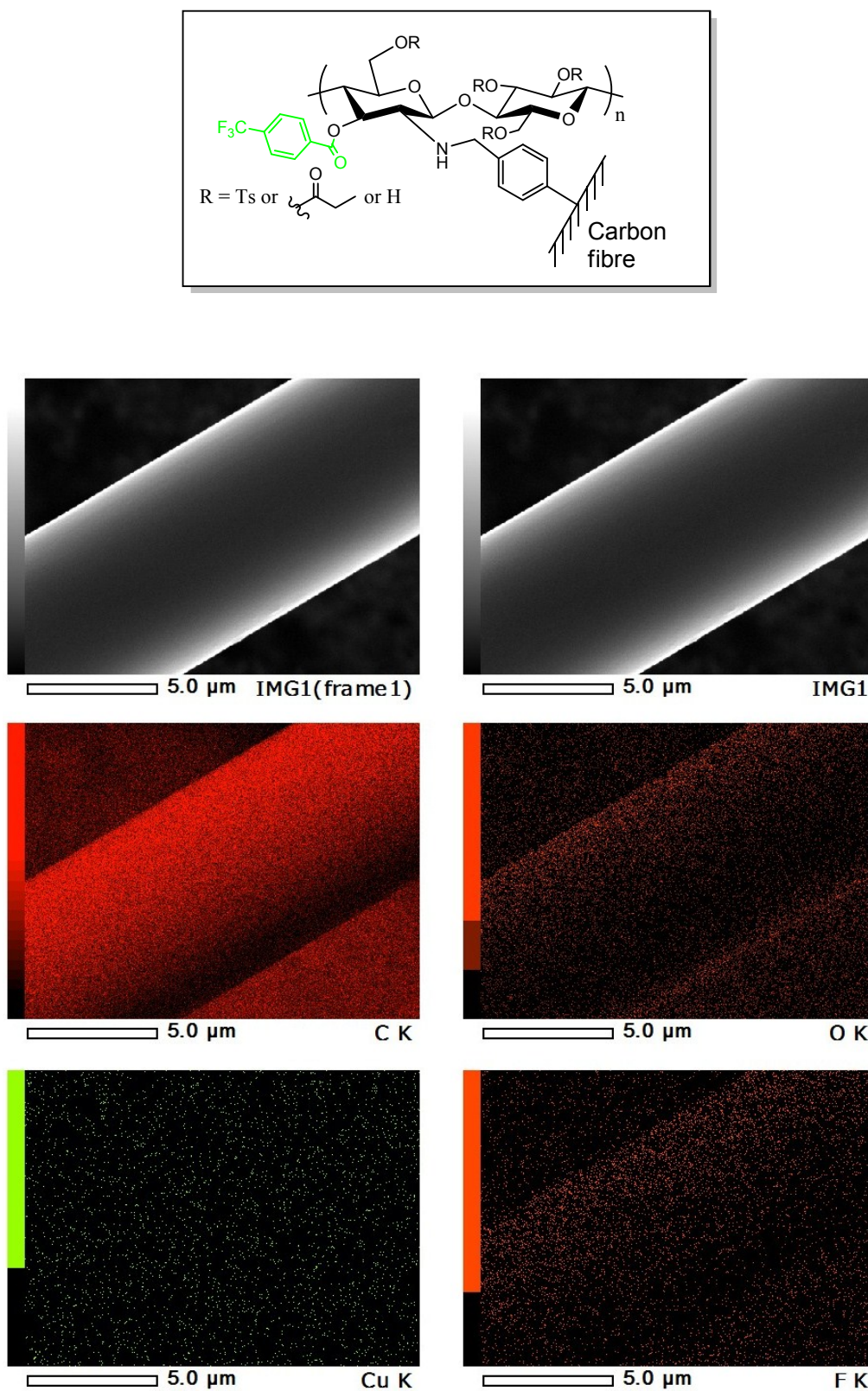


**Figure S12.** SEM images of control fibre (A), fibre functionalized with cellulose propionate (CF2) (B), benzoic acid-functionalized (CF3) (C), and 4-(aminomethyl)benzene-functionalized (CF1) fibre (D) (5 µm scale).

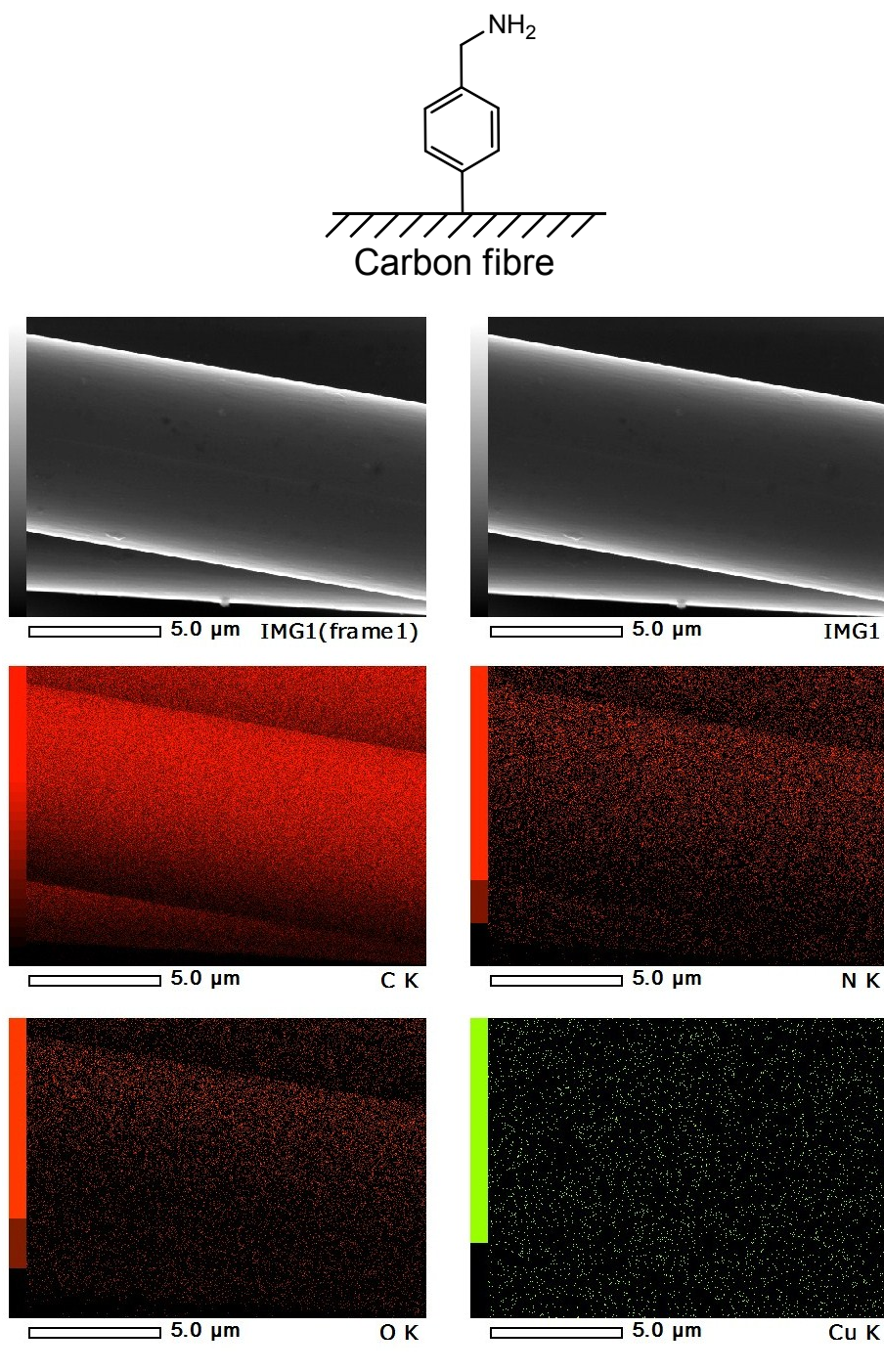
## 9. Chemical mapping of carbon fibre samples



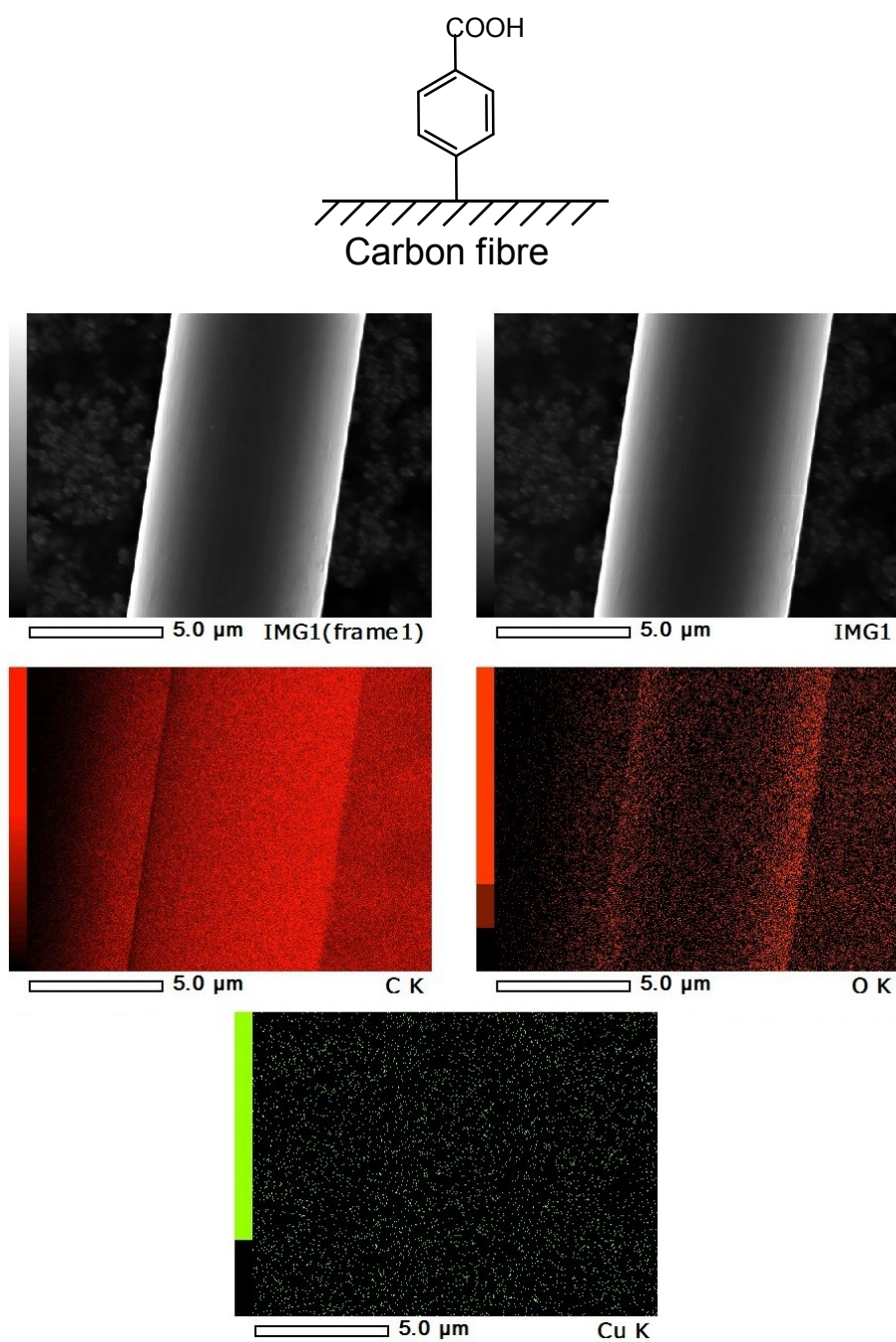
**Figure S13.** Chemical mapping performed on control carbon fibre sample. (Please note that copper background originates from the sample holder).



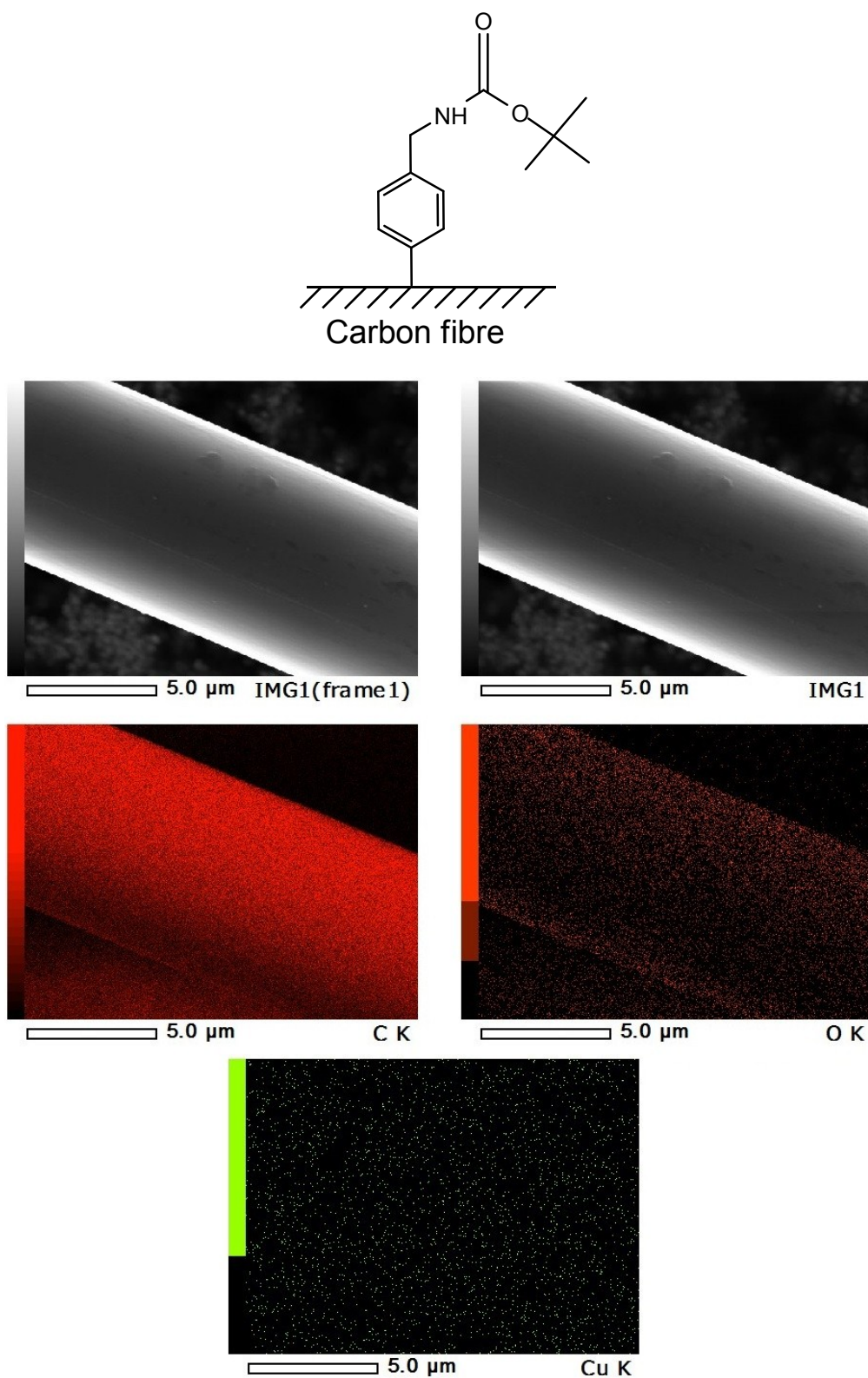
**Figure S14.** Chemical mapping performed on cellulose propionate-functionalized carbon fibre sample.



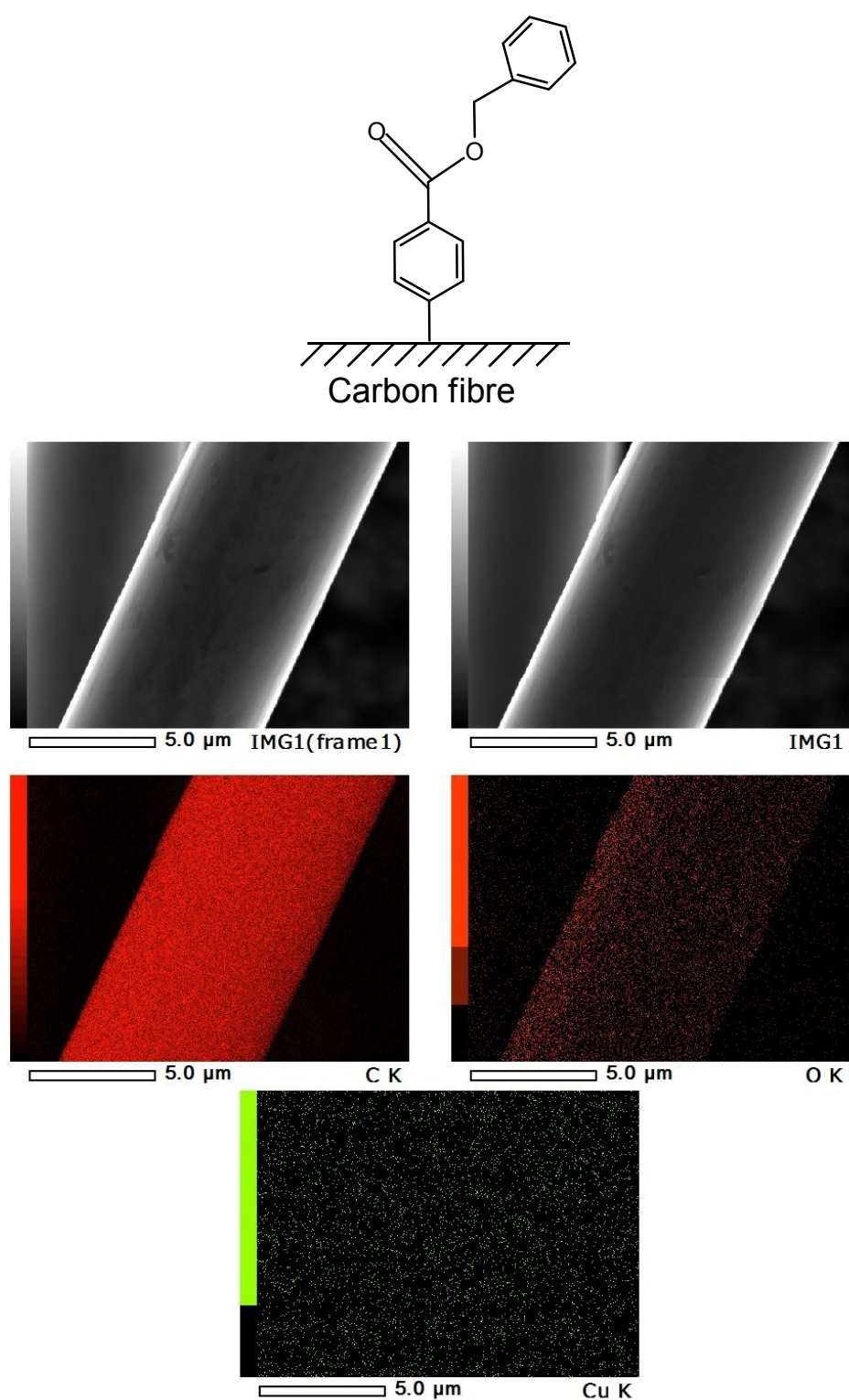
**Figure S15.** Chemical mapping performed on 4-(aminomethyl)benzene-functionalized carbon fibre sample.



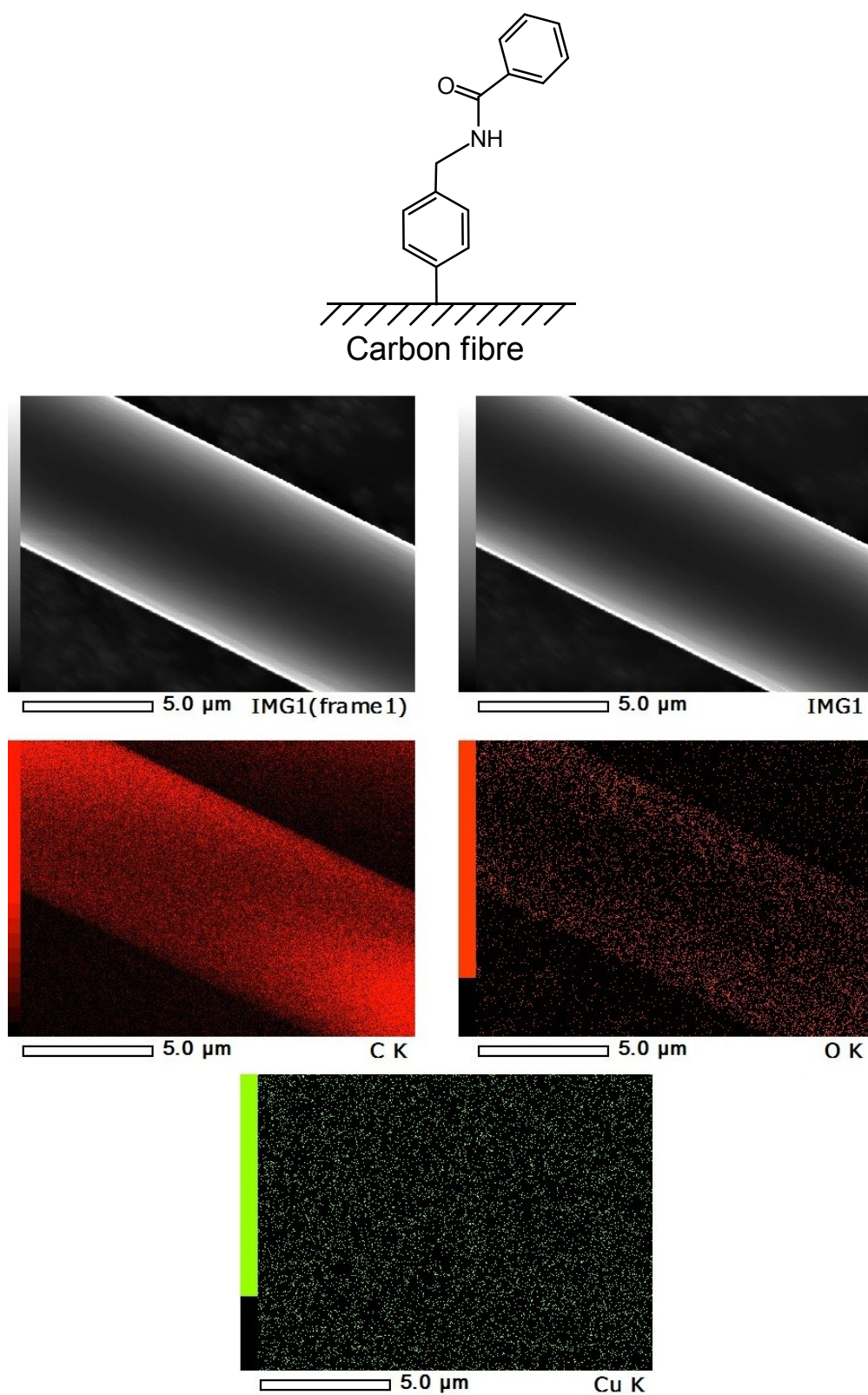
**Figure S16.** Chemical mapping performed on carbon fibre sample functionalized with benzoic acid moiety.



**Figure S17.** Chemical mapping performed on carbon fibre sample functionalized with 4-[(N-Boc)aminomethyl]benzene.

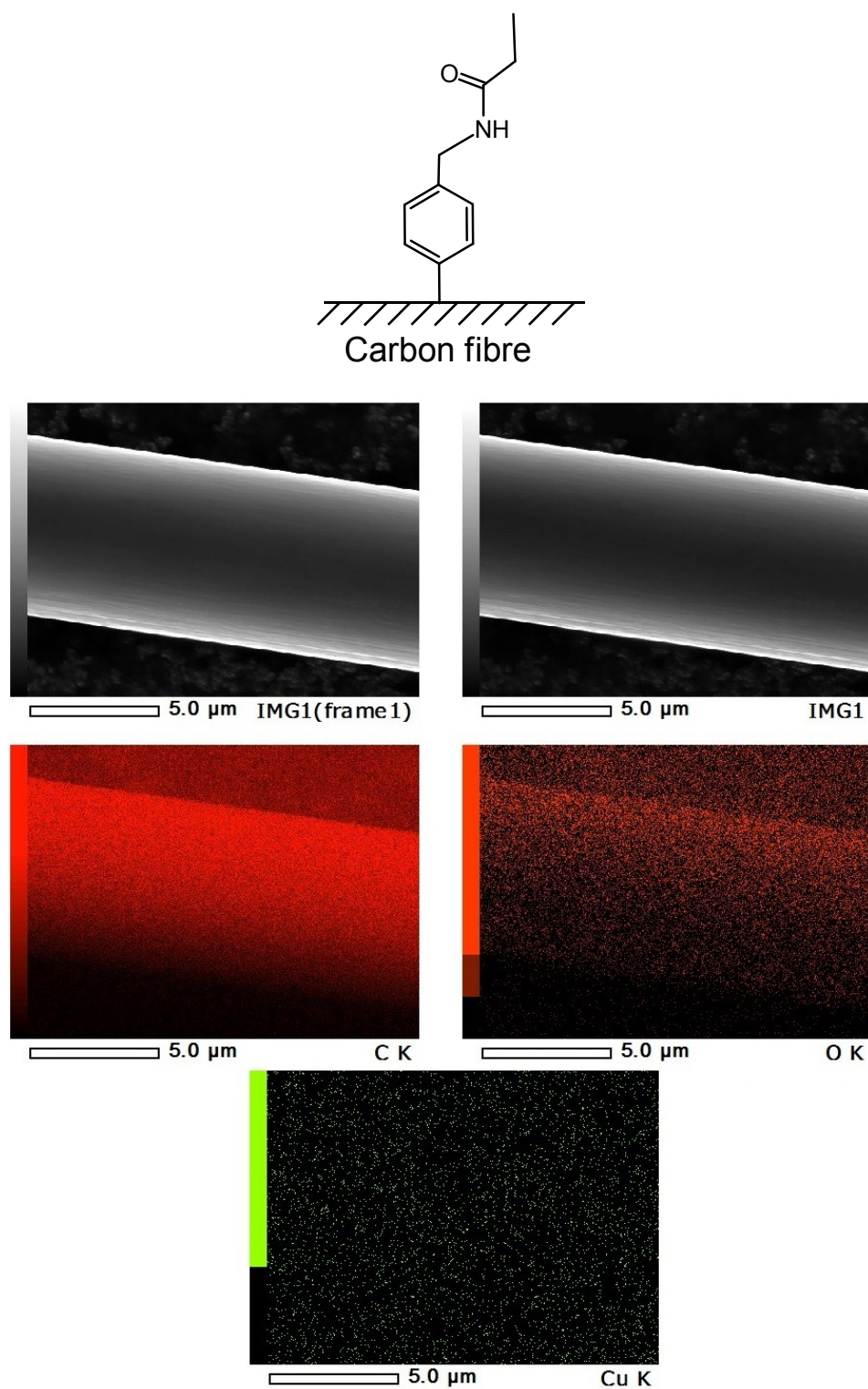


**Figure S18.** Chemical mapping performed on functionalized carbon fibre sample (structure is shown above).

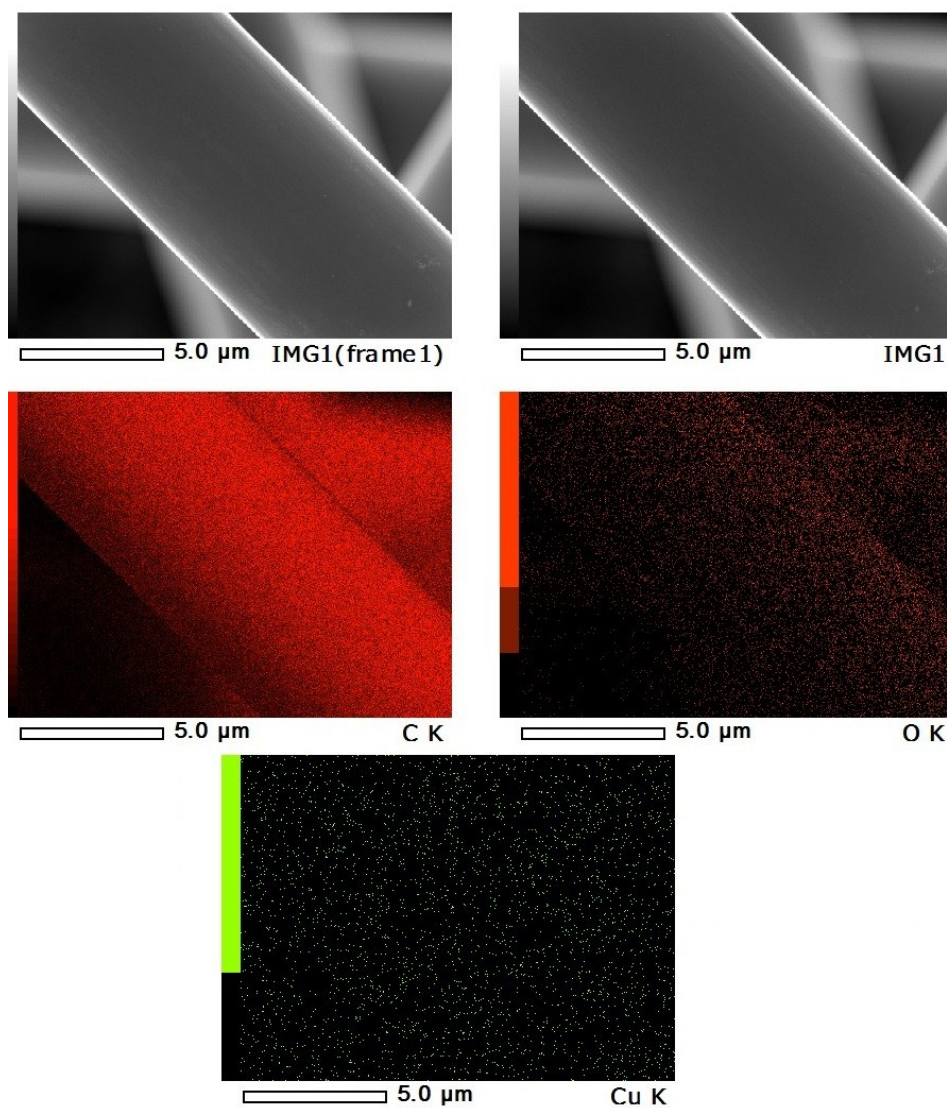
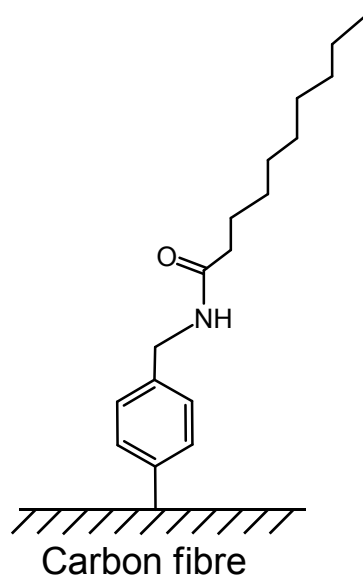


**Figure S19.** Chemical mapping performed on functionalized carbon fiber sample (structure is shown above).

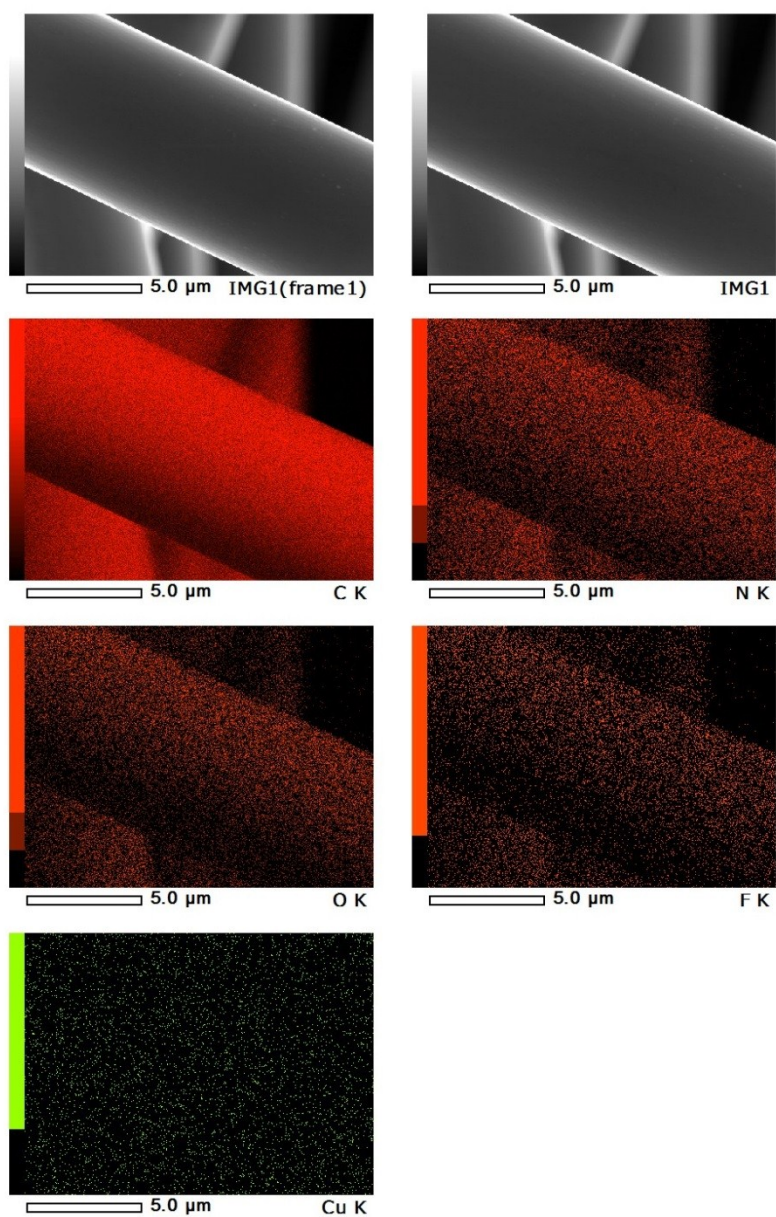
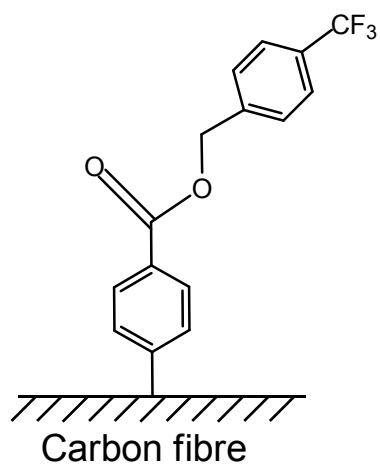




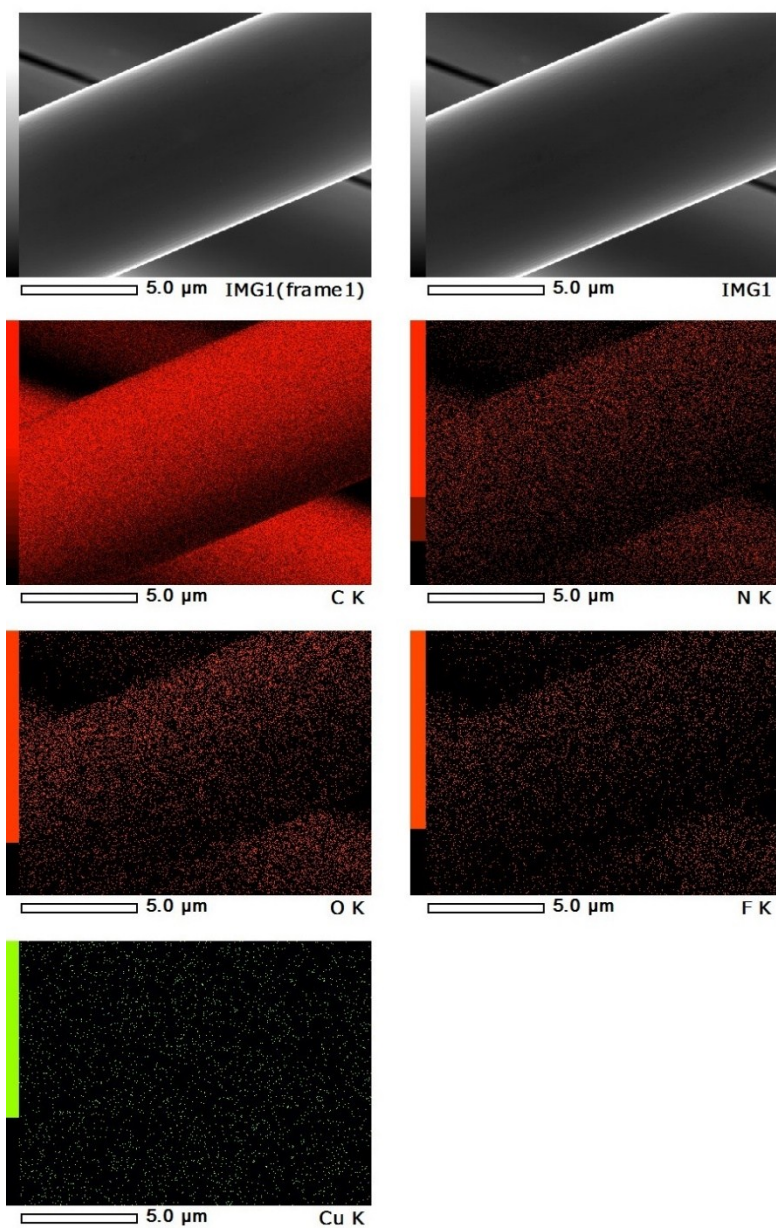
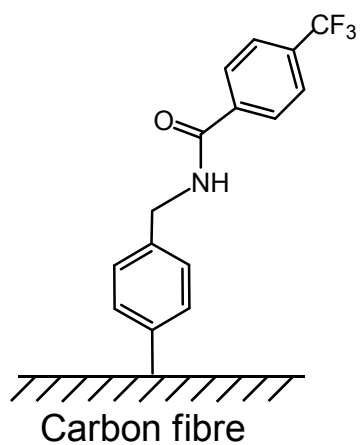
**Figure S20.** Chemical mapping performed on functionalized carbon fiber sample (structure is shown above).



**Figure S21.** Chemical mapping performed on functionalized carbon fibre sample (structure is shown above).

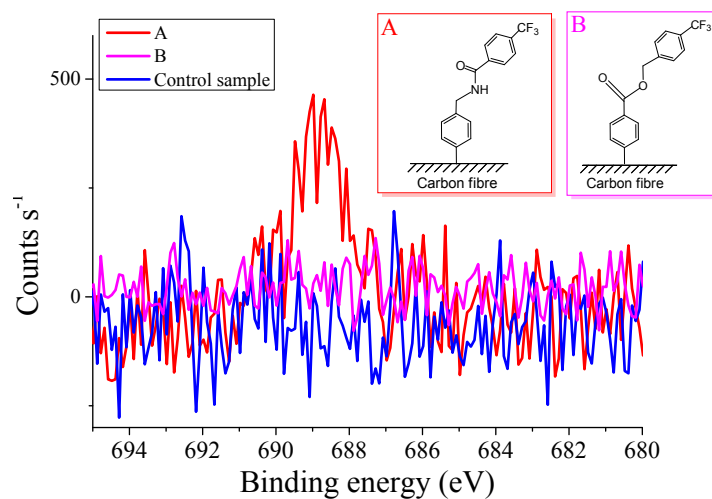


**Figure S22.** Chemical mapping performed on functionalized carbon fibre sample (structure is shown above).

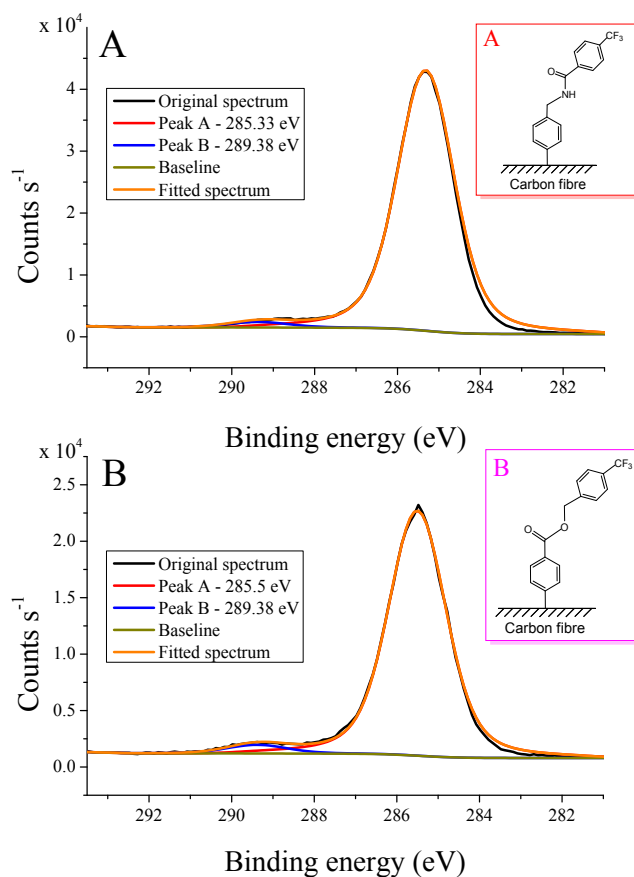


**Figure S23.** Chemical mapping performed on functionalized carbon fibre sample (structure is shown above).

## 10. XPS spectra of functionalized carbon fibre derivatives

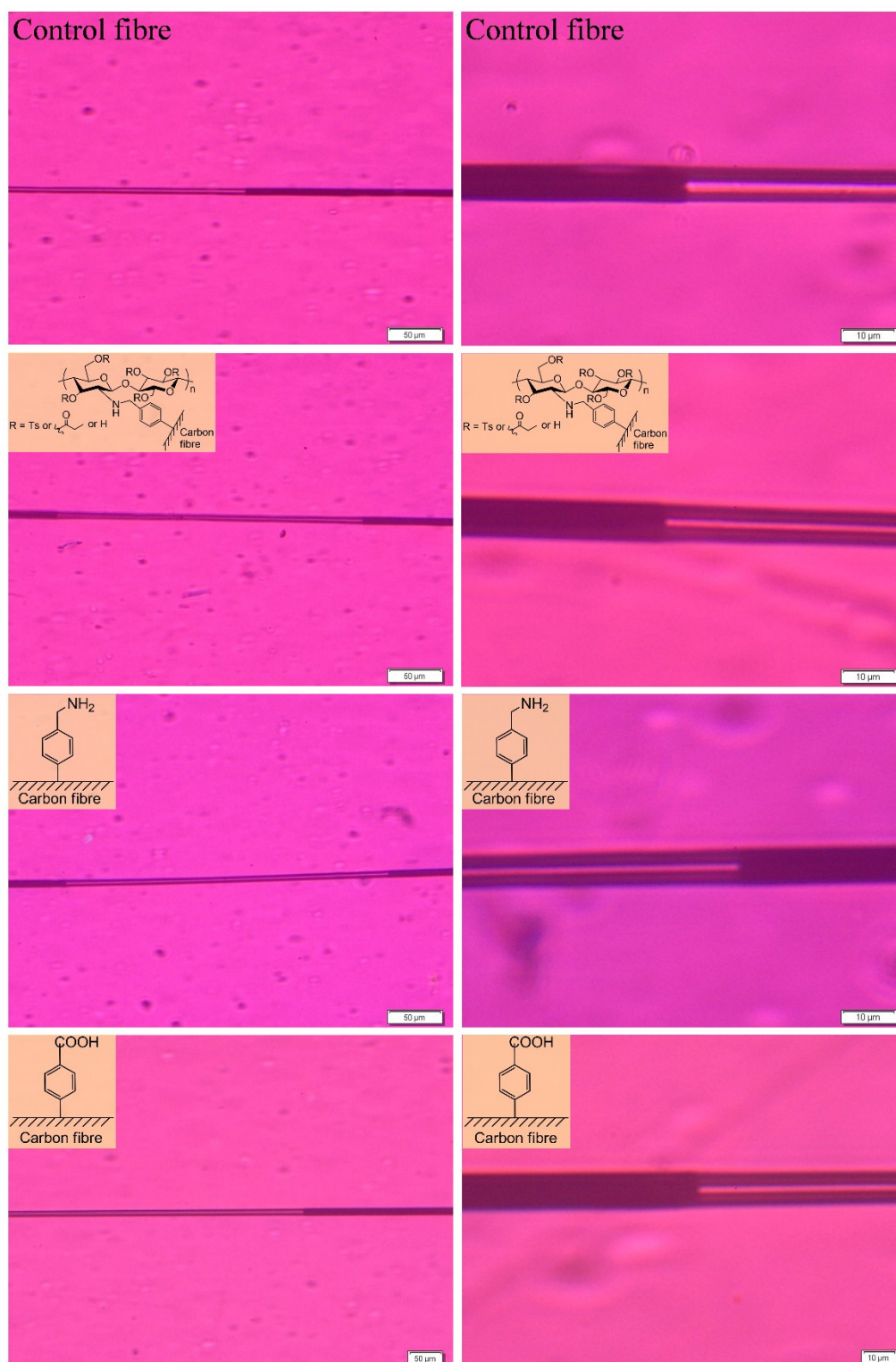


**Figure 24.** High-resolution F1s spectra of carbon fibre samples.

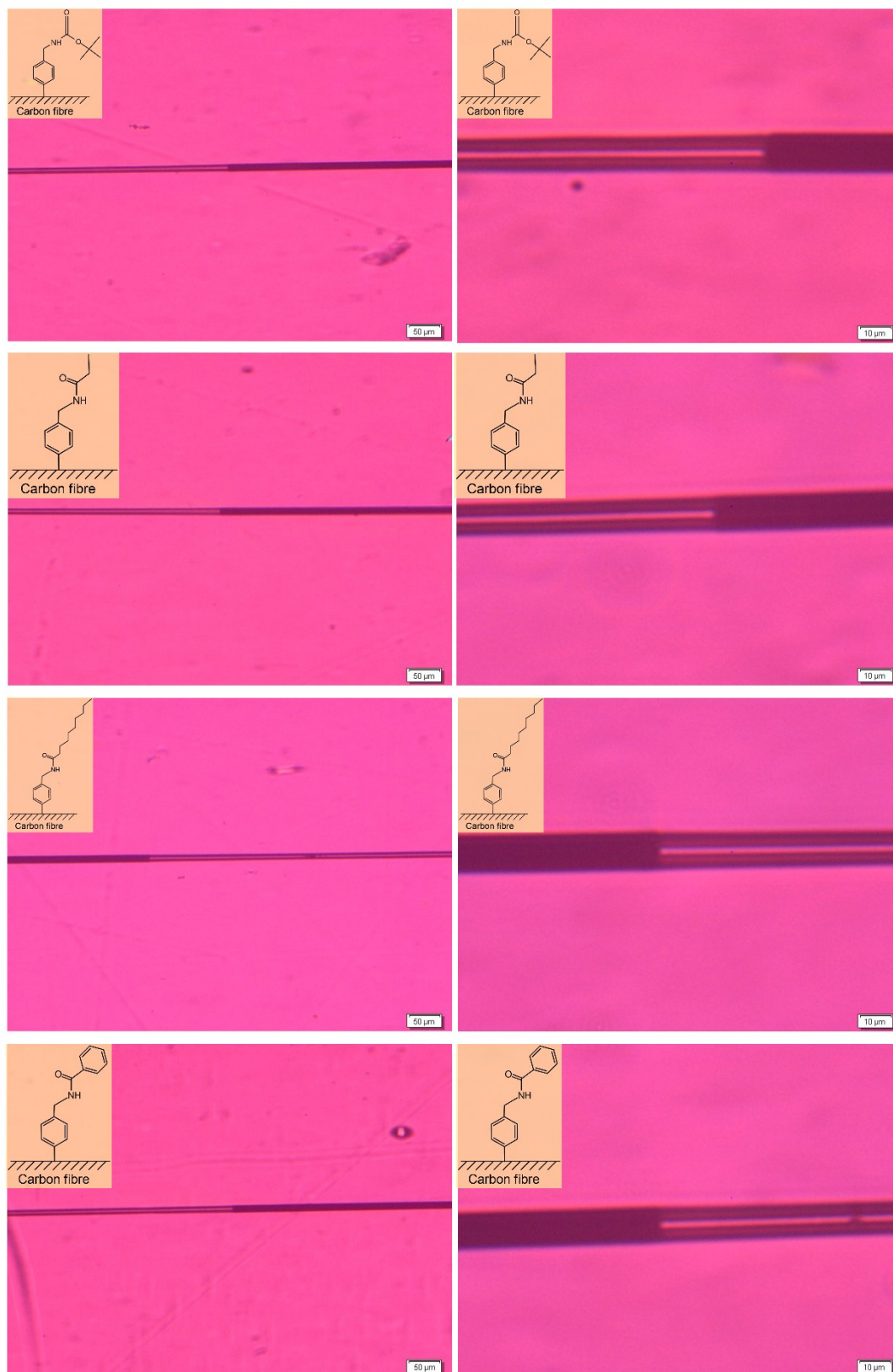


**Figure 25.** High-resolution C1s spectra of carbon fibre samples functionalized via N-acylation (A) and O-alkylation (B).

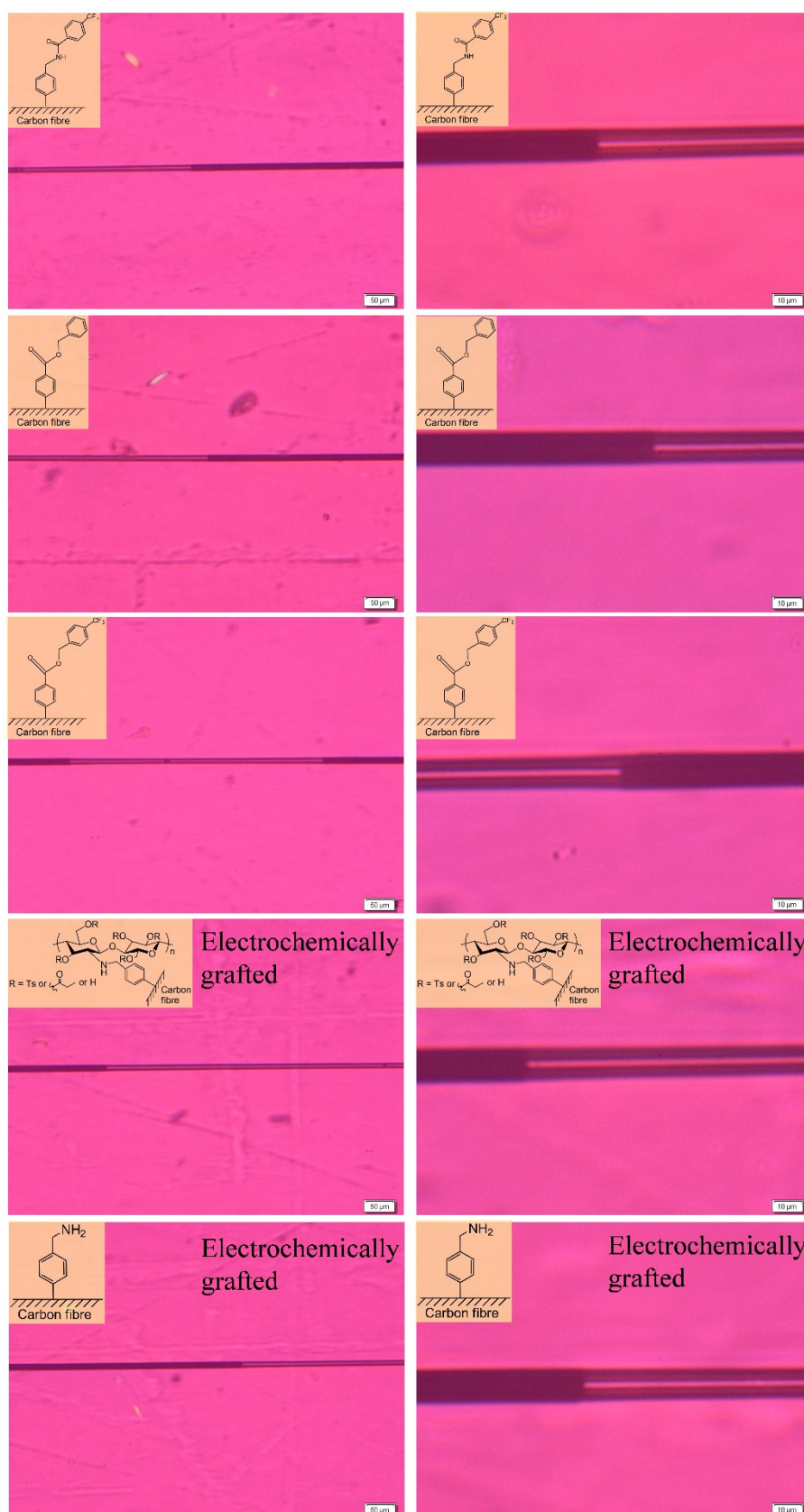
## 11. Optical microscopy



**Figure S26.** Optical micrographs of micromechanical failure at the saturation in the fragmentation test (samples from Figure 7).



**Figure S27.** Optical micrographs of micromechanical failure at the saturation in the fragmentation test (samples from Figure 8).

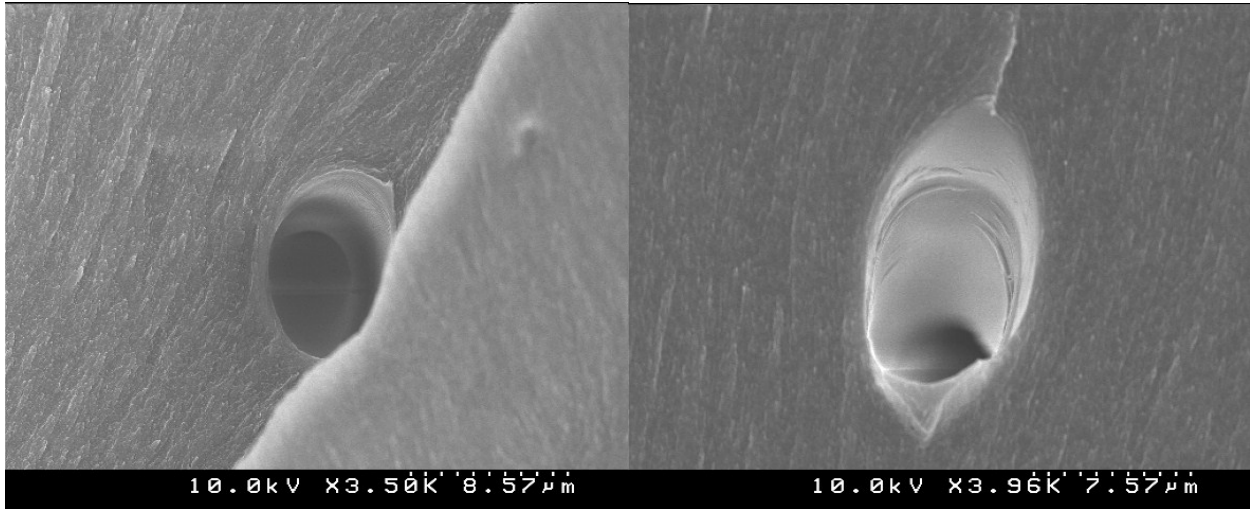


**Figure S28.** Optical micrographs of micromechanical failure at the saturation in the fragmentation test (samples from Figure 8 and 9).

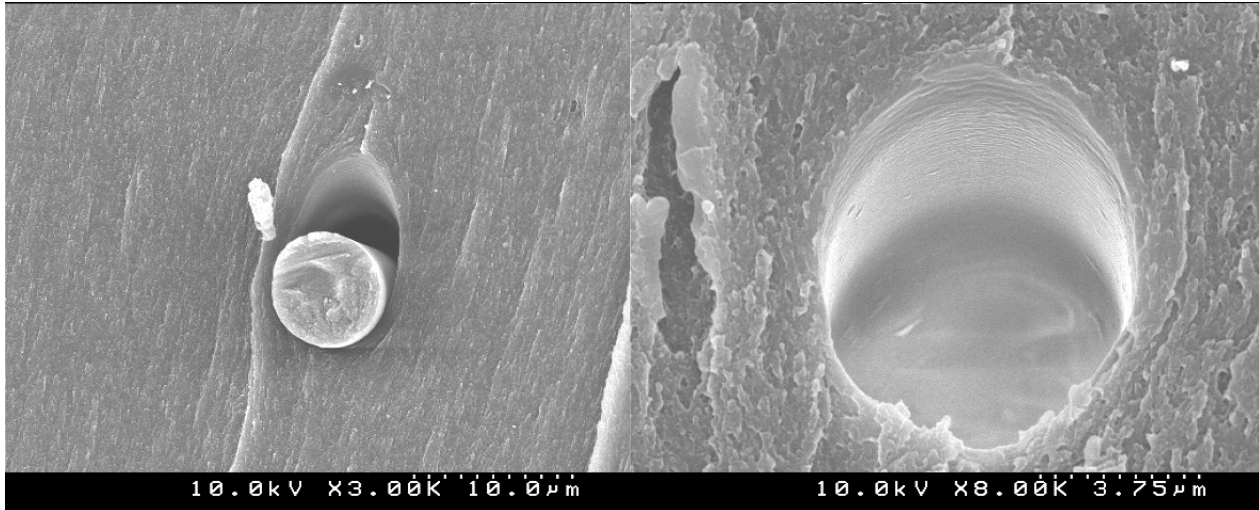


## 12. Fracture surfaces of single fibre composites

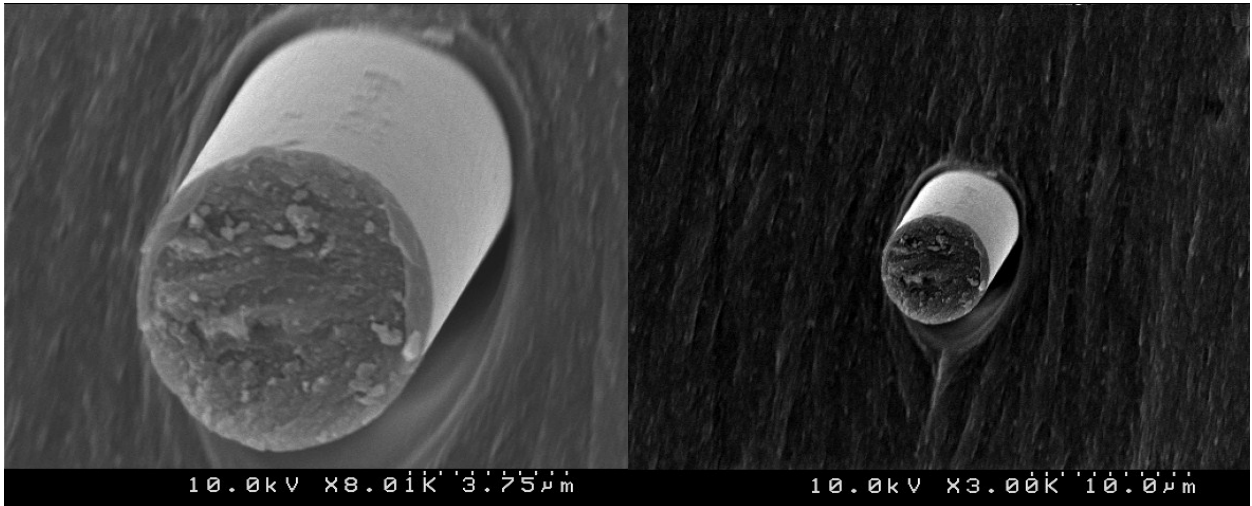
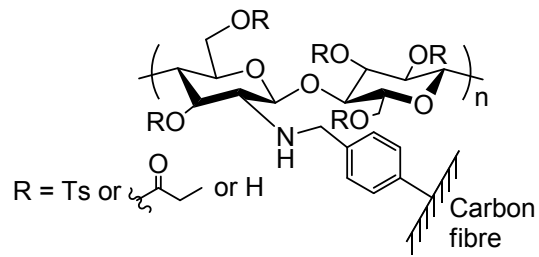
1. Fracture surfaces of two samples after the fragmentation test. Carbon fibre T700SC was used as single fibre. After delamination the fibre leaves a hole behind.



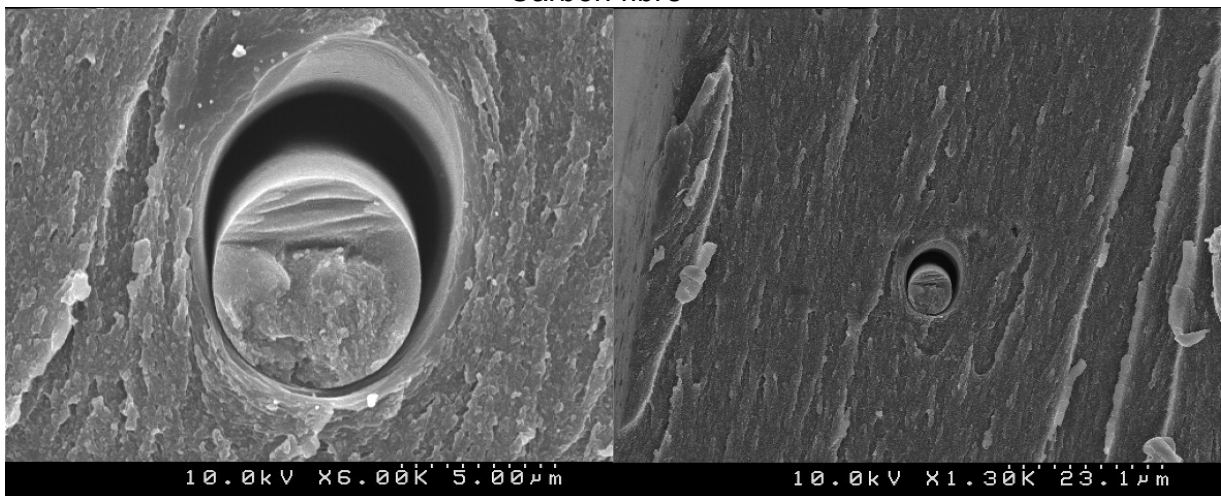
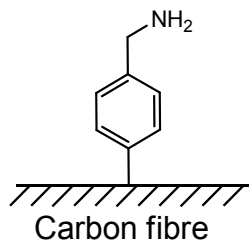
2. Fracture surfaces of two samples after the fragmentation test. Single fibre was a control sample prepared by cleaning carbon fibre T700 exhaustively (for further details please see the manuscript).



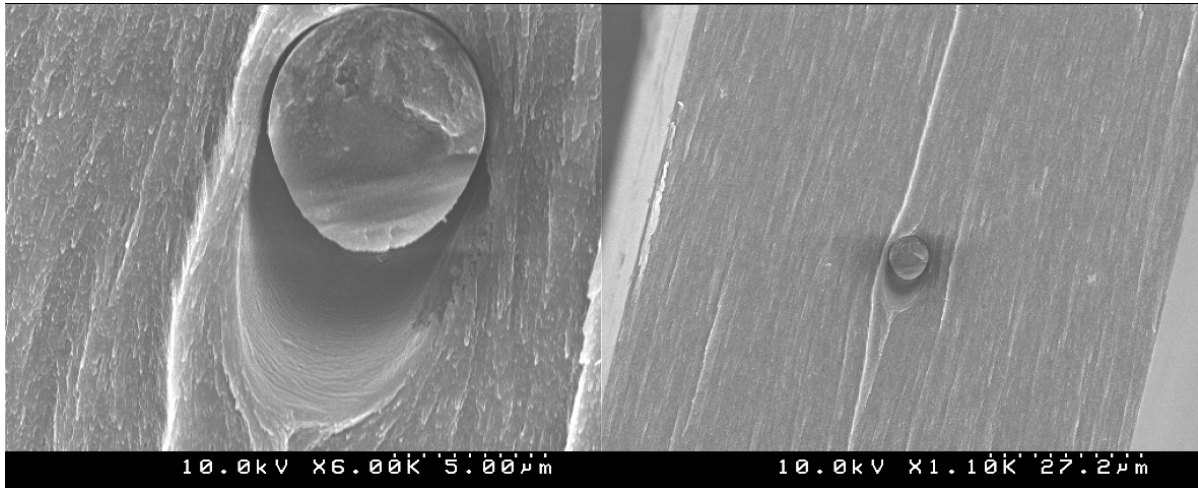
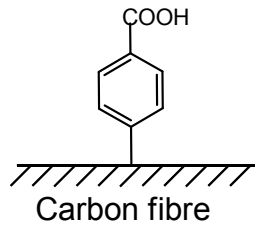
3. Fracture surfaces after the fragmentation test. Single fibre was functionalized as shown below on the structure.



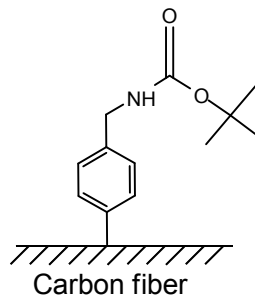
4. Fracture surfaces after the fragmentation test. Single fibre was functionalized as shown below on the structure.



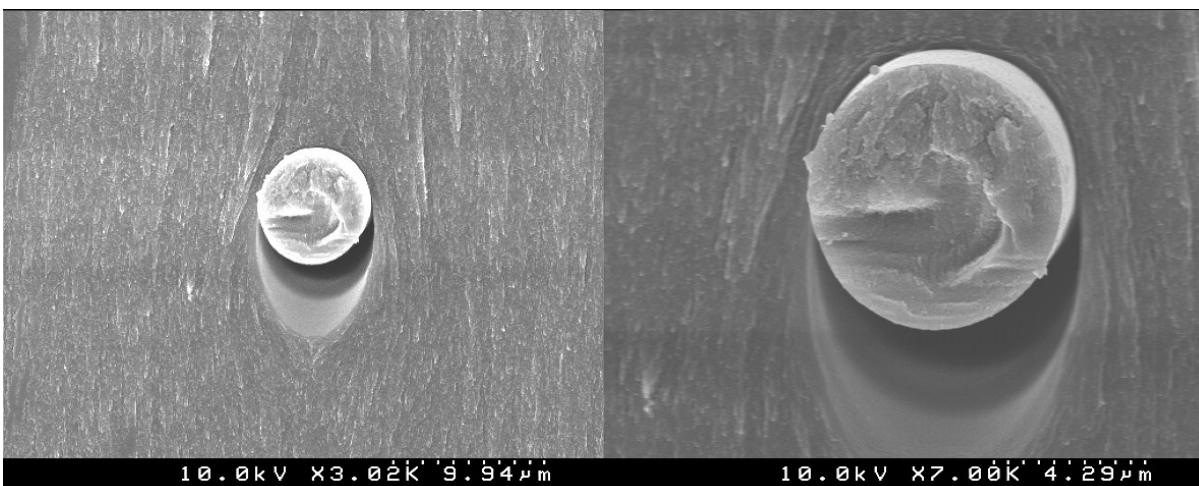
5. Fracture surfaces after the fragmentation test. Single fibre was functionalized as shown below on the structure.

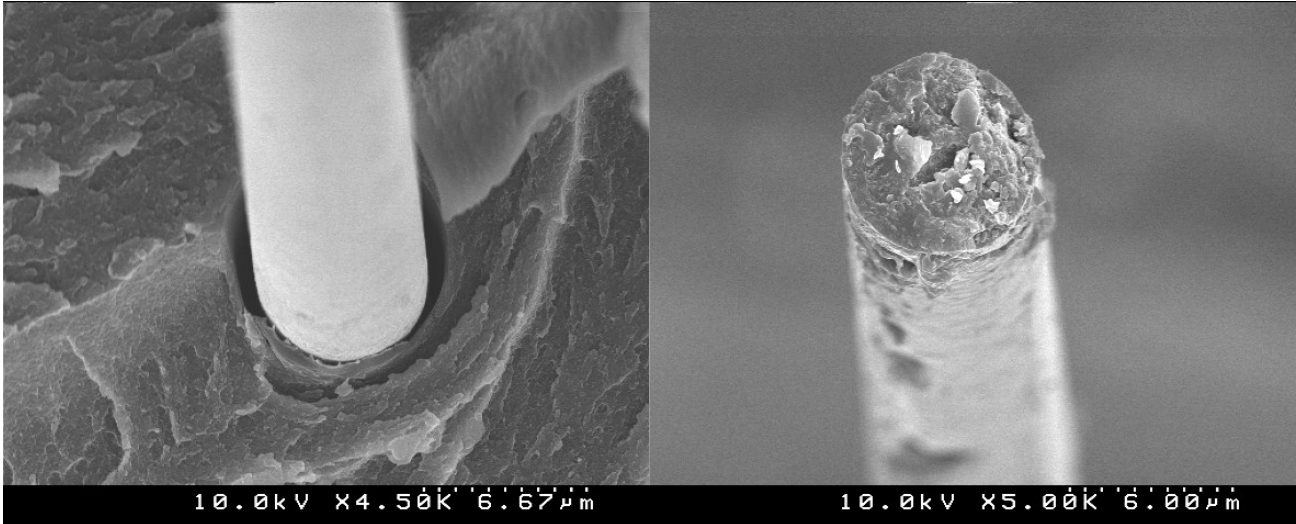
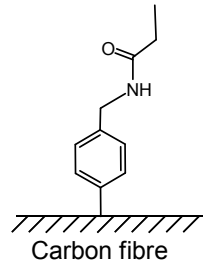


6. Fracture surfaces after the fragmentation test. Single fibre was functionalized as shown below on the structure.

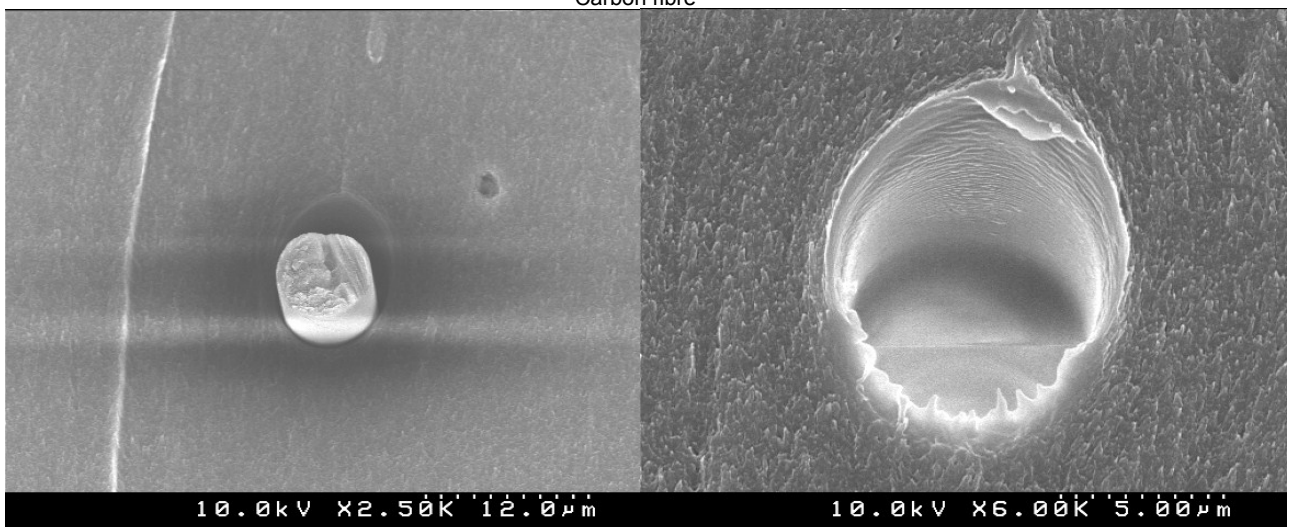
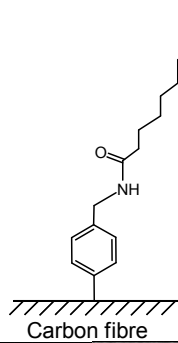


7. Fracture surfaces after the fragmentation test. Single fibre was functionalized as shown below on the structure.

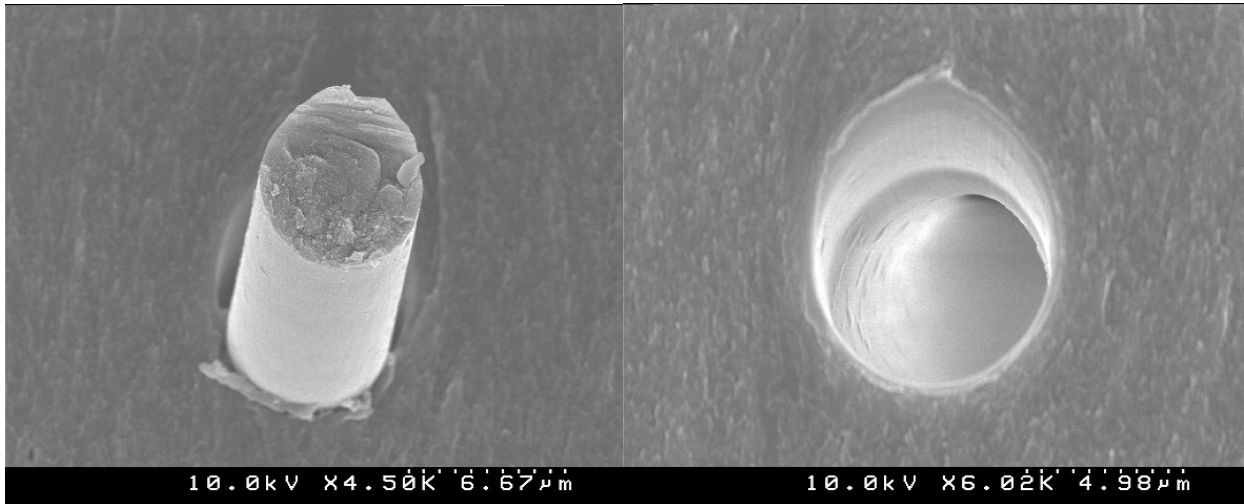
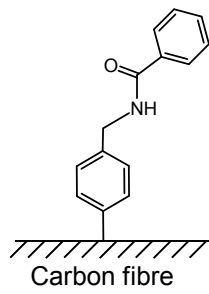




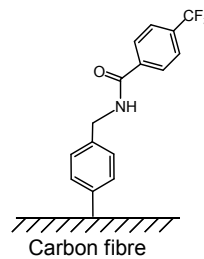
8. Fracture surfaces after the fragmentation test. Single fibre was functionalized as shown below on the structure.



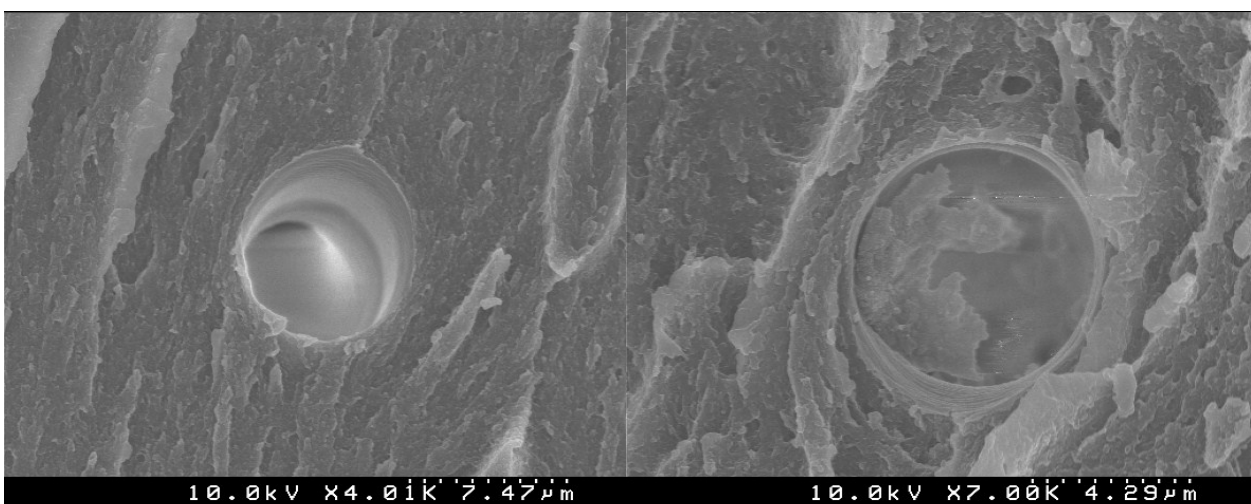
9. Fracture surfaces after the fragmentation test. Single fibre was functionalized as shown below on the structure.

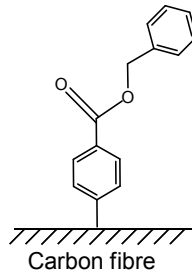


10. Fracture surfaces after the fragmentation test. Single fibre was functionalized as shown below on the structure.

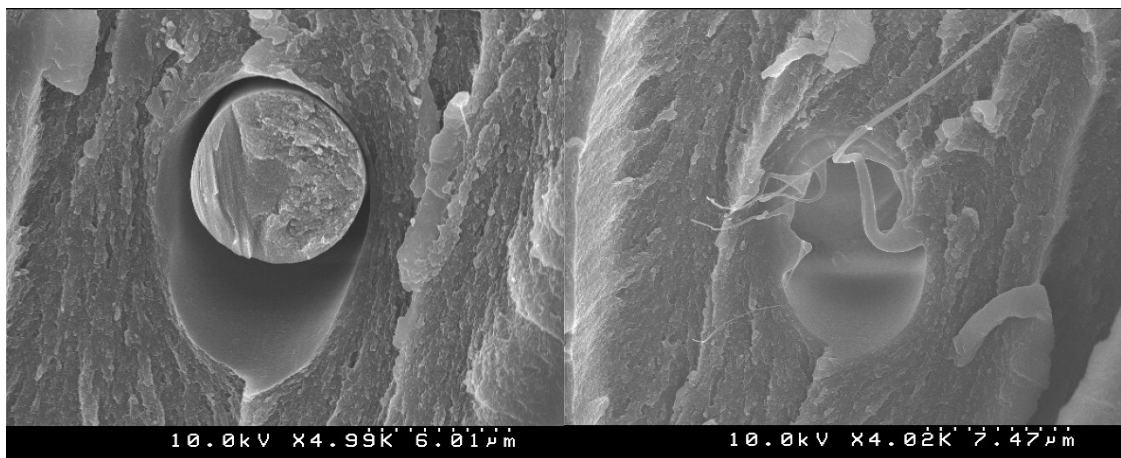
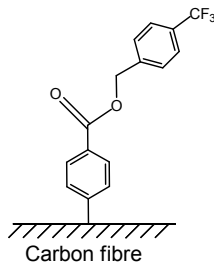


11. Fracture surfaces after the fragmentation test. Single fibre was functionalized as shown below on the structure.

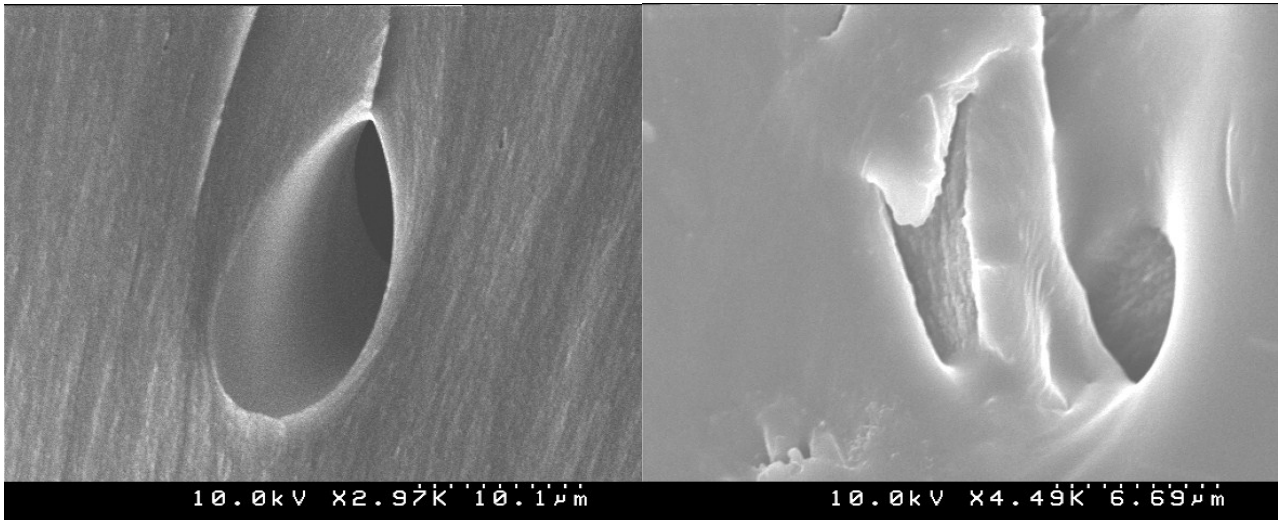
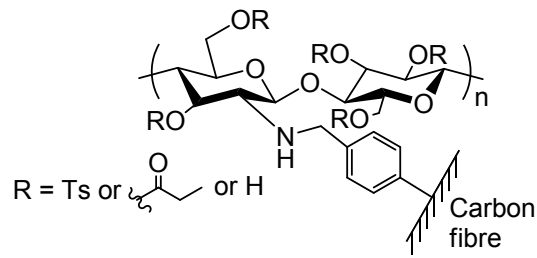




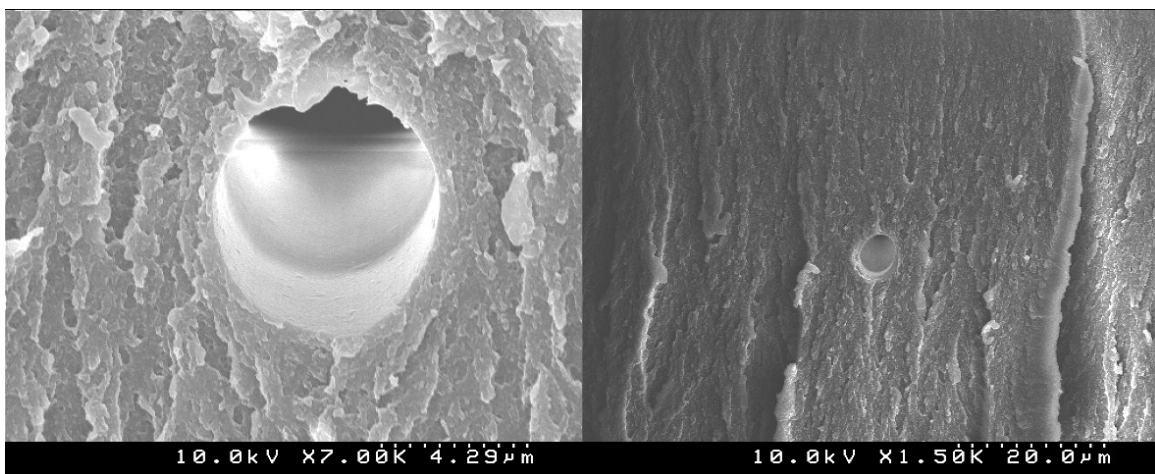
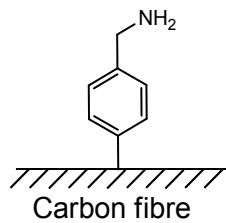
12. Fracture surfaces after the fragmentation test. Single fibre was functionalized as shown below on the structure.



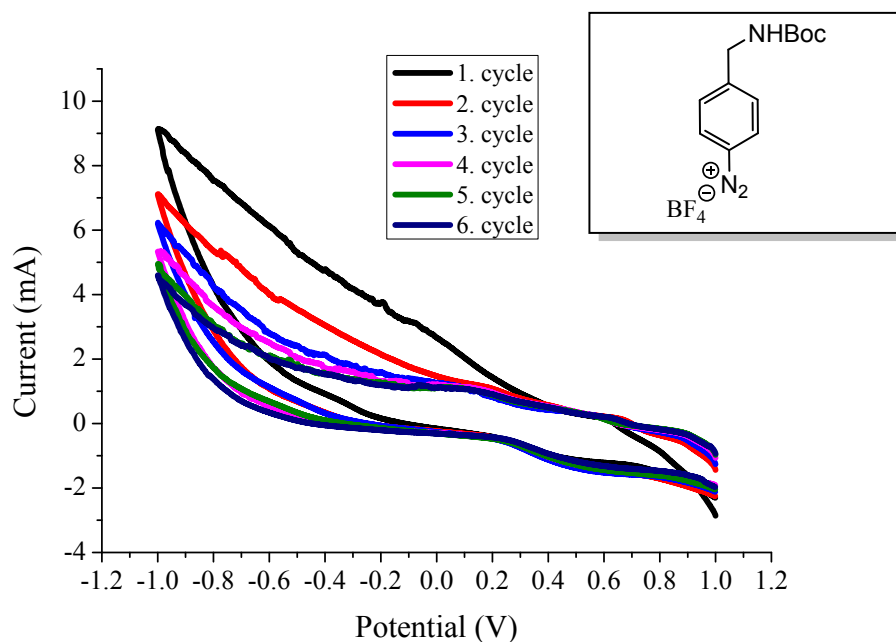
13. Fracture surfaces after the fragmentation test. Single fibre was functionalized as shown below on the structure using electrochemical grafting procedure.



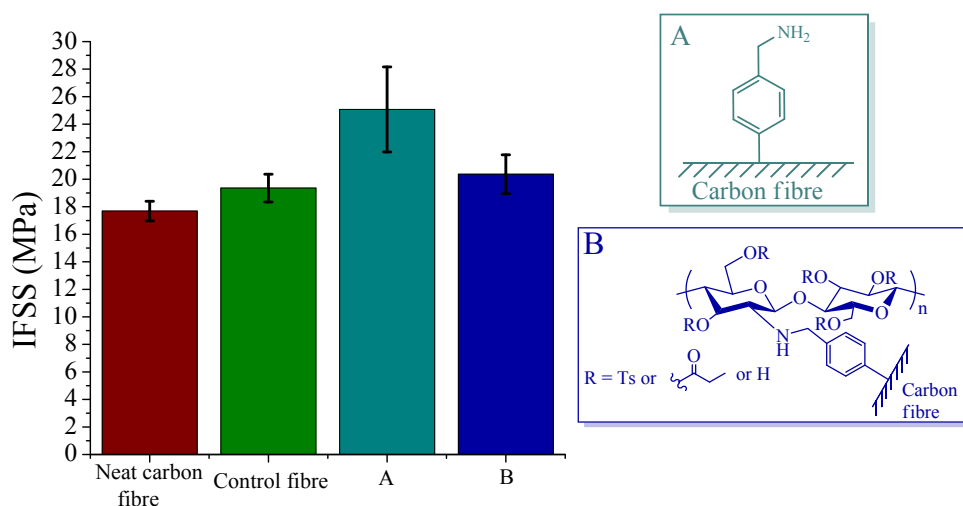
14. Fracture surfaces after the fragmentation test. Single fibre was functionalized as shown below on the structure using electrochemical grafting procedure.



### 13. Cyclic voltammogram



**Figure S29.** Cyclic voltammogram for grafting the corresponding diazonium salt (shown in the top-right) on the carbon fibre surface.



**Figure S30.** Interfacial shear strength (IFSS) of carbon fibre reinforced cellulose composites - electrochemical grafting. Neat carbon fibre denotes carbon fibre T700 as received, with sizing agent on the surface.



## 14. References

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