Supporting Information

Chemically reactive spinning dope for significant improvements in wet spun carbon nanotube fibres

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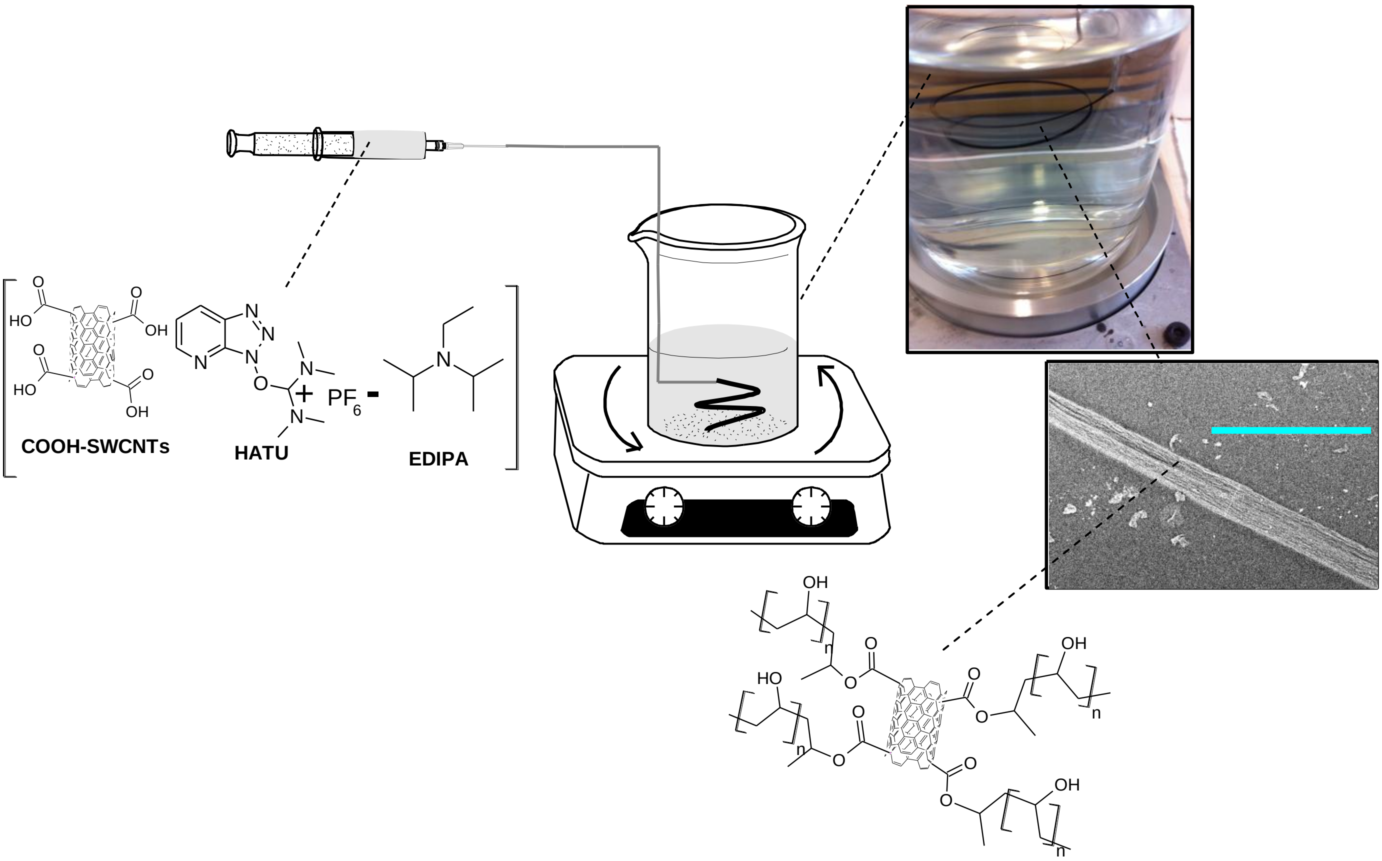

Scheme 1. Diagram representing the fibre spinning setup, the chemical approach, real image of the coagulated-spun fibres (upper right) and a scanning electron microscopy image of the 'COOH act. +' fibre sample (rightmost image), whose scale bar (in cyan) corresponds to 200 μm.

Experimental

Materials and Reagents: SWCNTs (AP-SWNT grade) were purchased from Carbon Solutions Inc., Riverside, California. This SWCNT powder material is synthesized by the electric arc reactor method using Ni/Y catalyst and contains ~30 wt.% metal residue.

These SWCNTs were purified in-house by air oxidation (350ºC, 2h) followed by reflux in HCl (3M, 2h). Purified SWCNTs were taken as the starting material and their fibres were considered as the baseline for comparative purposes. PVA was acquired from Kuraray America Inc., in the form of Mowiol® commercial product (195000 g/mol, 98 mol.% hydrolysis rate). PVA aqueous solution was prepared at 5 wt% by slowly dissolving solid PVA in deionized water at 90ºC under constant magnetic stirring for 45 min, and leaving the solution to cool down in ambient conditions. HATU and EDIPA were purchased from Sigma Aldrich in reagent grade, and used without further purification.

SWCNT functionalization, dispersion and activation: Purified SWCNTs were subjected to a wet oxidative treatment by reflux in a 3M H_2SO_4 / HNO_3 mixture (50:50 ratio, 3h). Then, after rinsing with deionized water and oven-drying, the obtained material was dispersed in sodium dodecyl sulphate (SDS). Characterization of these SWCNTs can be found in Supporting Information. The dispersion process was carried out in batches of 10g, in which SWCNTs (either purified or carboxylated) were added at 0.5wt% and SDS at 1wt% (the term ‘0.5%’ in samples nomenclature alludes to the initial SWCNTs ratio in the dispersion process, despite it does not reflect the final ratio wthin PVA fibres). This mixture was tip-sonicated (Branson 250A, 40W) for 1.5h at 25% amplitude and externally cooled with a water/ice bath. Then, the dispersion was centrifuged at 3000 rpm for 30 min and the supernatant was carefully decanted. These supernatants were directly injected into the coagulation spinning system to fabricate PVA composite fibres. In the cases where covalent linking was intended, these supernatants were treated before the fibre formation. For this purpose, ~8 mg (12 eq.) of HATU were dissolved in the supernatant containing SDS-dispersed carboxylated SWCNTs by stirring in a water/ice bath for 45 min. Afterwards, 240 μL of EDIPA were added to the cooled mixture and stirring was kept during 2h. Then, the supernatant was used to fabricate fibres without further treatment. A blank sample containing EDIPA but not HATU was identically prepared for comparative purposes (so-called ‘Blank EDIPA’).

Fibre manufacturing: The process by which PVA fibres were produced was that proposed by Vigolo et al.[1] Briefly, it consists in the controlled injection of the SDS-dispersed SWCNT supernatants (at 50 mL/h rate) through a 1.2 mm diameter needle into a rotating bath of 5 wt.% PVA solution (100 rpm). The needle was horizontally aligned with the bath diameter and set at about 2 cm from the edge. Upon injection, the SDS dispersion collapses by effect of the PVA stream and the fibre is formed. Around 10 cm-long fibres were produced in periods of 3s injection. These fibres were transferred to a deionized water bath at room temperature, left there for several minutes, and then hanged to an elevated platform. By sequentially lifting up the platform, the fibres were slowly pulled out from the water bath and thus dried at ambient conditions. In attempt to assess the influence of the contact time in the PVA bath, one sample was left inside the PVA bath for 24h before proceeding to its washing and drying (so-called ‘COOH act. +’).

Characterization techniques: FTIR spectra were obtained with a Bruker Vertex 70 instrument. All the samples were prepared as pellets by cryo-milling and compression with spectroscopic grade KBr. XPS spectra were registered with an ESCAPlus Omicron spectrometer using a monochromatized Mg X-ray source (1253.6 eV). The analysis area was 1.75mm×2.75mm. Peak deconvolutions were carried out using Gaussian/Lorentzian (75/25) functions with no asymmetry corrections. Tensile

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1 B. Vigolo, A. Penicaud, C. Coulon, C. Sauder, R. Pailler, C. Journet, P. Bernier, P. Poulin, *Science* 2000, **290**, 1331.

mechanical properties were measured to ~4 cm-long pieces of fibre, in a Zwick Z2.5/TN1S equipment, at a strain rate of 1 mm/min, which approximately corresponds to a strain rate of 2.5%/min. All those samples that did not break around the central region were automatically discarded. At least five successful measurements were utilized to obtain average values. Electrical resistance values were obtained with a Keithley 6221 source, in a two-point probe configuration, to small pieces of fibre (at least five) which were previously attached to a glass slide by using silver painting in their extremities. Electrical resistivity values were calculated from resistance data through normalization according to fibre length and section diameter. SEM images were taken with a Hitachi TM1000 device, provided with tungsten filament, and with an acceleration voltage of 15kV. Different magnifications were checked, ranging from 30X to 10000X. Fibre samples were not coated with any metal prior to their observation as they showed sufficient conductivity. Raman spectroscopy was performed with a HORIBA Jobin Yvon Raman spectrometer model HR 800 UV, working with a 532 nm laser (working at 25 mW). The spectra were analyzed, base-line corrected and normalized with the NGS LabSpec software. The calculations of the *S* parameter were performed over an average of 5-7 specimens in each sample. Thermogravimetric analyses (TGA) were performed under nitrogen atmosphere (60 mL/min flow), and registered with a SETARAM Setsys Evolution 16/18 device at a heating rate of 10ºC/min.

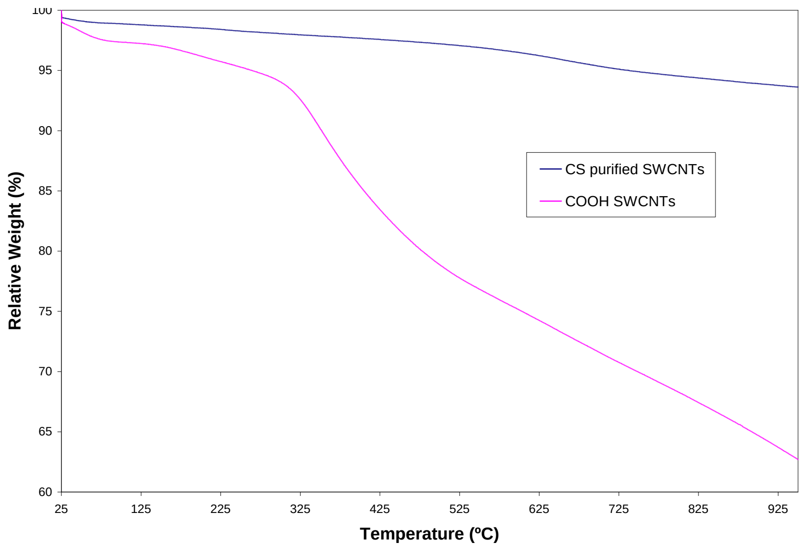

Figure S1. TGA plots for the two kinds of SWCNTs employed in this study

From these thermograms it can be seen that CS-SWCNTs possess a very low of functional groups in their surface. The oxygen groups incorporated upon air oxidation are mostly removed during the HCl reflux. However, the remaining groups are not negligible, as observed in FT-IR spectra. The COOH-SWCNTs present a large amount of surface groups, which are thermally desorbed during thermal treatment. One can estimate the COOH amount by considering their release to be happening at 150-300 ºC. With this, and the molecular weight of the COOH moiety,[2] we would have a nominal content on carboxylic groups of 0.66 mmol/gSWCNT. However, between 300 and 500ºC, there is a visible weight loss which corresponds to the desorption of other oxygen groups, mostly quinones, phenols and acid anhydrides.[3] Specifically, these latter groups, are able to spontaneously hydrolyze in aqueous medium to yield carboxylic acid groups, so the effective content in COOH is expected to be higher than initially

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[2] A. Anson-Casaos, J. M. Gonzalez-Dominguez, E. Terrado, M. T. Martinez, *Carbon* **2010**, *48*, 1480.

[3] a) P. Canete-Rosales, V. Ortega, A. Alvarez-Lueje, S. Bollo, M. Gonzalez, A. Ansón, M. T. Martinez, *Electrochim. Acta* 2012, **62**, 163; b) A. Ansón-Casaos, M. Gonzalez, J. M. Gonzalez-Dominguez, M. T. Martinez, *Langmuir* **2011**, *27*, 7192-7198.

estimated. Thus, the added reagents for the esterification reaction were put in enough excess according to this fact.

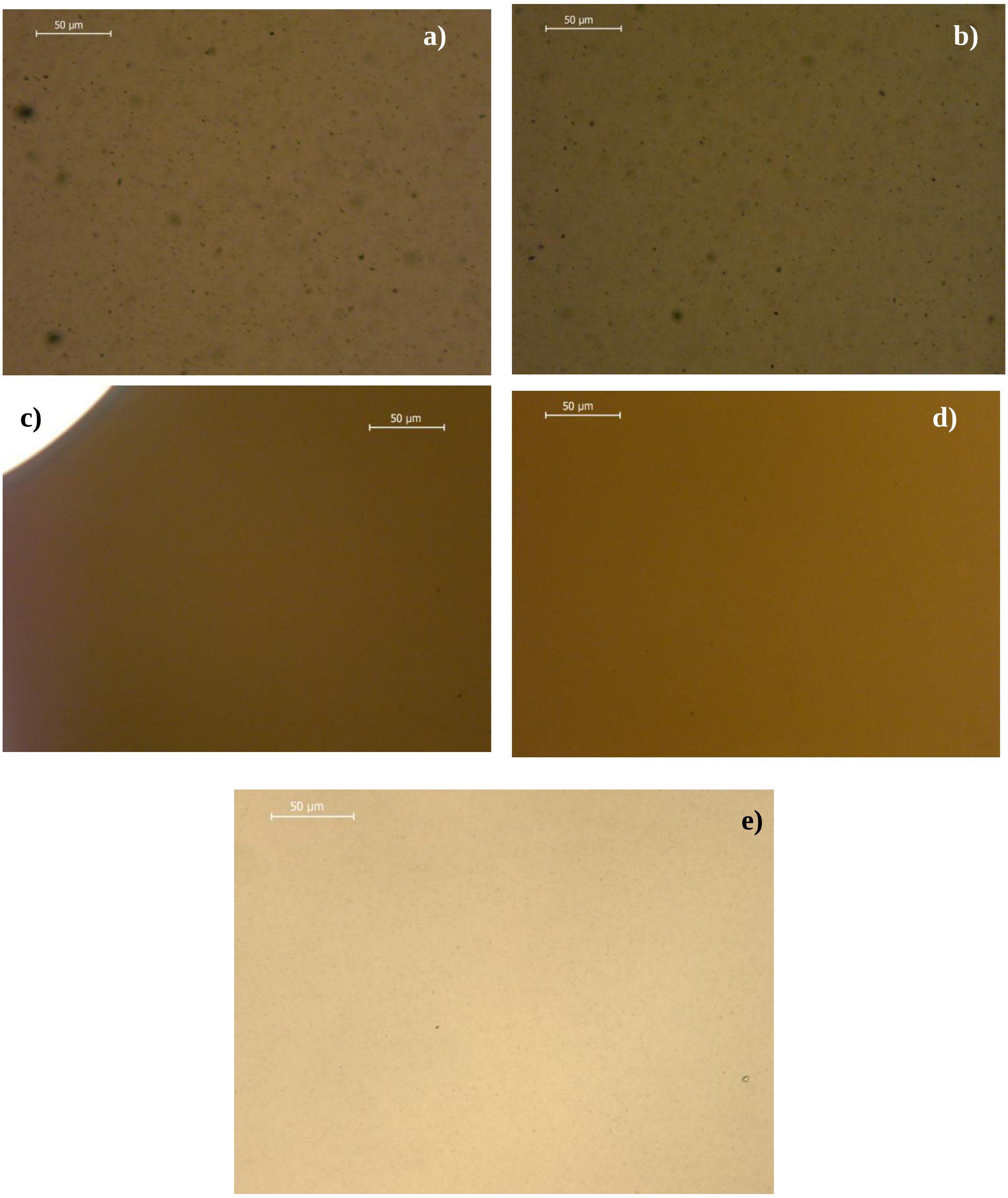

Figure S2. Optical images of several SWCNTs dispersions in SDS. a) CS-SWCNTs at 0.5 wt% nanotubes; b) COOH-SWCNTs at 0.5 wt% nanotubes; c) the supernatant liquid obtained after centrifugation of sample depicted in S2a; d) the supernatant liquid obtained after centrifugation of sample depicted in S2b; e) the supernatant liquid in S2d after adding HATU and EDIPA.

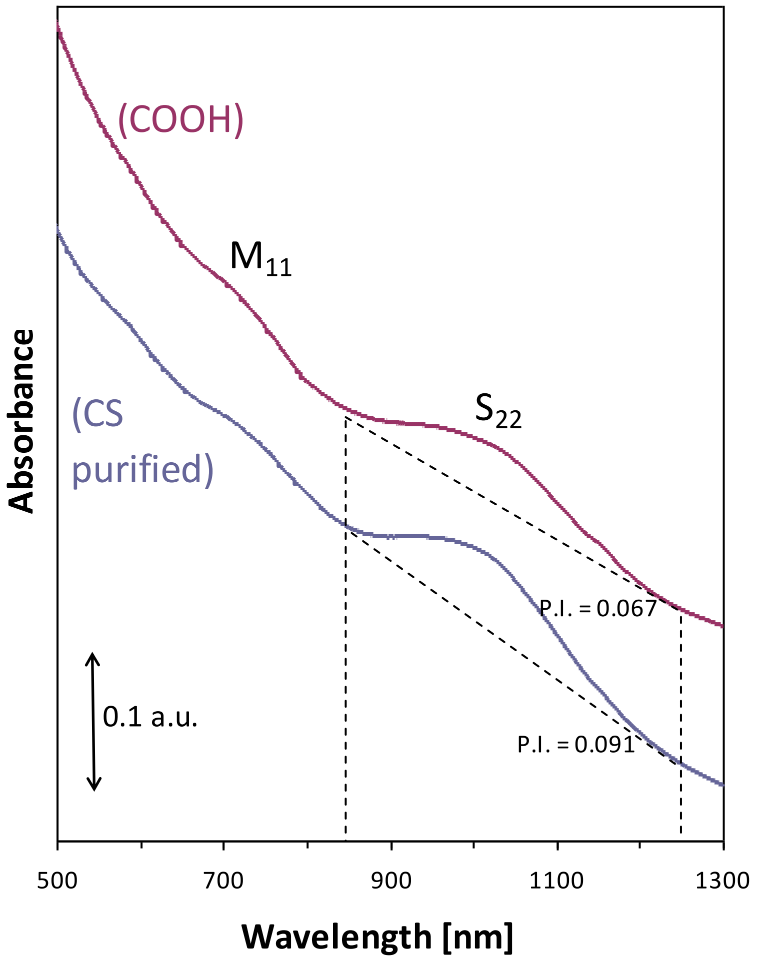

Figure S3. Vis/NIR absorption spectra of CS-SWCNTs and COOH-SWCNTs and their corresponding P.I. values. Transitions corresponding to semiconductor (S_{22}) and metallic (M_{11}) SWCNTs are observable.

The supernatants obtained after centrifugation at 3000 rpm have been spectroscopically characterized in the Vis/NIR region by applying the Itkis method.[4] In this way, we were able to obtain the so-called 'Purity Index' (P.I.) of each dispersion (consisting of the ratio between the peak area and the full area under the curve in the S_{22} semiconductor transition), which is related to the amount of isolated / individually-suspended SWCNTs and the carbonaceous purity of the sample after dispersion (since the final SWCNT wt% will vary from the initially set due to centrifugation). From Fig. S3 it is visible that the CS purified SWCNTs retain more nanotubes in suspension after the dispersion process

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[4] M. E. Itkis, D. E. Perea, R. Jung, S. Niyogi, R. C. Haddon, *J. Am. Chem. Soc.* **2005,** *127*, 3439-3448.

than their carboxylated counterparts. This could be ascribed to the worse dispersibility of acid-treated SWCNTs due to sample compaction caused by oxygen groups.[2,5] It is worth noting that, consequently, the SWCNT concentration (despite being unknown) will be lower in COOH-SWCNTs as compared to the CS ones.

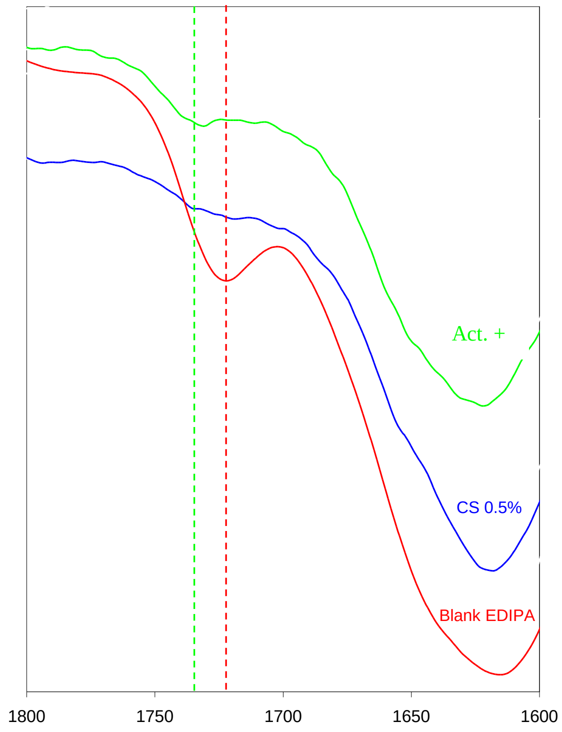

Figure S4. Magnification of FT-IR spectra of SWCNT/PVA fibres in the region of the carbonyl bands.

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[5] a) M. T. Martinez, M. A. Callejas, A. M. Benito, M. Cochet, T. Seeger, A. Anson, J. Schreiber, C. Gordon, C. Marhic, O. Chauvet, J. L. G. Fierro, W. K. Maser, *Carbon* 2003, **41**, 2247; b) J. M. Gonzalez-Dominguez, A. Ansón-Casaos, A. M. Díez-Pascual, B. Ashrafi, M. Naffakh, D. Backman, H. Stadler, A. Johnston, M. A. Gomez, M. T. Martinez, *ACS Appl. Mater. Interfaces* 2011, **3**, 1441.

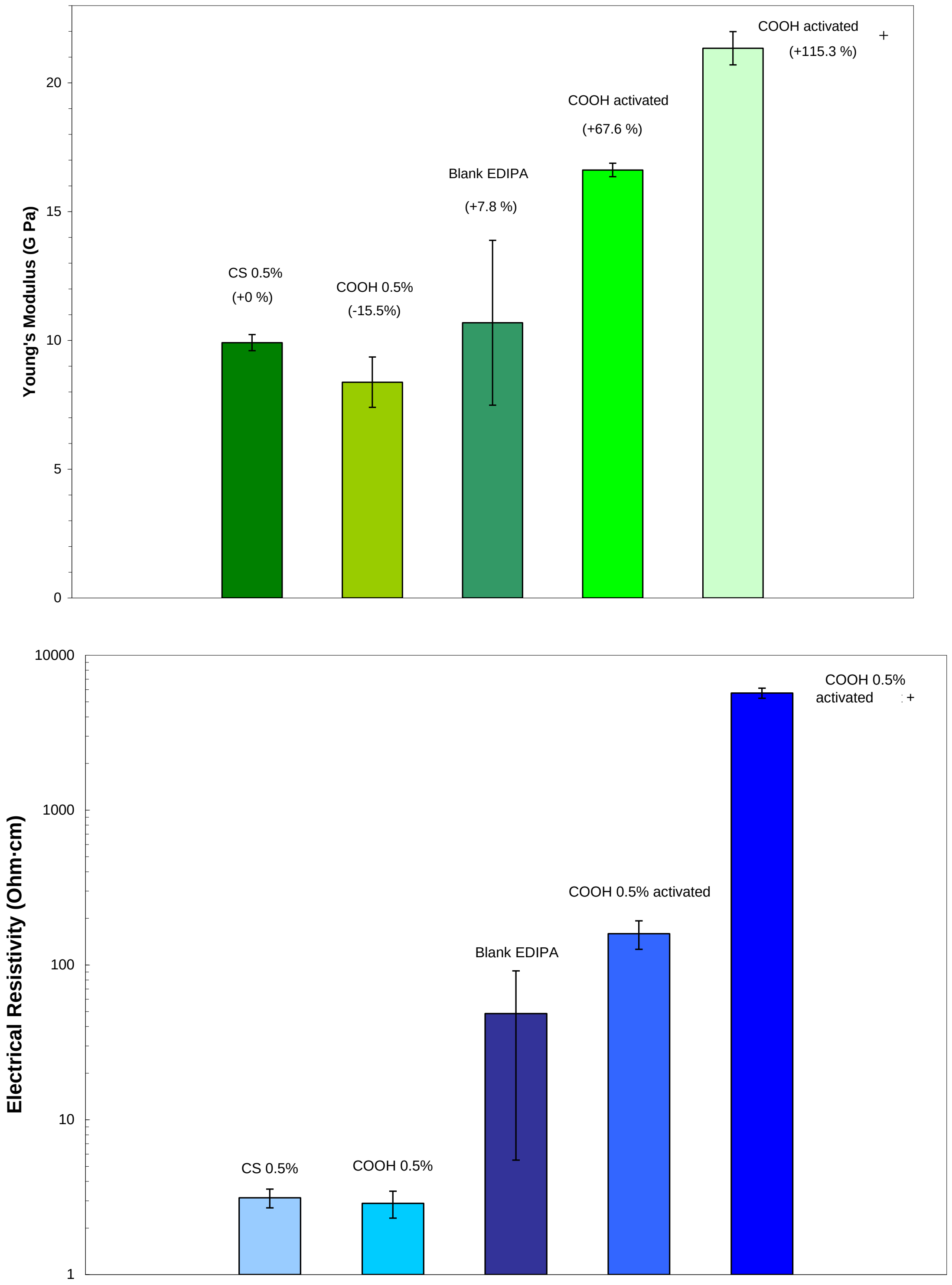

Figure S5. Mechanical (YM) and electrical (resistivity) measurements in all nanocomposite fibre samples. The percentages in YM graphic correspond to the improvements attained in comparison to the CS baseline fibre.

The Young’s Modulus (YM) value for the baseline fibre sample, which contains CS-SWCNTs, is 10GPa. This belongs to the same order than those YMs obtained for conventional fibres without physical post-treatments.[1] For ‘COOH 0.5%’ fibres, however, this value slightly decreases (-15.5% in comparison to the ‘CS 0.5%’ fibre, see Supporting Information), probably due to the lower effective content in SWCNTs in this sample or the SWCNT partial degradation after carboxylation. As seen for tensile strength, PVA fibres covalently bound to SWCNTs exhibit dramatic increases in YM, ultimately reaching a 115% increase (for ‘COOH act. +’) regarding the baseline fibre. This represents a significant improvement, considering that there was no post-treatment, so this is exclusively ascribed to the ester bonds.

On the other hand, the electrical resistivity values of these fibres were consistent with mechanical measurements. An increase of up to ~3 orders of magnitude was observed for the covalently-bound fibres, pointing to greater level of SWCNT integration and intimate contact with the PVA matrix (which would wrap around and isolate SWCNTs, obstructing the conductive pathways formation); and also, to a higher degree of alignment (as will be shown below), as it could happen in hot-drawn CNT/PVA films, which tend to lose electrical conductivity due to an excessive SWCNT alignment that hinders the intertube connection.[6]

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6 C. Mercader, P. Poulin, C. Zakri, in: Polymer/Carbon nanotube nanocomposites, Chapter 11th: *Synthesis and Properties of PVA/Carbon nanotube nanocomposites* 2010, Ed. Scrivener Publishing (Salem, USA), Wiley, 315-343, ISBN: 9780470625927.

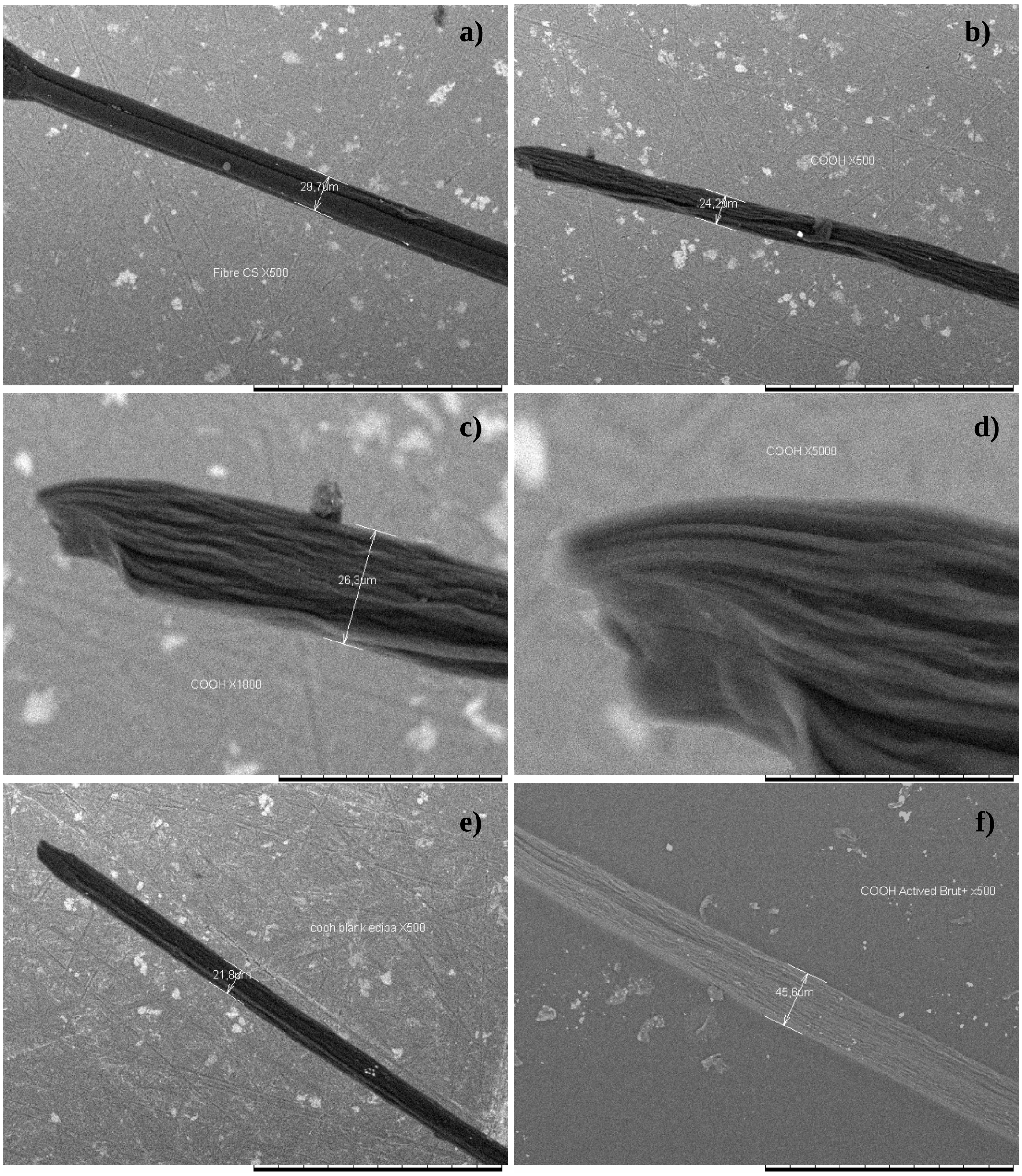

Figure S6. SEM images of different SWCNT/PVA fibre samples: a) CS, scale bar = 200 µm; b) COOH, scale bar = 200 µm; c) COOH, scale bar = 50 µm; d) COOH, scale bar = 20 µm; e) Blank EDIPA, scale bar = 200 µm; f) COOH act. +, scale bar = 200 µm.

Effect of the ester bonds in the SWCNTs orientation along the fibre

The esterification would aid the SWCNT orientation along the PVA stream during the injection process and also during the drying stage, improving their longitudinal alignment. Indeed, alignment is induced by shear during fibre spinning. The neat alignment of SWCNT in wet fibres results from a competition of Brownian diffusive rotation and shear forces. Brownian motion is reduced when the particles coagulate. Coagulation is expected to take place faster in the chemically reactive dope in comparison to non reactive materials. Therefore the effect of shear forces is likely to be more pronounced for the COOH act + materials. Nevertheless one has also to consider that shear-induced alignment is also partially lost during fibre drying when the nanotubes collapse to form a dried fibre. But again cross-linking is expected to favour a better alignment. Indeed, the loss of alignment during drying is likely to be reduced for the cross-linked fibres since nanotube rearrangements are limited by the presence of covalent bonds. The dominant mechanism is not yet known but the observed better alignment in COOH act + fibres would explain the results attained in mechanical and electrical properties.

These fibres could find use in advanced textiles and in electrochemical applications where creep is an issue. This includes for example electromechanical actuators.[7] Cross-linking is expected to reduce creep and to provide greater life expectancy. Nevertheless, it is also observed that cross-linking is associated to an increase in electrical resistivity (Fig. S5) which can lead to slower response times of actuators. Future work is needed to validate the potential for these applications.

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[7] L. Viry, C. Mercader, P. Miaudet, C. Zakri, A. Derre, A. Kuhn, M. Maugey, P. Poulin, *J. Mater. Chem.* 2010, **20**, 3487

SWCNT content within fibres

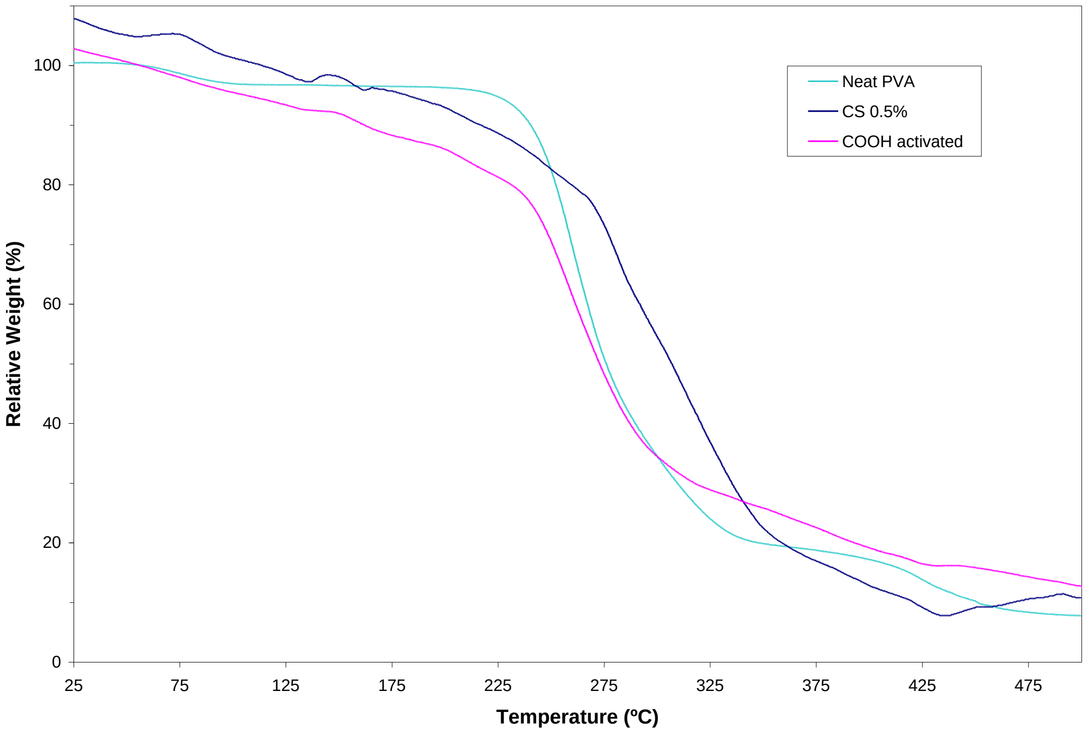

Figure S7. TGA curves for neat PVA and two representative fibre samples

The composition of the studied fibres (in terms of SWCNT and PVA percentage) was ascertained by using thermogravimetric analysis in inert atmosphere. In Fig. S7, some TGA curves are depicted. It is visible that the two represented fibre samples have a very similar residue (corresponding to 10.8 and 12.4 wt% for 'CS 0.5%' and 'COOH' activated fibres, respectively), thus it would be sensible to expect that the rest of fibre samples ('COOH 0.5%', 'Blank EDIPA' and 'COOH act.+') would exhibit similar residues since these other fibres came from the same supernatant as 'COOH activated'.

Considering the thermal profile of neat PVA, we could roughly estimate that the fibre composition is, in general, between 3 and 5 wt% of SWCNTs (and the rest would correspond to PVA). These values would be lower than those reported by Vigolo and co-workers,[1,6] but this could be explained since in this case, SWCNTs dispersions were centrifuged before injection and spinning.