Supplementary Information:
Wettability of carbon nanotube-grafted carbon fibers and their interfacial properties in polypropylene thermoplastic composite

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Sample Key

Sized CF, as-received sized carbon fiber
Unsized CF, as-received unsized carbon fiber
HRBC-CF, heated and reduced bi-catalyst coated carbon fiber
CNT-g-CF, carbon nanotube-grafted-carbon fiber

S1 Length of carbon nanotubes which are synthesized on the carbon fiber surface

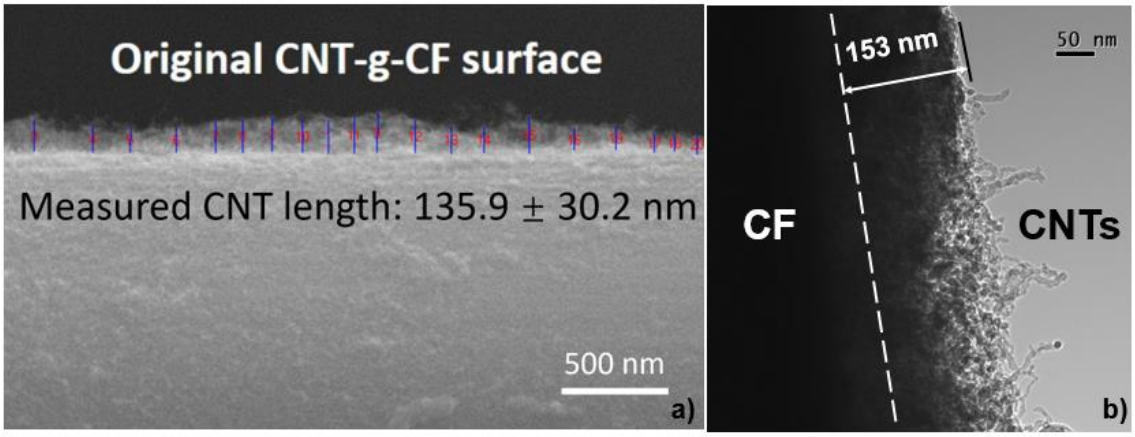


Figure S1 a) Scanning electron microscopy of the surface of carbon nanotube-grafted-carbon fiber (CNT-g-CF) sample, b) transmission electron microscopy of CNT-g-CF sample. Carbon nanotube (CNTs) growth on the carbon fiber (CF) surface perpendicular to the fiber axis were measured from the micrograph as indicated.

S2 Additional fibre surface contact angle measurements via Wilhelmy method

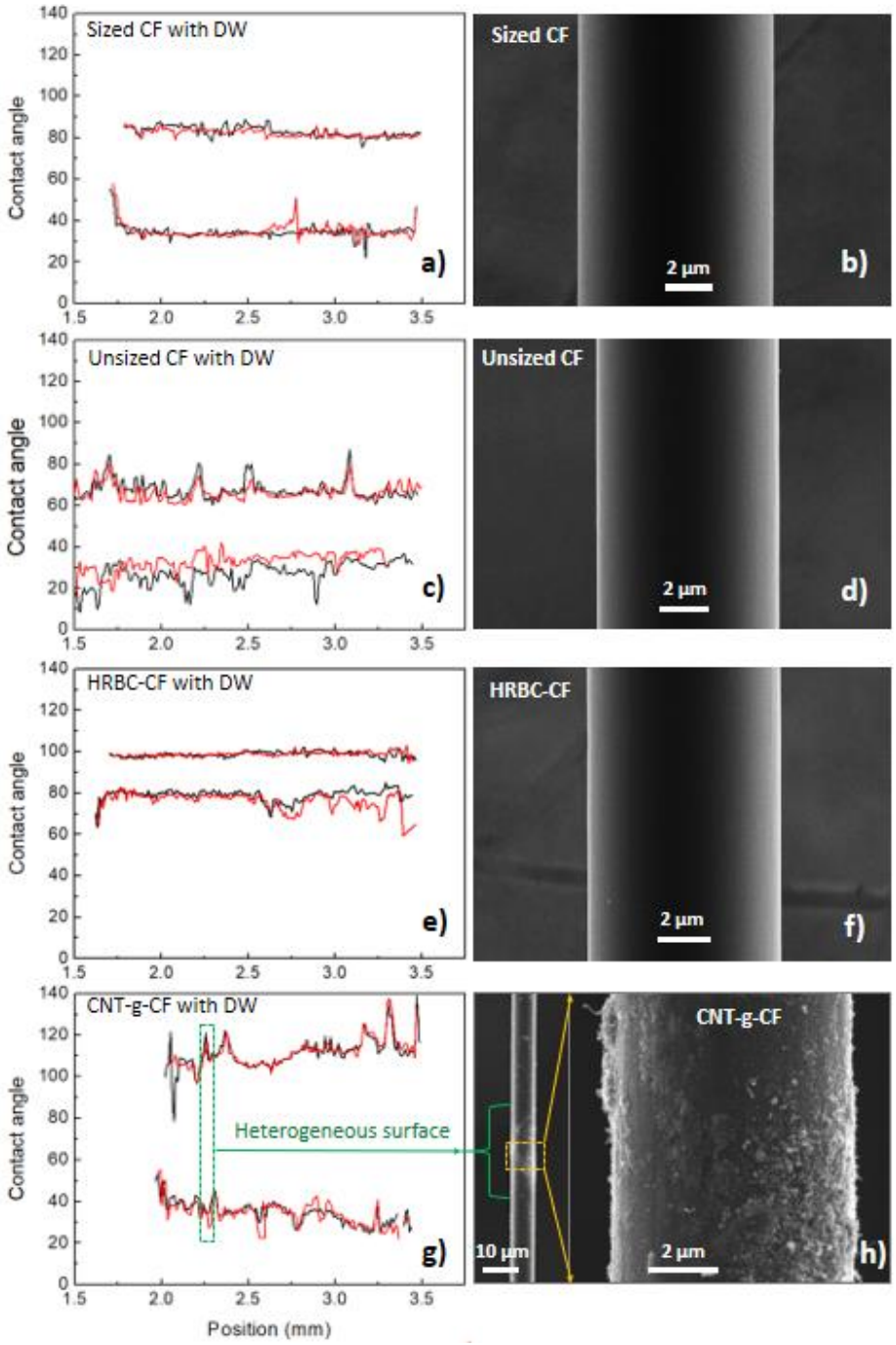


Figure S2 Contact angles determined for fiber samples using the Wilhelmy method, a) sized CF, c) unsized CF, e) HRBC-CF, and g) CNT-g-CF with deionized water (DW) for cycle 2 and 3 shown with black and red lines, respectively. Micrographs (post wetting evaluation) of the fiber surfaces are shown adjacent, with b) sized CF, d) unsized CF, f) HRBC-CF, and h) CNT-g-CF. The heterogeneous surface on h) CNT-g-CF sample can be directly associated with features in the g) wetting cycles.

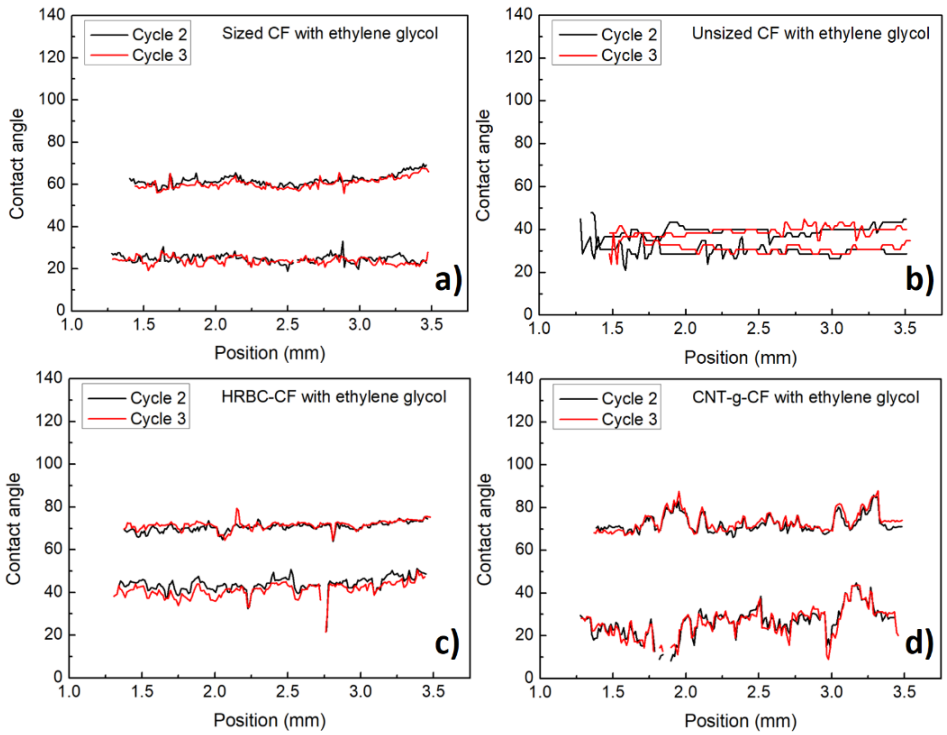


Figure S3 Additional contact angle wetting cycle results for fiber samples with ethylene glycol.

S3 Composition analysis of the fiber surfaces

The XPS spectra of the four CF samples, and the spectral deconvolution of C(1s) and O(1s) peaks are shown in Figure S.4, with the peak positions, their attributions [1] and the carbon-containing functional group concentrations given in Table S.1. The sized CFs and CNT-g-CFs have higher concentrations of functional groups, e.g. C-O and C-N, related to the peak C3 with a binding energy of ~286.9 eV. Despite the total oxygen concentrations on the surface of CNT-g-CFs (CNTs) being small, at 3.15 at.%, the percentage of peak C3 related functional groups is surprisingly high at 9.4 % of the associated carbon-containing groups. XPS C(1s) peak fitting is not able to distinguish between functional groups with similar binding energies [2], and this result suggests other functional groups than C-O bonds are present. As shown in Table S.2, the O (1s) peaks were composed mainly of oxygen bonded in C-O (peak O2, ~532 eV), in nitrogen-containing functional groups (peak O3, ~532.6 eV) and in C=O (peak O4, ~533 eV). The peak O1 (~531.4 eV) observed for HRBC-CFs can also be related to the oxygen bonded in the metal oxides, due to the presence of catalyst nanoparticles. In general, polymers have an acidic or basic character or a combination, except for saturated hydrocarbons for example polypropylene [3]. However, it is not possible to clearly identify the acidity or basicity of these carbon fibers simply from XPS results since the nature of functional groups are not known [4].

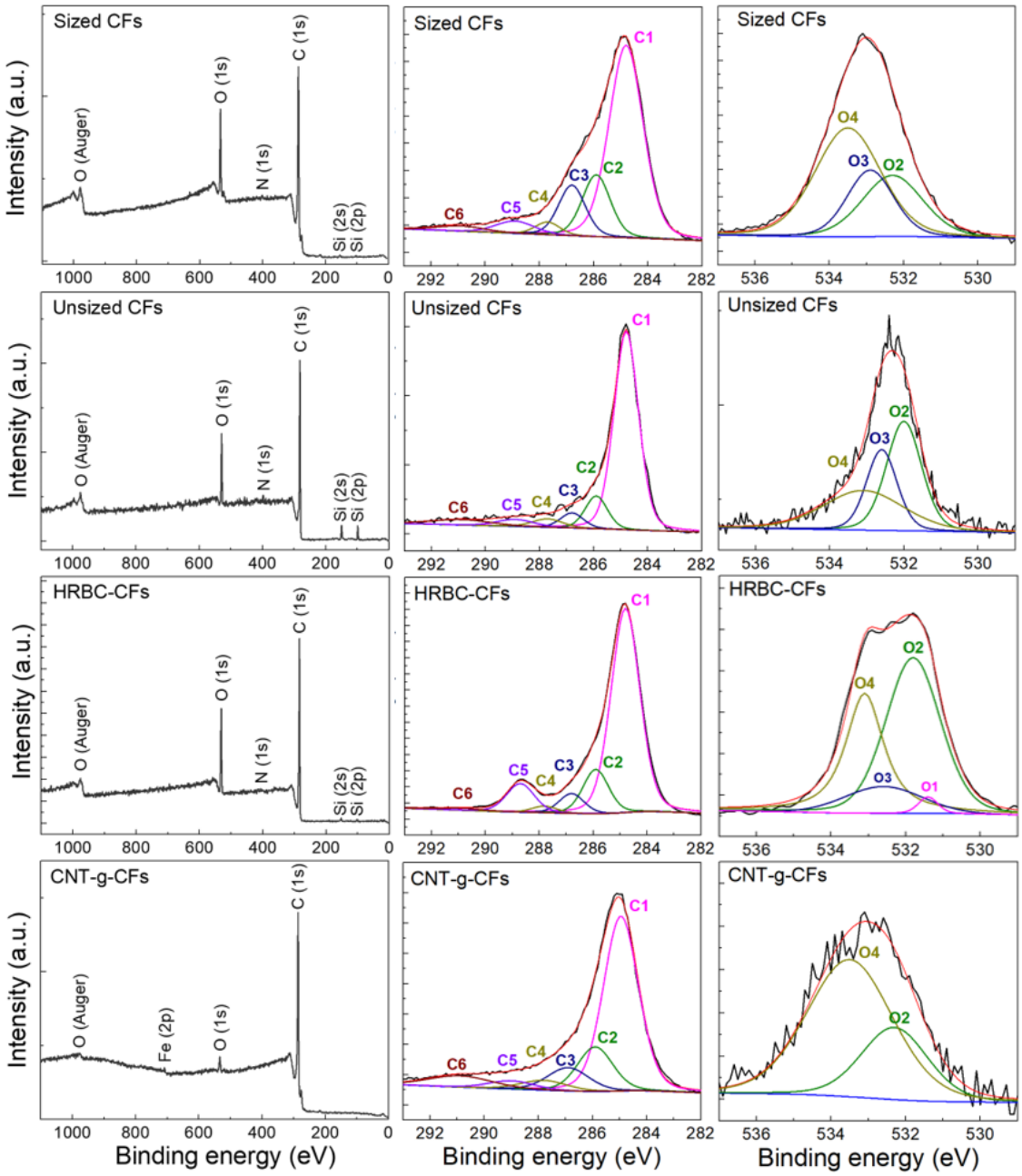


Figure S4 Left: XPS wide scan spectra, Centre: deconvoluted C(1s) and Right: O(1s) XPS spectra (black line) of various CFs. Peak-fitting curve red line, C1/O1 peak magenta line, C2/O2 peak olive line, C3/O3 peak blue line, C4/O4 peak dark yellow line, C5 peak purple line, and C6 peak wine line, respectively. [Color image]

Table S1 Deconvolution of C(1s) and the concentration of relevant functional groups for the fiber samples from XPS.

The deconvolution of C 1s peaks			% Surface functional group concentration			
Peak no.	**Binding energy (eV)**	**Attributions**	**Sized CFs**	**Unsized CFs**	**HRBC-CFs**	**CNT-g-CFs**
C1	~ 284.8	sp^2 carbon	61.37	71.72	68.57	59.95
C2	~ 285.9	sp^3 carbon	16.18	10.70	13.27	15.35
C3	~ 286.9	C-O, C-NR_2, surface free radical sp^3 bonds	12.61	5.09	5.71	9.40
C4	~ 287.7	C=O	2.94	3.80	1.93	4.43
C5	~ 288.9	O-C=O	4.48	3.88	9.22	3.73
C6	~ 290.9	π–π* interband	2.41	4.81	1.29	7.14

Table S2 Deconvolution of O(1s) and the concentration of relevant functional groups for the fiber samples from XPS.

The deconvolution of O 1s peaks			% Surface functional group concentration			
Peak no.	**Binding energy (eV)**	**Attributions**	**Sized CFs**	**Unsized CFs**	**HRBC-CFs**	**CNT-g-CFs**
O1	531.4	Metal oxides	-	-	1.89	-
O2	531.8-532.3	C-O	26.54	40.44	51.66	29.04
O3	532.6-532.9	-N, -Si	22.22	26.02	11.39	-
O4	533.1-533.5	C=O	51.24	33.54	35.06	70.96

S4 Microdroplet fiber-polypropylene determined interfacial shear strength

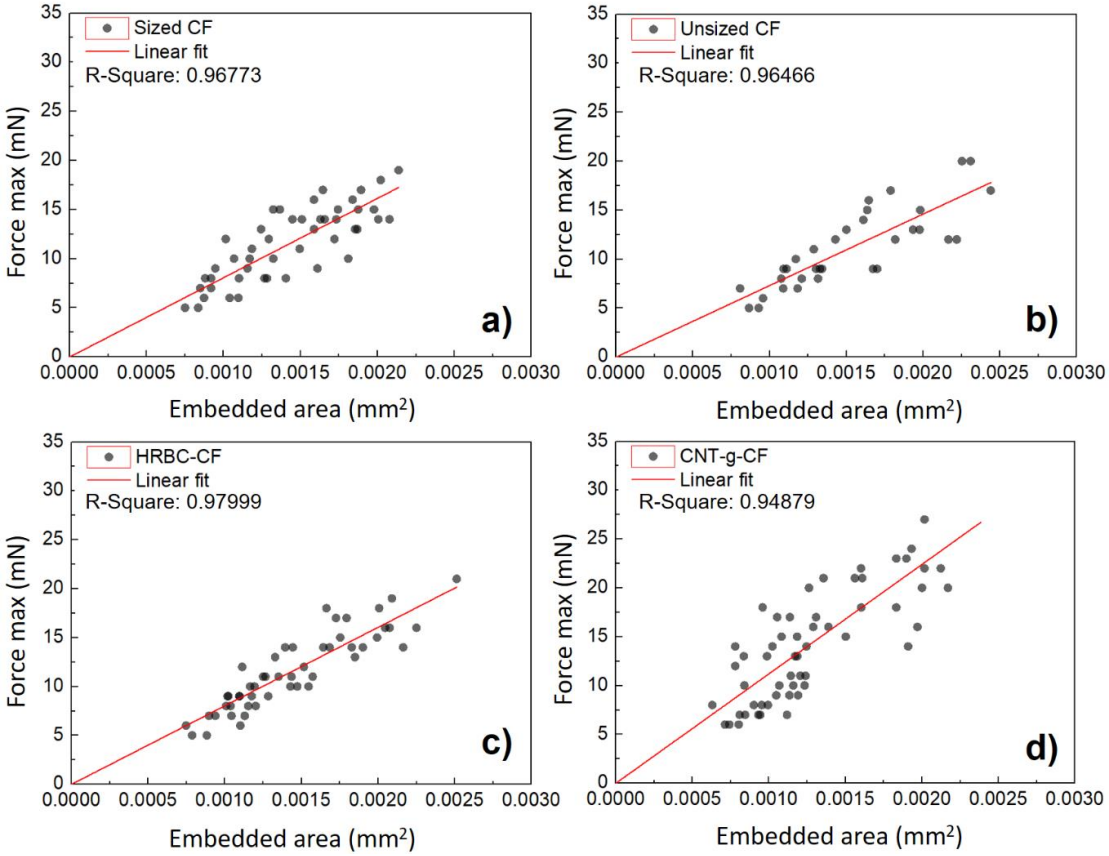


Figure S5 Microdroplet fiber-polypropylene tests results including a gradient of linear fit which corresponds to the average apparent interfacial shear strength as tabulated in Table 8. a): Sized CF, b): Unsized CF, c): HRBC-CF and d): CNT-g-CF.

References

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[2] K.A. Wepasnick, B.A. Smith, J.L. Bitter, D. Howard Fairbrother, Chemical and structural characterization of carbon nanotube surfaces, Anal. Bioanal. Chem. 396 (2010) 1003–1014. https://doi.org/10.1007/s00216-009-3332-5.

[3] F.M. Fowkes, Quantitative characterization of the acid-base properties of solvents, polymers, and inorganic surfaces, J. Adhes. Sci. Technol. 4 (1990) 669–691. https://doi.org/10.1163/156856190X00595.

[4] N. Dilsiz, J.P. Wightman, Effect of acid-base properties of unsized and sized carbon fibers on fiber/epoxy matrix adhesion, Colloids Surfaces A Physicochem. Eng. Asp. 164 (2000) 325–336. https://doi.org/10.1016/S0927-7757(99)00400-8.

Acronyms and symbols

A, acidity

A_e, embedded fiber area

AFM, atomic force microscopy

A_g, geometrically projected area

B, basicity

CF, carbon fiber

CFRTP, carbon fiber reinforced thermoplastic composites

CNT, carbon nanotube

CNT-g-CF, carbon nanotube-grafted-carbon fiber (* indicating roughness corrected where appropriate)

CVD, chemical vapor deposition

d_f, carbon fibre diameter

DIM, diiodomethane

DW, deionized water

EG, ethylene glycol

F_{max}, peak debonding force

γ^{AB}, acid-base surface energy components

γ^{LW}, Lifshitz-van der Waals surface energy component

γ^{+}, Lewis acid surface energy parameters of the solid surface free energy

γ^{-}, Lewis base surface energy parameters of the solid surface free energy

HRBC-CF, heated and reduced bi-catalyst coated carbon fiber

IFSS, interfacial shear strength

l, liquid

l_e, embedded length

PAN, polyacrylonitrile

PP, polypropylene

θ, equilibrium contact angle

θ_a, dynamic advancing contact angle

θ_{equ}, equilibrium contact angle

$\theta_{equ\ (CNT)}$, equilibrium contact angles on individual carbon nanotubes

$\theta_{equ\ (CNT-g-CF)}$, equilibrium contact angle on carbon nanotube-grafted carbon fiber

$\theta_{equ\ (CNT-g-CF*)}$, equilibrium contact angles on “roughness corrected carbon nanotube-grafted carbon fiber”

$\Delta\theta$, contact angle hysteresis

θ_r, receding contact angle

r, surface area ratio

R_a, arithmetic average roughness

s, solid

S, spreading coefficient

SEM, scanning electron microscopy

W_a, work of adhesion

XPS, X-ray photoelectron spectroscopy