Electronic Supplementary Information

for

Oxidised carbon nanotubes as dual-domain synergetic stabilizers

in electroconductive carbon nanotube flexible coatings

Artur P. Herman^{1,2}, Sławomir Boncel^{1,*}

¹Silesian University of Technology, Department of Organic Chemistry, Bioorganic Chemistry

and Biotechnology, Krzywoustego 4, 44-100 Gliwice, Poland

² Wroclaw University of Science and Technology, Faculty of Fundamental Problems of Technology, Department of Experimental Physics, Wybrzeże Wyspiańskiego 27, 50-370

Wroclaw, Poland

1. Materials and methods

The reagents were delivered by *Sigma Aldrich*. Aqueous suspension of acrylic resin was delivered by *Sico Screen Inks NV* (SX 150). PET non-woven support was delivered by *Miranda Ltd Co*. (Turek, Poland).

Grinding of MWCNT powders was performed using *Bosch* grinder MKM6003 (180 W). Ultrasonication was performed with *Bandelin Sonorex* Super RK31 (30 W, 35 kHz). Thermogravimetric analyses (TGA) were performed on a *Mettler Toledo* thermobalance (TGA/DSC 2). Two-point resistance measurements were performed using Sinometer MS8230B. Dimensions of samples necessary for calculation of specific resistance were taken from SEM measurements (SEM/FIB, FEI Helios NanoLab 600 Dual-beam). EDX spectra were recorded using Phenom PRO microscope. Low resolution SEM pictures of nanocomposites on PET supports were taken using Phenom Pro SEM. TEM images were acquired using Tecnai F20 FEGTEM.

2. Synthesis and purification of MWCNTs

A solution of ferrocene in toluene (5.5 wt.%) was injected at 5.6 mL/h flowrate into an argon atmosphere. The c-CVD process was conducted in a tube furnace at 760 °C for 5 h. After cooling to room temperature, the solid product was peeled of the quartz tube and purified from low-molecular and amorphous carbon contaminants following this procedure:

5.000 g of MWCNTs was added to a round bottom flask containing 250 mL of hydrogen peroxide ($H_2O_{2(aq)}$ 30 wt.%). The resulting suspension was sonicated for 24 h at room temperature, filtered off over PTFE filter membrane, washed thoroughly with distilled water and dried in a laboratory oven for 24 h. The solid material was Soxhlet-extracted with methanol and dried to constant weight. Yield: 4.853 g.

3. Synthesis of O-MWCNTs

5.000 g of MWCNTs, 32 mL of concentrated nitric acid (68 wt. %) and 96 mL of concentrated sulphuric acid (98 wt. %) were added to a round-bottom flask equipped with reflux condenser. The mixture was refluxed for 20 min and then poured on ice-cooled water (200 mL). After cooling to room temperature, the solid product was filtered off over PTFE filter membrane and washed with water until the pH of filtrate became neutral. Then it was placed in a laboratory oven and dried to the constant weight at 100 °C. Yield 3.337 g.

4. Characterization of O-MWCNTs (TGA + Boehm titration)

Thermal analysis was conducted under argon atmosphere, samples were heated in 70 µL platinum crucibles. Heating rate 10 °C min⁻¹. The results (**Fig. S1**) showed that pristine MWCNTs are thermally stable up to 800 °C. In case of *O*-MWCNTs, one can observe three desorption processes. The first process observed (below 150 °C) may be ascribed to the desorption of water. Then, for *O*-MWCNTs one can observe distinct (about 10%) weight loss between 150 and 450 °C. It is believed that in such a temperature range decarboxylation occurs.¹ Further gradual weight decrease (3.2%) may be assigned to desorption of phenolic moieties as it is generally more energy-demanding process.



Fig. S1 Thermogravimetric curves of O-MWCNTs (red) and pristine MWCNTs (blue). 1st derivative (black) of O-MWCNTs TG curve is also shown

The modified Boehm titration (BT) of O-MWCNTs was conducted according to the procedure by Scheibe et al.² The results of titration and thermal analysis are presented in **Table S1**.

Table S1 Analysis of functionalisation of O-MWCNTs using Boehm titration (BT) and thermogravimetric analysis (TG)

COOH (mmol g ⁻¹)		OH (r	OH (mmol g ⁻¹)	
TG	ВТ	TG	BT	
2.3	2.5 ± 0.3	1.9	1.6 ± 0.2	

5. Demonstration setup



Fig. S2 (A) Experimental setup for demonstration of conducting properties of screen printed *O*-MWCNT/MWCNT paths; low-magnification SEM images of PET textile (B) and the interphase of the printout (C)

6. Video files

V1 1_Switch.mp4 Demonstration of *O*-MWCNT/MWCNT thin film on a PET textile substrate serving as a flexible conductor in the electrical circuit

V2 2_Bending.mp4 Demonstration of performance of *O*-MWCNT/MWCNT thin film on a PET textile substrate after bending

V3 3_Various PETs Demonstration of performance of *O*-MWCNT/MWCNT thin film on various PET textile substrates including woven, non-woven and openwork textiles

7. ESI References

- 1. V. Datsyuk, et al. Carbon N. Y. 2008, 46, 833-840.
- 2. B. Scheibe, E. Borowiak-Palen, R. J. Kalenczuk, Mater. Charact. 2010, 61, 185–191.