**Supporting information**

**Locating carbon nanotubes (CNTs) at the surface of polymer microspheres using poly(vinyl alcohol) grafted CNTs as dispersion co-stabilizers**

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**Materials.**

Vinyl acetate (>99%, Aldrich), methyl methacrylate (>99%, Aldrich) were dried over calcium hydride, degassed by several freeze–thawing cycles before being distilled under reduced pressure and stored under argon. α,α′-azoisobutyronitrile (AIBN) (Fluka), 2,2′-Azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70) (Wako) and cobalt(II) acetylacetonate (Co(acac)2) (>98%, Merck) were used as received. Multi-Walled Carbon Nanotubes (CNTs) produced by Chemical Vapor Deposition (CVD) were provided and purified by FutureCarbon. Poly(vinyl acetate) (PVAc) was purchased from Aldrich. Poly(vinyl acetate-co-vinyl alcohol) (P(VAc-co-VA) (68% hydrolysis degree) was prepared by partial hydrolysis of polyvinylacetate (PVAc, Aldrich). 1.25g of PVAc is placed in a 50 ml round-bottomed flask. Acetic acid (16ml), distilled water (8 ml) and concentrated hydrochloric acid (1 ml) are then added and the solution is heated at 90°C for 5h. The mixture is then neutralized by a 33% solution of NaOH and the polymer is precipitated in acetone. The polymer was then washed several times by dissolution in methanol and precipitation in acetone.

**Synthesis of PVAc-Co(III) and grafting on carbon nanotubes**

1.233 g of cobalt(II) acetylacetonate (Co(acac)2) (4.8 $10^{-3}$ mol) and 4.8 g of 2,2′-Azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70) (1.56 $10^{-2}$ mol) are added in a 500 ml round-bottomed flask and degassed by several vacuum-nitrogen cycles. Vinyl acetate (45 ml) is then added and the mixture was heated at 30°C for 40h. A sample is picked out for the monomer conversion (45 %) and the SEC analysis (Mn = 6000 g/mol; Mw/Mn = 1.4). Residual monomer is then removed under vacuum followed by the addition of methanol (240 ml) at 0°C. 480 mg of CNTs are placed in a 500 ml round-bottomed flask and degassed by several vacuum-nitrogen cycles. The methanolic solution of PVAc-Co(acac)2 is then added to the fask containing the CNTs under nitrogen and the mixture is placed in an ultrasonic bath for 2 min followed by the addition of distilled water (2 ml). After 20 hour at 30°C, the mixture is cooled down to RT, diluted and filtrated. The CNTs are then washed several times with methanol to remove ungrafted PVAc. The washing steps consist in the dispersion of modified CNTs within methanol, the treatment in an ultrasonic bath for 10 min and filtration. After drying under vacuum for 24h at 40°C, the modified CNTs have been characterized by thermogravimetric analysis (TGA) in order to quantify the grafting degree (Figure 1S). The weight loss corresponding to the polymer is 20 wt% after one washing step and remains constant after further washing procedure which means that the coating is stable and permanent. The CNTs used for the partial hydrolysis and dispersion polymerization have been washed 5 times. For sake of comparison, CNTs and a commercially available PVAc that does not contain the cobalt complex (Co(acac)2) at the chain-end have been mixed in similar
conditions than the grafting procedure described above (in methanol for 20 hour at 30°C). TGA analysis clearly evidence that some PVAc chains are present on the CNTs surface after one washing step but the amount of PVAc adsorbed is decreased when increasing the number of washing steps (Figure 2S). After four washing steps, no more PVAc is adsorbed onto CNTs. This experiment demonstrates that PVAc physically adsorbed onto CNTs can be easily removed from CNTs by simply washing them with methanol. After 4 washing steps, all PVAc is removed in contrast to PVAc chemically grafted that remains on the CNTs surface (Figure 1S).

Figure 1S TGA curves of CNTs-g-PVAc after different number of washing steps.

Figure 2S TGA curves of CNTs that have been mixed with commercially available PVAc and washed several times with fresh methanol before each TGA analysis.
Partial hydrolysis of CNTs-g-PVAc

150 mg of CNTs-g-PVAc are placed in a 50 ml round-bottomed flask. Acetic acid (16ml) and distilled water (8 ml) are then added and the mixture is placed in an ultrasonic bath for 5 min. Concentrated hydrochloric acid (1 ml) is added and the solution is heated at 90°C for 5h. The mixture is then neutralized by a 33% solution of NaOH, filtrated and washed several times with water. The PVAc hydrolysis extent (72%) was determined by thermogravimetric analysis (TGA). For that purpose, the difference of weight loss at 500°C for CNTs-g-PVAc before and after hydrolysis corresponds to the weight amount of acetyl moieties removed during hydrolysis.

Dispersion polymerization of MMA

P(VAc-co-VA) (25 mg) and (modified) CNTs (15 mg) are added to 10 ml of methanol and placed in an ultrasonic bath for 30 min. 0.01g of AIBN and 1.5 g of MMA are then added and the solution is degassed by nitrogen. The mixture is heated at 60°C for 48h (yield ~ 95%) and then filtrated. After drying the polymer under vacuum, the polymer is dissolved in THF, filtered on a 0.2 μm Teflon filter and analyzed by SEC using a PMMA calibration. Mn = 89900, PDI = 2.78 in presence of pristine CNT and Mn = 60500, PDI = 2.78 in presence of CNTs-g-P(VAc-co-VOH).

Characterizations

Size exclusion chromatography (SEC) of poly(vinyl acetate) was carried out in tetrahydrofuran (THF) (flow rate : 1mL min⁻¹) at 40°C with a Waters 600 liquid chromatograph equipped with a 410 refractive index detector and styragel HR columns (four columns HP PL gel 5µm 10⁵Å, 10⁴Å, 10³Å, 10²Å). The molar mass of PVAc determined by SEC with PS calibration was in good agreement with that determined by ^1H NMR whenever the α-end group of the initiator (-OCH₃ at δ=3.13 ppm) could be observed and compared to the -CHOOCOCH₃ proton at δ =4.8 ppm of the monomer unit, as reported elsewhere²,³.
PMMA microspheres were observed with a scanning electron microscope (SEM; JEOL JSM 840-A) and with a transmission electron microscope PHILIPS M100 at an accelerating voltage of 100 kV. Thin sections (90 nm) were prepared by ultramicrotomy (ULTRACUT E from REICHERT-JUNG) at -130°C of PMMA microspheres compression-molded at 180°C for a short time (30 sec). Micrographs were analyzed by using the megaview GII (Olympus) software. CNTs-g-PVAC and CNTs-g-P(VAc-co-VA) were analysed with a Hi-Res TGA Q500 from TA Instruments at a heating rate of 20°C/min under nitrogen.

Electrical measurements were performed with a Vector Network Analyser Model Wiltron 360B operating over the frequency range 40MHz-40GHz. Each nanocomposite sample to be characterized consists of a thin plate of same thickness (1 mm) and surface (4x4 mm²) and is used as a microwave substrate on which a ground plane and a microstrip line are deposited.