

Electronic Supplementary Information

Materials

Sodium dodecyl sulphate, (SDS) (90%, Merck), copper (I) chloride (99.995+ %, Aldrich), 2,2'-bipyridyl (bipy) (99.9+ % GC grade, Aldrich), 1-phenylethyl chloride (PEC) (97%, Acros), 1,1,4,7,10,10-hexamethyltriethylenetetramine (97%, HMTETA) (Sigma), tetrahydrofuran (THF) (AR grade, Biosolve), toluene (AR grade, Biosolve) and 1,4-dioxane (AR grade, Biosolve) were used as received. Styrene (99% Merck), divinylbenzene (DVB) (Tech grade, Aldrich) and DMAEMA (98%, Aldrich) were passed over inhibitor remover columns before use. Azo (bisisobutyronitrile) (AIBN) (98%, Merck) was recrystallized from methanol and kept under refrigeration. The water used in all reactions was distilled de-ionized water obtained from a purification system. HiPCO® SWCNTs were purchased from Unidym Inc. According to the manufacturers, the carbonaceous impurities are approximately 10 – 15 wt% and metal catalyst content is around 5 wt%. SWCNTs were used as received.

Block copolymer synthesis by ATRP

PS-Cl macro-initiators were prepared via ATRP in solution. The catalyst/ligand/initiator system Cu(I)Cl/bipy/PEC was chosen. A theoretical $M_{n,theo}$ of 6000 g mol⁻¹ was targeted and [CuCl]:[bipy]:[PEC] was set at 1:3:1. CuCl and bipy were added to a 3:1 (vol%) styrene/toluene mixture, degassed (three freeze-pump-thaw cycles) and heated to 110 °C. The injection of PEC starts the reaction and conversion was monitored via gas chromatography (GC). The final reaction mixture was diluted with THF and passed over a basic alumina column. The PS-Cl macro-initiator was isolated by removing copper from the mixture via column chromatography over basic alumina, and subsequent precipitation into methanol. The molecular weight distribution was determined by size exclusion chromatography (SEC). Chain-extension was performed using the catalyst/ligand system Cu(I)Cl/HMTETA so as to afford maximum control

over the molecular weight^[1]. A theoretical $M_{n,theo}$ for the block copolymers of 20000 g mol⁻¹ was targeted. CuCl and the PS-Cl macro-initiator were dissolved in a 1:1 (vol %) DMAEMA/1,4-dioxane mixture, degassed and heated to 90 °C. The injection of the HMTETA starts the reaction and the conversion was monitored by GC. The final reaction mixture was diluted with THF and passed over a basic alumina column. Any residual PS macro-initiator was removed via precipitation into methanol. The polymer was dried via rotary evaporation, refluxed in heptane to remove last impurities and finally isolated via filtration. SEC was used to confirm a successful chain-extension and to measure the final molecular weight distribution.

SEC analysis of the PS-Cl macro-initiator yielded a $M_{n,exp}$ of 3 500 g.mol⁻¹, and polydispersity index (PDI) of 1.67. For the final block copolymer, values of 25 000 g.mol⁻¹, and 1.8 for the $M_{n,exp}$, and PDI respectively were determined.

SWCNT exfoliations in water

Exfoliations of SWCNTs were performed in water using ultrasound provided by a Sonics Vibracell VC750 horn sonicator with a 10 mm tip diameter. The sonication power was maintained at 20 W during the exfoliation, and the solution was cooled in an ice-bath to minimize nanotube damage. Solutions of 1.2 wt% (w.r.t. water) PS – *b* – PDMAEMA were prepared at a pH of 3. These solutions were used to prepare 0.1 wt% (w.r.t. water) SWCNT dispersions. As a control system, one 0.1 wt% aqueous SWCNT dispersion was prepared with 0.4 wt% SDS. Samples were taken at various times during sonication (diluted 150 times) for UV-Vis spectroscopy. The UV-Vis absorbance of the samples at a set wavelength (500 nm) was recorded using appropriate blanks (appropriate surfactant solutions). The optimal exfoliation was determined by monitoring the increase in the UV-Vis absorbance with time. At a certain value of energy added, the UV-Vis absorbance levels off and this point was then taken as the required time for maximum exfoliation. Following from the Lambert-Beer law, the plateau reached is

directly proportional to the concentration of exfoliated (single) SWCNTs, since only individual SWCNTs absorb in this range. The final absorbance value is similar for the two exfoliations, implying a similar degree of exfoliation. The energy requirement for maximum exfoliation is determined to be 50 kJ for dispersions prepared with SDS (approx. 1 hour) and 200 kJ for dispersions prepared with the block copolymer (approx. 3 hours).

PolyHIPE – SWCNT composite preparation

HIPEs were prepared by subjecting an oil/water mixture to high shear for 5 minutes at 600 – 800 rpm, supplied by a Kika Labortechnik overhead stirrer. A total reaction mixture volume of 10 ml was prepared, with a 75:25 (w/o) v/v ratio of the water and oil phases. The oil phase (2.5 ml), consisting of 50/50 (v/v) styrene/DVB mixture and 18 mg AIBN, was placed in a reactor equipped with baffles. While shearing, the water phase (total of 7.5 ml) consisting of water and an appropriate concentration of block copolymer-stabilized SWCNTs, was added drop-wise whilst simultaneously raising the pH to 10. The concentration of the block copolymer-stabilized SWCNTs was varied such that a loading of CNTs to the final composite foam mass (after abstraction of the continuous aqueous phase) ranged between 0 and 0.35 wt%. To prepare this mixture, an appropriate volume of the block copolymer-stabilized SWCNT dispersion was diluted with DDI water. A thick pre-emulsion was formed and transferred into a cylindrical poly(vinyl chloride) mold which was then sealed and placed in an oven at 65 °C for 36 – 48 hours. The mold was then opened and returned to the oven (now under vacuum) for an extra 24 hours to dry the foam. The foams were removed and cleaned via soxhlet extraction with water. The cleaned foams were once again dried overnight at 60 °C in a vacuum oven.

Mercury intrusion porosimetry measurements

During the extrusion cycle, voids that are connected with narrow throats tend to evacuate at lower pressures when compared to the pressure at which they had been filled during the intrusion cycle. All the samples show similar hysteresis patterns except for the foam prepared with the lowest SWCNT loading. For the composite foam with 0.01 wt% SWCNTs, a large drop in intruded volume is seen at the beginning of the extrusion cycle. This corresponds well with the value of the pore diameter. Large voids connected with large throats allow for fast evacuation during extrusion resulting in a large hysteresis.

Analysis

Size exclusion chromatography

Size exclusion chromatography (SEC) was performed using a Waters GPC equipped with a Waters model 510 pump and a model 410 differential refractometer. Two mixed bed columns (Mixed-C, Polymer Laboratories, 30 cm, 40 °C) were used. THF stabilised with 3,5-di-tert-butyl-4-hydroxytoluene was used as the eluent at a flow rate of 1.0 mL min⁻¹, and the system was calibrated using narrow molecular weight PS standards ranging from 600 to 7 x 10⁶ g mol⁻¹.

Gas chromatography

Gas chromatography (GC) measurements were performed on a Hewlett-Packard 5890 series II apparatus containing an Ultra 1, silicon type column (25 x 0.32 mm) and a flame ionization detector (FID).

UV-Vis spectroscopy

UV-Vis spectroscopy was performed on a Hewlett-Packard 8453 spectrometer (range of 200 to 1100 nm).

Conductivity measurements

Cylindrical shapes were cut from the polyHIPE foams. The flat edges were painted with colloidal graphite and aluminium foil was taped to these edges to act as the two electrodes for

subsequent direct current (DC) conductivity measurements. The resistivities of the composites were measured with a Keithley 6512 programmable electrometer. The conductivity was calculated using Equation 1 in conjunction with the determined resistivities and the dimensions of the foams.

$$\rho = R \cdot \frac{A}{d} \quad (1)$$

where ρ and R are the sheet resistance and measured resistance respectively. The dimensions A and d are the foam circular surface area (top of cylinder) and the foam length respectively.

Scanning electron microscopy (SEM)

SEM micrograph shown in Figure 2 A - C were taken using a Phenom table top SEM (Fei Co.). A back-scatter detector was used and the beam acceleration voltage was kept at 5 kV. The micrograph shown in Figure 4 was taken using a Phillips XL 30 ESEM-FG (Fei Co.) SEM. A secondary electron detector was used and the beam acceleration voltage was kept at 20 kV (spot size of 3).

Mercury intrusion porosimetry (MIP)

Mercury intrusion porosimetry measurements were performed using a Micrometrics Instrument Corporation, USA AutoPore IV 9500 V1.05.