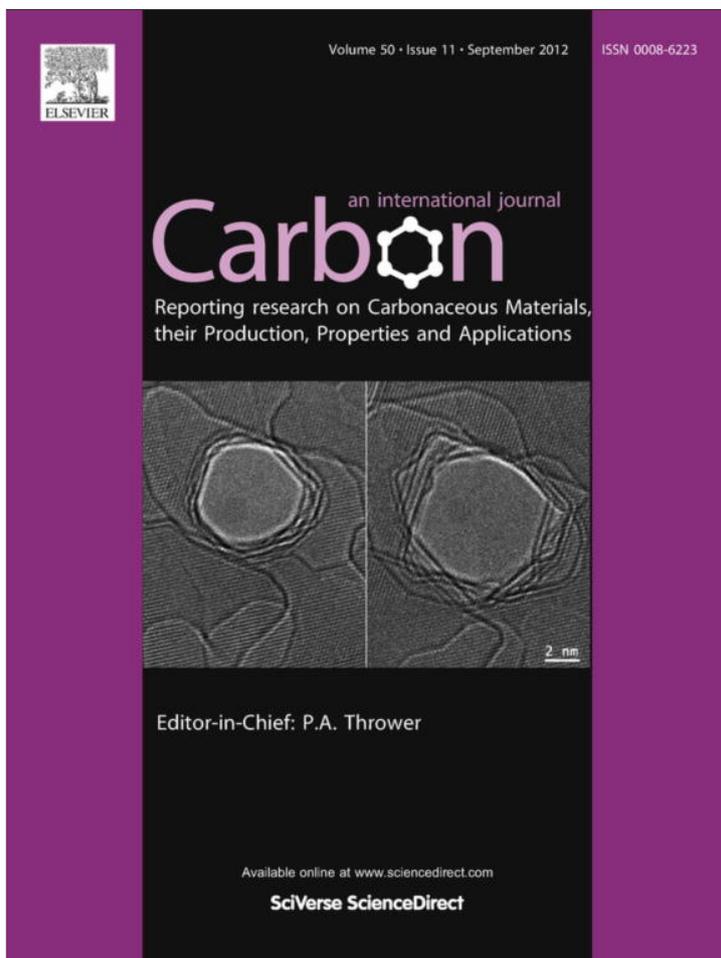


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Letter to the Editors

Polymer–nanotube interaction in MWCNT/poly(vinyl alcohol) composite mats

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ABSTRACT

Strong polymer–MWCNT interactions in millimeter-high MWCNT/poly(vinyl alcohol) composite mats of vertically aligned tubes are reported. SEM and TEM imaging revealed extensive polymer sheathing to have occurred homogeneously over the nanotubes in the mats without influencing their morphology, alignment or physical characteristics. A 7- to 10-fold increase in the apparent nanotube diameter due to poly(vinyl alcohol) sheathing was measured. Thermogravimetric analysis showed that the composite mats were thermally more stable than the pure polymer. Differential scanning calorimetry results were compatible with a crystallinity increase of the polymer phase due to the presence of CNTs of the order of 18%. Potential applications of the produced composites include filters, components for sandwich panels and sensors.

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The ability to control CNT morphology, alignment and orientation within a continuous polymer medium is today one of the most sought-after endeavours in the field of nano-reinforced composite materials. On the other hand, understanding the phase interactions and the nature of the polymer sheathing mechanism is key to characterizing the mechanical performance of emerging CNT/polymer systems [1]. It is now well established that the addition of carbon nanotubes in poly(vinyl alcohol) (PVA or PVOH) provides composites of superior mechanical and electrical properties compared to the pure polymer [2,3]. It has also been demonstrated that CNTs can act as nucleating agents for PVA crystals and could lead to the overall increase of PVA crystallinity in PVA/CNT composites [2–5]. Such observations have been made possible

mostly by experimental investigation of composite fibres and thin composite films.

Herein, we report the manufacturing of millimetre-high, vertically-aligned-MWCNT/poly(vinyl alcohol) composite mats, provide direct evidence of extensive polymer–CNT interactions by means of SEM and TGA tests, and examine the effect of the tubes on PVA crystallization by means of DSC testing. The composites were made possible by straightforward soaking, into aqueous PVA solutions, of acetone-wet mats grown by CVD with the use of an environmentally-friendly carbon precursor, camphor. The procedure did not evolve any chemical modification or oxidation of the surface of the tubes.

In our procedure, a 20:1 gas mixture of an economical, commercially available and green [6] carbon source, camphor,

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and the catalyst, ferrocene, is introduced into a 1.2 m long quartz CVD reactor hosting 150 mm × 38 mm × 0.725 mm ($l \times w \times t$) silicon substrates and operating at 850 °C. Running times of 60 min yielded 2.0- to 2.5-mm high deposits (hereon referred to as mats, Fig. 1) of vertically-aligned MWCNTs on the wafers; the corresponding growth rate was ca. 0.7 $\mu\text{m/s}$. The gaseous product of the decomposition was purged of phenanthrene, naphthalene and other polycyclic aromatic hydrocarbons (PAH) under open flame, and then purified through a HEPA-filter before being released to the environment. Free-standing as-grown mats of approximate dimensions 40 mm × 35 mm, separated from the substrates using a razor blade, were soaked into pure acetone, then immersed into an aqueous 1% wt. PVA solution ($M_w = 85,000$) for 1 h and then dried for 8 hr in a vacuum oven. The resulting MWCNT/PVA composites were cut into plates of approximate dimensions 10 mm × 10 mm.

The untreated/as-grown CNT mats were strongly hydrophobic, as expected for a graphitic material [7]. However, soaking the CNTs with acetone rendered the tubes friendly to the water-based PVA solution. We attribute this rather unexpected finding to the physical absorption of the oxygen-rich acetone on the nanotubes' surface during the soaking phase; the mechanism enriches the tubes with oxygen atoms that can form hydrogen bonds with PVA. Another explanation could be that the oxygen species that are imparted to the CNT surface by the acetone help to reduce the surface energy of the CNTs and thermodynamic wetting with PVA is thus significantly enhanced. This claim was verified experimentally by floating a CNT mat in a PVA solution that was previously wet in an oxygen-free substance, hexane, and observing that – contrary to the treatment involving acetone – the mat would not absorb the polymer and would remain afloat. PVA absorbed onto acetone-wet CNTs despite the fact that acetone is a poor solvent for PVA. This observation implies that acetone assists the sheathing mechanism indirectly, by providing an oxygen-rich (hence PVA-friendly) interphase that reconciles the chemical affinity of two otherwise incompatible media.

CNT diameter in the as-grown mat ranged between 30 and 45 nm. Three main observations were made possible under SEM. First, polymer sheathing extended only on the CNT surfaces and no polymer coagulates were found in other locations (Fig. 2a). It is argued that the new hydrophilic interphase around the tubes is responsible for promoting the PVA adsorption mechanism preferably on the CNT surface, as op-

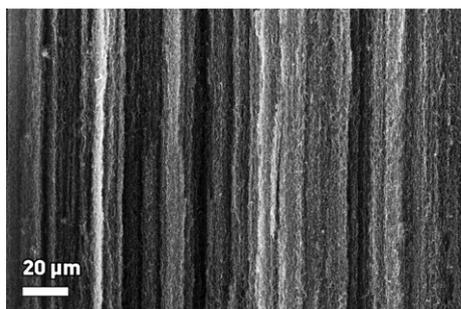


Fig. 1 – SEM micrograph of vertically aligned CNTs in the as-grown mat.

posed to CNT interaction with other polymers, such as with epoxy resin, for which pockets of the polymer coagulate independently of filler morphology [8].

A second observation was that sheathing had accumulated in the form of annular layers around the tubes' surface, as evidenced at loose ends of PVA-coated MWCNTs where protruding carbon cores and concentric layers of polymer sheathing were visible (Fig. 2b and c). The diameters of the PVA-coated CNTs, of the order of 300 nm, were 7–10 times larger than the diameters of the as-grown tubes. The thickness of the polymer sheath around the tubes is controlled by the concentration of polymer within the aqueous solution; this concentration then also controls the open porosity of the composite. This feature can be exploited in obtaining materials of custom porosity: by using different polymer concentrations in the drencher solution, mats of tunable pore size for filtering applications are achievable. Moreover, the PVA-sheathed CNT mat is now hydrophilic and can interact naturally with more water-soluble media. Extending the same notion, the porosity of the mat can be completely replaced by PVA to produce, for example, sandwich panel composite elements of z-reinforcements.

The third observation relates to the composites' morphology with respect to the as-grown highly-organized product. It was noted that the vertical alignment was retained with sheathed tubes; the presence of the polymer did not promote coalescence of the nanotubes themselves nor changed the morphology of the MWCNT mat (Fig. 2d). This observation is important in view of the current challenge in maintaining custom nano-reinforcement orientation in polymer media.

Thermogravimetric analysis (TGA) showed that the as-grown material had the highest thermal stability in air compared to the polymer and the composite, owing to its highly-organized structure (Fig. 3). Carbon nanotubes did not exhibit significant mass loss due to oxidation up to 800 °C. The thermogravimetric mass loss curve for the polymer, exhibited two degradation stages at 230 and 470 °C, corresponding to the melting and complete decomposition phases of the PVA. The corresponding curve of the composite mats, was shifted to higher temperatures by approximately 200 °C due to the presence of nanotubes and showed two significant drops starting at 270 and 470 °C. While of different scales, these steps appear at temperatures consistent with the pure polymer, hence they must correspond to the melting and decomposition of the PVA in the composite. The residual mass found to occupy 7.2% of the composite weight, was identified by energy-dispersive X-ray spectroscopy as iron. Iron was introduced as catalyst during the tubes' synthesis and was not removed as the tubes did not undergo any chemical treatment. The mass fraction of PVA in the composite was calculated as 29% by interrogating the TGA curve of the composite at the polymer's decomposition temperature, 470 °C, and further corrected for the residual trace percentage.

The effect of nanotubes' presence on polymer crystallization was examined under Differential Scanning Calorimetry (DSC) by heating samples of the pure polymer and composite mats to 250 °C, Fig. 4. The composite's DSC curve was corrected for the previously established value of polymer mass fraction in the composite mats. The MWCNT/PVA composite melting peak was found at ca 230 °C, 10 °C higher than the

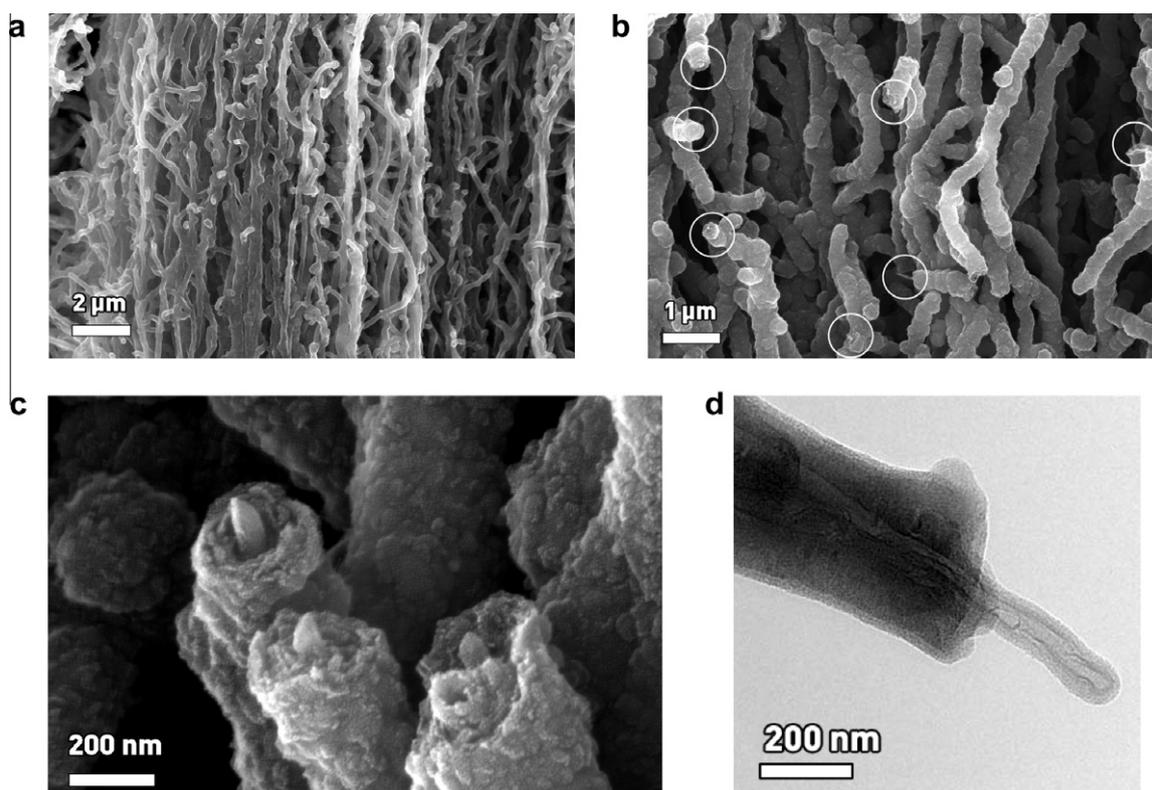


Fig. 2 – PVA-coated CNTs in the composite. (a) Vertical alignment of MWCNTs was retained in the composite mat. (b) Morphology at low-magnification. Open circles demonstrate nanotube core tips exposed through the surrounding polymer. (c) Close-up of tips showing layers of PVA absorbed around the tubes. (d) TEM image of PVA absorption around a carbon nanotube.

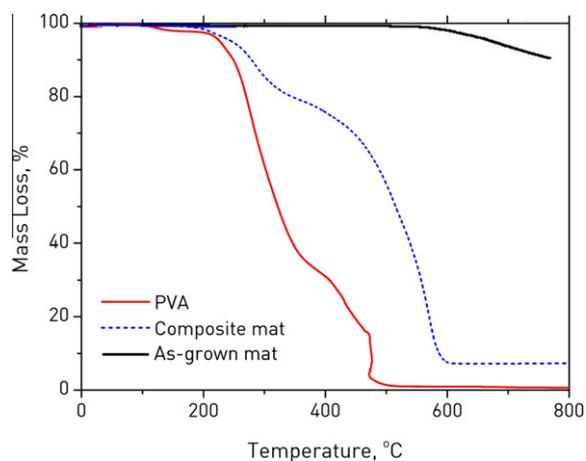


Fig. 3 – Thermogravimetric mass change curves for the pristine CNT mat, PVA and composite in air.

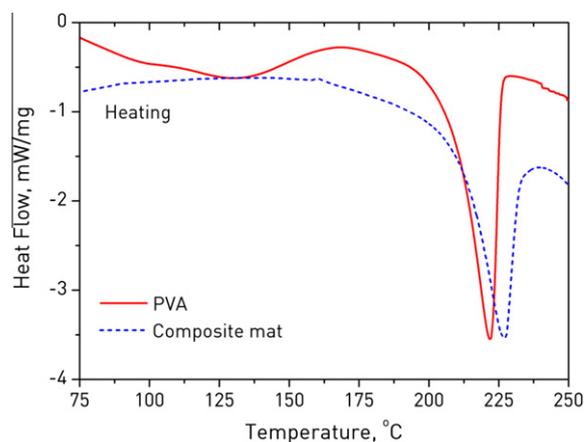


Fig. 4 – DSC curves for the pure polymer and composite mats.

corresponding peak of the pure polymer. This finding by itself indicates a good degree of bonding between the PVA and the nanotubes that effectively prevents the polymer from melting at its bulk melting temperature.

To compare the crystallinity of the pure polymer to that of the composite mat, enthalpy (ΔH) values were calculated by numerical integration of the area under the melting and crystallization peaks. The calculation was based on a stan-

dard melting enthalpy value for PVA of 155 J/g [5]. All experiments were conducted at the same heating rate. The results showed that neat PVA exhibited a relatively low crystallinity of 19% whereas the corresponding value for the composite mat was 37%. Given the fact that the PVA-soaking procedure of the mats did not involve thermal annealing or any other process that could independently increase the polymer's crystallinity [9], the observed crystallinity increase of 18% can be attributed exclusively to the presence of CNTs. The estab-

lished crystallinity value compares very well with the range of 2–36% that has been reported for thin CNT/PVA films [3,4].

Polymer-sheathed CNTs are promising materials for various sensing applications due to their large specific surface area and good electrical properties [10]. Aligned CNTs coated with conducting polymers can especially be used in glucose and complementary-DNA sensors of high accuracy and selectivity. PVA can also be utilized as protective/handling colloid for bulk CNTs similarly to its use as sizing medium in conventional fibres. From an application point of view, the observed increase in crystallinity due to the presence of nanotubes, could also have a beneficial effect in the mechanical properties of the composites.

We have proposed an approach for the production of MWCNT/PVA composite mats of vertically-aligned nanotubes by a straightforward methodology that does not affect the structure of the as-grown product nor the nanotubes' orientation. The presented results illustrate the extensive polymer sheathing mechanism and help understand the polymer-CNT interaction and the potential of the material system. MWCNT/PVA composites can be designed to meet specific needs of various applications such as filters of tunable pore size, composite panel components and sensing applications.

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Chiral-selective growth of single-walled carbon nanotubes on stainless steel wires

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ABSTRACT

Single-walled carbon nanotubes (SWCNTs) were successfully grown on calcined stainless steel wires at 700 °C using CO as the carbon source. By contrast, the raw stainless steel wires produced only necklace-like multi-walled carbon nanotubes. Photoluminescence spectroscopy studies showed that SWCNTs grown from calcined stainless steel have a narrow diameter distribution and a high chiral selectivity of (6,5) nanotubes. The pre-growth

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