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# Aligned carbon nanotube webs embedded in a composite laminate: A route towards a highly tunable electro-thermal system

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ABSTRACT

Highly aligned CNT webs, with an areal density of 0.019 g/m$^2$, were produced by direct drawing of CNT 'forests' grown by chemical vapor deposition, to form a conductive heating element. These were subsequently inserted between pre-cured layers of unidirectional carbon fibre reinforced polymer (CFRP) and the electrical and thermal conductivity of the combined system were assessed under different curing conditions. Control composites specimens, cured under high-pressure, demonstrated a higher fibre volume fraction, as well as higher electrical and thermal conductivities. With a single CNT 20-layer web interlayer added, the electrical conductivity increased by 25% when the CNT web alignment was perpendicular to that of the fibres, and by 15% when the CNT web alignment was parallel to the fibres. In addition, three types of CNT interlayer distribution were investigated. Through tailoring the pressure, carbon fibre layup and CNT interlayer, an efficient electro-thermal system was obtained which could be deployed as part of an ice-protection system on aircraft.



## 1. Introduction

As an aircraft flies through clouds at temperatures below 0 °C, super-cooled water droplets may impinge upon vulnerable aerodynamic surfaces and accumulate as ice, especially on the leading edges of wings, fins, tails, jet intakes or propellers [1]. Ice accretion adds weight, increases drag, and may significantly reduce lift, leading to a complete loss of control [2]. Ice accretion has been a contributing factor in 9.5% of fatal air-carrier accidents [3], and has consequently attracted considerable research interest aimed at developing energy-efficient anti-icing (AI) and de-icing (DI) systems.

Carbon fibre reinforced polymer (CFRP) composites have become the predominant material on the primary structure of the latest generation of passenger aircraft, owing to their superior specific strength and stiffness compared to traditional metallics. In the latest generation of wide-body passenger aircraft, e.g. Airbus A350 XWB and Boeing 787, more than 50 wt% [4] CFRP composite has been utilised in their primary structure. However, the relatively low thermal conductivity and the ever-greater emphasis on energy efficiency, demand a new approach to prevent ice accretion on susceptible aerodynamic surfaces. One of the most widely used anti-icing/de-icing (AI/DI) techniques is the hot-air-bleed system. The air is bled from the engine compressor stages, piped to vulnerable areas and expelled through small holes to the inner surface of the leading edge skin to heat the outside surface by thermal conduction [5,6]. As CFRP composites have much lower thermal conductivity compared to metals, more hot air is required, leading to higher thermal losses and energy consumption. In addition, air-bleed decreases the efficiency of the engines, and the piping network adds weight and maintenance costs [7].

In recent years, diverse ice protection systems have been investigated, including electro-thermal systems [6–12], electro expulsive systems [13], superhydrophobic coatings [14–16] and flexible pneumatic boots [17]. Among these, an electro-thermal system can be used for both anti-icing and de-icing, where a moderately conductive foil or wire element is commonly embedded in the critical surface and resistively heated. As current passes through the element, the heating weakens the bonding between the ice and impinged surfaces and the ice is consequently dislodged by the airflow [18]. The electrical heating element is the key component for this system. Metal is currently used for this function (eg. Boeing 787) but suffers from bonding, weight and

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heating uniformity problems [19]. As a consequence, alternative materials have been investigated, including carbon nanotubes (CNTs) [6,9–11,20–25], carbon fibre (CF) [12] and electro-conductive textiles [7].

Although CNTs possess excellent electrical conductivity at the individual level, macroscopic constructs of CNTs entail innumerable resistive contacts which can be utilized to produce an electro-thermal heating element. The macroscopic magnitude of the resistance can be tailored by functionalization but also, and more readily, by varying the amount or concentration of CNTs with virtually no weight penalty, given their vanishingly small mass. This, together with their exceptional specific strength and stiffness and compatibility with CFRP composites allows CNT heaters to be designed and shaped to optimize energy use to achieve anti-icing/de-icing while maintaining the structural integrity of the CFRP composite structure.

Dispersed CNTs have been widely investigated as the heating element [10,20,21], and applied through different methods. However, as dispersed CNTs present numerous challenges, such as achieving uniform dispersion, and difficulty in tuning for specific properties, aligned CNTs have emerged as potential efficient heating elements. Janas and Koziol et al. [22,23] have developed CNT films and CNT wires, which were directly spun from an aerogel produced by chemical vapor deposition (CVD) and continuously deposited onto a rotating winder [26]. However, the resulting CNT assemblies have high loading of catalyst and amorphous carbon as well as disordered CNTs. Wardle et al. [6,9,24] conducted research on the electro-thermal properties of a heating system with aligned 'knocked-down' CNTs as the heating element, and proposed a thermal-mechanical de-icing system which employed aligned CNT as the heating element. Knocked-down CNTs are obtained through pressing down and shearing aligned CNTs in one direction. As a result, there is very little that can be done to adjust the resistance. Fuzzy fibres [27], i.e., growth of CNTs on CF fabrics, is attractive for some applications but entails both extensive processing and often significant damage to the CF performance.

A uniquely useful form of high purity, highly specified CNT material is as 'directly drawable forests' of CNTs grown on a substrate such as silicon wafer, achieved through a carefully controlled CVD process [28] available within the Advanced Composites Research Laboratory at the Queen's University Belfast. Many other CNT products are heavily loaded with iron or other catalysts. Leaving the catalyst in place can result in gradual oxidation, leaching, and incompatibility between the CNTs and CFRP composites, however methods used to remove it are onerous and can damage and tangle the CNTs in the process. In contrast, directly drawable CNTs are essentially catalyst-free and require no purification. A fine, continuous film or web of CNTs can be drawn horizontally from the vertically aligned forest and used as-formed or laterally condensed into yarn [29]. The web is typically only around 50 nm thick when densified, has an areal density of approximately 2 μg/cm$^2$ and the CNTs are highly aligned and conductive along the draw direction.

As illustrated by Musameh et al. [30], the resistance of a laminated CNT web decreases inversely to the number of layers. Also, within a single web, the length of CNTs can be controlled during the CVD procedure. Accordingly, by controlling these three parameters (number of layers, orientation and length of CNTs), the desired electro-thermal properties of the CNT web can be achieved. Directly drawn carbon nanotube (CNT) web is a promising alternative to metal heating elements in that it adds very little weight, is compatible with composites and indeed may contribute to the structural performance, and, being highly anisotropic, flexible and adaptable, offers exceptional flexibility in design and fabrication to optimize performance. In this work, heating elements comprising CF laminates alone and in combination with interlaid CNT web are investigated. The effects of curing pressure on CFRP composite fibre volume fraction, resistance and thermal conductivity, with and without CNT web interlayers, as well as the effects of different CNT layer morphologies, are discussed.

## 2. Experiments

### 2.1. Materials

Aerospace grade IM7/977-2 carbon fibre/epoxy unidirectional prepreg (Cytec/Solvay), was used in this work. The CNT forests were fabricated by CVD of acetylene at 700 °C, grown on a silicon wafer with iron catalyst [28,29]. The obtained CNTs, with an average length of 300 μm, and an average diameter of 10 nm (Fig. 1a), were drawn directly into a fine continuous web of aligned CNTs and wound onto mounting frames (Fig. 1b) to the required thickness. As noted [30] the resistance of CNT web falls in inverse proportion to the number of layers (ie two layers have half the resistance of one, and twice the resistance of four). Web comprising 20 layers of CNT, wound as a single sheet or as multiple sheets summing to 20 layers, was chosen for this investigation. Strips of 10 mm wide copper foil (Alfa Aesar, 0.025 mm thick, annealed, uncoated, 99.8%) were used as the electrical buses to connect samples and power supply.

### 2.2. Sample preparation

Composite laminates (100 mm × 70 mm), made of 18 plies of prepreg were cured at 177 °C for 3 h using a platen press (COLLIN P200P), combined with vacuum. Copper buses were placed 40 mm apart between plies 9 and 10 to create a heater area of 40 mm × 70 mm (Fig. 1c). Specimens with carbon fibre (CF) perpendicular (⊥) or parallel (//) to the buses were made under high ('HP') and low ('LP') curing pressures (Table 1). HP samples with CNT web (denoted 'NT″, one web comprising 20 layers) placed perpendicular to the buses (Fig. 1c) and embedded in the middle of HP samples were also prepared. Subsequently, the effect of CNT webs placed as two webs each of 10 layers, or 5 webs of 4 layers was studied (Fig. 7). The buses are all in the middle, i.e. with 9 layers of CF on each side.

### 2.3. Characterization

A Hitachi FlexSEM1000 Scanning Electron Microscope (SEM) was used to observe the morphology of CNTs and cross section of the specimens. Thermogravimetric analysis (TGA, TA Instruments SDT-Q600) was used to find the fibre volume fraction and an Agilent 34450A 5½ Digital Multimeter to measure the resistance of the samples using the 4-wire method. Thermal conductivity of the samples was measured by a TC analyzer (TCi Mathis) using a modified transient plane source (MTPS) technique. In this test, the heat generated by the heating element of the sensor, with a known applied current, yields a temperature rise, at the interface between the sensor and the sample, which causes a change in the voltage drop of the sensor element. The rate of the voltage rise is used to determine the thermal conductivity of the sample. Before the thermal conductivity measurement, the surface roughness, $R_a$, of the samples was reduced by sanding to less than 1 μm for a more uniform contact between sensor and specimen surface.

The resistive heating performance of the composites, including temperature vs. time and temperature distribution, were investigated. The current was supplied by a DC power supply, and the temperature of the samples recorded by RS-1384 4 Input Data Logging Thermometers using K-type thermocouples (TCs) (Fig. 2). Six thermocouples were placed at different locations on the