An advanced anti-icing/de-icing system utilizing highly aligned carbon nanotube webs

Yao, X., Hawkins, S. C., & Falzon, B. G. (2018). An advanced anti-icing/de-icing system utilizing highly aligned carbon nanotube webs. *Carbon*, 136(Sept 2018), 130. <https://doi.org/10.1016/j.carbon.2018.04.039>

Published in:
Carbon

Document Version:
Peer reviewed version

Queen's University Belfast - Research Portal:
[Link to publication record in Queen's University Belfast Research Portal](#)

Publisher rights

Copyright 2018 Elsevier Ltd. All rights reserved.

This manuscript is distributed under a Creative Commons Attribution-NonCommercial-NoDerivs License

(<https://creativecommons.org/licenses/by-nc-nd/4.0/>), which permits distribution and reproduction for non-commercial purposes, provided the author and source are cited.

General rights

Copyright for the publications made accessible via the Queen's University Belfast Research Portal is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy

The Research Portal is Queen's institutional repository that provides access to Queen's research output. Every effort has been made to ensure that content in the Research Portal does not infringe any person's rights, or applicable UK laws. If you discover content in the Research Portal that you believe breaches copyright or violates any law, please contact openaccess@qub.ac.uk.

Accepted Manuscript

An advanced anti-icing/de-icing system utilizing highly aligned carbon nanotube webs

Xudan Yao, Stephen C. Hawkins, Brian G. Falzon

PII: S0008-6223(18)30398-1

DOI: [10.1016/j.carbon.2018.04.039](https://doi.org/10.1016/j.carbon.2018.04.039)

Reference: CARBON 13076

To appear in: *Carbon*

Received Date: 16 February 2018

Revised Date: 24 March 2018

Accepted Date: 15 April 2018

Please cite this article as: X. Yao, S.C. Hawkins, B.G. Falzon, An advanced anti-icing/de-icing system utilizing highly aligned carbon nanotube webs, *Carbon* (2018), doi: 10.1016/j.carbon.2018.04.039.

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

An Advanced Anti-icing/De-icing System Utilizing Highly Aligned Carbon Nanotube Webs

Xudan Yao¹, Stephen C. Hawkins^{1,2}, and Brian G. Falzon^{1,*}

¹School of Mechanical and Aerospace Engineering, Queen's University Belfast, UK, BT9 5AH

²Dept. of Materials Science and Engineering, Monash University, Clayton, Vic., Australia, 3800

*Corresponding Author: Fax: +44 (0)28 9097 4148

E-mail address: b.falzon@qub.ac.uk (B.G. Falzon)

Abstract

A carbon nanotube (CNT) web is a horizontally oriented continuous film, obtained by drawing CNT forests produced by chemical vapour deposition (CVD). As the CNTs are highly conductive and predominantly aligned along the draw direction, by controlling the aspect ratio of these CNTs and the number of stacked web layers, a tailored resistance can be achieved. Layers of CNT web are compared to plies of carbon fiber (CF), as the heating elements within a glass fiber laminate assembly. Compared with the CF-heater as well as existing state-of-the-art heating systems, the highly aligned CNT-web-heater possesses negligible weight (e.g. compared with eight CF plies (3633.8 g m^{-2}), an equivalent 20-CNT-web heater (0.38 g m^{-2}) is $\sim 10^4$ times lighter), rapid and uniform heating, efficient energy consumption and its electro-thermal behaviour can be tuned to suit any surface and power requirement to achieve rapid anti-icing/de-icing. Both anti-icing and de-icing performance

have been verified and in particular, for de-icing, with a constant 4.9 kW m^{-2} power supply, the GF laminate with 40 layers of CNT web could remove accreted ice within 15 seconds.

1. Introduction

In cold and cloudy conditions, aircraft are susceptible to ice accumulation on aerodynamic surfaces which can lead to loss of efficiency or loss of flight control [1]. In the latest passenger aircraft, e.g. the Airbus A350 XWB and Boeing 787, more than 50 wt. % carbon fiber reinforced polymer (CFRP) composite has been used in the primary structure. As discussed in our previous paper [2], the development of an energy efficient, low maintenance and compatible system to prevent icing or to remove accumulated ice (i.e. anti-icing/de-icing or AI/DI), for composite aircraft is an urgent problem.

AI/DI is conventionally achieved by bleeding hot air from the engine compressor stages where it is ducted along piping to the inside of the leading edges and the heat transferred to the outside surface by thermal conduction [3]. The spent bleed air is subsequently exhausted through small holes in the wing. This adds weight and maintenance requirements, and is energy inefficient [4]. Such a system is even less efficient for composite wings which are less thermally conductive than metal. Electro-thermal (i.e. resistance heater) systems that are applied to or within the surfaces are an attractive alternative. They can deliver higher energy efficiencies, low maintenance requirements and the absence of bleed exhaust holes, airplane drag and noise are improved. Various materials have been investigated as the heating element, including carbon nanotubes (CNTs) [5–16], graphene [17–21], carbon fiber (CF) [22], sprayable metal layer [23], electro-conductive textile [4] and constantan wires [24]. Among the materials, metal layers and wires are relatively heavy, incompatible with CFRP materials leading to interface problems, and do not enhance structural properties. Carbon-based electro-thermal heating elements [25,26] for AI/DI are attractive alternatives to metals as they are

compatible with the CFRP matrix and potentially contribute to the structural properties of the material. Different forms of CF, such as woven fabric, unidirectional (UD) fabric and short fiber mats, have been used as the heating element both for AI/DI as well as for curing the composites [27], and UD fabric will be used as the comparison material in this work.

CNTs have generated a great deal of interest over recent decades owing to their high thermal and electrical conductivities and extraordinary specific strength and stiffness. Although individually conductive, macroscale assemblies of relatively short CNTs have multiple resistive contacts and thus are a promising material for AI/DI. When applied as a dispersion in the resin matrix, this approach requires first that the CNTs used be readily dispersible and amenable to uniform distribution. Such particles must be relatively very short and, with productivity considerations, tend to be the commodity level CNTs with high levels of tangling and defects, and carbon and metal contaminants. A more fundamental problem is that dispersions above a few weight percent, especially of the longer and better dispersed CNTs, become unmanageably viscous, severely limiting the loadings that can be used and incurring significant penalties of resin enrichment and weight. CNTs applied as a ‘buckypaper’ also require dispersion in a solvent followed by filtration [28]. More controlled morphologies such as ‘fuzzy fibers’ (CNTs grown directly onto CF) [29], continuously aerogel-formed CNT films [16,30,31] and ‘knocked-down’ or ‘domino-tipped’ forests of CNTs [13,14,32] have been studied by different research groups, but face problems of processing, purity, orientation, weight and adjustability as discussed in our previous work [2].

A ‘CNT web’ is produced, in-house, by drawing a continuous sheet or film of horizontally oriented CNTs from specially grown CNT forests, with controlled diameter and length, produced by chemical vapour deposition (CVD) [33]. The directly drawn CNT web is highly aligned and conductive along the draw direction, and the resistance of a laminated CNT web can be easily adjusted through varying the number of layers [2,34]; meanwhile, the length of

constituent CNTs can be controlled by the CVD procedure. Furthermore, the design of the heater may be optimised according to specific requirements, e.g. the leading edges, where more power is needed, may incorporate additional layers of CNT webs. Owing to the adaptability and conformability of the system, any thermo-electrical response could be obtained and applied to any location as required.

In a previous study [2], CNT heaters were integrated within a CFRP layup, analogous to a structural component, to investigate the characteristics, advantages and problems with that approach. This work reports a separate heating element which could be applied to the outer surface of an aerostructure to improve the ice protection efficiency without affecting the mechanical properties and without requiring the entire component to be heated. Woven glass fiber (GF) prepregs were used to support and insulate the extremely thin CNT which were co-cured with the laminate. The heating element, GF and distribution buses were combined to provide a thin, light and efficient anti-icing/de-icing system. For comparison, GF laminates were also produced with CF plies as the heating element. Composites with different layers of CNT web as well as different plies of CF were prepared and assessed for their heating performance, and anti-icing and de-icing capability. The highly aligned CNT-web-heater presents negligible weight, uniform heating, efficient energy consumption and rapid anti-icing/de-icing.

2. Experimental section

2.1 Materials

Gurit SE84LV/HMC CF/epoxy unidirectional prepreg and SE84LV/RE295 GF/epoxy woven prepreg were used to prepare the heater specimens. Strips of copper foil (Alfa Aesar, 25 micron thick) of 10 mm width were used as the electrical buses to connect the samples to a power supply. The CNT forests were fabricated by CVD of acetylene at a temperature of

700 °C, grown on a silicon wafer with iron as the catalyst [35], yielding an average CNT length of 300 μm and an average diameter of 10 nm. The obtained CNTs (Fig. 1a) were drawn directly into a fine continuous web (Fig. 1b). Through winding onto open aluminium frames (Fig. 1c), CNT webs with a desired number of layers can be obtained.

Figure 1. (a) Scanning electron microscopy (SEM) image of drawable CNT forests (b,c) CNT webs (d) GF/CNT/GF epoxy composite (e) Cross-section SEM of the sample with 10 layers of CNT web (f) GF/CF/GF epoxy composite

2.2 Sample preparation

CNT web (10 to 40 layers) (Fig. 1d) and CF prepreg (1 to 16 layers) (Fig. 1f) of size 70 mm $\times$ 50 mm were embedded between two plies of woven GF prepreg (100 mm $\times$ 70 mm). Copper foil buses were placed between the heating element and GF, leaving a test area of 50 mm $\times$ 50 mm (Fig. 1d,f). The Cu buses are normal to the direction of CNT webs while parallel to the

direction of CF, owing to their appropriate electrode resistance in these respective directions. After the layup, the composites were cured at 120 °C for 1 hour using the ‘vacuum bagging’ method, and the basic parameters were measured (Table 1). The SEM image of the cross section of the CNT 10 sample (Fig. 1e) indicates the thickness of 10 layer resin-impregnated CNT web is ~6 μm .

Table 1. Samples properties of CNT web or CF plies between two layers of GF

Specimen	Heating element	Mass (g)	Thickness (mm)
Control (GF only)	-	6.13 $\pm$ 0.20	0.45 $\pm$ 0.01
CNT 10	10 layer CNT web	6.10 $\pm$ 0.31	0.46 $\pm$ 0.01
CNT 20	20 layer CNT web	6.15 $\pm$ 0.21	0.46 $\pm$ 0.01
CNT 30	30 layer CNT web	6.18 $\pm$ 0.09	0.46 $\pm$ 0.01
CNT 40	40 layer CNT web	6.21 $\pm$ 0.11	0.46 $\pm$ 0.01
CF 1	1 layer CF	7.75 $\pm$ 0.12	0.73 $\pm$ 0.01
CF 2	2 layer CF	9.27 $\pm$ 0.09	1.01 $\pm$ 0.01
CF 4	4 layer CF	12.62 $\pm$ 0.20	1.59 $\pm$ 0.03
CF 8	8 layer CF	19.14 $\pm$ 0.16	2.79 $\pm$ 0.03
CF 12	12 layer CF	24.52 $\pm$ 0.25	3.86 $\pm$ 0.03
CF 16	16 layer CF	31.21 $\pm$ 0.44	5.08 $\pm$ 0.04

2.3. Characterization

A JSM-6500F Field Emission Scanning Electron Microscope was used to observe the morphology of CNTs (Fig. 1a,b,e). An Agilent 34450A 5½ Digit Multimeter was employed to

measure the resistance of the samples, using the four-probe method. Samples for resistive heating performance were held horizontal at ambient temperature. The current was supplied by an EA Elektro-Automatik PS 3016-20B Digital Bench Power Supply, the temperatures of the samples were recorded by RS-1384 4 Input Data Logging Thermometers using four K-type thermocouples (TCs) applied to the front (top) of the samples, and the temperature distribution was monitored by an FLIR SC640 thermal imaging (IR) camera.

For the anti-icing and de-icing test, a 3 mm high dam was created around the heated area of 25 cm² and filled with 7.5 mL water for each sample. For anti-icing, each sample was mounted horizontally to hold the liquid water added at 0 °C immediately prior to testing. For de-icing, the water was pre-frozen and the sample mounted vertically. A thermocouple was applied to the back of each sample to monitor the temperature variation during the AI / DI testing which was conducted in an environmental chamber at -12 °C to -25 °C with a digital camera set to monitor the procedure at 10 s intervals (Fig. 2).

Figure 2. Experimental setup for de-icing

3. Results and Discussion

3.1. Heating Performance

3.1.1. Heating Rate

The resistance (bus to bus) of the CF and CNT web composites with GF showed the expected inverse relationship with number of layers (Fig. 3a). Samples with ten, twenty, thirty and forty layers of CNT web have very similar resistance to samples with four, eight, twelve and sixteen layers of CF respectively. For the heating performance, a constant voltage, 16 V, was applied with current and therefore power limited by the sample resistance. Thus, samples with lowest resistance reached the highest temperatures. The temperature at central points of the samples (Fig. 3b) showed that, with CNTs as the heating element (CNT 10, CNT 20, CNT 30 and CNT 40) the samples attained higher heating and cooling rates and a higher plateau temperature than CF samples with comparable resistances (CF 4, CF 8, CF 12 and CF 16 respectively) and hence energy dissipation. The heating/cooling rate curves of samples CNT 40 and CF 16, derived from the temperature profiles (Fig. 3b), illustrate the much higher peak rate of the former ($2.6\text{ }^{\circ}\text{C s}^{-1}$) compared with the latter ($0.7\text{ }^{\circ}\text{C s}^{-1}$) and quicker equilibration (Fig. 3c).

The temperature-time (T-t) curves of all specimens in the first 30 seconds of heating (Fig. 3d) all show a linear trend. The slopes (i.e. initial heating rate) for the CNT samples are higher and strongly correlated with the number of web layers (Table 2) whereas for the CF samples, there is not a clear relationship. Thus after only 30 seconds, the CNT 10, CNT 20, CNT 30 and CNT 40 samples reached $46\text{ }^{\circ}\text{C}$, $66\text{ }^{\circ}\text{C}$, $85\text{ }^{\circ}\text{C}$ and $95\text{ }^{\circ}\text{C}$ respectively, whereas the highest

temperature the CF samples reached is only 39 °C for the CF 12 sample followed by the CF 16 and CF 8 samples.

Figure 3. (a) The resistance variation with the change of CNT web or CF layer (b) Room temperature heating performance of samples with different layers of CNT web or CF plies as the heating element, under a constant voltage 16 V (c) Heating/cooling rate of sample CNT 40 and CF 16 (d) Heating profile of CNT and CF samples for the first 30 seconds.

Table 2. Parameters of linear trendlines in Fig. 3c, a is the heating rate

Specimen	T = at + b	
Type	a (°C/s)	b (°C)
CNT 10	0.80	21.79
CNT 20	1.45	23.37
CNT 30	2.13	22.28
CNT 40	2.38	26.55
CF 1	0.17	22.05
CF 2	0.28	21.05
CF 4	0.29	21.70
CF 8	0.44	20.68
CF 12	0.56	22.39
CF 16	0.47	22.17

The strong relation of the heating rate with CNT web number reflects both the extremely low thermal mass of the CNT component, but also the reliability of the construct. The CNT web connectivity is established and stable prior to its insertion in the laminate, hence the resistance and heating are predictable and reproducible. The CF conductive structure by contrast depends upon the establishment of CF-CF contacts during the layup and cure phase and is strongly influenced by the fiber volume fraction [2], which is acutely sensitive to factors such as the initial value, the fiber alignment and the curing pressure and temperature profile.

3.1.2. Heating Uniformity

In order to investigate the uniformity of heat distribution, four thermocouples were applied to each sample with TC1 on the top of the Cu bus and TC3 at the sample center (Fig. 4), while an IR camera was used to monitor the general heat distribution. Samples with eight layers of CF (Fig. 4 a, d); twenty layers of CNT web (Fig. 4 b, e); and, from a published report [24], constantan wires (Fig. 4 c, f) as the heating element, were compared. Although having closely similar resistance, the CNT web structure had a higher heating and cooling rate (Fig. 4b) and final temperature than the CF (Fig. 4a), which indicates that it needs less time and energy to reach the desired temperature, meeting the requirement of rapid de-icing. Moreover, the temperature variation across the CNT web specimen, as shown by IR imaging (Fig. 4e) with the contour plot, is negligible compared with that for CF (Fig. 4d) which also displays greater heating at the buses because of the relatively higher contact resistance there. In comparison with CNT web, the constantan wire-heated specimen [24] shows significant uneven temperature distribution (Fig. 4 c, f). In addition, compared with eight CF plies (3633.8 g m^{-2}), the 20-CNT-web heater (0.38 g m^{-2}) is $\sim 10^4$ times lighter.

Figure 4. Temperature history and distribution at 16 V, and TC locations for (a, d) GF laminate with 8 layers of CF (b, e) and GF laminate with 20 layers of CNT web; (c, f) [24] temperature distribution of device with constantan wires as the heating element.

3.1.3. Energy Consumption

By conservation of energy, the input power ($\dot{q}_{in}$) from the power supply equals the output power ($\dot{q}_{out}$), which comprises the energy absorbed by the structure ($cm \frac{dT(t)}{dt}$), heat conduction ($\dot{q}_{cond}$), convection ($\dot{q}_{conv}$) and heat radiation ($\dot{q}_{rad}$) to the environment (Eq. 1-4):

$$\dot{q}_{in} = \frac{U^2}{R} \quad (1)$$

$$\dot{q}_{out} = cm \frac{dT(t)}{dt} + \dot{q}_{cond} + \dot{q}_{conv} + \dot{q}_{rad} \quad (2)$$

$$\dot{q}_{out} = cm \frac{dT(t)}{dt} + kA \frac{T_s - T_\infty}{\Delta x} + hA(T_s - T_\infty) + \varepsilon\sigma A(T_s^4 - T_\infty^4) \quad (3)$$

$$\dot{q}_{in} = \dot{q}_{out} \quad (4)$$

Where U is the input voltage (16 V) and R the sample resistance; c , m and T are the specific heat capacity, mass and temperature of the sample respectively, and A is the heating area. T_s and T_∞ represent the sample surface temperature and the environmental temperature respectively; Δx is the distance between the surface of the sample and the environment; k , h , ε and σ are the thermal conductivity of air ($0.024 \text{ W m}^{-1} \text{ K}^{-1}$), heat transfer coefficient of air, emissivity (1 was selected according to the calibration between the IR camera and TCs) and Stefan–Boltzmann constant ($5.67 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$) respectively.

The heat transfer of the sample structures (Fig. 5a) can be homogenised as all the samples have been prepared between two layers of GF which can be combined with the heating element to form a simplified heating system (Fig. 5b).

Figure 5. Schematic of the heat transfer of (a) the real heating system (b) the simplified heating system.

The heat distribution of the sample ‘system’ at the steady state temperature (Fig. 6a) can be divided into radiative (Fig. 6b) and convective (Fig. 6c) components as well as conduction and absorption within the system. Heat conduction to the air can be neglected as the thermal conductivity of the air is only $0.024 \text{ W m}^{-1} \text{ K}^{-1}$. Radiation is proportional to the fourth power of the absolute temperature (Fig. 6b), however the relatively modest temperatures and differences encountered in this work ensure that the major energy loss is through convection (Fig. 6c).

During the steady-state, the temperature of the sample is stable, thus (Eq. 5, 6):

$$cm \frac{dT(t)}{dt} = 0 \quad (5)$$

$$\dot{q}_{conv} = \dot{q}_{in} - \dot{q}_{rad} \quad (6)$$

The slope of the $\dot{q}_{conv}/A - \Delta T$ curve is the heat transfer coefficient of air, $h = 20.12 \text{ W m}^{-2} \text{ K}^{-1}$ (Fig. 6d), for this particular system (i.e. free convection from a horizontal surface) which can be applied for the initial heating stage calculation.

Figure 6. (a) Steady-state temperature with the CNT web and CF layer. (b) Radiative and (c) convective heat loss at the steady-state. (d) Convection density changes with the temperature difference between the surface of the sample and the environment.

In the initial (30 s) linear heating phase the energy input (Q_{in} , Eq. 7) is distributed primarily to convection (Q_{conv} , Eq. 8, with h obtained as 20.12), radiation (Q_{rad} , Eq. 9) and absorption (Q_{abs} , Eq. 10). The distribution for the CNT samples (Fig. 7a) shows both the very minor radiative component and the substantial amount of energy absorbed (Eq. 10) to heat the sample, but with already a significant convective component. In contrast, the CF samples (Fig. 7b) absorb almost all the input energy that goes to heating the sample with very little available for convective heating from the surface.

$$Q_{in} = \frac{U^2}{R}t$$

(7)

$$Q_{conv} = \int hA(T_s - T_{\infty})dt$$

(8)

$$Q_{rad} = \int \varepsilon\sigma A(T_s^4 - T_{\infty}^4)dt$$

(9)

$$Q_{abs} = Q_{in} - Q_{conv} - Q_{rad}$$

(10)

Figure 7. Energy distribution of (a) CNT web and (b) CF samples in the initial 30 seconds.

(Q_{in} : input energy, Q_{abs} : sample absorbed energy, Q_{conv} : heat convection, Q_{rad} : heat radiation)

Table 3. Thermal mass of CNT web and CF samples

Sample	CNT 10	CNT 20	CNT 30	CNT 40	CF 1	CF 2	CF 4	CF 8	CF 12	CF 16
C_{th} (J/°C)	2.82	3.04	2.92	3.76	4.18	6.09	9.89	11.34	23.09	33.77

Samples with CNT web as the heating element absorbed up to 70% of input energy while CF samples absorbed up to 96%. Accordingly, CF samples need to expend more energy to heat up the sample before they could remove the ice. This is reflected in the thermal mass C_{th} (Table 3) or energy per degree of temperature rise which is governed both by the overall mass of the sample and the heat capacity of the components.

3.2. Anti-icing

To test the anti-icing performance, samples, with a thermocouple attached to the center of the surface on the under-side, were fixed horizontally in an environmental chamber (-18 °C to -25 °C). A bund was formed around the edges on the top surface and, after precooling, water at 0 °C (7.5 mL) poured on, to a depth of 3 mm. A constant voltage, 10 V, was then immediately applied to the samples and the temperature history recorded (Fig. 8) over a period of nine hours.

Over the full 9 h period, (Fig. 8a), composites with 20, 30 and 40 layers of CNT web, as well as twelve and sixteen layers of CF, displayed a similar trend, characterized by three stages. The first stage is heating until the samples and water reached a steady state temperature (second stage) (Fig. 8b) during which evaporation of water balanced heat inflow. As water was depleted and dry patches appeared, the temperature increased to a higher steady-state value (third stage).

During the first heat-up stage, the CF sample heats more quickly and to a higher temperature than the equivalent CNT sample (Fig. 8b). However this appears to be an artefact of the TC placement on the underside of the sample. A significant thermal gradient is thought to develop in the CF sample because of its thickness, such that the temperature of the under-side is significantly higher than that of the top-side from where water is evaporating. This becomes

evident when dry patches appear on the CF 16, 12, and 8, and CNT 40, 30 and 20 samples and temperature rise for the CNT samples is much faster and to a higher value than for the equivalent CF samples (Fig. 8a). Samples with 16 and 12 layers of CF, and with 40 and 30 CNT web layers dried fully. However the unevenness of the CF heating is illustrated by the icing appearance of the CF 8 sample which becomes ice free only in the very center but freezes in the periphery whereas the CNT 20 equivalent is ice free over a much larger area (Fig. 8c).

Figure 8. Temperature history during the anti-icing procedure at 10 V (a) for the whole 9 hours (b) for the first hour. (c) Images of the final ice performance.

Composites with one, two and four layers of CF or 10 layers of CNT web also exhibited the heat-up and plateau stages however the input power was not sufficient to prevent the water from freezing (Fig. 8c). After all the water was frozen, the absorbed heat and the released heat reached a new thermal equilibrium. Thus under this condition, laminates with one, two, or four layers of CF or 10 layers of CNT web could not achieve effective anti-icing.

3.3. De-icing

De-icing requires additional energy to overcome the latent heat of melting compared with anti-icing, so a higher constant voltage, 16 V, was used. To test the de-icing performance, a layer of ice was formed on one side of the samples in advance, and, with a thermocouple attached to the center of the surface on the other side, the samples were fixed vertically in an environmental chamber at -12 °C. When the interfacial ice melts and gravity overcomes the interfacial tension, the ice slips off and the temperature of the sample increase abruptly, as would occur in practice and illustrated for the CNT 30 sample (Fig. 9). As the power is applied, the melted ice contributes to the darker colour. With more and more interfacial ice melted, the whole ice layer started to move at 60 seconds and separated at 70 seconds. For the CNT 40 sample, this occurred in just 30 seconds, whereas for twelve and sixteen layers of CF, it needed 80 and 60 seconds respectively. Samples with 20 layers of CNT web or eight layers of CF, having similar resistance, needed 150 s and 190 s respectively, while samples with 10 layers of CNT web or four layers of CF needed around 300 s. Composites with one or two layers of CF were unable to shed the ice. When it comes to actual flight conditions, the air flow would dislodge the ice when the interfacial ice melts and the temperature reached zero degree, which would bring the de-icing time down to 15 s (CNT 40), 25-35 s (CF 16, CNT 30, CF 12, CNT 20), 60-70 s (CNT 10, CF 8, CF4) and 135s (CF 2).

Figure 9. Temperature history during the de-icing procedure at 16 V (a) for the whole 500 s (b) for the first 100s. (c) The evolution of de-icing for the CNT 30 sample during the de-icing at 16 V. Darkening of sample results from melting interface until ice layer slips (70 s).

3.4. A Comparison of Electro-Thermal Systems

From a comparison of the diverse electro-thermal systems (Table 4), nanomaterials including graphene and CNTs contribute to thinner, lighter, compatible, rapid and energy efficient heaters. Among them, the highest heating rate reached $3500\text{ }^{\circ}\text{C s}^{-1}$ by the aligned CNTs heated at a power density of 33.3 kW m^{-2} , however with no substrate [16]. In order to apply the heater to different applications, various substrates have been studied. With PET, glass or PI applied as the substrate to form a transparent film heater, a rate of $37.5\text{ }^{\circ}\text{C s}^{-1}$ has been reached at 30 kW m^{-2} power supplied [8]. In practice, application to a CFRP as in this work,

heating rate reached $2.6\text{ }^{\circ}\text{C s}^{-1}$ under only 4.9 kW m^{-2} , whereas dispersed CNTs reached $0.8\text{ }^{\circ}\text{C s}^{-1}$ under 3.7 kW m^{-2} [15] and CF reached $0.7\text{ }^{\circ}\text{C s}^{-1}$ under 6.5 kW m^{-2} . Graphene ink applied on the top of peel ply and CFRP composites reached $3.4\text{ }^{\circ}\text{C s}^{-1}$ under 4.0 kW m^{-2} [20]. However, it is applied on the surface without any coverings, moreover, its heating uniformity is much worse than the CNT web.

Table 4. Comparison between diverse heating elements of electro-thermal systems.

Material	Comment	Substrate	Thickness (μm)	Sheet resistance ($\Omega\text{ sq}^{-1}$)	Power density (kW m^{-2})	Max heating rate ($^{\circ}\text{C s}^{-1}$)	ΔT_{max} ($^{\circ}\text{C}$)	Ref.
Metal layer (Boeing 787)	Hand spray	GF fabric + CF/epoxy prepreg	-	-	3.6-11.8	-	24	[36]
Constantan wires	From Omega	GF/epoxy prepreg Resin film + insulating polymer	250	-	5.0-8.3	-	27-82	[24]
Electro-conductive textile	From Gorix		-	70-92.5	0.3-1.2	~ 0.1	10-37	[4]
CF	UD ¹ (0°)	No	150	4.6	0.5-6.5	-	13-115	[22]
	UD (90°)	GF/epoxy prepreg	283-4620	15.8-264.5	0.4-6.5	0.2-0.7	15-132	This work
Graphene	LbL ² doping	Glass, PET ³	-	43-403	0.2-5.7	~ 3	80-98	[17,18]
	Spin coating	PI ⁴	34-37 ($\times 10^{-3}$)	0.6-6.1 ($\times 10^3$)	20	16	185	[19]
	Printing	Peel-ply + CF/epoxy prepreg	11	~ 30	4.0	3.4	104	[20]
	Spray coating	PU ⁵ coated PI	0.1-0.2	1020-4970	3.9	-	-	[21]
Dispersed CNTs	Vacuum filtration	Glass or PET	188-250	230-3500	3.2-6.4	1.3	95-120	[5]
	Spray coating	Glass	0.55	130-190	7.6-11.1	-	140	[6]
	Dip coating	Glass	7-25 ($\times 10^{-3}$)	22.6-54.6 ($\times 10^3$)	0.02-1.6	2	21	[7]
	Suspension	Epoxy +	70	4	0.4-3.7	0.8	10-	[15]

	filtration	GF					100	
	Knocked-down	Epoxy film	80	5.9-12.8	0.3-1.3	-	4-14	[13,14]
	Directly spun from CVD	No	-	-	33.3	3500	375	[16]
Aligned CNTs	Directly drawn	PET or glass or no	-	172-3180	0.5-30	3.5-154	55-120	[8-12]
	Directly drawn	GF/epoxy prepreg	6-24	20.9-76.0	1.3-4.9	0.9-2.6	54-140	This work

¹unidirectional; ²Layer-by-layer; ³poly (ethylene terephthalate); ⁴polyimide; ⁵polyurethane.

It was assumed that the current system used on the Boeing 787 (metal spray), requires a steady state temperature of 6 °C for effective anti-icing under -18 °C operational ambient conditions, expending 11.8 kW m⁻² without considering the energy absorbed by the composite structure [36]. A comparison between CNT web and CF samples (Fig. 6) shows that the CNT web samples exhibited lower absorbed thermal energy owing to their lower thermal mass. Moreover, considering that a heating element, comprising 20 layers of CNT web, has an areal density of 0.38 g m⁻² and a thickness of 12 μm, if a sprayed lightweight metal could be deposited, to the same thickness, (e.g. aluminum, 2.7 g cm⁻³), the areal density would be 32.4 g m⁻², 85 times heavier. As a consequence, the CNT-web-heater is lighter, requires less energy consumption and has better compatibility with composite materials in which it is embedded, ensuring structural integrity. Having already established rapid heating rate and uniformity, tunability, compatibility and energy efficiency, CNT web is a promising heating element for an electro-thermal anti-icing/de-icing system.

4. Conclusions

CNT web was utilized as an electro-thermal heating element for anti-icing and de-icing of composite structures. The weight required compared with a carbon fiber equivalent is ~10⁴ times less. The temperature level and uniformity achieved are superior and benefits are

observed in flexibility and bus-contact resistance. The high heating rate, reliable and predictable performance and low thermal mass of the CNT web structure are particularly suited to the AI/DI application. In order to verify the CNT web's function as an effective heating element for ice protection, both de-icing and anti-icing studies were conducted. The results show that the GF laminate with 30 and 40 layers of CNT web, as well as twelve and sixteen layers of CF, reached both anti-icing and de-icing successfully. However, the heating and cooling rate, which relates to the speed of the ice protection, of the laminate with CNT web as the heating element is higher than the CF one. In particular, for de-icing, with a constant 16 V voltage supply, the GF laminate with 40 layers of CNT web could remove accreted ice within 15 seconds under $-12\text{ }^{\circ}\text{C}$ ambient temperature with 4.9 kW m^{-2} .

Compared with existing state-of-the-art heating systems, the highly aligned CNT-web-heater possesses negligible weight, rapid and uniform heating, efficient energy consumption, higher compatibility with CFRP, and can be tuned both in terms of shape and performance to suit any surface and power requirement to achieve rapid AI/DI. Directly drawn CNT web is essentially catalyst and damage free and is of great potential utility for a number of other functions such as structural health monitoring, lightning strike protection and interlaminar fracture toughness enhancement. Thus having it also applicable as an electro-thermal element whether for AI/DI or for any heating application within an aero-structure is a particularly attractive and efficient option. It is recognized that the foregoing study has focused on unidirectional CNT webs where the electro-thermal properties have been assessed along the 'draw' direction. Their electro-thermal properties are, indeed, highly orthotropic which suggests that the stacking of these webs, at different orientations, provides an added level of electro-thermal tuning. A detailed study of laminated multi-directional CNT webs has been completed and will be presented in a paper to follow.

Acknowledgements

The authors would like to acknowledge the financial support received from the European Union's 7th Framework Programme for Research under the Marie Curie Career Integration grant agreement No. 630756.

References

- [1] Napier D, Son. Electro-thermal heating system for protection of aircraft and ships against icing. *Polar Rec* 1958; 9:36–9.
- [2] Yao X, Falzon BG, Hawkins SC, Tsantzalis S. Aligned carbon nanotube webs embedded in a composite laminate: A route towards a highly tunable electro-thermal system. *Carbon* 2018; 129:486–94.
- [3] Thomas SK, Cassoni RP, Arthur CD Mac. Aircraft Anti-Icing and De-Icing Techniques and Modeling. *J Aircr* 1996; 33:841–54.
- [4] Falzon BG, Robinson P, Frenz S, Gilbert B. Development and evaluation of a novel integrated anti-icing/de-icing technology for carbon fibre composite aerostructures using an electro-conductive textile. *Compos Part A Appl Sci Manuf* 2015; 68:323–35.
- [5] Yoon YH, Song JW, Kim D, Kim J, Park JK, Oh SK, et al. Transparent film heater using single-walled carbon nanotubes. *Adv Mater* 2007; 19:4284–7.
- [6] Kim D, Lee HC, Woo JY, Han CS. Thermal behavior of transparent film heaters made of single-walled carbon nanotubes. *J Phys Chem C* 2010; 114:5817–21.
- [7] Kang TJ, Kim T, Seo SM, Park YJ, Kim YH. Thickness-dependent thermal resistance of a transparent glass heater with a single-walled carbon nanotube coating. *Carbon* 2011; 49:1087–93.
- [8] Liu P, Liu L, Jiang K, Fan S. Carbon-nanotube-film microheater on a polyethylene terephthalate substrate and its application in thermochromic displays. *Small* 2011; 7:732–6.

- [9] Feng C, Liu K, Wu JS, Liu L, Cheng JS, Zhang Y, et al. Flexible, stretchable, transparent conducting films made from superaligned carbon nanotubes. *Adv Funct Mater* 2010; 20:885–91.
- [10] Jang HS, Jeon SK, Nahm SH. The manufacture of a transparent film heater by spinning multi-walled carbon nanotubes. *Carbon* 2011; 49:111–6.
- [11] Jung D, Kim D, Lee KH, Overzet LJ, Lee GS. Transparent film heaters using multi-walled carbon nanotube sheets. *Sensors Actuators, A Phys* 2013; 199:176–80.
- [12] Im H, Jang EY, Choi A, Kim WJ, Kang TJ, Park YW, et al. Enhancement of heating performance of carbon nanotube sheet with granular metal. *ACS Appl Mater Interfaces* 2012; 4:2338–42.
- [13] Buschhorn ST, Lachman N, Gavin J, Wardle BL. Electrothermal Icing protection of Aerosurfaces Using Conductive Polymer Nanocomposites. 54th AIAA/ASME/ASCE/AHS/ASC Structures, Structural Dynamics, and Materials Conference, Boston, MA, USA., April 8-11, 2013.
- [14] Brampton CJ, Pickering SG, Bowen CR, Kim AH, Buschhorn ST, Lee J, et al. Actuation of Bistable Laminates by Conductive Polymer Nanocomposites for use in Thermal-Mechanical Aerosurface. 55th AIAA/ASME/ASCE/AHS/ASC Structures, Structural Dynamics, and Materials Conference, National Harbor, MD, USA., January 13-17, 2014.
- [15] Chu H, Zhang Z, Liu Y, Leng J. Self-heating fiber reinforced polymer composite using meso/macropore carbon nanotube paper and its application in deicing. *Carbon* 2014; 66:154–63.
- [16] Janas D, Koziol KK. Rapid electrothermal response of high-temperature carbon nanotube film heaters. *Carbon* 2013; 59:457–63.
- [17] Bae JJ, Lim SC, Han GH, Jo YW, Doung DL, Kim ES, et al. Heat dissipation of transparent graphene defoggers. *Adv Funct Mater* 2012; 22:4819–26.
- [18] Kang J, Kim H, Kim KS, Lee SK, Bae S, Ahn JH, et al. High-performance graphene-based

- transparent flexible heaters. *Nano Lett* 2011; 11:5154–8.
- [19] Sui D, Huang Y, Huang L, Liang J, Ma Y, Chen Y. Flexible and transparent electrothermal film heaters based on graphene materials. *Small* 2011; 7:3186–92.
- [20] Glover ENK, Bowen CR, Gathercole N, Pountney O, Ball M, Spacie C, et al. Graphene based skins on thermally responsive composites for deicing applications. *Proc SPIE* 2017; 10165:101650G–4.
- [21] Volman V, Zhu Y, Raji ARO, Genorio B, Lu W, Xiang C, et al. Radio-frequency-transparent, electrically conductive graphene nanoribbon thin films as deicing heating layers. *ACS Appl Mater Interfaces* 2014; 6:298–304.
- [22] Kim T, Chung DDL. Carbon fiber mats as resistive heating elements. *Carbon* 2003; 41:2436–40.
- [23] Sloan J. 787 integrates new composite wing deicing system. *CompositesWorld* 2008.
- [24] Mohseni M, Amirfazli a. A novel electro-thermal anti-icing system for fiber-reinforced polymer composite airfoils. *Cold Reg Sci Technol* 2013; 87:47–58.
- [25] Du J, Pei S, Ma L, Cheng HM. 25th anniversary article: Carbon nanotube- and graphene-based transparent conductive films for optoelectronic devices. *Adv Mater* 2014; 26:1958–91.
- [26] Sun X, Sun H, Li H, Peng H. Developing polymer composite materials: Carbon nanotubes or graphene? *Adv Mater* 2013; 25:5153–76.
- [27] Joseph C, Viney C. Electrical resistance curing of carbon-fibre/epoxy composites. *Compos Sci Technol* 2000; 60:315–9.
- [28] Zhang J, Jiang D, Peng H-X, Qin F. Enhanced mechanical and electrical properties of carbon nanotube buckypaper by in situ cross-linking. *Carbon* 2013; 63:125–32.
- [29] Pozegic TR, Hamerton I, Anguita J V., Tang W, Balocchi P, Jenkins P, et al. Low temperature growth of carbon nanotubes on carbon fibre to create a highly networked fuzzy fibre reinforced composite with superior electrical conductivity. *Carbon* 2014; 74:319–28.
- [30] Janas D, Koziol KK. A review of production methods of carbon nanotube and graphene thin

- films for electrothermal applications. *Nanoscale* 2014; 6:3037–45.
- [31] Li Y, Kinloch IA, Windle AH. Direct Spinning of Carbon Nanotube Fibers from Chemical Vapor Deposition Synthesis. *Science* 2004; 304:276–8.
- [32] Lee J, Stein IY, Kessler SS, Wardle BL. Aligned carbon nanotube film enables thermally induced state transformations in layered polymeric materials. *ACS Appl Mater Interfaces* 2015; 7:8900–5.
- [33] Huynh CP, Hawkins SC, Gengenbach TR, Humphries W, Glenn M, Simon GP. Evolution of directly-spinnable carbon nanotube catalyst structure by recycling analysis. *Carbon* 2013; 62:204–12.
- [34] Musameh M, Notivoli MR, Hickey M, Kyratzis IL, Gao Y, Huynh C, et al. Carbon nanotube webs: A novel material for sensor applications. *Adv Mater* 2011; 23:906–10.
- [35] Atkinson KR, Hawkins SC, Huynh C, Skourtis C, Dai J, Zhang M, et al. Multifunctional carbon nanotube yarns and transparent sheets: Fabrication, properties, and applications. *Phys B Condens Matter* 2007; 394:339–43.
- [36] Meier O, Scholz D. A Handbook Method for the Estimation of Power Requirements for Electrical De-Icing Systems. DLRK, Hamburg, 31 Aug-02 Sep, 2010.