Improvement in electrical characteristics by surface modification of multi-wall carbon nanotube based buckypaper for de-icing application

Francesco Zangrossi, Barun Ghosh, Fang Xu, Nick Warrior and Xianghui Hou

Abstract
Icing hazards often cause severe mobility concerns, safety risks, and even accidents in modern industries. Various ice mitigation strategies have been employed. Electro-thermal heating approach is a popular measure for ice protection, in which heat is generated electrically by internal components and then transferred to the outer surface for anti-icing and de-icing operation. Given the increasing usage of composites in aircraft structures, self-heating fibre reinforced polymer composite has been studied as an ice protection solution for the new generation aircraft. The present work focuses on improving electrical characteristics of carbon nanotube (CNT) based buckypaper (via surface functionalization) and the heating performance with an ice-phobic resin. The results indicated that surface functionalization of multi-wall carbon nanotubes (MWCNTs) was effective in obtaining MWCNT buckypaper (CNP) with improved electrical conductivity. The de-icing test confirmed the electro-thermal heating performance of the CNP based composite in a climate chamber at −20°C. The utilisation of surface modified MWCNTs in self-heating composites could be a promising strategy for maintaining lightweight and efficiency for electro-thermal systems to mitigate icing hazards.

Keywords
Multi-wall carbon nanotubes, buckypaper, electrical resistance, surface modification, de-icing

Introduction
Fibre-reinforced polymer composites are gaining an increasing attention in modern industries like aerospace, automobile, and wind energy, because of their high mechanical strength and light weight. However, in a cold region or environment, icing accretion on the composite surface often cause severe mobility concerns, safety risks, and even fatal accidents. Significant attention has been paid for developing smart de-icing systems to protect from the ice hazards in many industrial applications, including aircraft, telecommunications, and power transmission. Electro-thermal heating is one of the most popular approaches for the ice protection of polymer composites due to its capability of integration and controlling heat dissipation. Typically an electro-thermal structure consists of a metal framework and an inorganic insulator which is normally complicated and heavy. Incorporating a traditional metal foil heater in a composite structure may create a weak layer, especially under inter-laminar shear force. Thus, conductive nanomaterials into the composite structure has received increasing interest in the last decade, which could provide excellent self-heating capabilities for ice protection without sacrificing structure integration.

Carbon nanotube (CNT) is one of the most promising materials for electro-thermal heating elements of composite structures. Since the discovery of CNTs in 1991 by Iijima, CNTs have been using in various applications because of their excellent mechanical and chemical properties, high electrical and thermal conductivity. Various applications of carbon nanotubes have been reported, from antiballistic vests to electro-thermal elements. High electrical conductivity makes CNTs more attractive for electro-thermal application. Aouraghe et al. developed a flexible carbon nanotube film that could reach a steady-state temperature (>300°C) at low voltage, even after mechanical deformation and On/Off voltage switching.
cycles. Li et al.\(^{21}\) produced a transparent, flexible thin heater based on graphene and CNT sheets using a dry spinning technique. The film revealed defrosting performance at 12 V and uniform thermal distribution even after bending for 10,000 cycles. Sun et al.\(^{22}\) developed a CNT/thermoplastic polyurethane composite via a ball mixing and compression molding method. The obtained composite exhibited an electrical conductivity of 142.6 Sm\(^{-1}\) and a steady temperature of 65°C under 6 V applied voltage. Further attempts have been made to improve the intrinsic electrical conduction of CNT-based structures through surface modification of CNTs using different acid treatment. The addition of functional groups (-OH/-COOH) on the surface of CNTs can significantly increase the electrical conductivity because of the increased mobility and charge carrier concentration, thus enhancing the metallic behaviour of the nanotubes.\(^{23-25}\)

It was reported that the functional groups located at the contact area between the CNTs serve as conductance paths with lower electrical resistance.\(^{26}\) Zhang et al.\(^{27}\) showed an increase in electrical conductivity of MWCNT buckypaper from 1.3 × 10\(^{4}\) Sm\(^{-1}\) to 3.8 × 10\(^{4}\) Sm\(^{-1}\) after surface functionalization by acid treatment. Hong et al.\(^{28}\) produced a transparent de-icing CNT film by spin-coating on glass substrate. Its effective de-icing capability under a freezing condition of −20°C was demonstrated with 80 V of applied voltage. Chu et al.\(^{10}\) fabricated single-wall carbon nanotubes (SWCNTs) based composites for electro-thermal heating and de-icing applications. The SWCNTs were used to produce a buckypaper (SW-CNP), by filtration technique in glass fibre (GF) fabrics. The SW-CNP/GF/epoxy composites exhibited excellent heating performance in the temperature range of −22°C−15°C with a wind speed of 14 m/s, and the de-icing time 4−7 min. Rashid et al.\(^{29}\) produced a CNT heater by a roll-to-roll slot-die coating process. The coating sample kept the heated area ice-free and further ice accretion was prevented with 40 V applied voltage. Yao et al.\(^{30}\) developed a horizontally oriented CNTs film by chemical vapour deposition and embedded it in glass fibre fabrics to prepare composites for the de-icing purpose. During the de-icing test, the CNT/GF composites removed accreted ice within 15 s under a constant voltage of 16 V. Zhao et al.\(^{31}\) developed a multi-layered ice protection coating by a combination of MWCNTs heating element with a super-hydrophobic layer. Compared to the traditional heating element, super-hydrophobic electric heating element showed up to 58% reduction in energy consumption. Recently, fibre reinforced polymer composites embedded with CNPs have been fabricated by pre-preg and resin impregnation methods, and excellent electro-thermal characteristics has been demonstrated.\(^{32}\) Though the CNTs based self-heating element has demonstrated much improved heating performance, the overall electrical resistivity of the CNTs-based structure can be further lowered to increase the power density substantially.

The present work investigates the effect of surface functionalization on the microstructure of CNT based buckypaper and its effect on e-heating performances when impregnated with an ice-phobic resin. The acid treated buckypapers have been integrated into a composite structure by laminating the buckypaper with GF fabric followed by the impregnation in thermosetting resin (EL2 Epoxy laminating resin and Silikopon EF). EL2 Epoxy lamination resin is a commercial product used as a reference for comparison with the icephobic Silikopon EF.\(^{33}\) Microstructures and defect states of MWCNTs before and after acid treatment were systematically investigated. The self-heating element, consisting of surface-modified MWCNTs and the corresponding composites using advanced icephobic resin, could be a promising electrical heating strategy to maintain lightness and efficiency in ice mitigation.

**Experimental details**

**Raw materials**

Multi-wall carbon nanotubes (95% purity) were purchased from Merck KGaA (Darmstadt, Germany). The nanotubes had an average outer diameter of 6–15 nm and length 2.5–20 μm. Nitric acid (70 wt%) was supplied by Fisher Chemical UK Ltd (Loughborough, UK). Triton X-100 (C14H22O(C2H4O)\(_n\)) was provided by Merck KGaA (Darmstadt, Germany). The glass fibre fabric (GF, thickness 0.185 mm), EL2 laminating resin and its hardener AT30 SLOW were purchased from Easy Composite (Stoke-on-Trent, UK). Silikopon EF resin was provided by Evonik Industries AG (Essen, Germany), which was considered as an icephobic resin.

**Acid treatment**

100 mg of pristine MWCNTs were dispursed in 50 mL nitric acid. The suspension was ultrasonicated in a bath for 2 h, followed by magnetically stirring for another 2 h. At the end of the acid treatment, the suspension was filtered, washed with distilled water until pH reached 7 and then dried at 60°C overnight. The obtained product was named as NACNT.

**Preparation of carbon nanotube buckypaper**

To obtain carbon nanotube buckypaper (CNP), which was a macroscopic aggregate of CNTs, a water-based dispersion of MWCNTs (100 mg, untreated or modified) and surfactant (0.1 wt% Triton X-100) was filtered through a PTFE membrane (Omnipore Membrane Filter PTFE, 1 μm pores). The CNP layer was peeled off from the membrane after drying at 35°C overnight. The CNP layer with desired
 dimension (55 mm × 55 mm) was obtained. The thickness of the buckypaper was measured in nine different positions by a digital feeler gauge.

**Composite fabrication**

The composite samples were fabricated by laminating the buckypaper between two GF fabric layers (60 mm × 60 mm square). The GF/CNP structure was soaked in 1.5 g resin (EL2 or Silikon EF). Two copper electrodes (5 mm × 140 mm × 0.2 mm) were placed between the first GF layer and the CNP. This basic composite configuration was used to understand the effect of surface functionalization on the electro-thermal performance of the buckypapers. An optimised device configuration has to be considered to minimise the occurrence of thermal and mechanical stresses before being implemented on the industrial scale. A quick-drying silver paint from Agar Scientific was manually applied to the copper electrodes to attach with the CNPs to minimise the electrical resistance at the contact areas. The mould was made of two PTFE sheets covered with aluminium plates fixed with clamps. A schematic representation of the mould and the lay-up configuration is represented in Figure 1. The mould was made of two PTFE sheets covered with aluminium plates fixed with clamps. A schematic representation of the mould and the lay-up configuration is represented in Figure 1. The composites were heat-treated in an oven with different curing cycles. Silikon EF resin was used as icephobic matrix. The soaked GF/CNP was placed in the mould and cured at 110°C for 16 h, with a heating ramp of 1°C/min. While for EL2 laminating resin, it was mixed with AT30 SLOW hardener, with a weight ratio of 100:30, and stirred at 200 rpm for 30 min. The soaked GF/CNP was placed in the mould and cured in the oven at 65°C for 12 h, with a heating ramp of 1°C/min.

**Characterisation**

**Microstructural characterisation.** The microstructural characterisation was performed using Scanning electron microscopy (SEM), Transmission electron microscope (TEM), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS) and confocal microscope. TEM analysis was carried out by a Jeol 2100F FEG-TEM with field emission electron gun (FEG) providing electron source at 200 kV, equipped with a GATAN Orius SC1000 camera for high angle angular dark field (HAADF). A high definition field emission scanning electron microscope (JSM - 7100F) was used for morphological characterisation of the buckypaper and the corresponding composite samples. Raman spectra were collected at room temperature using a triple monochromator (T-64,000, Jobin-Ivon/Horiba Group, Kyoto, Japan) equipped with a charge-coupled device (CCD) detector. The excitation source used a 532 nm Nd:YVO₄ diode pumped solid-state laser (SOC JUNO, Showa Optronics Co Ltd, Tokyo, Japan) operating with a nominal power of 200 mW. The lateral resolution of the Raman microprobe was in the order of 1 μm. XPS analysis was performed by a photoelectron spectrometer JPS-9010 MC (JEOL Ltd, Tokyo, Japan) with an X-ray source of monochromatic MgKα (output 10 kV, 10 mA). The testing chamber was controlled under a vacuum level of 2 × 10⁻⁷ Pa. To neutralize the surface charge during data acquisition, a low-energy electron flood gun was used to deliver the electrons to the sample surface. A 3D laser scanning confocal microscope (Keyence VK-X150K) was used to analyse the surface rugosity of the buckypaper.

**Electrical resistance.** Figure 2 shows an assembled CNP heating device for testing the electrical resistance of the buckypaper. The device was composed of two Polyether Ether Ketone (PEEK) films (70 mm × 70 mm × 100 μm) placed in between two aluminium sheets (60 mm × 60 mm × 2 mm), one CNP layer in contact with two T-shape copper electrodes. The CNP films were laminated between the two PEEK sheets. Clamps were used to fix the devices and to keep the buckypaper in contact with the electrodes.

The prepared CNP and the respective composite samples were connected to a power supply (linear DC bench power supply CSI530S, by Circuit Specialists) that provided a constant electrical potential difference (5 V) between the two electrodes. The electrical current was recorded and the resistivity of the sample was calculated by Ohm’s law

\[ V = I R \]  \hspace{1cm} (1)

\[ R = \rho \frac{L}{S} \]  \hspace{1cm} (2)

where \( V \) is the voltage (V), \( I \) is the electrical current (A), \( R \) is the electrical resistance (Ω), \( \rho \) is the resistivity (Ω m), \( L \) is the length of the sample (mm) and \( S \) is the cross section of the sample (mm²).

**Figure 1.** Schematic diagram of the layer-up configuration in the mould.
De-icing evaluation. The composite samples were placed in a cold chamber at $-20^\circ C$ and 100 mL of distilled water were nebulized and delivered into the chamber. A 2 mm thick rim ice layer was formed on the top surface of the samples. Then an electrical potential of 5 V was applied until the ice fully disappeared from the surface. An IR thermo-camera (FLIR E4, operating in Multi-Spectral Dynamic Imaging mode) was used to measure the temperature of the sample surface every 15 s from the start of the heating.

Results and discussion

Buckypaper

To study the microstructures MWCNTs after acid treatment, Raman spectroscopy has been used and the data is presented in Figure 3 after normalization. Both samples showed similar responses from the Raman spectra. The main features in the spectra are: D band, D' band and G band. The D band, at 1350 cm$^{-1}$, is caused by disordered structure or discontinuity/defect in the carbon nanotube network. The presence of disorder in sp$^2$-hybridized carbon systems results in resonance Raman spectra. The G band at 1580 cm$^{-1}$ is induced by the crystalline graphitic structure. The distributed impurities, or defects in the nanotube structure, can cause the G-peak to split into two peaks, G-peak (1580 cm$^{-1}$) and D-peak (1610 cm$^{-1}$). The split is due to the interaction between the vibrational modes of the impurities and the carbon atoms of the nanotubes structure. The intensity ratio between G and D peaks remains the same in MWCNT and NA-CNT, further indicating that the amounts of amorphous and crystalline carbon remain almost unchanged. The reason behind this unchanged amorphous and crystalline carbon after acid treatment was confirmed from the TEM studies as discussed in the next paragraph.

Figure 4 shows the TEM images of untreated and acid treated MWCNTs. The amorphous carbon content on the surface of NA-CNT (Figure 4(b)) is lower than the untreated one (Figure 4(a)). The oxidant treatment could have reduced the amorphous carbon. An obvious structural change occurred in NA-CNT due to acid treatment, as observed in Figure 4(c) and (d). The graphene layers of CNT present different misalignments. The red circles highlight the area in which the acid may have attacked the nanotubes and the functional groups may attach onto the external wall of CNTs. Raman spectra indicates that the relative ratio between the amorphous/disordered and crystalline carbon did not change, i.e., the loss of amorphous carbon was compensated by the defect generation.

The changes in chemical states and bonding nature on the surface of carbon nanotubes have been analysed from the XPS study of C 1s core-level spectra. The deconvolution of the C 1s peak (Figure 5) helps to quantify the concentrations (at%) of oxygen containing groups (C-O, C=O and -COOH) in the samples, which is given in Table 1. NA-CNP corresponds to buckypaper made of nitric acid-treated CNTs; while MWCNP refers to buckypaper fabricated from untreated CNTs. The acid treatment creates defect sites on the graphitic network. The defects can be attributed to the result of carbon atoms being replaced by functional groups such as carboxylic acid (-COOH) and hydroxyl (-OH) on the CNT surface. The binding energy of the possible oxygen-containing groups is 286.0 eV for C-O, 287.1 eV for C=O and 288.8 eV for -COOH respectively. Any signal with eV > 289 could be classified as p-p* transition. Due to the acid treatment, the concentration of the functional groups on NA-CNT is higher than that on MWCNT confirming the successful addition of the functional groups on the surface of CNTs.

The characteristics of the buckypaper like surface area, thickness, surface roughness and their standard deviations are listed in Table 2. ΔThickness is the change in thickness compared with MWCNPs.

Figure 6 shows the SEM images of the two types of buckypaper. It is observed that nanotube aggregates are randomly distributed on the surface of MWCNP (Figure 6(a) and (b)), with length ranging from half to one
Figure 3. Normalized Raman spectra for multi-wall carbon nanotube (blue line) and NA-CNT (green line).

Figure 4. Transmission electron microscope images of: (a) untreated multi-wall carbon nanotubes; (b,c) defects (red circles) on multi-wall carbon nanotubes walls after nitric acid treatment; (d) a magnified image of one acid attacked position.
micron. However, the amount of aggregates seems to be significantly reduced on the NA-CNP surface (Figure 6(c) and (d)), which could be attributed to the oxidation effect of MWCNTs. Nitric acid is a strong oxidizing agent, so that some amorphous carbon would be removed, making NA-CNP surface much flatter than MWCNP. The reduction of amorphous carbon allows a more compact (around 32% less thickness) configuration in NA-CNP, without sacrificing the electrical conductivity, as noticed from the electrical resistances in Table 3. HNO₃ oxidation freed the MWCNTs from the entanglements, causing a reduction of the CNTs aggregates. The lower surface roughness of NA-CNP than MWCNP, as observed from the laser microscope measurement, also confirms the reduced amount of nanotube aggregates in NA-CNP, which allows more compactness with reduced thickness.

The electrical properties of buckypaper are listed in Table 3, including electrical resistance and the standard deviation, electrical resistivity $\rho$, and electrical conductivity $\sigma$. $\Delta \rho$ and $\Delta \sigma$ are the changes in electrical resistivity and electrical conductivity, respectively, compared with the reference MWCNP. A wide range of power densities of self-heating elements have been reported in the literature. The power density values of 4–12 kW/m² for metallic self-heating elements (e.g., Boeing 787 wings), and 1–33 kW/m² for nanomaterial based self-heating elements (e.g., carbon nanotubes and graphene) were reported. The power density values of MWCNP and NA-CNP based self-heating elements are in same range of 1.5–1.6 kW/m². Metallic self-heating elements are the standard products currently in use. In terms of energy consumption, nanomaterial based self-heating elements develop more heat than the metallic one with the same applied voltage thus could develop higher power density values.

The acid treatment has effectively reduced the electrical resistivity of the CNP layer and consequently, 35% increment in electrical conductivity is achieved in NA-CNP. Although the untreated and nitric acid-treated samples show close electrical resistances, a much thinner and more compact structure is formed using the acid-treated nanotubes. As a consequence, a significantly reduced electrical resistivity is obtained. Thus, nitric acid-treated CNTs are more effective for the construction of thin-layer of electrically conducting nanostructure network.

Table 1. Quantitative results from C1s scan.

| Samples   | C=C (at%) | C-C (at%) | C-O (at%) | C=O (at%) | -COOH (at%) | p-p* (at%) |
|-----------|-----------|-----------|-----------|-----------|-------------|------------|
| MWCNT     | 51.6      | 34.7      | 3.8       | 2.7       | 1.8         | 3.5        |
| NA-CNT    | 61.9      | 7.9       | 13.7      | 12.3      | 2.1         | 2.1        |
Table 2. Characteristics of carbon nanotube buckypaper.

| Samples   | Surface area (m²) | Thickness (mm) | Thickness St. dev (mm) | ΔThickness (%) | Surface roughness (μm) | Surface roughness St. dev (μm) |
|-----------|-------------------|----------------|------------------------|----------------|-------------------------|---------------------------------|
| MWCNP     | $3 \times 10^{-3}$ | 0.120          | 0.010                  | 0.0            | 0.98                    | 0.18                            |
| NA-CNP    | $3 \times 10^{-3}$ | 0.081          | 0.012                  | −32.2          | 0.57                    | 0.05                            |

Figure 6. Scanning electron microscopy images of: (a) ×10000 MWCNP; (b) ×30000 MWCNP; (c) ×10000 NA-CNP; (d) ×30000 NA-CNP.

Table 3. Electrical properties of carbon nanotubes buckypaper.

| Samples | Resistance (Ω) | Resistance St. dev (Ω) | $\rho$ (10$^{-3}$ Ω m) | $\Delta\rho$ (%) | $\sigma$ (S/m) | $\Delta\sigma$ (%) |
|---------|----------------|------------------------|------------------------|------------------|----------------|------------------|
| MWCNP   | 5.5            | 0.5                    | 0.66                   | 0.0              | 1513.2         | 0.0              |
| NA-CNP  | 6.0            | 0.8                    | 0.49                   | −26.0            | 2045.3         | 35.2             |

Characterisation and performance of the composites

The composite samples have been named based on the used thermosetting resins and buckypaper: EF-MWCNP for untreated buckypaper soaked in Silikopon EF resin; EL2-MWCNP for untreated buckypaper soaked in EL2 laminating resin and the similar for NA-CNP. The thickness of the composites is listed in Table 4. To obtain the thickness of the impregnated CNP, the GF fabrics thickness has been subtracted. The resin impregnation would slightly increase the

Table 4. Characteristics of the fabricated composites.

| Sample   | Composite thickness (mm) | CNP/resin thickness (mm) | St. dev (mm) |
|----------|--------------------------|--------------------------|--------------|
| EF-MWCNP | 0.618                    | 0.248                    | 0.019        |
| EF-NA-CNP| 0.589                    | 0.219                    | 0.018        |
| EL2-MWCNP| 0.645                    | 0.275                    | 0.020        |
| EL2-NA-CNP| 0.564                   | 0.194                    | 0.016        |
CNP thickness. The increase in GF thickness caused by the resin impregnation has been considered negligible.

Figure 7 shows SEM images of EF-MWCNP (Figure 7(a)), EF-NA-CNP (Figure 7(b)), EL2-MWCNP (Figure 7(c)) and EL2-NA-CNP (Figure 7(d)). From the SEM images, random distribution of the nanotubes impregnated with the thermosetting resin is observed. The buckypaper has been produced by filtration of nanotube dispersion (functionalised or untreated) and then impregnated with the resin. Both processes do not prompt any particular orientation or regular distribution of the carbon nanotubes. It is hard to notice clear differences in the distribution of the nanotubes.

Despite the similar surface morphology, the composites have different electrical characteristics. The electrical properties of the composites samples are listed in Table 5. The composites demonstrate higher electrical resistivities than the CNP (MWCNP and NA-CNP) layer themselves. The comparison of electrical resistivity between CNP and their corresponding composites is illustrated in Figure 8. The impregnation of the insulating resin decreases the contact of the neighbouring CNTs, increasing the electrical resistivity of the CNP layer. In each type of resin, the composites based on NA-CNPs exhibit a larger increase in electrical resistance. MWCNTs are randomly distributed in each conductive layer, which creates pathways for the electrical currents. The increase in electrical resistivity is due to the electrically insulating effect from the thermosetting resin that penetrates into the inner space of CNP and aggregates MWCNTs in bundles. As NA-CNP are more compact than MWCNP (as demonstrated by lower thickness), the resin would impregnate with more difficulty through the NA-CNT bundles. This may disturb the intra-bundle interactions and increase the electrical resistivity of the respective composites. The electrical resistivity of the composites impregnated with the icephobic Silikopon EF resin (MWCNP or NA-CNP) is lower than those of the samples impregnated with EL2. The impregnation of EF resin reduced the formation of CNTs bundles than that of EL2 resin, leading to a smaller increase in electrical resistivity.

Table 5. Electrical properties of the fabricated composites.

| Sample       | R (Ω) | St. dev (Ω) | ρ (10^{-3} Ω m) | σ (S/m) |
|--------------|-------|-------------|-----------------|---------|
| EF-MWCNP     | 11.8  | 1.2         | 2.9             | 345.8   |
| EF-NA-CNP    | 36.7  | 2.5         | 8.0             | 125.0   |
| EL2-MWCNP    | 15.8  | 1.8         | 6.1             | 190.2   |
| EL2-NA-CNP   | 51.5  | 1.5         | 10.0            | 100.6   |

Figure 9 shows the photos of de-icing tests and the corresponding IR thermal images during the ice melting. The composites were covered by rime ice at −20°C and a
5 V electrical potential was applied to provide the heating. This test condition was used to simulate an electro-thermal ice protection system under de-icing configuration.

Figure 10 shows an increase in surface temperature of two samples (EF-MWCNP and EL2-MWCNP) during the de-icing test. The ice melting time is defined as the moment in which the temperature rises above 0°C. The ice melting time is characterised by a plateau of temperature values, i.e., from 50 s to 315 s, which is visible in Figure 10. During the ice melting, the measured temperature was slightly below 0°C (around −1°C ~ −2°C). The IR camera measured the temperature at the centre of the sample during the ice melting (as shown in Figure 9(e)), where an ice/water mixed phase was observed. The ice melting started when melting spots appeared on the sample surface, as shown in Figure 9(b) and the procedure continued until all the ice disappeared from the sample surface, as shown in Figure 9(c). As the EF-MWCNP have an average electrical resistance lower than EL2-MWCNP, the ice melting of EF-MWCNP samples (~ 200 s) is faster than

![Figure 8. Comparison of electrical resistance between buckypapers and the composite samples with different resins.](image)

![Figure 9. Optical images (first row) and the corresponding IR thermal imaging (second row) of the de-icing test for an EF-MWCNP sample: (a, d) at the beginning of the heating; (b, e) during the ice melting; (c, f) at the end of the ice melting.](image)
that of EL2-MWCNP (~ 315 s), which is highlighted by the shorter plateau in Figure 10 (from 50 s to 200 s). NA-CNP based composites have not been tested due to higher electrical resistance. A high electrical resistance would cause longer ice melting time.

The power densities during the de-icing test are listed in Table 6. The surface of the sample is approximately 0.003 m². Both power densities were lower than 1 kW/m². A higher power density value was obtained when using Silikopon EF resin (0.68 kW/m²) over EL2 epoxy (0.52 kW/m²). Power density values around 2kW/m² were often reported in the literature.9,10,30 For a more efficient ice-protection system supplied with constant voltage, the electrical resistance of the composite should be further reduced to increase the power density and reduce the ice melting time. The formation of CNT bundles due to resin impregnation increases the electrical resistance: bigger bundles will lead to a higher electrical resistance. The electrical resistance along CNT is much lower than the junction resistance. The electrical resistance in the CNP network can be illustrated by a series of resistors, consisting of compactly connected CNT bundles. Each bundle is like a node of this continuous network. The bundles are sets of joint areas made of nanotube agglomerates. The smaller size of these agglomerates, the lower will be the electrical resistance of these nodes. During the resin impregnation, a lower viscosity may allow the resin to penetrate into the CNP and create small CNT bundles, reducing the increment in electrical resistance.

Conclusions

This work investigates the microstructural changes in CNT based buckypapers due to surface functionalization by acid treatment and the effect on heating performance when impregnated with an ice-phobic resin. The composites have been prepared by laminating the CNPs (both acid treated and untreated) with glass fibre fabric followed by the impregnation in thermosetting resin (EL2 Epoxy laminating resin and Silikopon EF resin).

The results indicated that surface functionalization of MWCNTs was effective in obtaining MWCNT buckypaper with improved electrical conductivity. The composites impregnated with Silikopon EF have lower electrical resistivity than the composites impregnated with EL2. The impregnation of EF resin reduced the formation of big CNTs bundles. The composites based on NA-CNPs exhibit a higher increase in electrical resistance with both resins. This was probably due to the more compact structure of the NA-CNP. It would be more difficult to impregnate the resin through the NA-CNT bundles. Diluting the thermosetting resin would allow it to penetrate into the CNP and reduce the increment in electrical resistance. The de-icing test confirmed the electro-thermal heating performance of the CNP based composite in a climate chamber at −20°C, indicating the potential to be integrated into composite structures for ice protection purposes.

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Table 6. Power densities of heating elements in the de-icing test.

| Sample     | Power density (kW/m²) | St. dev (kW/m²) |
|------------|-----------------------|-----------------|
| EF-MWCNP   | 0.68                  | 0.09            |
| EL2-MWCNP  | 0.52                  | 0.05            |

Figure 10. Temperature versus heating time during the de-icing test of EF-MWCNP and EL2-MWCNP samples.
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Appendix

Abbreviations

CNP carbon nanotubes buckypaper
CNT carbon nanotube
EF-MWCNP untreated buckypaper soaked in Silikopon EF resin
| Abbreviation | Description |
|--------------|-------------|
| EF-NA-CNP    | acid treated buckypaper soaked in Silikopon EF resin |
| EL2-MWCNP    | untreated buckypaper soaked in EL2 laminating resin |
| EL2-NA-CNP   | acid treated buckypaper soaked in EL2 laminating resin |
| GF           | glass fibre |
| MWCNP        | multi-wall carbon nanotube buckypaper |
| MWCNT        | multi-wall carbon nanotube |
| NA-CNP       | buckypaper made with acid treated multi-wall carbon nanotubes |
| NA-CNT       | multi-wall carbon nanotube treated with nitric acid |
| PTFE         | polytetrafluoroethylene |
| SW-CNP       | buckypaper made with single-wall carbon nanotubes |
| SEM          | scanning electron microscope |
| TEM          | Transmission electron microscope |
| XPS          | X-ray photoelectron spectroscopy |