Roll to Roll coating of carbon nanotube films for electro thermal heating

Taimur Rashid[1], Hsin-Ling Liang[2], Nicolò Chiodarelli[2], Hassan Abbas Khawaja[1], Kåre Edvardsen[1], Michael De Volder[2]

[1] Department of Engineering and Safety, UiT-The Arctic University of Norway, Hasen Hans Veg 18, 9018, Tromsø, Norway

[2] Department of Engineering, University of Cambridge, 17 Charles Babbage Road, Cambridge, CB3 0FS, United Kingdom

Abstract

Carbon nanotube (CNT) films are gaining traction in applications such as transparent conductive films, electro-magnetic shields and thin film heaters. However, to date, few cost-effective large-area CNT coating methods have been reported. Here, we present a roll-to-roll (R2R) slot-die coating process for thin film CNT heaters. In this process, a continuous CNT suspension is coated on a PET film substrate, subsequently dried and packaged. This process allows for continuous square-meter-size coating. The electrical resistance and thermal signatures of these samples are measured by high definition infrared (IR) thermography. Anti-/de-icing demonstrations of R2R CNT coated samples are performed inside a cold room and outdoor atmospheric icing conditions. The successful R2R coating of CNTs and anti-/de-icing demonstrations show promise for applications, such as the de-icing of ships, which comes under strict regulations for vessels operating in polar waters.

1. Introduction

Because of their unique mechanical, electrical and thermal properties, carbon nanotubes (CNTs) have attracted substantial research and commercial interest (Janas and Koziol, 2014; De Volder et al., 2013; Hierold et al., 2007). In particular, the increase in production volumes and the reduction in CNT cost means that CNTs can now be commercially attractive for a wider variety of applications (De Volder et al., 2013). Furthermore, the availability of large CNT quantities facilitates the development of applications requiring, for instance, large-area coatings of CNTs such as transparent conductors (Wu et al., 2004; Zhang et al., 2006), electromagnetic shields (Li et al., 2006; Liu et al., 2007; Glatkowski et al., 2001) and electro-thermal heaters (Kang et al., 2011; Yoon et al., 2007; Gbordzoe et al., 2016; Janas and Koziol, 2013; Kim et al., 2011; Kim et al., 2010). The latter have gained popularity, and efforts are being made to scale up their fabrication, for instance by coating them on fabrics (Fugetsu et al., 2011).

CNT thin films are generally prepared using either solution processing of CNT suspensions or dry spinning methods. Solution-processed CNT films are fabricated by dip coating (Mirri et al., 2012), spin coating (LeMieux et al., 2008), spray coating (Ramasamy et al., 2008), vacuum filtration (Song et al., 2009), in-jet printing (Kordás et al., 2006) and electrophoretic deposition (Boccaccini et al., 2006). The dry spinning approach relies on the processing of CNT vertically aligned forests (Lepró et al., 2010) and direct spinning methods from a CVD reactor (Li et al., 2004; Sun et al., 2011; Janas and Koziol, 2014). For a more detailed description of these methods, we refer to (Lu et al., 2012). While the dry spinning method has resulted in some of the best film properties and can be implemented in a continuous manufacturing process (Li et al., 2004), it does not profit from the cost benefits of commercial CNTs produced on a large scale. Roll-to-Roll (R2R) coating allows for a cost-effective continuous coating of CNT suspensions. Roll-to-Roll (R2R) coating refers to a family of manufacturing techniques, in which a flexible substrate is coated continuously as it is unwound from a stock roll and transferred to a rewinding roll. This process is particularly suited to large-area coating and has previously been used for coating CNTs in RFID tags (Jung et al., 2010), active matrices for multi-touch sensors (Lee et al., 2015), but, to our knowledge, R2R coating of CNT dispersion has not yet been used for CNT heaters.

Large-area, low-cost heaters are particularly interesting for anti-/de-icing of ships entering the Arctic region. This is due to ship ice accretion caused by sea spray. Icing can affect the ship's operations, risking human and machine safety (Wiersema et al., 2014; Marchenko, 2012). Since the number of shipping operations inside Arctic regions is rising, reliable de-icing techniques are becoming increasingly important. In order to improve the ice protection on ships, the International Maritime Organization (IMO) published the International Code for Ships Operating in Polar Waters (Polar Code) (IMO, 2016), which has been in effect since 2017 and demands the monitoring and mitigation of ice accretion. At present, ice on ships is removed manually and/or by applying heat (Samuelsen, 2017), and real-time monitoring of icing parameters (such as ice detection, ice thickness) is being developed (Rashid et al., 2018). This study shows that continuous CNT films can be coated on PET substrates, using a standard slot-die R2R coating system. These CNTs films have then been used to demonstrate their thermal anti-/de-icing capability.

2. Methods

A MWCNT ink (Electra Colour™ – CNTBlack) provided by Owen Research was used with varying CNT concentrations. Prior to use, the CNT suspension was sonicated for two hours in a bath sonicator and centrifuged for about 10 min at 8000 rpm. The CNT ink was coated on a

PET foil, using slot-die coating on a roll-to-roll coater (Easycoater, Coatema®). The viscosity of the CNT ink was adjusted by varying the surfactant composition, in order to make it suitable for R2R coating. To perform a single coating run on an R2R coater, 250ml of CNT ink was prepared.

The coater was used to coat lengths of to 2 meters at a time, which were then dried at room temperature. A removable protective film was then laminated on the R2R coating for safe handling of the CNT films. For coating, the ink was pumped at a rate of 1.9 ml/min into the slot-die head. The head was fixed at a gap of 1.4 mm from the substrate. The width of the coating was 10 cm. The coating setup is shown in Figure 1a and 1b and a coated sample is shown in Figure 1c. Finally, electrical connections were applied on the CNT films, using RS Pro® silver conductive adhesive paint. Silver tracks were drawn in the CNT coating direction. Figure 2 shows complete method of R2R coating and characterization of CNTs on a PET substrate.

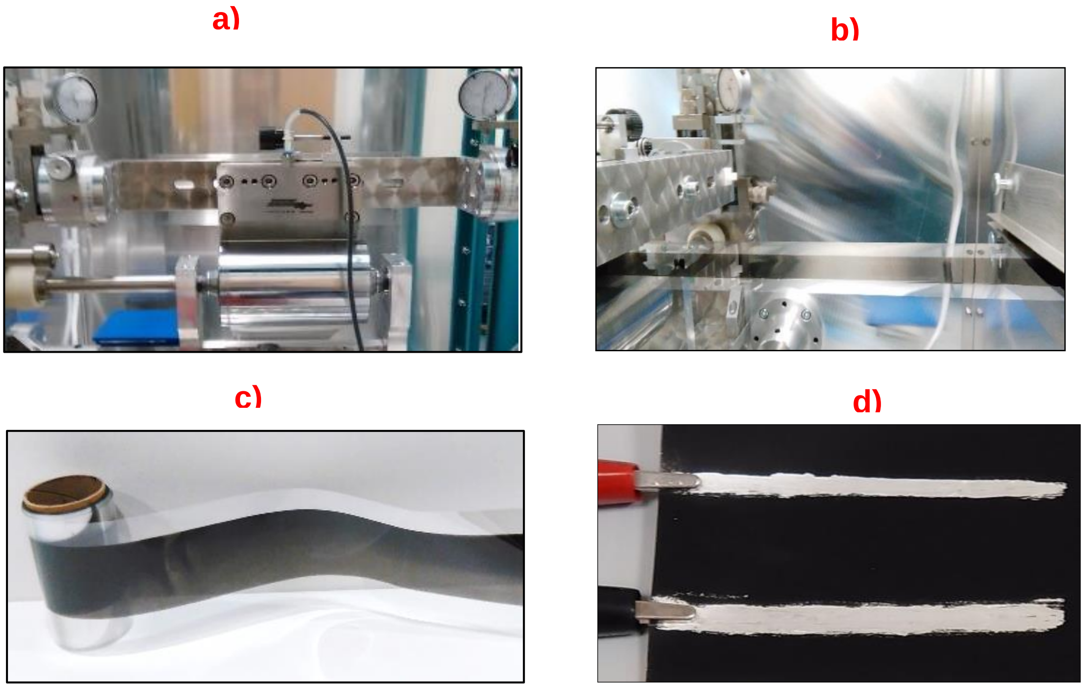

Figure 1: (a) Pumping CNT ink into slot die coating; (b) coating onto PET substrate, (c) CNT coated roll; (d) drawing conductive Ag ink on the CNT coating

After coating and connecting the CNT film, a DC electrical power supply (TENMA® 75-8695) was used for joule heating the films. The infrared thermography (IRT) of CNT samples was observed using a high definition infrared camera, FLIR® (T1030Sc). The IR image post processing and analysis was performed using FLIR® ResearchIR software.

Qualitative anti-/de-icing tests were performed on the R2R coated CNT films inside a cold room and outdoors in atmospheric icing conditions. Ice was frozen on the reverse side of the CNT coated film, while the surrounding temperature was -2°C. Similarly, an anti-/de-icing experiment was performed outdoors. The atmospheric temperature was -1.5°C with a humidity of 88% (source: www.yr.no).

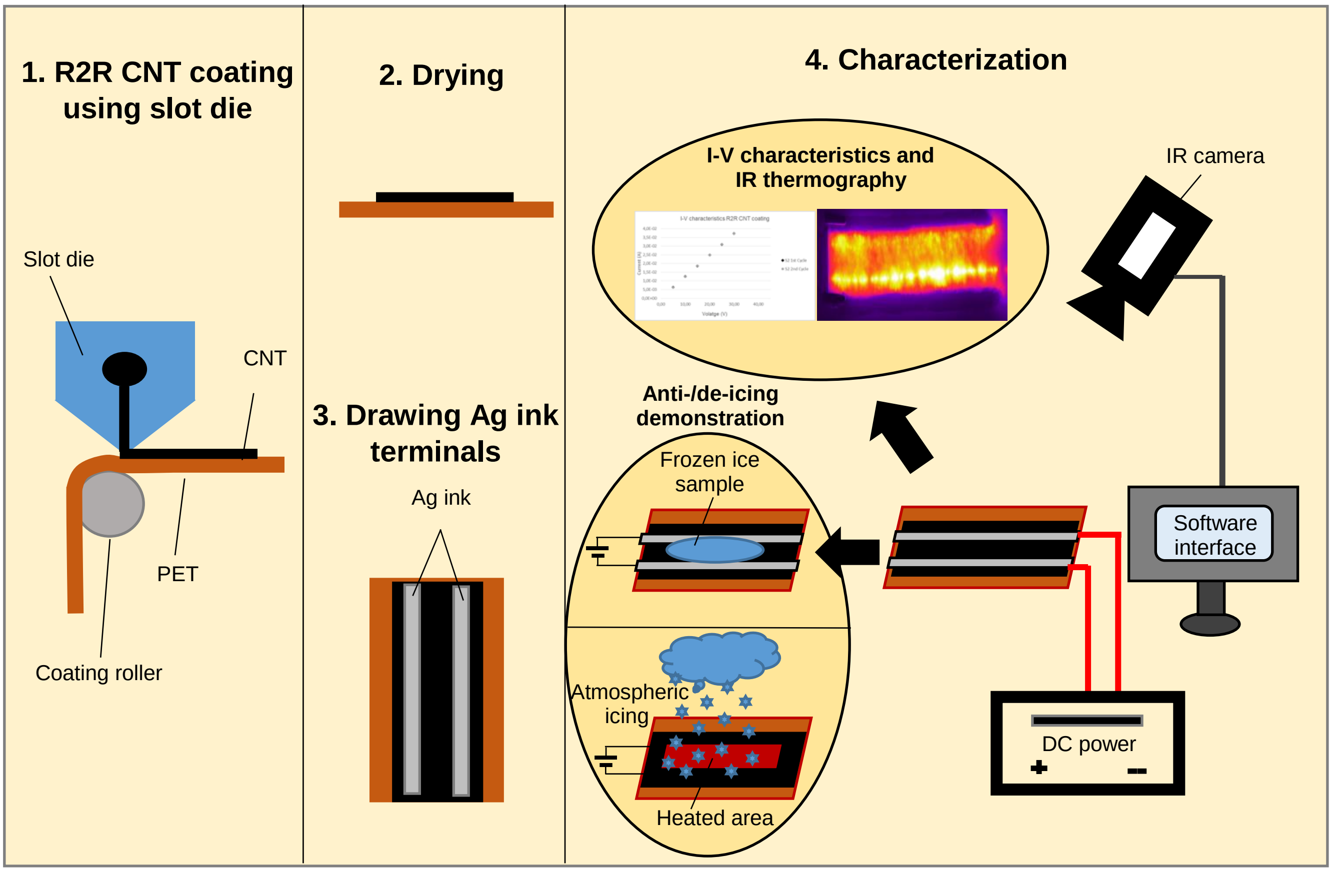

Figure 2: Roll to roll coating and characterization of CNTs on a PET substrate

3. Results and Discussion

Four different CNT suspensions (1wt.% to 4wt.%) were processed to obtain coatings, named S1 to S4, respectively. The electrical and thermal response was measured for these samples. Of these samples, only S2 and S3 gave satisfactory results and are presented here. The current and voltage characteristics of samples S2 and S3 are shown in Figure 3. A linear I-V response was obtained for both samples. The electrical resistance values at the terminals of S2 and S3 are found to be 806Ω and 23.2KΩ, respectively.

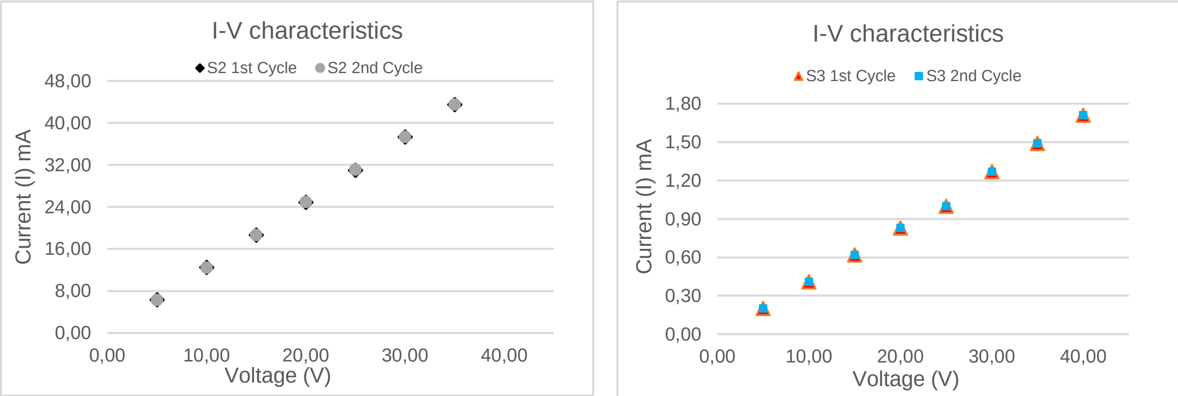

Figure 3: I-V characteristics of R2R CNT coated samples (S2 and S3)

Figure 4 shows the surface IRT of S2 and S3 at 25V, 30V, and 35V. An average surface temperature of up to 50.3ºC ± 3.8ºC was observed on S2, compared to the 22.8ºC ± 0.7ºC on sample S3 at 35V. A summary of the samples' average surface temperatures, observed at the particular voltages applied, is given in Table 1.

Table 1: Current and temperature parameters of samples S2 and S3 at different voltages (dc)

Current (I)			**Average surface temperature of R2R CNT coated sheet (8.5cm x 3cm)**		
Voltage (dc)	**Sample**		**Voltage (dc)**	**Sample**	
	S2	**S3**		**S2**	**S3**
10 V	12.44 mA	0.41 mA	25 V	35.32V±2.7 V	22.10±0.4 V
20 V	24.94 mA	0.83 mA	30 V	42.57±3.6 V	22.72±0.6 V
30 V	37.30 mA	1.27 mA	35 V	50.0±3.8 V	22.84±0.7 V
40 V	-	1.71 mA	40 V	-	23.15±1.0 V

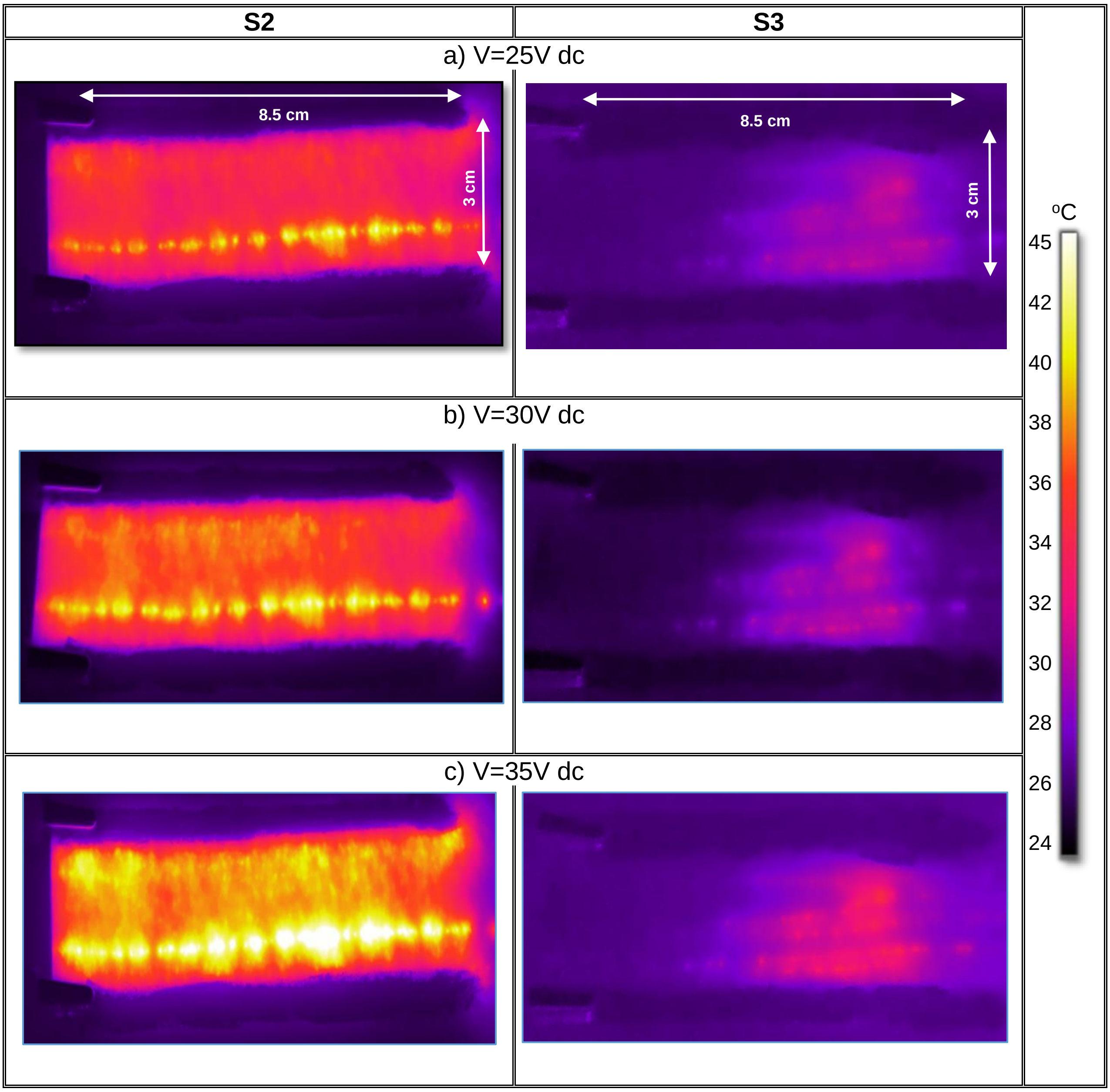

Figure 4: Surface infrared thermography (IRT) of S2 and S3 at
a) V=25V dc b) V=30 V dc c) V=35V dc

A qualitative de-icing demonstration, using the R2R CNT coated sample S2 (area 25.5 cm^2), was performed inside the cold room, as shown in Figure 5. Time-elapsed photos and IR images were taken at 60-second intervals to show the process of de-icing over the CNT film surface (Figure 5). The IR image of Figure 5a shows the ice and PET sheet at a surrounding temperature of -2°C. Similarly, Figure 6 shows an outdoor de-icing experiment in Tromsø, Norway (25-11-2018, GMT18:20). The coating sample kept the heated area ice-free and prevented further ice accretion (Figure 6c).

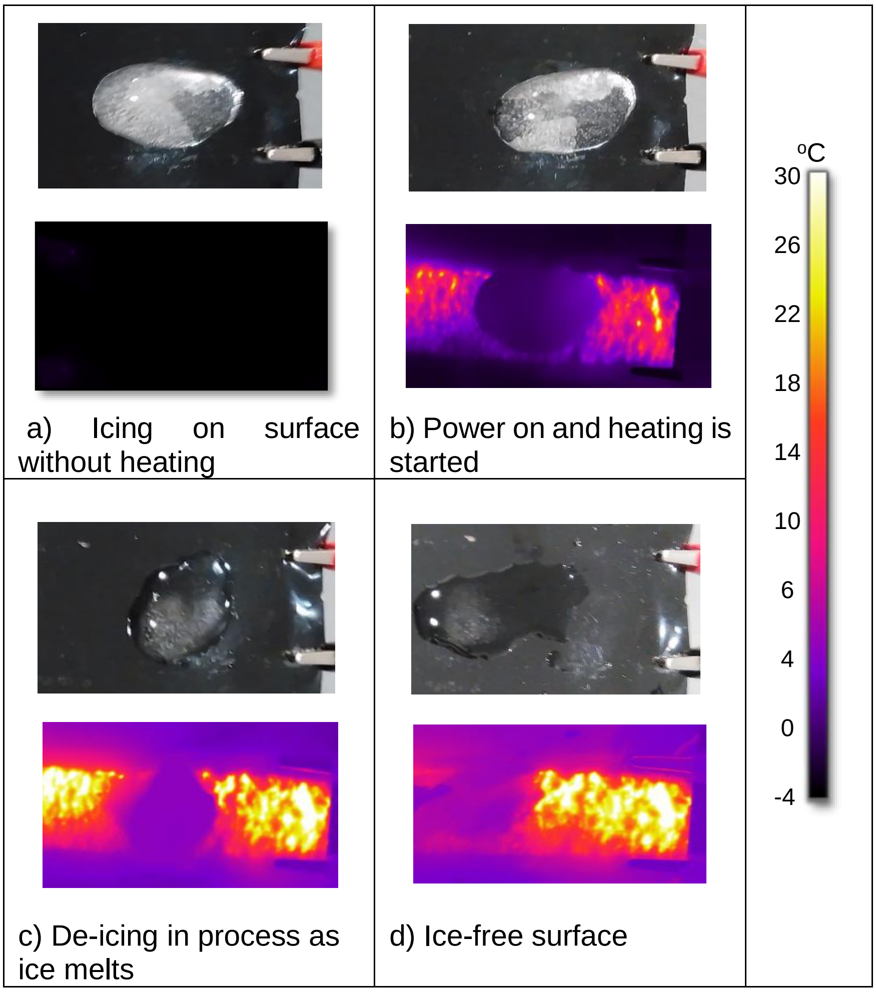

Figure 5: De-icing demonstration of R2R CNT coated sheet (IR and colour images), when ice is frozen inside cold room at steady state temperature of -2°C

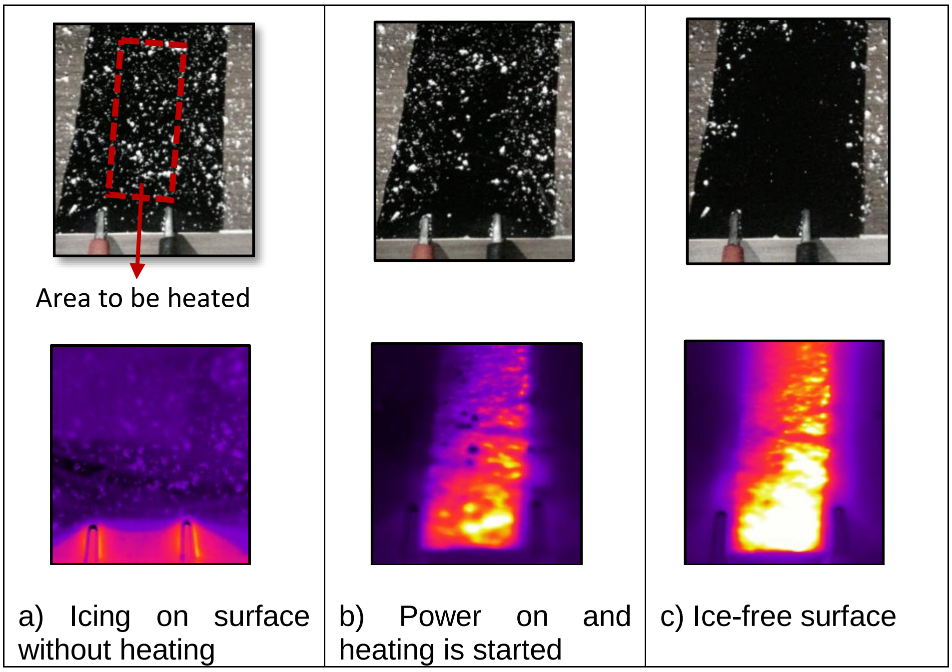

Figure 6: Anti-/de-icing demonstration of R2R CNT coated sheet (IR and colour images) in atmospheric icing conditions (Tromsø, Norway, 25-11-2018, GMT: 18:20)

4. Conclusion

The anti-/de-icing of ships in the Arctic Circle requires large-area cost-effective heating systems. In this paper, we demonstrate that R2R coating of CNT ink on a PET substrate allows for the continuous fabrication of heaters, which show promising properties for this application. CNT suspensions with different viscosities were coated and tested electrically and thermally. In addition, qualitative anti-/de-icing demonstrations are presented, both in a climate chamber and outdoors using natural snow. These heaters, therefore, show promise for the anti-/de-icing of ships in arctic waters.

References

Boccaccini AR, Cho J, Roether JA, et al. (2006) Electrophoretic deposition of carbon nanotubes. *Carbon* 44: 3149-3160.

De Volder MF, Tawfick SH, Baughman RH, et al. (2013) Carbon nanotubes: present and future commercial applications. *science* 339: 535-539.

Fugetsu B, Tarumoto N, Yano Y, et al. (2011) Planar heating element obtained using dispersion of fine carbon fibers in water and process for producing the planar heating element. Google Patents.

Gbordzoe S, Malik R, Alvarez N, et al. (2016) Flexible Low-Voltage Carbon Nanotube Heaters and their Applications. *Advances in Carbon Nanostructures.* InTech.

Glatkowski P, Mack P, Conroy JL, et al. (2001) Electromagnetic shielding composite comprising nanotubes. Google Patents.

Hierold C, Jungen A, Stampfer C, et al. (2007) Nano electromechanical sensors based on carbon nanotubes. *Sensors and Actuators A: Physical* 136: 51-61.

IMO. (2016) International code of safety for ships operating in polar waters (polar code). London, UK: International Maritime Organization.

Janas D and Koziol K. (2014) A review of production methods of carbon nanotube and graphene thin films for electrothermal applications. *Nanoscale* 6: 3037-3045.

Janas D and Koziol KK. (2013) Rapid electrothermal response of high-temperature carbon nanotube film heaters. *Carbon* 59: 457-463.

Jung M, Kim J, Noh J, et al. (2010) All-Printed and Roll-to-Roll-Printable 13.56-MHz-Operated 1-bit RF Tag on Plastic Foils. *IEEE Transactions on Electron Devices* 57: 571-580.

Kang TJ, Kim T, Seo SM, et al. (2011) Thickness-dependent thermal resistance of a transparent glass heater with a single-walled carbon nanotube coating. *Carbon* 49: 1087-1093.

Kim D, Lee H-C, Woo JY, et al. (2010) Thermal behavior of transparent film heaters made of single-walled carbon nanotubes. *The Journal of Physical Chemistry C* 114: 5817-5821.

Kim D, Zhu L, Han C-S, et al. (2011) Raman characterization of thermal conduction in transparent carbon nanotube films. *Langmuir* 27: 14532-14538.

Kordás K, Mustonen T, Tóth G, et al. (2006) Inkjet Printing of Electrically Conductive Patterns of Carbon Nanotubes. *Small* 2: 1021-1025.

Lee W, Koo H, Sun J, et al. (2015) A fully roll-to-roll gravure-printed carbon nanotube-based active matrix for multi-touch sensors. *Scientific Reports* 5: 17707.

LeMieux MC, Roberts M, Barman S, et al. (2008) Self-sorted, aligned nanotube networks for thin-film transistors. *science* 321: 101-104.

Lepró X, Lima MD and Baughman RH. (2010) Spinnable carbon nanotube forests grown on thin, flexible metallic substrates. *Carbon* 48: 3621-3627.

Li N, Huang Y, Du F, et al. (2006) Electromagnetic Interference (EMI) Shielding of Single-Walled Carbon Nanotube Epoxy Composites. *Nano letters* 6: 1141-1145.

Li Y-L, Kinloch IA and Windle AH. (2004) Direct spinning of carbon nanotube fibers from chemical vapor deposition synthesis. *science* 304: 276-278.

Liu Z, Bai G, Huang Y, et al. (2007) Reflection and absorption contributions to the electromagnetic interference shielding of single-walled carbon nanotube/polyurethane composites. *Carbon* 45: 821-827.

Lu W, Zu M, Byun J-H, et al. (2012) State of the Art of Carbon Nanotube Fibers: Opportunities and Challenges. *Advanced Materials* 24: 1805-1833.

Marchenko N. (2012) *Russian Arctic Seas: Navigational conditions and accidents*: Springer Berlin Heidelberg.

Mirri F, Ma AW, Hsu TT, et al. (2012) High-performance carbon nanotube transparent conductive films by scalable dip coating. *ACS nano* 6: 9737-9744.

Ramasamy E, Lee WJ, Lee DY, et al. (2008) Spray coated multi-wall carbon nanotube counter electrode for tri-iodide (I3-) reduction in dye-sensitized solar cells. *Electrochemistry Communications* 10: 1087-1089.

Rashid T, Khawaja HA and Edvardsen K. (2018) Measuring thickness of marine ice using IR thermography. *Cold Regions Science and Technology*.

Samuelsen EM. (2017) Prediction of ship icing in Arctic waters-Observations and modelling for application in operational weather forecasting. Norway, Doctoral Thesis, UiT-Norway.

Song X, Liu S, Gan Z, et al. (2009) Controllable fabrication of carbon nanotube-polymer hybrid thin film for strain sensing. *Microelectronic Engineering* 86: 2330-2333.

Sun D-m, Timmermans MY, Tian Y, et al. (2011) Flexible high-performance carbon nanotube integrated circuits. *Nature Nanotechnology* 6: 156.

Wiersema E, Lange F, Cammaert G, et al. (2014) Arctic Operations Handbook JIP. *OTC Arctic Technology Conference.* Offshore Technology Conference.

Wu Z, Chen Z, Du X, et al. (2004) Transparent, Conductive Carbon Nanotube Films. *science* 305: 1273-1276.

Yoon Y-H, Song J-W, Kim D, et al. (2007) Transparent Film Heater Using Single-Walled Carbon Nanotubes. *Advanced Materials* 19: 4284-4287.

Zhang D, Ryu K, Liu X, et al. (2006) Transparent, conductive, and flexible carbon nanotube films and their application in organic light-emitting diodes. *Nano letters* 6: 1880-1886.