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

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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 CNT suspension is continuously coated on a PET film substrate and subsequently dried and packaged. This process allows for continuous square-meter-size CNT coating. The electrical resistance and thermal map 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 application of CNTs in large area applications, such as the de-icing of ships, for which strict regulations are put in place for vessels operating in polar waters.

1. Introduction

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., 2019). 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.

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). Further, 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), Li-Ion batteries (Jo et al., 2020) 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), ink-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: Zhang et al., 2006: Li et al., 2004: Zhang et al., 2004: Zhang et al., 2005). 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. 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), Li-Ion batteries (Jo et al., 2020) active matrices for multi-touch sensors (Lee et al., 2015), manufacture hybrid materials as transparent electrodes (Hu et al., 2014: Shin et al., 2016), to our knowledge, R2R coating of CNT dispersion has not yet been used for CNT heaters. Other CNT preparation methods for ice removal are reported using flexible transparent heating (Zhou et al., 2019) for rapid de-icing (Janas and Koziol, 2013: Yao et al., 2018), wind turbine de-icing (Fischer et al.; 2017) and smart de-icing (Jang and Park, 2018).

2. Methods

A MWCNT ink (Electric 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 (PMX727 71 µm, HIFI Industrial Film), using slot-die coating on a R2R coater (Smartcoater, Coatema GmbH). 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 Figure 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 2a).

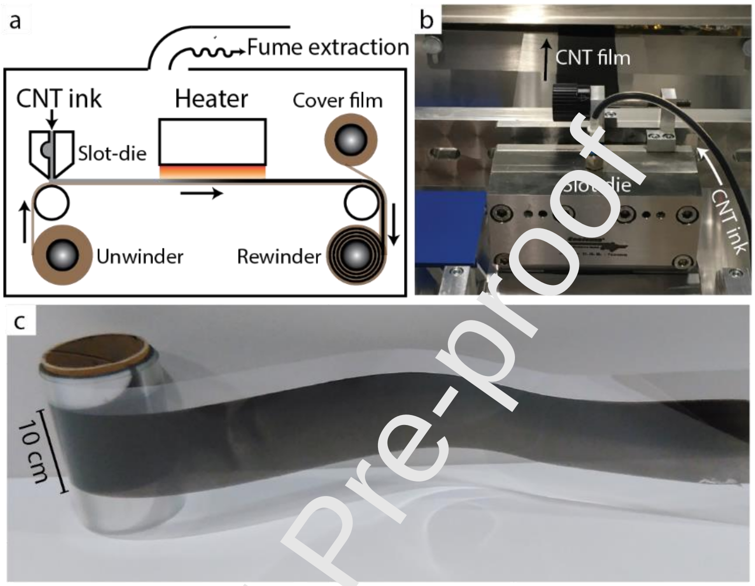

Figure 1: (a) R2R coater block diagram; (b) CNT ink pumped into slot die coating; (c) CNT coated roll

After coating and connecting the CNT film, a DC electrical power supply (TENMA® 75-8695) was used for joule heating the films (Figure 2a). 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).

3. Results and Discussion

Three different CNT suspensions (1, 2 and 3 wt.%) were processed to obtain coatings, named S1 to S3, respectively. The electrical and thermal response was measured for these samples. Of these samples, only S2 and S3 gave satisfactory results (i.e. average surface temperature above 22^{o}C) and are presented here. In our experiments, it seems S1 had insufficient CNTs to form a good percolated network of CNTs for heating. On the other hand, the higher concentration inks tend to have CNT aggregates, which cause defects during coating that are aggravated during the drying process. This lead to a poor film quality and reproducibility and are therefore not used in our de-icing study. The current and voltage characteristics of samples S2 and S3 are shown in Figure 2b. 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 806 Ω and 23.2 kΩ, respectively. The average sheet resistance (from 4-point probe method) for the samples S2 and S3 are calculated as 6.53kΩ/sq and 20.54kΩ/sq respectively.

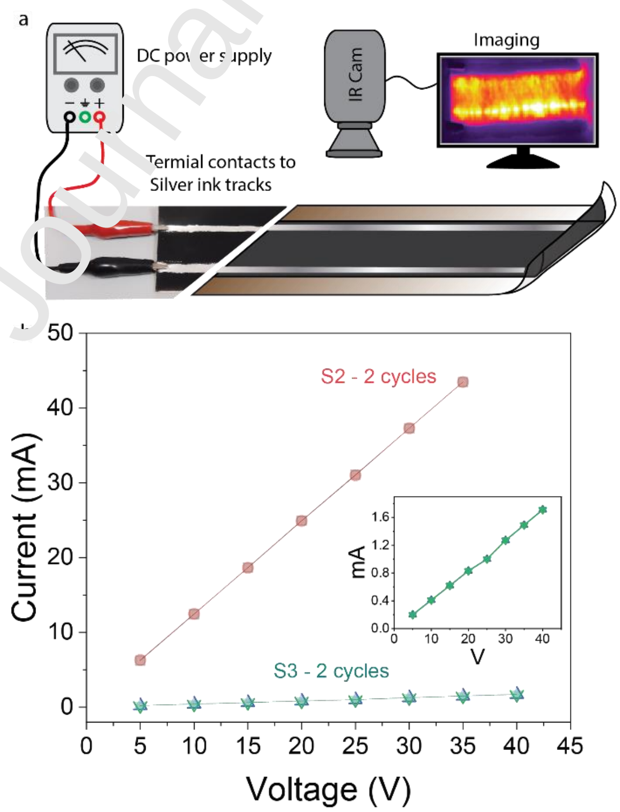

Figure 2: I-V characteristics of R2R CNT coated samples (S2 and S3)

Figure 3 shows the surface infrared thermography (IRT) of S2 and S3 at 25V, 30V, and 35V. An average surface temperature of up to 50.3°C ± 3.8°C was observed on S2, compared to the 22.8°C ± 0.7°C on sample S3 at 35V. A summary of the samples' average surface temperatures, observed at the particular voltages applied at room conditions 22°C, is given in Table 1.

Table 1: Current and temperature parameters of samples S2 and S3 at different voltages (dc) at room conditions 22°C

Current (I)			**Average surface temperature of R2R CNT coated sheet (8.5cm x 3cm) at room conditions 22°C**		
Voltage (dc)	**Sample**		**Voltage (dc)**	**Sample**	
	S2	**S3**		**S2**	**S3**
10 V	12.44 mA	0.41 mA	25 V	35.32 ±2.7°C	22.10±0.4°C
20 V	24.94 mA	0.83 mA	30 V	42.57±3.6°C	22.72±0.6°C
30 V	37.30 mA	1.27 mA	35 V	50.0±3.8°C	22.84±0.7°C
40 V	-	1.71 mA	40 V	-	23.15±1.0°C

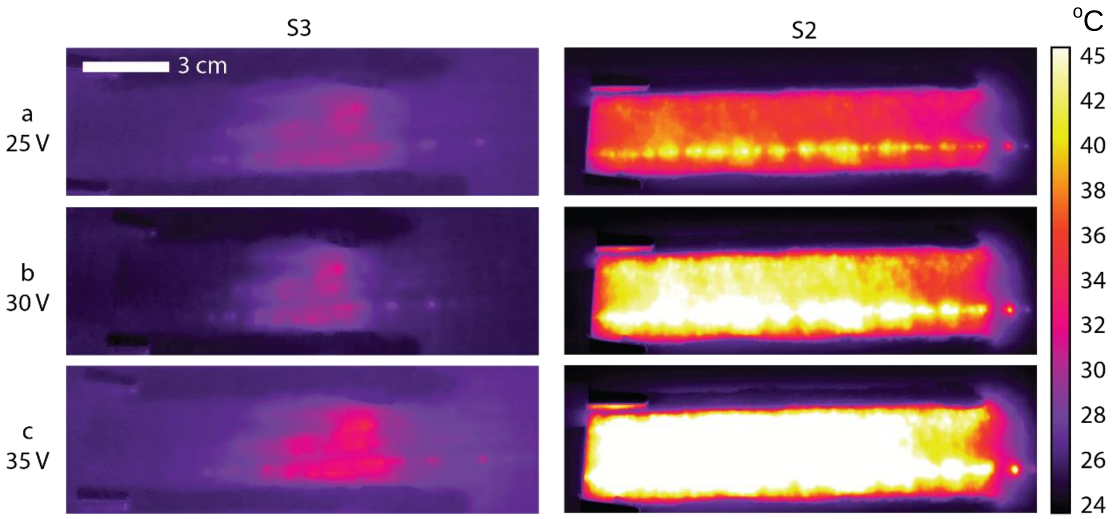

Figure 3: Surface infrared thermography (IRT) of S2 and S3 at different applied voltages:

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 (see Figure 4a). The operating temperature range of the cold room is down to -20^{o}C, which is within the range where most ship icing occurs (Samuelsen, 2017). 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 4b to 4e). The IR image of Figure 4b shows the ice and PET sheet at a surrounding temperature of -2^{o}C. In this experiment an ice block of 12 gram was molten in 3 min at an applied voltage of 40V dc.

It is worth noting that applications of CNT coated samples for anti-/de-icing developed in this study would be applied on parts of the ship above the sea water level, such as the ship deck, railings, pathways etc. These are the areas recommended for ship anti-/de-icing by the International maritime organization (IMO, 2016). Therefore, fouling by algae and degradation by electrolytes will not affect the CNT heaters.

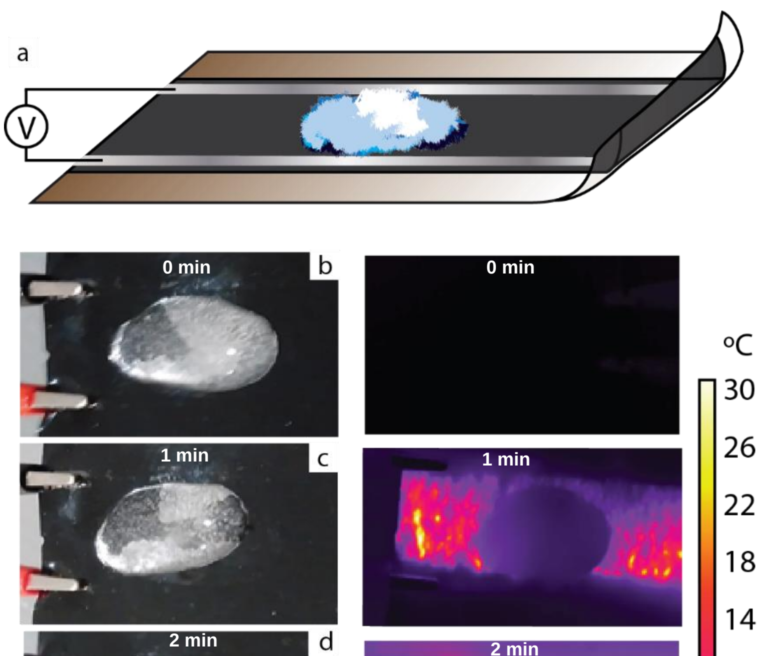

Figure 4: De-icing demonstration of R2R CNT coated sheet (IR and colour images), when ice is frozen inside cold room at steady state temperature of -2^{o}C.

Figure 5a to 5d 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 5d). In this experiment, 40V dc was applied to the film. These experiments illustrate that the developed CNT films can be used both to remove ice deposits (Figure 4) and to prevent snow from accumulating (Figure 5).

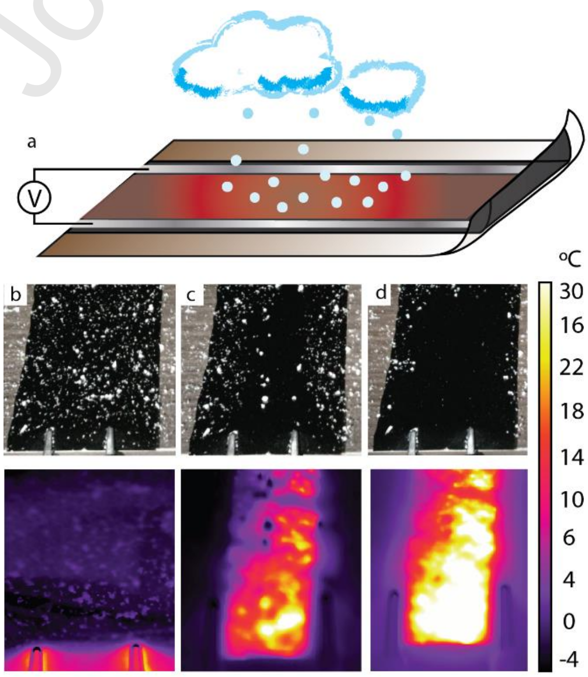

Figure 5: Anti-/de-icing demonstration of R2R CNT coated sheet (IR and colour images) in atmospheric icing conditions (Tromsø, Norway, 25-11-2018, GMT: 18:20)

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 and further studies applying the heater to ships in real-life conditions requires further experiments.

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Highlights

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