Breathing Life into Transport Infrastructure: Development of a Hydrophobic, Freezing Temperature Sensing, and Self-Heating Road Coating System

DfT Transport Technology Research Innovation Grant (T-TRIG 2018) Final Report

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1. Project Summary

1.1. Timeframe of the project and date of the report

Work Packages	**3**	**4**	**5**	**6**	**7**	**8**
Work 1: CNT/PU coating materials	🟨	🟨				
Work 2: Hydrophobic test			🟨			
Work 3: Freezing temperature sensing			🟨	🟨		
Work 4: Self-heating					🟨	🟨
Milestones	**M1** Effective fabrication procedure for CNT/PU coating materials **M2** Non-slippery transport roads by hydrophobic properties of CNT/PU coating materials **M3** Freezing temperature detectable transport roads system **M4** Self-heating (De-icing) transport roads system					

1.2. Location of the project

University of Plymouth, Plymouth, Devon, UK

1.3. Names and organisations of project team

Dr Sung-Hwan Jang, Civil & Coastal Engineering, School of Engineering, University of Plymouth

2. Executive Summary

In the UK, it is often wet and cold during the winter, creating a major transport challenge, through slippery conditions, which, cause widespread disruptions, with dozens of rail service and flights cancelled and thousands of highways closed. Currently, salting spray on major transport roads is one of effective and practical ways for winter service in Department of Transport in UK, leading to many issues of negative environmental impact, enormous wasting sources such as salts, gritting vehicles and manpower, and dramatic traffic congestion. Therefore, new innovate transport road system will be required to achieve two DfT priorities such as 1) improving journeys and safe and 2) safe, secure and sustainable transport. In this project, we will develop novel multifunctional transport road coating system with hydrophobic, freezing temperature sensing, and self-heating properties for smart transport road systems. The project exploits properly the excellent properties of carbon nanotubes (CNTs) in polyurethane (PU) resin for the development of the transport road coating with freezing temperature sensing and self-heating capabilities.

The primary aim of this project is to develop smart road coating materials with hydrophobic, freezing temperature sensing, and self-heating properties for winter-proofed next-generation transport road systems. Characterisation and laboratory testing of coating materials will be conducted through experimental tests, which are outlined in the following tasks:

Work 1: Fabrication of CNT/PU coating materials

Work 2: Characterisation of hydrophobic of CNT/PU coating materials

Work 3: Characterisation of freezing temperature sensing of CNT/PU coating materials

Work 4: Characterisation of self-heating capabilities of CNT/PU coating materials

As this project aimed to develop smart transport road coating system capable of hydrophobic, freezing temperature sensing and deicing, it was decided that the best method was to take a mixed methods approach. This involved the design and use of a quantitative equipment.

3. Aims/Objectives of the study

The primary aim of this project is to develop smart road coating materials with hydrophobic, freezing temperature sensing, and self-heating properties for winter-proofed next-generation transport road systems. The new innovate transport road coating system will be required to achieve two DfT priorities such as 1) improving journeys and safe and 2) safe, secure and sustainable transport. Characterisation and laboratory testing of coating materials will be conducted through experimental tests, which are outlined in the following tasks:

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Work 3: Characterisation of freezing temperature sensing of CNT/PU coating materials

Work 4: Characterisation of self-heating capabilities of CNT/PU coating materials

4. Outline of the concept (including scientific basis)/ methodology for how the technology is going to help to solve a transport problem:

4.1. Carbon nanotubes (CNTs) reinforced polymer-based composites

In general, thermal decomposition temperature of polymer is found to be affected by the CNT concentration in matrix. In addition, glass transition temperature and melting temperature of polymer may be altered by CNT incorporation. The rheological properties of CNT reinforced nanocomposites depend on factors such as the characteristic of filler loading, dispersion, aspect ratio, and molecular weight of polymer. Rheological exploration of polymer composite is an efficient method for the inference of processing behaviour and microstructure parameters.

4.2. Contact angle and wetting properties

Consider a liquid drop resting on a flat, horizontal solid surface as shown in Figure 1. The contact angle is defined as the angle formed by the intersection of the liquid-solid interface and the liquid-vapour interface. The interface where solid, liquid, and vapour co-exist is referred to as the “three-phase contact line”. A small angle is observed when the liquid spreads on the surface, while a large contact angle is observed when the liquid beads on the surface. More specifically, a contact angle less than 90° indicates that wetting of the surface is favourable, and the fluid will spread over a large area on the surface; while contact angles greater than 90° generally means that wetting of the surface is unfavourable so that fluid will minimized its contact with the surface and form a compact liquid droplet.

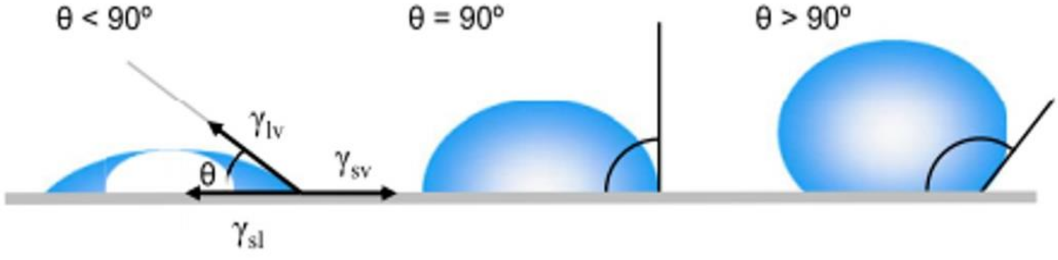


Figure 1. Schematic illustration of contact angles formed by liquid drops on a smooth homogeneous solid surface.

4.3. Joule heating

Nanomaterial reinforced polymer-based composites have shown promising results for creasing electrically conductive polymers. Electrical current induces the Joule heating effect, or self-heating, into nanomaterial reinforced composites. This heating can be used for different applications such as self-post-curing treatment of composite structures or adhesives and de-icing coatings. Joule heating depends on both the electrical and thermal conductivities of the composites, which are strongly influenced by the characteristics of nanomaterials. The thermal conductivity of multi-walled carbon nanotubes is around 3000 W/mK at room temperature.

Those material characterisations of CNT reinforced composite materials would be beneficial to future transportation infrastructure. Related to our research project, those coating materials can be used for temperature sensing as well as heating element for future winter maintenance system. Our developed CNT/PU coatings are electrically conductive. Also, their resistance depends on temperature, proving more accurate temperature information because they are located just above transport roads. Therefore, CNT/PU coatings could use accurate temperature sensor for transport roads to monitor freezing temperature.

In addition to freezing temperature sensing, CNT/PU coatings can generate amounts of heat when subjecting the external voltages/currents by Joule heating effect. Therefore, our proposed materials can be directly applied to transport roads covered with ice during winter season. Then, the materials melt ice layers on the transport roads, eliminating drivers' concern for icy roads. Therefore, DfT could consider the proposed CNT/PU coatings for advanced winter maintenance system in UK transportation.

5. How the idea was generated (e.g. is it an application from another industry) and any intellectual property rights:

5.1. Carbon nanotubes based cementitious-based materials

Conductive cementitious-based materials are promising multifunctional materials for future construction materials. Many researchers have developed highly conductive cementitious-based materials by using carbon-based materials such as multi-walled carbon nanotubes and graphene (Konsta-Gdoutos et al., 2010). Most of research show significant enhancement in mechanical properties of CNT reinforced concrete at small CNT concentration because of CNT network in cement matrix. Those CNT reinforced concretes can be used as a strain & pressure sensors due to highly conductive CNTs (You et al., 2017).

5.2. Carbon nanotubes based heater

Recent studies have revealed the development of optically transparent heaters using carbon nanotubes due to their excellent optical transparency, high electrical conductivity, mechanical flexibility, and the abundance of availability (Jang et al., 2011). Recent patent showed that it was possible to use carbon nanotubes as a windshield heater for demisting and defrosting. The defrosting window includes transparent glass, an adhesive layer on which a carbon nanotube film is attached, two electrodes and a protective layer. The top surface was a transparent substrate and a protective layer was used to isolate the carbon nanotube heater from atmospheric contact (Wang and Liu, 2013).

6. Assumptions made:

1) The electrical conductivity of multi-walled carbon nanotubes (CNTs) is the same as provided manufacturer.
2) Dispersion of CNTs is uniform.
3) Materials properties of polyurethane (PU) are not changed due to dispersion process.
4) Production of CNT/PU coatings could be scaled up.

7. Technologies/equipment used

7.1. Materials

Multi-walled carbon nanotubes produced by thermal chemical vapour deposition were obtained from Nanolab (Waltham, Massachusetts, USA), which showed an average length and a diameter of 15.0 μm and 10.0 nm, respectively. For matrix, polyurethane (PU) consisting of a base elastomer (part A) and a curing agent (part B) was purchased from Easy Composites (Staffordshire, UK). High purity chloroform and acetone were used as a solvent.

7.2. Characterisation

The thickness of the CNT/PU coatings was measured by a digital calliper. The microstructure of the CNT/PU coatings was observed using a scanning electron microscopy (FEI Sirion 600, JEOL, Tokyo, Japan). The electrical resistance of the composite was measured by a two-point probe method using two different digital multimeters at room temperature. The high resistance above 10^9 Ω of the coatings was measured by a high resistance meter (Keithley 6517B, Solon, Ohio, USA), whereas nominal resistance of the composites was measured by a precision multimeter (Keithley 2700, Ohio, USA). The electrical conductivity of the composite was calculated as $\sigma = L/(AR)$, where A and L are the area and the length of the sample, respectively, and R is the resistance.

The temperature dependence of the electrical properties was measured by placing the samples in an environmental chamber. A set of five specimens was used for each test to evaluate the electrical properties. For heating performance by Joule heating, a direct current power supply (Sorensen XPH35-4D, San Diego, California, USA) was used to provide heat by controlling the input voltage. Two pieces of copper tape were attached to both ends of the CNT/PU coatings to be used as electrodes, and the input voltage (approximately 0–75 V) was applied to the composite to induce heat, creating uniform heat distribution. A temperature profile was obtained using a digital thermocouple logger (SL500TC, Supco, Manasquan, New Jersey, USA). In addition, thermal images of the samples during Joule heating were recorded using a thermal infrared camera (FLIR A325sc LWIR Wilsonville, Oregon, USA) for heat distribution. For the defrosting performance, Joule heating was applied to the CNT/PU coatings coated on a glass slide in the area of 50 × 50 mm^2. Then, the samples were wetted by a water and frozen at -20 °C in an environmental chamber for 24 h to clearly form the frost on the surface.

(a) Ultrasonicator (b) Contact angle measurer

(c) Power supply (d) Multimeter

Figure 2. Equipment used in this project

8. Outcome of the project/findings:

Work 1: Fabrication of CNT/PU coating materials

CNT/PU coatings were fabricated by solution casting method as previous works. Figure 3 showed a fabrication procedure for CNT/PU coatings. Different concentrations (approximately 0–7.0 wt.%) of CNTs were carefully weighed with a precision weight scale and directly mixed with part A of the PU and different solvent using an horn-type ultrasonicator (ARE 301, Thinky Corporation, Tokyo, Japan). In this study, it operated at pulsed mode (45 seconds on and 15 seconds off) with 90% amplitude for 30 min. After fully evaporation of solvent in the mixture, Part B of the PU was added into the mixture with a weight ratio of 10:1 and then mixed again using the same mixer for another 3 min, followed by degassing under vacuum for 10 min in order to eliminate the air bubbles captured in the matrix that generally could cause low electrical conductivity than desired. Finally, the mixture was cured at 100 °C for 24 h at the room temperature. Then, the cured CNT/PU composite coatings were left at room temperature for further cooling and curing for a day.

Figure 4 showed the electrical conductivity of CNT/PU coatings fabricated by different solvent such as acetone and chloroform. Percolation threshold of CNT/PU coatings with two solvent occurred at around 0.5 wt.% of CNTs. The CNT/PU coatings with chloroform presented higher electrical conductivity than those with acetone. Using chloroform is effective to achieve uniform CNT dispersion in the matrix. However, chloroform is one of toxic materials so that, in this study, we will use an acetone in further experiments. Figure 5 showed the electrical conductivity of CNT/PU coatings (5.0 wt.% CNT/PU) with acetone at different ultrasonication power. The electrical conductivity of CNT/PU coatings increased as increasing ultrasonication power because of the higher power introduced in the system. In this study, we found the optimum power level of 10,000 J. Figure 6 showed a SEM image of CNT dispersion in the matrix. All of charge moves to fully interconnected CNT network, leading to higher electrical conductivity.

In conclusion, Work 1 focused on development of CNT/PU coating materials. Materials properties of CNT/PU coatings significantly depends on the fabrication procedure. Material design and optimisation of CNT/PU coatings were studied in this section.

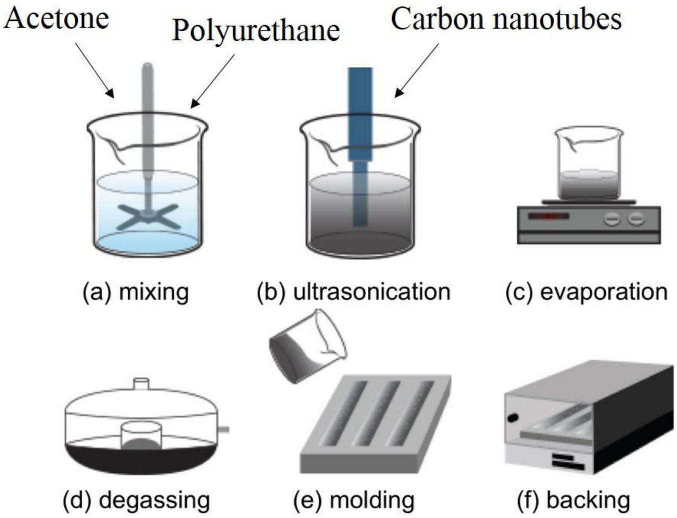


Figure 3. Fabrication of CNT/PU coating materials.

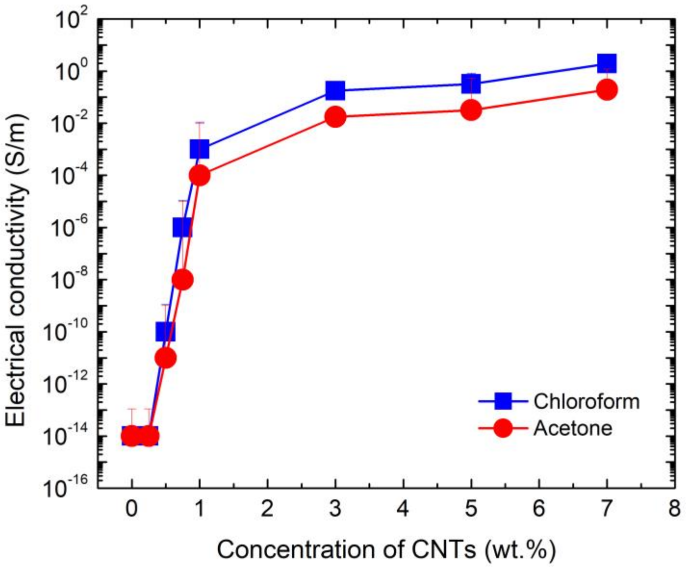


Figure 4. Electrical conductivity of CNT/PU coating materials.

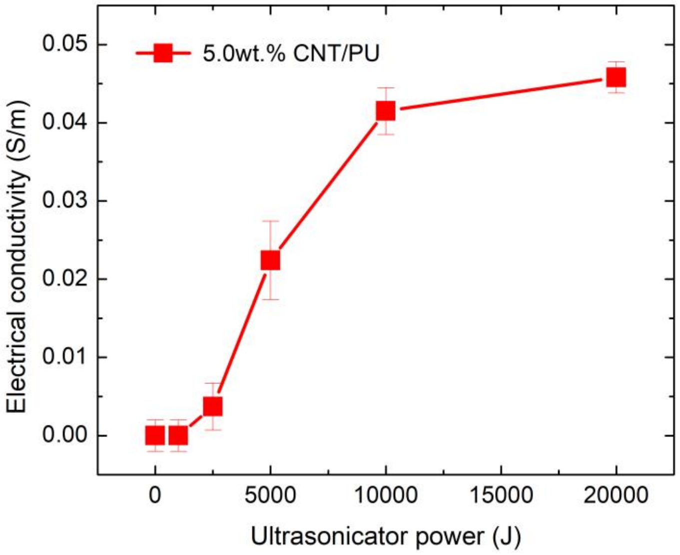


Figure 5. Electrical conductivity of CNT/PU coating materials with different power of ultrasonicator.

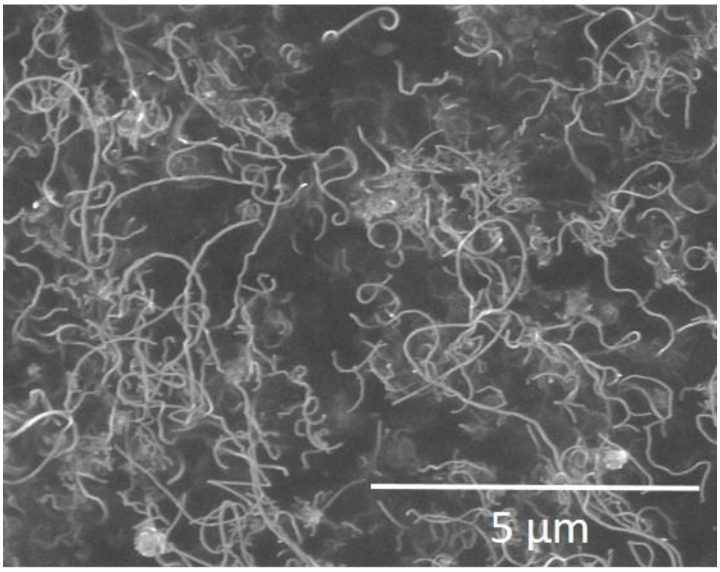


Figure 6. SEM image of CNT/PU coating.

Work 2: Characterisation of hydrophobic of CNT/PU coating materials

Wetting for transport road has received tremendous interest because it directly relates to safety for drivers. Wettability studies usually involve the measurement of contact angles as the primary data, which indicates the degree of wetting when a solid and liquid interact. Small contact angles (< 90°) correspond to high wettability, while large contact angle (> 90°) correspond to low wettability. In general, transport road materials show very high wettability. Developed CNT/PU coating materials presented hydrophobic surface. Figure 7 showed the images of water droplet on CNT/PU coatings. It was clearly seen that contact angle of water droplet increased as increasing CNT concentrations. Figure 8 showed the contact angle of water droplet on slide glass and different CNT/PU coatings.

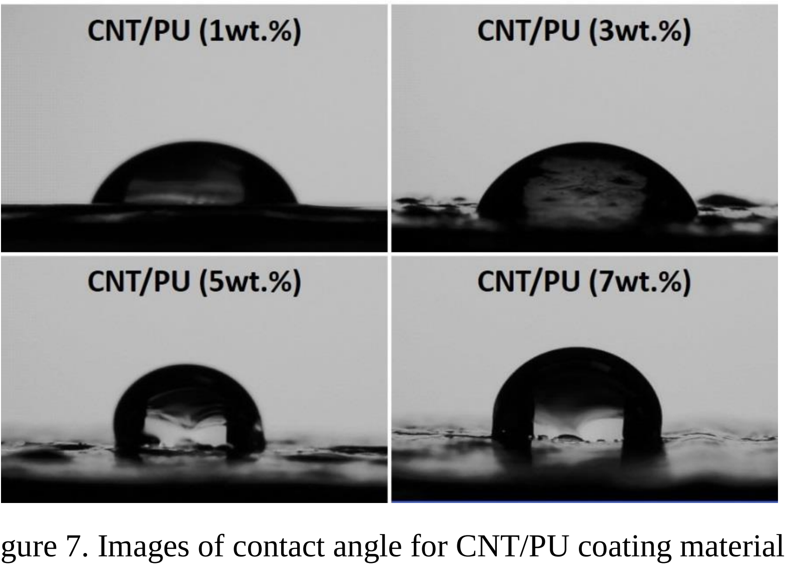


Figure 7. Images of contact angle for CNT/PU coating materials.

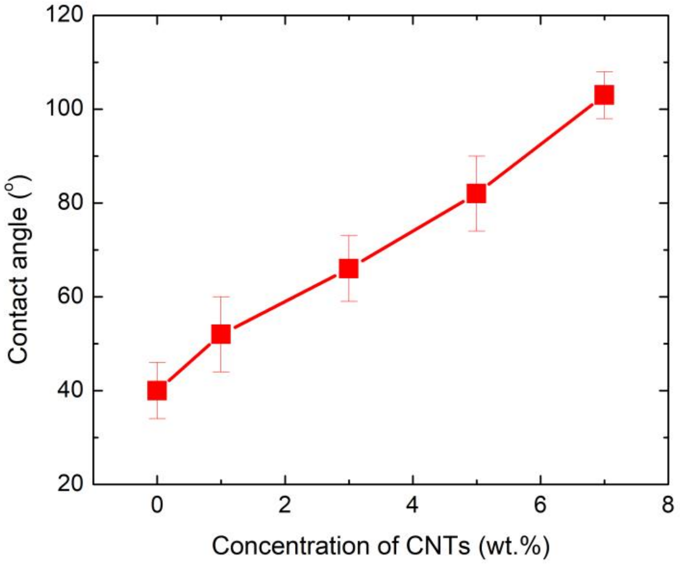


Figure 8. Contact angle for CNT/PU coating materials as a function of CNT concentration.

Work 3: Characterisation of freezing temperature sensing of CNT/PU coating materials

Developed CNT/PU coatings can be used to sense the freezing temperature because they have temperature dependent resistance behaviour. Figure 9 showed the resistance change of CNT/PU coatings as a function of temperature. In this study, temperature gradually reduced to -20 °C from the room temperature. It was clearly seen that the resistance of all CNT/PU coatings increased with a decrease in temperature. This is because CNT/PU coatings have a negative temperature coefficient. Also, CNT/PU coatings with higher CNT concentrations are sensitive to given temperature.

Figure 10 showed dynamic temperature sensing for CNT/PU coatings. We placed commercialised temperature sensor and our samples (5.0 wt.% and 7.0 wt.% CNT/PU coatings) in the environmental chamber of -20 °C. 7.0 wt.% CNT/PU coating showed faster response to given temperature compared to 5.0 wt.% CNT/PU because of higher thermal conductivity.

In conclusion, developed CNT/PU coatings can be used as freezing temperature sensing. It provides more accurate temperature information than commercialised sensors which are generally located far from the surface. Our developed CNT/PU coating also can be extended to IoT system.

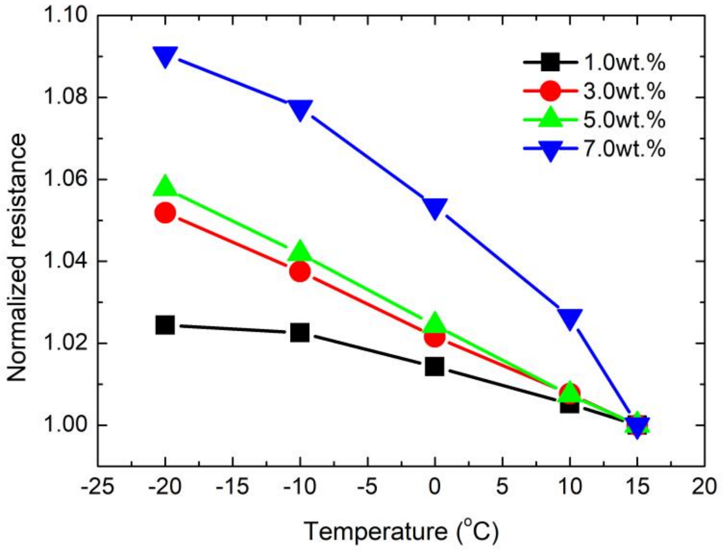


Figure 9. Freezing temperature sensing for CNT/PU coating materials.

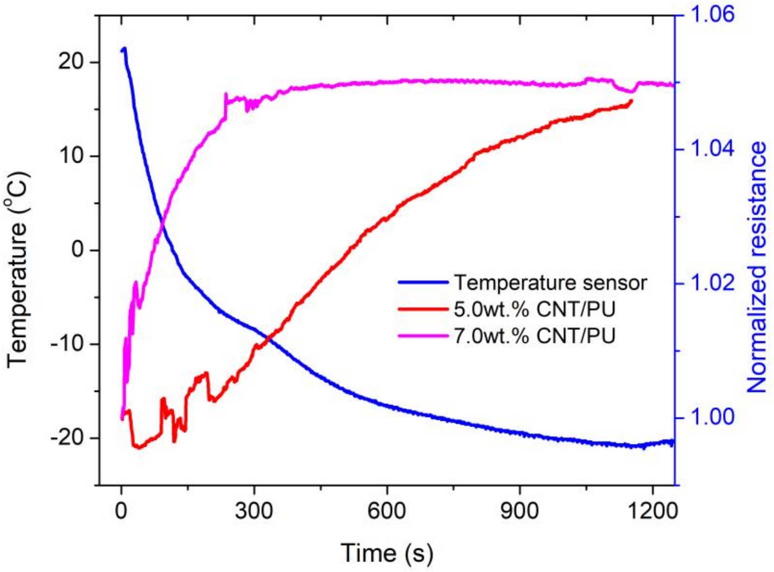


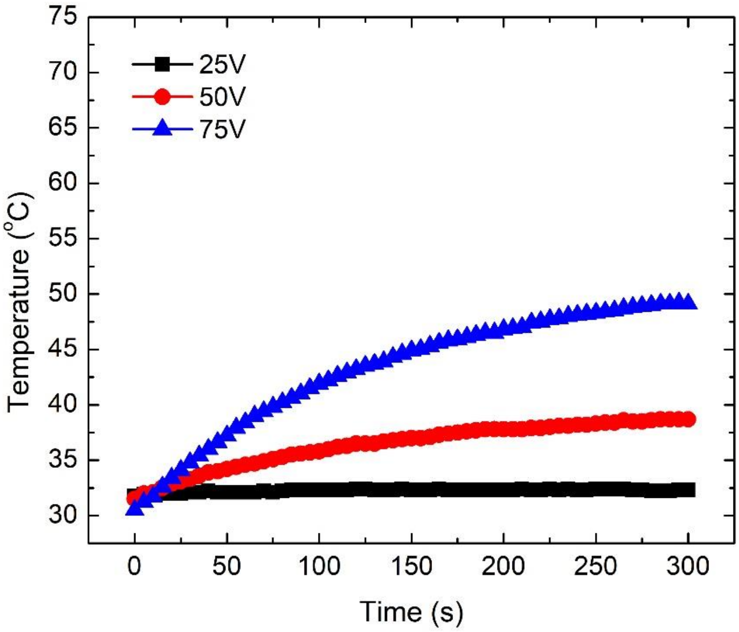
Figure 10. Dynamic temperature sensing of CNT/PU coating materials.

Work 4: Characterisation of self-heating capabilities of CNT/PU coating

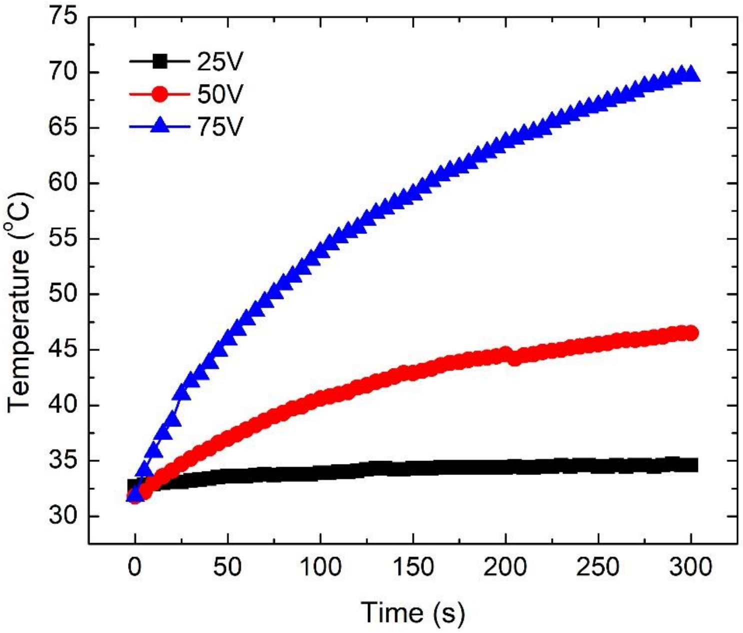
Developed CNT/PU coatings can be used a heat element based on Joule heating. The power increased according to $P = IV = V^2 / R$, where V is the applied voltage, I is the applied current, and R is the resistance of the CNT/PU coatings, which is converted to heat though the Joule heating effect. In this study, we prepared CNT/PU coatings with an area of $30 \times 30 \times 0.5 mm^3$ for the heat characterization. Figure 11 showed the temperature profile for

CNT/PU coatings at different applied voltages. It was clearly seen that CNT/PU coatings with higher CNT concentrations presented faster heat evolution. Figure 12 presented the heat performance of various CNT/PU coatings at 75 V.

Figure 13 demonstrated the heat performance of CNT/PU coating covered with ice. We spayed water on the surface and freeze it in environmental chamber of -20 °C for 24 h. Then, we applied voltage (75 V) to the CN/PU coating and monitored temperature changes. All ice on CNT/PU coating were completely melt within 30 min because of Joule heating of CNT/PU coating. Therefore, proposed CNT/PU coating can be used smart coatings on all types of transport road system such as highways, cyclic roads, and airways in the future.

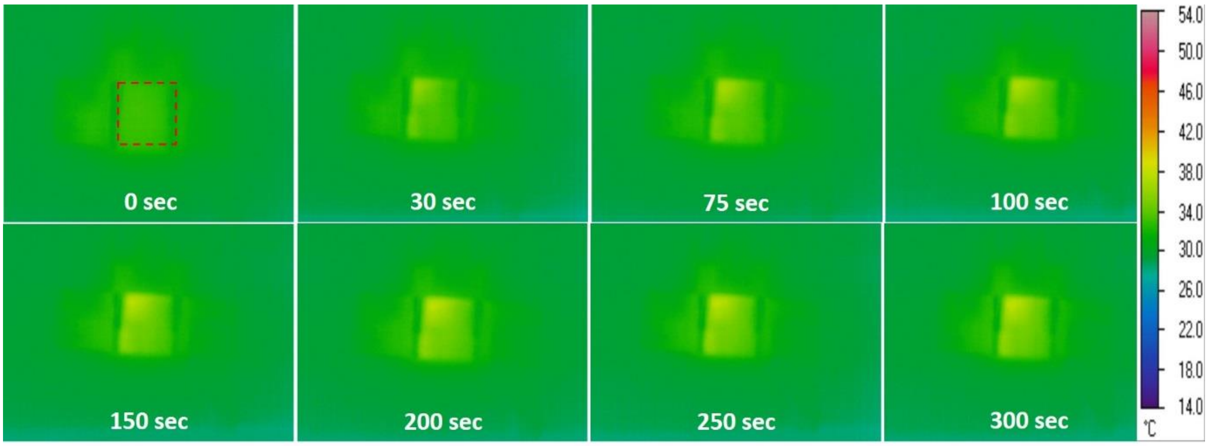


(b) 5.0wt.% CNT/PU coating

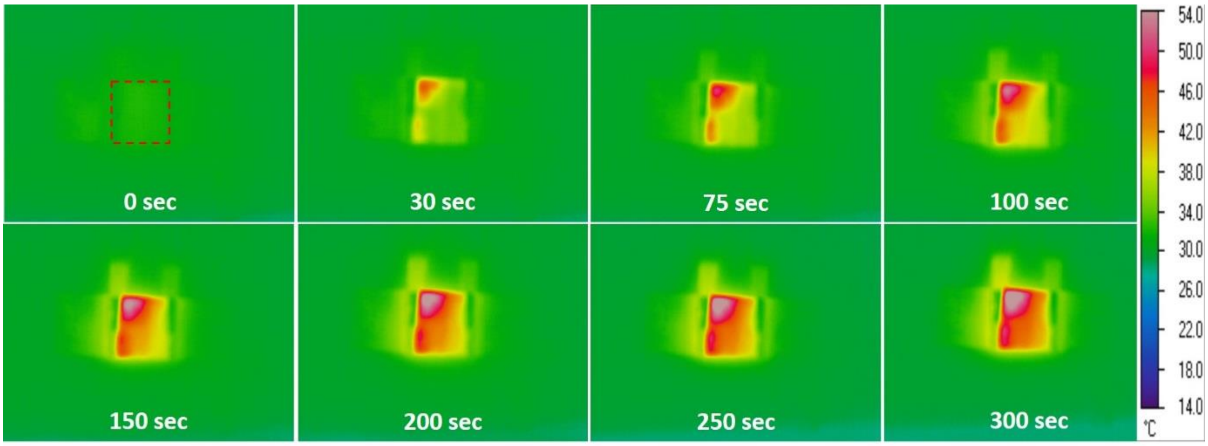


(c) 7.0wt.% CNT/PU coating

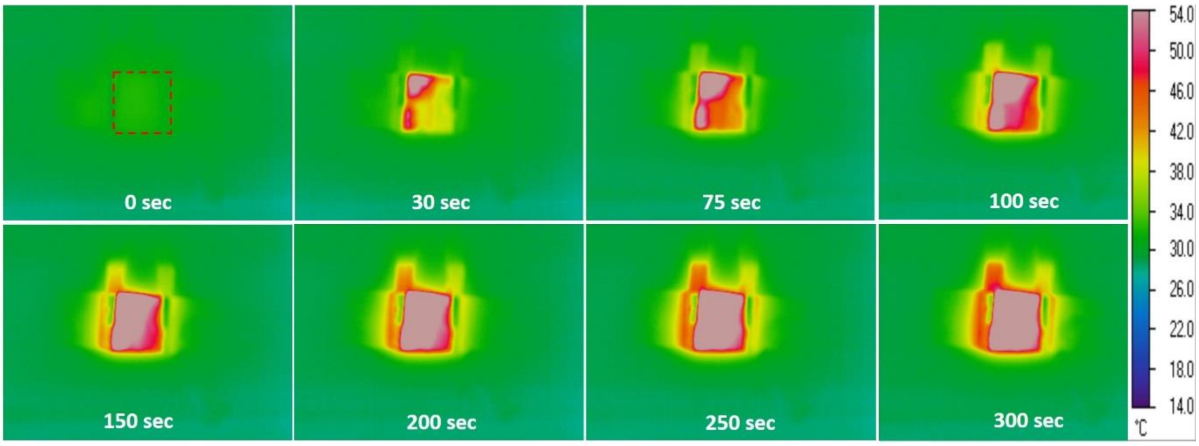
Figure 11. Temperature profile for CNT/PU coatings at different voltages.



(a) 1.0wt.% CNT/PU coating



(b) 3.0wt.% CNT/PU coating



(c) 7.0wt.% CNT/PU coating

Figure 12. Temperature evolution of CNT/PU coatings at 75V.

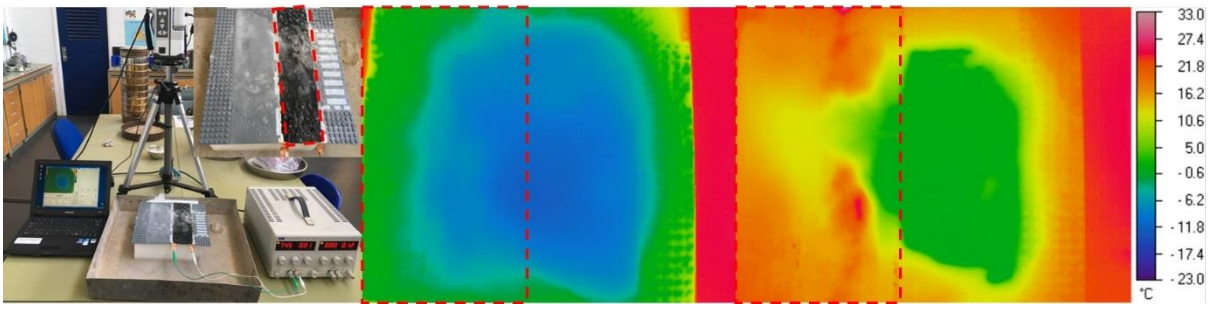


Figure 13. Temperature profile for CNT/PU coatings at different voltages.

9. Limitations:

9.1. Large quantities of CNT/PU coating materials

Currently the maximum volume of CNT/PU coating materials is around 1 litre, which mainly depends on the equipment. For example, current equipment (QSonica – Q700) with ½” diameter probe supported by T-TRIG produce the maximum volume of 1 litre. However, the maximum volume could be increased up to 5 litre when additional accessory (High Volume Flocells) is equipped with our equipment, which will overcome production issue for real application. For construction application such as coating on the highways and cyclic roads, it requires high amount of volume of our coating materials. Therefore, ultrasonicator with higher volume capacity will be required for real application. Also, PI will contact several coating companies in UK.

9.2. Power supply

As increasing total area of CNT/PU coating, total resistance also increased. According to $P = IV = V^2 / R$, dissipated heat from the coating will be reduced. Therefore, we need to increase the external power to enhance the heat. Considering long highways, high power capacity will be required for the heating over large area of transport roads.

10. Practical applications of the concept to the UK transport system (including costs):

Future application can be smart coating system on any kind of transport road system such as highways, airway runaway and cyclic roads during winter season. Polyurethane materials have currently used in transport road coating application with desirable material properties and durability. According to published report, addition of CNTs in the polyurethane could provide enhanced material properties in terms of mechanical, electrical and thermal properties. Therefore, CNT/PU coatings will be applied to any type of transportation system such as highway and cyclic roads. Although future research will be required in order to investigate long-term performance, proposed CNT/PU coatings will be survived for winter seasons, which applied once a year for targeted road paths. For coating issue, we used industrial type of multi-walled carbon nanotube, costing only $1,000 per 1 kg. Considering that our CNT/PU coating only requires 5.0 wt.%, the total cost of CNT/PU coatings is not big issue for future application. Although the price of CNT/PU coatings will be higher than pristine PU coating due to CNT additive, proposed CNT/PU coatings have other innovative functions such as temperature sensing and self-heating. Therefore, the price of CNT/PU coatings includes temperature sensing devices as well as enormous resources for winter maintenance such as huge amount of salt, trucks and drivers, and additional storage for equipment for winter maintenance. Considering those cost, I believe that proposed CNT/PU coatings will be promising solution for future winter maintenance system in UK transport.

11. Next steps/Recommendations for testing and implementation:

The results of the reported research can be used to manufacture a new-generation of smart transport road coating system capable of hydrophobic, freezing temperature sensing and self-heating. Investigation on the abrasion resistance for developed coating materials is required to understand the life cycle analysis. Also, the influence of freezing and thawing exposure will be investigated. Moreover, optimisation of smart transport road coating in terms of lower resistance and high power is required for real application. In the future, field tests on transport roads such as airways and highways are desired to understand the benefits of our developed coating materials in this research.

12. Conclusions:

This project showed the feasibility of carbon nanotubes reinforced polymer-based coatings for smart transport road system capable of hydrophobic, freezing temperature sensing, and self-heating. Electrically conductive CNT/PU coatings were fabricated using a horn-type ultrasonicator. The results confirmed that the electrical conductivity of the CNT/PU coatings increased as CNT concentrations increased. Also, other manufacturing parameter such as type of solvent and equipment power dramatically affects the electrical conductivity of the CNT/PU coatings. It was also shown that the nonlinear change in resistance of all CNT/PU coatings were observed with decrease of temperature. The self-heating performance of the CNT/PU coatings was investigated by the Joule heating effect. CNT concentrations of the CNT/PU coatings significantly affected the temperature profile when varying voltage was applied. Finally, we demonstrated the defrost performance of the CNT/PU coatings covered with ice. The CNT/PU coatings successfully melted the ice in a short period of time. Therefore, developed CNT/PU coatings have a great potential in smart transport road coatings for hydrophobic, detecting the freezing temperature, and deicing by self-heating in any type of transport road systems.

13. Annexes:

13.1. References

Jang, H.S., Jeon, S.K., and Nahm, S.H., “The manufacture of a transparent film heater by spinning multi-walled carbon nanotubes,” Carbon 49, Vol. 1, 2011, pp. 111-116.

Wang, Y. Q., and Liu, L., Beijing Funate Innovation Technology Co., Ltd., Washington, DC, U.S. Patent Application for a “Carbon nanotube defrost windows,” No. 8426776, filled on 29 Dec. 2009.