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Abstract: Abstract: The surface ice formation is an important phenomenon which affects multiple aspects of human daily activities. The icing has remarkable impact on certain industrial sectors such as aerospace, naval, construction and energy. A good example is the ice formation on airplanes and Unmanned Aerial Vehicles (UAVs) where it could endanger enormously planes´ aerodynamic efficiency and thus can even provoke accidents with severe consequences or cancelation of drones´ mission. Another problem is the loss of efficiency and safety risks related to ice formation on the surface of wind turbines, especially on blades. To deal with ice-formation several systems has been developed that are able to prevent ice accumulation or to facilitate its removal. Hereby, we report on novel active heated systems based on chemical modification of carbon nanotubes (CNTs) and organofluorine polymers based on the Joule effect.

Suggested Reviewers:

Tables (if any)

Dear Sir/ Madam,

Please find enclosed manuscript with the title: “Innovative coatings for advanced applications – Development of active anti-ice coatings”.

We present this manuscript due to an invitation of the Committee of the ICCG12 International Conference on Coatings on Glass and Plastics held in July 11 to 15 in Würzburg, Germany. The manuscript describes part of the results published in the oral presentation with number 5.4.

I hope the topic and specially the obtained results are interesting enough to be considered for publication in Thin Solid Films VIS ICCG12.

Sincerely yours,

Pavel Bartovký

***Highlights (for review)**

HIGHLIGHTS

- Carbon nanotube-based active systems prevent surface ice-formation
- Combination of carbon nanotubes and fluorinated polymers results in dual solutions
- Chemical modification and use of silica nanoparticles enhances the thermal efficiency of the system
- Homogeneous and efficient heating is achieved

Innovative coatings for advanced applications - Development of active anti-ice coatings

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Abstract: The surface ice formation is an important phenomenon which affects multiple aspects of human daily activities. The icing has remarkable impact on certain industrial sectors such as aerospace, naval, construction and energy. A good example is the ice formation on airplanes and Unmanned Aerial Vehicles (UAVs) where it could endanger enormously planes´ aerodynamic efficiency and thus can even provoke accidents with severe consequences or cancelation of drones´ mission. Another problem is the loss of efficiency and safety risks related to ice formation on the surface of wind turbines, especially on blades. To deal with ice-formation several systems has been developed that are able to prevent ice accumulation or to facilitate its removal. Hereby, we report on novel active heated systems based on chemical modification of carbon nanotubes (CNTs) and organofluorine polymers based on the Joule effect.

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1. Introduction

Ice formation over different surfaces can affect in many ways our daily life. In fact, it is common to observe ice appearance of frost in geographical areas where continental climate conditions predominate. The ice cause traffic jams and accidents on the roads, pipeline freezing and obstructions, windshield freezing and many more troubles. From the industrial point of view the icing is associated to safety risks as well as increasing costs of operations, time-losses and stops. Some sectors are highly sensible to the icing phenomenon. Among them the most representative are energy (specially wind energy), aerospace industry, naval industry (in cold climate) and railway [1].

The aerogenerators ("windmills") face an increasing challenge due to the more and more growing production capacity together with their usual extreme location. Depending on its geographical emplacement and climate condition the windmills should deal with diverse ice conditions ranging from few days a year as occurs for example in certain areas in central and northern Spain, to three or four months of freeze as happens in northern Europe area, namely Sweden, Norway and Finland.

Regarding aeronautical sector, it is worth to mention that commercial airplanes often struggles against weather conditions that implicates ice risk. However, conventional airplanes are equipped with technology that allows to destroy (melt) the ice formed on leading edge of the wings or to prevent its formation due to use of heated systems [2].

In the last 10 years, the introduction of unmanned aerial vehicles (UAVs) has gained higher interest in civil and military sector due to their versatility and low human risks. In the present exists a variety of UAVs of different types and size from various tons to few kilograms. The small-and medium size UAVs (Type I and Type II respectively) are able to perform missions covering up to 600 km distance [3], [4]. Nevertheless, statistics show that from 10 to 15% of mission is cancelled due to ice deposition on the leading edge and wing surface. Type I and II UAVs cannot bear common de-icing systems because of its weight and elevated energy consumption.

For all these reasons, it its crucial to improve the operative capacity of the UAVs through development of novel materials able to prevent and/or reduce ice formation over drone surface.

2. Dual active anti-icing systems development

The aim of this work was to develop heated anti-ice solutions that can be applied as coatings and/or as internal heated layer of multilayer film. From the technical point of view, two possible coating types were considered for aeronautical and wind energy sectors. Thus, polyurethanes and polyacrylate based coatings were modified with carbon nanotubes (CNTs) along with organofluorine polymers to obtain the desired double impact: to reduce ice adhesion and to prevent ice formation or melt already accumulated ice by induced surface heating [5].

3. Results and discussion

3.1 Anti-ice active systems.

Active anti-ice system development requires to transform a non-conductive material (polymer) into a conductive one in order to allow electrical heating promoted by the Joule effect. For this reason, we have incorporated carbon nanotubes and chemically modified (functionalized) carbon nanotubes at different ratios in the polymer matrix.

3.1.1 Carbon nanotubes functionalization.

Step 1: The CNT functionalization is performed via surface oxidation process using ozone. Typically, 2 grams of multi-walled nanotubes (MWNT; Nanocyl 7000) was placed in one-neck round-bottom reaction flask. Then 300 ml of methanol was added and the CNTs are dispersed using powerful ultrasonic equipment. The reaction mixture was cooled down to 0^{o}C in ice-bath. Bubbles of an O_3/O_2 (10-90) mixture obtained in ozone generator was purged into the flask during 5 hours at flow rate of 200-300 ml/min. Once the reaction time was over, the mixture was stirred 30 minutes at room temperature to eliminate excess of ozone, then the reaction mixture was filtered, and the obtained residue was dried in vacuum oven over 5 hours at 110^{o}C at 0,1 mbar pressure. The surface functionalization grade has been checked by measuring the hydroxyl value following the ASTM E1899 norm.

N the second step of the functionalization we have modified the CNTs with a perfluoroalquilic chain with 17 fluorine atoms to improve CNTs´ compatibility with the polymer.

Step 2: First, 1 gram of oxidized CNTS obtain in the first step was placed in a two-neck round-bottom flask together with 100 ml of dichloromethane. The mixture was stirred and 1.8 g of perfluorooctanol, 0.61 g of DMAP (dimethylaminopyrridine) and 0.78 ml of DIC (diisopropylcarbodiimide) has been added to the flask. The reaction was maintained under stirring at room temperature during 48h. Then the crude reaction mixture was filtered, and the solid residue was washed with 50 ml of DCM and after that again with 2x50 ml of methanol. Finally, the obtained solid was dried under vacuum during 5 hours at 110^{o}C at 0,1 mbar pressure.

3.1.2 Work up for heated carbon nanotube coatings

First step to obtain heated coatings was to disperse the functionalized nanotubes in butyl acetate in the ratio 95% (p/v) together with silica nanoparticles (Sigma-Aldrich, 200 nm) using ultrasound dispersion (Bandelin Sonoplus UW200) for 20 seconds. The dispersion was incorporated into Dupont perfluoroalquilic polymer (Capstone ST-110) and a bicomponent polyurethane (Hidromar Polyurethane – 10% Hardener). Then the coating was applied over an epoxy resin probe.

In the table 1 we present results on heating capacity of the developed materials and temperature reached after 24V current application for 10 seconds.

Table 1. Heating capacity of developed coatings

SAMPLE	%CNT	%CNT-F	% Silica	Surface Heating	Temperature (^{o}C)
1	0	0	8	No	-
2	0	1	0	No	-
3	0	2	0	Yes	35-40
4	0	4	0	Yes	65-70
5	4	0	0	No	-
6	0	4	0	Yes	70-75
7	0	4	2	Yes	75-80
8	0	4	4	Yes	75-80
9	0	4	8	Yes	85-90
10	0	8	8	-	-

In view of the obtained results it is worth to mention that CNT functionalization is an indispensable requirement for the obtention of more efficient heated CNT system (results 5-6, table 1). It was observed that contain of more than 4% of active component in the coating is needed to reach temperature above 65^{o}C. If the concentration is lower than the surface heating is not homogeneous, and/or the temperature barely overcomes 40^{o}C (results 2-4, table 1). Using 4% of modified CNTs results in adequate heating behaviour that can be even improved by using silica. The use silica nanoparticles allow to improve CNT dispersion in the matrix due to the dispersant and disaggregation effect of the silica. A significant increase of the heating efficiency (from 5 to 10 ^{o}C) has been observed using silica nanoparticles together with CNTs. Finally, the concentration upper limit has been established by adding 8% of CNT and 8% of nanosilica (result 10, table 1). In this case, it was not possible to measure the heating capacity because of the poor quality of surface coating. Numerous cracks and surface imperfections were produced that destroy the conductivity of the layer. A thermography image of the sample 9 is shown below. In this concrete case the temperature reaches up to 90^{o}C in 10 seconds. It should be highlighted that the temperature distribution is homogeneous without any cold nor overheated areas.

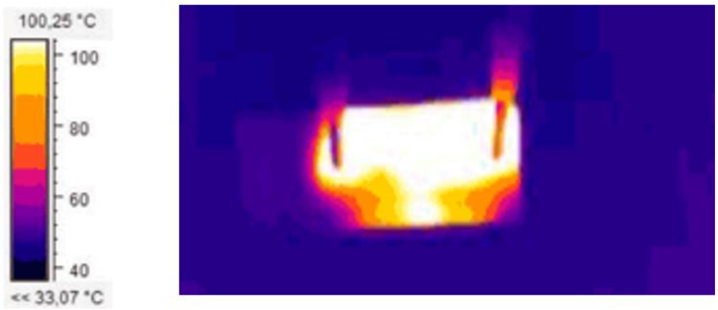

Fig 1. Thermography image of sample 9 coating

4. Conclusions

In this paper we have described novel active anti-ice heated coatings which can either melt accumulated ice or prevent the ice formation on treated surface. Its efficiency has been improved by an adequate functionalization of the CNTs as well as by presence of silica nanoparticles.

Acknowledgements

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Figures (if any)
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