Lubricated icephobic coatings prepared by flame spraying with hybrid feedstock injection

Valentina Donadei*, Heli Koivuluoto, Essi Sarlin, Petri Vuoristo

Materials Science and Environmental Engineering, Faculty of Engineering and Natural Sciences, Tampere University, P.O. Box 589, FI-33014 Tampere, Finland

ABSTRACT

Lubricated icephobic coatings were fabricated by flame spraying with hybrid feedstock injection. In this one-step process, composite coatings were produced by spraying a matrix material from a combustion flame spray gun and a lubricating additive from an injector, externally to the flame. External injection avoided possible thermal degradation of the heat sensitive additive during spraying. Inexpensive and widely available feedstock materials were used, polyethylene as the matrix and solid cottonseed oil as the lubricating additive. The coating properties were investigated by thermal and chemical analyses, surface roughness and wettability measurements at room temperature and in cold conditions. The icephobic behaviour was evaluated by accreting ice from supercooled water droplets in the icing wind tunnel. Ice adhesion was measured by the centrifugal ice adhesion test. The results showed that lubricant addition improved the icephobic performance of the coatings. Moreover, cooling the flame temperature with compressed air addition reduced thermal degradation of polymers. This was beneficial for the icephobic behaviour, thus lowering the shear ice adhesion strength down to 23 kPa ± 6 kPa. In conclusion, lubricated icephobic coatings were successfully produced by combining the hybrid feedstock injection and the thorough optimization of process parameters. This approach provides a potential surface engineering solution for the industrial sectors facing icing problems.

1. Introduction

In recent years, the demand for icephobic surface solutions has increased in industrial applications facing icing problems, such as power lines [1,2], wind turbines [3,4], solar panels [5,6], telecommunication and transportation in outdoor environments [7–9]. The accumulation and accretion of ice on functional surfaces represent a serious risk for several applications. For example, accumulation of ice on infrastructure can compromise their mechanical stability and, eventually, cause their collapse [10]. Moreover, accretion of ice on aircraft structures can modify the aerodynamics, endangering flight operations [7]. For this reason, the development of icephobic surface solutions is fundamental to solve this problem affecting industrial applications. Different strategies have been adopted to face icing problems, namely active and passive methods of ice removal. Active methods involve physical removal of ice by scraping operation and/or mechanical vibration, melting of ice by thermal heating or application of de-icing chemicals on surfaces [11,12]. However, these active methods require repetitive manual operations, waste of resources, environmental pollution and, consequently, additional costs [13–15]. Considering these disadvantages, an alternative strategy is represented by passive methods. These consist of smart paints, coatings and surface modifications [16], which lower the ice adhesion of surfaces and, then, easily promote passive ice removal. Recently, passive icephobic solutions have been developed to address industrial needs [17–20]. These include the availability of coatings or surface treatments, which show permanent icephobicity and withstand severe weather conditions, such as exposure to ultraviolet (UV) light radiation, changes of temperature and humidity, wind, rain, sandstorm, or some combination of these. Furthermore, the industry requires suitable coating techniques, which should preferably be fast, scalable, versatile and cost-efficient.

Different surface designs have been proposed in the literature with potential icephobic properties to reduce ice accumulation and/or ice adhesion on surfaces [21]. For example, superhydrophobic surfaces (SHS) (water contact angle ≥ 150°) effectively reduce the accumulation of ice compared to untreated metal surfaces [22,23]. The hierarchical micro/nanostructure of SHS helps to repel water droplets approaching the surface. Moreover, if water droplets are deposited on SHS, their hierarchical structure delays ice nucleation [24,25]. However, researchers have demonstrated that the icephobic properties of SHS are
severely damaged in high humidity and sub-zero conditions because of water condensation within surface features [26,27]. Therefore, alternative surface solutions are under consideration. Another surface design, namely slippery liquid-infused porous surface (SLIPS) [28], has been proposed as a solution for facing icing problems. SLIPS commonly consist of a micro/nanostructure infused with a liquid lubricant. These surfaces show potential anti-icing and anti-frost properties due to the presence of the liquid layer, which promotes the inhibition of ice nucleation [29,30]. Furthermore, once the ice forms on SLIPS, the extremely smooth layer of lubricant serves as a protection of the surface structure by preventing mechanical interlocking between the ice and the surface [31,32]. However, if the liquid lubricant is depleted, the surface experiences degradation of its icephobicity [21]. To solve this challenge, different strategies have been developed to improve the stability of liquid lubricant in SLIPS [32,33]. For example, one common strategy consists of entrapping the liquid lubricant within a network of cross-linked elastomers [34,35]. Furthermore, lubricant in the form of solid is infused within the coating structure to improve lubricant stability and thus obtaining long-term icephobicity [36,37].

Inspired by the infusion of solid lubricant, we fabricated a composite coating, composed of a matrix material and a lubricating additive, hereafter termed lubricated icephobic coating (LIC). Lubricating additives, in the form of liquid oil [34,38], grease paste [17] and solid wax [36,39], have shown potential icephobic behaviour [40]. In the present study, the matrix material is made of low-density polyethylene (LDPE), previously used to produce flame sprayed icephobic coatings [41–43]. The lubricant, namely fully hydrogenated cottonseed oil, represents the solid additive of LICs. The hydrogenated cottonseed oil consists of a hydrophobic waxy solid [44], generally employed as a coating release agent [45] or taste masking tool [46] for pharmaceutical purposes. Additionally, this specific combination of materials, namely polyethylene and liquid cottonseed oil, has been successfully used in SLIPS for packaging applications because of their excellent chemical compatibility [47].

In the last decades, icephobic coatings have been fabricated with different techniques, consisting mainly of laboratory-scale coating synthesis [21,34] and paint technology [48,49]. However, these methods require post-curing with evaporation of volatile organic compounds (VOCs), large waste of chemicals, and/or controlled environmental conditions. Therefore, alternative coating technologies are under consideration. Recently, icephobic coatings have been manufactured using different thermal spray techniques, such as suspension plasma spray [50], high-velocity oxygen-fuel (HVOF) spray [51–53], and flame spray processes [41,42,45,54]. However, some of these require a post-treatment to render the surface water repellent [50,53] or to infuse the liquid lubricant [54]. In this study, we propose a one-step flame spray process as a potential method to produce icephobic coatings, thus eliminating VOCs, post-curing and need for controlled environments [56]. We modified flame spraying by adding an injector externally to the flame spray gun. Matrix material was sprayed with the flame spray gun and lubricating additive was fed with an external injector. This protects the heat sensitive lubricant from the flame torch, thus limiting its degradation. We referred to this method as the flame spray process with hybrid feedstock injection. The objectives of the study were to (1) modify flame spray technique to process such heat sensitive materials and to produce lubricated coatings in one-step, (2) optimise the processing parameters for these specific materials to produce coatings with enhanced icephobic properties, (3) study the effect of process parameters on coating properties, such as surface chemistry, topography and wettability, and (4) evaluate the icephobic behaviour of lubricated coatings, understanding possible correlations between surface properties and icephobicity.

2. Experimental procedure

2.1. Materials and coating manufacturing

Commercially available low-density polyethylene (LDPE) powder (Plascoat LDPE, Plascoat Europe BV, The Netherlands) was used as a feedstock material to produce the lubricated coatings. This represents the main component of the coatings, considered as the matrix material of the composite structure. A solid lubricant (Lubritab® capsules, JRS PHARMA GmbH & Co. KG, Germany), made of fully hydrogenated cottonseed oil, was used as the lubricating additive. The lubricated icephobic coatings (LICs) were manufactured by the flame spray process with hybrid feedstock injection, which is schematically represented in Fig. 1.

A similar approach has been used to produce low friction coatings by externally feeding additives in the form of suspension [57,58]. In our study, the dry additive was fed externally to the spray gun to avoid direct contact with flame. The solid lubricant, made of hydrocarbons, can serve as a fuel in the flame and, therefore, its interaction with the combustion flame should be avoided. In this hybrid process, the matrix powder was sprayed by an oxygen-acetylene flame spray gun (CastoDyn DS 8000, Castolin Eutectic, Switzerland). This was axially fed using a powder feeder (Sulzer Metco 4MP, Oerlikon Metco, Switzerland) with
compressed air as a carrier gas. Simultaneously, the lubricating additive was sprayed from an injector mounted on the left side of the gun. The external injector was oriented towards the gun with its axis intersecting the flame spray gun axis at the distance of about 280 mm from the flame spray nozzle. The lubricant was fed using a powder feeder (PT-10 Twin powder feeder, Oerlikon Metco, Switzerland) with argon as a carrier gas, to further protect the additive from thermal oxidation. Mechanical sieving prior to spraying was necessary for the additive to increase its flowability and ensure continuity during powder feeding. The spray gun was mounted on a single-arm robot (ABB IRB 4400/60, ABB Robotics, Sweden), controlling traverse speed and spray distance during coating production. The process parameters used for the fabrication of LICs are listed in Table 1.

Table 1

<table>
<thead>
<tr>
<th>Process parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Castodyn DS 8000 – flame spray gun</td>
<td>SS M10</td>
</tr>
<tr>
<td>Nozzle model</td>
<td>250 mm</td>
</tr>
<tr>
<td>Combustion gases</td>
<td>250 mm</td>
</tr>
<tr>
<td>Oxygen pressure [bar]</td>
<td>4.2</td>
</tr>
<tr>
<td>Acetylene pressure [bar]</td>
<td>0.7</td>
</tr>
<tr>
<td>Compressed air pressure [bar]</td>
<td>2, 4</td>
</tr>
<tr>
<td>Gun spray distance [mm]</td>
<td>500, 700, 900</td>
</tr>
<tr>
<td>Gun traverse speed [mm/s]</td>
<td>5</td>
</tr>
<tr>
<td>Step size [mm]</td>
<td>5</td>
</tr>
<tr>
<td>Number of coating layers</td>
<td>5</td>
</tr>
<tr>
<td>Sulzer Metco 4MP-8500 dual powder feeder - matrix powder</td>
<td>20 mL/min</td>
</tr>
<tr>
<td>Matrix material feed rate [g/min]</td>
<td>11</td>
</tr>
<tr>
<td>Carrier gas (air) flow rate [L/min]</td>
<td>6</td>
</tr>
<tr>
<td>Carrier gas (argon) input pressure [bar]</td>
<td>5</td>
</tr>
<tr>
<td>PT-10 twin powder feeder – additive powder</td>
<td>26</td>
</tr>
<tr>
<td>Lubricating additive material feed rate [g/min]</td>
<td>1</td>
</tr>
<tr>
<td>Carrier gas (argon) flow rate [L/min]</td>
<td>6</td>
</tr>
</tbody>
</table>

Coatings were deposited on stainless steel substrates (EN 1.4301/2K (4N)), 30 mm × 60 mm × 1.5 mm in dimensions. The steel substrates were grit-blasted prior to spraying using aluminium oxide powder (grit size of 54 mesh), resulting in surface roughness of Ra = 2.8 μm. The substrates were pre-heated by flame to ensure good adhesion between coating and substrate. The substrate temperature was monitored during pre-heating by a thermal imaging camera (TI300 Infrared Camera IR Fusion Technology, Fluke Corporation, United States). The thermal camera was calibrated for the substrate material prior to spraying. Coating deposition started when the substrate exceeded the melting range of the matrix powder. This monitoring avoided the overheating of the substrate, which could cause polymer degradation [59].

From technical datasheets of the feedstock materials, the lubricant has a lower melting temperature range (57–70 °C) compared to the polyethylene material (107 °C). This requires the adjustment of the process parameters to reduce the heat load transferred to different polymeric materials. To achieve this, the following process parameters were varied (Table 1). Firstly, compressed air was added to the flame with variable pressure, namely 0, 2 and 4 bar. Addition of air reduces the flame temperature with the increase of pressure used. Secondly, a higher gun traverse speed was employed when no additional compressed air was added to the flame to reduce the heat load on the polymeric materials. The traverse speed was gradually reduced when compressed air was added to the combustion gasses. Finally, the post-heating by flame was performed for one selected coating to study its effect on the surface properties. The gun spray distance was fixed to 250 mm, according to our previous studies [42,43]. Fig. 2 summaries the process parameters used for LICs, flame-sprayed polyethylene coating (FS-PE1) and plain lubricant coating without matrix material (L4). L4 was produced to better understand the effect of lubricant addition on the properties of LICs. The FS-PE1 sample was fabricated with the same process parameters of the best polyethylene icephobic surface reported in our previous study [42], avoiding the post-heating by flame in this work.

2.2. Structural and thermal characterization of the powders and coatings

The morphology of the powders was analysed by a scanning electron microscope (SEM, Jeol, IT-500, Japan). The particle size distribution was measured by a laser diffraction analysis using dry powder method (LS 13 320 Laser Diffraction Particle Size Analyser, Beckman Coulter, Inc., United States). The coating thickness was estimated by a digital micrometre (293-676 micrometre IP54 SPC, Mitutoyo, United States). The results were obtained by the average and standard deviation of nine measurements. The thermal characterization of as-received powders and coatings was carried out by differential scanning calorimetry (DSC, Netzsch DSC214 Polyma, Netzsch, Germany). The specimens were weighed (approximately 10 mg) and placed in a concave aluminium pan for the thermal analysis. Dynamic heating was performed at 20 °C/min from −30 °C to 150 °C in a nitrogen atmosphere (40 mL/min nitrogen flow in addition to 60 mL/min protective nitrogen flow) to evaluate melting range and peak melting temperatures of as-received feedstock powders and coatings. The thermal stability of the powders was investigated by thermogravimetric (TG) analysis (Netzsch TGA209F Tarsus, Netzsch, Germany). The specimen weight was approximately 10 mg and placed in a concave aluminium pan for the thermal analysis. Dynamic heating was performed at 20 °C/min from −30 °C to 150 °C in a nitrogen atmosphere (40 mL/min nitrogen flow in addition to 60 mL/min protective nitrogen flow). The onset decomposition temperature, T onset, was evaluated for the powders from the dynamic TG curve according to the standard ISO 11358-1. This temperature is used as an indicator of the thermal stability of materials. Moreover, the maximum degradation rate temperature of the powders was measured at the peak of the first derivative of the TG curve (DTG curve). The DTG curve represents the rate of mass loss of the material versus temperature.

2.3. Characterization of the coating surfaces

The surface topography was analysed using an optical profilometer.
The areal roughness parameters (Sa, Sq, Sx) were evaluated with 20× objective magnification on 2 mm × 2 mm areas at different locations of the surface, according to the standard ISO 25178-3. The areal roughness values were obtained by the average and standard deviation of three measurements from corrected and filtered surface datasets. The chemical characterization of the coatings was carried out by Fourier-transform infrared spectroscopy (FTIR, Bruker Tensor 27 FT-IR spectrometer, Bruker, Sweden) and compared to the data obtained from the feedstock powders. For this analysis, an attenuated total reflectance (ATR) sample holder (GladiATR, PIKE Technologies, United States) was used with a diamond crystal. This allows the recording of FTIR spectra directly on the pristine material surface without any sample preparation. The FTIR absorbance spectra were measured in the wavenumber range 4000 cm−1 to 600 cm−1 in air at room temperature by recording 32 scans with a resolution of 4 cm−1. For the measurements, the coating surface was directly placed in contact with the crystal. The measurements were performed at 15 different locations of the coating surface for each sample.

The wetting behaviour of the coating surfaces was evaluated by a droplet shape analyser (DSA100, Krüss, Germany) in controlled conditions (22 °C ± 1 °C temperature and 60% ± 3% relative humidity). Static contact angles were measured by placing 10 μL droplets of ultrahigh purity water (MilliQ, Millipore Corporation, United States) onto the surfaces. The apparent water contact angle was estimated using the tangent method (polynomial fit of droplet shape). The dynamic wetting behaviour was evaluated by tilting experiments. The 10 μL droplet was placed onto the coating surfaces, which were tilted until the droplet rolled off. The roll-off angle was recorded when no droplet pinning was observed during tilting experiments. Both static contact angle and roll-off angle were calculated as the average of at least five measurements on different locations of the sample. Moreover, the wetting behaviour was evaluated at −10 °C, which corresponds to the temperature we used for the ice adhesion test. For this purpose, a temperature control chamber was installed (Krüss TC40, Krüss, Germany) on the stage of the droplet shape analyser. The chamber includes a movable Peltier plate unit, which temperature is adjusted and monitored by a glycol bath circulator (F12-MA, Julabo GmbH, Germany) and a temperature controller (2216e controller, Eurotherm Controls LTD, United Kingdom), respectively. The sample was placed on the Peltier stage, gradually cooling the surface from room temperature to −10 °C ± 1 °C. Coating surface temperature was monitored by a type K thermocouple with a digital thermometer (Fluke 51 II digital thermometer, Fluke Corporation, United States). After the surface reached the desired temperature, the static contact angle and roll-off angle were measured by depositing 10 μL water droplet. The results were evaluated as the average of at least three measurements. During this experiment, a dry atmosphere was maintained in the chamber by continuously flushing dry nitrogen to avoid water condensation. The air temperature of the chamber was monitored with a temperature sensor (Pt-100, Krüss TP20, Krüss GmbH, Germany) and measured to be around 11 °C ± 1 °C at 10 mm distance above the sample. The chamber was preventedly sealed with paraffinic laboratory film to further insulate it from the surrounding environment.

The icephobic behaviour of the coating was evaluated by using the icing wind tunnel (IWIT) and the centrifugal ice adhesion test (CAT) facilities at Tampere University. The test equipment sits in a climate-controlled cold room with monitored temperature and relative humidity (−10 °C ± 1 °C and 80% ± 5%). The test apparatus is described in detail in previous studies [38,60,61]. Mixed-glaze type of ice was accreted from supercooled water droplets on 30 mm × 30 mm sample areas in the IWIT at −10 °C. After accretion, the ice adhesion strength was measured with the CAT at the same temperature. In the centrifugal method, the specimen with accreted ice, placed on a blade and carefully counterweighted, is spun with a constant acceleration rate until the ice detaches. An acceleration sensor records the value of the rotational speed, which corresponds to the ice detachment. The shear ice adhesion strength is evaluated as the ratio of the centrifugal force, F [N] at the moment of ice detachment, to the area of the iced surface, A [m²]. Eq. (1) estimates the shear ice adhesion strength, $\tau_{\text{ice}}$ [kPa], as follows:

$$\tau_{\text{ice}} = \frac{F}{A} = \frac{m_{\text{ice}} \omega^2 r^2}{A}$$

where $m_{\text{ice}}$ [kg] is the known mass of the accreted ice on the specimen, r [m] is the radial spinning length and $\omega$ [rad/s] is the rotational speed. The ice adhesion of the coating was evaluated as the average and standard deviation of four parallel samples during icing accretion events. A reference surface, namely Teflon tape (TT, 3M, United States), was tested to monitor the ice adhesion variation during ice accretion. The use of the reference material is essential to ensure the repeatability of the test results because of variability in ice adhesion strength for different icing conditions [60,62,63].

3. Results and discussion

3.1. Structural and thermal properties of the feedstock powders

Fig. 3a shows the morphology of LDPE powder. The shape of the particles varied from blocky irregular grains to long stretched flakes, produced by the powder manufacturing process. Conversely, the hydrogenated cottonseed oil powder showed particles with spherical shape (Fig. 3b) and capsule geometry (Fig. 3c). The particle analysis revealed a broader size distribution for the LDPE powder ($\sim 482 \pm 154 \mu m$) compared to the lubricant powder ($\sim 152 \pm 34 \mu m$).

The thermal analysis of the as-received powders represents a powerful tool to understand the thermal behaviour of polymeric materials, especially when their processing involves high-temperature flame and oxidative atmosphere. The main purpose was to drastically reduce or, in the best case, avoid thermal degradation, which has been demonstrated to negatively affect the icephobicity of flame sprayed polyethylene.
coatings [42]. Fig. 4a shows the DSC curves of both as-received powders, highlighting two distinct melting temperature ranges. The lubricant had a lower melting range (two different melting peaks at around 55 °C and 66 °C) compared to LDPE (melting peak at around 111 °C). Moreover, the TG analysis of the powders revealed the onset temperatures ($T_{\text{onset}}$) of 458 °C and 398 °C for the LDPE and lubricant degradation, respectively (Fig. 4b). Above $T_{\text{onset}}$, the material decomposes, and this temperature should not be exceeded during processing. Both TG and DTG curves confirmed that the thermal degradation process in inert conditions happened in one stage for both powders. The rate of weight loss was maximum at 482 °C and 435 °C for the LDPE and lubricant, respectively. These two maximum degradation temperatures were used to identify the presence of these components in the coating once the powders were flame sprayed.

These analyses highlight the differences in dimensions and thermal properties of the feedstock powders, resulting in their different thermal behaviour in contact with the flame. In particular, the lubricant has smaller particle size distribution, lower melting range and thermal stability than polyethylene. This implies that the chance of thermal degradation is higher for the additive during spraying, and justifies our decision to use an external injector for it.

3.2. Structural and thermal properties of the coatings

Fig. 4a shows the DSC curves of both as-received powders, highlighting two distinct melting temperature ranges. The lubricant had a lower melting range (two different melting peaks at around 55 °C and 66 °C) compared to LDPE (melting peak at around 111 °C). Moreover, the TG analysis of the powders revealed the onset temperatures ($T_{\text{onset}}$) of 458 °C and 398 °C for the LDPE and lubricant degradation, respectively (Fig. 4b). Above $T_{\text{onset}}$, the material decomposes, and this temperature should not be exceeded during processing. Both TG and DTG curves confirmed that the thermal degradation process in inert conditions happened in one stage for both powders. The rate of weight loss was maximum at 482 °C and 435 °C for the LDPE and lubricant, respectively. These two maximum degradation temperatures were used to identify the presence of these components in the coating once the powders were flame sprayed.

These analyses highlight the differences in dimensions and thermal properties of the feedstock powders, resulting in their different thermal behaviour in contact with the flame. In particular, the lubricant has smaller particle size distribution, lower melting range and thermal stability than polyethylene. This implies that the chance of thermal degradation is higher for the additive during spraying, and justifies our decision to use an external injector for it.

Fig. 5a shows the visual appearance of two coating surfaces and Fig. 5b represents the schematic structure of LICs. The lubricant addition rendered the surface visually opaquer compared to the glossy black polyethylene coating, FS-PE1. Moreover, this addition helped to obtain a visually smoother surface topography (LIC1 compared to FS-PE1, sprayed with identical process parameters). Fig. 5c shows the measured coating thicknesses.

The used process parameters influenced the coating thickness. The lower the gun traverse speed, the greater the deposited amount of material per unit length. This resulted in increased coating thickness. Producing the plain lubricant coating was challenging because the melted additive was continuously dripping down from the substrate. Therefore, an uneven coating layer was produced (L4 thickness around 20 μm ± 6 μm). The deposition of lubricant improved the coating build-up when this was simultaneously sprayed with LDPE, as can be seen from the difference in thickness between FS-PE1 and LIC1. For the coatings sprayed with a gun traverse speed of 900 mm/s, the increased cooling effect of the flame (from 0 to 4 bar air pressure) resulted in gradually higher thicknesses. The cooling effect might reduce the degree of melting of polyethylene splats and the in-flight degradation of powders, especially for the lubricant. Both of these factors led to an
3.3. Surface topography and surface chemistry of the coatings

The areal roughnesses (Sa, Sq, Sz) are summarised in Table 2. From the results, the process parameters greatly influenced the obtained surface topography. As a rule of thumb for thermal spraying of polymers, the higher the temperature reached by the polymer during processing, the greater the smoothness obtained for the surface [56,66]. For this reason, the higher the gun traverse speed, the lower the temperature in which the polymers are heated, thus producing a rougher coating surface (LIC4 compared to LIC3). Moreover, the greater the cooling effect of the flame, the lower the degree of melting for the polymer matrix, thus newly resulting in rougher surfaces (LIC1 compared to LIC4). The addition of lubricant reduced the coating roughness when identical process parameters were used (LIC1 compared to FS-PE1), as confirmed by visual inspections in Fig. 5a. This was probably caused by the complete melting of lubricant, which filled the surface topography of flame sprayed polyethylene. Furthermore, if post-heating was performed, this smoothened the coating surface because of re-melting and re-solidification of the polymers (LIC3 compared to LIC3*). Similar behaviour has been reported when using different post-heating treatments to re-melt the surface of thermally sprayed polymer coatings [67]. Finally, L4 resulted in the smoothest surface because of the lubricant dripping down from the substrate during spraying.

The presence of thermal degradation was further investigated by the chemical characterization of the coating surfaces, considering the feedstocks as reference materials. The infrared (IR) spectra of LDPE and lubricant powders are represented in Fig. 8. Compared to LDPE, the lubricant had additional peaks at 2955 cm$^{-1}$ ($=C$–H cis stretching vibration), at 1737 cm$^{-1}$ ($=C$=O ester stretching vibration), and in the fingerprint region from 1200 cm$^{-1}$ to 800 cm$^{-1}$.

From the comparison between the feedstock powders and corresponding coatings, little chemical modifications were detected for FS-PE1. These chemical modifications produced an increase in peak absorbance at 1713 cm$^{-1}$. This indicated the presence of carbonyl compounds formed by thermal oxidation when no additional air was used in the flame [42]. Moreover, weak peaks appeared around 1600 cm$^{-1}$. The signals corresponded to the vibrations in C=C bonds, revealing the presence of alkene compounds (unsaturated carbon-carbon covalent bond). Alkenes constitute an initial product of thermal degradation of polyethylene [68]. Fig. 8c shows representative FTIR spectra of the lubricated coatings. The characteristic peaks of both matrix and additive materials were revealed for every coating, confirming that the materials (and surely the lubricant) were evenly distributed on the coating surface. However, LIC1 and LIC3* showed alkene signals, similarly to FS-PE1. This demonstrated that little thermal degradation of the polymers occurred when both post-heating and no additional cooling were used, as confirmed by thermal analyses. Additionally, the presence of the carbonyl peak (signal at 1713 cm$^{-1}$) was impossible to reveal for the coating surfaces because it overlaps the strong ester signal of the lubricant in the same region.

3.4. Wetting properties of the coatings

The analysis of the wetting properties serves as a preliminary investigation to understand the tendency of the surface to like or dislike water. This tendency is commonly evaluated by measuring the water contact angle (WCA) formed by the water droplet with the surface. If the surface likes water, this angle lies between 0° and 90° (i.e., the hydrophilic case). Conversely, if the surface dislikes water, this angle is higher than 90° (i.e., the hydrophobic case) and even greater than 150° for strong water repellency (i.e., the superhydrophobic case) [69]. Since ice is the solidified form of water, the wetting behaviour has been
90°. The wettability of the surfaces generally fell with lowering the surface for the other coatings, resulting in roll-off angles higher than 31° ± 1.5°. Conversely, 10 μL water droplets were pinned onto the mical analyses. At room temperature, L4 showed a roll-off angle of presence of the additive on the coating surfaces, as confirmed by che the lubricant coating (L4). This wetting behaviour was justified by the coating. LICs showed intermediate wetting properties, more similar to grit-blasted substate (Ra ≈ 2.8 μm) beneath the uneven lubricant state [73]. This wetting state was promoted by the microroughness of underneath the water droplet, which was in a Cassie−Wenzel mixed wetting surface was partially wetted. Air pockets were probably trapped be approximately 120° in the Wenzel state [69,74], this suggested that the flat solids (fluorinated materials) the contact angle never exceeds ap

reached WCA of 146° ± 3°. Being aware that on the most hydrophobic

graphy, remaining in a Wenzel wetting state [73]. Conversely, L4
character with WCA of 84° ± 3°. Here, the water droplet probably was

for its presence on the mixed wettability of surfaces [12,70]. Fig. 9a shows the apparent WCA at different surface temperatures of the coating surfaces. The apparent WCA, which is schematically defined for a non-ideal surface in Fig. 9b, was measured both at room temperature and in cold conditions of the surface. The sub-zero temperature of −10 °C was chosen, which corresponds to the icing test temperature. A few studies have recommended performing wetting measurements at conditions as similar as possible to icing test environments [71] or real icing conditions [72] to better understand the icephobicity of surfaces.

From the results at room temperature, FS-PE1 showed a hydrophilic character with WCA of 84° ± 3°. Here, the water droplet probably was in intimate contact with the valleys and peaks of the surface topography, remaining in a Wenzel wetting state [73]. Conversely, L4 reached WCA of 146° ± 3°. Being aware that on the most hydrophobic flat solids (fluorinated materials) the contact angle never exceeds approximately 120° in the Wenzel state [69,74], this suggested that the surface was partially wetted. Air pockets were probably trapped beneath the water droplet, which was in a Cassie−Wenzel mixed wetting state [73]. This wetting state was promoted by the microroughness of grit-blasted substate (Ra ≈ 2.8 μm) beneath the uneven lubricant coating. LICs showed intermediate wetting properties, more similar to the lubricant coating (L4). This wetting behaviour was justified by the presence of the additive on the coating surfaces, as confirmed by chemical analyses. At room temperature, L4 showed a roll-off angle of 31° ± 1.5°. Conversely, 10 μL water droplets were pinned onto the surface for the other coatings, resulting in roll-off angles higher than 90°. The wettability of the surfaces generally fell with lowering the substrate temperature. This can be explained by considering the cold experimental conditions. When water, at room temperature, is deposited on a cold surface, a temperature gradient is generated between the droplet and the surface. The higher the gradient, the greater the induced formation of water nuclei (water condensation phenomenon), which grow beneath the drop on the surface [75]. The water condensation phenomenon is schematically shown in Fig. 9c. This effect is reduced when no temperature gradients exist between the water droplet and the surface [75], which is ideally the case of our room temperature experiments. Therefore, the water condenses within the microstructure, eliminating the presence of air pockets and thus resulting in lower apparent contact angles [71,76]. In our study, this explained the more evident drop in WCA for some surfaces (L4, LIC3*, LIC2 and LIC1), in which air pockets were still trapped beneath the water drop at room temperature. No evident drop in WCA was revealed for other surfaces (LIC3 and LIC4) when the droplet might be already in a Wenzel state at room temperature. However, it cannot be excluded that water might also condense onto the surface from the humid air of the chamber during sample cooling, despite the presence of continuous nitrogen flow. The roll-off experiments in cold conditions were also influenced by the condensation phenomenon, showing systematically pinning of the water droplets for every coating surface.

The wetting properties at room temperature demonstrated the presence of air pockets trapped beneath the drop for some coatings. This air volume was filled with water in cold temperature experiments, thus causing a general decrease in WCA. The effect of the areal roughness on the wetting properties was evaluated in this study. The apparent WCA measured at different temperature is plotted as a function of the areal roughness Sa for the lubricated coatings, as shown in Fig. 10.

In the room temperature experiments, the WCA decreased with areal roughness (Fig. 10a). This behaviour can be explained by understanding the wetting regime of water droplets. If a fixed water volume is deposited on the surface, a higher apparent WCA is measured when the surface is partially wetted (Cassie–Wenzel mixed wetting state for L4). Conversely, a lower apparent WCA is revealed when the surface is completely wetted (Wenzel wetting state for LIC4). The transition from a partial non-wetting to a complete wetting state is influenced by the surface geometry (relative size of surface features and drop dimension) and by gravity effects [69]. Until a certain limit of roughness, the hydrophobicity of the surface was enhanced allowing air pockets to be stably trapped beneath the drop. After that limit, the increased roughness produced a larger surface area, which geometrically enhanced the Wenzel state [69]. In the cold temperature

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>FS-PE1</td>
<td>31 ± 3</td>
<td>39 ± 5</td>
<td>214 ± 10</td>
</tr>
<tr>
<td>LIC1</td>
<td>12 ± 2</td>
<td>15 ± 3</td>
<td>75 ± 9</td>
</tr>
<tr>
<td>LIC2</td>
<td>14 ± 3</td>
<td>18 ± 5</td>
<td>115 ± 23</td>
</tr>
<tr>
<td>LIC3</td>
<td>18 ± 2</td>
<td>23 ± 4</td>
<td>160 ± 42</td>
</tr>
<tr>
<td>LIC3*</td>
<td>10 ± 0.2</td>
<td>12 ± 0.5</td>
<td>76 ± 15</td>
</tr>
<tr>
<td>LIC4</td>
<td>37 ± 4</td>
<td>47 ± 6</td>
<td>282 ± 38</td>
</tr>
<tr>
<td>L4</td>
<td>0.9 ± 0.3</td>
<td>1 ± 0.3</td>
<td>64 ± 10</td>
</tr>
</tbody>
</table>

Table 2

Average and standard deviation of the areal roughness: average height (Sa), root-mean-square height (Sq) and maximum height (Sz) evaluated for the coating surfaces.

Fig. 7. Surface topography of the coatings measured by optical profilometer analysis.

7
experiments, the decrease of WCA with areal roughness was less pronounced (Fig. 10b). Here, water condensation forced the droplet in a Wenzel state, thus being the variation of WCA less dependent from the roughness in these conditions. Several studies on the influence of surface roughness on wettability have shown an increase of WCA (reaching superhydrophobicity) when passing from a flat and to a rougher surface. This has been verified for the same material in the range of surface roughnesses below 5 μm [77–79]. Increased hydrophobicity was also observed for the same range of roughnesses in this study, as can be seen for L4 in Fig. 10a. Above surface roughnesses of 5 μm, we observed a gradual decrease of WCA with increasing roughness. To the best of the authors’ knowledge, no studies correlating wetting properties and surface roughness were presented in the literature for the range of roughnesses considered in this work.

3.5. Icephobic behaviour of the coatings and influence of the surface properties

The icephobic behaviour is defined as the intrinsic ice-repellency of the surface, generally resulting in low ice adhesion strength below to 50 kPa. The value represents the low ice adhesion limit defined for this ice adhesion test [38]. Firstly, LICs generally showed lower average ice adhesion compared to the polyethylene coating. Secondly, the ice adhesion further decreased with the increased cooling effect of the flame (from LIC1 to LIC3). Thirdly, optimised process parameters allowed the best icephobic surface of this study, lowering the ice adhesion strength down to 23 kPa ± 6 kPa. If post-heating was performed, the ice adhesion increased approximately 61% (LIC3* compared to LIC3). Moreover, if a rougher surface was produced, the ice adhesion rose again approximately 35% (LIC4 compared to LIC3). Finally, L4 showed average ice adhesion in the same range of LIC3 with a broader standard deviation. This was probably caused by the unevenness of the lubricant coating, increasing the standard deviation of the results [63].

Different material properties have been shown to influence ice adhesion strength, such as chemical composition, surface topography, stiffness and thermal expansion, without considering the effect of the test variables as well [80]. Concerning surface topography, several researchers have demonstrated that roughness affects the icephobicity of
surfaces [77,81,82]. Ice adheres on surface features, forming intimate mechanical interlocking and thus increasing ice adhesion [83]. The ice adhesion strength increases with surface roughness when coatings with identical surface chemistry are considered [81,82,84,85]. However, no similar relationship is found when other factors are influencing the icephobic behaviour of surfaces [81,86]. In this study, no clear correlation was found between areal roughness and ice adhesion strength for the lubricated coatings. Firstly, the ice adhesion decreased from LIC1 to LIC3 while areal roughness increased. Secondly, the ice adhesion surprisingly increased for the smoother surface LIC3*. Finally, the roughest surface of this study (LIC4) showed ice adhesion lower than the post-heated coating. This implied that another dominant factor was influencing icephobicity. In particular, the coating chemistry, which is directly correlated with coating degradation, could determine the icephobic behaviour of the surface. We measured the highest ice adhesion strength for degraded LICs, such as LIC1 and LIC3*. The degradation was caused by the absence of additional air in the flame and performed post-heating. The coatings experienced thermal degradation and

Fig. 9. Results of the wetting experiments: a) apparent WCA at room temperature and cold (−10 °C) surface conditions, b) schematization of a water droplet on a real surface with the definition of apparent water contact angle, and c) transition from Cassie-Wenzel mixed wetting state at room temperature to Wenzel wetting state at cold temperature surface (θ1 > θ2). Description of the water nuclei formation (water condensation) under the drop during wetting experiments in cold surface conditions.

Fig. 10. Correlation between the apparent water contact angle and the areal roughness a) at room temperature, and b) at −10 °C.

Fig. 11. Ice adhesion strength and areal roughness Sa of the coatings. Teflon tape (TT) represents the reference material for the ice adhesion test.
possible surface embrittlement, which have been shown to negatively affect icephobicity [42]. Conversely, the cooling effect of the flame was beneficial for the icephobic behaviour (gradual decrease of ice adhesion passing from LIC1 to LIC3). Finally, the ice adhesion increased with areal roughness, passing from LIC3 to LIC4 samples. This increase was probably caused by the formation of mechanical interlocking. We can assume that when no degradation was revealed, surface roughness might become the main factor influencing icephobicity. However, further analyses are required to define this specific correlation.

Concerning surface wettability, several studies have found a relationship between apparent WCA and ice adhesion strength [26,70,87]. Conversely, other researches have claimed no clear correlation between these properties [88–91]. Fig. 12 shows the ice adhesion strength plotted as a function of the apparent WCA at room temperature and in cold conditions.

Three different coating groups were distinguished for the wettability at room temperature, namely FS-PE1, LICs and L4. We noticed that the icephobic behaviour was enhanced when passing from a hydrophilic surface (FS-PE1 with WCA below 90°) to a more hydrophobic surface (LICs and L4), confirming the benefits of lubricant addition. This tendency has been reported in previous studies [70,86,87]. No clear relationship could be established between ice adhesion strength and WCA at room temperature and cold conditions. However, the wetting properties in cold conditions showed a narrower distribution of the data compared to the results at room temperature (distribution of star symbols narrower than that of square symbols). The data reported here appear to support the assumption that wetting properties, evaluated in conditions similar to icing test, might provide useful information on the icephobic behaviour of surfaces [71,72]. However, this requires additional research and further development of the actual test equipment. Furthermore, other factors could influence icephobicity. Several recent studies have demonstrated the dependence of the icephobic behaviour from mechanical properties, such as Young modulus [92,93], shear modulus [34,94,95], interfacial toughness [19], and other physical-chemical properties of materials [87,96,97]. In this study, we cannot exclude the influence of these beforementioned factors on the icephobicity of presented coatings. Therefore, further investigations are needed to understand possible correlations with these other influencing factors.

3.6. Icephobic performance of lubricated coatings compared to polyethylene coatings

Fig. 13a summarises the results of the ice adhesion strength plotted as a function of the areal roughness $S_a$ for lubricated coatings (in orange) and LDPE coatings (in black). Fig. 13b shows the corresponding process parameters. The lubricated coatings were manufactured by modifying the traditional flame spray process, previously used to produce the LDPE coatings [42,43]. In this study, the hybrid feedstock injection system was added to the flame spray gun to feed the lubricating additive. The spray distance was constant at 250 mm for the compared samples.

From the comparison of the results, we can draw the following conclusions. Firstly, the addition of selected lubricant further enhanced the icephobic behaviour of flame sprayed polyethylene coatings (orange squares versus black squares). This was achieved by using flame spraying with hybrid feedstock injection when such heat sensitive materials were involved in the process. The roughest lubricated coating
showed icephobicity below the limit of low ice adhesion strength. This implied a great influence of the surface chemistry over the roughness on the icephobic behaviour of the coatings. Secondly, the thermal degradation of the polymers was identified as another factor negatively influencing the icephobicity. Material degradation was reduced by cooling the flame and avoiding post-heating. The avoided post-heating was beneficial to the icephobicity, when the lubricant was present in the coating structure (ice adhesion of LIC3 compared to LIC3*). In this case, the post-heating probably produced degradation and partial vaporisation of the surface components, thus compromising the icephobicity. Conversely, the post-heating enhanced the coating icephobicity in the case of flame sprayed polyethylene (ice adhesion of FS-PE1 compared to C1*). Here, a smoother surface was beneficial to reduce the ice adhesion. In conclusion, a full investigation of the chemical and thermal properties of the sprayed coatings is strongly recommended. In our study, this supports the optimization of process parameters to obtain high quality icephobic coatings for the selected materials.

4. Conclusions

This research work presented the one-step fabrication of lubricated icephobic coatings by flame spraying with hybrid feedstock injection. In this process, the matrix material and the lubricating additive with different thermal properties were simultaneously sprayed to form a composite coating. The higher melting temperature polymer, namely matrix material, was sprayed from the oxy-acetylene gun. Differently, the lower melting temperature polymer, namely lubricating additive, was externally fed by an injector. This protected the additive from thermal degradation. The main conclusions of this study can be summarised as follows:

- Processing of heat sensitive materials, such as lubricants in solid form, was achieved by flame spray technology with hybrid feedstock injection. This was done to enhance the icephobicity of flame sprayed polyethylene coatings. The use of this process and further cooling of the flame allowed the protection of sprayed materials from thermal degradation, ensuring the production of good quality coatings.
- The optimization of process parameters was carried out by comparing chemical and thermal properties of materials before and after spraying. The results demonstrated that cooling of the flame was beneficial to reduce the thermal degradation of polymers.
- The surface topography was tailored by the chosen process parameters. The lower the heat load involved in the process, the rougher the obtained surface. The post-heating treatment produced smoothening of the coating surface caused by re-melting effects.
- Lubricated coatings showed enhanced hydrophobic character compared to the plain polyethylene coatings. Additionally, the surface topography influenced the surface wettability. The greater the roughness, the lower the apparent WCA for both room and cold temperature experiments. The hydrophobic character of the surfaces fell in cold temperature because of water condensation within surface features.
- The ice adhesion was mainly influenced by both thermal degradation and surface chemistry of the coatings. The lubricant addition enhanced the icephobic behaviour of the coatings. The thermal degradation compromised the icephobic performance of surfaces. The degradation was avoided by optimising the process parameters, which lowered the ice adhesion down to 23 kPa ± 6 kPa.

Future studies will focus on the fabrication of thermally sprayed coatings made of different combinations of materials to further tailor the surface icephobicity. Moreover, the icing durability of the coatings will be investigated under repeated icing/de-icing cycles in cold conditions.

CRediT authorship contribution statement

Valentina Donadei: Conceptualization, Methodology, Investigation, Visualization, Writing - original draft. Heli Koivuluo: Conceptualization, Supervision, Funding acquisition, Resources, Writing - review & editing. Essi Sari: Supervision, Writing - review & editing. Petri Vuoristo: Supervision, Funding acquisition, Resources, Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgement

Authors thank the LubISS (Lubricant Impregnated Slippery Surfaces) project that has received funding from the European Union’s Horizon 2020 research and innovation programme under the Marie Sklodowska-Curie Grant Agreement No. 722497. Mr. Anssi Metsiönekala and Mr. Jarkko Lehti, of Tampere University, are acknowledged for technical support in the flame spray process. Moreover, the authors acknowledge M.Sc. Matteo Orlandini, of Millidlyne Oy, for the particle size analysis. Prof. Shrikant Joshi, of University West, and M.Sc. Saurabh Nath, of ESPCI Paris, are thanked for the stimulating discussions. M.Sc. Henna Niemelä-Anttonen and B.Sc. Enni Hartikainen, of Tampere University, are thanked for assisting the icing testing.

References
