Heterogeneous freezing on pyroelectric poly(vinylidene fluoride-co-trifluoroethylene) thin films

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Active deicing of technical surfaces, such as for wind turbines and heat exchangers, currently requires the usage of heat or chemicals. Passive coating strategies that postpone the freezing of covering water would be beneficial in order to save costs and energy. One hypothesis is that pyroelectric active materials can achieve this because of the surface charges generated on these materials when they are subject to a temperature change. High-quality poly(vinylidene fluoride-co-trifluoroethylene) (P(VDF-TrFE)) thin films with a high crystallinity, prefered edge-on orientation, low surface roughness, and comprised of the $\beta$-analogous ferroelectric phase were deposited by spin-coating. Freezing experiments with a cooling rate of 1 K min$^{-1}$ were made on P(VDF-TrFE) coatings in order to separate the effect of different parameters such as the poling direction, film thickness, used solvent, deposition process, underlying substrate, and annealing temperature on the achievable supercooling. The topography and the underlying substrate significantly changed the distribution of freezing temperatures of water droplets in contact with these thin films. In contrast, no significant effect of the thickness, morphology, or pyroelectric effect of the as-prepared domain-state on the freezing temperatures was found.

KEYWORDS
electric double layer, heterogeneous freezing, parameter study, pyroelectric effect, P(VDF-TrFE)

1 | INTRODUCTION

The ferroelectric properties and pyroelectrically generated surface charges of poly(vinylidene fluoride-co-trifluoroethylene) (P(VDF-TrFE)) have created interest in their application in aqueous surroundings. It is assumed that the surface charges generated due to the combination of the pyroelectric effect and a temperature change can influence processes in the electrochemical double layer (EDL) (Figure 1) and, therefore, result in thermally switchable surface chemistry.\textsuperscript{1,2} Using P(VDF-TrFE) thin films as active materials in aqueous environments is expected to enable new applications, such as passive anti-ice surfaces,\textsuperscript{3-5} pyrocatalytic materials,\textsuperscript{6} and materials affecting cell proliferation.\textsuperscript{7} The surface charge generated by the pyroelectric effect during a temperature change might postpone the freezing of water droplets on technical surfaces. This would be beneficial in order to save costs and energy in applications such as for wind turbines and heat exchangers. P(VDF-TrFE) is a semicrystalline thermoplastic random copolymer comprised of vinylidene fluoride and trifluoroethylene monomers.

Abbreviations: AFM, atomic force microscopy; CH, cyclohexanone; DC, dip-coating; DSC, differential scanning calorimetry; EDL, electrochemical double layer; IQR, interquartile range; IRRAS, grasing incidence infrared reflection absorption spectroscopy; MEK, butan-2-one; n, number of independent droplets; PMMA, polymethylmethacrylate; P(VDF-TrFE), poly(vinylidene fluoride-co-trifluoroethylene); $P_s$, spontaneous polarisation; p, pyroelectric coefficient; $R_a$, arithmetic average of the roughness profile; SC, spin-coating; T, temperature; $T_c$, Curie temperature; $T_m$, melting temperature; THF, tetrahydrofuran; 2D-GIWAXS, two-dimensional grasing incidence wide angle X-ray spectroscopy.

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trifluoroethylene units that spontaneously crystallize in its ferroelectric and, therefore, pyroelectric phase for a TrFE content of between 0.18 ≤ x ≤ 0.45. The positively charged hydrogen and negatively charged fluorine atoms form molecular dipoles with two possible but opposing alignment directions when the material is below its Curie temperature $T_c$. The Curie temperature $T_c$ marks the transition between the ferroelectric phase of P(VDF-TrFE) at lower temperatures and the paraelectric phase at higher temperatures. Cooling a ferroelectric material below its Curie temperature results in a randomly oriented multidomain state. A poling treatment is required in order to align the direction of the spontaneous polarisation of the domains perpendicular to the substrate surface to achieve positively or negatively polarised surfaces during $\Delta T$. The poling treatment orients the dipoles according to the direction of an externally applied electric field when the field strength is above the material-specific coercive field. The pyroelectric effect, inherent to all ferroelectric materials, is defined as the change of the spontaneous polarisation $\Delta P_s$ due to a change in temperature $\Delta T$ multiplied by a factor called the pyroelectric coefficient $p$ according to Equation (1).

$$\Delta P_s = p \cdot \Delta T.$$  

Highly crystalline P(VDF-TrFE) has a pyroelectric coefficient of -31 μC m$^{-2}$ K$^{-1}$ at room temperature. Ideal pyroelectric behaviour of thin P(VDF-TrFE) films is only achieved when the polymer chains are oriented parallel to the underlying substrate, the so-called edge-on orientation (Figure 2). Since the molecular dipoles are oriented approximately perpendicular to the polymer chain, the edge-on orientation will result in the highest possible surface charge during $\Delta T$.

The freezing of water to ice $I_h$ occurs, due to supercooling, below the thermodynamic phase transition temperature of 0 °C. Without any foreign surfaces or vibrations, a supercooling of -37 °C is possible before the water freezes spontaneously (homogeneous nucleation). The achievable supercooling of water droplets in contact with a foreign surface is usually smaller (heterogeneous nucleation).

There are ongoing discussions as to what extent certain parameters affect the freezing temperatures of water in contact to different surfaces and how to design efficient anti-ice coatings. Furthermore, most studies focus only on a single parameter and not on the effect size of different parameters. Parameters with a small effect on the achievable supercooling might be masked by parameters that strongly affect the freezing temperature distribution. The goal of this study is to quantify the effect of different film parameters on the achievable supercooling of water droplets on top of P(VDF-TrFE) thin films, such as the poling direction, film thickness, solvent used during the deposition process and underlying substrate.

2 | MATERIALS AND METHODS

2.1 | Materials

Granules of P(VDF-TrFE) with a ratio of 70:30 of the co-monomers (Solvane Powder from Solvay) and 99.9 wt% pure tetrahydrofuran (THF), butan-2-one (MEK) or cyclohexanone (CH) (Fisher Scientific) were used to prepare spin- and dip-coating solutions with polymer concentrations of between 0.1 and 10 wt%. The Curie temperature $T_c$ = 108.5 °C and melting temperature $T_m$ = 143.8 °C of the granules was determined by differential scanning calorimetry (DSC) using a DSC Q 2000. The majority of the freezing experiments were done on P(VDF-TrFE) thin films that were deposited on Silicon substrates (Silicon Materials µ/Bor, polished) after a cleaning step with oxygen plasma and ultrasonic cleaning three times in ethanol for 10 min each time. For the purpose of comparison, thin P(VDF-TrFE) films were deposited on stainless steel and aluminium sheets polished with 1 µm diamond paste as well as microscope glass slides and sand-blasted titanium samples.

2.2 | Thin film fabrication and characterization

For the spin-coating a spin-coater (PoloSpin150i), a maximum spin speed of 2500 r min$^{-1}$ and acceleration of 1000 r min$^{-1}$ s$^{-1}$ for 10 s was used. A withdrawing speed of 1.2 mm s$^{-1}$ was used for the dip-coated samples. The polymer film thickness varied from 5 to 500 nm as a function of the concentration and parameters of the deposition processes and was measured on Si substrates with an ellipsometer SE 402. The coating procedure was directly followed by an annealing step for 1 h in a cabinet dryer under slight vacuum using different temperatures below and above the Curie $T_c$, and melting temperature $T_m$. The crystallinity index and orientation of the polymer chains inside the thin films was estimated by 2D gracing incidence wide-angle X-ray spectroscopy (2D-GIWAXS) and gracing incidence infrared reflec-
tion absorption spectroscopy (IRRAS) with an incidence angle of 80°. Surface morphology images and phase images were recorded simultaneously with an atomic force microscope (AFM) Dimension 3100 nanoScope IIIa and V, and the roughness $R_a$ was determined using the images with a 10 $\mu$m edge length. Poling experiments were performed with a voltage of 5 kV or -5 kV on P(VDF-TrFE) thin films deposited on Al substrates and placed inside a capacitor setup with a small air gap between the surface of the thin film and the counter electrode to prevent possible damage of the films. The poling was done inside the cabinet dryer whilst the samples cooled down from an annealing step at 140 °C in order to ease the polarisation.

2.3 | Freezing experiments

For the freezing experiments, a LINKAM LTS 350 cooling chamber with LINKAM TMS 94 and LINKAM LNP subunits were used. The P(VDF-TrFE)-coated specimen were placed directly on top of the cooling stage inside the chamber and one to three drops of 10 $\mu$l deionized water were deposited on the sample surface using a METTLER TOLEDO pipette. A thermocouple was placed inside an additional droplet of water on the specimen to record the temperature close to the solid-liquid interface. The distance in between the droplets, and between the droplets and the samples edge, was at least one droplet diameter. The specimen inside the closed LINKAM chamber was cooled to 5 °C and held for 10 min before the experiment started. The chamber was then cooled with 1 K min$^{-1}$ to at least -25 °C, and the temperature shown from the thermocouple was noted when each of the three measurement droplets changed completely from transparent to opaque, signalling the occurrence of the freezing event. The experiment was repeated five times with the same set of droplets and the freezing temperatures of each droplet were averaged.

The graphs in the result section show experiments on comparable samples where only one parameter was varied at a time with the others remaining the same. The distribution of the averaged freezing values of independent droplets is shown as box plots where the box encloses the upper and lower quartiles and is horizontally divided at the median value. The upper and lower whiskers mark the highest and lowest of the averaged freezing temperatures within a distance of 1.5 times the interquartile range (IQR) from the box boundaries. Values above or below these are classified as outlier. The arithmetic mean of the averaged freezing temperatures is marked with a diamond.

Statistical tests were performed on the averaged values of the freezing temperatures in order to decide whether a parameter has a significant influence on the distribution of the achievable supercooling on the P(VDF-TrFE) films or not. The Anderson-Darling normality test was used to evaluate the probability for a normal distribution of the samples of averaged freezing temperatures on each surface. A probability of 0% was frequently found for the samples and therefore nonparametric rank sum tests were used to test the null hypothesis $H_0$ (all freezing temperatures are from the same statistical population, and the parameter does therefore not affect the freezing behaviour). For the comparison of only two treatments, the Mann-Whitney U-Test, and for the comparison of three to five different treatments, the Kruskal-Wallis H-Test were used. The number of averaged freezing values for each test as well as the resulting p values are noted inside each graph. Significant effects are marked with * for $p<0.05$, ** for $p<0.01$, and *** for $p<0.001$, according to their significance level $\alpha$.

3 | RESULTS AND DISCUSSION

Heterogeneous freezing experiments were performed for a variety of different parameters of the P(VDF-TrFE) thin films. It was confirmed in preliminary tests with 2D-GIWAXS and IRRAS that the annealing temperature affects the orientation of the polymer chains inside the P(VDF-TrFE) thin film. Both solvent-based deposition processes result in an edge-on orientation of the polymer chains (Figure 2) and high

**FIGURE 2** Poly(vinylidene fluoride-co-trifluoroethylene) (P(VDF-TrFE)) thin films with the orientation of the polymer chains in parallel to the substrate surface (edge-on) are preferential for pyroelectric applications compared to thin films with the polymer chains oriented perpendicularly to the substrate (face-on).
crystallinity of the P(VDF-TrFE) films. Both properties are slightly enhanced during an annealing step below $T_c = 108.5 \degree C$ and greatly enhanced after annealing the films at temperatures between the Curie temperature $T_c$ and the melting temperature $T_m = 143.8 \degree C$. The edge-on orientation is preferred for a good polarisability of the pyroelectric polymer, but this orientation is lost after an annealing above the melting temperature. Figure 3a shows that no difference in freezing temperatures was found between the two edge-on oriented samples (annealed at 70 °C and 130 °C), but the water droplets on the samples annealed above $T_m$ froze at significantly higher temperatures (the median temperature is 1.5 K higher). It is therefore assumed that the freezing temperature is either affected by the polymer chain orientation or by the change in surface roughness accompanying the annealing. The roughness changes from $R_a(70 \degree C) = 0.62 \text{ nm}$ to $R_a(130 \degree C) = 1.45 \text{ nm}$ and increases significantly to $R_a(150 \degree C) = 9.85 \text{ nm}$ (Figure 3bc). The recrystallisation after cooling the polymer from the melt state might create a topography that provides nucleation sites preferable for viable ice nuclei.
Performing repetitive freezing experiments on the same sample results in higher median freezing temperatures as a function of the run number (a more than 0.5 K higher median temperature after each run, see Figure 4a). The samples were blown dry in between the experiments before a fresh droplet of deionized water was deposited. Possible explanations for the deteriorated anti-ice performance are the swelling of the polymer film when in contact with water or the deposition of dust particles or other contamination during the handling in air that provide additional nucleation sites themselves. Another parameter that was identified during the experiments to significantly affect the freezing temperature is the substrate beneath the P(VDF-TrFE) film during dip-coating (the median temperature on P(VDF-TrFE) on glass is more than 3 K higher than the median temperature on P(VDF-TrFE) on Al, see Figure 4b). The different surface energy and roughness of the substrates might result in a different wetting behaviour during the dip-coating process, since the P(VDF-TrFE) films for this part of the experiment had a film thickness well below 100 nm. Partial de-wetting might result in additional three-phase boundaries between the polymer, water, and substrate material and might provide additional nucleation sites with a varying probability for heterogeneous nucleation. Microscopy images of de-wetted glass surfaces can be seen in Spitzner et al.

The solvent used during the deposition process was found to not significantly influence the film properties in such a way that the freezing behaviour of water on these films (Figure 4c) is affected, when P(VDF-TrFE) is dip-coated on polished Al substrates to the same thickness of about 150 nm. The deposition process was also found to not significantly influence the heterogeneous freezing, shown here for 130 nm films spin- and dip-coated from solutions of P(VDF-TrFE) in THF onto polished steel substrates (Figure 4d). High-quality P(VDF-TrFE) films with smooth surfaces were achieved by dip- and spin-coating in a broad thickness range. Changing the thickness of the polymer film was found to not influence the heterogeneous freezing of water significantly (Figure 4e). However, films well below 100 nm and well above 1 μm thickness resulted in a broader distribution of the freezing temperatures.

In contrast to the results from Ehre et al.1 and Spitzner et al.4 the polarisation direction and, therefore, the sign of the surface charge generated during the cooling process has no significant effect on the heterogeneous freezing (Figure 4f). Neither a significant difference between a positive and negative polarised pyroelectric film nor between a polarised and nonpolarised film was found in our experiments. A possible explanation could be that the coercive field required to completely align the dipoles of the spontaneous polarisation perpendicular to the substrate was not reached inside the P(VDF-TrFE) film during the polarisation treatment. The result would be an imperfect domain-state in contrast to the single domain thick-films used by Ehre et al.1 However, the results might as well be caused by the negligible effect of the pyroelectrically generated surface charges on the heterogeneous freezing process when a successful polarisation is assumed. The maximum temperature change during the cooling process is ΔT=20 K, resulting in a change of the spontaneous polarisation according to the equation for the pyroelectric effect (Equation (1)) of the following:

\[ \Delta P = \Delta T \cdot p = 20 \, K \cdot 31 \, \mu C \cdot m^{-2} \cdot K^{-1} = -620 \, \mu C \cdot m^{-2} = -0.062 \, \mu C \cdot cm^{-2}. \] (2)

It is expected that the value of the surface charge actually generated during the cooling is less, since the pyroelectric coefficient of P(VDF-TrFE) decreases strongly with decreasing temperature below Tc. In contrast, the surface charge built up on common surfaces such as metal oxides and minerals in contact with low molarity electrolytes is typically between 1 and 20 μC·cm⁻² and therefore many orders of magnitude higher. It is therefore assumed that any effect of pyroelectric generated surface charges might be usually masked by parameters that were found to much stronger affect the distribution of freezing temperatures on solid substrates, such as the topography/roughness and possible contamination.

4 CONCLUSIONS

We were able to successfully quantify the effect of different parameters of P(VDF-TrFE) thin films on the achievable supercooling of water droplets in contact with these surfaces. The loss of the preferred edge-on orientation after annealing above the melting temperature Tm results in a higher freezing temperature of water droplets compared to the edge-on oriented films. Higher freezing temperatures are also found for repetitive runs of the freezing experiments on the same samples. The strongest effect was seen by using different substrates beneath the P(VDF-TrFE) thin films that can result in a more than 3 K higher median freezing temperature, possibly caused by a de-wetting effect that has occurred during the dip-coating process. In summary, the highest supercooling of water droplets in contact with P(VDF-TrFE) thin films and therefore best anti-ice performance is achieved on clean and edge-on-oriented P(VDF-TrFE) films with a low surface roughness deposited on Al or Si substrates. The polarisation direction of the as-prepared domain state of the pyroelectric polymer was not able to significantly change the median freezing temperatures in our experiments. This contradicts the results found in the literature where negatively charged pyroelectric materials were able to postpone the heterogeneous freezing of water. The film thickness and the deposition process were additionally shown to have no significant effect on the freezing behaviour of water on thin P(VDF-TrFE) films. The occurrence of topographic structures that promote the formation of viable ice nuclei have been suggested to be the main parameter affecting the heterogeneous freezing of water on foreign surfaces.

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FINANCIAL DISCLOSURE

None reported.

CONFLICT OF INTERESTS

The authors declare no potential conflict of interests.

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