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New insight into icing and de-icing properties of hydrophobic and hydrophilic structured surfaces based on core-shell particles†

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Icing is an important problem, which often leads to emergency situations in northern countries. The reduction of icing requires a detailed understanding of this process. In this work, we report on a systematic investigation of the effects of geometry and chemical properties of surfaces on the formation of an ice layer, its properties, and thawing. We compare in detail icing and ice thawing on flat and rough hydrophilic and hydrophobic surfaces. We also show advantages and disadvantages of the surfaces of each kind. We demonstrate that water condenses in a liquid form, leading to the formation of a thin continuous water layer on a hydrophilic surface. Meanwhile, separated rounded water droplets are formed on hydrophobic surfaces. As a result of slower heat exchange, the freezing of rounded water droplets on a hydrophobic surface occurs later than the freezing of the continuous water layer on a hydrophilic one. Moreover, growth of ice on hydrophobic surfaces is slower than on the hydrophilic ones, because ice grows due to the condensation of water vapor on already formed ice crystals, and not due to the condensation on the polymer surface. Rough hydrophobic surfaces also demonstrate a very low ice adhesion value, which is because of the reduced contact area with ice. The main disadvantage of hydrophobic and superhydrophobic surfaces is the pinning of water droplets on them after thawing. Flat hydrophilic poly(ethylene glycol)-modified surfaces also exhibit very low ice adhesion, which is due to the very low freezing point of the water-poly(ethylene glycol) mixtures. Water easily leaves from flat hydrophilic poly(ethylene glycol)-modified surfaces, and they quickly become dry. However, the ice growth rate on poly(ethylene glycol)-modified hydrophilic surfaces is the highest. These results indicate that neither purely (super)hydrophobic polymeric surfaces, nor "antifreeze" hydrophilic ones provide an ideal solution to the problem of icing.

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1. Introduction

The future development towards a sustainable society requires, among others, new solutions of environmental and energetic problems. Thus, the exploitation of environmentally friendly alternative energy sources like wind and solar energy is highly favourable. Icing of rotor blades in the wind turbines, however, limits the use of wind as an energy source. Icing is also a major problem in other fields, such as transport (aircrafts, cars), and energy supply (high-voltage power lines, air conditioning), where it causes increased energy consumption and failure. The most favourable solution of the icing problem is the design of passive polymeric or polymeric/hybrid anti-icing coatings, *i.e.* coatings

which prevent icing and do not require power consumption.^{1,2} Such surfaces are typically based on the reduction of ice adhesion, or inhibition of the ice growth.

Reduced ice adhesion can be achieved by the design of hydrophobic³ and superhydrophobic surfaces,^{4–12} or the use of hydrophobic lubricants.¹³ In the first case (hydrophobic and superhydrophobic surfaces), the contact area between the surface and the ice is simply reduced.^{14–16} Ice adhesion is also low when hydrophobic lubricants are deposited on surfaces. Thus, ice can be easily removed.^{7,13,17,18} Reduced ice growth can be achieved in two ways. The first way is to use the colligative properties of solutions.^{19,20} For example, hydrophilic polymers reduce the freezing point of water, and ice crystals can simply slide off due to the presence of an unfrozen water layer.²¹ The second way is to use antifreeze proteins, which kinetically decrease the ice crystal formation rate.²²

In fact, an efficient development of passive anti-icing coatings requires deep understanding of the interactions of the surfaces with ice: its nucleation, growth, adhesion, and thawing. A detailed investigation of the synergistic effects of chemical and

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mechanical properties as well as the geometry/topography of structured surfaces is necessary in order to address these questions. Since icing is related to the wetting of surfaces, investigation of the water contact angle dependence on temperature is important.²³ It was found that the adhesion of ice to superhydrophobic surfaces may be large¹⁶ or small, depending on the surface roughness.²⁴ The second important phenomenon is ice nucleation. It was found that the ice nucleation rate on an unmodified hydrophilic silicon wafer surface is about 1 order of magnitude lower than that on the hydrophobic surface at the same temperature.²⁵ Freezing time increases with the increasing contact angle on hydrophobic surfaces,^{15,26} and decreases with the increasing roughness on hydrophilic surfaces.²⁶

Thus, surface topography and hydrophobicity/hydrophilicity play a crucial role in the icing process. On the other hand, the structure of such surfaces is typically irregular^{10,14,15,24,26} which makes the comparison of different kinds of rough surfaces difficult. Herein, we report on the design and systematic investigation of the effects of the geometry/topography and chemical properties of surfaces on the formation of an ice layer, its growth, adhesion, as well as thawing. In particular, we prepared robust well-defined chemically and topographically structured surfaces using colloidal particles of different sizes and designs (spherical and raspberry-like ones). The advantage of such systems is that roughness parameters are defined by the size of the particles, and can easily be predicted. Moreover, particles are usually used in industrial coatings as additives and fillers, which makes the investigation of icing on surfaces based on colloidal particles of high practical importance.

2. Experimental section

Materials and methods

Highly polished single-crystal silicon wafers of (110) orientation (Semiconductor Processing Co.) were used as substrates. Ethanol abs. (EtOH, VWR, 99.9%), 3-aminopropyltriethoxysilane (APS, ABCR, 97%), hydrogen peroxide (VWR, 30%), ammonia hydroxide (Acros Organics, 28–30 wt%), α -bromoisobutyl bromide (Aldrich, 98%), ethyl- α -bromoisobutyrate (EBiB, Aldrich, 98%), anhydrous dichloromethane (Fluka), triethylamine (Fluka), copper(II) bromide (Aldrich, 99.999%), tin(II) 2-ethylhexanoate (Aldrich, 95%), N,N,N',N'',N''' -pentamethyldiethylenetriamine (PMDTA, Aldrich, 99%), N,N -dimethylformamide (DMF, Aldrich, 99.8%), toluene

(Aldrich, 99.8%), chloroform (Aldrich, 99.8%), anisole (Aldrich, 99%), L-ascorbic acid (Aldrich), and poly(glycidyl methacrylate) (PGMA, M_n : 48 000, Polymer Source) were used as received. Poly(ethylene glycol)methyl ether methacrylate (M_n = 500 g mol⁻¹, PEGMA, Aldrich), styrene (Aldrich), and monomethacryloxypropyl-terminated PDMSMA (asymmetric 6–9 cSt PDMS, Gelest) were filtered prior to polymerization through acidic, neutral, and basic aluminum oxides. Millipore water was obtained from Milli-Q (Millipore). Conductivity: 0.055 μ S cm⁻¹.

Modification of surfaces and preparation of coatings

Polymer brushes were synthesized on flat and particle-based surfaces using surface-initiated ATRP as described in ref. 27. The particle layers were prepared using a solvent casting method,²⁸ and a floating technique.²⁹ Briefly, for solvent casting we took a 10 wt% dispersion of polymer-modified particles and dried it on the surface of a PGMA-coated wafer. We deposited particles on a Si wafer tilted to 45° when the floating technique was used, which lead to the formation of a well-ordered particle layer. The particle layer was eventually on a PGMA coated wafer. Afterwards, the prepared rough surfaces were annealed at 150 °C in a vacuum oven for 2 h. Finally, the samples were immersed in an ultrasonic bath in the same solvent for several seconds to remove weakly-attached particles. The quality of the prepared particle-covered substrates was checked by SEM and AFM measurements. A list of samples tested in this paper is given in Table 1.

Ellipsometry

The thickness of polymer layers on wafers in the dry state was measured at λ = 632.8 nm and a 70° angle of incidence using a null-ellipsometer (Multiscop, Optrel Berlin, Germany) in a polarizer-compensator-sample-analyzer configuration as described elsewhere.^{30,31}

Thermogravimetric analysis (TGA)

Thermogravimetric analysis was performed to measure the thickness of the polymer layer on the particle surface. All these measurements have been conducted in an air atmosphere using a TGAQ5000IR device (TA Instruments Co). The thickness of the grafted layer was determined using the following equation:

$$H_{\text{POL}} = \frac{1}{S_{\text{BET}} \cdot \rho_{\text{POL}}} \frac{m_{\text{POL}} - m_{\text{BrIn}}}{100\% - m_{\text{POL}}} \quad (1)$$

Table 1 List of samples

Sample	Designation
Flat P(PEGMA)	F-P(PEGMA)
Flat P(PDMSMA)	F-P(PDMSMA)
Flat PLMA	F-PLMA
Flat PS	F-PS
Particles 1000 nm	R-1000-P(PEGMA), R-1000-P(PDMSMA), R-1000-PLMA, R-1000-PS
Particles 200 nm	R-200-P(PEGMA), R-200-P(PDMSMA), R-200-PLMA, R-200-PS
Particles 20 nm	R-20-P(PDMSMA)
Inverse, 1000 nm	Inv-1000-PS
Inverse, 200 nm	Inv-200-PS
Raspberry-like, 200 nm on 1000 nm	Rsp-1000/200-P(PDMSMA)
Raspberry-like, 100 nm on 1000 nm	Rsp-1000/100-P(PDMSMA)

where S_{BET} is the surface area of silica particles, ρ_{SiO_2} and ρ_{POL} are the mass densities of particles and polymers, respectively (either PS, P(PDMSMA), PLMA, or P(PEGMA)), and m_{BrIn} and m_{POL} are the mass loss values in the TGA experiments for the particles before and after polymer grafting on the particle surface, respectively. The reliability of the polymer shell thickness estimation using TGA was proved in our previous paper.³²

Topographic characterization of surface coatings

The topography of surfaces was recorded by using a scanning electron microscope (SEM), an atomic force microscope (AFM), and the optical imaging device Nano focus (Fries Research & Technology GmbH, Bergisch Gladbach, Germany).

Scanning electron microscopy (SEM, cryo-SEM)

All scanning electron microscopy (SEM) images were acquired using a NEON 40 EsBv Crossbeam scanning electron microscope (Carl Zeiss NTS GmbH), operating at 3 keV in the secondary electron (SE) mode. To enhance the electron density contrast, samples were coated with platinum (3.5 nm) using a Leica EM SCD500 sputter coater.

Cryo-SEM

The following procedure was implemented for the preparation of samples for cryo-SEM imaging. First, the wafer with an anti-ice coating was cooled down in liquid nitrogen and was then brought under ambient conditions. As a result, a layer of ice was formed on the surface of the wafer. The ice eventually melted and formed water droplets on the surface. The wafer was then quickly immersed in liquid nitrogen and transferred to the Leica EM SCD500 sputter coater, where it was coated with platinum for 30 seconds at $-130\text{ }^{\circ}\text{C}$ (estimated thickness of the platinum layer – 3.5–4.0 nm). The Leica EM VCT100 vacuum cryo-transfer system was used to load the sample in the SEM. Imaging was performed at $-135\text{ }^{\circ}\text{C}$ at 0° and 45° tilt angles.

Atomic force microscopy (AFM)

AFM studies were performed in the dry state by using a Dimension 3100 (Veeco Instruments, USA) microscope. All the images were taken in the tapping mode with a silicon tapping mode tip (resonance frequency 200–400 kHz, and spring constant of $1.5\text{--}6.3\text{ N m}^{-1}$). Imaging was conducted at scanning rates in the range of 1–2 Hz. The root mean square roughness (R_q) values were calculated from topography images ($10 \times 10\text{ }\mu\text{m}^2$) with the help of WSXM software.

The roughness characteristics were also obtained from Nano focus images ($160 \times 160\text{ }\mu\text{m}^2$). The resolution of these images was 512×512 lines. Arithmetical roughness (R_a), root mean square roughness (R_q), roughness factor (RF), as well as fractal dimension (FD) were calculated from Nano focus data. We applied the box counting method (FRT Mark III software) to the cross section of the investigated films to find the fractal dimension of the prepared coatings.

Contact angle measurements

The contact angles (advancing, receding) of DI water were measured using the sessile drop method and a conventional drop shape analysis technique (Krüss DSA 10, Hamburg, Germany). $10\text{ }\mu\text{L}$ water droplets were dropped gradually onto the surface, and the average values of advancing and receding contact angles were measured at five different places on each sample. Sliding water contact angles were measured with different droplet volumes: $5\text{ }\mu\text{L}$, $10\text{ }\mu\text{L}$, and $20\text{ }\mu\text{L}$. All measurements were carried out at $24\text{ }^{\circ}\text{C}$ and a relative humidity of $40 \pm 3\%$, which were kept constant.

Icing and thawing tests

The measurements were performed in a special chamber (LHU-113, ESPEC, Japan) with controlled temperature and humidity (Fig. S1, ESI†). Temperature in the chamber could be controlled in the range between $+50\text{ }^{\circ}\text{C}$ and $-20\text{ }^{\circ}\text{C}$ (with $\pm 0.5\text{ }^{\circ}\text{C}$ accuracy), and humidity could be controlled in the range between 30% and 90% RH (with $\pm 2\%$ accuracy). Samples were mounted on a flat copper plate by using thermally conductive double sided copper tape. The temperature of the copper plate was maintained by using a Peltier element with a thermoelectric temperature controller (TC/TPC 150, Data Physics, Germany), and a cooling thermostat (Alpha RA 8, Lauda, Germany). For all the experiments humidity of the chamber was accurately maintained at a constant relative humidity (RH) of 80%, while the temperature was gradually decreased from $+15\text{ }^{\circ}\text{C}$ to $-15\text{ }^{\circ}\text{C}$ with a cooling rate of $2\text{ }^{\circ}\text{C min}^{-1}$. After cooling to $-15\text{ }^{\circ}\text{C}$, the temperature was kept constant for 20 min. Finally, the samples were heated to $+15\text{ }^{\circ}\text{C}$. We recorded the whole process of the freezing and melting of ice with the help of a digital camera (DMC-TZ31, Panasonic). All the samples (fabricated on $2\text{ cm} \times 1\text{ cm}$ silicon wafers) were mounted vertically at a 90° tilt angle on the cooling plate.

Kinetics of ice growth

The experiments were carried out by taking seven identical samples ($2\text{ cm} \times 1\text{ cm}$) from each set, and mounting them horizontally onto the cooling plate within the temperature and humidity controlled chamber. Kinetics of ice formation on different surfaces was measured at $-2\text{ }^{\circ}\text{C}$ under high humidity conditions (80% RH) by measuring the weight of the surfaces after certain time intervals. The weight difference of the samples before and after frost formation corresponds to the amount of ice formed with time. After the removal of each sample, five minute stabilization time was required to maintain the appropriate conditions for testing.

Ice adhesion strength measurements

Ice adhesion measurements were performed in the temperature and humidity controlled chamber; the temperature of the chamber was maintained at $-10\text{ }^{\circ}\text{C}$. A cylindrical ice column was prepared on the sample surface by using a hydrophobic syringe, which was filled with fresh deionized water (Milipore, Milli-Q). The diameter of the ice cylinder on the substrate was 16 mm, and its weight was approximately 1.4 g. Ice cylinders

were kept inside the chamber for 16 h at $-10\text{ }^{\circ}\text{C}$, then they were mounted on a beam inside a home-made centrifuge apparatus (Fig. S2, ESI†). Counterweight with a reference sample was always used at the opposite end of the beam to balance the weight during spinning. The samples were spun inside the centrifuge situated in the chamber at $-10\text{ }^{\circ}\text{C}$ to determine the rotational speed at which the detachment of the ice cylinder occurred. The time at which the ice cylinder was detached from the surface was detected by a sound from the microphone sensor, which was ingrained into the centrifuge setup. The ice adhesion force of the sample surfaces was presumed to be equivalent to the centrifugal force, $F = m\omega^2 r$, where m is the mass of the ice cylinder, ω is the rotational speed, and r is the radius of the centrifuge beam. Subsequently, the ice adhesion strength, which is a shear stress, was calculated using the equation $\tau = F/A$, where $A = (\pi d^2)/4$ is the contact area of the ice cylinder on the substrate, and d is the diameter of the ice cylinder.

3. Results

In this work, we prepared surfaces with different topographies and geometries using particles of different sizes (1000, 200, and 20 nm), shapes (spherical and raspberry-like ones), and grafted polymers. In particular, polymers with different hydrophobicities/hydrophilicities, such as polystyrene (PS), poly(polydimethylsiloxane methacrylate) (P(PDMSMA)), poly(lauryl methacrylate) (PLMA), and poly(polyethylene glycol methacrylate) (P(PEGMA)) were grafted on the surface of the particles. From the point of view of the water contact angle values, PS is on the edge between hydrophobic and hydrophilic substances (both advancing and receding contact angles on a flat PS surface are *ca.* 90°). On the contrary, P(PDMSMA) and PLMA are highly hydrophobic polymers (advancing and receding contact angles on flat P(PDMSMA), and PLMA surfaces are *ca.* 110°). P(PEGMA) is a highly hydrophilic swellable polymer (advancing contact angle on a flat P(PEGMA) surface is *ca.* 30°), and its mixtures with water have very low freezing points (Fig. S3, ESI†). The polymers were grafted onto the particles using a previously reported approach based on ATRP.³³

We fabricated three kinds of rough structured surfaces with a well-defined geometry using colloidal particles (Table 1).

Fig. 1 Schemes and representative illustrations of different kinds of rough surface morphologies prepared using colloidal particles: (a) – regular array of spherical particles; (b) inverse structures (inset is a side view); (c) raspberry-like particles formed by immobilization of small particles on large ones. More representative SEM and AFM images of surfaces based on particles of different sizes are presented in the ESI,† Fig. S4–S6.

Table 2 Theoretically estimated and measured roughness parameters of layers prepared from spherical particles and inverse structures

Surface	R_q , nm		r_s	
	Estimated	Measured	Estimated	Measured
Particles 1000 nm	270	120	1.9	1.3–1.4
Particles 200 nm	54	30	1.9	1.2
Particles 20 nm	5.4	600	1.9	1.6
Inverse, 1000 nm	150	300	1.9	1.7
Inverse, 200 nm	30	89	1.9	1.3

Rough surfaces of the first kind are layers of spherical polymer-modified particles with the sizes of 20 nm, 200 nm, and 1000 nm (Fig. 1a and Fig. S4, ESI†). These surfaces were prepared by simple drying of particle dispersions on a silica wafer coated by a thick layer of poly(glycidyl methacrylate), which served as an adhesion promoter and prevented disintegration of the particle layers in tests. We observed that 1000 nm large particles tend to form more ordered layers than 200 nm large particles (Fig. S4, ESI†). The smallest particles (20 nm) form very rough layers, in which particles are unordered. The second kind of rough surfaces are inverse films (Fig. 1b). Such surfaces were prepared using ordered arrays of spherical particles on silica wafers as templates. The interstices between the particles were filled with a polymer, and finally the particles were removed by etching with a HF solution. Surfaces of the third sort are the ones made from raspberry-like particles,³⁴ which are obtained by chemical immobilization of small particles on the surface of larger ones (Fig. 1c). The surfaces of all particles were chemically modified by grafted polymer chains: PS, P(PDMSMA), PLMA, or P(PEGMA).

Such three kinds of surfaces are model surfaces since their roughness parameters as well as their wetting properties can be estimated on the basis of their geometry. In particular, surfaces made from spherical particles, and inverse surfaces possess the same roughness factor $r_s = 1.9$ (ratio between the real surface area and the projected one), which is independent of the particle diameter. The RMS roughness of the layers of well-ordered particles is $R_q = 0.54R$.³⁵ The RMS roughness of inverse structures, which was estimated in a similar way, is $R_q = 0.3R$ (R is the particle radius). The values of roughness obtained from AFM measurements (Table 2) are always lower than the estimated ones because of the specific resolution of AFM, which is limited by the shape of the tip.

The roughness factor of the surfaces prepared using raspberry-like particles is $r_s = 1.9$.³⁶ Prediction of the RMS roughness of surfaces with raspberry-like particles is very difficult.

Wettability of surfaces

Next, we investigated the wetting properties of the prepared flat and rough structured surfaces. We found that the advancing contact angle on a rough particle-PS-modified surface is *ca.* 130° , and the receding one is in the range of $60\text{--}90^{\circ}$ (Fig. 2a). The receding contact angles on surfaces with inverse patterns are slightly higher than on surfaces formed by particles. In fact, PS is not a truly hydrophobic polymer ($\cos \theta = 0$), and, according to the equation of Wenzel and Cassie–Baxter,^{37,38} the

Fig. 2 Wetting properties (a – advancing and receding contact angles, b – sliding angle) of P(PDMSMA), PLMA, PS and P(PEGMA)-modified flat and rough structured surfaces.

contact angle on a PS surface must be independent of roughness. The experimentally observed deviations from the predictions were already reported in our previous work, and their origin is a deviation of the contact angle from the equilibrium state.³⁶ Wetting of P(PDMSMA)-based and PLMA-based surfaces differs from the wetting of PS-based ones. On a P(PDMSMA) surface made from 1 μm, or 200 nm large particles both water advancing and receding angles are generally higher than those on PS. We also observed that some P(PDMSMA)-based surfaces (surfaces made from 20 nm particles, as well as raspberry-like ones) are really superhydrophobic, where both advancing and receding contact angles are greater than 150°. In fact, superhydrophobic behaviour of surfaces made from raspberry-like particles is known, and is present due to the hierarchical structure of the surface.³¹ Superhydrophobic behaviour of surfaces formed by 20 nm large particles can be explained by the tendency of particles to spontaneously form aggregates, which have structures similar to raspberry-like particles.³⁹

All P(PEGMA)-based flat and rough surfaces are very hydrophilic with low advancing and receding contact angles. Thus, based on the values of advancing and receding water contact angles, we can summarize that hydrophobicity of the surfaces decreases in the sequence: P(PDMSMA)-based irregular (20 nm, raspberry-like) > regular rough P(PDMSMA), and PLMA (1000 nm and 200 nm) > PS all > P(PEGMA) all.

We also assessed the wetting properties by measuring the values of sliding angles of water droplets of different sizes: 5 μl, 10 μl, and 20 μl (Fig. 2b). We observed that the values of sliding angles on all PS surfaces (flat and rough), P(PDMSMA)-based flat ones, and the ones prepared using 200 nm, and 1000 nm particles are high (> 40°), which indicates a high water adhesion. On the contrary, the values of sliding angles on irregular P(PDMSMA) surfaces based on 20 nm large particles, as well as

on the ones made of raspberry-like particles, are very low (< 2°). This means that water adhesion to these surfaces is low, and water droplets slide off easily. The sliding of water droplets on P(PEGMA) surfaces could not be measured due to their high hydrophilicity, as well as strong water spreading and penetration. Thus, the values of sliding angles confirm that hydrophobicity of the surfaces decreases in the sequence: P(PDMSMA)-based irregular (20 nm, raspberry-like) > regular rough P(PDMSMA), and PLMA (1000 nm and 200 nm) > PS all > P(PEGMA) all.

Formation of ice

Next, we investigated the formation of ice (Fig. 3). A gradual decrease in the temperature of the Peltier element, on which the samples were mounted, results in an increase in the relative humidity around it, and water droplets start to condense on

Fig. 3 Formation of ice layers. Optical microscopy images (a, b, d and e) of water droplet condensation and their freezing on flat (a and d) and rough (b and e) hydrophilic P(PEGMA) (a and b) as well as hydrophobic PLMA (d and e) surfaces. Cryo-SEM images (c and f) of frozen water droplets on surfaces formed by 1000 nm large particles modified by P(PEGMA) (c) and PLMA (f) with different magnifications. Kinetics of ice growth (g – change of ice weight with time, h – ice growth rate measured during first 500 s of freezing) of P(PDMSMA), PLMA, PS and P(PEGMA)-modified flat and rough structured surfaces.

the surfaces. The type of condensation depends, however, on the properties of the surface. We did not observe individual droplets on the P(PEGMA) surface, but rather a thin continuous water layer, which immediately gets frozen in a few seconds (Fig. 3a). Rough P(PEGMA) surfaces demonstrated a similar behaviour (Fig. 3b). Compact water droplets were observed on flat and rough hydrophobic PLMA, P(PDMSMA), and PS surfaces (Fig. 3d and e). We found that these droplets are initially small (2–3 μm), then they grow, and meanwhile new droplets are formed due to water condensation. At some point we did not observe the formation of new water droplets, but only the growth and merging of the existing ones. Further cooling led to freezing of the droplets. Notably, freezing of water droplets on hydrophobic surfaces occurred much later (*ca.* 1–2 min) than on hydrophilic P(PEGMA)-modified ones, and the freezing on the rough surfaces occurred later than on the flat ones, which correlates nicely with previous observations of Boinovich *et al.*⁴⁰ Further freezing led to an increase in the amount of ice formed on both hydrophobic and hydrophilic surfaces. However, the mechanism of ice growth is different. The results suggest that ice growth on hydrophobic surfaces is due to the growth of already formed ice crystals. No ice formation on naked polymer surfaces was observed. On the other hand, new ice crystals are formed on hydrophilic polymer surfaces, and on already formed ice crystals. This is particularly visible in the cryo-SEM images of frozen droplets on hydrophobic, and hydrophilic surfaces (Fig. 3c and f). Frozen ice droplets are covered by small ice crystals, while no small ice crystals were observed on hydrophobic surfaces (Fig. 3f). On the other hand, small ice crystals are formed on frozen ice droplets and hydrophilic surfaces (Fig. 3c).

We also observed that the ice growth rate on all surfaces is linear in the beginning (0–1000 s), and comes to its saturation after 4 hours, when no further ice growth was detected (Fig. 3g). We explain the plateau with the thermal insulation of polymer substrates by the formed ice layer that increases the temperature on the surface of the growing ice layer, and thus slows down its growth. We found that the ice growth rate, which was calculated as an angle of inclination in Fig. 3g, during first 1000 s on hydrophobic surfaces is lower than that on hydrophilic ones, and more ice is condensed on hydrophilic surfaces before saturation (Fig. 3h).

Moreover, the ice growth rate on rough surfaces is typically lower than that on flat ones. These results suggest that flat and rough hydrophilic P(PEGMA) surfaces freeze first, while flat and rough hydrophobic ones freeze with some delay. Ice growth on hydrophobic surfaces is provided by the growth of already formed ice crystals. On hydrophilic surfaces, ice grows on both naked polymer surfaces, and on already formed ice crystals. As a result, ice growth on hydrophilic surfaces is faster than on hydrophobic ones.

Ice adhesion strength

We found that the ice adhesion strength on all hydrophobic flat polymer surfaces (P(PDMSMA), PS, and PLMA) is nearly the same, and is about 100 kPa, which can be explained by similar hydrophobicity of the polymers (Fig. 4). We observed that roughness either increases the adhesion strength of ice on PS

Fig. 4 Summary of ice adhesion strength measured on different polymeric surfaces.

surfaces (in the case when the surfaces are formed by plain 1000 nm particles, or inverse surfaces with the same dimension), or remains unchanged (in the case when the surfaces are formed by planar 200 nm particles, or inverse surfaces with the same dimension). We also observed that increasing roughness results in an increase in the ice adhesion strength in the case of PLMA. However, we observed an opposite trend in the case of P(PDMSMA)-modified surfaces, *i.e.* increasing roughness decreases the adhesion strength, whereas minimal adhesion is observed in the case of superhydrophobic surfaces formed by 20 nm, and raspberry-like particles. The flat P(PEGMA) surface demonstrated a very low ice adhesion (< 50 kPa), while increasing roughness dramatically increased ice adhesion. Thus, surfaces with the lowest ice adhesion are superhydrophobic P(PDMSMA) based ones (20 nm, and raspberry-like particles), and flat P(PEGMA). The maximal ice adhesion strength was observed for rough P(PEGMA) surfaces, and rough PS surfaces prepared from 1000 nm particles, and inverse structures with 1000 nm pores.

An increase in the temperature results in the melting of ice, which occurs independently of the surface nature at 0 °C (Fig. 5).

Fig. 5 Optical microscopy images during ice melting on flat PLMA and P(PEGMA) surfaces: (a–d) – small magnification; (e–h) – large magnification – melting of ice on the PLMA surface; (i–k) – large magnification – melting of ice on the superhydrophobic 20 nm P(PDMSMA) surface; (l–m) – large magnification – melting of ice on the P(PEGMA) surface.

The melting ice forms a continuous water layer on hydrophilic surfaces, which easily leaves the surface (Fig. 5a–d, i and j). On the hydrophobic surfaces, molten ice crystals merge (Fig. 5a–d and e–h), and form droplets with the size of 20–50 μm formed by fused ice crystals (Fig. S12, ESI†). These droplets remain pinned and can be removed from the surfaces only by strong shaking. A similar behaviour was observed on rough surfaces formed by 1000 nm, and 200 nm particles, as well as superhydrophobic surfaces (Fig. 5i–k). These small droplets, which remain immobile, can freeze again upon second cooling. The shape of frozen droplets is rounded as the shape of water droplets. Further cooling results in their anisotropic growth and formation of crystals; however, no formation of ice crystals on naked polymer surfaces was observed. It is interesting that the small droplets, which are formed on superhydrophobic surfaces after ice thawing, are also very immobile and can be removed only by strong shaking. Thus, thawed water more easily leaves the hydrophilic surfaces than from hydrophobic ones.

4. Discussion

The values of sliding angles show that hydrophobicity of the surfaces decreases in the sequence: P(PDMSMA)-based irregular (20 nm, raspberry-like) > regular rough P(PDMSMA), and PLMA (1000 nm, and 200 nm) > PS all > P(PEGMA) all modified surfaces. In order to explain this sequence one has to consider two effects: chemical structure of polymers, and roughness. The polarity of polymers increases in the sequence P(PDMSMA) $\rightarrow$ PLMA $\rightarrow$ PS $\rightarrow$ P(PEGMA), as it can be concluded from the values of contact angles on corresponding flat surfaces. Roughness enhances the intrinsic properties of the polymers, and makes intrinsically hydrophilic surfaces even more hydrophilic and hydrophobic surfaces superhydrophobic. Therefore, rough P(PDMSMA) surfaces are the most hydrophobic, and rough P(PEGMA) surfaces are the most hydrophilic ones.

We observed that water droplets on flat and rough hydrophilic P(PEGMA) surfaces freeze first, while they freeze with some delay on flat and rough hydrophobic ones. The delayed freezing of hydrophobic surfaces can be explained by considering the shape of the water droplets: water droplets on hydrophilic surfaces are flattened, while the droplets on hydrophobic ones are more spherical. Therefore, the contact area of the droplets with the same volume on hydrophilic surfaces is larger than that on hydrophobic ones, and their cooling is faster.

The mechanisms of ice growth on hydrophilic and hydrophobic surfaces are, however, different. On hydrophobic surfaces, ice growth is provided solely by the growth of already formed ice

crystals. On hydrophilic surfaces, ice grows both on the naked polymer surface, and on the already formed ice crystals. The difference in ice growth mechanisms can be explained by considering the polarity of polymers: P(PEGMA) is hydrophilic, and water molecules like to adhere to it by forming hydrogen bonds with polymer molecules. P(PDMSMA), PLMA, and PS are hydrophobic, and are unable to form hydrogen bonds. As a result, ice grows faster on hydrophilic surfaces than on hydrophobic ones.

Surfaces with the lowest ice adhesion strength are superhydrophobic P(PDMSMA)-based ones (20 nm, and raspberry-like particles), and flat P(PEGMA). The maximal ice adhesion was observed on the rough P(PEGMA) surfaces, and rough PS surfaces prepared from 1000 nm particles, as well as on inverse structures with 1000 nm pores. High adhesion on PS surfaces formed by large particles can be explained by the penetration of water through the pores between the particles due to gravity. On the other hand, freezing results in the formation of a strong mechanical contact between the ice and the surface. Apparently, water droplets cannot penetrate in the narrow pores between the 200 nm large particles, which reduces ice adhesion. High adhesion of ice on rough P(PEGMA) surfaces can be explained in a similar way: water simply penetrates between P(PEGMA)-modified particles that build very strong mechanical contact between the ice and the surface. Low adhesion of ice to superhydrophobic surfaces can be explained by a small real contact area between the ice and the polymer surface. Low adhesion of ice to the flat P(PEGMA) surface can be explained by the “antifreeze” properties of P(PEGMA) – the freezing point of poly(ethylene glycol)–water solutions is $-10\text{ }^{\circ}\text{C}$ to $25\text{ }^{\circ}\text{C}$ (Fig. S3, ESI†). We believe that the hydrated P(PEGMA) brush does not freeze, and this liquid layer serves as a lubricant and facilitates the removal of ice from the surface.

Melting of ice leads to the formation of small individual droplets, which are immobile on hydrophobic surfaces, and form a thin mobile water layer on hydrophilic ones. The difference in the droplet shape formed by ice molten on hydrophilic and hydrophobic surfaces arises due to the difference in their wetting properties: water contact angles on P(PDMSMA), PLMA, and PS surfaces are high, and the difference between advancing and receding angles (contact angle hysteresis) is also large, which does not allow the droplet to slide off easily. The contact angle on the P(PEGMA) surface is low, and water droplets are flattened, which facilitates their evaporation (because of the high surface to volume ratio). The summary and comparison of advantages and disadvantages of flat/rough hydrophilic, and hydrophobic surfaces is given in Table 3.

We investigated the correlation between the wetting properties of the surfaces and their icing behaviour (ice growth rate,

Table 3 Advantages and disadvantages of (super) hydrophobic and hydrophilic surfaces with respect to their anti-icing properties

(Super) hydrophobic (flat and rough) surfaces	Flat hydrophilic surfaces
+ slow ice growth (growth only on existing ice crystals, no growth on naked polymer)	– fast ice growth (growth on existing ice crystals and naked polymer)
+ low ice adhesion (reduced contact area)	+ low ice adhesion (low freezing point)
– pinning of water droplets after thawing	+ easier removal of water after thawing

Fig. 6 Correlation between ice adhesion, ice growth rate and cosine of the advancing contact angle for different surfaces.

and adhesion). It was found that the increase in the cosine of advancing contact angles (decrease of advancing contact angles) results in a slight decrease of ice adhesion (Fig. 6a), and a strong increase of the ice growth rate (Fig. 6d). On rough surfaces, an increase in the cosine of advancing contact angles results in an increase of both ice adhesion (Fig. 6b and c), and the ice growth rate (Fig. 6e and f).

Finally, we correlated the results of ice adhesion and the ice growth rate in one plot (Fig. 6g). From this plot one can clearly see that the superhydrophobic surfaces demonstrated the best anti-icing behaviour, and have the lowest ice adhesion and ice growth rate. The rough hydrophilic surfaces are the worst ones, since both ice adhesion and ice growth rate are the largest.

5. Conclusions

In this paper, we thoroughly investigated the effects of geometry/roughness and chemical properties of flat and structured surfaces on their icing and thawing behavior. We found that the freezing of water droplets on a hydrophobic surface occurs later

because of their round shape and slower heat exchange. Moreover, the growth of ice on hydrophobic surfaces is slower than that on hydrophilic ones, because ice grows either on already formed ice crystals, or on a hydrophilic surface, but not on the naked hydrophobic polymer. We have demonstrated that superhydrophobic rough surfaces, and the flat poly(ethylene glycol)-based surface demonstrate the lowest ice adhesion strength (<50 kPa). The reason for the low ice adhesion is the low freezing point of water–poly(ethylene glycol) mixtures in the case of flat hydrophilic surfaces, and the small contact area with ice in the case of superhydrophobic surfaces. We conclude that the use of (super)hydrophobic and hydrophilic polymers is promising for the design of anti-icing surfaces. However, each of these kinds of polymers has advantages but also disadvantages (Table 3), and neither purely (super)hydrophobic polymeric surfaces, nor “anti-freeze” hydrophilic ones provide an ideal solution for the problem of icing.

These findings might initiate a new platform for scientific discussion and the search for alternative approaches for solving the problem of icing. These could lead to the design of novel effective anti-icing coatings in the near future.

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