

SUPPORTING INFORMATION

Superhydrophilic Polyelectrolyte Brush Layers with Imparted Anti-Icing Properties: Effect of Counter ions

Sergey Chernyy¹, Mikael Järn², Kyoko Shimizu³, Agne Swerin^{2,5}, Steen Uttrup Pedersen^{3,4}, Kim Daasbjerg^{3,4}, Lasse Makkonen⁶, Per Claesson^{2,5}, Joseph Iruthayaraj^{7,4*}

¹ Technical University of Denmark, Department of Micro- and Nanotechnology, Produktionstorvet, 2800 Lyngby, Denmark

² SP Technical Research Institute of Sweden – Chemistry, Materials and Surfaces, , Box 5607, SE-114 86 Stockholm, Sweden

³ Department of Chemistry, Aarhus University, Langelandsgade 140, DK-8000 Aarhus, Denmark

⁴ Interdisciplinary Nanoscience Center (iNANO), Department of Physics and Astronomy, Aarhus University, Ny Munkegade 120, DK-8000 Aarhus C, Denmark

⁵ KTH Royal Institute of Technology, Department of Chemistry, Surface and Corrosion Science, SE-100 44 Stockholm, Sweden

⁶ VTT Technical Research Centre of Finland, Box 1000, 02044 VTT, Finland

⁷ Biological and Chemical Engineering Division, Aarhus University, Høngøvej 2, 8200 N, Aarhus, Denmark

Keywords

ATRP isopropanol-water, polyelectrolyte brushes, ion exchange, anti-icing, superhydrophilic surfaces, ice adhesion

Corresponding author

Joseph Iruthayaraj

Email: ji@eng.au.dk

1. X-ray photoelectron spectroscopy (XPS). A Kratos Axis Ultra-DLD instrument operated with a monochromatic Al K α X-ray source at a power of 150 W was employed for the XPS analysis. Survey scans were acquired by accumulating two sweeps in the 0–1100 eV range at a pass energy of 160 eV. High-resolution scans were acquired at a pass energy of 20 eV. The pressure in the main chamber during the analysis was in the order of 10^{-11} bar. The generated XPS data were processed using the CasaXPS software. Atomic surface concentrations were determined by fitting the core spectra using Gaussian line shapes and a linear background. Binding energies of the components in the spectra were determined by calibrating against the C–H/C–C peak in the C1s spectra at 285.0 eV. The systematic error is estimated to be of the order of 5–10%.

2. Ellipsometry. Film thicknesses below 50 nm were measured by means of a rotating analyzer ellipsometer (Dre, Germany) with a HeNe laser ($\lambda = 632.8$ nm) at 75° angle of incidence. The ellipsometric parameters of the bare (Δ_s, ψ_s) and grafted (Δ_g, ψ_g) substrates were measured in air at ambient temperature, where Δ is the phase shift and $\tan(\psi)$ is the amplitude ratio upon reflection. The complex refractive index of the bare substrate was calculated from the measured Δ_s and ψ_s values. A three-layer optical model^{1,2} consisting of a substrate with a complex refractive index, the grafted layer given by its refractive index and thickness and the surrounding medium (air) was used to calculate the overall reflection coefficients for in-plane (R_p) and out-of-plane (R_s) polarized lights. The real and the imaginary parts of the refractive index of the bare substrate were obtained by measuring the clean plates prior to modification. Ellipsometric measurements were performed on the same area of the plates before and after electrografting. Because the measurements are carried out on a dried and thus collapsed film, the refractive index of the layer is fixed at a constant value (real = 1.55; imaginary = 0), independent of the thickness. The average and the standard deviation values reported correspond to data points obtained from measuring three spots on each plate.

3. Profilometry. Film thicknesses above 50 nm were measured by means of a Dektak 150 Surface Profiler by scanning the surface of the substrate across the grafted and non-grafted parts. In the case of bad contrast the grafted material was scratched off by a plastic spatula and the scan was

made across the scratch. Typically, 3 runs with $2.9 \times 10^{-5} \text{ kg m s}^{-2}$ styles force, $40 \mu\text{m s}^{-1}$ scanning speed, and $1200 \mu\text{m}$ scanning distance were used in order to obtain an average thickness value and standard deviation.

4. Ice adhesion profiles. The representative ice adhesion strength vs. time profiles are shown for all strong anionic (Figure 1), strong cationic (Figure 2), weak anionic (Figure 3) and nonionic polymer brushes (Figure 4). Zero values of the ice adhesion strength correspond to a situation when the cuvette with ice was not yet in contact with the pulling arm and/or the ice cuvette was peeled from the surface. The peak force was used as a characteristic value for ice adhesion strength.

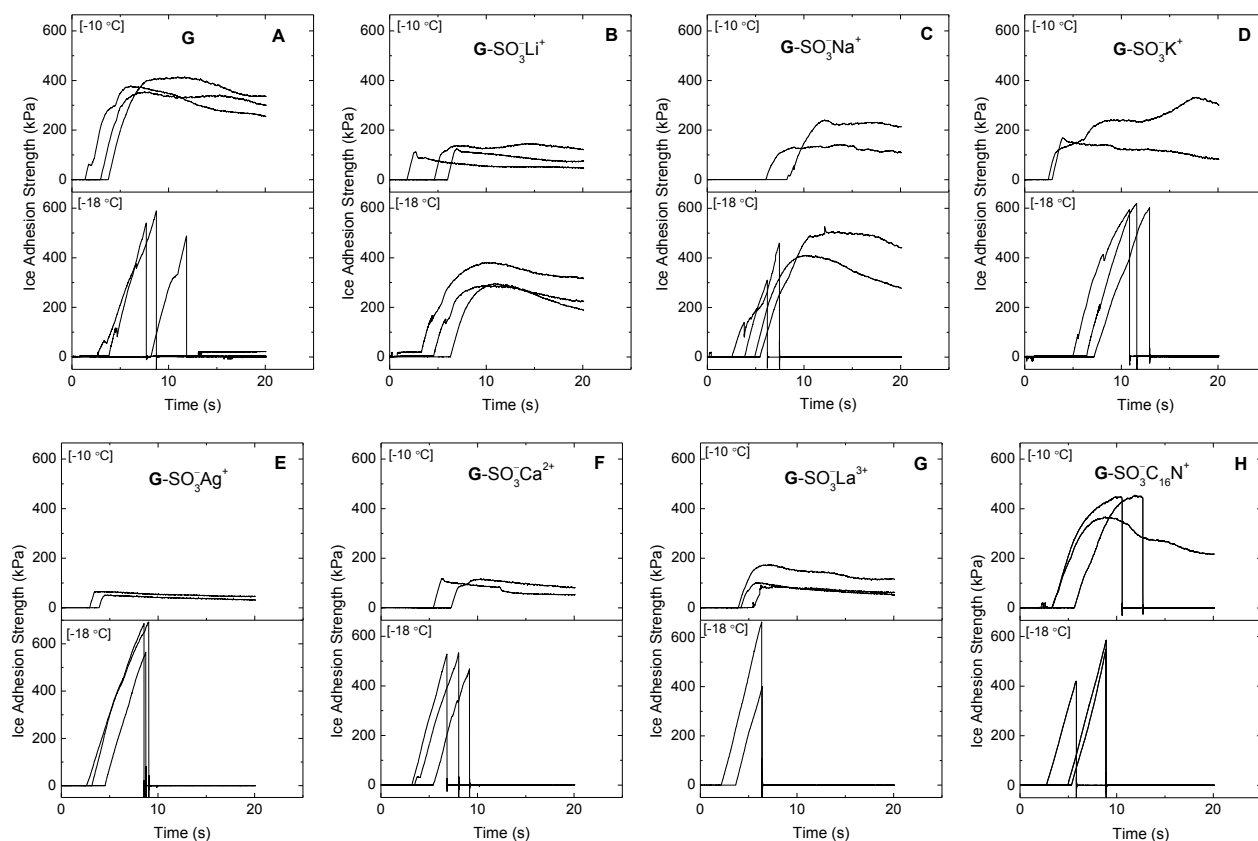


Figure 1. Ice Adhesion Strength measured at $-18\text{ }^{\circ}\text{C}$ and $-10\text{ }^{\circ}\text{C}$ on bare glass (G) and strong anionic ($\text{G-SO}_3^- \text{X}^+$) polyelectrolyte brush layers comprising of different types of counter ions ($\text{X}^{n+} = \text{Li}^+, \text{Na}^+, \text{K}^+, \text{Ag}^+, \text{Ca}^{2+}, \text{C}_{16}\text{N}^+, \text{La}^{3+}$)

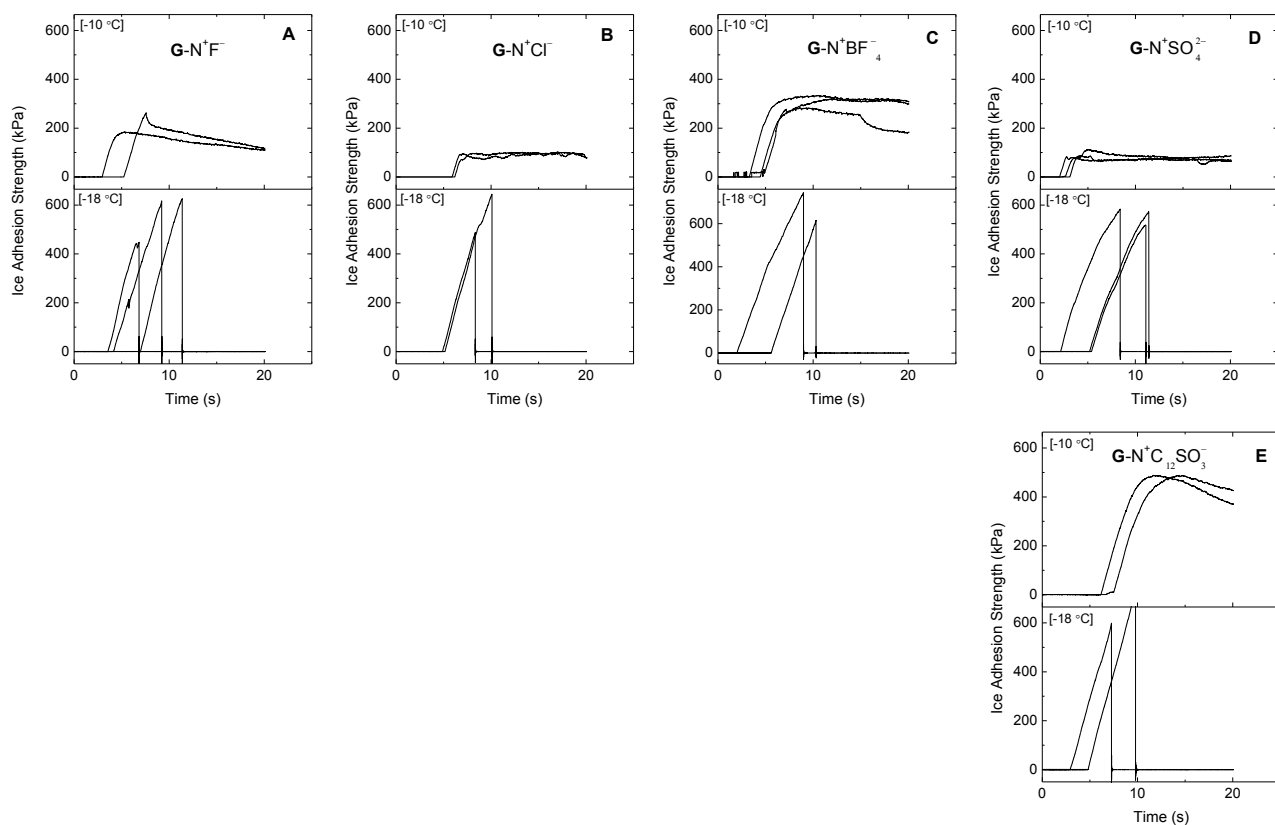


Figure 2. Ice Adhesion Strength measured at -18 °C and -10 °C on strong cationic ($\text{G-N}^+\text{Y}^{\text{n-}}$) polyelectrolyte brush layers comprising of different types of counter ions ($\text{Y}^{\text{n-}} = \text{F}^-, \text{Cl}^-, \text{BF}_4^-, \text{SO}_4^{2-}$)

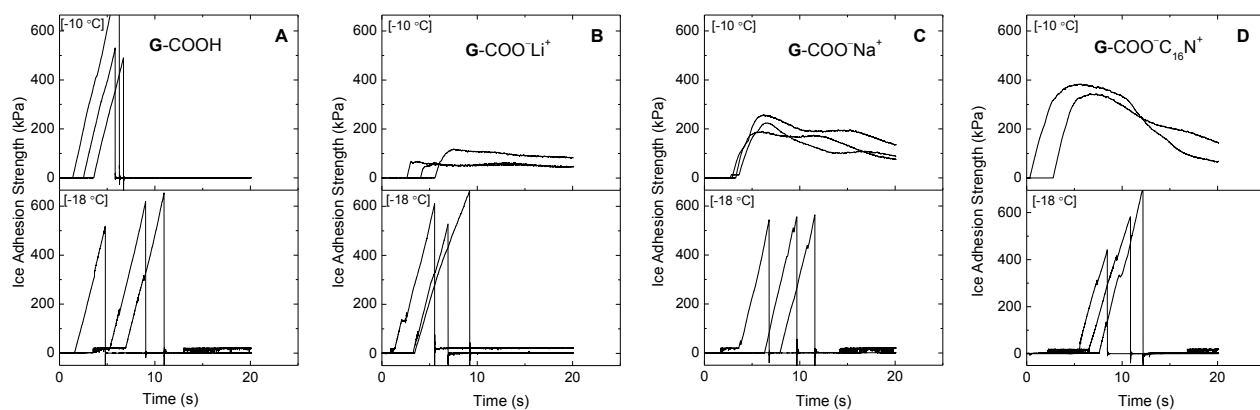


Figure 3. Ice Adhesion Strength measured at -18 °C and -10 °C on weak anionic ($\text{G-COO}^-\text{Z}^+$) polyelectrolyte brush layers comprising of different types of counter ions ($\text{Z}^+ = \text{H}^+, \text{Li}^+, \text{Na}^+$)

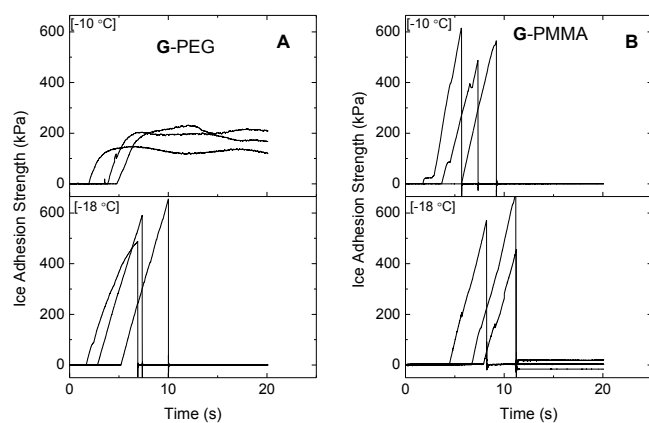


Figure 4. Ice Adhesion Strength measured at -18 °C and -10 °C on poly(ethylene glycol) [G-PEG] and poly(methyl methacrylate) [G-PMMA] brushes

References

1. Tiberg, F.; Landgren, M. Characterization of Thin Nonionic Surfactant Films at the Silica/Water Interface by Means of Ellipsometry. *Langmuir* **1993**, *9*, 927-932.
2. Landgren, M.; Jonsson, B. Determination of the Optical Properties of Silicon/Silica Surfaces by Means of Ellipsometry, Using Different Ambient Media. *J. Phys. Chem.* **1993**, *97*, 1656-1660.