Hierarchically structured polymer surfaces: Curved surfaces and sliding behavior on ice

Kati Mielonen

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Hierarchically structured polymer surfaces: Curved surfaces and sliding behavior on ice

Kati Mielonen

Department of Chemistry
University of Eastern Finland
Finland

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ABSTRACT

The surface properties of polymers can be modified by physical patterning without changing the chemical characteristics of the polymer material. Functional surface properties usually originate from highly developed natural surfaces, and by way of structuring techniques, similar properties have been achieved with various polymeric base materials. Besides the well-understood wetting properties of hierarchically structured surfaces, the effects of structuration on other surface phenomena have also been increasingly studied. The practical application of artificial structured surfaces requires flexible and scalable fabrication methods.

A common limitation is that fabrication methods are not suitable for curved surfaces. This study demonstrates the fabrication of curved and structured mold inserts to be used in polymer injection molding. Spherically and cylindrically symmetrical millimeter-scale curvatures with both convex and concave orientations were applied. Hierarchical two- and three-level structures were replicated on the curved polypropylene surfaces, and replication quality depended on the injection molding parameters as well as demolding. The curved hierarchically structured surfaces were highly hydrophobic, and their planar references were characterized as superhydrophobic.

Surface structuration also provides an approach to modify the frictional properties of polymers on ice. This study shows how microstructuration on three polymer materials of different hardnesses influences ice sliding friction. In addition to the microstructure type, ice friction behavior was also studied with respect to ice temperature and applied load. All polymer materials reached superhydrophobicity with the hierarchical microstructures, but the ice friction behavior did not exhibit regularity between polymer types. Different microstructure types affected the frictional behavior in a manner that was dependent on the polymer mechanical properties and prevailing conditions at the contact interface.
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The dissertation is based on the following publications and manuscript, referred to by the Roman numerals I–III.


The main ideas for the topics of Papers I–III were derived from discussions between the author and co-authors. The author planned and developed the fabrication of curved mold inserts and the method for measuring ice friction. The author performed all experiments and prepared the three manuscripts with comments from the co-authors.
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INTRODUCTION

Every natural material and surface has one or more functional purposes. Seven-level hierarchies in human bone and the deep-sea glass sponge are examples of complex evolutionary achievements. Similarly, animals and plants have evolved to survive and adapt in their environments taking advantage of various structured surfaces. The two most frequently referenced examples of such surfaces are the three-level-structured gecko toe and the two-level-structured lotus plant leaf. By means of surface engineering, similar functional properties have been aspired on synthetic materials.

1.1 Hierarchically structured polymer surfaces

Chemical composition and physical structure together define the surface properties of a polymer. Topographical surface modification is an effective way to manipulate the surface functionality while still maintaining the inherent chemical properties of the material. Structural surface features are typically generated by replication or direct surface manufacturing processes. Replication processes, which include molding and embossing techniques, are based on transferring the master geometry to the substrate surface, whereas in direct surface manufacturing, the tool geometry directly determines the surface features. Structure fabrication methods can also be classified into top-down and bottom-up approaches; the former denoting the removal of building blocks from the substrate surface and the latter the construction of structures on the surface.

The significance of hierarchical structuration lies in the distinct roles of the structural levels. The lower base structural level is usually responsible for the mechanical surface properties such as strength and stability, and the upper structural level provides the surface with specific functional properties. Hierarchical structures on polymer surfaces have most commonly consisted of micro- and nanostructures, and numerous studies have demonstrated functional two-level micro-nano structured polymer surfaces. Until recently, micro-nano structures in particular have been considered necessary for obtaining structure-induced surface functionalities, the typical example being superhydrophobicity. However, multiscale hierarchical structures combining different microscales have been shown to exhibit similar surface functionalities, but with improved robustness. The weakness of nanostructures is that they are typically fragile. Mechanically durable hierarchically structured surfaces are needed to support practical applications. As a potential approach to improving surface durability, larger-scale sacrificial structures have been demonstrated to protect smaller hierarchical structures from mechanical pressure and abrasive wear.

Structural hierarchies in nature are not restricted to two levels. Similarly, for artificial functional surfaces, multilevel structures have been suggested to further support the achievement of desired surface properties. Hierarchical three-level structures have been fabricated as fiber arrays on polyurethane, three-dimensional wrinkles on polydimethylsiloxane, and sequentially imprinted ridges and pillars on polystyrene.
1 INTRODUCTION

Every natural material and surface has one or more functional purposes. Seven-level hierarchies in human bone\textsuperscript{1} and the deep-sea glass sponge\textsuperscript{2} are examples of complex evolutionary achievements. Similarly, animals\textsuperscript{3–5} and plants\textsuperscript{6,7} have evolved to survive and adapt in their environments taking advance of various structured surfaces. The two most frequently referenced examples of such surfaces are the three-level-structured gecko toe\textsuperscript{8} and the two-level-structured lotus plant leaf\textsuperscript{9}. By means of surface engineering, similar functional properties have been aspired on synthetic materials.

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The significance of hierarchical structuration lies in the distinct roles of the structural levels. The lower base structural level is usually responsible for the mechanical surface properties such as strength and stability, and the upper structural level provides the surface with specific functional properties.\textsuperscript{13,14} Hierarchical structures on polymer surfaces have most commonly consisted of micro- and nanostructures, and numerous studies have demonstrated functional two-level micro–nano structured polymer surfaces.\textsuperscript{15–20} Until recently, micro–nano structures in particular have been considered necessary for obtaining structure-induced surface functionalities, the typical example being superhydrophobicity.\textsuperscript{21,22} However, multiscale hierarchical structures combining different microscales have been shown to exhibit similar surface functionalities, but with improved robustness.\textsuperscript{23–25} The weakness of nanostructures is that they are typically fragile.\textsuperscript{26} Mechanically durable hierarchically structured surfaces are needed to support practical applications. As a potential approach to improving surface durability, larger-scale sacrificial structures have been demonstrated to protect smaller hierarchical structures from mechanical pressure and abrasive wear.\textsuperscript{27}

Structural hierarchies in nature are not restricted to two levels. Similarly, for artificial functional surfaces, multilevel structures have been suggested to further support the achievement of desired surface properties.\textsuperscript{28} Hierarchical three-level structures have been fabricated as fiber arrays on polyurethane\textsuperscript{29}, three-dimensional wrinkles on polydimethylsiloxane\textsuperscript{30}, and sequentially imprinted ridges and pillars on polystyrene and...
poly(methyl methacrylate)\textsuperscript{31}, and have also been fabricated by combined multiplex lithography and imprinting on various polymers\textsuperscript{32}.

### 1.2 Properties of structured polymer surfaces

Polymer surfaces have been structurally modified to achieve specific desired surface properties, many of which originate from the functions of natural surfaces. Adjustable wettability\textsuperscript{33}, smart adhesion\textsuperscript{34}, structural coloration\textsuperscript{35}, anti-reflection\textsuperscript{36}, and drag reduction\textsuperscript{37} are examples of such biomimetic properties. Surface structures can be applied to tune the friction and wear rate of polymer surfaces\textsuperscript{38} and to prevent microbial growth\textsuperscript{39}. Structural modification is also one of the approaches in the development of anti-icing surfaces.\textsuperscript{40,41}

Superhydrophobicity, an extreme wettability property, is typically considered a prerequisite to other functional surface properties.\textsuperscript{42,43} Specific design requirements including hierarchy and appropriate structural proportions have been suggested for roughness-induced superhydrophobic surfaces fabricated from materials that were initially hydrophobic.\textsuperscript{44} The fabrication of superhydrophobic surfaces with self-cleaning functionality is straightforward, but issues that remain to be resolved include improvements to their multifunctionality and robustness. Instead of solely being a property of the outermost surface, superhydrophobicity that extends deeper into the material could advance the use of such surfaces in practical applications.\textsuperscript{45}

### 1.3 Curved polymer surfaces

Various fabrication methods for structured polymer surfaces have been introduced throughout recent decades, but they have typically been demonstrated to be suitable only for planar surfaces. These techniques, especially those based on direct mechanical machining which require accurate structural alignment, are seldom easily adaptable to curved or multifaceted surfaces. Appropriate and flexible methods to produce three-dimensional structured surfaces are obviously needed in order to fully exploit the possibilities of functional surfaces in practical applications. Curved functional surfaces have been suggested to be applicable in hydrodynamic drag reduction\textsuperscript{46}, liquid transportation\textsuperscript{47,48}, controlled liquid overflow\textsuperscript{49,50}, climbing robots and similar applications requiring strong grip\textsuperscript{51–53}, and medical equipment such as implants and devices\textsuperscript{53,54}. Very small liquid volumes need to be transported without loss in fluidic applications. Lossless droplet transportation has been demonstrated with curvature-driven switching between pinned and roll-down superhydrophobic states of the structured polymer film.\textsuperscript{47} Curved hierarchically structured polymer tracks have been used to directionally move droplets.\textsuperscript{48}
Despite the limited methods available, a few manufacturing processes for curved structured polymer surfaces have been introduced. These processes can be roughly categorized as having to do with coatings, bendable soft substrates, and pattern transfers onto curved objects. Furthermore, molding has been applied to obtain free-standing but flexible polymer surfaces with cylindrical and spherical curvatures as well as rigid cylindrical surfaces. Microstructuration of the complex three-dimensional mold cavity for polymer injection molding has been demonstrated in three ways: separate structured mold inserts, direct laser machining, and anodization.

Macrosopic surface curvature can affect, for example, surface hydrophobicity by changing the contact interaction through alteration of the structural spacing and reorientation of the contact line. In particular, the dimensions, orientation, and tip geometry of the structures define the achievable contact area. Due to practical difficulties in the unambiguous determination of the contact angle for curved surfaces, theoretical models have been developed to estimate the relationships between surface curvatures and apparent contact angles.

### 1.4 Ice friction of polymer surfaces

Various practical motivations, including advancements in tire traction, footwear grip, and winter sports technologies, inspire surface scientists to study the complex friction phenomena which occur at the polymer–ice interface. A peculiarity of friction on ice is that a layer of water is naturally present on the surface of the ice. The water layer mainly originates from frictional heating during the sliding contact, while the role of pressure melting is considered minor. Three friction regimes, namely boundary, mixed, and hydrodynamic friction, can be characterized with respect to the thickness of the water layer, which is closely related to the nature of the contact. Contact between solid asperities of the ice surface and the sliding surface is dominant in boundary friction, whereas in hydrodynamic friction, no solid contact occurs and friction instead arises from the shearing of the viscous water layer. Mixed friction is an intermediate between these two regimes; the load of the sliding surface is partly supported by solid–solid contact and partly by the water layer. Two competing mechanisms exist in mixed friction; sliding is favored by the increased water lubrication but counteracted by the developing capillary bridges, and thus the minimum friction is case-specific and is attributed to the balance of the contributions of these two factors. The lowest friction coefficient for polymers has typically been observed at ice temperatures in the range of −7 °C to −2 °C, depending on other conditions.

A complex combination of various system- and surface-related parameters makes ice friction an intricate interaction, not in the least due to the metamorphic nature of ice. The effects of ice temperature, sliding velocity, normal load, and ice type have been widely studied as system-related parameters. An increase in ice temperature, sliding velocity, or normal load typically decreases the friction coefficient. On the other hand, the hardness and surface wettability of polymer surfaces.
of polymer sliders have been studied as material-related parameters. Ice friction has most often been measured with custom-made linear\textsuperscript{69,72,82,85,87,88} or rotational\textsuperscript{77,79,80,83} friction testers, typically tribometers, but field tests\textsuperscript{69,71,78} have also been utilized. The vast variety of measurement methods available and the numerous interrelated parameters involved limit the comparison of experimental results to observed trends. An example of ambiguity in such measurements regards the ice temperature; its value has always been reported but the measurement location has rarely been specified.

Surface structuration of the polymer slider offers an additional way to affect its frictional behavior on ice. Ice friction has been controlled with differently oriented structures depending on the dominant friction regime\textsuperscript{80,92}. Grooves in rubber surfaces have been demonstrated to control the onset of frictional sliding\textsuperscript{93}, and the degree of friction in grooved rubber has been shown to be determined by the sliding velocity\textsuperscript{69,94}. At the comparatively low sliding velocity, the flat rubber surface has exhibited higher friction than the grooved surface, while at the higher velocities, the grooved rubber surface has shown higher friction than the flat surface due to a plowing effect\textsuperscript{69}. Composites of rubber and protruding fibers have exhibited high friction due to enhanced mechanical interlocking and roughness-induced hydrophobicity\textsuperscript{95–97}.

1.5 Aims of the study

The study summarized in the dissertation had two distinct objectives, both of which are related to the application of hierarchically structured polymer surfaces. The first aim concerned the fabrication of such surfaces with additional curvature, and the second aim was to explore the frictional behavior of microstructured polymer surfaces on ice. The following specific topics will be considered:

- the effect of each hierarchical level on the surface hydrophobicity in three-level-structured polypropylene surfaces
- the possibility to fabricate curved, hierarchically structured mold inserts and use them in polymer injection molding
- the replicability of microstructures onto rubber surfaces
- tribological study of the ice friction of microstructured polypropylene and rubber surfaces
- the effects of microstructure levels, ice temperature, and normal load on the ice friction behavior of polymer surfaces
2 CURVED HIERARCHICALLY STRUCTURED POLYPROPYLENE SURFACES

Four different combinations of micro- and nanoscale structures were fabricated on polypropylene surfaces by means of injection molding using structured mold inserts. The wettability properties of the planar polymer surfaces were characterized, and the roles of the hierarchical levels in surface hydrophobicity were examined. Corresponding structures were applied to spherically and cylindrically curved polypropylene surfaces.

2.1 Surface structures and their effect on surface wettability

All structures of the polymer surfaces were protrusions which were replicated from indentations fabricated on the mold inserts. Micropit structures were machined with a microworking robot (RP-1AH, Mitsubishi Electric) on aluminum foil, using hard-metal working needles of different shapes and sizes. For the hierarchical two-level structures, the second structural level was fabricated with a smaller needle tip inside the larger micropits of the first level. The third hierarchical level was a layer of porous anodic aluminum oxide (AAO) produced via single-step anodization in polyprotic acid. The four structured surface types employed in this study were one multiscale (MS), two micro–micro structured (MM1, MM2) and one micro–micro–nano structured (MMN). MS, MM1, and MM2 are originally presented in the publication I and MMN in the publication II.

SEM micrographs of the structures on injection-molded polypropylene (PP) surfaces are shown in Figure 1. The MS structures consisted of a microroughness structure protected with larger square-shaped micropillars (Figure 1 A). The protective pillars had a surface coverage of 15%, which is the level that was previously demonstrated to shelter the small and fragile roughness structure from mechanical wear while still retaining the surface wettability properties. Both hierarchically MM structured surface types had regularly arranged pillar patterns (Figures 1 B and C). The area fraction, i.e., the ratio of the area of the pillar tops to the projected surface area, was 0.12 for the MM1 pattern (Figure 1 B) and 0.11 for the MM2 pattern (Figure 1 C). The third hierarchical level of the MMN surface consisted of bump-like nanostructures which covered the micropillar tops, walls, and the base between them (Figure 1 D). While the microstructural levels of the MMN pattern resembled those of the MM1 pattern, their dimensions are not similar and thus they could not be directly compared. The area fraction of the MMN surface was estimated to be approximately 0.07, indicating that the topmost contact area decreases with an increasing number of hierarchical levels. The replication quality of the nanostructures depends on the injection molding parameters, in particular the mold temperature; this has also been reported previously. At high enough mold temperatures, the polymer melt can flow into the smallest nanocavities, and consequently, nanostructures are replicated even on top of the smallest micropillars of the second level.
Static contact angles (CA), contact angle hystereses (CAH), and sliding angles were determined for the four structured surface types, using the flat unstructured PP surface as a reference. Table 1 presents the wettability characteristics of the surface types. The added roughness further improves the hydrophobicity of the inherently hydrophobic PP surface. The microroughness structure of the MS surface increased the static contact angle to over 150°, but the hysteresis and sliding angle, both of which indicate droplet adhesion, were comparable to those of the flat surface, and in fact the droplet got stuck to the MS surface. However, larger manually applied droplets easily slid on the MS surface. Droplet mobility has been shown to depend on the droplet size, initial droplet position, and overall measurement procedure.\textsuperscript{100,101} Both micro–micro structured surfaces, MM\textsubscript{1} and MM\textsubscript{2}, were similarly hydrophobic. More precisely, they are considered superhydrophobic since their CAs are larger than 150° and the hystereses and sliding angles are lower than 10°. Different microstructural arrangements can thus result in similar area fractions, as presented above, as well as similar wettability characteristics. The third structural level further improved the surface water repellency, and the role of each hierarchical level of the MMN surface is demonstrated below.

Figure 1. SEM micrographs of four structural patterns on injection-molded PP surfaces: (A) multiscale structures MS; (B) and (C) hierarchical micro–micro structures MM\textsubscript{1} and MM\textsubscript{2}, respectively; (D) hierarchical micro–micro–nano structures, MMN, where the inset represents the nanobump structures.

<table>
<thead>
<tr>
<th>Surface</th>
<th>Static contact angle (°)</th>
<th>Contact angle hysteresis (°)</th>
<th>Sliding angle (°)</th>
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<tbody>
<tr>
<td>Flat</td>
<td>105 ± 1</td>
<td>18 ± 1</td>
<td>&gt; 90</td>
</tr>
<tr>
<td>MS</td>
<td>151 ± 1</td>
<td>15 ± 1</td>
<td>&gt; 90</td>
</tr>
<tr>
<td>MM\textsubscript{1}</td>
<td>160 ± 2</td>
<td>7 ± 2</td>
<td>8 ± 2</td>
</tr>
<tr>
<td>MM\textsubscript{2}</td>
<td>165 ± 1</td>
<td>5 ± 3</td>
<td>9 ± 2</td>
</tr>
<tr>
<td>MMN</td>
<td>170 ± 2</td>
<td>5 ± 1</td>
<td>6 ± 3</td>
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The graph shown in Figure 2 illustrates how the three hierarchical levels of the MMN pattern gradually increased the CA and decreased the CAH of the PP surface. The base microstructures of the first level had the largest single contribution to CA, but the superhydrophobic state was only achieved for the two- and three-level hierarchical structures. The comparatively large CAH and standard deviation for the one-level structural surface was explained by the stepwise moving Wenzel-type droplet, whereas on the hierarchically structured surfaces, the droplet expanded and contracted smoothly on top of the structures. Two properly designed hierarchical levels are thus sufficient for imparting functional water repellency, and three-level structural surfaces can be considered less prone to losing their superhydrophobicity.
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![Graph showing the effect of hierarchical structural levels on PP surface wettability](image)

**Figure 2.** The effect of hierarchical structural levels on PP surface wettability. Static contact angle (CA) and contact angle hysteresis (CAH) values are presented with standard deviations (deviations of ± 1° are not shown for the sake of clarity).
2.2 Fabrication of curved surfaces

Curved structured PP surfaces were injection molded on inversely curved structured aluminum mold inserts. Applied curvatures were cylindrically or spherically symmetrical (so-called halfpipe and dome shapes, respectively), both in convex and concave manners. The structures were oriented either radially or vertically with respect to the curvature, depending on the structuration procedure. Figure 3 summarizes the fabrication steps and presents the method used to curve the aluminum foil. Curvature was induced in the planar foil simply by pressing the foil with the steel sphere against the hole, or against the gap in the case of the steel rod. Multiple adjacent dome shapes were produced when the balls and holes were arranged in a $3 \times 3$ square.

To obtain radially oriented surface structures, the foil was microstructured with the microworking robot prior to being bent. The micropit structures were filled and protected with a sacrificial polymer film made of a commercial polymer solution, and the film supported the structures against flattening during the mechanical bending of the foil. Besides the nature of the protective film, the degree of curvature achievable also depends on the foil material and thickness, the bending shape and size, and the applied force. For instance, it is easier to bend the foil one-directionally into a cylindrical shape than three-dimensionally into a spherical shape. In this study, the force applied to the 0.2-mm-thick aluminum foil was $50 \pm 100$ N, depending on the bending shape and size. Nanostructuration was fabricated on the curved foil surface by an anodization process after removal of the sacrificial polymer film. The layer of nanoporous AAO is too brittle to be bent.

Direct microstructuration on the curved foil surface produces vertically oriented structures, since the microworking robot works in the vertical direction. However, achieving precise hierarchical structuration on steeply curved surfaces is difficult. When the working needle faces the sloping surface from above, the position of the micropit slightly shifts downwards, and the alignment of the second structural level inside the pits of the first level becomes inaccurate.
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**Figure 3.** Schematic presentation of the fabrication steps for the curved structured mold inserts and polymer surfaces: (A) radially oriented structures; (B) vertically oriented structures.

2.3 Two-level structures on curved surfaces

The hierarchical MM₁ and MM₂ structure types were fabricated on convex and concave spherically symmetrical surfaces with curvature radii of 4.2 mm and 7.7 mm, and convex and concave cylindrically symmetrical surfaces with curvature radii of 1.7 mm. Vertical microstructures were demonstrated with the MS structure type on the concave cylindrical PP surface with a radius of curvature of 2.7 mm. **Figure 4** presents a selective representation of the fabricated two-level-structured surfaces.

All two-level structures were successfully replicated on the curved PP surfaces by injection molding. The use of the protective polymer film and a sufficient but non-excessive bending force were critical for ensuring that the structures of the mold inserts were not damaged (**Figure 4 B**). Further, instant demolding of the PP samples from the mold inserts was essential for structure replication. Immediately following the injection

![Diagram showing fabrication steps and schematics of structures](attachment:image.png)
Figure 4. Photograph and SEM micrographs of the curved two-level structured surfaces: (A) curved mold inserts and dyed water droplets on the PP surfaces; (B) convex cylindrical mold insert with 1.7 mm curvature radius and MM$_1$ structure type; (C) injection-molded PP replica of the mold insert described in (B); (D) convex cylindrical PP surface with 1.7 mm curvature radius and MM$_2$ structure type; (E) concave spherical PP surface with 4.2 mm curvature radius and MM$_2$ structure type; (F) concave cylindrical PP surface with 2.7 mm curvature radius and vertically oriented MS structure type. The insets of (C) and (D) show a 5 μl water droplet on the surfaces.
phase, the polymer was still elastic and the radially oriented structures were successfully
demolded, even for the most steeply curved surfaces (Figures 4 C and D). In Figure 4 E, the concave spherically curved surface with square-shaped structures demonstrates
that the micropit structures had retained their squareness in the mold insert during the
three-dimensional bending. The multiscale structuration was comprised of the
superimposed protective micropillars on the microroughness structure, and the
fabrication process for this structure is not as sensitive or elaborate as the centering of
the hierarchical microstructures. The vertical multiscale structures were therefore easily
produced on the curved mold insert, and the injection-molded PP replica was detached
without effort, as the structures were oriented parallel to the demolding direction (Figure 4 F).

Spacing between surface structures changes when the structured substrate was curved.
Concave curvature decreases the structure spacing, while convex curvature increases it.
Structure-induced surface properties such as wettability typically depend on the
dimensions and arrangement of the structures.\textsuperscript{100,102} The macroscopic curvature of the
microstructured surface changes the solid–droplet interaction and thus influences
wettability.\textsuperscript{59} Taking the effect of curvature into account, the structure spacings were
adjusted so that they corresponded to those of the planar surfaces. However, the droplet
still interacts with a different number of structures on the curved surfaces than on the
planar surfaces, as the insets of Figures 4 C and D demonstrate. The concave surface in
particular resembles the droplet shape and results in a larger contact area, undoubtedly
affecting the droplet mobility. Determination of the contact angle is ambiguous if the
droplet cannot be clearly observed from a side view or if the droplet settles
asymmetrically with respect to the curvature. The inset of Figure 4 D, however, shows
the ideally settled 5 μl droplet, the size which was used in the CA measurements, on the
convex cylindrical PP surface. Similar apparent CA and air entrapment under the droplet
were obtained for the planar surface.

2.4 Three-level structures on three-dimensional surfaces

Structuration of four length scales was achieved when the hierarchical MMN structures
were combined with the curvature at the millimeter scale on the PP surfaces. Figure 5
presents the surface features from macro- to nanoscale. Nine dome shapes with curvature
radii of 2.2 mm were arranged in a square array, in both convex and concave orientations.
A close-up image of the side of the convex dome shown in Figure 5 E reveals the three-
dimensionally oriented microstructures. The nanostructuration covered even the corners
and sidewalls of the second-level micropillars across the surface (Figure 5 F), clearly
indicating that the layer of AAO can be formed on freely-curved surfaces.

Optimum injection molding parameters are necessary for the creation of well-replicated
structures. Both the melt and mold temperatures, as well as the injection pressure, should
be high enough to completely fill the multi-level micro- and nanoscale cavities of the
mold insert. The melt and mold temperatures are polymer-specific parameters which
cannot be increased excessively without weakening the mechanical properties of the final polymer.\textsuperscript{103,104} Larger structured areas require higher injection pressure for complete filling.

Favorable molding parameters also depend on the surface structures. Typically, the nanostructuration of the mold insert is susceptible to spoiling under unsuitable molding conditions. The polymer can stick to the nanopores and break during demolding, which prevents repeated nanostructure replication. For example, when the MMN structures were repeatedly and successfully replicated from the curved area, the surface of the mold insert outside of this area, where only nanostructures were present, began to be spoiled by the broken nanostructures. Thus, the molding conditions suitable for the three-level structures were too harsh for the one-level nanostructures.

The surface wettability was assessed with manually deposited droplets and droplet sliding tests. The microliter-sized droplet could not be deposited on top of the convex dome, as it slid to the valley between the domes (Figure 5 A). On the concave surface, the droplet tended to settle at the bottom of the depression (Figure 5 B). For these reasons, CAs could not be measured for the curved surfaces. However, as the microdroplets easily slid over the curved structured areas and the structure dimensions corresponded to those of the planar surface, the curved surfaces were also considered superhydrophobic. Droplet size, structure dimensions, and the extent of surface curvature together with the substrate material determine the behavior of the droplet on the curved structured surface. Superhydrophobicity was entirely based on the hierarchical three-level structures and the inherently hydrophobic nature of PP since no chemical surface treatments were applied.
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3 ICE FRICTION OF STRUCTURED POLYMER SURFACES

Microstructurally modified surfaces made of PP and two rubber compounds were tribologically tested against the ice surface. The effects of the microstructure type, ice temperature, and applied load on the ice sliding friction were studied.

3.1 Microstructured polypropylene and rubber surfaces

Micropillar patterns were replicated from the aluminum mold inserts which were micropit-structured with the microworking robot. The three micropattern types included
one-level microstructures, hierarchical two-level micro–micro structures, and protected micro–micro structures. The one-level microstructure also served as the base structural level for the hierarchical structures. The base microstructures were arranged in an equilateral radial array of circles in order to achieve isotropic sliding in the friction tests. The round micropillars had 200 μm-wide bases, height of 70 μm, and were spaced 70 μm apart from each other. Seven hexagonally arranged second-level micropillars, with diameter of 25 μm and height of 30 μm, were centered on top of each base micropillar. For the protected MM structures, 25% of the base microstructures were replaced with a protective microstructure of the same width but with a height of 120 μm. The equally distributed taller micropillars were expected to shelter the second-level micropillars from abrasive wear during the ice friction tests. Similar protective structures have previously been demonstrated to increase the mechanical robustness of hierarchically structured PP surfaces during abrasion against a rough steel surface. The microstructures were injection molded on PP surfaces and hot embossed on rubber sheets of two different hardnesses; the hard rubber had a Shore hardness of A71 and the soft rubber a Shore hardness of A56. The softer rubber was obviously more flexible than the harder rubber. The hot embossing process was performed by Nokian Tyres plc.

Selected polymer samples and their microstructures are illustrated in Figure 6. All three micropattern types are presented for PP (Figures 6 B–D), while only the protected micro–micro structures are shown for the hard rubber (Figure 6 E) and the soft rubber (Figures 6 F and G). As expected, all structures were easily replicated on the PP surfaces. Similar microstructures were also successfully fabricated on both rubber materials by hot embossing. Closer observation revealed differences in the fine surface structures of the materials. PP samples clearly exhibited the smoothest surface qualities. Bump-like surface features existed on both rubber compounds, and the protuberances were attributed to the composition and processability of the rubber materials.

Static CAs and CAHs were determined in order to characterize the wettability of the fabricated surfaces; results are shown in Figure 7. Since the CAs of the flat surfaces were above 90°, all three materials were naturally hydrophobic. The flat rubber surfaces were more hydrophobic than the flat PP surface, which was attributed to the combined effect of the chemical composition and the fine surface structure. The bar graph demonstrates how micro- and micro–micro structures increase the CAs and decrease the CAHs in a stepwise manner. Unexpectedly, the effect of the protective micropillars on wettability was negligible. Both with and without the protective pillars, all hierarchical micro–micro structured surfaces exhibited superhydrophobicity. The taller protective structures increased the area fraction and therefore should theoretically diminish the hydrophobicity. In fact, nine wetting modes exist for the hierarchical two-level-structured surfaces, differing from each other in the way the droplet fills the structural levels. However, determination of the prevailing wetting mode is not possible due to the poor resolution of the CA images.
The one-level microstructure also served as the base structural level for the hierarchical structures. The base microstructures were arranged in an equilateral radial array of circles in order to achieve isotropic sliding in the friction tests. The round micropillars had 200 μm-wide bases, height of 70 μm, and were spaced 70 μm apart from each other. Seven hexagonally arranged second-level micropillars, with diameter of 25 μm and height of 30 μm, were centered on top of each base micropillar.

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Figure 6. Circular polymer samples and SEM micrographs of the microstructures: (A) PP and rubber samples; (B) microstructures on PP; (C) micro–micro structures on PP; (D) protected micro–micro structures on PP; (E) protected micro–micro structures on hard rubber; (F) protected micro–micro structures on soft rubber; (G) close-up of (F).
3.2 Tribological measurements

Ice friction measurements were performed with a pin-on-flat tribometer (CSM Instruments TRN S/N 18-347), in which a linearly reciprocating ice surface slid against a static planar sample. Figure 8 illustrates the main components of the measurement apparatus. Circular 10 mm-diameter samples of PP and both rubber compounds were glued to sample holders, and the rigid PP samples were padded with a layer of flexible silicone rubber to ensure parallel contact with the ice surface. The rubber samples were intrinsically flexible, allowing them to follow the ice surface level more easily. A specific cooling system was developed to freeze the water, maintain the ice temperature, and cool the surrounding air. The ice surface was prepared in a steel rink under which a coolant was circulated, and the intended ice temperature was attained by regulating the coolant temperature. The air around the tribometer was cooled down via circulation of precooled compressed air inside the transparent plastic chamber. The air temperature and relative humidity inside the chamber were regulated to correspond to an absolute humidity of 4–7 g/m³. A new ice surface was prepared, leveled, and polished for each friction test. The inner ice temperature was measured with a contact thermometer, and the ice surface remained stable within the temperature range of $-10^\circ C$ to $-3^\circ C$. Another
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A new ice surface was prepared, leveled, and polished for each friction test. The inner ice temperature was measured with a contact thermometer, and the ice surface remained stable within the temperature range of $-10$ °C and $-3$ °C. Dead weights were used to apply normal loads of 20 N and 40 N, which corresponded to nominal contact pressures of 255 kPa and 510 kPa, respectively, calculated for the flat samples. The sliding friction coefficients were taken as averages of the friction coefficient values in the middle part of the 40 mm sliding track ($\pm 4$ mm from the center) over the total sliding length of 300 m. Static friction is a transient stage which typically lasts for 10–100 ms. Besides the short duration, condition-related factors have been demonstrated to hinder the reliable determination of static friction on ice. Thus, this study focused on the ice sliding friction; the reported sliding friction coefficients are averages taken over the distance of 100–300 m where the friction was stabilized. Wear behavior of the fabricated surfaces could not be quantitatively analyzed. The micrometer-scale height changes could not be explicitly accounted for by the height loss of the microstructures, but were affected by possible height losses on the ice surface. The wear of the friction-tested samples was, however, qualitatively studied by scanning electron microscopy.

Ice sliding friction of the microstructured polymer surfaces was studied with respect to the ice temperature and applied load. The inner temperatures of the ice were $-10$ °C and $-3$ °C. Dead weights were used to apply normal loads of 20 N and 40 N, which corresponded to nominal contact pressures of 255 kPa and 510 kPa, respectively, calculated for the flat samples. The sliding friction coefficients were taken as averages of the friction coefficient values in the middle part of the 40 mm sliding track ($\pm 4$ mm from the center) over the total sliding length of 300 m. Static friction is a transient stage which typically lasts for 10–100 ms. Besides the short duration, condition-related factors have been demonstrated to hinder the reliable determination of static friction on ice. Thus, this study focused on the ice sliding friction; the reported sliding friction coefficients are averages taken over the distance of 100–300 m where the friction was stabilized. Wear behavior of the fabricated surfaces could not be quantitatively analyzed. The micrometer-scale height changes could not be explicitly accounted for by the height loss of the microstructures, but were affected by possible height losses on the ice surface. The wear of the friction-tested samples was, however, qualitatively studied by scanning electron microscopy.

Ice friction behavior at temperatures closer to the ice melting point was studied in collaboration with V-Research GmbH in Austria. With the properly insulated and cooled instrumentation, an inner ice temperature of $-2$ °C was achieved, which was the highest possible temperature that could be stably maintained during the friction tests. The inner ice temperature of $-2$ °C corresponded to an ice surface temperature of $-0.5$ °C outside of the measurement track. The flat and protected micro–micro structured surface types on all three materials were friction-tested at $-2$ °C under a normal load of 20 N.
Comparative ice friction tests were performed to verify correspondence between the two measurement methods.

### 3.3 Ice sliding friction of polymer surfaces

Three microstructured surface types were used in the ice friction tests, and an unstructured flat surface served as a benchmark. The average coefficients of friction (COF) for the ice sliding and their standard deviations for the PP, hard rubber, and soft rubber surfaces at different load and ice temperature conditions are presented as bar graphs in Figure 9.

The PP surfaces exhibited lower ice sliding friction than the rubber surfaces. The sliding friction of the flat PP surface was dependent on the ice temperature. Lower friction values were recorded on the warmer ice (−3 °C), where more lubricating water was available to facilitate sliding, than on the colder ice (−10 °C). The one-level microstructures decreased the sliding friction notably at −10 °C, and only marginally at −3 °C, when compared to the flat benchmark. At −10 °C, the smaller contact area between the microstructured surface and the dry ice surface resulted in the decreased friction, whereas at −3 °C, the melt water increased the contact area between the microstructure and the ice surface and counteracted this reduction in friction. The microstructured PP surfaces themselves exhibited similar sliding friction behaviors with respect to the varying conditions. The second microstructure level increased friction at the lower ice temperature and under the higher applied load. Under a load of 20 N, the increased polymer–ice interlocking resulted in a sliding friction coefficient which was two-fold higher on the −10 °C ice than on the ice at −3 °C. The interlocking was determined via observations of a continuous scratching noise and the evolution of abraded ice flakes around the sliding track. Stick-slip behavior was not, however, observed under the 20 N load at either temperature. Under a 40 N load, the stick-slip phenomenon was observed with both ice temperatures, and the sticking tendency increased the total sliding friction coefficient for the micro–micro structured surface. Under the same 40 N load, the protected micro–micro structured surface showed similar stick-slip behavior at −3 °C, but only a temporary stick-slip behavior for the first 15 meters at −10 °C. This 15 m ‘running-in period’ was not included in the reported COF value, which was calculated over the distance of 100–300 m, but is marked with (#) in Figure 9. A similar running-in period was observed for the one-level microstructured surface under the same conditions. The large microstructures presumably first scraped away the roughness features of the ice surface and then slid over the smoothed ice, resulting in the low total sliding friction under 40 N at −10 °C.
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**Figure 9.** Average sliding friction coefficients for the (A) PP, (B) hard rubber, and (C) soft rubber surfaces at different load and ice temperature conditions. Under the bars of the graphs, # denotes stick-slip behavior during the entire measurement and (#) indicates stick-slip only at the beginning.
The bar chart in Figure 9 B summarizes the ice sliding friction behavior for the hard rubber surfaces. The temperature effect was the most significant under the 20 N load. A COF at least three times higher was recorded on the cold and dry ice at $-10 \, ^\circ\text{C}$ compared to that on the wetter ice at $-3 \, ^\circ\text{C}$. The structuration did not induce any additional effect under the 20 N load. The increased load has been demonstrated to facilitate sliding on cold ice by shifting the friction towards the lubricated regime.\textsuperscript{78} The lower friction values for the flat and microstructured surfaces under the higher 40 N load at $-10 \, ^\circ\text{C}$ can be explained by load-induced lubrication. The hierarchically microstructured surfaces again tended to stick to the ice under a 40 N load at $-10 \, ^\circ\text{C}$, and in contrast to the PP surfaces, the stick-slip behavior was occasional and partly one-directional. The irregular sliding under the heavier load was ascribed to the bendable second-level microstructures and protective micropillars, which resulted in the high sliding friction values. No stick-slip behavior was observed under the same 40 N load on the wetter ice at $-3 \, ^\circ\text{C}$, in which case the lubrication prevented the onset of stick-slip.

The sliding friction coefficients for the soft rubber are shown in Figure 9 C. Distinct trends in the ice friction behavior can be concluded with respect to ice temperature, applied load, and surface structuration. The ice temperature effect was the strongest for the soft rubber amongst all the materials studied. The sliding friction was lower at warmer ice temperature for each surface type under a given load. Correspondingly, friction decreased with increasing load for a particular surface type at the same ice temperature. The effect of the microstructures on the sliding friction was dependent on both ice temperature and applied load, both of which clearly influence the amount of water lubrication. On one hand, enhanced lubrication can make sliding easier, while on the other hand, the water layer can induce resistive forces of capillary drag and viscous shearing. At $-3 \, ^\circ\text{C}$, all the microstructured surfaces exhibited higher COFs than the flat surface. Besides the presumable occurrence of capillary drag between the microstructured surfaces and the ice, it was considered that bending of the soft micropillars added resistance to the sliding. The higher contact pressures of the structured surfaces compared to that of the flat surface also promoted melting of the ice, which further increased the capillary drag. The flat surface instead benefited from the lubrication available at $-3 \, ^\circ\text{C}$. The flat soft rubber surface could tightly flatten against the less-lubricated and rougher ice at $-10 \, ^\circ\text{C}$, resulting in the highest friction values recorded amongst all the surfaces studied. For the structured surfaces, the contact areas were smaller, and the contact pressures were therefore higher. The low sliding friction coefficients were attributed to the reduced contact area and local melting under the areas of the microstructures contacting the ice surface. Considering the standard deviations, the structured surface types did not exhibit significantly different sliding behaviors. Nonetheless, the hierarchically structured surfaces are advantageous due to their water repellency.
The flat and protected micro–micro structured surfaces of all three materials were tribologically tested on ice near its melting point. Figure 10 illustrates the average sliding friction curves as functions of the total sliding distance, along with the average sliding COFs, for each material. The first notable observation was the unexpected oscillating behavior in all the friction curves. A comparison of the friction curves of the flat surfaces (black curves in Figure 10) reveals that the oscillation amplitude increased with increasing material compliance. The amplitude was the lowest for the rigid PP and highest for the soft rubber. This behavior was a result of the thermostatic controller, which cyclically regulated the ice temperature around the value of −2 °C. The inner ice temperature oscillated between −2.3 °C and −1.5 °C during the test periods, and thus small ice-temperature-induced fluctuations in the sliding friction coefficient were captured by the high-accuracy load cell of the tribometer. The actual friction coefficients at −2 °C are thus between the lowest and highest recorded values.

The structured surfaces showed higher sliding COFs than their flat counterparts for all three materials. The increased material compliance enabled larger contact areas with the ice surface and yielded higher friction coefficients. The structured PP surface demonstrated the most striking friction behavior, which is seen as a high-amplitude fluctuation in the friction curve. The oscillation frequency is the same for all curves, and it was thus concluded that the variations in friction originated from the oscillating ice temperature. The highest transient friction was recorded every time the ice temperature was closest to the melting point (−1.5 °C), and the lowest friction was recorded each time the ice temperature reached the minimum of −2.3 °C. The sliding friction tests also made a creaky noise cyclically, becoming louder when the ice temperature approached −1.5 °C and quieting down as it reached −2.3 °C. The temporarily elevated sliding friction coefficient and the simultaneous noise were explained by the increased viscous shearing and drilling of the stiff PP micropillars into the softened ice surface. Neither of the structured rubber surfaces exhibited behavior similar to that of the PP surface, which may have been due to their softness and elasticity.

Figure 10. Average sliding friction coefficients for the flat and protected micro–micro structured PP, hard rubber, and soft rubber surfaces on the ice at −2 °C under a 20 N load. The friction curves and COF values are averages of three tribological tests, and COFs were averaged over the distance 50–150 m.\textsuperscript{III}
3.4 Wear resistance of the structures and comparison of the friction results

Pristine rubber samples with protected micro–micro structures were imaged under 20 N and 40 N loads to observe how the microstructures carry the static applied load (Figure 11). Protective pillars on the hard rubber carried most of the load under 20 N load (Figure 11 A), but on the soft rubber, the load was also carried by the smaller micropillars (Figure 11 C). Figures 11 B and D demonstrate that the protective pillars were flattened to the level of the lower microstructures under the 40 N load. However, the protective pillars on PP carried both static loads easily. Tribologically tested polymer samples were imaged with SEM to qualitatively evaluate structure durability (Figure 12). The microstructures of the PP surfaces best endured the ice friction tests under all experimental conditions. No abrasive wear was observed under the 20 N load, but under the 40 N load, some of the protective pillars had wear debris on them (Figures 12 A and B). Some of the protective PP micropillars were pristine after the 300 m friction test under the 40 N load at −10 °C, and thus presumably the roughness features of the hard ice only partially scraped the structures. The 40 N load was excessively high for both rubber compounds, and due to the insufficient load-bearing capacity of the rubber protective pillars, the second-level microstructures collapsed entirely. The protective pillars, however, successfully supported the 20 N load and the hierarchical microstructures largely maintained their shape and size (Figures 12 C and D). Some second-level microstructures of the soft rubber surface, as shown in Figure 12 D, were bent and asymmetric after tests under the 20 N load. Therefore, the protective micropillars could have been fabricated to be taller on the soft rubber to prevent the deformation of the smaller microstructures. The sliding direction can be observed as

Figure 11. Optical microscopic images of hard and soft rubber compounds with protected micro–micro structures under two loads: hard rubber under (A) 20 N and (B) 40 N loads; soft rubber under (C) 20 N and (D) 40 N loads. Scale bar: 200 μm.iii
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When comparing the friction results of the polymers, the PP surfaces generally showed the lowest sliding friction values. PP was also the only material for which the structure-induced stick-slip or distinct resistive behavior was observed at all tested ice temperatures. Both rubber compounds exhibited clearly different friction phenomena. The harder rubber exhibited lower friction than the softer rubber, as expected. The microstructuration did not noticeably affect the sliding performance, except at the coldest temperature and under the heavier load, where the hierarchical structures induced occasional stick-slip sliding. For the soft rubber, the microstructuration instead increased friction at temperatures near the ice melting point (−3 °C and −2 °C) and decreased it at −10 °C. Variances in the ice sliding friction properties of the similarly microstructured polymer surfaces were concluded to originate from the different hardnesses and elasticities of the polymer materials.
4 CONCLUSIONS

The thesis has demonstrated the applicability of hierarchically structured polymer surfaces in two ways. Different structural hierarchies were accomplished on curved polymer surfaces via injection molding, and the effect of microstructuration on ice friction behavior was explored for three different polymer materials.

Curved hierarchically structured metal mold inserts were developed and successfully employed in polymer injection molding. Different micro–micro hierarchies and a micro–micro–nano hierarchy were first fabricated on planar PP surfaces, and superhydrophobicity was shown to be improved by the added hierarchical levels. Planar structured metal foils were simply bent into spherically or cylindrically symmetrical curvatures to obtain the curved mold inserts, and the micropit structures remained undamaged during the mechanical stress on account of the incorporated sacrificial polymer film. Successful replication with fully filled protruding surface structures was ascribed to appropriate injection molding parameters; in particular, melt and mold temperatures, injection pressure, and proper demolding were critical. Curved hierarchically structured PP surfaces exhibited similar wettability to their planar counterparts. As an ultimate example, the three-dimensionally curved surface with hierarchical micro–micro–nano structures facilitated the repellence of water droplets. The results demonstrate that multilevel structures on three-dimensional polymer surfaces can be mass-produced by injection molding, and that such functional surfaces could be applied to facilitate and direct water movement.

A conventional linear tribometer was equipped with a cooling system in order to determine the ice sliding friction behavior of microstructured PP and two rubber compounds. Ice friction is a highly sensitive surface phenomenon, and reproducible and reliable results can only be obtained under strictly controlled experimental conditions. One-level microstructures, hierarchical micro–micro structures, and protected micro–micro structures were each replicated on PP by injection molding, and on hard and soft rubber compounds by hot embossing. All three materials with hierarchical structures showed superhydrophobicity. The polymer material itself, surface structure types, ice temperature, and applied load all affected the ice sliding friction behavior. Since similar microstructuration resulted in similar wetting characteristics but different dynamic ice friction properties, the diverse frictional behavior was attributed to differences in the mechanical properties of the polymer materials themselves. Taller protective structures were critical in sheltering the functional hierarchical structures from abrasive wear, and their dimensions and surface coverage can be adjusted to achieve adequate protection on a case-specific basis. Structural modification of polymer surfaces is thus an effective method for controlling their frictional behavior on ice. Overall, the results contribute useful perspectives to the understanding of the complex concept of ice friction.

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