Experimental Investigation of a Polymer Coating in Sliding Contact with Skin-Equivalent Silicone Rubber in an Aqueous Environment

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A study on the effect of a brush coating of polyacrylic acid (PAA) grafted with poly(ethylene glycol) (PEG) (PAA-g-PEG) on friction was done for a sliding system that involves silicone skin L7350: a silicone rubber used by the Fédération Internationale de Football Association (FIFA) for the determination of skin–surface friction in combination with artificial grass. Friction experiments were carried out using a reciprocating flat-on-flat test setup with the selected brush coating and compared with PAA-coated and fluoroalkane-coated samples. The experiments were focused on the effect of water. Results for the coatings tested at dry conditions showed a coefficient of friction above 1. Effective lubrication by water was able to reduce friction to a coefficient of friction below 0.01 at low sliding velocities. The results are currently used to further develop low-friction products for sliding interactions with human skin; for example, artificial grass and possibly medical textiles.

KEY WORDS

Boundary Lubrication Friction; Water; Coatings; Friction Reducing

INTRODUCTION

Material selection for sport and personal care products can be done by optimizing the complex interaction between manufacturing costs, functionality, and, for example, environmental impact, durability, color aspects, and design aspects. An important requirement from the user's point of view, however, is the de-gree of comfort during use. This aspect is currently difficult to address in the engineering process, because design diagrams or design rules are missing. Comfort for products that involve static or dynamic contacts with the human skin is tightly linked to tribology of the human skin. Extensive research has been done on modeling and measuring the contact and friction behavior of the skin—see, for example, Zahouani, et al. *(1)*; Adams, et al. *(2)*; Derler, et al. *(3)*; Gitis and Sivamani *(4)*)—and on important topics such as the development of test methods for touch perception (Childs and Henson *(5)*; Barnes, et al. *(6)*; Gee, et al. *(7)*; Darden and Schwartz *(8)*). From these results and others it follows that in vivo testing with representative panels is preferred for measuring and evaluating the performance of products that are in contact with the human skin. Yet, in some cases in vivo testing is not an option; for example, when it inflicts damage to the human body or when panel tests are difficult to organize from a viewpoint of costs or time. An alternative approach is found in evaluation of skin penetration methods (Shergold and Fleck *(9)*), hair care products (Bhushan, et al. *(10)*), and textiles (Derler, et al. *(11)*) in which a skin equivalent or synthetic skin is used; that is, silicone rubber, polyurethane film, and polyurethane coated polyamide fleece, respectively.

The skin equivalent used in the present research is selected based upon the recommendation of the Fédération Internationale de Football Association (FIFA) for the determination of skin–surface friction of artificial football turf (FIFA *(12)*): one of the criteria for the quality of the grass. Low friction in the contact between the skin and the polymer fibers of the grass during sliding will avoid heat generation and high shear loads that otherwise can cause severe injuries to the players' skin. A similar situation exists for textiles, where low friction is beneficial in terms of comfort (Derlet, et al. *(11)*). Friction is an important parameter in the formation of pressure ulcers (Dinsdale *(13)*), and low friction during use of medical textiles is thought to be beneficial in prevention of these ulcers (Gerhardt, et al. *(14)*).
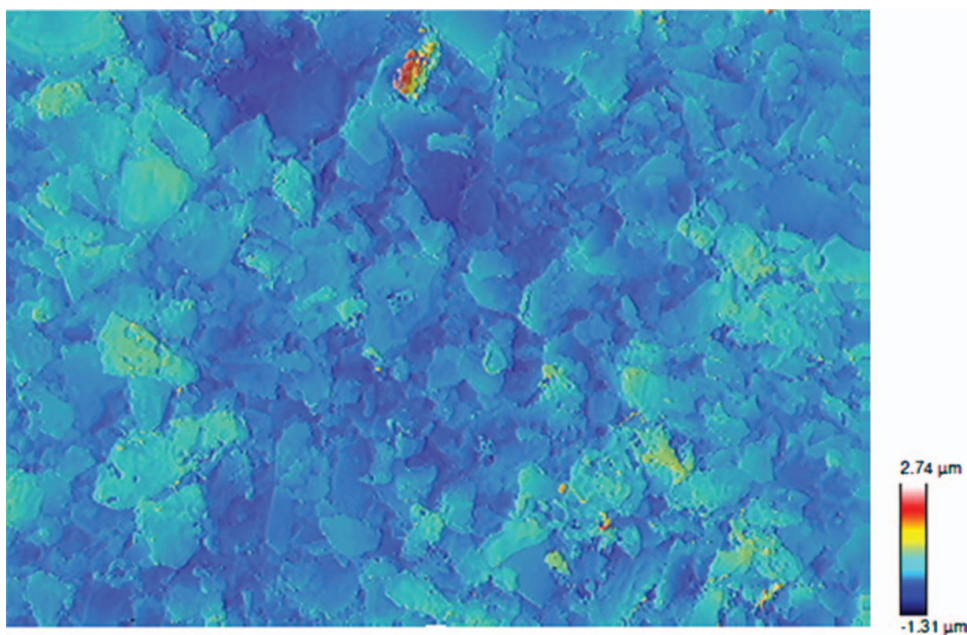
Fig. 1—Silicone Skin L7350 surface, 85 × 62 μm^2.

This work focuses on the friction between a polymer brush coating, polyacrylic acid (PAA) grafted with poly(ethylene glycol) (PEG) (PAA-g-PEG), in contact with silicone rubber as a skin equivalent. This polymer brush coating can be put on the surfaces of consumer products such as textiles. Polymer brush coatings represent a promising class of coatings for friction control (Klein, et al. *(15)*) and especially for friction reduction in an aqueous environment (Ikeuchi *(16)*). Extensive work on the lubricating action of polymer poly(L-lysine)-graft-poly(ethylene glycol) (PLL-g-PEG) layers confirmed the possibility of friction reduction at boundary lubrication conditions in an aqueous solution for glass–steel (Müller, et al. *(17)*; Müller *(18)*), polymers (Lee and Spencer *(19)*), and SiC and Si3N4 ceramics (Hartung, et al. *(20)*). The excellent lubrication properties of PLL-g-PEG have been ascribed to its dense, brush-like structure that is highly solvated under good solvent conditions. An alternative approach was found recently (Ten Cate, et al. *(21)*) by attaching PEG chains to a polyacrylic acid backbone by chemical coupling. This work describes research focused on the effect of water on the tribological performance of the previously developed and described PAA-g-PEG coating (Ten Cate, et al. *(21)*) at low sliding velocities.

EXPERIMENTAL

Materials

Test pieces were made, each 10 × 10 × 4 mm, from Silikon MVQ L7350 sheet, supplied by Maag Technic AG (Duebendorf, Switzerland). The shore hardness of this quality is 50 Shore A. This specific silicone rubber is selected based on a FIFA test in which Silicone Skin L7350 is taken as skin substitute for measurements with artificial turf (FIFA *(12)*). The two sides of the test sheet differ greatly in roughness. All tests were done using the smooth side of the test piece; see Fig. 1 for a representative view of a nontested surface. The centerline average roughness value based on area measurements of 85 × 62 μm^2 varied between 149 and 166 nm.

Standard laboratory glass with dimensions 76 × 26 × 1 mm was taken as counter material. A layer based on polyacrylic acid, polyacrylic acid grafted with polyethylene glycol, or a fluoroalkane monolayer was put on the glass substrate. Hence, three variants were evaluated:

1. Coated with PAA
2. Coated with PAA-g-PEG
3. Coated with fluoroalkane

Surface 2, coated with PAA-g-PEG, is the surface of interest. Surface 1 is an intermediate stage in the coating process. Because water lubrication is the focus of the research, we decided to compare the expected hydrophilic surfaces 1 and 2 with a strong hydrophobic surface; that is, coated with fluoroalkane, surface 3.

Functionalization of glass with amino moieties was selected as the first step for surfaces 1 and 2. Glass slides were cleaned using piranha acid (1:3 vol% H_2O_2:H_2SO_4) for a period of 30 min, after which they were washed extensively with demineralized and ultrapure water. These precleaned glass substrates were submerged in a fresh solution of 5 wt% 3-aminopropyltrimethoxysilane (APTMS) in isopropyl alcohol and sonificated for 20 min in an ultrasonic bath. The substrates were thoroughly washed (3×) with demineralized and ultrapure water followed by drying for 1 h in an oven at 60°C. Further functionalization with PAA was done by dipping of the amino-functionalized glass substrates in a solution of polyacrylic acid (Mw 1,080.000; Mn 135.000) in ultrapure water (0.5 wt%). The samples were subsequently dried in an oven at 100°C under reduced pressure (<100 mbar) for 4 h. The substrates were thoroughly washed (3×) with demineralized and ultrapure water to remove the physically adsorbed/not chemically bonded polyacrylic acid. The samples were dried using an

Fig. 2—Overview of the flat-on-flat contact between the silicone rubber test piece and the (coated) substrate.

N_2 flow. Further functionalization to a brush-like coating with a strong hydrophilic character based on PEG was done by dipping the PAA substrate in a solution of 1 wt% of monofunctionalized amino-PEG (Mw 5,400; Mn 5,000) in water. The samples were subsequently dried in an oven at 120°C under reduced pressure (<100 mbar) for 1 h. The substrates were thoroughly washed (3×) with demineralized and ultrapure water to remove the physically adsorbed/not chemically bonded PEG.

A strong hydrophobic surface was created by functionalization of glass with fluoroalkane. Glass slides were cleaned using piranha for a period of 30 min, after which they were washed extensively with water and dried using an N_2 flow. These pre-cleaned glass substrates were submerged in a fresh coating solution of 2% 1H-1H-2H-2H-perfluorodecyltrichlorosilane in dry toluene for 45 min while shaking modestly. The substrates were thoroughly washed (3×) with toluene followed by drying for 20 min in an oven at 60°C. APTMS, PAA, and PEG were obtained from Aldrich (Zwijndrecht, The Netherlands), Acros Organics (Geel, Belgium), and Polymer Source Inc. (Montreal, Canada), respectively.

No additional cleaning before testing was done for the coated surfaces, because it could alter the surface treatment.

Contact Angle Measurements

Contact angle (CA) measurements were carried out with a KRÜSS DSA 100 system (Hamburg, Germany). The contact angle was measured on static drops, by measuring the angle between the baseline and the tangent at the drop boundary directly after application. Two liquids were used for this: ultrapure water H_2O (3 μL drop) and diiodomethane CH_2I_2 (1.5 μL drop). Water was used to show hydrophilic–hydrophobic behavior, and diiodomethane was selected as an indicator for the presence of PEG.

Friction Tests with and without Water at Low Sliding Velocities

Friction tests were carried out at low sliding velocity with a reciprocating flat-on-flat test setup. This configuration was realized on the commercially available tribometer PLINT TE67 (Phoenix Tribology Ltd., Newbury, UK), for which a dedicated glass support unit was constructed; see Fig. 2. All experiments were carried

out at room temperature and in air. The humidity and the temperature of the room varied respectively between 20 and 40% and between 19 and 22°C. The track length was set to 40 mm for all experiments. Ten strokes were carried out per experiment (five from left to right and five from right to left), with a new silicone rubber sample. The sliding velocity v during the track was set to 1, 10, or 62 mm/s. The normal load Fn was applied by the mass of the specimen holder or by an additional dead weight to a resulting normal force of, respectively, 2.9 and 9.8 N or in terms of contact pressure p of 0.03 and 0.1 MPa. These contact pressures were higher than the 0.004 MPa reported as clinically realistic for supine persons on a foam mattress (Gerhardt, et al. *(14)*) and lower than the 0.23 MPa measured for highly stressed local contact at the forefoot during walking (Dai, et al. *(22)*). Tests were performed with and without demineralized water. The first condition is referred to as with water and the second as dry condition.

Each material combination was evaluated at the three selected sliding velocities, the two selected contact pressures, with water and at dry conditions, all twofold. Thus, 72 experiments were performed. The friction force was measured during these experiments and the average coefficient of friction was calculated over the full test cycle of 10 tracks. All experiments were conducted twofold; thus, two mean values were available for each combination. The average of the two was taken as ranking value and used to compare the results of the experiments.

RESULTS

Contact Angle Measurements

A summary of the contact angle measurements for ultrapure water H_2O and diiodomethane CH_2I_2 are given in Table 1.

The contact angle measurements clearly show the hydrophilic character of surfaces PAA and PAA-g-PEG and the hydrophobic character of the fluoroalkane surface and the silicone rubber surface. The contact angle measured for functionalization with PAA was 20°. No clear change in wettability using water drops occurred after further functionalization based on PEG. Using diiodomethane as liquid, different contact angles were found, indicating that PEG is indeed grafted on PAA. Contact angle measurements of water at the fluoroalkane-coated surface confirmed the expected hydrophobic behavior of the layer because a contact angle of 120° was found.

Sliding Friction

The results obtained for dry conditions and for water lubricated conditions are summarized by Figs. 3a–3c for the PAA-coated surface, the PAA-g-PEG–coated surface, and the

TABLE 1—OVERVIEW OF CONTACT ANGLE (CA) MEASUREMENTS

	Static CA (°)	
	H_2O	CH_2I_2
Silicon rubber	89–93	88–90
PAA coating	20	35–40
PEG coating	18	16–20
Fluoroalkane coating	120	106

(a)

× PAA (dry) □ PAA (water)

f [-]

v/p [m³/Ns]

(b)

× PAA-g-PEG (dry) □ PAA-g-PEG (water)

f [-]

v/p [m³/Ns]

(c)

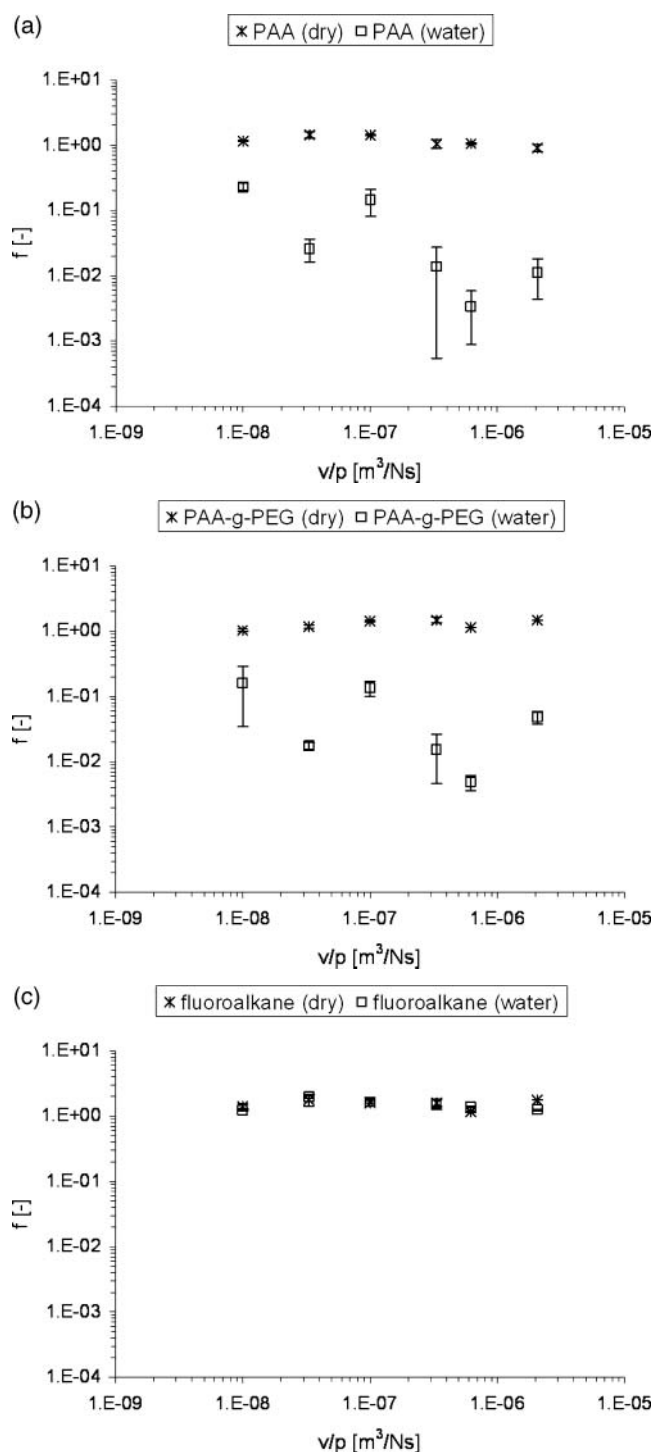× fluoroalkane (dry) □ fluoroalkane (water)

f [-]

v/p [m³/Ns]

Fig. 3—Friction values at dry conditions and at water lubricated conditions for (a) coated with PAA, (b) coated with PAA-g-PEG, and (c) coated with fluoroalkane substrates in combination with silicone rubber.

fluoroalkane-coated surface, respectively. The average friction data, with the standard deviation as error bar, is not plotted as a function of the usually selected Stribeck or Hersey number $H = \eta \, v/p$ (m) (see, for example, Schipper and de Gee (23)) because it has no relevance for the friction values measured at dry con-

ditions. Therefore, we decided to use the quotient v/p (m³/Ns) as operational number at the x-axis of the graphs (Bierlein, et al. (24)). Multiplying the x-axis values by the dynamic viscosity η of water in (Pa**cot**s) will give the Stribeck or Hersey number representation in the water-lubricated case.

The experimental results showed a dry coefficient of friction value $f \approx 1$ for all tribopairs. This level could not be reduced greatly by changing the operational conditions within the selected window. Yet, the presence of water had a great impact on the tribological behavior of the hydrophilic systems. A major reduction in friction was found for the PAA-coated and PAA-g-PEG–coated surfaces in the presence of water. The actual reduction varied with the operational conditions for both the PAA-coated surface (Fig. 3a) and the PAA-g-PEG–coated surface (Fig 3b), from at least 80% to a maximum reduction in friction of >99%. The lowest absolute values were found at a contact pressure of 0.1 MPa and at 62 mm/s sliding velocity: $f = 0.0034 \pm 0.0025$ and $f = 0.0049 \pm 0.0012$ for the PAA- and PAA-g-PEG–coated surface, respectively. For these systems, the water-lubricated friction coefficient was, respectively, 99.7 and 99.6% lower than the dry coefficient of friction.

The presence of water did not reduce friction for the fluoroalkane-treated substrates, as can be seen from Fig. 3c. Friction remains rather constant as a function of the quotient of velocity and pressure at $f \approx 1$.

DISCUSSION

With water, friction is reduced greatly for the hydrophilic PAA-coated and PAA-g-PEG–coated surfaces and remains constant for the hydrophobic fluoroalkane-coated surface. The measured friction reduction of more than one order of magnitude by changing a hydrophobic–hydrophobic tribopair to a hydrophobic–hydrophilic tribopair is in good agreement with the work of Bongaerts, et al. (25) on water-lubricated soft contacts. The hydrophilic character of the PAA- or PAA-g-PEG–coated surface causes a lubricating water layer to remain in the contact, whereas this layer is removed from the contact that involves hydrophobic surfaces only.

The effect of the operational number v/p on friction for the water-lubricated condition shows a similar pattern as a function of the parameter v/p for the PAA coating and the PAA-g-PEG coating. This pattern is related to the contact pressure that is used for the experiments. At 0.03 MPa contact pressure, friction changed as the sliding velocity was increased from 1 to 10 and 62 mm/s to, respectively, $f = 0.026$, $f = 0.014$, and $f = 0.011$ for PAA and $f = 0.018$, $f = 0.015$, and $f = 0.049$ for PAA-g-PEG. The mean value of friction increased when the contact pressure of 0.1 MPa was applied at 1 and 10 mm/s sliding velocity and decreased at 62 mm/s sliding velocity, compared to the same experiments at $p = 0.03$ MPa. This behavior resulted in the pattern that is visible in Fig. 3a and Fig. 3b. Furthermore, from the error bars in Fig. 3 it is shown that the mean friction value varies in case of the water-lubricated condition. The effect of the sliding velocity at $p = 0.03$ MPa and the relative importance of the standard deviation present at the water-lubricated conditions can be explained from the configuration that was used for the research;
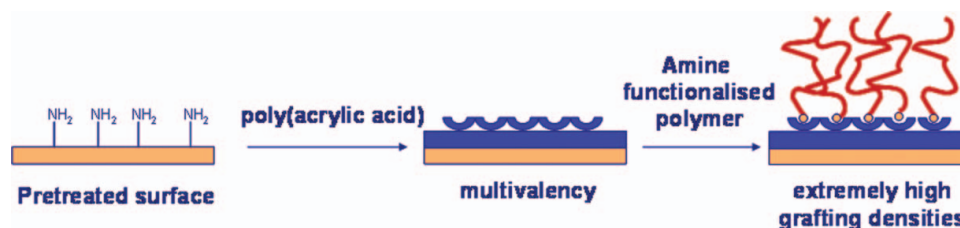
Fig. 4—Conceptual presentations of the different steps in coating preparation.

that is, a flat-on-flat contact. Hydrodynamic effects are excluded for this setup because all three effects (Czichos and Habig *(26)*) that could generate pressure based on the Reynolds equation are reduced to zero: the required wedge geometry is absent, there is no stretching in the plane of sliding during the test, and there is no squeezing action during the test. An increase in velocity will therefore not cause a transition from the boundary lubrication regime to the mixed lubrication regime by the introduction of hydrodynamic effects. Yet, small misalignments or small curvatures at the leading edge of the contact will directly introduce a water flow in the contact and consequently add a hydrodynamic component to the test results. Because the sliding velocities used were low, these effects were expected to be minimal, but from the low friction results it is clear that some variation was introduced. The specific effect of pressure in the current test setup is likely related to the lubricating properties of the film. An increase in friction occurred at $v = 1$ and $v = 10$ mm/s. A decrease in mean friction occurred when the sliding velocities increases to $v = 62$ mm/s for the PAA coating and for the PAA-g-PEG coating. This suggests an optimum in operating conditions.

The excellent lubrication properties of PAA-g-PEG in the presence of water can be explained further from its specific structure. Figure 4 conceptually depicts the different steps of the current coating process in which a layer of polyacrylic acid is covalently bonded to the glass surface by pretreatment with 3-aminopropyltrimethoxysilane. The polyacrylic acid coating serves as a primer layer for the relatively long polyethylene glycol chains, which are connected to the primer in a dense, brush-like structure. A comprehensive analysis of the prepared coatings by spectroscopic ellipsometry and X-ray photoelectron spectroscopy was previously conducted and reported (Ten Cate, et al. *(21)*). Ellipsometry on silicon wafer substrates showed PAA primer layers to be 6.8 ± 0.1 nm (three samples) and PAA-g-PEG layers that ranged between 13.6 and 22.1 nm (five samples), corresponding to a grafting density of 1.9 to 3.0 chains/nm^2 (Ten Cate, et al. *(21)*). Water added to the tribosystem is thought to be adsorbed by the layer and expand the polymer chains in a direction normal to the surface, forming a brush-like structure, similar to brush coatings that are based on adsorbed polymer chains onto negatively charged surfaces (Müller, et al. *(17)*).

Thus, the PAA-g-PEG coating does not only cause a lubricating water layer to remain in the contact by its hydrophilic character; it can also bond water in its structure. This combination can explain the large reduction in friction at low sliding velocities. The difference in velocity between two surfaces in sliding contact can now be accommodated by shearing of a thin water film that is cre-

ated in the contact area by applying a normal load. Such a layer is able to effectively separate the two tribological surfaces during sliding contact and as a consequence minimize the high adhesive contribution to friction that occurs for dry contact. The mechanism of release of water by applying pressure to the contact was referred to as *hydration lubrication* by Ikeuchi *(16)*. The capacity of the layer to adsorb or bond water seems more important at this point than the existence of a brush, because of the known capability of engineering surfaces containing absorbed or trapped fluids to reduce friction in general (Ikeuchi *(16)*). The results with PAA confirm this. This layer is also capable of reducing friction in the presence of water to the same low levels as PAA-g-PEG despite the fact that it cannot form a brush-like structure.

Hydration lubrication is not possible with the fluoroalkane coating because of its hydrophobic character. Water will be squeezed out of the contact, such that direct contact could occur, with related high friction.

CONCLUSIONS

The tribological performance of a polymer brush coating based on polyacrylic acid grafted with polyethylene glycol (PAA-g-PEG) was assessed in combination with a mechanical skin equivalent—Silicone Skin L7350—at dry and water-lubricated conditions. Experiments were performed with a PLINT TE67 tribometer with a flat-on-flat configuration at low sliding velocities. Comparative measurements were done with a PAA-coated substrate and a fluoroalkane-coated substrate. Results for the combinations at dry conditions showed a relatively high level of friction of $f \approx 1$. The use of water changed this for the two layers that are hydrophilic and able to capture water in their structure; that is, PAA and PAA-g-PEG. The actual reduction varied with the operating conditions for both coatings from at least 80% to a maximum reduction in friction of >99%. The lowest absolute values were found at a contact pressure of 0.1 MPa and at 62 mm/s sliding velocity: $f = 0.0034 \pm 0.0025$ and $f = 0.0049 \pm 0.0012$ for the PAA- and PAA-g-PEG–coated surface, respectively. The results confirmed the potential of the PAA and PAA-g-PEG coatings for boundary lubrication applications involving silicone rubber and an aqueous environment.

Hydration lubrication is not only promising from the viewpoint of low friction during skin–product interactions: The potential possibility to induce lower frictional behavior just by the application of water makes it especially attractive for applications in which the fluid can be removed from the system after use. Hence, creating a reversible system with two distinctively different friction levels. The next step in our research is to develop low-friction

products for sliding interactions with human skin, such as artificial grass or medical textiles, based on these results.

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