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Fluorine-Free Anti-Smudge Polyurethane Coatings

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Abstract: *Conventionally, low-surface-tension fluorinated reagents are incorporated into anti-smudge (oil- and water-repellent) coatings for oil repellency. However, fluorinated compounds are expensive and an environmental concern because of their high stability and bioaccumulation. These factors limit their widespread application. We report herein the development of fluorine-free anti-smudge polyurethane coatings that are clear at thicknesses up to tens of micrometers and are able to sustain extensive surface damage. We demonstrate that these coatings can be applied readily onto a diverse range of substrates.*

Self-cleaning windows, grease-repelling dining tables, stain-resistant automobile interiors, and graffiti-impeding walls help beautify the world around us. A cleaner world is possible with clear anti-smudge coatings that are highly repellent against water- and oil-borne contaminants. There have been many attempts to create such coatings. For example, fluorinated particles have been cast onto various substrates to yield nano- and microarchitectured coatings.[1–8] Although these coatings exhibit superior oil and water repellency, they (except in rare cases[9]) lack optical clarity and wear resistance.[10] Alternatively, fluorinated liquid polymers, such as perfluoropolyethers, can be grafted onto plain substrates to yield anti-smudge monolayers from which liquid droplets cleanly slide off upon substrate tilting.[11–13] The drawbacks in this case include the thinness of these monolayers and their lack of wear tolerance. In another approach, polyurethane (PU) formulations have been modified with fluorinated reagents to introduce anti-smudge or amphiphobic properties.[14,15] Although PU coatings can be applied at various thicknesses and bind well to many substrates,[15] past challenges had included their cloudy appearance and lack of long-term smudge repellency. These challenges have been overcome recently;[16] however, a major remaining hurdle is the use of perfluorinated moieties, which have been deemed essential for oil repellency because of their low surface tension. These species are about one hundred times more expensive than reagents typically found in commodity coatings, such PU coatings. Furthermore, they do not readily degrade and bioaccumulate, thus presenting an environmental concern.[17] These considerations limit the widespread application of fluorinated anti-smudge coatings. Therefore, inexpensive and environmentally friendly fluorine-free anti-smudge coatings are highly desirable. We report herein the preparation of fluorine-free anti-smudge PU coatings that are clear at thicknesses up to tens of micrometers and can preserve their key properties after extensive surface damage. We demonstrate that the new PU coatings can be readily applied onto diverse substrates. They do not surface-reconstruct and they retain their anti-smudge properties even after extended contact with test liquids.

Our investigation was inspired by reports from the McCarthy[18] and Hozumi groups,[19,20] who demonstrated that hexadecane, water, and other droplets cleanly glided down tilted silicon wafers that were grafted with monolayers of flexible organic compounds and poly(dimethylsiloxane) (PDMS) chains. Indeed, the water repellency of PDMS as observed by Hozumi and-co-workers was expected because PDMS possesses a room-temperature surface tension of 20 mN m^{-1},[21] which is much lower than that of 72.8 mN m^{-1} for water.[22] However, its repellency of hexadecane was surprising because PDMS and hexadecane are miscible liquids. Furthermore, the surface tension of 27.5 mN m^{-1}[22] of hexadecane is close to that of PDMS, and the static contact angle of hexadecane on the grafted PDMS layer was low at 33°.[20] Our rationalization of this observation was that the grafted PDMS chains existed as a nonswollen PDMS liquid film when in contact with an incompatible test liquid and as a swollen PDMS liquid film when in contact with a compatible test liquid. This liquid film converted a liquid/solid interface between the applied liquid and the substrate in the absence of the coating into a liquid/liquid interface. As is well-known, a liquid flows fastest in the center of a viscometer capillary and does not flow close to the capillary wall as the friction coefficient (typically known as viscosity) between two liquid layers is much smaller than that between a liquid and a solid.[23] Therefore, most applied liquids, including low-surface-energy liquids, readily slipped down a liquid PDMS coating, nonswollen or swollen, once the substrate was tilted.[19,24,25] Although the dynamic dewetting properties observed previously were striking, we imagined that these ultrathin monolayers would not survive many rubbing cycles when used on a substrate such as a touch screen. Furthermore, the grafting chemistry needed to be tailored for a particular substrate.

We hypothesized that we could overcome the shortcomings of the PDMS monolayer coatings by incorporating PDMS into thicker PU coatings that bind well to many substrates. We imagined that a PDMS monolayer would spontaneously form on the surface of a PDMS-containing PU film during coating formation owing to the self-stratification of PDMS.[26,27] PDMS would be a good alternative to fluorinated polymers because PDMS is an inexpensive commodity rubber and has been widely used, including in human bodies as breast implants. We further desired the following features for a superior coating: First, the coating

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should not undergo surface reconstruction, which involves the "sinking" of the PMDS chains into the coating matrix upon contact with a test liquid and thus the exposition of the other components, which do not dynamically repel the test liquid. Second, it should be optically clear even at thicknesses up to tens of micrometers. Third, the coating should retain its anti-smudge properties even after extensive surface wear.

We envisioned that surface reconstruction could be mitigated by heavily cross-linking the PU matrix. This strategy would also minimize the sorption of test liquids by the PU matrix and the embedded PDMS chains. Thus, a styrene/methacrylate oliogomer, P1-0, with multiple hydroxy groups per molecule was used as the polyol component (see Scheme S1 in the Supporting Information). The polyisocyanate component used was also multifunctional and was a hexamethylene diisocyanate trimer (HDIT; Figure 1 a). Aside from their high functionality, the two components were also chosen because they reacted with one another to produce a harmless clear PU that had been widely used as an interior coating for cars.

We further envisioned that clear coatings could be obtained by eliminating macrophase separation between the embedded PDMS chains and the PU matrix. Thus, PDMS−COCl (Figure 1 b) was treated with P1 (Figure 1 c), a purified and higher-molecular-weight version of P1-0, to yield a graft copolymer P1-*g*-PDMS$_{68\%}$, in which 68 % refers to the weight fraction of PDMS in the graft copolymer. To remove possible ungrafted PDMS chains from P1-*g*-PDMS$_{68\%}$, we purified it by fractional precipitation to yield P1-*g*-PDMS$_{29\%}$. At the weight fractions of 68 and 29 %, the average number of PDMS chains grafted per P1 chain was 1.2 and 0.22, respectively.

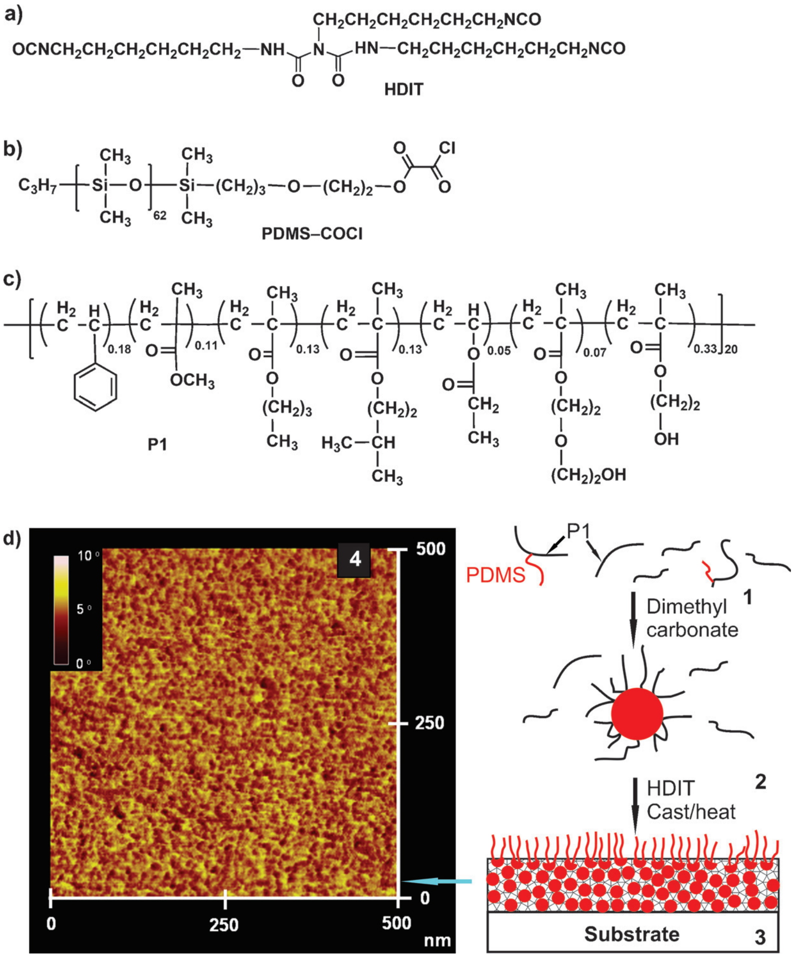

Figure 1. a–c) Chemical structures of HDIT, PDMS−COCl, and P1. d) AFM cross-sectional phase image of a P1-*g*-PDMS$_{68\%}$-modified coating containing 9.2 wt % PDMS, and schematic representation of the protocol used for preparing coatings from P1-*g*-PDMS$_{29\%}$, HDIT, and P1-0. The dispersion of P1-*g*-PDMS$_{29\%}$ and P1-0 in dimethyl carbonate yields P1-*g*-PDMS$_{29\%}$ micelles coexisting with P1 and P1-0 chains (**1**→**2**). Casting of the micellar mixture after HDIT addition, evaporation of the solvent, and then curing of the dried film at 120 °C yielded a coating with embedded PDMS nanodomains (**2**→**3**).

The PDMS mass fraction in the final PU coating was tuned by incorporating a controlled amount of P1-*g*-PDMS$_{68\%}$ or P1-*g*-PDMS$_{29\%}$ into the commercial HDIT and P1-0 coating mixture. We suspected that the reaction of P1-0 and P1-*g*-PDMS$_{68\%}$ (or P1-*g*-PDMS$_{29\%}$) with HDIT could still produce domains rich in reacted P1-0 and graft copolymer, respectively (see Table S3 in the Supporting Information). Thus, we avoided this complication by casting coating solutions from a selective solvent, such as acetonitrile or dimethyl carbonate, for P1-0, P1, and HDIT. We anticipated that in these solvents, the PDMS pendant chains of different graft-copolymer molecules would aggregate to form the cores of graft-copolymer micelles (structure **2**, Figure 1 d). Since the coronal P1 chains of the micelles and P1-0 were structurally similar, the micelles and P1-0 would mix well and their subsequent reaction with HDIT would yield films containing uniformly distributed PDMS nanodomains. Because the micellar domains would be small, the resultant coating would not scatter much light and would thus appear clear (structure **3**, Figure 1 d). We further anticipated that this nanostructured coating would be self-healing[28–30] and retain its anti-smudge properties even after surface wearing because the removal of a top layer would expose the embedded PDMS nanodomains (nanoreservoirs), which would release fresh PDMS chains to the newly generated surface.

By following the approach described above, we directly dispersed P1-*g*-PDMS$_{29\%}$ and P1-0 into hot acetonitrile or dimethyl carbonate at room temperature to yield a solution containing P1-*g*-PDMS$_{29\%}$ micelles (**1**→**2**, Figure 1 d). After the addition of HDIT, the solution was cast onto glass plates (see Table S3). Optically clear films were eventually obtained after solvent evaporation and coating curing at 120 °C for 12 h (**2**→**3**). Although the complete consumption of the isocyanate groups under these conditions was confirmed by a FTIR spectroscopic study (see Figure S6), we controlled the thickness of the coatings by adjusting the amount of PU precursor cast per unit glass surface area. However, P1-*g*-PDMS$_{68\%}$, owing to its high PDMS content, did not readily disperse in acetonitrile or dimethyl carbonate. Thus, a general protocol also suitable for preparing coatings containing P1-*g*-PDMS$_{68\%}$ involved first heating a graft copolymer and P1-0 with HDIT in acetone, a good solvent for all components, including PDMS, before evaporation of most of the acetone and the addition of acetonitrile or dimethyl carbonate (see the Supporting Information) to prepare a micellar solution. Heating of the graft copolymer in acetone led to the consumption of 19 mol% of the isocyanate units (see Figure S5 for FTIR spectroscopic evidence), the attachment of some HDIT units to the P1 backbone of P1-*g*-PDMS$_{68\%}$, and improvement of the dispersion of P1-*g*-PDMS$_{68\%}$ in acetonitrile or dimethyl carbonate. For consistency, we prepared all further coatings by this general protocol.

We confirmed micelle formation from P1-*g*-PDMS$_{29\%}$ and P1-*g*-PDMS$_{68\%}$ in acetonitrile and dimethyl carbonate by dynamic light scattering (DLS; see Table S1). For example, we prepared a coating solution of P1-*g*-PDMS$_{68\%}$, HDIT, and P1-0 by using the general protocol that involved prior heating in acetone and then acetone replacement with acetonitrile. DLS analysis of this sample detected micelles with an average hydrodynamic diameter of (85 ± 9) nm. This value decreased to (35 ± 5) nm for a P1-*g*-PDMS$_{29\%}$/HDIT/P1-0 mixture prepared in an analogous manner.

We confirmed the absence of large domains in the P1-*g*-PDMS$_{68\%}$-modified coatings at PDMS contents of 9.2 and 25 wt%. The coating samples were embedded between heated polystyrene plates and microtomed to yield thin sections. Topography and phase images of the thin sections were obtained by atomic force microscopy (AFM; see Figure S11). Figure 1 d shows an AFM phase image (labeled **4**) for a coating containing 9.2 wt% PDMS. Brown or yellow domains corresponding to regions of different hardness were clearly observed. More importantly, the domain sizes never exceeded about 30 nm. Therefore, macrophase separation did not occur in this sample. Furthermore, the internal morphology was similar from region to region in agreement with our hypothesized coating internal structure (structure **3**, Figure 1 d).

We also replaced P1-0 with other polyol precursors, such as a polytetrahydrofuran diol, and prepared coatings with different degrees of cross-linking (see Table S3). A systematic comparative study of the properties of the resultant coatings confirmed the importance of heavy PU cross-linking in the initial and long-term hexadecane repellency. At low PU cross-linking densities, PDMS incorporation did not offer hexadecane repellency. As the degree of matrix cross-linking increased, freshly dispensed hexadecane droplets were repelled. However, the droplets were pinned to the coatings after sitting on them for 24 h as a result of surface reconstruction. In contrast, hexadecane droplets that had sat for 72 h on coatings prepared from P1-*g*-PDMS$_{68\%}$ (P1-*g*-PDMS$_{29\%}$), HDIT, and P1-0 still cleanly glided down the surface without leaving a trace when the substrate was tilted slightly. Thus, the heavily cross-linked coatings exhibited no noticeable surface reconstruction even after prolonged contact with hexadecane.

The anti-smudge properties of some P1-*g*-PDMS$_{68\%}$-containing coatings were shown not to change over an observation period of 7 months under ambient conditions. Thus, the coatings did not undergo surface reconstruction during storage. We also attempted an unusual experiment in which we placed a coating sample under vacuum with a mechanical vacuum pump in the presence of the drying agent $CaCl_2$ for 6 h. This drying treatment also did not change the dewetting properties of the coatings.

By avoiding macrophase separation, we obtained clear PDMS-containing PU coatings. We measured the optical transmittance T at 500 nm for P1-*g*-PDMS$_{68\%}$- and P1-*g*-PDMS$_{29\%}$-modified PU coatings as a function of their thickness at 9.2 wt% PDMS and as a function of the PDMS mass fraction at a film thickness of (6.9 ± 0.5) μm (Figure 2 a,b). The results show that the P1-*g*-PDMS$_{68\%}$-containing coating had a transmittance close to 90% at a thickness of 10 μm and a PDMS amount of 9.2 wt%. More strikingly, a P1-*g*-PDMS$_{29\%}$-containing coating at 9.2 wt% PDMS and a thickness of 32 μm still had a transmittance of 95.5%. Thus, the P1-*g*-PDMS$_{29\%}$-containing coatings possessed superb optical clarity.

The P1-*g*-PDMS$_{29\%}$-modified coatings probably showed higher transmittance than their corresponding P1-*g*-PDMS$_{68\%}$-modified coatings for two reasons. First, the P1-*g*-PDMS$_{29\%}$ micelles in acetonitrile before casting were smaller than the P1-*g*-PDMS$_{68\%}$ micelles. Smaller micelles should lead to smaller PDMS domains in the cured PU coatings. Second, P1-*g*-PDMS$_{29\%}$ was purified by fractional precipitation and probably contained a lower molar fraction of free PDMS chains if any. Free PDMS impurities in P1-*g*-PDMS$_{68\%}$ could increase the size of the PDMS domains. Larger PDMS domains should scatter light more effectively.

Clean sliding of 15 μL water and hexadecane droplets was observed on a P1-*g*-PDMS$_{68\%}$-modified coating (Figure 3 a,b; see the Supporting Information for quantitative wetting properties, including the sliding angles for water, diiodomethane, and hexadecane droplets on a series of P1-*g*-PDMS$_{29\%}$-modified coatings as a function of the PDMS mass fraction, as well as the static, advancing, and receding contact angles and the sliding angles of these three test liquids for a series of P1-*g*-PDMS$_{68\%}$-modified coatings). Above their sliding angles, water, diiodomethane, and hexadecane droplets cleanly glided down all coatings with a PDMS content between 4.2 and 25.7 wt%. Furthermore, the sliding angle for 5 μL hexadecane droplets was decreased from 4.6 to 2.6° as the PDMS content increased from 4.2 to 12.3 wt% for the P1-*g*-PDMS$_{29\%}$-modified coatings. These low sliding angles exemplify the exceptional repellency of our coatings towards hydrocarbons. Finally, the lowest sliding angle observed for diiodomethane and water was 8 and 38°, respectively. Given that the highest static contact angle was 34 and 72°, respectively, for hexadecane and diiodomethane on these coatings, the liquids were repelled as a result of dynamic dewetting.

To determine the critical surface tension below which dynamic dewetting would not occur anymore, we investigated the sliding behavior of a series of liquids with decreasing surface tensions on a P1-*g*-PDMS$_{29\%}$-modified PU coating

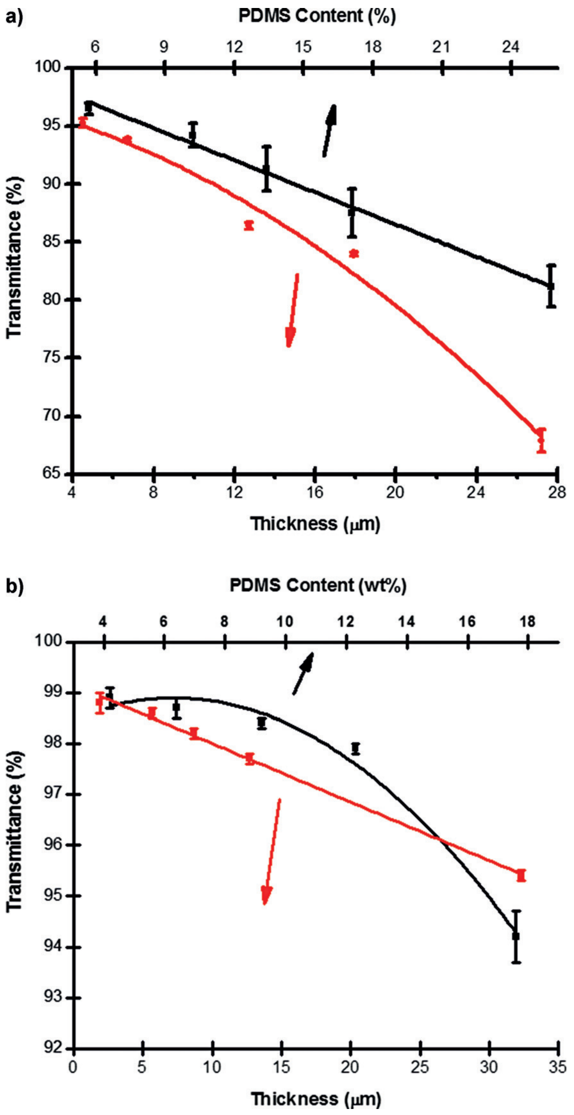

Figure 2. a) Transmittance variation at 500 nm for P1-*g*-PDMS$_{68\%}$-modified coatings as a function of film thickness at 9.2 wt % PDMS (red curve) and as a function of the PDMS mass fraction at a fixed thickness of (6.9 ± 0.6) µm (black curve). b) Transmittance variation at 500 nm for P1-*g*-PDMS$_{29\%}$-modified coatings as a function of film thickness at 9.2 wt % PDMS (red curve) and as a function of the PDMS mass fraction at a fixed thickness of (6.9 ± 0.5) µm (black curve).

containing 8.0 wt % PDMS. Whereas dodecane, decane, methanol, and ethanol with surface tensions[31] of 25.4, 23.4, 22.1, and 22.0 mN m^{-1} at 25 °C all glided down the coating at sliding angles less than 10°, octane, PDMS, and hexane with surface tensions[31] of 21.1, 20, and 17.9 mN m^{-1} spread over the coating and could not glide as whole droplets. Thus, the PDMS coatings repelled only liquids that had surface tensions at room temperature larger than or equal to 22.0 mN m^{-1}, which is slightly larger than the value of 20 mN m^{-1} for PDMS.

Figure 3 c shows the ink repellency of a P1-*g*-PDMS$_{68\%}$-containing coating. We coated only half of the glass cover of a wristwatch. When a permanent marker was dragged across the watch surface, a uniformly dark trace was left on the uncoated side of the cover. In contrast, the ink on the coated side contracted into a faint patchy trace. Moreover, the patchy trace was readily wiped off with a tissue after the ink dried. However, the trace on the uncoated side was "permanent" and could not be removed in this way. Thus, the coating not only inhibited ink deposition but also facilitated ink removal.

The P1-*g*-PDMS$_{68\%}$-containing coating also repelled an artificial fingerprint liquid consisting of lactic acid, acetic acid, sodium chloride, sodium hydrogen phosphate, 1-methoxy-2-propanol, hydroxy-terminated PDMS, and deionized water.[32] In this test, a rubber stamp bearing concentric rings was wetted with this liquid before it was pressed onto a test substrate. Figure 3 d shows the impressions left behind by the stamp on an uncoated glass plate, a plate bearing a commercial anti-fingerprint coating designed for smartphones and tablets, and a plate coated with P1-*g*-PDMS$_{68\%}$-modified PU. The concentric patterns of the stamp were transferred onto the uncoated plate owing to its facile wetting by the "fingerprint" liquid. On the commercial coating with repellency against the "fingerprint" liquid, undulations or beaded sections were seen in the stamped rings. Strikingly, the P1-*g*-PDMS$_{68\%}$-containing coatings strongly repelled the "fingerprint" liquid, even though the liquid contained 30 wt % PDMS.

The coating also repelled a commercial oil-based green paint that contained a mixture of acetone, toluene, ethyl 3-ethoxypropionate, and dimethyl carbonate as the solvent. A coated and an uncoated glass plate were sprayed with a similar amount of the green paint. The paint could not stick well to the coated plate and shrank into patches (Figure 3 e). In contrast, the paint spread uniformly on the uncoated plate. This result shows the potential of our coating in anti-graffiti applications.

The P1-*g*-PDMS$_{68\%}$- and P1-*g*-PDMS$_{29\%}$-modified coatings were found to be wear-tolerant. To intentionally inflict damage, we rubbed a P1-*g*-PDMS$_{68\%}$-containing coating with a rotating cotton-covered probe at an average pressure of 5.8×10^3 Pa for 19 200 cycles by using a home-built device (see Figure S1). This treatment created in the coating circular grooves that could be detected with the naked eye only at certain observation angles. Despite the damage, both water and hexadecane droplets cleanly glided down the coating. However, the contact angles of the liquids increased and their sliding angles decreased. For hexadecane droplets, for example, the sliding angle increased from (3.8 ± 0.2) to (13 ± 1.0)°, and their static contact angle decreased from (34.8 ± 0.8) to (32.1 ± 0.7)°. In a second test, we rotated a sandpaper-covered probe for 6 cycles on a P1-*g*-PDMS$_{68\%}$-modified coating at an average pressure of 5.0×10^3 Pa. In this case, the protruding sand particles created whitish circular grooves in the coating. Hexadecane droplets still glided cleanly down the severely damaged coating (Figure 3 f), although the sliding angle increased from (3.8 ± 0.2) to (16 ± 2.8)°.

The wear tolerance of our coatings must be due to their uniform internal structures, as depicted in structure **3** in Figure 1 d. With such a coating structure, wearing off of the surface layers exposes the PDMS nanoreservoirs embedded deep within the coating matrix. The newly exposed chains regenerate the coating surface with its anti-smudge properties.[28–30]

Despite the self-healing feature of our coatings, the anti-smudge properties of the worn surfaces still deteriorated, probably because of increased surface roughness, which would decrease the contact angle of test liquids in the Wenzel state[33] and increase the sliding angle owing to droplet pinning. A decrease in the surface PDMS content as a result of chain scission from abrasion is also possible (see Table S2).

Finally, our PU-based formulations could be applied by different methods onto different substrates to render smudge resistance. Both hexadecane and water glided cleanly on a coated a wooden plate and a coated stainless-steel disk (Figure 4 a,b; see the Supporting Information for coating methods). Water droplets readily rolled off rather than glided off coated cotton fabric (Figure 4 c), since water droplets on such rough substrates are in the Cassie state.[34]

Because of the facile applicability and excellent anti-smudge properties of our anti-smudge coatings, as well as the absence of fluorine, future variations should be affordable even for routine applications, such as the protection of metals against corrosion. For example, the P1-*g*-PDMS$_{68\%}$-containing coating was found to be effective in preventing iron etching and corrosion upon exposure to hydrochloric acid (Figure 4 d). In another experiment, one half of a cell phone was coated. The coating did not affect either the display quality or the electronic response of the touchscreen, as the letters o, l, j, u, h on the coated side of the "virtual" keyboard of the touchscreen were readily entered (Figure 4 e). Thus, the coatings can be used to coat hand-held electronic devices to reduce smudge deposition.

In summary, we have developed practical fluorine-free anti-smudge coatings. These coatings were prepared from a PDMS-grafted polyol, an HDIT, and

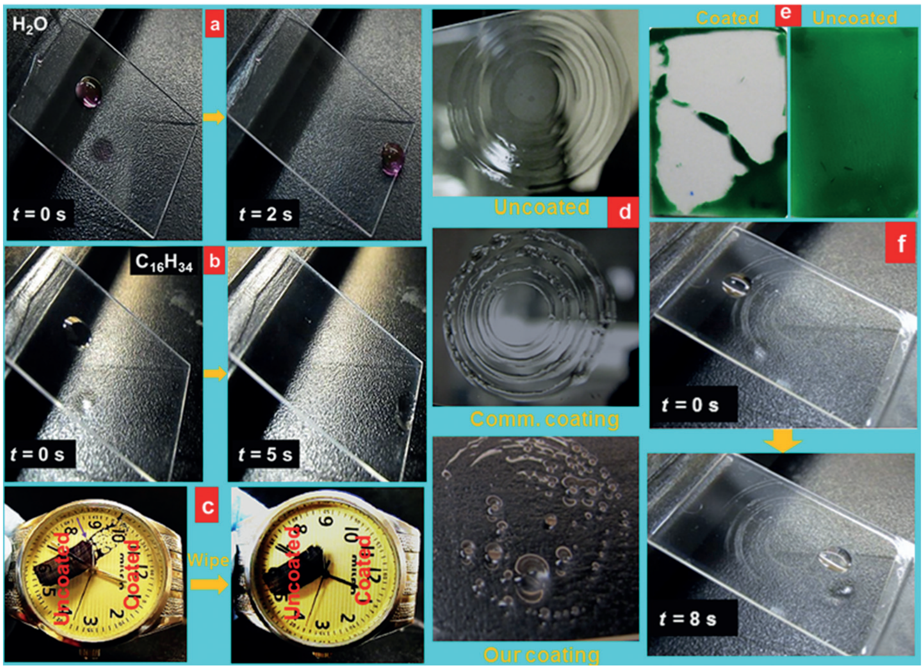

Figure 3. Properties of P1-*g*-PDMS$_{68\%}$-modified coatings containing 9.2 wt% PDMS. a,b) Snapshots of the sliding of water (a) and hexadecane droplets (b) on coated glass plates. c) Ink trace left by a permanent marker on the face of a wristwatch that was uncoated on the left-hand side but coated on the right-hand side, before and after cleaning with a tissue. d) Photographs of traces impressed by a stamp freshly wetted with an artificial fingerprint liquid on an uncoated glass plate (top), on a glass plate treated with a commercial anti-fingerprint coating (middle), and on a glass plate coated by P1-*g*-PDMS$_{68\%}$-modified PU (bottom). e) Coated and uncoated glass plates after spraying with a green paint. f) Sliding of hexadecane on a coating after wearing with a rotating sandpaper-covered probe.

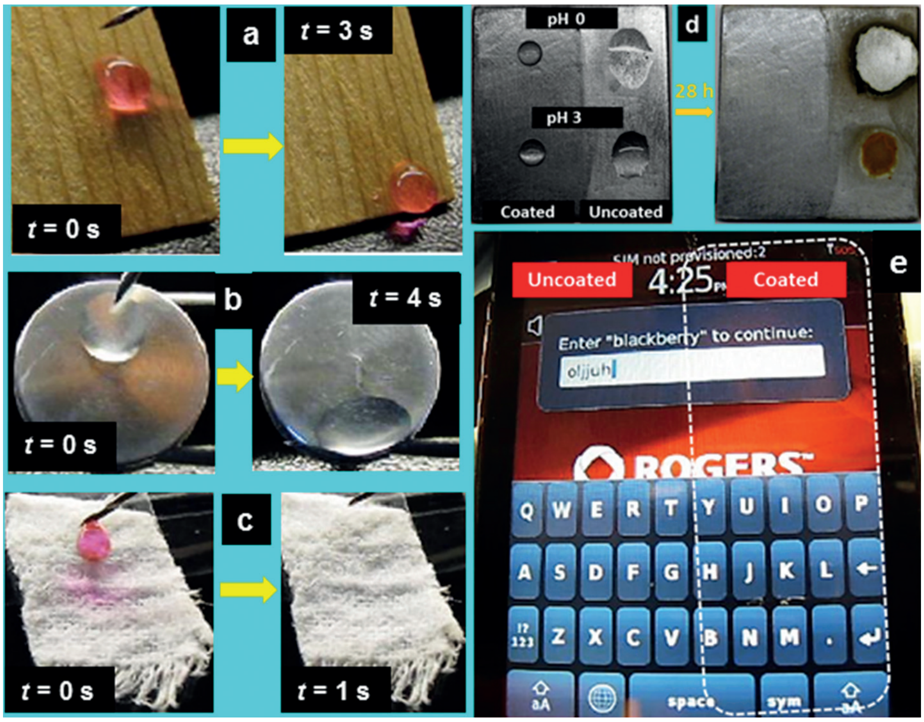

Figure 4. a–c) Snapshots of water sliding on a coated wooden plate (a), hexadecane sliding on a coated stainless-steel disk (b), and water rolling on coated cotton fabric (c). d) Photographs of a half-coated iron plate immediately and 28 h after the dispensing of aqueous HCl droplets at pH 0 and 3.0. e) A half-coated cell phone. The objects were coated with a P1-*g*-PDMS$_{68\%}$-containing coating at 9.2 wt% PDMS.

a polyol. High optical clarity was ensured by the use of polyols bearing a low weight fraction of PDMS and casting the coating solutions from a selective solvent for the polyol. The coatings did not undergo surface reconstruction upon extended contact with a test liquid owing to the heavy cross-linking of the PU matrix. The coatings exhibited superior dynamic dewetting properties against hexadecane and diiodomethane. Furthermore, they repelled ink, a "fingerprint" liquid, paint, and water. Moreover, these coatings retained their anti-smudge properties even after extensive wear. Because they do not need fluorine, these inexpensive anti-smudge coatings with superior properties will find widespread application.

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