Continuous Fabrication of Slippery Liquid-Infused Coatings on Rolls of Flexible Materials

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ABSTRACT: We report continuous, spray-based methods for the fabrication of anti-fouling 'slippery' liquid-infused porous surfaces (SLIPS) on rolls or sheets of thin, flexible materials relevant in a broad range of consumer and industrial applications. Our approach is based on the simultaneous spraying of two reactive polymers and leads to uniform and conformal coatings with (i) useful levels of nano- and microscale porosity and (ii) levels of residual azlactone reactivity that enable the facile introduction of hydrophobic character needed to infuse and retain lubricating oils. This approach can be used to fabricate transparent and mechanically robust SLIPS-based materials that resist fouling by a broad range of fluids and gels, including food-based substances, on rolls of polymer films and foils commonly used to design consumer packaging. These spray-on methods are compatible with continuous (e.g., roll-to-roll) processing approaches used in many commercial and industrial settings. We demonstrate proof of concept of this continuous approach to SLIPS fabrication using a benchtop roll-to-roll setup to coat meter-scale lengths of flexible plastic film. SLIPS-coated film produced using this roll-to-roll approach was then used to design models of flexible food packaging (e.g., transparent bags or sachets), containers, and adhesive 'SLIPS-strips' that can be affixed manually to secondary surfaces to impart temporary non-adhesive properties. The approaches reported here enable fabrication of anti-fouling materials on scales and in forms that would be difficult to achieve using many existing methods for the design of SLIPS, and open the door to additional potential practical applications of liquid-infused materials.

KEYWORDS: polymers, coatings, anti-fouling; slippery; packaging; roll-to-roll

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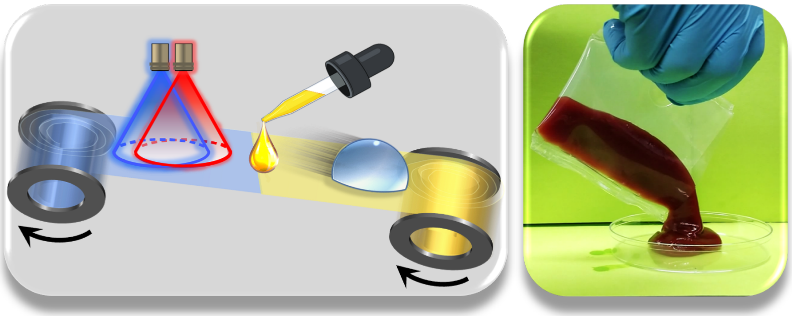

Introduction

Slippery liquid-infused porous surfaces (SLIPS) and lubricant-impregnated surfaces (LIS) constitute an emerging class of materials that exhibit unique and robust anti-fouling behaviors.[1-8] These materials have many interesting and useful properties, and address practical limitations, including physical and functional stability over extended periods, that are associated with many conventional anti-fouling or non-wetting materials, including, superhydrophobic, superoleophobic, and superomniphobic surfaces.[9-12] The design of these materials is based on the infusion of lubricating oily liquids into chemically compatible porous or micro/nano-textured surfaces,[1,2,7,8,13] resulting in the formation of a smooth and mobile liquid layer on the surface that allows a broad range of complex fluids and viscoelastic gels,[1,6,14,15] microorganisms,[4,16-20] and other contaminants to readily slide off.[3,5,8,21] Since the first report on the fabrication of SLIPS in 2011, many approaches have been reported for the design of these materials, rapidly expanding the combinations of porous/textured surfaces and lubricating liquids that can be used to assemble and manufacture liquid-infused materials.[7,8,22-27] These efforts have significantly improved the physical, chemical, and mechanical stability of these materials, leading to their recent adoption in various commercial contexts, including the prevention of fouling in marine environments and the design of slippery containers for the storage and dispensing of commercial liquids and gels. Continued development of scalable and efficient methods for the fabrication of SLIPS and LIS, including approaches that can be readily integrated with manufacturing processes commonly used in commercial contexts, will further expedite these efforts and open the door to the adoption of liquid-infused materials in other applied contexts.

In the context of the storage and transport of liquids and gels, many materials used for these purposes, including paper, plastic films, and foils, are often produced commercially in long, continuous sheets that are rolled up for further processing, handling, and transportation. The work reported here was motivated broadly by the potential positive impacts of processes that could be used to impart slippery character to the surfaces of these materials, including reduction or elimination of product wastage in consumer contexts, easier recycling of commercial packages and containers, and minimizing the use of other environmentally harmful 'non-stick' flexible packaging (e.g., per- and poly(fluoroalkyl) substances (PFAS)-based coatings, etc.). Several approaches have been reported for the fabrication of SLIPS on paper, plastic, and metal substrates,[7,8,21] but these methods are not, in general, well suited for integration with approaches to continuous or 'roll-to-roll' manufacturing that are used to process rolls of flexible materials in commercial and industrial settings.

In this paper, we report new approaches to the continuous 'spray-on' fabrication of SLIPS-based coatings. Our approach is based on the infusion of oils into nano and micro porous polymer coatings fabricated by the simultaneous spray-based assembly of two mutually reactive polymers, and leads to transparent slippery coatings that strongly resist fouling by a range of commercial substances and external contaminants, including microorganisms. In general, 'spray-on' approaches are well suited for the development of continuous coating processes. In the sections below, we report new methods for and meter-scale proof-of-concept demonstrations of continuous roll-to-roll processes for the fabrication of anti-fouling oil-infused coatings on thin sheets of flexible materials. These methods are straightforward to implement and can be used to fabricate physically and chemically durable SLIPS on a range of substrates, including paper, plastic, and foils used to design commercial packaging and containers. The approaches reported here thus have the potential to be integrated with processes for continuous manufacturing and could help address challenges associated with fouling in a broad range of consumer and industrial contexts.

Materials and Methods

Materials. Branched poly(ethyleneimine) (PEI, MW ~25 000), acetone, diethyl ether, dimethyl sulfoxide (DMSO), *N*,*N*-dimethylformamide (DMF), dimethylaminopropylamine (DMAPA), 1-aminodecane (*n*-decylamine), propylamine (98%), decanoyl chloride (98%), and *N*,*N*-diisopropylethylamine (Hünig's base, ≥ 99 %) were purchased from Sigma Aldrich (Milwaukee, WI). 7-Dimethylaminocoumarin-4-acetic acid succinimidyl ester, tetramethylrhodamine cadaverine (TMR-cadaverine), and SYTO-9 green fluorescent nucleic acid stain were Invitrogen brand and were purchased from Thermo Fisher Scientific (Waltham, MA). Hexanes solvent (Macron Fine Chemicals brand) was purchased from VWR International (Radnor, PA). Heptane (Fisher Chemical brand) was purchased from Fisher Scientific (Pittsburgh, PA). Lake water was locally sourced from Lake Mendota, Madison, WI. Ethanol (EtOH, 200 proof) was obtained from Decon Laboratories (King of Prussia, PA). Yogurt drink (Chobani mixed berry Greek yogurt drink), soy sauce (Kroger), spicy brown mustard (Kroger), and tomato ketchup (Heinz) were purchased from Pick 'n Save (Madison, WI). Double India Pale Ale beer (Double Dog IPA; Flying Dog Brewery) was purchased from a local liquor store (Madison, WI). Fresh porcine blood was collected in a 50 mL conical centrifuge tube with 3.4% sodium citrate in PBS at a ratio of 9:1 (blood:citrate) from the Meat Plant located in the Meat Science & Animal Biologics Discovery Building (UW-Madison, Madison, WI) and stored in a refrigerator until use. 3M Scotch Brite pads, honey, Elmer's school glue, and Empress standard foil roll (E121-S) were purchased from a local store (Madison, WI). Flexible polyester films (Grafix Dura-Lar; 0.005 in) and a Kuinensi Mini Sealer were obtained from Amazon.com, Inc. (Seattle, WA). 2-Vinyl-4,4-dimethyl azlactone (VDMA) was a kind gift from Dr. Steven M. Heilmann (3M Corporation, Minneapolis, MN). Poly(2-vinyl-4,4-dimethyl azlactone) (PVDMA, MW ~87, 000; PDI = 3.6) was synthesized by the free-radical polymerization of freshly distilled VDMA with 7 wt% oligo(2-vinyl-4,4-dimethyl azlactone) added, using procedures described previously.[28] Water with a resistivity of 18.2 MΩ was obtained using a Millipore filtration system. Brain heart infusion (BHI) medium was purchased from Teknova (Hollister, CA). Wild-type *S. aureus* (RN6390b; NTCC8325 cured of prophages) was used for all experiments with bacteria.[29] All materials were used as received without further purification unless noted otherwise.

General Considerations. Compressed air for drying samples was filtered through a 0.2 μm membrane syringe filter. Scanning electron micrographs were acquired using a LEO 1550 SEM at an accelerating voltage of 3 kV using an in-lens SEM detector. Coated substrates were cut into 0.5 × 0.5 cm sections for top-down SEM imaging. The samples were then mounted on a SEM stub using conductive carbon tape. Samples were coated with a thin layer of gold using a gold sputterer operating at 45 mA under a vacuum pressure of 50 mTorr for 2 min before imaging. Digital photographs and videos were acquired using either a Samsung Galaxy S8+ smartphone or a Google Pixel 3a smartphone. Contact angle measurements were made using a Dataphysics OCA 15 Plus contact angle goniometer at ambient temperature with 5 or 10 μL Milli-Q water droplets. The advancing and receding contact angles were measured by placing samples at an angle of approximately 15° and increasing Milli-Q water droplet size until sliding was observed. Fluorescence microscopy images were acquired using an Olympus IX70 microscope and were analyzed using the Metavue (version 4.6) software package (Universal Imaging Corporation).

All data were analyzed using Microsoft Excel for Office 360 and plotted using GraphPad Prism 7 (version 7.0h).

Fabrication of Simultaneously Sprayed PVDMA/PEI Coatings. Flexible polyester films (30 cm long; Dur-Lar clear) were cleaned with water, ethanol, and acetone, dried under a stream of filtered and compressed air, and oxygen plasma-treated for 600 s (Plasma Etch, Carson City, NV). The coatings were fabricated using an automatic SPALAS coating system (AGILTRON, Woburn, MA) with different nozzles for spraying PEI and PVDMA. In-house compressed air lines supplied pressurized gas with overpressure fixed at 20 psi and all nozzles were calibrated to flow rates of 3 mL/min ± 0.5 mL/min. Substrate films were positioned horizontally on the spraying platform and nozzles were aligned perpendicular to the film. One end of the film was attached to a motor set to pull it horizontally at a rate of ~0.64 cm/s. Solutions of PEI and PVDMA (20 mM in DMF) were sprayed through two different nozzles while the film was continuously pulled under the nozzles until the entire 30 cm length of the film was coated. After fabrication, films were cleaned with DMF and dried under a stream of filtered, compressed air and either functionalized immediately or stored in a vacuum desiccator until functionalization or further use in other experiments. For proof of concept roll-to-roll demonstrations, flexible polyethylene films (150 cm long) were coated using a similar procedure, except that the uncoated film was rolled onto a feed spool with the tail of the film attached to an uptake spool pulling the film at a constant rate of ~0.64cm/s under the spray nozzles (see Video S1). The wet coated film from the uptake spool was then cleaned with DMF and dried under a stream of filtered compressed air and either functionalized immediately or stored in a vacuum desiccator until functionalization or use in other experiments.

Post-Fabrication Functionalization and Chemical Patterning of Reactive Thin Films. Films containing unreacted azlactone groups, fabricated as described above, were further functionalized using the following general procedures. To functionalize small sections, coated substrates were first cut into approximately 1 × 2 cm pieces. These pieces were then immersed in a solution containing a primary amine-containing molecule (e.g., 20 mM DMAPA in heptane, or 20 mM *n*-decylamine in heptane, or 20 mM propylamine in diethyl ether). To functionalize longer film-coated strips, samples were sprayed with a 40 mM solution of *n*-decylamine in DMF using the same general spraying procedures and parameters detailed above, and then rinsed with DMF and acetone and dried with filtered air. Substrates that could not be readily sprayed with the *n*-decylamine solution were immersed in a 40 mM solution of *n*-decylamine in DMF for 1.5 minutes then rinsed with DMF and acetone and dried with filtered air. Post-fabrication functionalization by chemical modification of residual amine groups was performed using the following general procedure. Substrates were immersed in a solution of either propionyl or decanoyl chloride (20 mM) and DIPEA (35 mM) in heptane for 1.5 minutes, followed by thorough rinsing with acetone and drying under a stream of filtered air. Caution: Functionalization of latent amine reactivity with highly reactive acid chloride compounds should be performed with caution using adequate PPE. For functionalization of fabricated films with TMR cadaverine, a 10 μL drop of TMR cadaverine in DMSO (1 mg/mL) was spread on the surface of an approximately 1 cm x 1 cm section of a longer film-coated substrate. The droplet was allowed to sit on the film in the dark for 30 minutes, after which the TMR cadaverine solution was rinsed from the surface of the substrate using copious amounts of DMSO and acetone. The functionalized substrate was then dried under a stream of filtered air.

Characterization of Biofilm Adhesion on SLIPS-Coated Substrates. Characterization of the antibiofouling performance of SLIPS-coated substrates was performed using procedures reported previously.[20] Briefly, overnight cultures of *Staphylococcus aureus* were diluted 1:100 into fresh brain-heart infusion medium supplemented with 1% (w/v) glucose to prepare a *S. aureus* subculture. The subculture was then added to the wells of a 24 well plate (Falcon brand) that contained 1 cm x 1 cm pieces cut from larger PVDMA/PEI SLIPS-coated aluminum foil and PET substrates. The corresponding uncoated foil and PET substrates were also placed in the wells with *S. aureus* subculture. The well plate was then incubated under static conditions at 37 °C for 24 hours. After 24 hours, the culture solution was removed, and substrates were gently rinsed with 1 mL of Milli-Q water. The substrates were then stained with SYTO-9 according to the manufacturer's recommended protocol and imaged using an Olympus IX71 fluorescence microscope.

Fabrication of Simultaneously-Sprayed Model Food-Service Containers. To fabricate a model slippery plastic bag, the spraying procedure described above was followed with few modifications. Polyethylene films were pulled at a 15° angle to the ground to promote drainage of the spray solutions and the nozzles were held perpendicular to the substrate (15° angle to the vertical). The pull rate was adjusted to ~0.1 cm/sec and as the substrates were pulled in the *x*-direction, the nozzles moved in the *y*-direction back and forth over a length of ~10 cm. The coating was then rinsed with acetone and DMF and functionalized with *n*-decylamine and decanoyl chloride as described above. After functionalization, the substrates were folded in half lengthwise with the sprayed coating facing inward and two sides were heat-sealed using a Kuinensi Mini Sealer to create a package. The packs were then infused with silicone oil by pipetting the required number of drops into the pack and shaking it gently. After infusion, the bag was held upside down and the excess oil at the outside lip was wiped off with a kimwipe. Model aluminum foil containers were produced using the same SLIPS fabrication procedure described above for polyethylene films. SLIPS-coated foil was then stamped between two glass petri dishes, conforming the foil to the shape of the dishes. The resulting aluminum foil dish was then infused with silicone oil by pipetting several drops into the dish, tilting and shaking it gently, and then wiping off the excess oil with a kimwipe.

Physical Stability Tests. To characterize the physical performance of the SLIPS-coated substrates, the sliding times of 20 μL water droplets across the surface of a film held at an angle of 20° was measured and compared to sliding times of the same-sized droplet at the same angle after physically manipulating the film. In bending and twisting experiments, the films were bent until their two ends touched and then were allowed to relax back to a planar position. This procedure was repeated 30 times, and the films were then twisted by rotating one end of the film in a clockwise motion while rotating the other in a counterclockwise motion, followed by allowing the films to relax back to a planar position. This process was also repeated 30 times. Films were also manually smudged or abraded. For these experiments, a piece of Scotch Brite cleaning pad was placed onto a SLIPS-coated surface and a 50 g weight was placed on top of the pad. The pad was then pulled along the length of the film 10 times. To test the ability to withstand contact with running water, a fresh SLIPS-coated film was placed under a faucet with water flowing at a rate of ~50 mL/sec for one minute. For films that were permanently creased prior to characterization, films were creased at three points along the length of the film.

Results and Discussion

We recently reported an approach to the spray-based assembly of reactive polymer films that is useful for the fabrication of SLIPS on flexible and planar substrates.[30] That prior work was based on alternate or simultaneous spraying of solutions of poly(ethyleneimine) (PEI, Figure 1B) and the amine-reactive polymer poly(2-vinyl-4,4-dimethylazlactone) (PVDMA; Figure 1A). That approach leads to nano- and microporous polymer coatings that contain residual reactive azlactone groups that can be further functionalized, post-fabrication, to generate hydrophobic

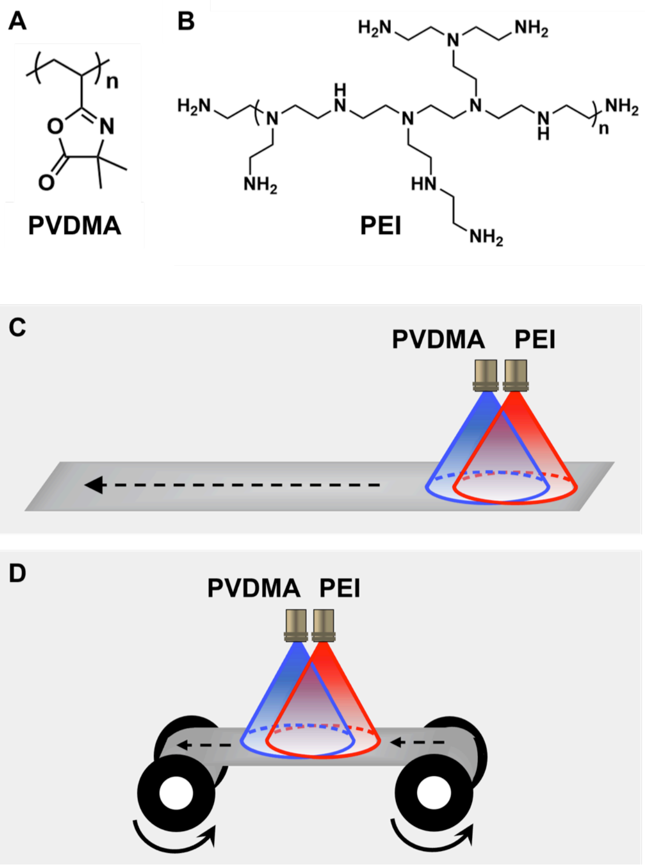

Figure 1. (A-B) Structures of the polymer building blocks used in this study: (A) poly(2-vinyl-4,4-dimethyl azlactone) (PVDMA) and (B) branched poly(ethyleneimine) (PEI). (C) Schematic showing simultaneous spraying of PVDMA (blue) and PEI (red) to continuously coat an underlying substrate (grey); in this process, the substrate was pulled under a continuous simultaneous spray. (D) Schematic showing simultaneous spraying of PVDMA and PEI in a roll-to-roll manner; in this process, the substrate was spooled on a supply roller (right) and pulled under a simultaneous spray by an uptake roller (left) used to collect the coated substrate.

coatings that can host and retain infused oils. Overall, that work demonstrated that exposure of substrates to multiple PVDMA/PEI spray cycles could be used to iteratively build up porous coatings with physical, chemical and functional properties and behaviors similar to those of reactive PVDMA/PEI films fabricated in past studies using immersion-based methods.[24,28,31-33] To determine whether this general ‘spray-on’ scheme could be adapted for the simultaneous and single-pass fabrication of nanoporous coatings (and, thereby, provide a platform for the development of continuous or roll-to-roll approaches to the fabrication of these materials), we performed an initial series of experiments using PVDMA and PEI solutions prepared in the non-volatile solvent DMF and an automated spray coating system with two different nozzles to affect the simultaneous and continuous spraying of both solutions. Thin strips of flexible polyester film (~30 cm long) were then pulled under the spray heads at a constant rate (~0.64 cm/s) while nozzles simultaneously sprayed polymer solutions at angles perpendicular to the test surfaces (as illustrated in Figure 1C; see Methods for additional details).

Figure 2A shows an image of a polyester film test strip coated after one pass under simultaneous PVDMA/PEI sprays, and reveals the presence of a transparent and colorless thin coating on the surface of the film that was difficult to discern by visual inspection. Treatment of these film-coated substrates with TMR-cadaverine, a primary amine-containing fluorescent probe that can react with residual azlactone groups in PVDMA, enabled further characterization of the uniformity of the coatings by fluorescence microscopy. Figure 2B shows a representative fluorescence microscopy image of a TMR-treated film segment and shows uniform red fluorescence; inspection of coating segments in other locations along the test strip, shown in Figure S1, revealed these films to be applied uniformly over the length of the 30 cm substrate. These results also confirmed the presence of residual amine-reactive azlactone functionality in

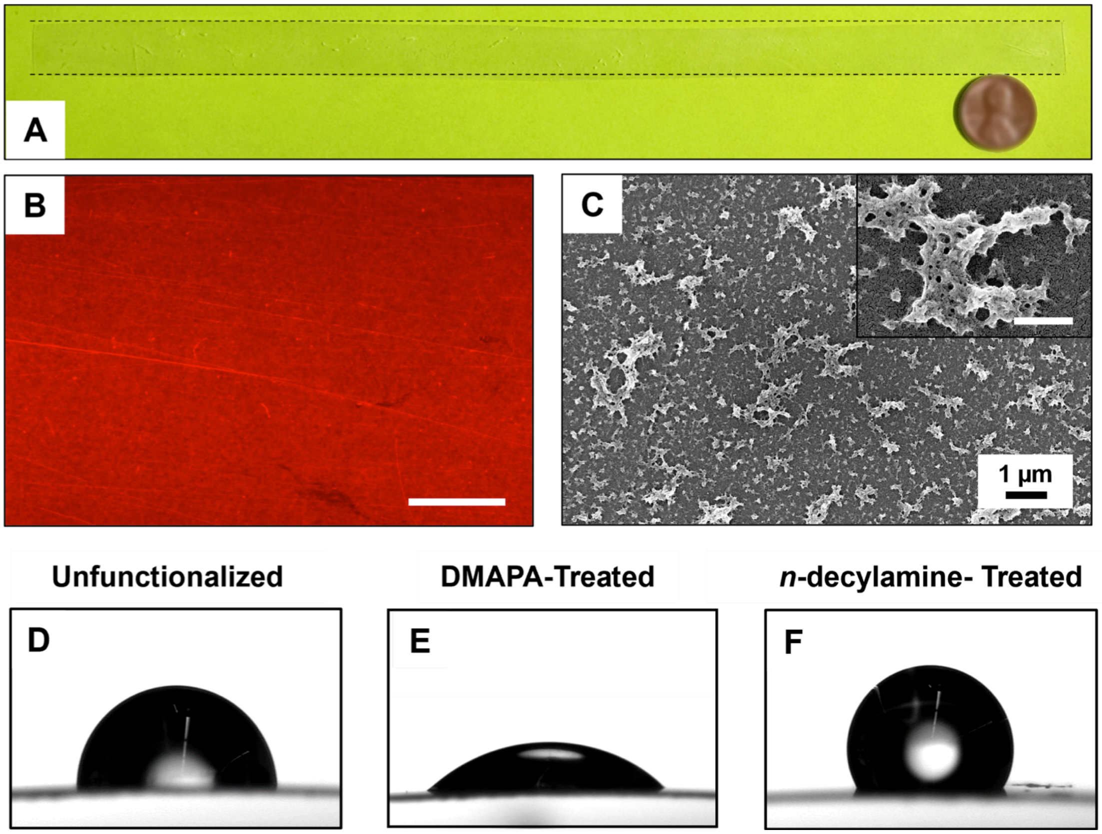

Figure 2. (A) Representative image of a 30 cm long segment of SLIPS-coated flexible polyester film; a U. S. one-cent piece is included to show scale and dotted lines are added to guide the eye. (B) Fluorescence microscopy image of a representative section of a segment of flexible film coated with a simultaneously sprayed PVDMA/PEI film after treatment with TMR-cadaverine. Scale bar = 400 µm; see also Figure S1. (C) Low- and high-magnification (inset) top-down SEM images of a representative section of flexible film coated with a simultaneously sprayed PVDMA/PEI film. Scale bar of inset = 400 nm; see also Figure S4. (D-F) Images showing contact angles of 5 µL water droplets on representative sections of flexible film coated with a simultaneously sprayed PVDMA/PEI film (D) before (θ ~86°) and after functionalization with (E) DMAPA (θ ~42°) or (F) *n*-decylamine (θ ~115°); see also Figure S2.

these single-pass coatings. Otherwise identical films that were pre-treated with propylamine to consume remaining azlactone functionality prior to functionalization with TMR-cadaverine showed no fluorescence, suggesting that the fluorescence observed in Figure 2B and Figure S1A-C arises from covalent immobilization and not physisorption.[30,31] This result is important, because remaining azlactone functionality provides means to modify and tune the interfacial properties of these materials[30,32,34] and, in the context of the design of SLIPS, can be used to render these materials more suitable for infusion with lubricating liquids.[24,30] Film-coated strips that were treated with solutions of DMAPA, a hydrophilic amine-based nucleophile, exhibited decreased water contact angles (θ ~42°, Figure 2E) compared to those of native films prior to functionalization (θ ~86°, Figure 2D). In contrast, treatment with *n*-decylamine, a hydrophobic amine-based nucleophile, resulted in a significant increase in water contact angles (θ ~115°, Figure 2F; these contact angles are representative of contact angles measured over the length of these coated test strips; see Figure S2). Results of additional experiments demonstrated that these coatings also contained unreacted amine functionality that can be functionalized by treatment with the hydrophobic electrophile decanoyl chloride to further tune chemical and interfacial properties after fabrication (see Figure S3 and additional discussion below).

Further characterization of these single-pass PVDMA/PEI coatings by SEM revealed them to be rough and porous with a morphology consisting of microscale and nanoscale aggregates (see Figure 2C and Figure S4). This overall morphology is consistent with simultaneously sprayed PVDMA/PEI coatings reported previously,[30] and likely arises from the deposition of PVDMA/PEI aggregates or complexes that form due to mixing of PVDMA and PEI solutions in the liquid film draining along the substrate during simultaneous spraying. We note that, although it is not visually apparent from the SEM images shown in Figure 2C, those past reports revealed larger aggregates similar to those observed here to be surrounded by a thinner and continuous polymer film covering the entirety of the underlying substrate and surrounding the salient micro-and nanoscale features[30] (this is also consistent with the presence of uniform red fluorescence observed in the results described above). Additional experiments described below demonstrated that the topographic features exhibited by these coatings and the hydrophobic character that can be imparted by post-fabrication functionalization are sufficient for the infusion and retention of oily lubricants.

Infusion of silicone oil into single-pass PVDMA/PEI coatings functionalized by immersion into solutions of both *n*-decylamine and decanoyl chloride (see Methods) resulted in coatings that allowed droplets of water to readily slide off the surface (in contrast, water droplets remained stuck and did not slide on uncoated substrates or on PVDMA/PEI film-coated substrates that were not infused with silicone oil). Figure 3A shows a series of images of a 100

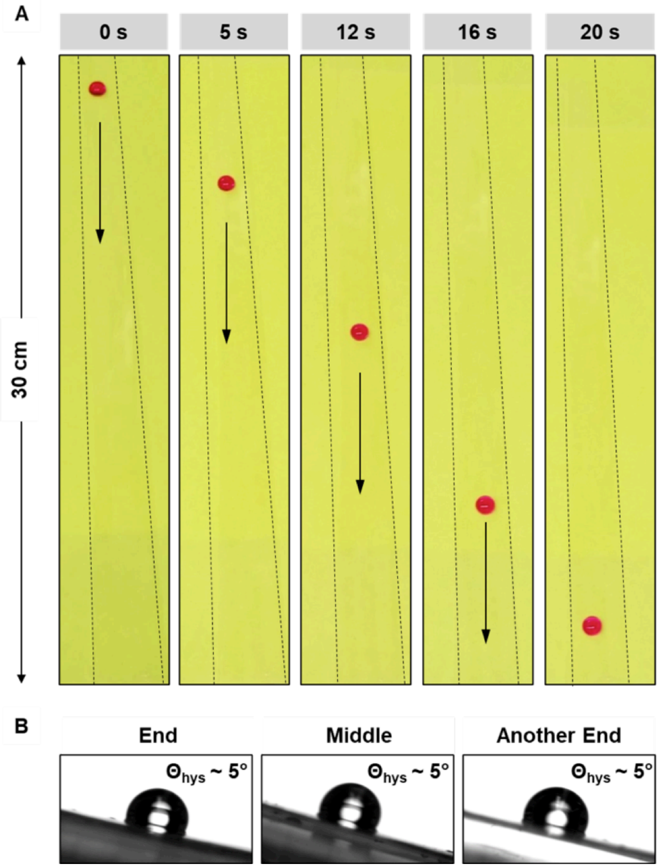

Figure 3. (A) Angled-top-down images showing a water droplet (100 µL; containing a pink dye to guide the eye) sliding, from top to bottom, on a 30 cm long segment of SLIPS-coated flexible polyester film (tilt angle ~10°). The dotted lines in each image mark the positions of the edges of the coated film and do not appear parallel because of the angle at which these long strips were imaged. Aqueous droplets did not slide on uncoated polymer films even at 90° tilt angles (not shown). (B) Images showing contact angle hysteresis (Θ_{hys}) at different points along the length of these SLIPS-coated polymer films (droplet size = 10 µL; angle of incline ~10°).

μL droplet of water (containing a pink-colored dye to aid visualization) placed at the upper end of an oil-infused, SLIPS-coated strip of plastic film 30 cm long tilted at an angle of ~10°; the droplet was observed to slide down the surface of the film at a rate of 1.5 cm s^{-1}. Contact angle hysteresis (θ_{hys}) measurements of water droplets (10 μL) at different locations along the film are shown in Figure 3B. In each case, low hysteresis (θ_{hys} ~5°) was observed, consistent with the presence of a uniform and conformal slippery coating across the entire length of the film. Functionalization of reactive PVDMA/PEI coatings with *n*-decylamine and decanoyl chloride to impart hydrophobic character can be achieved in a period of few minutes by immersion or by spraying. The contact angles of coatings sprayed with *n*-decylamine increased from ~50° to ~100° immediately after spraying (see Methods for additional details, and Figure S5 for the contact angle values; functionalization with decanoyl chloride produced similar results, but was achieved in the work reported here by immersion rather than spraying for safety reasons). These spray and immersion approaches to post-fabrication chemical functionalization, when combined with continuous spray-based procedures for the fabrication of reactive PVDMA/PEI coatings, provide a useful model for the development of continuous, end-to-end processes for the fabrication of liquid-infused surfaces.

Figure 4 shows that SLIPS-coated films fabricated using this approach were stable and remained slippery when contacted with a broad range of chemically complex liquids, including whole blood, tomato ketchup, soy sauce, and a liquid yogurt drink; also see Figure S6 for images of other liquids sliding on these SLIPS-coated films). These SLIPS-coated films also demonstrated robust anti-biofouling behavior and substantially prevented biofilm formation by the human bacterial pathogen *Staphylococcus aureus* (see Figure S7). These coatings maintained their slippery properties after exposure to other physical and chemical manipulation, including

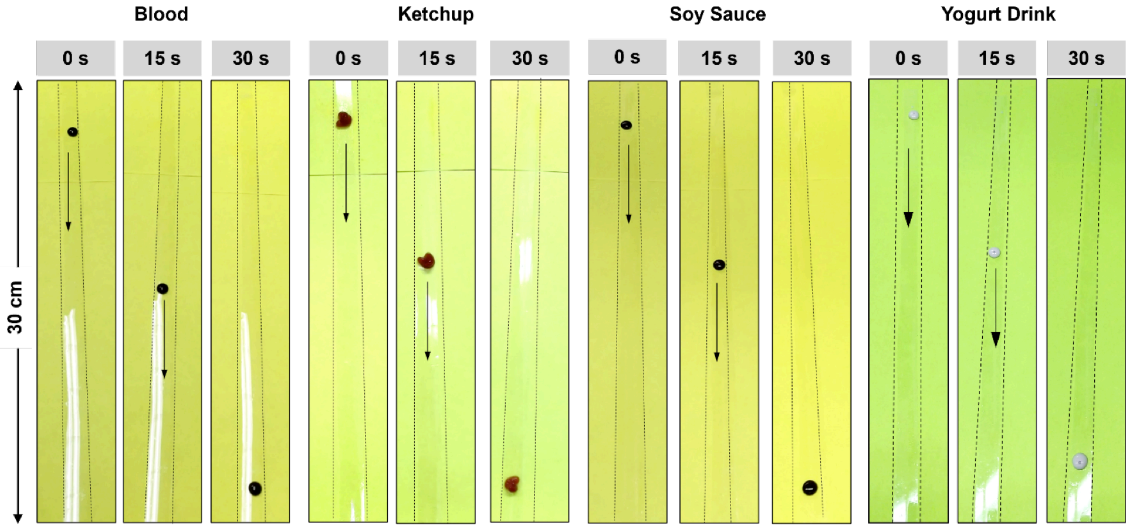

Figure 4. Angled-top-down images showing droplets of various chemically and compositionally complex fluids (blood, tomato ketchup, soy sauce, and a yogurt drink) sliding, from top to bottom, on 30 cm long SLIPS-coated strips of flexible polyester film; (droplet volumes = 100 µL; tilt angles ~10°). The dotted lines in each image mark the positions of the edges of the coated films and do not appear parallel because of the angle at which these long strips were imaged.

repeated bending and twisting, exposure to high shear, permanent creasing, and abrasion/scratching commonly encountered during the storage, processing, usage, and transport of plastic film in various real-world scenarios (see Methods for details).

The procedures reported here are also suitable for the continuous, spray-on fabrication of uniform and conformal SLIPS-based materials on a range of other flexible substrates. Figures 5A,B show representative SEM images of porous films fabricated on 30 cm long strips of aluminum foil and woven cotton fabric by a single pass of these substrates under simultaneous PVDMA/PEI sprays. Infusion with silicone oil resulted in foil and fabric surfaces that were slippery across the entire length of the coated strips (Figure 5C,D). Additional characterization of film uniformity and surface features for these coated surfaces is provided in Figure S8.

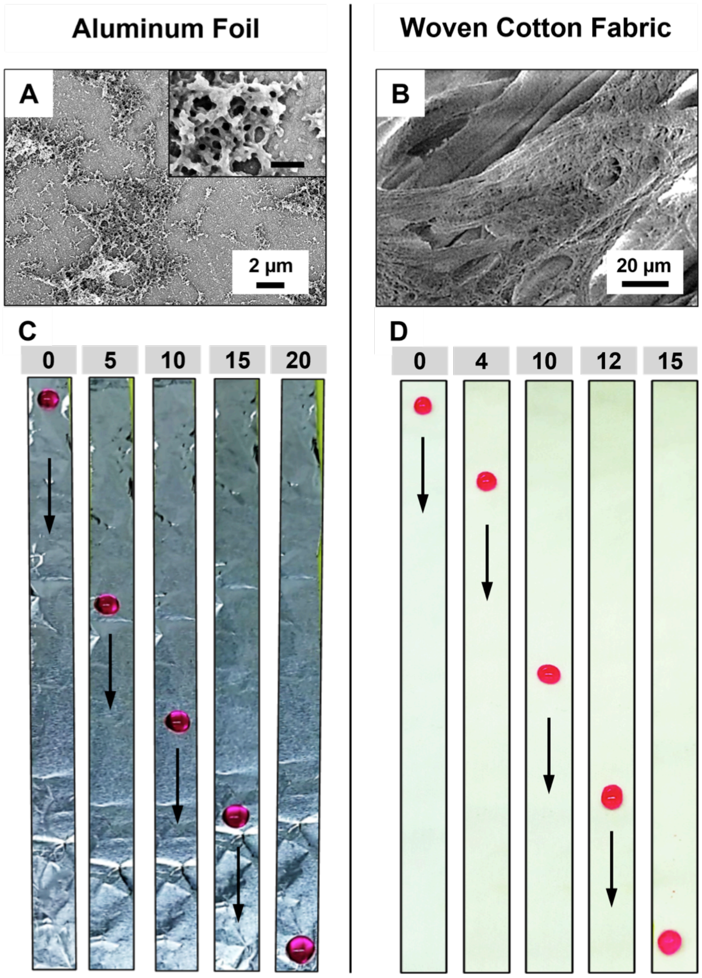

Figure 5. (A-B) Low and high (inset) magnification SEM images of PVDMA/PEI films fabricated on (A) aluminum foil (inset scale bar = 400 nm) and (B) woven cotton fabric. (C-D) Angled-top-down images of water droplets (100 µL, containing a pink dye to guide the eye) sliding on a (C) SLIPS-coated aluminum foil strip and (D) and a woven cloth fiber strip (tilt angles ~10°).

The single-pass simultaneous spray-based procedures described above can be combined with approaches for roll-to-roll processing to fabricate slippery and antifouling materials rapidly and continuously onto longer lengths of flexible materials. To explore the feasibility of this approach and demonstrate proof-of-concept, we designed a benchtop-scale laboratory model to continuously feed a 1.5 meter long roll of flexible plastic film through simultaneous sprays of PVDMA and PEI, using an uptake roller rotating a rate of ~10 rpm/sec to drive the feed (see Figure 6A and Video S1 for a photograph and representative video of this roll-to-roll setup).

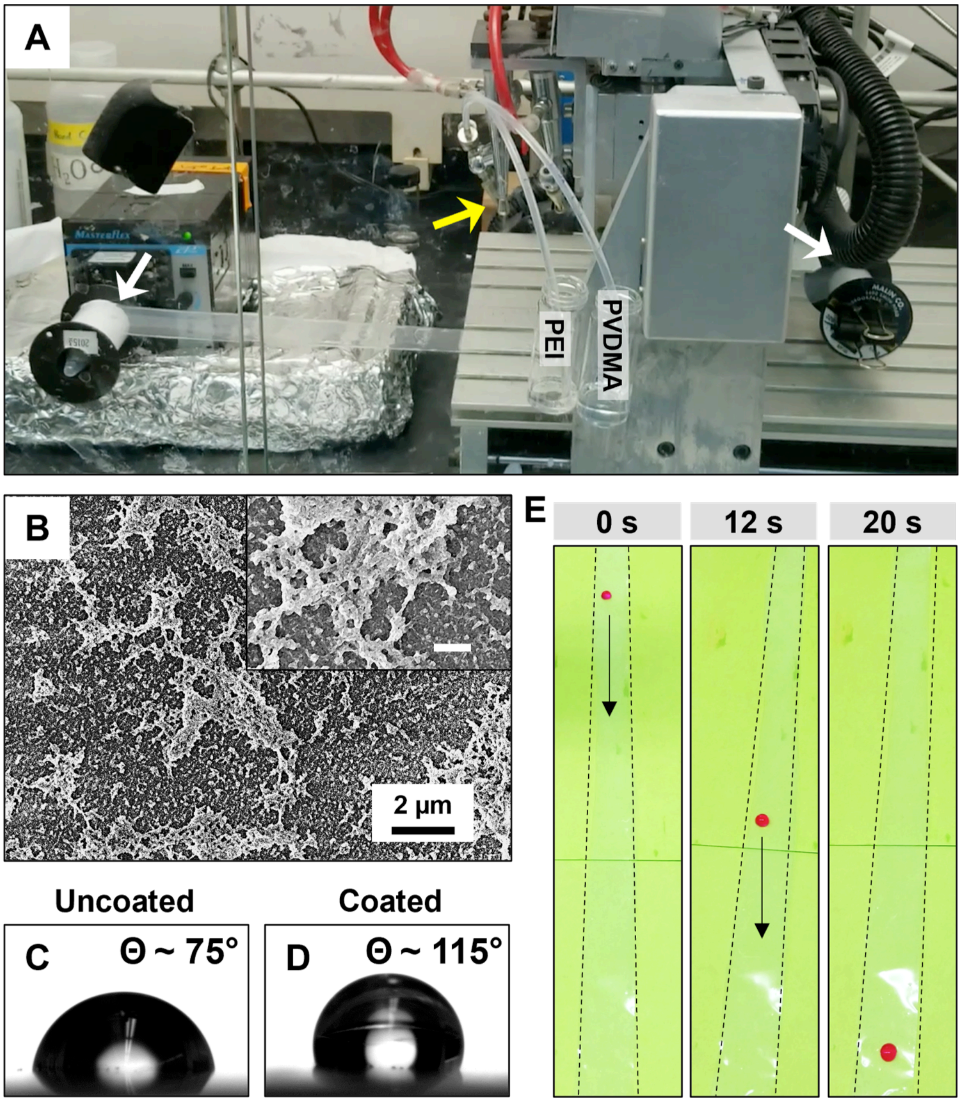

Figure 6. (A) Photograph showing the benchtop-scale roll-to-roll setup used to coat a spool of flexible polyethylene film. The white arrows point to the rollers used to hold the spool of the uncoated film (right) and the PVDMA/PEI-coated film (left). The roller on the left was connected to a motor and pulled the strip of film (at a rate of ~0.64 cm/s) under two spray nozzles (marked by the yellow arrow) simultaneously spraying PEI and PVDMA solutions. See also Video S1. (B) Representative top-down SEM image of a coated film obtained using the roll-to-roll fabrication process shown in (A); inset scale bar = 500 nm. (C,D) Representative images showing contact angles of 5 µL water droplets on (C) an uncoated polymer film substrate and (D) polymer film after coating with PVDMA/PEI films functionalized with *n*-decylamine and decanoyl chloride. (E) Series of photographs showing the sliding behaviors of aqueous droplets (50 µL; containing a pink dye to guide the eye)

After spraying, the wet roll of coated film was dried by unrolling the film and passing it under a stream of air. The film was then reacted with decylamine and decanoyl chloride, respectively, and rolled up again on the roller. Characterization of these roll-to-roll-coated strips by SEM and measurements of water contact angle revealed them to be coated uniformly and conformally along the length of the strip, with microscale and nanoscale features (Figure 6B) and interfacial wetting behaviors (θ ~115°; Figure 6D) similar to those described above (see Figure S9 for additional related results; θ ~75° for uncoated film (Figure 6C)). This result demonstrates that the roller-based substrate-winding collection process used here does not substantially impact the topographic features of these materials when rolled prior to or after film drying. Finally, infusion of silicone oil into these roll-to-roll coatings resulted in robust slippery behavior (Figure 6E shows a 50 μL droplet of water sliding on a representative 30 cm long section tilted to an angle of ~10°). When combined, these results provide useful proof of concept and suggest (i) that these continuous spray procedures could be integrated into larger-scale roll-to-roll processes for the rapid and continuous fabrication of SLIPS-coated film, and (ii) that physical flexing, bending, and coiling of freshly-fabricated wet film-coated strips or dry film-coated strips onto themselves does not adversely affect anti-fouling behavior, consistent with the physical stability results discussed above.

The approaches reported here for the fabrication of SLIPS-based coatings on strips of flexible materials open the door to new processes and potential applications for these antifouling films, including new approaches to the design of flexible non-stick packaging for the storage and transport of commercial liquids and gels. As a demonstration model of such an application, we designed a flexible plastic packet by strategically heat-sealing the edges of strips of SLIPS-coated plastic film fabricated by roll-to-roll assembly and then infusing the inside of the packet with silicone oil (see Methods for additional details). Figure 7A-C shows images of a SLIPS-coated pack filled with tomato ketchup. The SLIPS-coated package remained slippery and non-

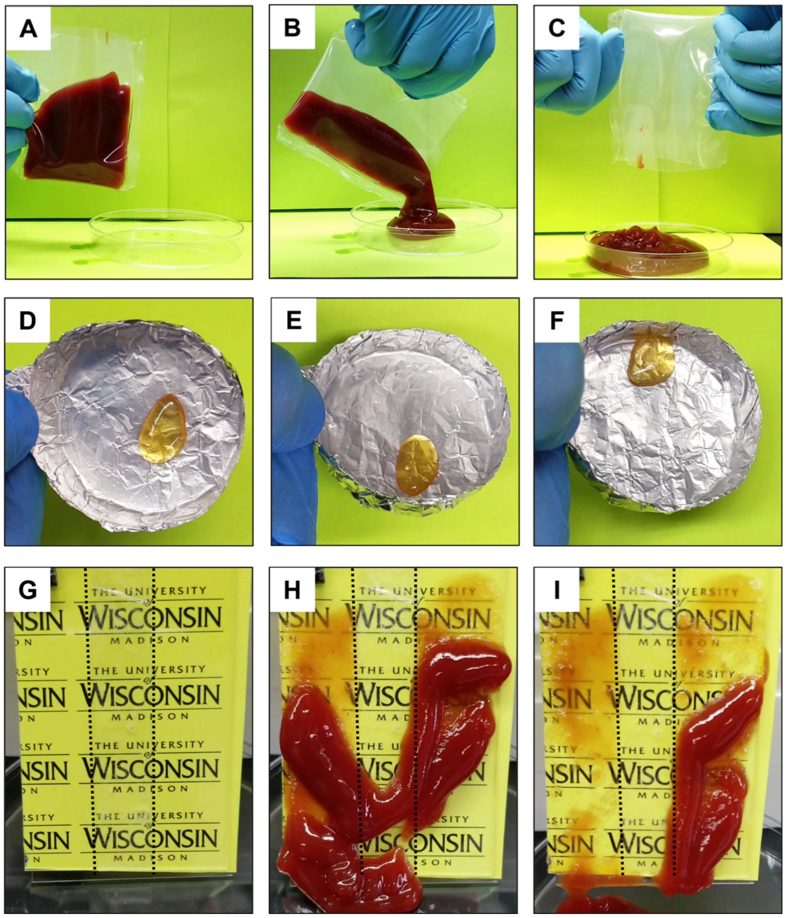

Figure 7. (A-C) Images of a slippery, non-fouling plastic bag fabricated by heat-sealing the edges of SLIPS-coated plastic film (see text). The bag is shown filled with tomato ketchup (A); ketchup was easily removed from the bag by gentle pouring and inversion, leaving no fouling or residue on the surface of the bag (B-C; see also Video S2). (D-F) Images of a sample of viscous honey sliding inside a foil container fashioned by pressing and shaping SLIPS-coated aluminum foil (see also Figure S11 and Video S3). (G-I) Images of a transparent glass substrate with a SLIPS-coated adhesive sticker-strip placed in the center (D; the strip is framed by dotted lines to guide the eye); panels H-I show the same substrate after ketchup was poured on the surface (see also Video S4).

fouling in contact with ketchup for extended periods and allowed the straightforward and complete removal of ketchup from the packet without the need for additional squeezing or shaking (see also Figure S10 and Video S2; in comparison, the surfaces of packets fabricated using uncoated plastic film were heavily fouled by ketchup, and large amounts of residual ketchup remained in the bag even after vigorous shaking).

As another demonstration, we designed SLIPS-coated foil containers by pressing or forming sheets of SLIPS-coated aluminum foils (see Methods). Figure 7D-F shows a sample of viscous honey sliding inside a SLIPS-coated foil container (see also Figure S11 and Video S3 for additional examples of other complex liquids; the surfaces of uncoated foil containers were readily fouled). Additional experiments demonstrated that these SLIPS-coated foil containers can prevent fouling by microorganisms, including *S. aureus* (Figure S12). When combined, these results demonstrate that the continuous-spray procedures reported here lead to films and coatings that exhibit and maintain robust antifouling and slippery behaviors after subjection to physical manipulation required to fashion them into useful containers and model stresses associated with potential applications. These proof of concept demonstrations suggest opportunities to design transparent and flexible packaging and containers that could help reduce wastage of food or other substances in consumer and industrial contexts (for example, in smaller single-use packets, or in larger, industrial-scale pouches used to dispense larger quantities of liquid foodstuffs or other consumer liquids and gels). This approach also has the potential to address challenges related to the recycling of materials that may otherwise be heavily fouled by residual product and improve consumer experience.

Finally, we used the continuous processes reported here to design flexible slippery stickers, or ‘SLIPS-strips’, having an adhesive underlayer masked by a protective, non-sticky backing. Removal of the protective backing resulted in slippery plastic strips that could be peeled off and readily affixed to a wide range of secondary substrates to endow them with anti-fouling behaviors. Figure 7G-I shows a glass surface with an optically transparent slippery sticker (framed with dotted lines to guide the eye) that was subsequently exposed to ketchup. Inspection of these images reveals that the region of the surface protected with the SLIPS-strip remained clear and free of ketchup, whereas other regions of the exposed glass surface were readily fouled (see also Video S4). The results of these experiments provide proof-of-concept demonstrations of spray-on and continuous approaches to the design of flexible sticky materials that can provide anti-fouling character to surfaces in ways that are temporary and can be defined conveniently by an end user and, if needed, easily removed, repositioned, or replaced after use.[15]

Summary and Conclusions

We have reported a continuous, spray-on method useful for the fabrication of slippery, oil-infused coatings on rolls of flexible materials relevant in a wide range of consumer and industrial contexts. Continuous and simultaneous spraying of two mutually reactive polymer building blocks was demonstrated to result in useful and uniform levels of nano- and microscale porosity as well as chemical reactivity that enabled the installation of hydrophobic functionality. These features, when combined, permit the continuous, single-pass, spray-on design of transparent and mechanically robust SLIPS-based materials. These methods are useful for the fabrication of SLIPS on long rolls of flexible plastic and other materials used to store, process, and distribute a broad range of viscous consumer products, and are compatible with continuous roll-to-roll approaches used to manufacture, functionalize, and transport flexible films in many commercial settings. We demonstrated proof of concept of this approach using a benchtop-scale roll-to-roll setup to coat meter-scale lengths of flexible plastic film. SLIPS-coated film produced using this method remained non-fouling to a wide range of common liquids and gels, including liquid foodstuffs, and could be readily fashioned into models of flexible food packaging (e.g., transparent bags or sachets) or lengths of adhesive slippery stickers that can be placed on and easily removed from other surfaces to temporarily impart non-fouling properties.

The approaches reported here enable fabrication of anti-fouling materials on scales and in forms that are likely to be useful for the commercial utilization of SLIPS-based materials. For example, the potential to integrate these approaches with continuous manufacturing processes could help address challenges associated with the fouling of flexible packaging in consumer and industrial contexts. We note that the work reported here demonstrated proof of concept using silicone oil as a model oily lubricant. Previous studies have demonstrated that nanoporous PVDMA/PEI coatings similar to those reported here could also be infused with a broad range of other lubricating liquids, including plant-based edible oils such as corn, canola, and almond oils to produce robust SLIPS.[24] It is likely that these and other natural and synthetic oils could be used effectively with the polymer coatings reported here, allowing the overall design to be selected based on the end use of the coatings. It should also be possible to strategically manipulate several different spray-process and roll-to-roll parameters, including polymer solution concentration, the number of spraying passes, spray angle, velocity, and size, or substrate speed to further tune coating properties, as demonstrated previously for the spray-based fabrication of coatings using multiple mutually-interacting polymers.[30,35-40] Finally, we note that these approaches and materials could also open the door to new and exciting designs and applications of slippery liquid-infused materials that are currently inaccessible or difficult to realize using other previously reported methods for SLIPS fabrication. The integration and controlled release of active agents into these polymer-based coatings, for example, as demonstrated in our previous work using layer-by-layer PVDMA/PEI coatings,[20,41] could provide new opportunities to enhance anti-biofouling performance, maintain food freshness, release fragrances, or introduce other useful active or passive functions to these oil-infused materials.

Acknowledgments. Financial support for this work was provided in part by the National Science Foundation through a grant provided to the UW–Madison Materials Research Science and Engineering Center (MRSEC; DMR-1720415), and by the UW-Madison Wisconsin Alumni Research Foundation (WARF) through grants provided by the WARF Accelerator Program and the Draper Technology Innovation Fund (Draper-TIF). The authors acknowledge the use of instrumentation supported by the NSF through the UW MRSEC (DMR-1720415). We thank Prof. Helen E. Blackwell and Thomas J. Polaske for assistance with bacterial assays and for many helpful discussions.

Supporting Information. Fluorescence and scanning electron microscopy images, contact angle measurements, digital images, and videos showing surface morphologies, interfacial properties, and results of anti-fouling assays for coatings prepared with and without infused oil (PDF). This material is available free of charge via the Internet.

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