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Nanoporous Glass Films on Liquids

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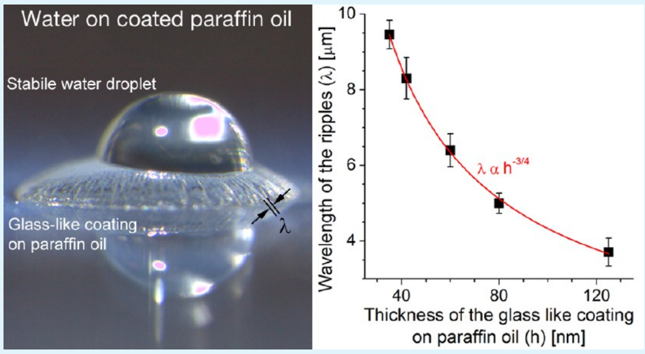
S *Supporting Information*

ABSTRACT: Glass-like thin films are used in many applications as dielectric layers, barrier coatings, abrasion-resistant films, and/or transparent films. We report the first direct application of such materials to liquid substrates using a plasma-deposition process at atmospheric pressure. The study demonstrates the broader utilization of these materials, for example, as robust membranes for water harvesting or drug delivery.



KEYWORDS: *PE-CVD, liquid substrates, thin films, membrane*

INTRODUCTION

Thin films fabricated by fragmenting and condensing (polymerizing) material through the use of plasmas have gathered great attention owing to the diversity of film properties attainable and their potential applications.[1] Variation of the plasma conditions and material to be fragmented provides the simplest means to create different thin films with varying properties. However, the vast majority of these films are deposited under reduced pressure or a vacuum environment,[2] which ultimately limits the possible substrate materials and thus the pool of potential applications. Herein, we present for the first time the deposition of glass-like thin films, tens of nanometers in thickness, onto a range of different liquid substrates, which was made possible through the development of a plasma polymerization reactor under atmospheric pressure.[3−5] Importantly, these films are connected in contrast to the "floating rafts" created by self-assembly of particulates best described by the "Cheerios" effect.[6] Comparison of the connected thin films on different liquid substrates (glycerol, an ionic liquid, heavy paraffin oil, and sucrose solution) opens the pathway to explore a range of exotic phenomena.

The use of plasma to assist in the deposition of material leads to a range of thin films possessing a multitude of differing properties.[7] Two processes that utilize plasma are magnetron sputtering and plasma-enhanced chemical vapor deposition (PE-CVD), typically requiring reduced pressure conditions under which to conduct the deposition. In magnetron sputtering, plasma is confined via a magnetic field to the surface of a bulk volume of the material to be deposited, leading to particles being ejected from the bulk and then proceeding via line of sight to condense or deposit on the given substrate. In contrast, PE-CVD uses plasma to fragment monomeric vapor, which then condenses onto the substrate as a thin film. To the best of our knowledge, the works of Ye et al., Borra et al., and Wender et al. are the only to report the plasma-assisted deposition of thin-film coatings onto liquid substrates, although they were limited to magnetron sputtering (performed under vacuum) of metals onto liquids of negligible vapor pressure (i.e., ionic liquids).[8−10] The reduced pressure conditions required for typical magnetron sputtering, or for that matter PE-CVD, limits the variety of liquids that can be used to those with negligible vapor pressure.

The motivation for this work was to use adapt recent advances in the PE-CVD process under atmospheric pressure made recently by Belmonte et al.[10] to produce polymeric coatings onto liquid substrates for the first time, opening a broad range of new applications. The monomeric material of choice in this investigation is a siloxane-based molecule that upon processing in a PE-CVD reactor leads to glass-like thin films. The question then arises as to whether this process for fabricating glass-like thin films can yield deposition on the surface of a liquid?

RESULTS AND DISCUSSION

To investigate this, a variety of four model liquids (glycerol, silicon oil, paraffin oil, and ionic liquid) were chosen that display dissimilar properties, such as polarity, organic/inorganic character, or viscosity. The presence of the glass-like film on the liquid substrate was visually observed as wrinkles on the liquid surface (inset in Figure 1). This was confirmed with energy-dispersive X-ray spectroscopy (EDXS, Figure S1a) that showed an elemental composition consistent with a thin film of glass-like material on the liquid. Taking into account the sensing

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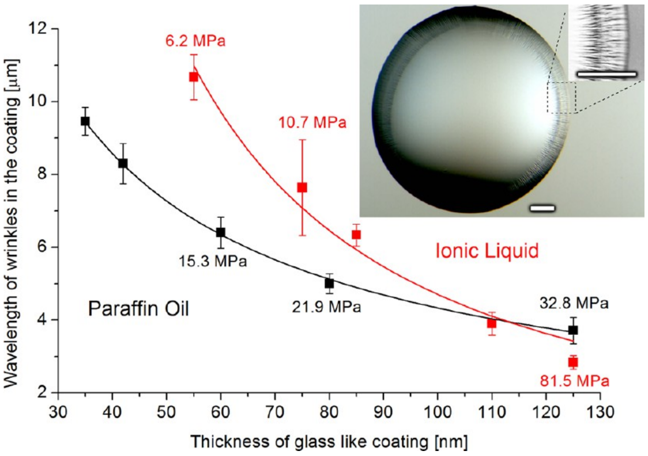

Figure 1. Wavelength of wrinkles, λ, observed at the edge of a paraffin oil and ionic-liquid drop coated with glass-like thin films as a function of the thickness, h, of these coatings. No buckling was observed for coatings thinner than 35 nm, which was most likely the result of a lack of a continuous coating. Coatings thicker than 120 nm displayed a rough surface and complex wrinkle shapes. By fitting the results with a power function, λ was found to be proportional to $h^{-3/4}$ for coating on paraffin oil and to $h^{-3/2}$ for ionic liquid (lines drawn in the graph represent fits of the data points). Numbers on the graph represent the value of the elastic modulus for a given sample. The photographic inset presents a drop of paraffin oil coated with a 35 nm thick glass-like coating. The scale bars in the inset are 200 μm.

depth of EDXS relative to the deposited film thickness, these results are in agreement with the composition of reference glass-like films on solid microscope slides from X-ray photoelectron spectroscopy (XPS, Figure S1b): 35.2% Si, 34.3% O, and 30.5% C.

Buckling of thin-film coatings has been recently observed in coatings on elastomer substrates[12] and liquid surfaces.[13] In these studies, the wavelength of the wrinkles, λ, was found to be proportional to the thickness, h, for coatings on elastomers and $\lambda \propto h^{3/4}$ for films on liquids. In contrast, $\lambda \propto h^{-3/4}$ was found to be the best fit for the glass-like thin films on paraffin oil as the liquid substrate and $\lambda \propto h^{-3/2}$ for coatings on ionic liquid (Figure 1). The contrast between the observed relationship and that described by Huang et al. is hypothesized to arise from the glass-like thin films being grown directly on the liquid substrate as opposed to the transfer of already-grown films from temporary supports onto the elastomers or liquids. When films are grown directly on the substrate of interest, their interaction throughout the growth phase plays a critical role in defining the final thin-film properties. Finally and most importantly, the model used by Huang et al. refers to thin rectangular sheets of polymeric material floating on a liquid substrate. It has translational symmetry that allows the surface-energy component of the Lagrange function for the system to be omitted. Because of the different symmetry and shape of the coatings on liquids described herein, this assumption may not be applicable and in turn would result in a different $\lambda(h)$ relation.

To examine this exotic buckling behavior, the elastic modulus of the coatings on liquid substrates was measured with AFM in the peak force mode using the Derjaguin, Muller, and Toporov (DMT) method.[14] The average modulus across the scanned areas was found to be proportional to the thickness of the thin film for all liquid substrates studied, contrary to the previously studied polymer films that had a constant modulus with thickness.[12] The topography and modulus images show these to be confluent films, with interconnected nanodots that merge into threads (Figure 2) when the film is thicker than 70 nm.

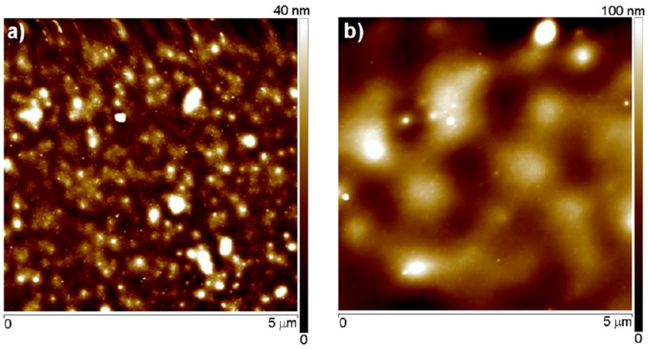

Figure 2. AFM images of coatings presented in Figure 1 on a glass substrate (measured several millimeters away from the droplets): (a) 55 nm thick glass-like coating and (b) 125 nm coating.

Importantly, these films are not merely assembled nanoparticles like those utilized to create liquid marbles.[15] In a review on the properties of liquid marbles, Aussillous and Quére[16] briefly discuss the interaction of liquid marbles with liquid substrates. When a liquid marble comes into contact with a dissimilar liquid (such as a coated water droplet contacting an oil droplet), the marble is spontaneously destroyed. To demonstrate the PE-CVD glass-like films studied here are connected, a film was deposited onto oil, onto which a water droplet was subsequently deposited (Figure 3a). The glass-like film remained stable, and the respective oil and water droplets remained separated indefinitely.

With respect to the film porosity, the boundaries between the threads potentially act as pores within the film, giving it membrane-like properties (an ability to transport material through the glass-like thin film). Films of 55 nm in thickness exhibit a porous structure with many open pores (Figure 3b,c). The modulus mapping of the thin films show the nanodots are of higher modulus and lower energy dissipation than the material connecting them together. A reference image of the glass-like film on the microscope slide adjacent to a paraffin oil droplet gives a structure in agreement with those reported by Belmonte et al.[11] for films deposited on solid substrates (Figure 2). Given the strong effect of the porosity on the value of the modulus observed by Stafford et.al.,[12] the complex morphology and porosity of the glass-like thin film deposited onto liquid substrates implies the elastic modulus is a dependent on the thickness of the film.

Interestingly, the glass-like thin film on the glycerol substrate also displayed some dynamic behavior, which is captured in Figure 4. In the first instance, water from the surrounding environment condenses on the glass-like thin film as micro-droplets as well as within the pores of the thin film because of capillary condensation. This adsorbed water is then transported through the pores, equilibrating within the volume of the main glycerol droplet (microdroplets on the surface decrease in volume). The glass-like thin film capping the main glycerol drop is pinned at its edges such that any increase in the droplet volume (uptake of water) leads to both a change in the contact angle at the pinned edge of the main droplet and a rise in the internal pressure of the droplet (Figure 4a). This rising pressure eventually reaches a high enough level to drive liquid from within the main droplet out through the pores, and the main

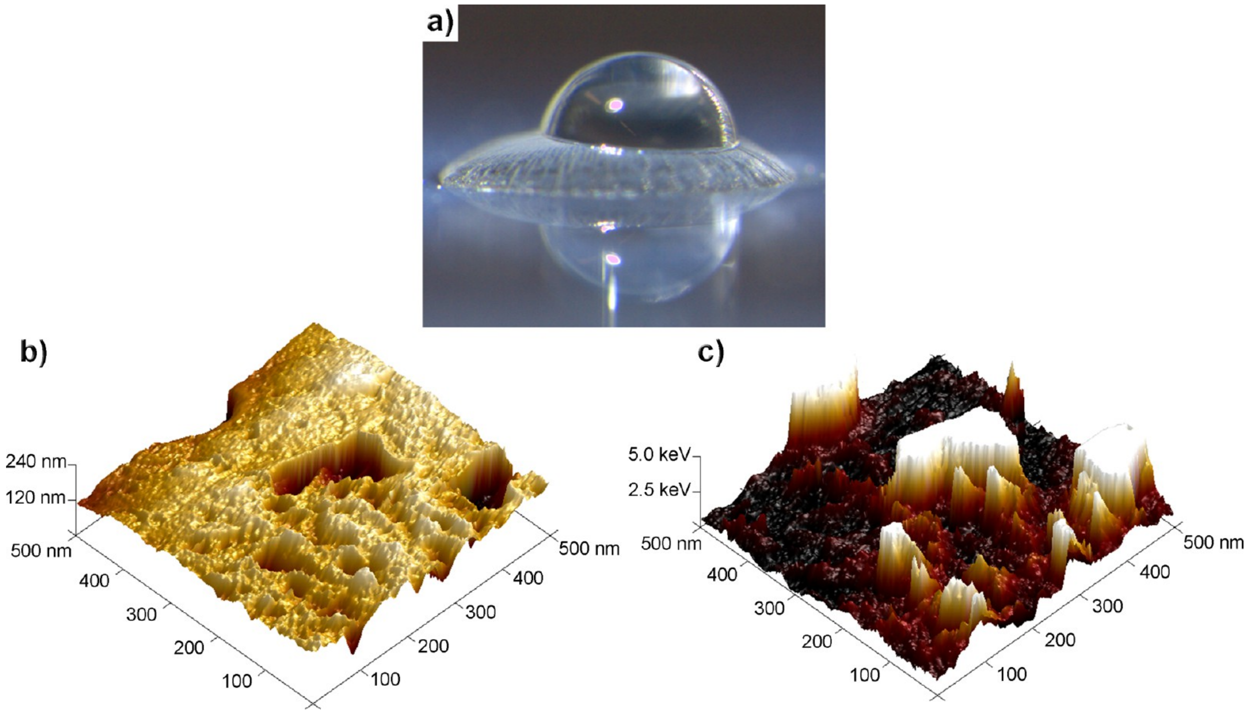

Figure 3. (a) Optical microscope image of a water droplet deposited onto an oil droplet, where the oil droplet was precoated with a glass-like film. AFM images of 65 nm thick porous glass-like thin films deposited onto an ionic liquid displaying (b) topography features and (c) energy dissipation. The energy-dissipation image confirms that the holes observed in the coating expose the liquid surface.

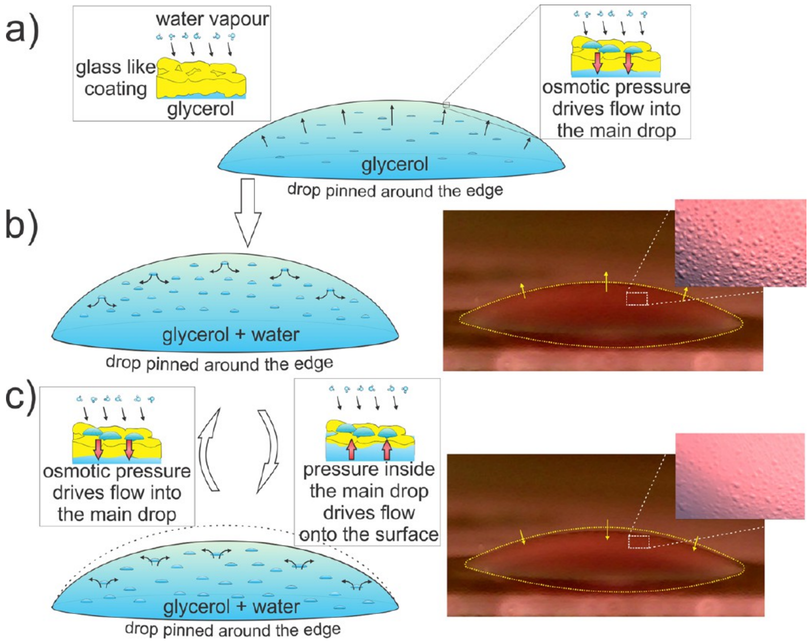

Figure 4. Schematic of the dynamic behavior of the glass-like thin film on a glycerol substrate. (a) Hygroscopic nature of the glycerol combined with the porous nature of the thin film allows water to be collected from the surrounding air environment. Initially water condenses on and in the pores of the glass-like surface. Osmotic pressure is created by the gradient in the water concentration between the adsorbed microdroplets and the glycerol substrate, driving liquid from the microdroplets into the substrate. (b) Liquid substrate expands in volume and increases in pressure until the pressure is high enough to drive liquid back from the substrate to the microdroplets. (c) Flow back to the microdroplets yields a decrease in the pressure and volume of the substrate and an increase in the microdroplet volume. The hygroscopic nature of glycerol allows further uptake of water from the humid surroundings into the microdroplets, creating the concentration gradient and osmotic pressure, and the cycle begins again.

droplet volume contracts (Figure 4b). The microdroplets on the surface of the thin film increase in volume, the content of which has a high glycerol concentration equivalent to that in the liquid droplet substrate. The exposure of these microdroplets to the humid environment allows for more water to be absorbed. This leads to a water concentration gradient between the microdroplets on the thin film and that within the liquid substrate droplet, creating osmotic pressure. To equilibrate the water concentration, liquid flows from the microdroplets back through the porous glass-like thin film into the bulk liquid substrate (Figure 4c). Again, the droplet substrate expands in volume, rising in internal pressure, and the microdroplets shrink (Figure 4b). This continues until the pressure raises enough to force liquid flow back through the thin film, expanding the volume of the microdroplets at the newly equilibrated concentration of water in glycerol. This cycling of liquid from within the liquid substrate to the microdroplets and back continues until the concentration of water in glycerol reaches its equilibrium for the given humidity level in the air. Interestingly, this cycling process is observed on the macroscopic scale as a breathing-like action by the thin-film/glycerol substrate, with the expansion and contraction of the droplet occurring over a time scale of approximately 1 h and continuing to cycle for many tens of hours, resulting in an increase of the volume of the microdroplets on the surface of the coating (Figure 5). The breathing-like action is captured in Movie S1 in the Supporting Information. Because of the hygroscopic nature of glycerol (glycerol is used as a humectant to reduce humidity), the glass-like thin-film membrane on a glycerol substrate can be used to harvest water from the surrounding air environment.[17] A question arising from this observation is whether this phenomenon can be utilized for mass transport through the glass-like membrane.

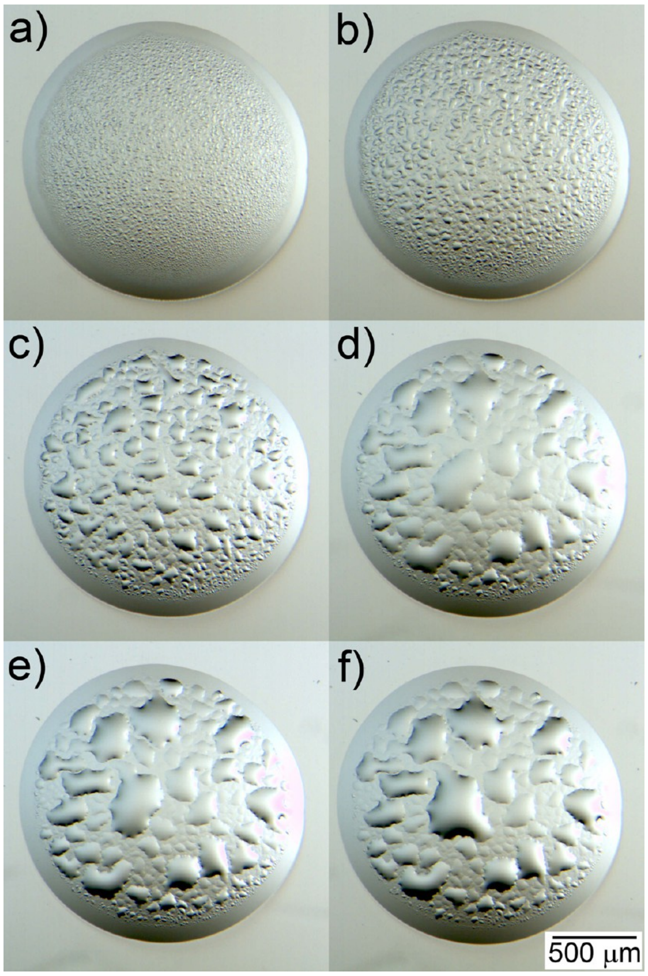

Figure 5. Optical microscope image of the glass-like thin film on a drop of glycerol measured (a) with minor delay after deposition or after (b) 90 min, (c) 18 h, (d) 42 h, (e) 72 h, and (f) 140 h.

To test this idea, glycerol was used as a carrier substance in a slow-release system. Iron(III) chloride hexahydrate, chosen as the transported substance, was dissolved in glycerol to create a 20 wt % solution. This substance was chosen because it is a common oxidant used in the vapor-phase polymerization of polypyrrole.[18] Drops of this solution were cast on a glass slide, and a glass-like coating was deposited onto the glycerol-based solution. Samples were then left for 24 h to enable transport of solution through the membrane. The presence of $FeCl_3 \cdot 6H_2O$ in the microdroplets that had bloomed at the surface of the coating was tested by exposing samples to pyrrole vapor for 10 min (in a similar way as described by Tan and Ge[17]). Because polypyrrole is a dark gray−brown polymer, it is easy to identify under an optical microscope and creates good contrast with the pale transparent yellow glycerol solution of $FeCl_3 \cdot 6H_2O$. The microscope image in Figure 6a,b presents the large drop as well as the microdroplets containing polypyrrole fibres dispersed in the solution with greater concentration of the polymer within the microdroplet (because of the darker color). This observation indicates that (i) $FeCl_3 \cdot 6H_2O$ can be transported through the membrane using the dynamic behavior of the glass-like thin film with glycerol as a carrier liquid and (ii) the membrane enables two-way transport because the monomer also diffused into the main drop. Following this experiment, the sample was stored under ambient conditions for 30 days to equilibrate. During this time, new microdroplets formed on the surface of the main drop. Figure 6c illustrates the presence of polypyrrole containing microdroplets and $FeCl_3 \cdot 6H_2O$-containing droplets, providing further evidence of the diffusion process transporting material from within the main drop and the microdroplets.

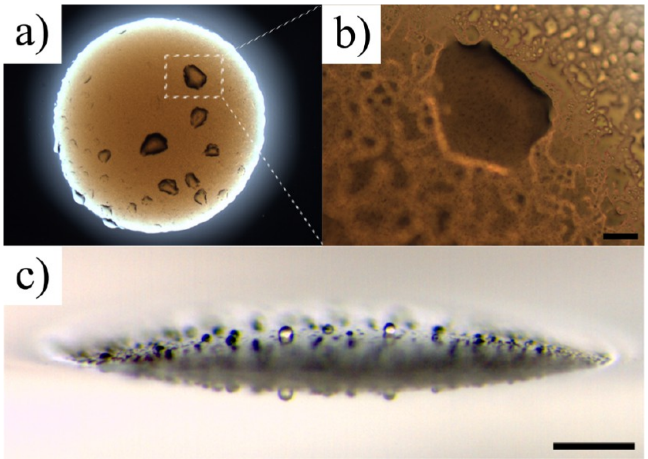

Figure 6. Optical microscope images of a drop of a glycerol-based $FeCl_3 \cdot 6H_2O$ solution coated with glass-like coating, containing vapor-phase polymerized polypyrrole as a proof of concept for a slow-release system. (a, b) Images displaying a microdroplet with polymer fibres within; the scale bar is 20 µm. (c) Image displaying the same drop after 30 days. Microdroplets with polypyrrole (dark) as well as microdroplets containing $FeCl_3 \cdot 6H_2O$ solution (clear) that bloomed to the surface after polymerization can be found; the scale bar is 200 µm.

The exotic dynamic behavior is not limited only to glycerol as the substrate. In the case of silicon fluid as the substrate, other interesting behavior is observed. Paraffin oil and silicon oil are two liquids of similar properties, with paraffin oil being of organic and silicon oil of inorganic nature. The measured static contact angles (Table 1) for both of them on glass were comparable (below 10°, equilibrating to approximately 2.5° over more than 10 min). However, contact angles measured on a glass-like coating were very dissimilar for these two liquids. Silicon oil displays the same value of contact angle as on glass, whereas the paraffin oil forms a drop with a 49° contact angle. A great affinity of silicon oil to both the glass and glass-like coating results, with the drop spreading after deposition of the coating (Figure 7), leaving the glass-like film physically intact.

Table 1. Static Contact Angle of Chosen Liquids on Glass and Glass-Like Coatings

	static contact angle	
	on glass (degrees)	on glass-like coating (degrees)
ionic liquid	21.5	19.5
glycerol	50.5	65.5
paraffin oil	<7	49
silicon oil	<7	<7

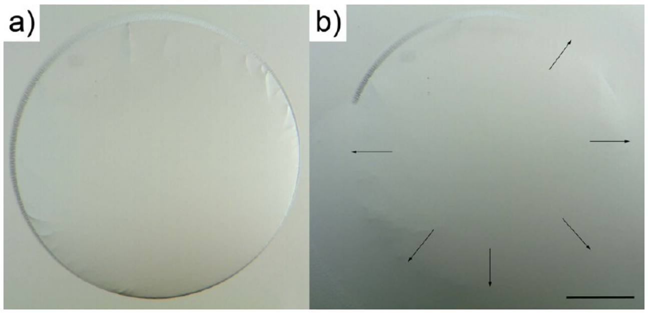

Figure 7. Optical microscope image of a thin film on a drop of silicone oil (a) taken with a minor delay after deposition and (b) 18 h after deposition. The scale bar is 500 μm.

The observed expansion of the area of the droplet can be explained either as silicon oil flowing through the pores in a similar way as glycerol or by silicon oil leaving between glass substrate and the coating. The first scenario is more probable because it can be justified by the coating morphology observations. This phenomenon could be utilized in a similar way as for glycerol, using silicon oil as a carrier liquid in slow-release or self-replenishing systems.

■ CONCLUSIONS

We have presented for the first time glass-like thin films deposited onto liquid substrates that exhibit exotic mechanical and flow behavior. Through careful selection of the liquid substrate along with the tuning of the thin-film material, many device innovations can be made. Exciting areas for exploration include (i) coating aerosols to encapsulate atomized droplets for airborne drug delivery, (ii) using the described effect with glycerol for self-replenishing coatings, (iii) in-water harvesting applications, and (iv) slow release of materials by loading glycerol with an active substance.

■ METHODS

Glycerol (analytical reagent grade) and paraffin oil heavy 68 (laboratory reagent grade) were obtained from Chem-Supply Pty Ltd. Silicone oil (200 fluid, 350 cS) was obtained from Ajax Finechem Pty Ltd. Preliminary results showed that the main selection criterion for a liquid substrate was volatility in high argon flow. Pyrrole was obtained from Merck, and ferric chloride hexahydrate was obtained from Chem-Supply. 1,1,3,3-Tetramethyldisiloxane (TDMS) obtained from Chem-Supply Pty Ltd. was used as a precursor in plasma polymerization to produce glass-like thin films. Thin films were deposited onto droplets of liquid cast onto microscope slides that were precleaned with a mild detergent and water followed by acetone, ethanol, and MiliQ water before flushing with deionized air.

The deposition chamber was an in-house built atmospheric microwave plasma reactor similar to the design described by Cardoso et al.[19] The main part of the reactor where the plasma discharge was generated is a fused quartz tube, 30 mm in o.d. and 26 mm i.d. This tube was inserted across a waveguide taped down to 5 mm in width to increase the intensity of the electric field. The tube expanded out of the waveguide for a length of 50 mm. Ar and O_2 were flushed through the quartz tube with the flow of 1500 and 5.5 L/h, respectively. The TMDS precursor was vaporized by flushing with Ar gas at 60 standard cubic centimeters per minute (sccm) flow and introduced into the quartz tube 25 mm away from the waveguide. Microwaves were generated using a switching power generator (SM 745) from Alter with a supplied magnetron head. The measured forward power was 450 W, and the reflected power with plasma discharge running was 60 W.

Samples were analyzed for composition by X-ray photoelectron spectroscopy (XPS, Specs) and by energy-dispersive X-ray spectroscopy (EDXS) on an FEI Quanta 450 environmental scanning electron microscope. The thickness of the coatings was measured with a Bruker DektakXT profilometer with 12.5 μm stylus under a 3 mg load. Optical microscope images were taken on an Olympus SZX7 with an Altra 20 camera. Optical microscope time-lapse videos were taken with a Nikon Eclipse 50iPOL with a QImaging camera and a USB microscope camera. The relative humidity during the tests with glass-like coatings on glycerol was in the range of 35 ± 5% at 22 ± 1 °C. Atomic force microscopy (AFM) analysis was performed with a Bruker Nanoscope V Multimode 8 in peak force mode using Bruker scanasyst air tips. Viscosity of the liquids was measured with a Brookfield DVDV-II +PX viscometer with the spindle rotating at 60 rpm. Because of the wide range of viscosity values, two spindles were used: LV2 for paraffin oil and ionic liquid and LV3 for glycerol. The viscosity values measured at 23 °C were 160 cP for paraffin oil, 77 cP for ionic liquid, and 945 cP for glycerol.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

EDXS and XPS spectra and a movie of the glass-like thin-film/glycerol substrate breathing. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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