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Liquid Secretion

Photoresponsive Sponge-Like Coating for On-Demand Liquid Release

Anne Helene Gelebart, Danqing Liu, Dirk J. Mulder, Kevin H. J. Leunissen, Jop van Gerven, Albert P. H. J. Schenning, and Dirk J. Broer*

Many publications report on stimuli responsive coatings, but only a few on the controlled release of species in order to change the coating surface properties. A sponge-like coating that is able to release and absorb a liquid upon exposure to light has been developed. The morphology of the porous coating is controlled by the smectic liquid crystal properties of the monomer mixture prior to its polymerization, and homeotropic order is found to give the largest contraction. The fast release of the liquid can be induced by a macroscopic contraction of the coating caused by a trans to cis conversion of a copolymerized azobenzene moiety. The liquid secretion can be localized by local light exposure or by creating a surface relief. The uptake of liquid proceeds by stimulating the back reaction of the azo compound by exposure at higher wavelength or by thermal relaxation. The surface forces of the sponge-like coating in contact with an opposing surface can be controlled by light-induced capillary bridging revealing that the controlled release of liquid gives access to tunable adhesion.

1. Introduction

Coatings form the outer skin of a surface, a device, or a construct. The general purpose is often mainly protection and/or decoration. For biological species, skins are given more functions. For instance, many amphibians secrete mucous for protection or lubrication. And even human skin secretes moisture for temperature regulation and antimicrobial liquids for protection against infections. Inspired by these natural functions, presently more functions are added to man-made coatings. For instance, phototunable adhesion is achieved by either creating a rough surface\(^1\) or by changing the chemical properties of a coating\(^2\) for application in microrobotics. Following the mentioned examples of natural skins, a property that is gaining more attention is the controlled release of fluid at the coating surface with prospects in a wide variety of applications. For example, a recent publication refers to self-lubricating surfaces by the release of a silicone based lubricant.\(^3\) The lubricant is slowly released from the coating which makes the surface extremely slippery avoiding adhesion of a variety of species. Other examples of releasing materials serve medical purposes such as controlled localized release of drugs for in-vivo medical treatment, both inside the body and at the human skin surface. Plasters for burn treatments that control humidity and antibiotics at the skin promote cure and avoid infections.\(^4\) In the in-vitro detection of medical analytes by microfluidic sensors, a timely release of reagents is necessary when the fluid is transported through the channels.\(^5\) Thinking somewhat further, one can imagine that controlled release of surfactants can be used for self-cleaning purposes of contaminant-sensitive surfaces. These applications become even more valuable when the releasing layers can be repeatedly re-filled. In addition, choosing light as a trigger to secrete the desired liquid allows for quick and remote control of both absorption and release.

Here we present a new approach to deliver liquids from a solid coating, both location- and time- controlled. The principle is based on a photosensitive liquid crystal network (LCN). LCNs doped with an isomerizable chromophore are widely known for their light-triggered geometrical deformation, either in free standing films\(^6-9\) or as coatings.\(^10,11\) Often the photosensitive component, typically being an azobenzene, is copolymerized to the LCN. The light-triggered trans-to-cis conversion alters the order parameter of the LCN, consequently inducing large geometrical changes. Besides, LCNs are also known for their ability to be polymerized in the presence of nonreactive species\(^12\) resulting in a composite, confining the nonreactive component in phase separated liquid crystal polymer elements.\(^13-15\) The latter property will be employed to create the on-command liquid releasing coating, further denoted as photosponge.

Dr. A. H. Gelebart, Dr. D. Liu, Dr. D. J. Mulder, K. H. J. Leunissen, J. van Gerven, Prof. A. P. H. J. Schenning, Prof. D. J. Broer Department of Chemical Engineering and Chemistry, Laboratory for Functional Organic Materials and Devices (SFD) Eindhoven University of Technology 5612 AZ Eindhoven, The Netherlands E-mail: D.Broer@tue.nl

Dr. A. H. Gelebart, Dr. D. Liu, Prof. A. P. H. J. Schenning, Prof. D. J. Broer Institute for Complex Molecular Systems (ICMS) Eindhoven University of Technology 5612 AZ Eindhoven, The Netherlands

Dr. D. Liu, Prof. A. P. H. J. Schenning, Prof. D. J. Broer SCNU-TUE Joint Lab of Devices Integrated Responsive Materials (DIRM) No. 378, West Waihuan Road Guangzhou Higher Education Mega Center 510006 Guangzhou, China

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/adfm.201705942.

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2. Results and Discussion

2.1. Design of the Photoresponsive Coating

The general objective of our work is to make a solid coating that reversibly releases and uptakes a liquid material thereby changing surface properties like adhesion or friction. For that we explore a liquid-filled smectic LCN coating. The smectic LCN consists of rod-like mesogenic units that are connected through acrylate polymer chains by a photopolymerization process. By polymerizing the liquid crystal monomers in the presence of the inert liquid, the liquid phase separates on microscale from the forming polymer network. The azobenzene containing monomer is copolymerized with the liquid crystal acrylate and provides the photosensitive function. For secretion of the liquid, we rely on the change of the average molecular orientation of the polymerized elements in response to light to induce dimensional changes of the network. The coating adheres firmly to its rigid substrate which results in strong contraction orthogonal to the surface while the lateral dimensions remain (mostly) unchanged. Thereby the liquid is squeezed out of the coating in a sponge-like manner and collects at the coating surface. The basic principle of this release is presented in Figure 1.

The materials and compositions we explored for our purpose are shown in Figure 2a. For this basic study, we employed 8CB as the releasing material. It has a moderate viscosity, has amphiphilic properties and, moreover, it is liquid crystalline, therefore it helps to obtain well aligned samples, needed for large release properties. Among various initial alignments and phases tested, homeotropic smectic LCNs, i.e., with the LC director perpendicular to the substrate, resulted in the largest contraction (see Table 1) although the difference with a frozen phase in nematic phase is marginal.

2.2. Structural Characterization of the Coating

We based our smectic photosponge coating on an LC mixture of azobenzene/diacrylate/monoacrylate (40/27/33) and various amounts of nonreactive mesogen, 8CB (Figure 2a). After polymerization and subsequent removal of 8CB by extraction in hexane, scanning electron microscopy (SEM) images of the polymer network reveal a porous structure (Figure 2b,c). The pore size varies roughly from 0.5 µm at the bottom to 0.1 µm at the top of the coating. The size difference might be attributed to the sample preparation where capillary forces contracts the network of the hexane near the interface with air. On the other hand, phase separation and gradient formation may occur during polymerization under the influence of polymerization-induced diffusion due to a gradient of UV light during the photopolymerization process.[16]

We also performed a structural characterization of the sponge by X-ray diffraction on the samples prior to removal of the 8CB. The smectic phase has an additional advantage that the lamellar spacing (d) gives information related to contraction of the network upon isomerization of the azobenzene moiety. For this measurement, we selected the sample with a ratio LCN/8CB of 30/70. The small angle 1D profile obtained from the Grazing-incidence small-angle scattering (GISAXS) measurements shows the presence of two diffraction signals. The peak at 3.1 nm is attributed to the 8CB dimer[1] while the peak at 3.9 nm is attributed to the network (Figure 2d), confirming the phase separation as observed with SEM images. The assignment of the peaks is supported by heating experiments reported in the SI. Above the smectic to nematic transition of 8CB the 8CB peak disappears while the network peak remains in place. On the other hand, when the network is exposed to 365 nm light, the network contracts due to contraction when the azobenzene undergoes its conversion from the trans to the cis form and the peak shifts to higher q. However, we may conclude that full phase separation does not occur and we rather suggest the presence of an LCN rich phase and an 8CB rich phase, based on literature on polymer stabilized liquid crystal devices.[17]

2.3. Light Induced Release

The photosresponse of the coating is investigated by exposing the sample to UV light (365 nm) in order to address the azobenzene.

![Figure 1. Principle of a photosponge coating. During the formation of the coating the mobile liquid is phase separated from the polymer network (left). The white area resembles here the continuous phase of the polymer network and the green area the phase separated 8CB molecules. The insert shows that both the network, consisting of the blue polymerized reactive mesogens, and the green unbound 8CB molecules have adapted the smectic order. Upon reduction of the molecular order by light the liquid is expelled at the surface in the form of initially small droplets (green) which may coagulate in a later phase to form a continuous wet film (right).](image-url)
At the illuminated regions a decrease of the coating thickness is observed, and interestingly, droplets of the nonreactive and liquid 8CB appeared at the surface in accordance with the model schematically depicted in Figure 1. We studied samples having different compositions with LCN/8CB ratios ranging from 100/0 to 30/70 (Figure S1, Supporting Information). The release is recorded in time by optical microscope (Figure 3a–c) and by interference microscope (Movie S1, Supporting Information). When the coating is illuminated, the formation of 8CB droplets at the surface occurs (Figure 3b). When the illumination stops, the droplets slowly diffuse into the coating again (Movie S1, Supporting Information). The size and number of droplets is linked to the initial amount of 8CB in the network. For the sample containing 70% of 8CB, the droplets grow until they suddenly coalesce and form a continuous liquid film at the surface of the sponge (Figure 3c; Movie S2, Supporting Information). Upon exposure to 455 nm light, the azobenzene isomerizes back to its initial trans isomer and the liquid layer is reabsorbed fully by the sponge-like coating in a reverse manner. The sponge-like character of the coating is also demonstrated in the scanning electron microscope images in Figure 3d. For this experiment we removed the 8CB by extraction in hexane while maintaining the morphology (left figure). It shows an open porous structure demonstrating the space initially taken by the 8CB molecules. After light exposure (left figure) the film collapses and the open pores compress as one would expect when wringing a sponge.

While 8CB forms droplets at the surface during the initial stage of UV triggered secretion, interestingly along the edges of a partially removed coating no droplets are formed at the glass substrate. Instead, the 8CB is emitted at the edges and wets the

**Table 1.** Influence of the liquid crystal phase and alignment prior to polymerization on the contraction of the network along its normal after removal of the expelled liquid. Measurements were performed on a sample containing 50 wt% of 8CB.

<table>
<thead>
<tr>
<th>Alignment</th>
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<th>Planar</th>
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<tr>
<td>Phase</td>
<td>Isotropic</td>
<td>Nematic</td>
</tr>
<tr>
<td>Deformation</td>
<td>−4%</td>
<td>−10%</td>
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glass surface to form a continuous 5 µm wide film adjacent to the coating. Because the secretion of 8CB occurs both at the edge and at the top, we investigated this feature to estimate whether it can be applied to control liquid release at a preferred position on a coating; for instance, to guide the liquid into prestructured channels at the surface. Thereto we fabricated coatings with motifs of various height and spacing, as shown in Figure 4a. When the pattern size, as defined by the pitch \( p \), is large (\( p > 100 \) µm), the influence of the release at the side of the structure is negligible and results in the formation of droplets in both top and bottom areas as seen in Figure 4b. At smaller distances \( p \), the amount of liquid released at the sides of the higher parts becomes relatively more dominant. Consequently, the channels between the elevated corrugations fill themselves with liquid and, driven by surface tension, form a meniscus against the standing walls as schematically shown in Figure 4c. When the distance between two motifs is of the order of 15 µm the side release is predominant, and driven by capillary forces the lower areas are preferentially filled with liquid 8CB. The process is fully reversible and under the influence of 455 nm light, the network goes back to its initial conformation, and the liquid is subsequently reabsorbed.

For implementation in practical systems the kinetics of the release and reabsorption are of eminent importance. It appears that both occur within a short lap of time. The photostationary state (accompanied by the contraction of the network and the release of the 8CB) is reached within 40 s exposure to 365 nm light with an intensity of 200 mW cm\(^{-2}\). An even shorter time (10 s) is needed for the azobenzene to relax to the trans state upon exposure to 455 nm light (Figure 5a). Visually, the release of droplets occurs quickly (within 10 s) in agreement with the isomerization of the azobenzene units and they coalesce to form a layer upon longer exposure. This can be explained by further conversion of the azobenzene units in the deeper layers of the film, subsequently releasing the extra amount of liquid needed to create the liquid layer (Figure 5a).

The contraction of the sponge-like coating scales with the amount of 8CB present (Figure 5b). Note that also the coating without 8CB tends to contract. This is enhanced by the presence of 8CB released during the contraction process. From the contraction observed, and by assuming that the expansion is limited in the \( xy \)-plane, we roughly estimate the amount of release for each coating to 0.072, 0.177, and 0.302 mm\(^3\) mm\(^{-2}\) for the coatings containing 30%, 50%, and 70% of 8CB, respectively. One should also note that the release can be triggered by an increase of temperature to the nematic and isotropic phase (Figure S2a, Supporting Information). In that case, a liquid layer is formed directly without having the intermediate step of droplet formation.

### 2.4. Photoresponse Mechanism

The mechanism of light driven release is investigated with X ray diffraction shown in Figure 6. Similar studies were performed for the temperature triggered release and can be found in the supporting information (Figure S2b, Supporting Information). By subjecting the coating to UV light, the peak attributed to the lamellar structure of the network shifts from 3.9 to 3.5 nm which corresponds to a contraction of the layer spacing (d) of 0.4 nm.
It can also be noticed that the peak broadens over q, meaning that the distribution in d-spacing varies throughout the thickness of the film, while the orientation of the layers remains barely affected. We postulate that, despite photobleaching by the transmission through the sample increases in time due to the disappearance of the trans absorption band of the azobenzene chromophore, the bottom layers contract less because of a gradient in absorption throughout the thickness. The peak at 3.1 nm, related to the dimension of 8CB dimers, remains mostly unaffected by the exposure to UV light. Only a small decrease in intensity can be noted, indicating a limited loss of order. Furthermore, on the 2D diffraction pattern, a sharp arc over θ appears upon exposure. We attribute this to the presence of smectic droplets of 8CB at the surface. The layer spacing is conserved and well defined, but since the layers are curved along the surface of the half sphere, the overall orientation is

Figure 4. Liquid release at structured surfaces. a) Picture of the structured indentations between cross polarizers. Homeotropic alignment is obtained over the whole area regardless the presence of structure. On the left, a stripe like indentation pattern with a pitch of 120 μm; in the center, a square motif of 100 μm squares separated by a 50 μm gap; on the right, holes with a diameter of 15 μm at an equidistance of 25 μm. b) 3D view of the surfaces before and after exposure to UV light. The reversible process can be obtained when exposed to 455 nm light. c) Schematic representation of the diffusion process leading to secretion of liquid for different pitches p. The yellow arrows indicate top emission; the green arrows side emission.

Figure 5. Response to light exposure. a) Kinetics of isomerization and relaxation of the azobenzene. Normalized absorbance at 365 nm upon illumination with 365 and 455 nm light. b) The contraction along the normal, given in percentage of the initial thickness, of coatings containing various amounts of 8CB. The average initial coating thickness is 18.4 ± 1.6 μm.
isotropic as explained in the insert of Figure 6. Upon exposure to 455 nm light, the peak returns to its initial position and intensity, confirming that the system is fully reversible. These experiments reveal that the mechanism behind the release of 8CB during exposure to UV light is mainly due to the contraction of the network induced by photoisomerization of the azobenzene moieties and resembles the release and uptake of water by an ordinary sponge (Figure 1).

2.5. Light Tunable Capillary Adhesion

In order to estimate whether the controlled release of liquids may lead to macroscopic and measurable phenomena we studied the tribological properties of the released 8CB between two parallel plates. Thereto friction measurements are carried out by sliding two sponge cladded glass plates against each other at a constant speed (Figure S3 in the Supporting Information and experimental description in ref. [1]). A constant normal load ($F_N$) of 0.5 N is placed on top of the coating during sliding and the kinetic friction force ($F_k$) was measured before and during UV exposure. The kinetic friction coefficient ($\mu_k$) is the ratio of friction force to the normal force. In the initial state, prior to the release of the 8CB liquid, $\mu_k$ is on the order of 0.4. Upon releasing 8CB by UV exposure, $\mu_k$ increases by a factor of 4 (position 2, Figure 7a).

The increased friction is attributed to the capillary pressure induced by the very thin film of released 8CB from the sponges. The liquid between the two plates forms a so-called capillary bridge of which the connecting force between the plates inversely scales with the thickness of the liquid film as derived from the Young–Laplace equation.23,24 Upon continuation of the UV exposure more 8CB is released and, eventually, the entire microsized gaps between two coating surfaces is filled with a thin liquid layer, but thick enough to enhance shearing of the two plates with a force about equal to the initial force (position 3, Figure 7a). The shear forces between two sliding surfaces can be regulated by dosing the amount of liquid release, for instance by balancing the dose of UV light and blue light as shown in the experiment presented in Figure 7b. When the friction force reaches its maximum, we switched the light source from UV to blue light. Consequently, the released fluid is sucked into the sponges. The corresponding friction force is further increased to a higher value (marked 4, Figure 7b,c).

We explain this significant increase of friction force by the formation of an ultrathin but continuous liquid film eventually followed by a liquid-maintained partial vacuum between the two coating surfaces while the liquid is further sucked in the polymer sponge. Even under the external mechanical force by shaking several cycles (position 4, Figure 7c), the coating still does not slide (Movie S3, Supporting Information). The principle has the potential to make a light-controlled soft robotic brake or temporary dynamic fixes in self-mounting systems.

We further studied the light-controlled static adhesion/detachment of two coatings surfaces. Two photosponges are placed on top of each other at a tilted angle, sliding does not occur (Figure 7c). Upon UV exposure, the two coatings adhere tightly by the capillary bridge and do not slide even by increasing the tilt angle to the vertical position (position 2, Figure 7c,d). It should be noted that the liquid layer in between the two plates is still in its smectic phase, with the planes of the smectic layers parallel to the surface. This means that the viscosity of the layer is considerable, i.e., at room temperature in the order of 0.05 Pa s.[18] Even so, the viscosity was found[18] to be thickness dependent for very thin films and tended to increase for lower thicknesses in the nanometer region which might be playing a role here as well. Upon longer exposure, when the released 8CB forms the thicker continuous layer between the coatings, the capillary pressure drops and the coating falls (position 3, Figure 7c,d; and Figure S4 and Movie S4, Supporting Information). In a control experiment, where the two coatings are placed onto each other and the table is tilted but without illumination, the top sponge slides freely (Figure 7c, and Figure S5, Supporting Information).

3. Conclusion

In conclusion, we developed a sponge-like coating that is able to release and absorb a liquid repeatedly and reversibly upon exposure to light. The amount of liquid that can be released is
considerably affected by the initial content. The type of release, either droplets or film, can be controlled be the dose of UV light. The release of liquid can be integral over the whole surface, can be local by directed exposure or can be channeled at or into dedicated areas by indentations integrated in the coating surface by reaction molding. The local release can be used to control the trajectory of liquid droplets at the surface of the coating (Figure S6, Supporting Information). Interestingly, we have also shown that we can control the formation of capillary bridges that determine the strength of adhesive forces between two parallel plates. Besides, as the secreting liquid can in principle be replaced by another liquid, eventually after adjustment...
of the physical properties of the network molecules with respect to polarity, the photosponge coatings have the potential for controlled localized release of drugs, release of reactants in, e.g., microfluidic reactors and self-cleaning coatings and antigraffiti solutions.

4. Experimental Section

Materials and Mixture Preparation: The three monomers described in Figure 2 were kindly supplied by Phillips and used as received. The nonreactive mesogen, 8CB, was purchased at Synthon and used as received. The photoinitiator (Irgacure 819) was purchased at Cibachem. The mixtures were prepared by dissolving the components in dichloromethane, and subsequently evaporating the solvent under an argon flow.

Cell Formation and Polymerization: Coatings with a uniform thickness were prepared by using LC cells where one side was provided with a monolayer of 3-(trimethoxysilyl)propyl methacrylate and the other side was coated with trimethoxy(octadecyl)silane. Such combination resulted in the coating being attached to one side preferentially upon opening the cell. The cells were formed by gluing together the two glass plates with a glue containing well-defined spacers of 20 µm to have a controlled gap. SU-8 negative photosets were used to create the mold when working with structured surfaces. SU-8 was purchased at MicroChem. To create the coating, the mixture was heated to the isotropic phase and the cell was subsequently filled by capillary forces. The filled cell is then cooled down to the desired phase. The sample was placed under an EXFO high pressure mercury lamp for 45 min to ensure full polymerization of the network. A 405 nm cutoff filter was used during the polymerization to prevent premature isomerization of the azobenzene. After polymerization the cell is open using a razor blade. Release of the liquid was performed by exposure to UV light using a 365 nm LED light from Thorlabs. To obtain the SEM pictures, 8CB was removed by soaking the coating in ethanol for about 10 min to obtain the porous structure.

Characterization: A Leica CTR 6000 microscope was used to characterize the phase and alignment of the mixture and visualize the release of liquid. A DSC-Q1000 from TA instruments was used at a rate of 5 °C min⁻¹. The second cycle was used for characterization. XRD experiments were performed at the DUBBLE-BM26B beamline at the ESRF, Grenoble, France. 2D images were recorded using a Pilatus 1M detector. SEM was performed on a Jeol 5600. Height profile was obtained using a Michelson interferometer (Fogale NanoTech zoomsurf 3D). The contraction is calculated as the ratio of the height after contraction over the initial height. Droplet formation is studied by digital holographic microscopy (Lyncée Tec SA.).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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