Compliance-Mediated Topographic Oscillation of Polarized Light Triggered Liquid Crystal Coating

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The ability to induce oscillating surface topographies in light-responsive liquid crystal networks on-demand by light is interesting for applications in soft robotics, self-cleaning surfaces, and haptics. However, the common height of these surface features is in the range of tens of nanometer, which limits their applications. Here a photoresponsive liquid crystal network coating with a patterned director motive exhibiting surface features that oscillate dynamically when addressed by light with modulated polarization is reported. By utilizing a compliant intermediate layer, the surface topographies increase with a factor 10, from roughly 70–100 nm to 1 μm. This increase in topography height is accompanied by a superimposed dynamic oscillation with an amplitude of ≈100 nm. These values can be translated to a 16.7% average static strain with 3.3% oscillations with respect to the coating thickness. Moreover, utilizing the complying support increases the maximum rotation speeds with an in-phase response from 2.5 up to 25° s⁻¹. However, at this maximized rotation speed the oscillation amplitude decreases to about half of the initial value.

1. Introduction

The surface of a material is the communication channel between its bulk property and the environment or between the function of a device and the human perception. The surface properties are largely determined by the hierarchical topographical landscape of the material, varying from nanometers to micrometers in height and from micrometer to centimeters in lateral direction. Controlling these landscapes in shape and size is crucial to tune the surface properties. The ability of surface topographies to respond to external triggers gives rise to new applications in the field of haptics, friction control, self-cleaning (by repelling or rejecting liquids and/or solids), structural color changes, and adaptive micro-optics.\(^1\) The next challenge is to achieve continuous oscillatory dynamic materials with large and fast responses. This type of response translates to a perpetual change upon continuous triggering and is interesting for applications such as haptics.

Polymers containing azobenzene light-responsive trigger molecules provide a basis for investigating different topographies on surfaces.\(^4\) The azobenzene molecules allow for controlled switching, based on the trans-to-cis and cis-to-trans isomerization. These can be controlled by selectively illuminating the azobenzene’s absorption bands, being 365 and 455 nm, respectively.\(^11-10\) However, it remains a challenge to obtain reversible and/or dynamic topographies at high respond speeds combined with large topographical changes. At most, the deformations achievable are up to a micrometer at best. These large topographies were only reported for chiral nematic liquid crystal (LC) coatings.\(^2,12\) For other glass-supported azopolymers, topographies are smaller, reaching up to only a few hundred nanometers.\(^13,14\) We have shown before that oscillations in glass-supported coatings are achievable by changing the polarization state of incident ultraviolet (UV) light.\(^11\) The azobenzene’s dichroism leads to a change in absorption and surface topography as response to the constant changing polarization of UV light. We observed localized topographies near the defect lines, where the largest stresses accumulate. However, depending on the desired application (haptics or friction control), the achieved topographies and oscillation amplitude can be rather small. It would be of great interest if the localized stresses could be expressed globally to enhance the topographies. Glass as a substrate limits and governs the topography size by suppressing lateral stresses. To express these stresses, harder responsive layers are typically deposited on soft substrates. Examples showing stress releases in coatings typically show wrinkling, as two layers between its bulk property and the environment or between the function of a device and the human perception. The surface properties are largely determined by the hierarchical topographical landscape of the material, varying from nanometers to micrometers in height and from micrometer to centimeters in lateral direction. Controlling these landscapes in shape and size is crucial to tune the surface properties. The ability of surface topographies to respond to external triggers gives rise to new applications in the field of haptics, friction control, self-cleaning (by repelling or rejecting liquids and/or solids), structural color changes, and adaptive micro-optics.\(^1\) The next challenge is to achieve continuous oscillatory dynamic materials with large and fast responses. This type of response translates to a perpetual change upon continuous triggering and is interesting for applications such as haptics.

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In this work, we present an approach to bridge the effects observed in freestanding films and the applicability of

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surface-attached coatings. For that, we created a layer stack with a soft compliant layer between glass and the photoresponsive glassy coating. Different compositions of soft layers were used based on acrylates to achieve an optimal actuation, focusing on a larger deformation and faster response depending on the domain size.

2. Results and Discussion

The detailed preparation of the azobenzene-containing liquid crystal network (azo-LCN) coatings supported by a soft compliant layer in between the coating and the glass substrate is described in the Experimental Section. Briefly, a nonpolymerized soft acrylate layer consisting of 2-ethylhexyl acrylate (EHA) and tetra (ethylene glycol) diacrylate (TEGDA) has been sandwiched between an acrylate functionalized glass plate and a pre-made 6 µm thick azo-LCN coating (Figure 1: Figures S1 and S2, Supporting Information). After photopolymerization of the soft compliant layer, a stable layer stack is obtained. By decreasing the cross-link density (expressed in vol% EHA), the modulus of the soft layer can be changed from 900 to ≈1 MPa (Figure S3, Supporting Information). We found that the azo-LCN polymer has a high storage modulus of ≈2.6 and 1.1 GPa, parallel and perpendicular to the director, in the absence of light. Upon illumination with UV and blue light, the modulus drops to 0.85 and 0.1 GPa for parallel and perpendicular director upon linear polarized UV (LPUV) irradiation parallel to the director (Figure S4, Supporting Information).

The azo-LCN coating is aligned in adjacent line domains with orthogonal director. The anisotropic expansion and contraction perpendicular and parallel to the director, respectively, induced by illumination are indicated with the red arrows in Figure 1.

In order to obtain the topographies, the azo-LCN bilayer is exposed with static polarized UV light (365 nm) and unpolarized blue (455 nm) light at an intensity ratio of 0.1. Earlier work has proven that this ratio leads to the largest deformation by continuous trans–cis–trans isomerization.[18] The angle of the polarizer is aligned at 90° to fully express the stress created by the contracting line. This alignment led to a maximum topography height. We also expect that part of the light will be absorbed by the 0° aligned line caused by the cosine-shaped intensity transmission of the polarizer and the distribution function of the azobenzene molecules with respect to their director. As can be seen in Figure 2a (Figure S3, Supporting Information), different topographical heights for 500 µm wide lines were obtained for the various compliant layers. Upon increasing the EHA content, and thus the compliance (the inverse of the tensile storage modulus), we observe an increase in the height of the topographical feature.

From previous work on glass-supported azo-LCN coatings, we know that most of the stresses and resulting strains are expressed near and at the boundaries of the aligned domains within a range of 20 µm. In our bilayer system, we see a similar response of the azo-LCN coatings on the higher cross-linked substrates (≤40 vol% EHA, ≥60 MPa). However, remarkably for the compliant substrates with lower cross-link density (≥60 vol% EHA, ≤15 MPa), a clearly distinguishable amplification of the structure height occurs. This makes us believe that the lateral stresses are propagated throughout the soft substrate layer to the neighboring domains. Figure 2a shows the profiles of the 500 µm wide domains for the different compliant bilayers under static polarized illumination.

The profiles of each bilayer, in Figure 2a, are centered at 500 µm and a mismatch is visible at 0 and 1000 µm. This observation is a direct confirmation of the stresses being transferred and expressed through the soft substrate leading to larger deformations with broadening and narrowing of the 0° and 90° line domains, respectively. This change in line width is plotted in Figure 2b as relative domain size (the width of the deformed topography divided by the pitch of the line pattern) as function of the compliance. Here we observe that the lateral

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**Figure 1.** a) Polarized micrographs of the azo-LCN acrylate bilayer at different polarization angle of the polarizer (P) and analyzer (A). b) Graphical representation of the line pattern alignment of the azo-LCN coating (top) and of the bilayer coating with the compliant layered sandwiched between the azo-LCN and the glass substrate (bottom). The red arrows indicate the stress induced by UV light as result of the alignment. The thickness of the azo-LCN coating is 6 µm and the soft layer is at least 70 µm. Typical line widths are 100 and 500 µm.
change levels off at increasing softness. The change relative domain sizes of both domains are a direct mirror image and diverge toward an expansion and shrinkage of \( \approx 3\%–4\% \) for the \( 0^\circ \) and \( 90^\circ \) domains, respectively. These values are larger than those found by van Oosten et al. for the contraction and expansion of freestanding uniaxial aligned azo-LCN films.\(^{[19]} \) It is important to realize that in our case the change in domain size is an interplay of both parallel contraction and perpendicular expansion, leading to these higher values.

Furthermore, we believe that the thickness of the sublayer plays an important role for less compliant layers. This thickness is chosen to be 10 times the thickness of the azo-LCN top coating. Especially for the softest sublayers, an onset of wrinkling-like phenomena might be observed at the larger periodicities, explaining the shift of the maximum deformation toward the center rather than at the edge of the director domain (ear shape structures).

Next, the polarization axis of the UV light is continuously rotated, in presence of a stationary blue light source, stimulating the trans–cis azobenzene conversion in specific domains. The blue light promotes the back reaction of the azobenzene. This combination provides a continuous shift of the balance between the forth and back reaction of azobenzene, forming a continuously changing stress between the two domains in the coating. In Figure 3, the height difference of these structures is shown as function of time under illumination with rotating
LPUV and unpolarized blue light. The definition of the height difference is given in the Experimental Section. Upon further investigation of the shape and velocity of the oscillation at the various compliances of the sublayer, we observed an asymmetric phenomenon. For the harder layers, the oscillation is symmetric, as indicated by the shape of the velocity profile in Figure 3b. For the softer compliant layers, we noticed that the oscillation has an inverted U-shape, and the velocity profile during time tends to form a sawtooth shape.

In order to investigate the stress-translating effect of the compliant layer in more detail, we studied the height difference and oscillation of different line widths (domain sizes). For a hard layer (0.9 GPa, 0 vol% EHA), we found a dependency of the lateral dimensions of the lines and concluded that smaller widths (~25 µm) lead to more expressed surface structures (Figure 4a). This finding is due to the local expression of the stress near the defect. In contrast, for the softest substrate (1 MPa, 95 vol% EHA), we observed a large increase in topography height by increasing domain size (Figure 4b). This observation confirms that the topographies created on soft layers are an expression of the lateral stresses induced by the adjacent domains. Figure 4c,d shows the topographies formed for both compliant layers with the same scale. For complete depiction of the oscillatory actuation, see video clips in the Supporting Information. The smaller topography size in the thinner domains (25 µm) is caused by the limited widening and thinning of the domain size through the limited shear applied by the smaller domain.

Lastly, we investigated the influence of the rotation speed of the polarizer for the softest sublayer (95 vol% EHA). The domains tested were 100 µm wide to ensure a full observation of the complete area with a 10x DHM objective. The optimal rotation speed was determined by plotting height and its derivative (speed) as function of time with increasing rotation speed of the polarizer every two full rotations (Figure 5). We observed a slight inverted U-shape oscillation for all oscillations and the derived speed confirms this asymmetry. From the bottom graph (II), it can be derived that the speed of the oscillations is asymmetric for all different speeds. Importantly, the topography size does not diminish with increasing rotation speed. The amplitude decreases from 96 to 57 nm upon increasing the rotation speed to 25° s⁻¹ (Figure S7, Supporting Information).

3. Conclusion

The use of a compliant sublayer for supporting a patterned azo-LCN coating has a large effect on the formation of topographical structures by light. We have demonstrated an amplification of a factor 10 for the height of the surface topographies and an increased oscillation speed when addressed by a polarization modulating light source. As result, topographies of 1 µm can be achieved in fully planar aligned azo-LCN coatings with oscillations reaching to ~100 nm in amplitude. This corresponds with a topographic structure of 16.7% oscillating at 3.3% of the
azo-LCN coating’s thickness. In contrast to LCN coatings directly on glass or on a stiffer sublayer, the patterned LCN coating on a low modulus sublayer gives the largest topographical heights for the larger domain sizes (0.5 mm), whereas for LCN coatings on a hard sublayer (0.9 GPa) the smaller domains (25 µm) perform best with respect to topography height and amplitude. Of relevance for applications, we have observed large deformations at much higher rotating speeds than in the absence of the soft sublayer. Increasing the rotation speed with a factor 10 only depletes the total topographical heights with 20 nm. However, the oscillation amplitude nearly drops to half of the original value. All these results show an interesting new design of materials to overcome the applicability issues of glass-supported azo-LCN coatings.

The improvements made by only implementing a soft support layer lead to the possibility to design new applications while having the ability to fine-tune the response without completely changing the chemistry. The much faster oscillations and larger topographies can further expand on applications in haptics, robotics, or even toward control of materials on surfaces.

4. Experimental Section

Materials: Azo-LCN coatings were made from a mixture of liquid crystalline acrylates and additives, as shown in Scheme 1, and have been described previously in more detail.[11] Monomers 1–3 were obtained from Merck UK. Monomer 4 was custom-synthesized by Syncom (Groningen, the Netherlands). Photoinitiator 5 was obtained from Ciba. The azo-LCN composition consists of 42 wt% monomer 1, 21 wt% monomer 2, 31 wt% monomer 3, 5 wt% monomer 4, and 1 wt% photoinitiator 5. The constituents were mixed homogeneously by dissolving in dichloromethane. The solvent was removed under a reduced atmosphere to achieve a reactive LC monomer mixture. The photoalignment layers used are Brilliant Yellow (BY) and PAAD-22. These materials were bought from Sigma Aldrich and BEAM Co, respectively. BY was dissolved at 1.5 wt% in dimethylformamide (DMF) and PAAD-22 was diluted 3 times in DMF prior to application. The soft layers were made from a mixture of EHA and TEGDA in a volume ratio of 0.95, 0.80, 0.60, 0.40, 0.20, and 0.00, respectively, with 1 wt% of photoinitiator 5. 2-(trimethoxysilyl) propyl methacrylate was bought from Sigma Aldrich and dissolved in ethanol at a 1 vol% concentration.

Preparation of the Patterned LCN Coatings on Soft Layers: Glass substrates (3 × 3 cm²) were cleaned by sonication using acetone and propanol-2 followed by UV ozone cleaning. The photoalignment material (BY or PAAD-22) and 2-(trimethoxysilyl) propyl methacrylate solution were spin-coated onto the cleaned substrates and baked for 10 min at 100 ºC. BY or PAAD-22 coated substrates were glued together using an adhesive containing 6 µm spacers. The BY or PAAD-22 surfaces of the thus obtained LC cells were patterned by a two-step exposure. For BY, in the first step, the sample was exposed to polarized light through a mask for 5 min. In the second step, the mask was removed and a shorter flood exposure, 2 min, was applied with light with polarization orthogonal to the first exposure. For PAAD-22, the patterning was performed in a two-step procedure as well. First, a flood exposure of 2 min in one polarization direction is performed followed by a masked 1.5-min orthogonal aligned polarization exposure. These LC cells were filled with the LC monomer mixture by capillary forces at 75 ºC. The filled cells were cured at 38 ºC with light >400 nm (EXFO Omnicure S2000). Afterward, one of the glass plates was removed leaving a coating adhering to glass on one side and with a free surface on the other side. This azo-LCN coated
substrate is glued to an acrylate-modified substrate with adhesive containing 70 μm spacers. This newly constructed cell is filled with the EHA-TEGDA mixture and polymerized with light >400 nm for 15 min at room temperature. Afterward the top glass plate with the alignment layer was removed and the desired layer stack was obtained. Figure S1 shows a scheme of the preparation of these layered coatings.

Characterization and Actuation of the Azo-LCN Soft Layered Coating: The monomeric LC mixture and azo-LCN coating were characterized using a crossed-polarized optical microscope (Nikon Ci Eclipse) equipped with a thermo-controlled stage (Linkam). For the monomeric mixture, the nematic to isotropic transition temperature is determined by cooling from the isotropic liquid to the nematic LC phase. Both the polymeric and monomeric transitions were confirmed using differential scanning calorimetry (DSC Q1000, TA Instruments). The mechanical properties of the individual polymer layers were measured with a dynamic mechanical thermal analyzer (DMTA, Q800 Dynamic Mechanical Analyzer, TA Instruments). The illumination of uniaxially aligned azo-LCN films during the modulus measurement in DMTA was performed with a 365 nm LED (M365L, Thorlabs) equipped with a thermo-controlled stage (Linkam). For the monomeric mixture, the nematic to isotropic transition temperature is determined by cooling from the isotropic liquid to the nematic LC phase. Both the polymeric and monomeric transitions were confirmed using differential scanning calorimetry (DSC Q1000, TA Instruments). The acquisition rate of the holograms was set to 0.5 frames real-time. The change in height was plotted as a difference between the 90° and the 0° domain. For smaller domains, the complete domain was monitored. The change in height was plotted as a difference between the 90° domain and the 0° domain. Changes of the surface were monitored in real-time. The acquisition rate of the holograms was set to 0.5 frames per second. This resulted in a captured hologram every 5° of rotation. Videos of the created deformations were constructed with ImageJ and sped up 50x.

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.

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