Functionalized polyamide membranes yield suppression of biofilm and planktonic bacteria while retaining flux and selectivity

Polarized light guiding anisotropic deformation and relaxation in photosensitive polymeric substrates

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Abstract. Light-responsive polymers offer unique possibilities for anisotropic manipulation of objects on the micron scale. Here we demonstrate the reversible anisotropic stretching of a polymeric surface made out of an azopolymer-elastomer blend, in response to green laser irradiation with varying polarization. We quantify the stretching parameters and the residual strain after relaxation by means of a Fourier-based analysis, which exploits a periodic 2D pattern imprinted onto the surface.

1 Introduction

Light-responsive polymers have recently attracted increasing attention due to their potential applications in areas such as smart micro-structured surfaces, adaptive optics, and biology. For applications necessitating contactless, anisotropic deformations, the subclass of sidechain azopolymers has been found of particular interest, as some of them tend to deform along the polarization axis of linearly polarized light. Application examples using directional deformation of azopolymer pillars range from inducing anisotropic behavior in living cells [1] to tuneable anisotropic surface wettability [2]. However, a major limitation of these types of microstructures is the limited reversibility of the induced plastic deformations. In a recent work carried out by Ryabchun et. al., the reversible deformation of single azopolymer domains sparsely dispersed in a Styrene-Ethylene-Butylene-Styrene (SEBS) thermoplastic elastomer matrix was reported. Pristine domain shapes were reobtained by heating or irradiation with circularly polarized light, making use of the strain stored in the elastomeric matrix surrounding the azopolymer domains [3]. Furthermore, an example of the potential use of this material system in a macroscopic actuator has been provided.

2 Results

Here, we study the deformation and reversibility of a light-responsive polymer slab whose top surface is patterned with a hexagonal array of cylindrical pillars (lattice constant $d = 6\ \mu$m). The sample is prepared by dissolving azopolymer poly[(methyl methacrylate)-co-(Disperse Red 1 methacrylate) (Sigma-Aldrich) and SEBS (Mediprene 500120M, kindly provided by Hexpol AB) in Toluene and casting the solution on a soft PDMS master, reaching a final concentration of 30 %wt azopolymer.

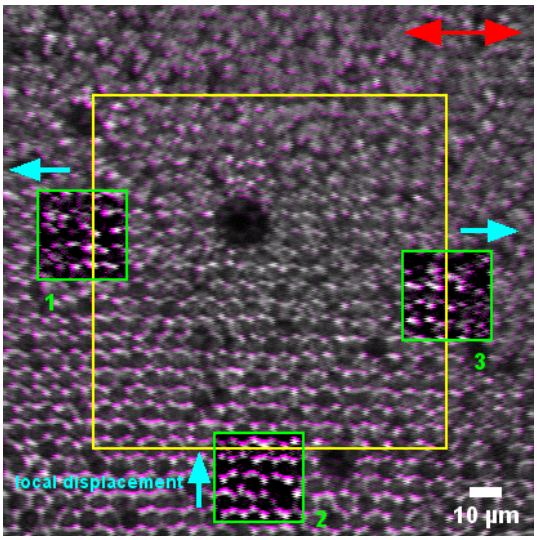

Figure 1. B/W: raw transmission image of the substrate top surface patterned with a hexagonal array of pillars. Magenta: pixels of transmission image after irradiation with horizontal polarization (red double-arrow), initial image subtracted. Yellow: Zone of irradiation. Green: Enhanced contrast regions.

Figure 1 shows the local displacement (magenta) resulting from the irradiation of the central area (yellow square) with a horizontally linearly polarized CW green laser (561 nm, 3 W/cm2, 15 s exposure) in a confocal microscope setup operating in continuous scanning mode. Enhanced contrast insets exemplify the local displacement of brighter spots, which extends also outside the directly irradiated region through strain propagation.

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An analysis in the Fourier space of the directly irradiated area allows to estimate the shifts of the peaks associated to the spatial harmonics of the periodic pattern (Figure 2, top). Fourier peaks moving inward/outward indicate real space stretching/compression along the horizontal/vertical axis, which is consistent with horizontally polarized irradiation [4]. Subsequent irradiation of the same area switching to circular polarization partially reverses the strain and the peak shifts associated thereto, as shown in Figure 2, bottom.

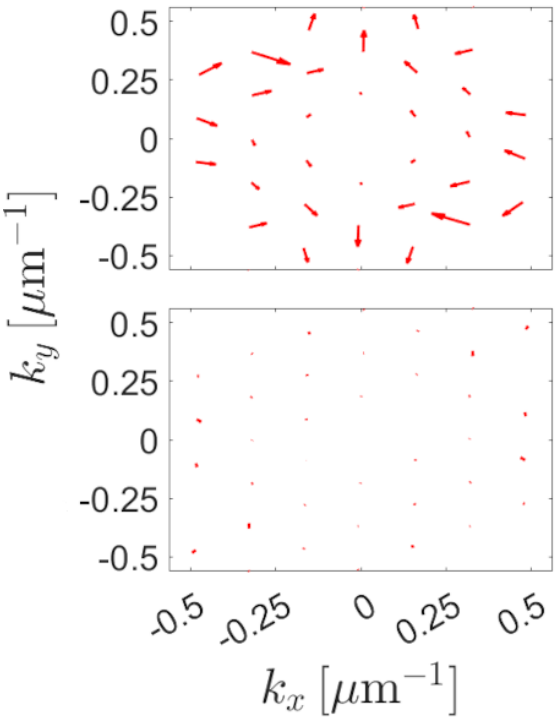

Figure 2. Arrows showing displacement of peaks in Fourier space before and after irradiation with linear polarization (top) and before and after a complete cycle of linear + circular polarization (bottom). Arrow magnification: x10.

A least squares algorithm with parameters θ (angle of strain- with respect to x-axis), ϵ_1 (strain along θ-axis) and ϵ_2 (strain along perpendicular axis) is implemented to fit the strain-associated shifts in Fourier space (Figure 2, top), aiming to quantify the expansive and compressive strain after exposure to linearly polarized light. The resulting parameter values are summarized in table 1, together with the respective sample standard deviation over five subsequent stretching cycles. The computed stretching axis angle θ is close to the horizontal axis, while the associated strains ϵ_1 and ϵ_2 signify stretching by (1.29 ± 0.25) % and compression by (-1.18 ± 0.05) % respectively. R^2-values of the fits are 0.71 ± 0.05, where R^2 has been defined as

$$R^2 = 1 - \frac{\sigma_{res}^2}{\sigma_{tot}^2} \tag{1}$$

with σ_{res}^2 being the squared residual norm of the fit and σ_{tot}^2 the squared sum of arrow magnitudes. Finally, while the shifts after a full cycle of irradiation with linearly and subsequently circularly polarized light are considerably smaller (Figure 2, bottom), it is known that circular polarization can lead to in-plane expansion of azopolymers [3]. Applying the same fitting algorithm to the full deformation cycle the relative area change can be calulated to the first order as:

$$\Delta A_{rel} = \frac{A_{new} - A_{old}}{A_{old}} = \frac{a(1+\epsilon_1)\cdot b(1+\epsilon_2) - a\cdot b}{a\cdot b} \approx \epsilon_1 + \epsilon_2 \tag{2}$$

where we have used a rectangular area of size $A = a \cdot b$ as example. The relative area change after deformation and subsequent relaxation is then found to be (0.17 ± 0.02) %, meaning there is a slight effect of in-plane area expansion. Although an order of magnitude smaller than the induced stretches, this means that the reversibility is not complete.

Table 1. Extracted Strain Parameters and Standard Deviation

	θ [deg]	ϵ_1 [%]	ϵ_2 [%]	R^2	ΔA_{rel} [%]
Value	-2.45	1.29	-1.18	0.71	0.17
St. Dev	2.94	0.25	0.05	0.05	0.02

3 Discussion and Outlook

Reversibility in anisotropic deformation of azopolymeric structures is a key issue for several potential applications and has received increasing attention in recent years. The approach presented above is a powerful tool to assess the quantitative degree of reversibility of such material systems. What's more, it will be useful for determining the effect of changing both material and experimental parameters such as azopolymer content and distribution, as well as irradiation time or intensity. We also note that the propagation of light-induced deformations outside of the irradiated area due to the propagation of strain in the SEBS matrix is an interesting feature.

In perspective, we aim to explore the use of similar substrates for biological applications, where inducing local surface stretches through either direct or indirect irradiation can be particularly advantageous for remote control of cell metabolism and behaviour. Furthermore, new types of actuators, which not only respond to radiation intensity, but also to its polarization, can be foreseen.

References

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