Supporting Information

Sub-100 nm wrinkling of polydimethylsiloxane by double surface oxidation

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Frontal coarse-grained model for PDMS plasma oxidation

PDMS oxidation via air/oxygen plasma and UVO can be described as a frontal process[1,2] using a minimal, spatiotemporal, model which borrows concepts from polymer solidification occurring via photopolymerisation[3]. The extent of PDMS surface conversion into a glassy-like layer is captured by an order parameter φ(z,t), varying in both space and time, with the z axis defined to be normal to the illuminated surface. Parameter φ(z,t) ranges from 0, corresponding to neat PDMS (φ(z,0)=0), to 1, corresponding to fully oxidised PDMS (φ(z,t→∞)=1). The equation of motion for φ(z,t) is written as

$$\frac{\partial \phi(z,t)}{\partial t} = K\,(1-\phi(z,t))I(z,t) \qquad (1)$$

where *K* is a kinetic constant related to the oxidation reaction, and *I* the plasma intensity. The evolution of the intensity with depth z is written as

$$\frac{\partial I(z,t)}{\partial z} = -\mu(z,t)I(z,t) \qquad (2)$$

which is analogous a Beer-Lambert law, and describes how the plasma/ozone penetrates in the material, where μ(z,t) is an attenuation coefficient, which is taken to be a constant, in first approximation. In these conditions, (1) and (2) can be solved analytically, and an expression for the thickness of the glassy layer as a function of time can be obtained

$$h = \frac{ln(t)}{\mu} - \frac{1}{\mu} ln\left(\frac{1}{KI_0} ln\left(\frac{1}{1-\phi_c}\right)\right) \qquad (3)$$

where I_0 is the intensity at the surface and φ_c is a critical value for the conversion required for film formation (analogous to a percolation threshold). The conversion profile as a function of z, at different times, is plotted in Figure SI1. The plot reveals the existence of three regimes, namely induction, formation and propagation. An 'induction regime', characterised by $\varphi < \varphi_c$, corresponds to low exposure times which do not allow to overcome the threshold required for the conversion of a skin layer at the PDMS surface. Greater values of φ, between φ_c and φ_s correspond to the 'skin formation regime', where the thickness of the glassy film slowly increases with time, as the film *simultaneously* densifies. As φ becomes greater than a saturation value φ_s (1 at completion), i.e. when the skin layer is fully oxidised, a 'propagation regime' corresponding to a steeper increase in the film thickness with time, as the front travels into the bulk PDMS.

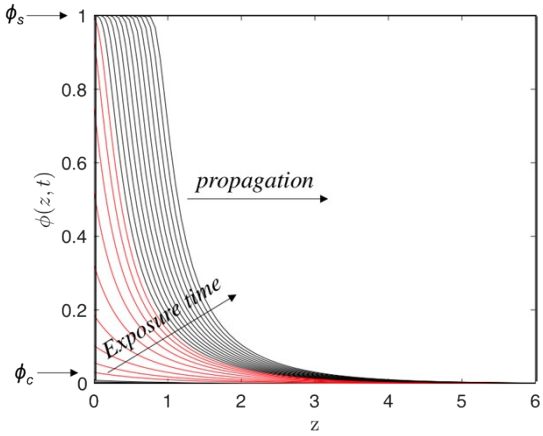

Figure SI1: PDMS to glassy-layer conversion φ as a function of normalised depth, z, for different times. Φ_c and φ_s indicate the transition between the induction ($\varphi<\varphi_c$), formation ($\varphi_c<\varphi<\varphi_s$, red curves) and propagation regimes ($\varphi>\varphi_s$).

The values of the experimentally-measured thicknesses, inferred from both wrinkling and reflectivity data on plasma oxidised PDMS specimens, confirm the logarithmic dependence with time as well as the three regimes described above, validating this coarse-grained model to describe the oxidation process.

Effect of PDMS crosslinking conditions on wrinkling of resulting bilayers by plasma oxidation

In the main paper, we showed how the crosslinking temperature or base:crosslinker ratio affect the PDMS mechanical properties, and thus the pattern dimensions obtained upon plasma oxidation. We performed a series of extra experiments to assess the limits of varying the crosslinking conditions in lowering the wavelength of the wrinkling patterns. The impact of the elastomer base to crosslinker ratio, crosslinking temperature and duration was evaluated as well as the combination of these. The results are shown in Figure SI2, where the wavelength of wrinkles obtained via plasma oxidation of PDMS slabs prepared at different conditions is compared to $\lambda_{conventional}$ (corresponding to $T_{crosslinking}$= 75˚C, $t_{crosslinking}$= 1 hour, base:crosslinker = 10:1). The oxidation was carried within a kHz chamber, at constant pressure P ≈ 0.2 mbar and variable dose. The wavelength reduction is in general more significant at high doses, decreasing at small doses. At these conditions, relevant when having to lower the minimum patterns' wavelength, the maximum wavelength reduction reaches only 35 %, when curing PDMS with a base:crosslinker ratio of 4.5, at 120˚C for 1 week.

We also performed experiments using the MHz plasma, to validate the results obtained with the KHz chamber. We prepared PDMS slabs at the optimal curing conditions identified before, and oxidised them at t = 180, 1200 s (P = 1.2 mbar, p = 7.16 W). Mechanical wrinkling was induced on the resulting bilayers. As expected and shown in Figure SI2, the increase in PDMS stiffness causes a decrease in wrinkling wavelength. The observed decrease is a function of plasma exposure time (dose), ranging from approximately 32% at high doses to 19% at low doses, confirming that modifying PDMS curing conditions alone is not effective at substantially reduce wrinkling wavelength.

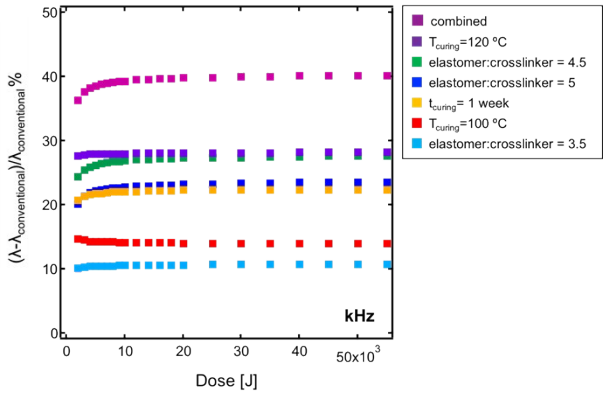

Figure SI2: Percentage variation of λ with oxygen plasma dose (P = 0.2 mbar, kHz) for different PDMS curing conditions, compared to unmodified (conventional) PDMS with 10:1 base:crosslinker ratio, cured at 75˚C for 1 hour. The 'combined' data refer to the optimal conditions for maximum wavelength reduction corresponding to $T_{crosslinking}$= 120˚C, $t_{crosslinking}$= 1 week, base:crosslinker = 4.5:1.

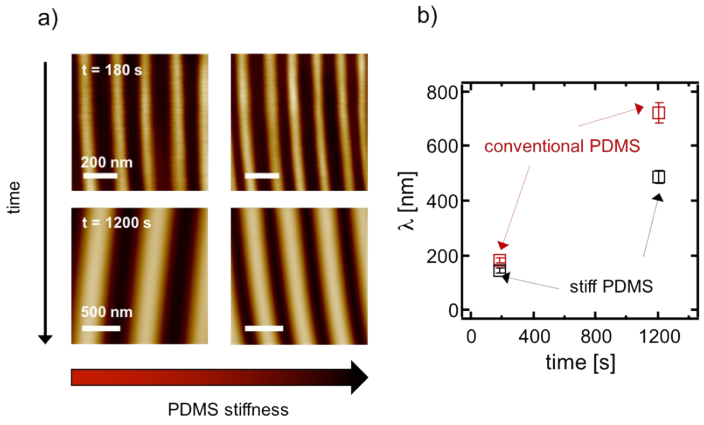

Figure SI3: a) AFM images of wrinkling patterns obtained on PDMS slabs cured at different conditions (Conventional: $T_{crosslinking}$= 75˚C, $t_{crosslinking}$= 1 h, base:crosslinker = 10:1, Stiff: $T_{crosslinking}$= 120˚C, $t_{crosslinking}$= 1 day , base:crosslinker = 4.5:1), prestretched by 20% and oxidised within a MHz plasma chamber for t= 180,1200 s (P = 1.2 mbar, p = 7.16 W) and b) corresponding wavelength of the patterns.

References

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3 J. Cabral, S. Hudson, C. Harrison and J. Douglas, *Langmuir*, 2004, **20**, 10020–10029.