Electronic Support Information for "Droplet-train induced spatiotemporal swelling regimes in elastomers" by Akshay Phadnis, Kenneth C. Manning, Ian Sanders, Timothy Burgin, and Konrad Rykaczewski^{*}

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1. Solvent uptake comparison and validation

Fig. S1 Comparison of solvent uptake with time between FE model predictions and the two experiments conducted on the cylindrical samples. On the right is the experimental setup used to measure the solvent uptake of PDMS.

The model predicted solvent uptake is compared with the experimentally measured values. The experiments were conducted on two different samples. The red line corresponds to the numerical values predicted by the COMSOL model. This is not done by fitting the experimental data but by using diffusion coefficient of 6.1×10^{-9} m²s⁻¹ and the appropriate boundary conditions. A slight deviation at higher time points is due to an additional solvent held in the convex shaped top surface resulting in higher values.

2. Equilibrium swelling ratio

The equilibrium swelling ratio defined as the ratio of swollen volume to the dry volume can be calculated from above results as follows:

Volume of the dry polymer = 1.055 cm^3

Volume of the solvent absorbed = 1.8 cm^3

$$S_{eq} = \frac{1.8 + 1.055}{1.055} = 2.71$$

At the same time, volumetric or bulk strain can be estimated as -

$$\epsilon_{bulk} = \frac{1.8}{1.055} = 1.706$$

3. Assumptions in the numerical model

It should be noted that the chemical potential in Equation 5b represents the chemical potential of solvent inside gel relative to that of the pure solvent. Thus, on the boundary, where the chemical potential of gel equilibrates with the outside solvent, we use $\mu = \mu_0 = 0$. However, assumption of a perfect equilibrium poses a challenge in terms of concentration of the solvent at the boundary. Consider free swelling of a cubical polymer sample when completely immersed in the solvent bath. At equilibrium, the stresses inside the gel vanish because of absence of any constraint and from Equations 5a and 5b we can write-

$$\mu_0 = RT \left(\log \left(\frac{\Omega J_0 c_{eq}}{1 + \Omega J_0 c_{eq}} \right) + \frac{1}{1 + \Omega J_0 c_{eq}} + \frac{\chi}{\left(1 + \Omega J_0 c_{eq}\right)^2} \right) + \frac{G\Omega}{\lambda_{eq}}$$
(6)

Where, ${}^{c_{eq}}$ is equilibrium concentration and ${}^{\lambda_{eq}}$ is the equilibrium stretching ratio such that equilibrium swelling ratio $J_{eq} = {}^{3}_{eq}$. For given values of T = 298 K and $\chi = 0.39$, G = 75 kPa and $\Omega = 3 \times 10^{-4}$ m³ mol⁻¹, the equilibrium concentration for hexane is ${}^{c_{eq}} = 22000$ mol m⁻³. This value is significantly higher than the expected concentration of 7650 mol m⁻³. This discontinuity is believed to be resulting due to assumptions associated with Flory-Rehner free energy calculation. This formulation neglects free energy of mixing underestimating the free energy resulting in higher concentration. We estimated that, $\mu_0 = -236$ J mol⁻¹ when $c_{eq} = 7650$ mol m⁻³ which is not considerably different from the ideal equilibrium. However, to be consistent with the literature we use $\mu_0 = 0$. Also, the effect of using $\mu_0 = -236$ J mol⁻¹ instead of ideal equilibrium value on displacement is within ± 0.15 mm.



4. FTIR-ATR experiments and results

Fig. S2 Measurement of the diffusion coefficient of n-hexane in PDMS using FTIR-ATR technique.

5. Hexane droplet spreading and absorption



Fig. S3 (a) High speed imaging of hexane droplet spreading on PDMS sample and (b) Images of absorption of hexane droplet in PDMS sample with time.

6. Wrinkle formation and crumpling of thin films (case (iv))



Fig. S4 Crumpling due to swelling instabilities in thin PDMS samples after injecting 3 - 5 drops of hexane (~30 - 50 μ L). Thickness of the film is 110 μ m.

The films are obtained by spin coating PDMS on glass slides of size 25.4×25.4 mm. We expect this to happen because for a thin film of thickness \ll droplet size, the solvent diffuses rapidly and fills the gap between PDMS and glass slide and results into inelastic crumpling instabilities.

7. Experimental setup



Fig. S5 Experimental setup used to measure the swelling of polymer samples.