A Simple Contact Mechanics Model for Highly Strained Aqueous Surface Gels

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Supplementary Materials

Nomenclature

E	elastic modulus
R	probe radius of curvature
ν	Poisson's ratio
d	indentation depth
z_o	indentation depth at maximum pressure
t	surface gel layer thickness
a	contact area radius
P	contact pressure
F	indentation force
η	viscosity
k	permeability
t_{dr}	draining time
Π	osmotic pressure

1. Contact Pressure and Draining Time Estimation

Hertzian contact mechanics were used to estimate contact pressures.[1]

$$P = \frac{3F}{2\pi a^2} \text{ where } a = \sqrt{Rd} \tag{S1}$$

The estimated contact pressures for the contact lens and polystyrene-molded hydrogel were plotted against the indentation depth to determine whether they exceeded the osmotic pressure. As shown in Fig. S1, both the contact lens and PS-molded hydrogel experienced contact pressures that surpassed the predicted elastic modulus of the surface gel layer. These results suggest that fluid flow due to draining was possible.

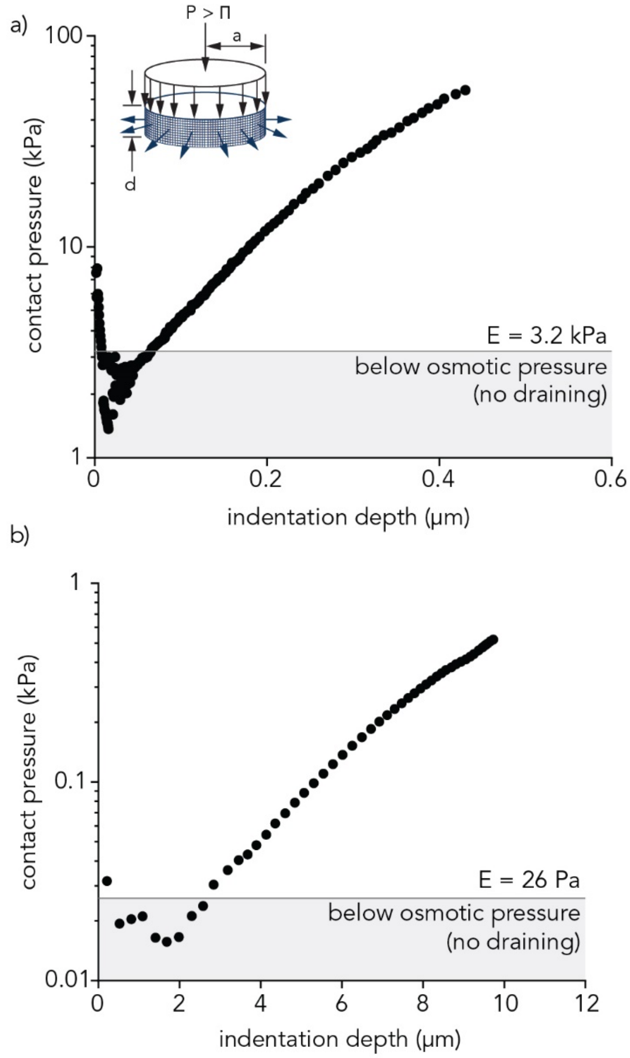

Fig. S1 Contact pressures estimated using Hertzian contact mechanics as a function of indentation depth for the (a) contact lens and (b) PS-molded hydrogel surface. After a critical indentation depth, the pressure surpasses the predicted elastic modulus of the system, indicated by the horizontal gray line. Based on scaling principles by de Gennes, the osmotic pressure, *Π*, scales with elastic modulus, and draining will occur once the contact pressure surpasses the osmotic pressure. The schematic indicates a unit volume draining as the contact pressure surpasses the osmotic pressure.

This estimation of contact pressures validates the use of our model by demonstrating the possibility of draining. For further validation, the draining time was estimated using Darcy's Law:[2]

$$\frac{V}{t_{dr}} = \frac{kAP}{\eta d} \rightarrow \frac{\pi a^2 d}{t_{dr}} = \frac{k(2\pi a d)P}{\eta d} \rightarrow t_{dr} = \frac{a d \eta}{2kP} \qquad \text{(S2)}$$

where V is the volume of hydrogel being drained (Fig. S1a schematic), A is the surface area of the volume, P is the contact pressure, a is the contact area radius, d is the indentation depth, η is the viscosity of the solvent, and k is the permeability of the hydrogel. The permeability of a hydrogel is on the order of magnitude of $k \sim 1$ nm^2, which is in agreement with values found in literature.[3] Using this estimation for k, Hertzian contact area and pressure (Eqn. S1), and the viscosity of water (η = 8.9 x 10^{-4} Pa·s), the estimated maximum draining time is t_{dr} = 0.006 s for the contact lens and t_{dr} = 300 s for the PS-molded hydrogel. With an indentation speed of 1 μm s^{-1}, draining was possible within the experimental conditions for the contact lens.[4]

2. Comparison of Contact Mechanics Models

2.1 Hertzian contact mechanics model[1]

The Hertz model is one of the most commonly utilized contact mechanics models, where the indentation force is related to the elastic modulus, indenter radius, and indentation depth by:

$$F = \frac{4E_{Hertz}R^{1/2}d^{3/2}}{3(1-v^2)} \tag{S3}$$

However, there are a few assumptions in the derivation that preclude its use in characterizing the mechanics of complex, heterogeneous systems[5]:

1. Strain and deformations must be small enough to stay within the linear elasticity theory ($d/t \leq 0.1$)
2. The substrate is an infinite half-space ($t >> R$)
3. There is no friction or adhesion at contact between the indenter probe and substrate

The first assumption is violated in both experiments by high strains (>60%) on the thin surface gel layer. The second assumption is violated by the structural anisotropy and heterogeneity of these systems. Therefore, Hertz cannot accurately capture the mechanics of these systems, leading to an overprediction in the elastic modulus.

2.2 Nonlinear elastic correction factor by Long *et al.*[5]

To account for the overprediction of the Hertz model, Long *et al.* developed a correction factor, ψ, using nonlinear elasticity and finite-element simulations.[5] This correction factor only applies in the regime of $0.5 \leq R/t \leq 12.7$ and $d/t \leq \min(0.6, R/t)$:

$$\psi = \frac{E_{Long}}{E_{Hertz}} = \frac{1 + 2.3\omega}{1 + 1.15\omega^{\frac{1}{3}} + \alpha\omega + \beta\omega^2} \tag{S4}$$

where $\omega = \left(\frac{Rd}{t^2}\right)^{\frac{3}{2}}$. Depending on the R/t regime, α and β will have different values (Table S1).

Table S1. Table of values for α and β depending on the *R/t* ratio. These values assume frictionless contact between the indenter and substrate.

R/t ratio	$\boldsymbol{\alpha}$	$\boldsymbol{\beta}$
$0.5 \leq R/t \leq 2$	$10.05 - 0.63\sqrt{t/R}\,(3.1 + t^2/R^2)$	$4.8 - 4.23\,t^2/R^2$
$2 < R/t < 12.7$	9.5	4.212

To determine whether the parameters of the contact lens and PS-molded hydrogel experiment fit within the regime of the correction factor, *d/t* and *R/t* were estimated using the maximum indentation depth value and surface gel layer thickness value predicted by our proposed model (*t* = 0.5 µm and *t* = 12 µm for the contact lens and PS-molded hydrogel, respectively). As shown in Table S2, the maximum *d/t* ratio for both the contact lens and PS-molded hydrogel is larger than the maximum allowable *d/t* ratio of 0.6. The authors note that the behavior of the system may not be accurately captured at strains higher than 0.6 due to the inability of neo-Hookean models to fully capture the amount of strain hardening that occurs at large deformations.[5]

Table S2. Comparison of the *R/t* and *d/t* ratios for the two surface gel layer surfaces from literature.

	R/t **ratio**	***d/t*** **ratio**
delefilcon A contact lens[4]	5	0.86
PS-molded hydrogel[6]	1.2	0.81

2.3 Winkler foundation model[7,8]

The Winkler foundation model was developed for layered systems, such as a rigid thin film on a soft substrate, and takes into account the thickness of the system when relating indentation force to the elastic modulus, indenter radius, and indentation depth.

$$F = \frac{\pi R d^2 E_{Winkler}}{t(1 - v^2)} \tag{S5}$$

While this model works well for thin films, it does not fully capture the mechanics of heterogeneous film layers because the main assumption in this model depends on the linear elasticity of the substrate.

2.4 Poroelastic model for thin gel films by Hu *et al.*[9]

To account for relaxation in thin films of crosslinked polymer networks on rigid substrates, Hu *et al.* developed a poroelastic model for the short- and long-time limit.[9] The indentation force is related to the shear modulus, *G*, contact area radius, surface gel layer thickness, and indentation depth as:

$$F = \frac{8Gda}{3(1 - v)}\left[\frac{2.36\left(\frac{a}{t}\right)^2 + 0.82\left(\frac{a}{t}\right) + 0.46}{\frac{a}{t} + 0.46}\right] \tag{S6a}$$

where $a = \sqrt{Rd}$ and the shear modulus can be related to the elastic modulus as $G = \frac{E}{2(1+v)}$, leading to:

$$F = \frac{4E_{Hu}d\sqrt{Rd}}{3(1-v^2)}\left[\frac{2.36\left(\frac{\sqrt{Rd}}{t}\right)^2 + 0.82\left(\frac{\sqrt{Rd}}{t}\right) + 0.46}{\frac{\sqrt{Rd}}{t} + 0.46}\right] \quad \text{(S6b)}$$

During the short-time limit of instantaneous compression, the gel is assumed to be incompressible and v = 0.5, leading to:

$$F = \frac{16E_{Hu}d\sqrt{Rd}}{9}\left[\frac{2.36\left(\frac{\sqrt{Rd}}{t}\right)^2 + 0.82\left(\frac{\sqrt{Rd}}{t}\right) + 0.46}{\frac{\sqrt{Rd}}{t} + 0.46}\right] \quad \text{(S6c)}$$

During the long-time limit of stress relaxation, F takes the form of Eqn. S6b, where v is not assumed. Eqns. S6b and S6c only apply for intermediate values of $\sqrt{Rd}/t$ when the contact area radius and gel thickness are comparable. When $\sqrt{Rd}/t \rightarrow 0$, F approaches Hertzian contact mechanics, and when $\sqrt{Rd}/t \rightarrow \infty$, F approaches Winkler mechanics.

Because v = 0.5 was used to estimate the elastic modulus using the different contact mechanics models, the short-time limit equation (Eqn. S6c) was implicitly used. This corresponds well with the nanoindentation experimental conditions for both the contact lens and PS-molded hydrogel surface, which underwent compression with indentation velocities of 1 μm/s.

3. Metric for Determining Best Fit

To fit the models to the experimentally gathered force-indentation curves, the sum of squares of the residual was minimized ("least squares fitting") for each model using Eqns. S3, S5, and S6b. This error was used as the metric to determine the "best-fitting" model.

$$SSE = \sum_i \left(F_{model,i} - F_{data,i}\right)^2 \quad \text{(S7)}$$

The lsqcurvefit function in MATLAB was used to fit the model to the entire approach curve of the experimental data and minimize the SSE. A two-parameter fit was used for the contact mechanics models that were functions of both *E* and *t* (Table S3). A one-parameter fit was also tested by setting either *E* (Table S4) or *t* (Table S5) as a known value and solving for the other.

Table S3. Comparing the predicted elastic modulus, surface gel layer thickness, and SSE values for the two surface gel layer systems when using a two-parameter fit for the entire approach curve. A Poisson's ratio of $v = 0.5$ was used to estimate the elastic modulus. Our proposed model had the lowest SSE while Hertz had the highest.

Contact Mechanics Model	Contact Lens			PS-molded hydrogel surface		
	Predicted elastic modulus (kPa)	Predicted surface gel layer thickness (μm)	SSE	Predicted elastic modulus (kPa)	Predicted surface gel layer thickness (μm)	SSE
Hertz	106	--	1.3×10^4	0.54	--	9.5×10^4
Long *et al.*	6.5	--	--	0.16	--	--
Winkler	30	0.58	4.5×10^3	13	603	5.0×10^4
Hu *et al.*	5.5	0.10	4.4×10^3	0.028	1.3	5.0×10^4
Model	3.2	0.54	2.1×10^3	0.026	12	7.5×10^3

Table S4. Comparing the predicted surface gel layer thickness and SSE values for the surface gel layer systems when using a one-parameter fit to solve for t when given E. In this test, $E = 3.2$ kPa for the contact lens and $E = 0.026$ kPa for the PS-molded hydrogel.

Contact Mechanics Model	Contact Lens			PS-molded hydrogel surface		
	Elastic modulus (kPa)	Predicted surface gel layer thickness (μm)	SSE	Elastic modulus (kPa)	Predicted surface gel layer thickness (μm)	SSE
Hertz	3.2	--	1.0×10^5	0.026	--	1.1×10^6
Long *et al.*	0.2	--	--	0.008	--	--
Winkler	3.2	0.06	4.5×10^3	0.026	1.2	5.0×10^4
Hu *et al.*	3.2	0.06	4.4×10^3	0.026	1.2	5.0×10^4
Model	3.2	0.54	2.1×10^3	0.026	12	7.5×10^3

Table S5. Comparing the predicted elastic modulus and SSE values for the surface gel layer systems when using a one-parameter fit to solve for E when given t. In this test, $t = 0.54$ μm for the contact lens and $t = 12$ μm for the PS-molded hydrogel. A Poisson's ratio of $v = 0.5$ was used to estimate the elastic modulus.

Contact Mechanics Model	Contact Lens			PS-molded hydrogel surface		
	Predicted elastic modulus (kPa)	Surface gel layer thickness (μm)	SSE	Predicted elastic modulus (kPa)	Surface gel layer thickness (μm)	SSE
Hertz	--	--	--	--	--	--
Long *et al.*	--	--	--	--	--	--
Winkler	28	0.54	4.5×10^3	0.26	12	5.0×10^4
Hu *et al.*	28	0.54	4.9×10^3	0.24	12	5.9×10^4
Model	3.2	0.54	2.1×10^3	0.026	12	7.6×10^3

To determine whether the best-fitting contact mechanics model changed based on the portion of the indentation curve analyzed, the approach curve was fit by incrementally increasing the displacement along the curve by 20 data points. The SSE was plotted against % strain for both surface gel layer systems, where % strain = *d/t* x 100 and *t* is the predicted surface gel layer thickness when the entire approach curve is analyzed (*t* = 0.5 µm for the contact lens and *t* = 12 µm for the PS-molded hydrogel surface) (Fig. S2). Our proposed model was able to capture the behavior of the system at all strains for the contact lens and higher strains (> 40%) for the PS-molded hydrogel comparably better than the other contact mechanics models tested.

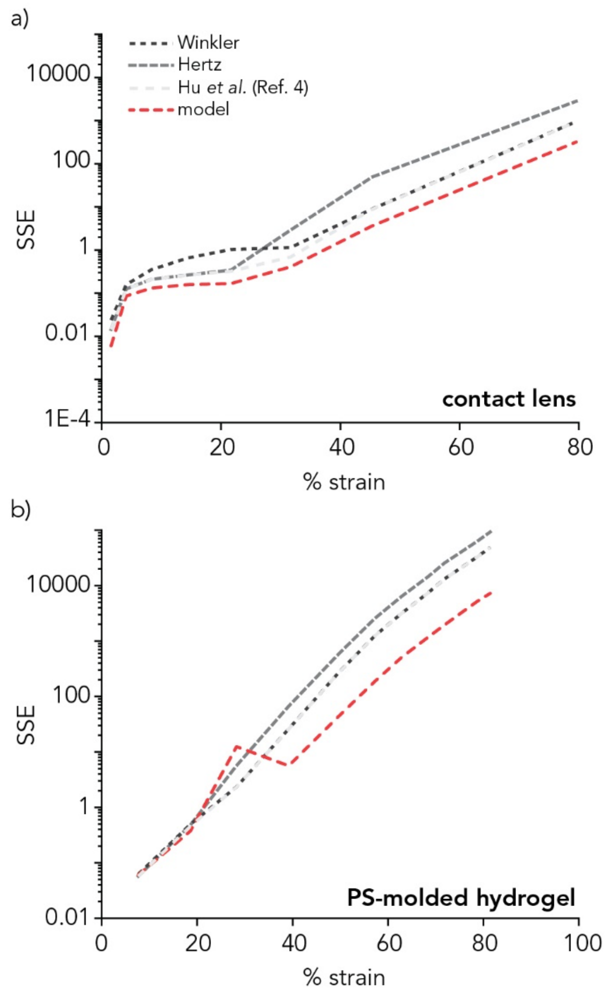

Fig. S2 Comparison of the sum of squares of the residual as the maximum indentation depth of the approach curve is incrementally increased for the (a) contact lens and (b) PS-molded hydrogel surface. (a) At low strains (< 20%), the poroelastic model proposed by Hu *et al.* closely follows Hertzian mechanics but switches to Winkler-like mechanics when strain > 40%. Within 20-40% strain, the model proposed by Hu *et al.* had lower SSE values, indicating a better fit. However, our proposed model had the lowest SSE values for all strains. (b) The poroelastic model proposed by Hu *et al.* follows Hertzian mechanics between 10-20% strain and Winkler mechanics thereafter. Our proposed model has the lowest SSE values for both low (< 20%) and high (>40%) strain.

The change in predicted E and t values based on the portion of the indentation curve analyzed was also analyzed for the contact lens (Fig. S3a, b) and PS-molded hydrogel surface (Fig. S3c, d).

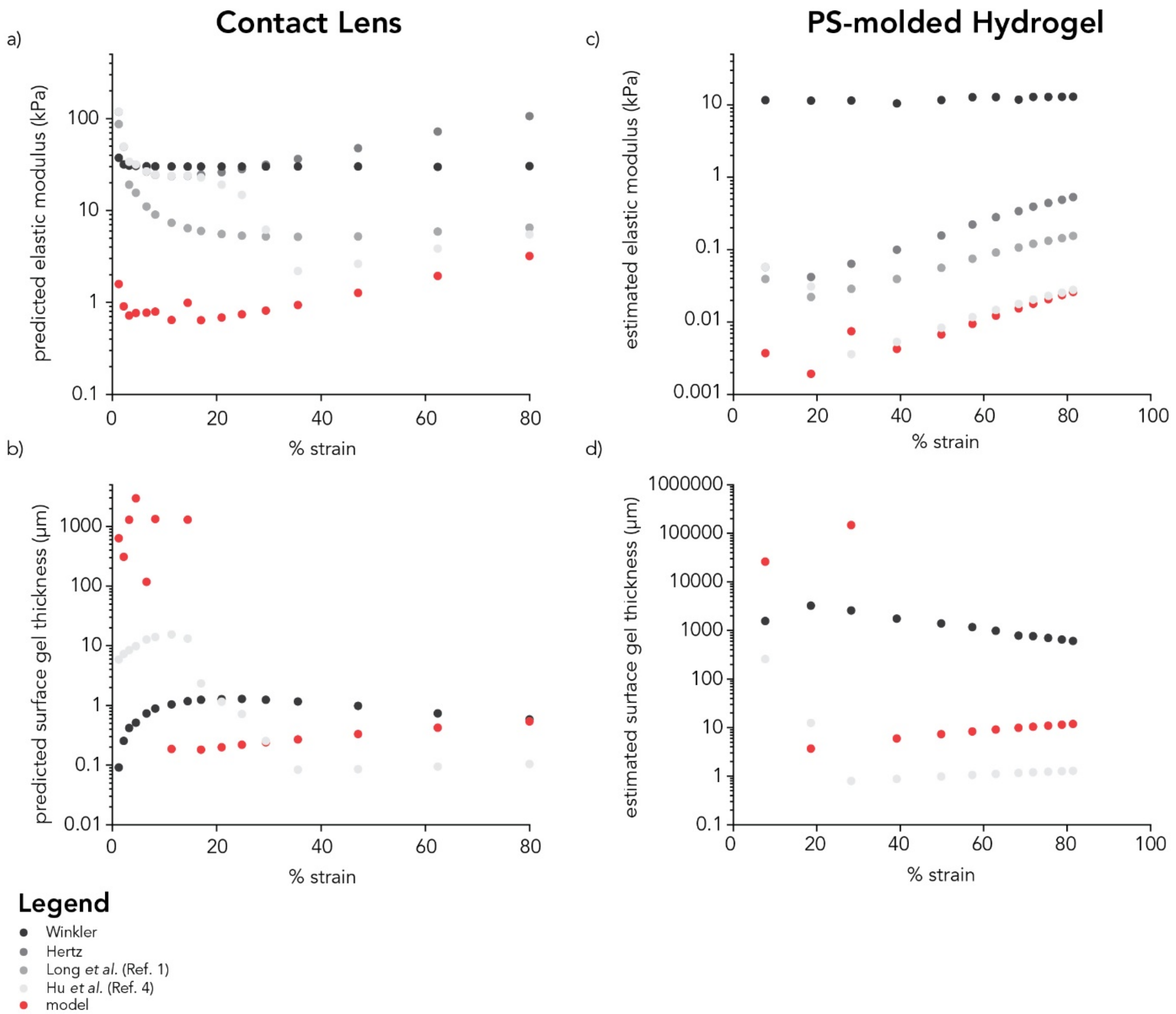

Fig. S3 Change in the predicted elastic modulus and surface gel layer thickness values of the best fit line as the maximum indentation depth of the approach curve is incrementally increased by (a,b) 10 data points for the contact lens and (c,d) 20 data points for the PS-molded hydrogel surface. Each data point represents the predicted E and t value of the best fit line for that portion of the curve. (a,c) Below 20% strain, the elastic modulus values predicted by the poroelastic model by Hu *et al.* (lightest gray circles) are similar to those predicted by Hertz (gray circles), Winkler (black circles), and the corrected elastic modulus values by Long *et al.* (light gray circles). Above 30% strain, the elastic modulus values of the poroelastic model by Hu *et al.* are closer to those predicted by our proposed model (red circles). (b,d) Below 20% strain for the contact lens and <30% strain for the PS-molded hydrogel, our model predicted non-physical surface gel layer thicknesses. However, at higher strains, the predicted surface gel layer thicknesses are within the range of those predicted by Winkler and the poroelastic model by Hu *et al.*

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