Published in final edited form as:

Langmuir. 2013 February 5; 29(5): 1407–1419. doi:10.1021/la303810d.

Large Deformation and Adhesive Contact Studies of Axisymmetric Membranes

Evan J. Laprade^a, Rong Long^b, Jonathan Pham^c, Jimmy Lawrence^c, Todd Emrick^c, Alfred Crosby^c, Chung-Yuen Hui^b, and Kenneth R. Shull^{a,*}

^aDepartment of Materials Science and Engineering, Northwestern University, Evanston, Illinois 60208, USA

^bSibley School of Mechanical and Aerospace Engineering, Cornell University, Ithaca, NY 14853, USA

^cPolymer Science and Engineering Department, University of Massachusetts Amherst, Amherst, MA 01003, USA

Abstract

A model membrane contact system consisting of an acrylic copolymer membrane and polydimethyl-siloxane substrate was utilized to evaluate a recently developed nonlinear large-deformation adhesive contact analysis. Direct measurements of the local membrane apex strain during non-contact inflation indicated that the neo-Hookean model provides an accurate measure of membrane strain and supports its use as the strain energy function for the analysis. A time dependent modulus emerges from the analysis, with principal tensions obtained from a comparison of predicted and experimental membrane profiles. A displacement controlled geometry was more easily modeled than the pressure controlled geometry, the applicability of the analysis was limited by wrinkling instabilities. The substantial viscoelastic behavior of these membranes made it difficult to describe the entire membrane with a single modulus, given the nonuniform deformation history of the membranes. Given the difficulty in determining membrane tension from the measured pressure and profile fits using the model, the peel energy was used as a simpler measure of adhesion. Using an analytical balance in the displacement controlled geometry, the membrane tension at the contact line was directly measured. Coupled with contact angle imaging, the peel energy was determined. For the model membranes studied, this peel energy described the membrane/substrate adhesive interactions quite well, giving well-defined peel energies that were independent of the detailed strain state of the membrane.

1 Introduction

A widely used technique to measure the adhesive interactions between soft materials is the approach developed by Johnson, Kendall, and Roberts (JKR) [1], in which an elastic hemispherical indenter is brought into contact with a flat rigid substrate. If the interaction between the two contacting surfaces is adhesive, the resulting contact area will be larger than that given by the Hertzian prediction. The size of this contact region is governed by a balance between the adhesive energy of the surface interaction, which works to increase the contact area, and the elastic deformation energy of the indenter, which resists this deformation. Approaches that minimize this deformation energy create a larger and more easily measurable contact area for a given adhesive interaction, and could therefore increase the technique's sensitivity to weak adhesive interactions. Following this principle, a number

*k-shull@northwestern.edu.

of adhesion tests utilizing highly compliant film probes, have been introduced [2–10], beginning with the pressurized polymeric bubble test described by Shanahan [2].

Subsequent membrane contact work can be divided into two categories: small deformation, where a linear mechanics approach can be used, and large deformation where membrane nonlinearity must be taken into account. Small deformation and adhesion contact between thin films and substrates finds particular applicability in both biological and micro-electro-mechanical systems (MEMs). Recent studies in this area have looked at the adhesive contact of a thin film using flat punch systems [5–8], as well as the adhesive contact of a pressurized thin film [10]. These previous experiments were done in what can be viewed as a 'stiff membrane' limit, where the strains are small and a linear elastic analysis can be applied. Indeed, work over the past 10 years has created a library of models for thin film adhesion under different geometrical assumptions [5,6,10–15], but all of these studies avoided the complications associated with large deformation behavior by examining deflections that were much smaller than the membrane's radial dimension. Under these conditions, small deformation approximations such as linear membrane, linear plate, or von-Karman plate theory, could be utilized.

The assumption of linear behavior places strict limitations on the conditions for which small deformation analysis can be applied. Large strains on the other hand occupy a larger subset of membrane deformations, and in some cases can provide easier experimental design and implementation. The focus of this paper is on the large deformation and adhesive contact of membranes, such as that exhibited by the pressurized elastomers in the technique developed by Flory *et al.* [9]. Flory proposed an approximate analysis to address large deformations, using a numerical solution to the axisymmetric Laplace equation [9], but this method suffered from several critical drawbacks. Perhaps most importantly, the analysis required an assumption of uniform equibiaxial tension, a condition that is strictly valid only at the center of the contact region. More recently Guvendiren *et al.* employed a similar geometry, which utilized a dihydroxyphenylalanine (DOPA)-functionalized membrane to measure the strength of DOPA-titanium and DOPA-tissue interactions under different environmental conditions [16]. The authors used the measured pressure at pull-off to compare the adhesive interactions in their DOPA-functionalized membrane studies, but while a pull-off force measurement can provide a simple figure of merit, it is difficult to directly relate this quantity to a peel energy or energy release rate.

Recently a full formulation was presented by Long *et al.* [17], who addressed the nonlinearity of this problem with their model describing the large deformation and adhesive contact of a hyperelastic membrane with a rigid substrate. Here we present the first experimental implementation of Long *et al.*'s large deformation analysis using a model membrane contact system consisting of an acrylic-copolymer membrane and polydimethylsiloxane (PDMS) substrate. Two membrane contact geometries, exhibiting significantly different strain distributions during withdrawal, are investigated. The first, examines the wet contact of an air pressurized membrane, referred to here as a *pressure controlled geometry*. The second looks at the dry contact of a fluid deformed membrane, in a geometry where a stepping motor controls membrane-substrate separation, referred to here as a *displacement controlled geometry*. Compared to the pressure controlled geometry, this second configuration stretches the membrane in a predominately tensile manner, which reduces potential complications due to compressive stresses and buckling instabilities.

In this last part of this work, a simplified analysis for extracting a peel energy from these membrane contact geometries is presented. The method employs a standard laboratory analytical balance and utilizes a free body analysis to directly measure the membrane

tension at the point of contact with substrate. This simple and direct measure of adhesion is expected to be a particularly useful application of this technique for non-specialists.

Membrane contact experiments such as those performed by Guvendiren et al. [16] provide an excellent example of the advantages offered by this type of peel geometry, namely that the highly compliant nature of the membrane allows for intimate contact, under uniform and low (100–300 Pa) applied pressures with substrate that aren't perfectly smooth or flat, such as tissues and structured surfaces. Coupled with the ability to test in aqueous environments, membrane contact experiments are particularly well suited for investigating weak adhesive interactions that are biologically relevant. The ability to understand and quantify the molecular origins of adhesion to soft biological tissues is of great importance in a number of potential applications. These applications include for instance, to control the adhesive interactions between natural tissues and synthetic biomedical devices, or similarly to optimize the performance of surgical adhesive for internal suturing. Standard industrial peel measurements can be difficult to implement with soft biological tissues and may lack adequate sensitivity, making membrane contact an attractive alternative for investigating these types of interactions.

With these potential biomedical applications motivating the further development of the membrane contact technique, we present the outline for this paper as follows: In section 2 the analysis of Long *et al.* is reviewed and our numerical solution procedure is briefly described. In section 3 we describe the sample preparation procedures and the methods used to perform the membrane contact experiments. Section 4 is a presentation of the experimental results, evaluating them using both the Long *et al.* model and the analytical balance free body analysis.

2 Analysis

2.1 Background

Figure 1 shows a schematic of the general contact configuration. A thin incompressible polymeric membrane with an undeformed thickness h , is clamped to the edge of a cylindrical tube of inner diameter $2R_m$. A substrate is placed below the undeformed film at a separation of δ_m . An external pressure ΔP is applied, deforming the membrane, creating contact with the flat substrate below. This circular contact region is defined by the contact radius, a . Once the desired contact coverage is achieved, the pressure is reduced (pressure controlled test) or the inflation tube-substrate separation is increased (displacement controlled test) to detach the membrane from the substrate.

In their recent work, Long *et al.* [17] provide a rigorous treatment of the large deformation mechanics of contact adhesion between an inflated hyperelastic membrane and a rigid substrate. This section provides a general overview of this analysis and we refer the reader to their original publication [17] for a full description and derivation. Their formulation employs finite strain hyperelastic membrane theory to accommodate the difficulties of nonlinear deformation. We also note that this membrane theory neglects bending deformation, a reasonable approximation given the membrane's very high aspect ratio (lateral dimension $\sim 1\text{ cm}$ and thickness $\sim 1\mu\text{m}$) [18].

The initial configuration for this treatment is a flat, undeformed, circular membrane which lies on the plane $z = 0$, clamped along the edges at $r = R_m$. A positive pressure difference, ΔP , is applied to the membrane's top surface causing deformation. The arc length of the deformed membrane profile is denoted by ξ ($\xi = 0$ at $r = 0$). The angle made by the tangent to this curve at (r, z) with respect to the horizontal is denoted by α . For an incompressible material, two principal stretches describe deformation: λ_ξ the longitudinal stretch along the

membrane cross section in the $r-z$ plane, and λ_ϕ , the latitudinal stretch, in the direction normal to the $r-z$ plane.

Two force balances are needed to define the membrane's equilibrium configuration. The first of these is the familiar Laplace pressure equation, which can be viewed as a force balance in the direction normal to the inflated membrane:

$$\Delta P = \frac{T_\xi}{R_\xi} + \frac{T_\phi}{R_\phi}, \quad (1)$$

where R_ξ and R_ϕ are the principal radii of curvature. The second force balance is within the ξ direction, *i.e.*, along the membrane contour in the $r-z$ plane:

$$\frac{d}{dr}(rT_\xi) = T_\phi \quad (2)$$

A third force balance, in the ϕ direction, is automatically satisfied by the axial symmetry of the problem.

2.2 Role of Elasticity

In general, the tension consists of two components: an equibiaxial pretension, T_s , which is due to the surface energetics and is independent of the strain state of the membrane, and an elastic contribution T_{el} which may be different in the ξ and ϕ directions, and is determined by the elastic strain energy function that is used:

$$T_\xi = T_s + T_{\xi,el} \quad T_\phi = T_s + T_{\phi,el} \quad (3)$$

Here we use a neo-Hookean model for an incompressible elastomeric material, where the elastic strain energy per volume, W_{el} , is given by the following expression:

$$W_{el} = \frac{E}{6} \left(\lambda_\xi^2 + \lambda_\phi^2 + 1/(\lambda_\xi \lambda_\phi)^2 - 3 \right), \quad (4)$$

where E is the small strain Young's modulus and the neo-Hookean principal line tensions are

$$T_{\xi,el} = \frac{h \partial W_{el}}{\lambda_\phi \partial \lambda_\xi} = \frac{Eh}{3} \left(\frac{\lambda_\xi}{\lambda_\phi} - \frac{1}{\lambda_\xi^3 \lambda_\phi^3} \right), \quad (5)$$

$$T_{\phi,el} = \frac{h \partial W_{el}}{\lambda_\xi \partial \lambda_\phi} = \frac{Eh}{3} \left(\frac{\lambda_\phi}{\lambda_\xi} - \frac{1}{\lambda_\xi^3 \lambda_\phi^3} \right). \quad (6)$$

2.3 Adhesion and Calculation of the Energy Release Rate

A primary motivation for this work is to determine the adhesion between the membrane and the substrate surface. Our starting point is the energy release rate expression for a perfectly elastic membrane. This expression accounts for the fact that, in the presence of adhesive interactions, the longitudinal membrane tensions and extension ratios are not necessarily continuous across the contact lines. The respective longitudinal tensions on the contact and non-contact sides of the contact line are T_ξ^- and T_ξ^+ . Similarly, the respective longitudinal extension ratios on the contact and non-contact sides of the contact line are λ_ξ^- and λ_ξ^+ . The

general expression from for the energy release rate, $\mathcal{G}$ from the work of Long *et al.* [17] can be written in the following form:

$$\mathcal{G} = T_{\xi}^{+}(1 - \cos(\theta)) - \Delta W_{el} h_d^{-} + \varepsilon_c T_{\xi,el}^{+}. \quad (7)$$

Here $\Delta W_{el} \equiv W_{el}^{+} - W_{el}^{-}$ *i.e.*, the difference in the stored elastic energy density between the contact side (W_{el}^{-}) and non-contact side (W_{el}^{+}) of the contact line, and ε_c is the elastic strain applied across the contact line:

$$\varepsilon_c = \left(\frac{\lambda_{\xi}^{+}}{\lambda_{\xi}^{-}} - 1 \right). \quad (8)$$

The quantity h_d^{-} is the deformed membrane thickness on the contact side of the contact line:

$$h_d^{-} = \frac{h}{\lambda_{\xi}^{-} \lambda_{\phi}}. \quad (9)$$

The first term in Eq. 7 describes the work done by the longitudinal tension in moving the contact line. The second term accounts for the fact that some of this work is expended in the elastic extension of a portion of the membrane as the contact line passes through it. The third term in Eq. 7 accounts for the elastic contribution to the longitudinal tension, which represents an elastic potential that is also able to do work. The equivalence of these last two terms to previous expressions for the energy release rate [19, 20] for an elastic membrane is discussed by Long *et al.* [17] in their derivation of Eq. 7. We also note that the reference area for this definition of the energy release is the area of the membrane on the contact side of the contact line.

The energy release rate is fully determined by the longitudinal component of the tension at the contact line, T_{ξ}^{+} , the contact angle, θ , and the values of λ_{ξ}^{-} and λ_{ξ}^{+} , which in turn determine the values of W_{el} and $T_{\xi,el}^{+}$ through Eqs. 4 and 5. An important assumption of this contact theory is that the membrane is a perfectly elastic material and that energy dissipation only occurs in the close vicinity of the contact line. Since most membranes possess some degree of viscoelastic character, the applicability of Eq. 7 must be evaluated carefully for each system. In section 4 we discuss in more detail the case for membranes, such as the acrylic copolymer membranes utilized in this study, where viscoelastic contributions become significant and it is more useful to define an adhesion energy using the first term in Eq. 7, equivalent to an elastic peeling term described previously [19].

2.4 Fit to Experimental Data

Membrane contact experiments consist of two stages that require modeling: non-contact deformation and contact deformation. Both stages are governed by four ordinary differential equations (ODEs) (see Appendix for more details) that describe the membrane's large deformation equilibrium configuration. The independent variable in this formulation is ρ ($0 \leq \rho \leq R_m$), the material coordinate of a point on the membrane in the undeformed, flat reference configuration. A material point located at $(r = \rho, z = 0)$ in the unpressurized state is displaced to the point $(r = r(\rho), z = z(\rho))$ in the deformed configuration. We numerically integrate the four governing ODEs using MATLAB's boundary value problem solver *bvp4c*, subject to the appropriate boundary conditions for each stage of deformation. The appropriate boundary conditions for the non-contact and contact stages of the deformation are described below.

2.4.1 Non-contact deformation—During non-contact deformation six boundary conditions are defined:

$$\lambda_\phi(\rho=R_m)=1(a) \quad z(\rho=R_m)=0(b) \quad \alpha(\rho=0)=0(c) \quad z(\rho=0)=-\delta(d) \quad \lambda_\phi(\rho=0)=\lambda_0(e) \quad \lambda_\xi(\rho=0)=\lambda_0(f) \quad (10)$$

where 10(a,b) pertain to the clamped edge of the membrane, and 10(c–e) define behavior at the apex. The apex displacement, δ , (see Figure 1a) is measured from images of the deformed membrane. In addition to these boundary conditions, the pressure difference across the membrane, ΔP (a known, experimentally measured quantity), places an additional constraint on the problem. Two unknown parameters are allowed to float in order to assure that a solution can be found that is consistent with the boundary conditions. These parameters are λ_0 , the stretch ratio at the apex, and Eh , the small strain Young's modulus multiplied by the undeformed thickness. The model is formulated under that assumption that the membrane is a purely elastic material, implying that Eh must be a constant and therefore should not be a floating parameter. In practice though, most membranes possess some degree of viscoelastic character such that a time-dependent modulus would be more appropriate. By allowing Eh to float as a parameter, this constant modulus requirement can be relaxed, and viscoelastic behavior can be incorporated into the analysis. This adaption of the model is clearly not a rigorous treatment of viscoelasticity but it can provide a simple first order approximation utilizing the original framework of the analysis.

2.4.2 Contact deformation—During contact deformation the clamped boundary conditions are still given by 10(a,b), but the remaining boundary conditions are replaced by the following:

$$\alpha(\rho=\rho^*)=\theta(c) \quad z(\rho=\rho^*)=-\delta_m(d) \quad \lambda_\phi(\rho=\rho^*)=r^*/\rho^*(e) \quad (11)$$

Here ρ^* is the undeformed coordinate of the material element at the contact line, θ is the contact angle, and δ_m is the membrane holder-substrate separation. We determine ρ^* from the contact phase of the experiment, assuming a no-slip boundary condition as described by Long *et al.* [21] and in the 7. Outside the contact region the material can stretch without the frictional constraint of the substrate, so λ_ξ is generally discontinuous across the contact line. As with the non-contact case, Eh is obtained as the value that enables a solution to the governing equations to be obtained.

2.4.3 Fitting Procedure—The first step in modeling a membrane contact experiment is to extract the full experimental profile in each image using a MATLAB image processing routine. From this profile four boundary condition parameters can be measured: R_m , δ (non-contact only), θ (contact only), and δ_m (contact only). In addition to these experimentally measured parameters, a value for membrane pretension, T_s and the density difference between the pressurizing fluid and external fluid environment, $\Delta\zeta$ must be specified. For the acrylic copolymer membranes used in this work, the assumed membrane pretension was $T_s = 0.07 \text{ N/m}$, and the density difference for air inflation in water was $\Delta\zeta = 1000 \text{ kg/m}^3$.

We numerically integrate the governing ODEs using MATLAB's boundary value problem solver *bvp4c*, subject to the boundary conditions defined above. The value of Eh that emerges from the solution is found to be time dependent, as one would expect for a viscoelastic membrane. The quality of the profile fits for the contact experiments is optimized outside of the ODE solver with an iterative routine that adjusts the contact angle boundary condition to minimize the residuals for the full profile. Experimental contact angle measurements may vary as much 5–10 degrees between the left and right sides of the membrane profile. This iterative routine makes small adjustments to the contact angle until a “best fit” solution is found. “Best fit” is determined by minimizing Λ_{res} , the sum of the

residuals between the model and experimental profiles. This quantity is defined in the following way:

$$\Lambda_{\text{res}} = \frac{1}{NR_m} \sum_{i=1}^N d_i, \quad (12)$$

where d_i is the normal distance between the model and experimental profile at each model profile point $(r(i), z(i))$, and N is the total number of points along the profile.

3 Experimental

In this section we describe membrane fabrication, general procedures for performing the pressure controlled and displacement controlled experiments, and the protocol for tracking apex area strain during non-contact inflation.

3.1 Membrane Preparation

An acrylic triblock copolymer, poly(methyl methacrylate)-poly(n-butyl acrylate)-poly(methyl methacrylate) (PMMA-PnBA-PMMA, 25k-116k-25k g/mol), whose bulk structure and mechanical properties was well characterized previously [22], was utilized as a polymeric membrane for this work. This A-B-A type copolymer consists of glassy "A" end blocks and an elastomeric "B" midblock. Thermodynamics drive microphase separation into a physically crosslinked elastic network consisting of glassy endblock domains bridged by midblock segments. Membranes were spun cast from 10 wt% polymer solutions in toluene onto the surface of a sodium chloride crystal (International Crystal Laboratories), creating $\sim 1\mu\text{m}$ thick films. These films were floated off the salt crystals and onto a water bath so that they could then be transferred to the end of a cylindrical inflation tube.

To reduce the mechanical hysteresis of this membrane system, a hybrid diblock-triblock copolymer blend was developed. Blend membranes were created from a 10 wt% polymer solution in toluene of blended diblock (PMMA-PnBA, Kuraray 1114, 4.9k–65k g/mol) and triblock. Figure 2 shows the non-contact deformation behavior for 5 membranes, with compositions ranging from 100/0 wt% triblock/diblock to 75/25 wt% triblock/diblock. The hysteresis decreased significantly with relatively low amounts of added diblock copolymer. The experiments discussed below utilize a diblock-triblock blend of 90/10 wt% triblock/diblock, which offer an appropriate combination of stiffness and low hysteresis.

Figures 3(a) and (b) demonstrate the large-strain non-contact deformation behavior of these blend membranes. In (a), 3 identically prepared membranes were subjected to the same pressurization protocol and exhibit very similar apex displacement behaviors. In (b), a single blend membrane was inflated for 3 successive cycles, with no delay in between cycles. These results indicate that the strains are completely recoverable. We also see from Figure 3(b) that the pressure to reach a given apex displacement is higher for the first inflation than it is for subsequent inflations, but that these subsequent inflations give a very reproducible behavior.

3.2 Pressure Controlled Geometry: Air-Filled Membrane in Water

Figure 4 shows a schematic of the pressure controlled membrane contact geometry. This apparatus consists of an experimental chamber, pressurization devices, video recording and a data acquisition system. The membrane is clamped to the bottom of a cylindrical aluminum tube with a diameter, $2R_m$, of 11.75 mm, situated in the center of the experimental chamber, at a fixed separation from the substrate. The unpressurized experimental chamber is partially filled with water, fully immersing both the membrane and

the substrate. Two circular quartz windows allow video recording of the membrane profile shape, contact angle, and contact radius with a CCD camera (Adimec 1000m, Adimec Inc., Stoneham, MA). A syringe pump (NE-1000, New Era Pump Systems Inc, Wantagh, NY) is used to pressurize the membrane with air and a differential pressure transducer (PX653, Omega Inc., Stamford, CT), with a capacity of 0.6 kPa , is used to measure the pressure inside the membrane. A MATLAB (Mathworks) programming interface controls the syringe pump and camera and allows for simultaneous video and pressure data acquisition.

Figure 5(a) shows the evolution of pressure during a typical pressure controlled experiment for contact between an acrylic copolymer membrane and a PDMS substrate. Side view images of the membrane profile at specific time points are shown in Figure 4(b). The contrast in these images arises from the difference in refractive index between the pressurizing medium (air) and the surrounding chamber environment (water). After the syringe pump begins pressurization ($t = 10\text{ s}$), the membrane continues to undergo non-contact deformation until $t = 519\text{ s}$ where the membrane initially contacts the substrate. The contact area increases as the membrane is further deformed until the syringe pump is stopped at $t = 686\text{ s}$. For $686\text{ s} < t < 2022\text{ s}$, the syringe pump is stopped to allow the membrane to relax while in contact. Though no pumping occurs during this period, the pressure decreases slightly and then plateaus. This decrease in pressure results from a combination of membrane relaxation (membrane strains continue to increase) and system leaks. Additionally, since the contact area continues to grow slightly during this period, we refer to this stage as a “hold in contact” period rather than an equilibration period. At $t = 2023\text{ s}$ the syringe pump begins to depressurize the membrane, and the contact area decreases. Membrane “pull-off” occurs at $t = 2438\text{ s}$, identifiable by a characteristic spike in the pressure versus time data.

3.3 Displacement Controlled Geometry: Fluid-Filled Membrane in Air

Figure 6 shows a schematic of the displacement controlled membrane contact geometry. This apparatus consists of a glass inflation tube, stepper motor, analytical balance, a video capture and data acquisition system. The membrane is fixed to the bottom of a cylindrical glass tube, $2R_m = 15\text{ mm}$, which is attached to a linear stepper motor (Burleigh Instruments, Fishers, NY). The membrane is centered over the substrate, which is fixed to an analytical balance (ALF 100, Ohaus Corporation, Parsippany, NJ) so that contact forces can be measured directly. A video camera records the water level in the glass inflation tube, in addition to the full membrane profile, from which the membrane contact angle and contact radius are extracted. A MATLAB programming interface controls the stepper motor, balance, and camera, allowing simultaneous video and force data acquisition.

Figure 7(a) shows the displacement and contact force history during a contact experiment between an acrylic copolymer blend membrane and a PDMS substrate. Side view images of the membrane profile at selected time points are shown in Figure 7(b). Approximately 1 ml of water is added to the open end of the glass inflation tube, deforming the membrane into a spherical cap. The deformed membrane is allowed to relax for 10 minutes prior to changing the membrane tube-substrate separation, δ_m , with the stepper motor. The stepper motor is turned on at time $t = 0\text{ s}$ and moved down at a velocity of $0.80\text{ }\mu\text{m/min}$. At $t = 32\text{ s}$ in Figure 7, the membrane initially contacts the substrate, and contact continues to increase until the stepper motor is stopped at $t = 164\text{ s}$. For $164\text{ s} < t < 1917\text{ s}$ the contact area is allowed to stabilize at fixed displacement. Though displacement is fixed during this period, membrane relaxation causes the contact area to continue growing before eventually stabilizing. At $t = 1917\text{ s}$ the stepper motor is reversed, moving at a rate of $0.80\text{ }\mu\text{m/min}$. Membrane pull-off occurs at $t = 2560\text{ s}$.

3.4 Apex Strain Tracking

To clarify our definitions and notations for strain, we list here the different measures of strain that are used to characterize the membrane. As mentioned in section 2.1, the full strain state of the membrane is specified by the values of λ_ξ and λ_ϕ for all locations along the membrane surface. The product of these two principle extension ratios can be used to determine a local membrane area strain:

$$\varepsilon_A = \lambda_\xi \lambda_\phi - 1 \quad (13)$$

We are particularly interested in the following three specific values of ε_A :

- ε_∞ , the difference in area strains across the contact line, given by Eq. 8
- ε_0 , the area strain at the membrane apex
- ε_{avg} , an average area strain for the whole membrane, given by the following expression:

$$\varepsilon_{avg} = A / \pi R_m^2 - 1, \quad (14)$$

where A is the surface area of the membrane.

Local strain measurements of a flat circular membrane subjected to non-contact inflation have been described previously in the literature, where this geometry is often used to characterize materials at large deformations [23–30]. If a suitable grid pattern can be applied to the membrane surface, local strains can be directly measured using optical imaging systems. Such a measurement is particularly useful for assessing the validity of our assumption that these acrylic copolymer membranes can be modeled with a neo-Hookean elastic strain energy function.

In this work we utilize a fluorescent nanoparticle grid, transferred directly on to the membrane (Figure 8(a)), to achieve our goal of measuring the area strain at the apex, ε_0 . The nanoparticle grids were fabricated via a flow coating technique, specific details of which can be found in recent publications [31,32]. The grids used in this work consisted of fluorescent CdSe quantum dots (QD) functionalized with undecenylthiol ligands. The QD particles were deposited on to a sacrificial poly(acrylic acid) film in a square grid pattern with $50\mu m$ spacing, line width of $2 - 3\mu m$, and line thickness of $45 - 55 nm$. An acrylic copolymer membrane was pressurized to a very small deformation and brought in to contact with the grid until approximately 80% of the membrane was contacting the substrate. The membrane and QD substrate were then submerged in water for 30 minutes to dissolve the poly(acrylic acid) layer. The membrane was then depressurized to separate the membrane and transferred grid from the substrate. Apex strains were measured during non-contact inflation using fluorescence microscope images of the apex region obtained with a reflected fluorescence microscope (Zeiss Axiovert 100A equipped with a Hamamatsu CCD camera).

4 Results and Discussion

4.1 Non-contact Inflation

We begin our investigation with the non-contact deformation of an acrylic copolymer blend membrane in the water filled experimental cell shown in Figure 4. The membrane was pressurized with air and expanded to a surface area strain of $\varepsilon_{avg} = 1.87$ (Figure 9(a), $0s < t < 1050s$). During a 25 minute “hold” period ($1050s < t < 2550s$) the membrane was allowed to relax, reaching a maximum area strain of $\varepsilon_{avg} = 1.92$. After the hold period the membrane

was depressurized ($2550s < t < 3335s$), and deflation proceeded in a controlled manner until approximately $t = 3200s$, at which time buckling and wrinkling instabilities were observed.

Treating E as a function of time, Long *et al.*'s analysis was applied to this experiment using the procedure outlined in section 2. Calculated membrane profiles were obtained for the majority of the experiment ($0 < t < 3157s$), but during the last portion of deflation ($3157s < t < 3335s$) the ODE solver was unable to converge on a solution that satisfied the experimental constraints. Figure 10 shows the model result for an image at the end of the hold period ($\epsilon_{avg} = 1.92$, $t = 2382s$). The experimental and model profiles are compared in Figure 10(a), where the model fit is plotted over the image of the deformed membrane. A closer inspection of the model and experimental profiles in Figure 10(b) shows they exhibit excellent agreement. We also observe in Figure 10(c) that even though the condition of equibiaxial tension is only valid at the apex, the principal tensions remain nearly uniform until the clamp edge is approached. This is consistent with the analysis of Long *et al.* who showed that for a neo-Hookean solid, the tensions are insensitive to the stretch ratios, provided that the stretch ratios are sufficiently large. As a result, the membrane tensions are roughly independent of position and are given by $Eh/3$. During the pressurization/depressurization cycle, the apex tension initially increased during inflation, followed by a slight decrease to a plateau during the hold period, and finally continuously decreased during deflation, as shown in Figure 11(a). Values for the apex strain, ϵ_0 , given by Long *et al.*'s model and also measured directly using the QD grids, are plotted as function of ϵ_{avg} in Figure 11(b). For clarity only the inflation strains are shown. Agreement between the modeled and measured apex strains, coupled with the quality of the profile fits (Figure 9(c)), indicates that the simple neo-Hookean assumption for this copolymer membrane system provides an accurate description of the strain state of the membrane.

Difficulties fitting the the last portion of deflation can be rationalized by looking at the model results in more detail. It's clear from Figure 9(c) that the agreement between the model and experimental profiles begins to increase during deflation, and the largest profile residuals are observed as the model begins to break down. In Figure 9(b) the area modulus, Eh , is plotted versus time and depicts the significant stress relaxation that occurs throughout the experiment. The area modulus decays during the inflation phase of the experiment before quickly plateauing and approaching a relaxed modulus of $0.36N/m$ during the hold phase. Difficulties arise though as the membrane deflates, particularly as tensile stresses approach zero and wrinkling instabilities develop. These conditions are troublesome for a pure elastic formulation to accommodate as they force Eh to approach zero. At this point the ODE solver can no longer converge on a solution and the analysis ultimately breaks down.

4.2 Pressure Controlled Geometry: Adhesive Contact and Withdrawal

For adhesive contact experiments two additional stages must be analyzed; contact deformation (increasing contact area) and contact withdrawal (decreasing contact area). We begin our contact investigation with the pressure controlled geometry, utilizing the acrylic copolymer blend membrane - PDMS substrate system as a model contact system. In this experiment, the membrane was air pressurized into contact with a submerged PDMS substrate in the experimental setup shown in Figure 4. The membrane was inflated until a contact radius of $a = 3.93 \text{ mm}$ ($t = 760s$ in Figure 12(a)) was achieved and then held in contact for 20 minutes ($760s < t < 2016s$), during which contact radius continued to increase slightly to $a = 4.01 \text{ mm}$. After this hold period, the membrane was deflated, decreasing its contact area until it was completely detached from the substrate at $t = 2438s$.

The analysis was applied to this experiment using the procedure outlined in section 2. Model fits were obtained for $0 < t < 2250s$, but for $2250s < t < 2438s$, the ODE solver was unable to converge. It is important to note that this portion of the experiment where our solution

fails to converge corresponds to the majority of withdrawal ($0 < a/a_{max} < 0.975$). Figure 12(b) shows model profile fits plotted over experimental images at selected time points during the membrane contact experiment. The model fits show decent agreement with the experimental profile for the contact portions of the experiment, though it is clear from Figure 12(a) that the residuals during contact inflation and deflation are higher than those of non-contact inflation.

As illustrated in Figure 12(a) the area modulus behaves in a similar manner to that observed for the non-contact experiment. The model captures the stress relaxation that occurs during the non-contact and contact inflation phases, with $E(t)h$ eventually plateauing during the hold period. As the pressure is reduced during withdrawal, the principal tensions quickly decrease as shown in Figure 13, and this in turn forces $Eh \rightarrow 0$ (Figure 12(a)). The development of compressive stresses, observable in the contact configuration as wrinkling instabilities in the circumferential (ϕ) direction, limit the applicability of the analysis to only a small portion of the withdrawal ($0.975 < a/a_{max} < 1$). The depressurization process of the pressure controlled geometry induces a circumferential compression during withdrawal, suggesting that a geometry that is dominated by tensile deformation may provide a more tractable analysis.

4.3 Displacement Controlled Geometry: Adhesive Contact and Withdrawal

The results described in the previous section motivate the development of a displacement controlled geometry to avoid the complications of compressive stresses that develop in the pressure controlled geometry. The acrylic copolymer blend membrane - PDMS substrate model system was tested in the displacement controlled geometry described in Figure 6. In this configuration, approximately 1 ml of water was added to the open end of the glass inflation tube, deforming the membrane into a spherical cap. The deformed membrane was allowed to relax for 10 minutes before the stepper motor was initiated and then the membrane was brought into contact with the substrate. The membrane was held in contact for 30 minutes with $a_{max} = 4.56\text{mm}$, and then the stepper motor was reversed and the membrane was pulled off. The entire contact and withdrawal process was analyzed, but the 10 minute relaxation period before contact was not included in the analysis.

As expected, the tensile nature of the displacement controlled geometry provides a more suitable deformation for application of the analysis of Long *et al.* In comparison to the pressure controlled geometry where the withdrawal regime $0 < a/a_{max} < 0.97$ could not be analyzed, model solutions were obtained for the entire displacement controlled pull-off. Figure 14(b) shows model profile fits plotted over experimental images at several time points during the membrane contact experiment. The model fits show decent agreement with the experimental profile for the non-contact and contact inflation portions of the test. During withdrawal though, the quality of the fits become increasingly worse, as evident in the residual plot shown in Figure 14(a). We attribute this disagreement to the difficulty in describing the entire membrane by a single relaxation modulus, given the different deformation histories experienced by the in-contact and out-of-contact portions of the membrane. Figure 14 (a) shows the area modulus fit given by the analysis. The area modulus is relatively constant during the contact inflation and contact “hold” stages, indicating the membrane has fully relaxed. During withdrawal the area modulus remains at 0.7 N/m until decreasing slightly right before pull-off. In this configuration the area modulus does not decay to zero because the principle tensions remain positive throughout withdrawal.

4.4 Direct Membrane Tension Measurement

The discussions above highlight the difficulty in accurately determining membrane tension from the profile fits and measured pressure using the analysis. These issues, coupled with the overall complexity of the analysis, motivate the formulation of a simplified method for extracting a membrane peel energy. To accomplish this goal, the displacement controlled geometry described in the previous section incorporates a laboratory analytical balance as shown in Figure 6. In this configuration, it is possible to simply measure the membrane tension using a free body analysis. A force balance at the membrane contact plane gives

$$T_{\xi}^{+} \sin \theta (2\pi a) - \rho g h_w (\pi a^2) = m_{\text{balance}} g. \quad (15)$$

Rearranging for T_{ξ}^{+} , ξ tension at the contact line, gives

$$T_{\xi}^{+} = \frac{m_{\text{balance}} g a + \rho g h_w (\pi a)}{\sin \theta (2\pi)}, \quad (16)$$

where θ is the contact angle, a is the contact radius, ρ is the density of water, h_w is the height of the column of water, g is the gravitational acceleration and m_{balance} is the mass reading from the balance.

The acrylic copolymer membrane - PDMS substrate experiment shown in Figure 14 was interfaced with an analytical balance, allowing the calculation of T_{ξ}^{+} according to Eq. 16. Figure 16 compares the tension predicted by the analysis with the result from Eq. 16. The contact line tension given by the analysis closely agrees with the measured tension during the contact inflation and hold period. During withdrawal the analysis slightly underestimates the contact line tension, consistent with the observed difference between the predicted and experiment profiles in Figure 14. With the ability to simply and directly measure membrane tension we can now proceed to discuss how this measurement can be used to quantify an adhesion energy for this geometry.

4.5 Peel Energy Measurements

4.5.1 Definition and use of the Peel Energy—The displacement controlled geometry was evaluated on two different substrates: a “weakly” adhesive untreated PDMS substrate (referred to hereafter as “PDMS”); and a “strongly” adhesive PDMS substrate, with a higher surface energy via a 15 minute UV-ozone treatment (referred to hereafter as “PDMS-UVO”). For the “strongly” adhesive substrate a pure acrylic triblock membrane was used rather than the 90 wt% triblock copolymer/10 wt% diblock copolymer blend membrane employed previously. The higher modulus acrylic triblock membrane was necessary because the stronger adhesive interaction was difficult to separate with the more compliant acrylic blend membranes. Membranes that consisted of the 90/10 triblock/diblock blend are referred to below as “blend membranes” and the pure triblock copolymer membranes are referred to as “triblock membranes”

For adhesive contact of an ideally elastic membrane in contact with a rigid surface, the energy release rate is given by Eq. 7. As with most membranes, our acrylic copolymer membranes are viscoelastic and therefore one must carefully evaluate whether conditions are appropriate for applying Eq. 7. Figure 17(a) plots the magnitude of the three terms on the right hand side of Eq. 7, using the results from Long *et al.*'s analysis for the displacement controlled experiment analyzed in section 4.3. As discussed in section 2.3, the first term describes work done by the longitudinal tension at the contact line, the second term accounts for the work expended in the elastic extension of the membrane segment that the contact line passes through, and the third term accounts for the elastic potential due to the elastic

contribution to the longitudinal tension which is also able to do work. In Figure 17(a) we see that during withdrawal these last two terms have magnitudes several times greater than that of the first term, and therefore tend to dominate the behavior of $\mathcal{G}$ as given by Eq. 7. The quantitative significance of these contributions to the energy release rate is unclear, however, because the membranes are viscoelastic. As discussed above, the elastic moduli in our analysis are actually fitting parameters that enable the membrane tensions and strains to be determined from the experimental data. These moduli are not expected to give a reliable quantification of purely energetic quantities. We do expect that the values of the contact strains, ϵ_c , are reliable, and these are plotted for three membrane/substrate combinations in Figure 17(b). The comparison between the blend and triblock membranes on PDMS is particularly interesting, because the adhesive interactions for these two situations are expected to be very similar, yet the values of ϵ_c for these two situations are quite different from one another. These results indicate that the commonly used peel energy, given by the first term in Eq. 7 and defined in our notation as $\mathcal{G}_\xi^*$, is the relevant parameter describing the adhesive interactions in these systems:

$$\mathcal{G}_\xi^* = T_\xi^+ (1 - \cos(\theta)), \quad (17)$$

Our justification for this statement comes from a comparison of Figure 17(b) with Figure 18, which shows the measured peel energies for this same set of experiments. The following observations can be made:

- During contact inflation the peel energy is low (0.02 J/m^2) and relatively constant for both substrates.
- During withdrawal the peel energy is also well behaved and relatively constant, but there is nearly an order of magnitude difference between the peel energies for the PDMS and PDMS-UVO substrates.
- For a given type of interfacial interaction (membrane/PDMS or membrane/PDMS-UVO), the peel energy is independent of the contact line strain, ϵ_c .

Our justification for the use of the peel energy as the appropriate measure of adhesion in these viscoelastic systems is based on the fact that the peel energy depends only on the type of interfacial interaction and not on ϵ_c . This behavior is exactly what one would expect for a true measure of the interfacial adhesion.

4.5.2 Thickness and Velocity Dependence of the Peel Energy—The last part of this work investigates the role of membrane thickness and debonding rate on the measured peel energy. The appropriate measure of debonding rate in these experiments is the crack velocity, defined as rate of change of the contact radius. The crack velocity varies to some extent within a given experiment, and a broader range of crack velocities can be obtained by controlling the rate at which the substrate is pulled from the experiment. The results for wide range of systems are summarized in Figure 19. The most significant changes in $\mathcal{G}_\xi^*$ are obtained by changing the substrate from PDMS (weaker adhesion) to PDMS-UVO (stronger adhesion). Increases in the membrane thickness also increase the peel energy, presumably due to the increased viscoelastic dissipation that occurs in thicker membranes. The crack velocity was determined by fitting a second order polynomial to the withdrawal portion of contact radius vs time data, as shown in Figure 7(a). Some dependence on the crack velocity is observed, although the scatter in the measured values for the peel energy make it difficult to draw any definitive conclusions regarding rate effects.

5 Conclusion

The focus of this article has been on the analysis of an axisymmetric membrane-based peel test. A model membrane contact system consisting of an acrylic copolymer membrane and PDMS substrate was utilized to evaluate the large deformation and adhesive contact analysis developed by Long *et al.* Direct measurements of the local membrane apex strain during non-contact inflation demonstrated that the neo-Hookean model provides an accurate measure of membrane strain for this acrylic copolymer system. Predicted membrane profiles were compared to experimental profiles and principal tensions were calculated, enabling the more detailed constitutive behavior of these viscoelastic membranes to be quantified. These results can be summarized as follows:

- Wrinkling instabilities in the pressure controlled geometry limit the applicability of the numerical analysis
- The displacement controlled geometry was more easily modeled than the pressure controlled geometry, but the viscoelastic character of the membranes made it difficult to describe the entire membrane with a single modulus, given the spatially non-uniform deformation history of the membrane.

For this reason a conceptually simpler method based on the direct measurement of the membrane tension and contact angle was utilized as well. The following points regarding this method can be made:

- The traditional peel energy defined using this direct measurement was found to give a measure of adhesion that was independent of the strain applied across the contact line
- Correction terms to the full energy release rate expression for an elastic membrane depend on this contact line strain. Our results indicate for these model membranes, a consistent, well-defined value for the membrane/substrate adhesion is obtained when these correction terms are ignored.

Acknowledgments

K.R. Shull acknowledges support by the National Institutes of Health under Grant 5R37DE014193-08. C.Y. Hui acknowledges the support by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under Award DE-FG02-07ER46463

Appendix

7.1 Governing Differential Equations

Four ODEs describe the membrane's large deformation equilibrium configuration:

$$\frac{d\lambda_\xi}{d\rho} = \frac{\lambda_\xi(T_\phi - T_\xi)\cos\alpha - \lambda_\phi(\partial T_\xi/\partial\lambda_\phi)(\lambda_\xi\cos\alpha - \lambda_\phi)}{\rho\lambda_\phi(\partial T_\xi/\partial\lambda_\xi)} \quad (a) \quad \frac{d\alpha}{d\rho} = \frac{\Delta P\rho\lambda_\phi\lambda_\xi - \lambda_\xi T_\phi\sin\alpha}{\rho\lambda_\phi T_\xi} \quad (b) \quad \frac{d\lambda_\phi}{d\rho} = \frac{\lambda_\xi\cos\alpha - \lambda_\phi}{\rho} \quad (c) \quad \frac{dz}{d\rho} = \lambda_\xi\sin\alpha \quad (d) \quad (18)$$

where 18(a),(b) are equilibrium equations derived from Eq.1 and Eq.2, and 18(c), (d) are geometric relations. For a neo-Hookean membrane, T_ξ and T_ϕ are defined by Eq.5 and Eq.6.

7.2 Evaluation of Boundary Condition 11(e)

In 11(e) r^* can be measured experimentally, but ρ^* depends on the history of contact and has to be determined incrementally using the following procedure. The starting point is when the apex of the membrane just touches the substrate ($i = 0$). We seek the solution at the

($i+1$)th step assuming the solution at the i th step has been determined. We can use the following relation for contact inflation where λ_ξ is continuous across the contact line and the contact angle is close to zero:

$$\rho_{i+1}^* = \rho_i^* + (r_{i+1}^* - r_i^*) / \lambda_{\xi i}^*, \quad (19)$$

where $\lambda_{\xi i}^*$ is the ξ -principal stretch ratio at the contact line for the previous step.

During contact withdrawal λ_ξ is no longer continuous across the contact line, but since λ_ϕ is always continuous across the contact line we can use Eq.20 to incrementally determine ρ_{i+1}^* .

$$\rho_{i+1}^* = r_{i+1}^* / \lambda_{\phi i}^*. \quad (20)$$

References

1. Johnson K, Kendall K, Roberts A. Surface energy and contact of elastic solids. Proceedings of the Royal Society of London. 1971; 324(1558):301–313. URL <http://dx.doi.org/10.1098/rspa.1971.0141>.
2. Shanahan MER. A novel test for the appraisal of Solid/Solid interfacial interactions. The Journal of Adhesion. 1997; 63(1):15. URL <http://dx.doi.org/10.1080/00218469708015211>.
3. Shanahan MER. Adhesion of a punch to a thin membrane. Comptes Rendus de l'Académie des Sciences - Series IV - Physics. 2000; 1(4):517–522. URL <http://dx.doi.org/10.1080/00218469708015211>.
4. Shanahan MER. Adhesion of a liquid-filled spherical membrane. Journal of Adhesion. 2003; 79(10):881–891. URL <http://dx.doi.org/10.1080/714906141>.
5. Wan K-T. Adherence of an axisymmetric flat punch on a thin flexible membrane. The Journal of Adhesion. 2001; 75(4):369. URL <http://dx.doi.org/10.1080/00218460108029611>.
6. Ju B-F, Ju Y, Saka M, Liu K-K, Wan K-T. A systematic method for characterizing the elastic properties and adhesion of a thin polymer membrane. International Journal of Mechanical Sciences. 2005; 47(3):319–332. URL <http://dx.doi.org/10.1016/j.ijmecsci.2005.02.006>.
7. Raegen A, Dalnoki-Veress K, Wan K, Jones R. Measurement of adhesion energies and young's modulus in thin polymer films using a novel axi-symmetric peel test geometry. The European Physical Journal E: Soft Matter and Biological Physics. 2006; 19(4):453–459. URL <http://dx.doi.org/10.1140/epje/i2005-10069-7>.
8. Ju B-F, Liu K-K, Wong M-F, Wan K-T. A novel cylindrical punch method to characterize interfacial adhesion and residual stress of a thin polymer film RID b-2903-2010. Engineering Fracture Mechanics. 2007; 74(7):1101–1106. WOS:000245129000009. URL <http://dx.doi.org/10.1016/j.engfracmech.2006.12.010>.
9. Flory AL, Brass DA, Shull KR. Deformation and adhesive contact of elastomeric membranes. Journal of Polymer Science Part B: Polymer Physics. 2007; 45(24):3361–3374. URL <http://dx.doi.org/10.1002/polb.21322>.
10. Xu D, Liechti KM. Analytical and experimental study of a circular membrane in adhesive contact with a rigid substrate. International Journal of Solids and Structures. 2011; 48(20):2965–2976. URL <http://dx.doi.org/10.1016/j.ijsolstr.2011.06.014>.
11. Wan K-T, Liu KK. Contact mechanics of a thin-walled capsule adhered onto a rigid planar substrate. Medical & Biological Engineering & Computing. 2001; 39(5):605–608. URL <http://dx.doi.org/10.1007/BF02345154>. [PubMed: 11712660]
12. Plaut RH, White SA, Dillard DA. Effect of work of adhesion on contact of a pressurized blister with a flat surface. International Journal of Adhesion and Adhesives. 2003; 23(3):207–214. URL [http://dx.doi.org/10.1016/S0143-7496\(03\)00013-7](http://dx.doi.org/10.1016/S0143-7496(03)00013-7).
13. Wan K-T, Kogut L. The coupling effect of interfacial adhesion and tensile residual stress on a thin membrane adhered to a flat punch. Journal of Micromechanics and Microengineering. 2005; 15(4):778–784. URL <http://dx.doi.org/10.1088/0960-1317/15/4/015>.

14. Jin C. Theoretical study of mechanical behavior of thin circular film adhered to a flat punch. *International Journal of Mechanical Sciences*. 2009; 51(6):481–489. URL <http://dx.doi.org/10.1016/j.jmecsci.2009.04.003>.
15. Wan K-T, Dillard DA. Adhesion of a flat punch adhered to a thin pre-stressed membrane. *Journal of Adhesion*. 2003; 79(2):123–140. URL <http://dx.doi.org/10.1080/00218460309573>.
16. Guvendiren M, Brass DA, Messersmith PB, Shull KR. Adhesion of DOPA-Functionalized model membranes to hard and soft surfaces. *The Journal of Adhesion*. 2009; 85(9):631. URL <http://dx.doi.org/10.1080/00218460902997000>. [PubMed: 21461121]
17. Long R, Shull KR, Hui C-Y. Large deformation adhesive contact mechanics of circular membranes with a flat rigid substrate. *Journal of the Mechanics and Physics of Solids*. 2010; 58(9):1225–1242. URL <http://dx.doi.org/10.1016/j.jmps.2010.06.007>.
18. Begley MR, Mackin TJ. Spherical indentation of freestanding circular thin films in the membrane regime. *Journal of the Mechanics and Physics of Solids*. 2004; 52(9):2005–2023. URL <http://dx.doi.org/10.1016/j.jmps.2004.03.002>.
19. Kendall K. Thin-film peeling-the elastic term. *Journal of Physics D: Applied Physics*. 1975; 8(13):1449–1452. URL <http://dx.doi.org/10.1088/0022-3727/8/13/005>.
20. Chen B, Wu P, Gao H. Pre-tension generates strongly reversible adhesion of a spatula pad on substrate. *Journal of The Royal Society Interface*. 2009; 6(35):529–537. URL <http://dx.doi.org/10.1098/rsif.2008.0322>.
21. Long R, Hui C-Y. Axisymmetric membrane in adhesive contact with rigid substrates: Analytical solutions under large deformation. *International Journal of Solids and Structures*. 2012; 49(3–4):672–683. URL <http://dx.doi.org/10.1016/j.ijsolstr.2011.11.008>.
22. Seitz ME, Burghardt WR, Faber KT, Shull KR. Self-assembly and stress relaxation in acrylic triblock copolymer gels. *Macromolecules*. 2007; 40(4):1218–1226. URL <http://dx.doi.org/10.1021/ma061993+>
23. Jones A, Shaw J, Wineman A. An experimental facility to measure the chemorheological response of inflated elastomeric membranes at high temperature. *Experimental Mechanics*. 2006; 46(5):579–587. URL <http://dx.doi.org/10.1007/s11340-006-9111-8>.
24. Hsu F, Liu A, Downs J, Rigamonti D, Humphrey J. A triplane video-based experimental system for studying axisymmetrically inflated biomembranes. *Biomedical Engineering, IEEE Transactions on*. 1995; 42(5):442–450. URL <http://dx.doi.org/10.1109/10.376148>.
25. Galliot C, Luchsinger R. Uniaxial and biaxial mechanical properties of ETFE foils. *Polymer Testing*. 2011; 30(4):356–365. URL <http://dx.doi.org/10.1016/j.polymertesting.2011.02.004>.
26. Drexler E, Finch D, Ivy D, McColskey J, McCowan C, Quinn T, Shandas R, Slifka A, Wright J. An experimental method for measuring mechanical properties of rat pulmonary arteries verified with latex. *Journal of Research of the National Institute of Standards and Technology*. 2003; 108(3) 183+, 183. URL <http://dx.doi.org/10.6028/jres.108.018>.
27. Downs J, Halperin H, Humphrey J, Yin F. An improved video-based computer tracking systems for soft biomaterials testing. *Biomedical Engineering, IEEE Transactions on*. 1990; 37(9):903–907. URL <http://dx.doi.org/10.1109/10.58600>.
28. Reuge N, Schmidt FM, LeMaout Y, Rachik M, Abbé F. Elastomer biaxial characterization using bubble inflation technique. i: Experimental investigations. *Polymer Engineering & Science*. 2001; 41(3):522–531. URL <http://dx.doi.org/10.1002/pen.10749>.
29. Li Y, Nemes JA, Derdouri AA. Membrane inflation of polymeric materials: Experiments and finite element simulations. *Polymer Engineering & Science*. 2001; 41(8):1399–1412. URL <http://dx.doi.org/10.1002/pen.10840>.
30. Mott P, Roland C, Hassan S. Strains in an inflated rubber sheet. *Rubber Chemistry and Technology*. 2003; 76(2):326–333. URL <http://dx.doi.org/10.5254/1.3547746>.
31. Kim HS, Lee CH, Sudeep PK, Emrick T, Crosby AJ. Nanoparticle stripes, grids, and ribbons produced by flow coating. *Advanced Materials*. 2010; 22(41):4600–4604. URL <http://dx.doi.org/10.1002/adma.201001892>. [PubMed: 20848596]
32. Lee DY, Pham J, Lawrence J, Lee CH, Parkos C, Emrick T, Crosby AJ. Macroscopic nanoparticle ribbons and fabrics. (under review).

Figure 1.

Side view schematic of the axisymmetric membrane inflation geometry: (a) non-contact geometry, (b) contact geometry. Typical experimental values: inflation pressure range 0.1 kPa – 0.3 kPa; $2R_m$ diameter of the undeformed membrane = 11.75 mm for pressure controlled geometry, 15 mm for displacement controlled geometry;

Figure 2.

Non-contact inflation in water of air pressurized membranes: pressure vs. apex displacement data for a pure triblock membrane and blend membranes of varying diblock content. $2R_m = 11.75$ mm.

Figure 3.

(a) Pressure vs apex displacement data for three identically prepared blend membranes (90 wt% triblock, 10 wt% diblock, $\sim 1.0\mu\text{m}$ thick). Membranes were air pressurized and inflated in water. (b) Multiple inflation cycles for the same membrane. The second and third inflation cycles were initiated immediately after the previous cycle's completion. $2R_m = 11.75$ mm.

Figure 4.
Pressure controlled membrane contact geometry

Figure 5. (a) Pressure evolution during a pressure controlled membrane contact experiment, (b) selected side view images of pressure controlled membrane contact experiment. The membrane was a blend membrane consisting of 90 wt% triblock copolymer, 10 wt% diblock copolymer spuncast to a thickness of $1.0\mu m$.

Figure 6.
Displacement Controlled Geometry: Fluid-Filled Membrane

Figure 7.

(a) The separation distance, δ_m (top) and contact radius, a , (bottom) between the glass inflation tube and substrate during a displacement controlled experiment. The membrane was a blend membrane consisting of 90 wt% triblock copolymer, 10 wt% diblock copolymer spuncast to a thickness of $\sim 1.0\mu\text{m}$. Stepping motor velocity was $0.80\mu\text{m}/\text{min}$. The solid curve (blue online) on the contact radius plot is a second order polynomial fit used to calculate the crack velocity during peel-off. (b) Side view images: *A* ($t = 0\text{ s}$, $\delta_m = 4.47\text{ mm}$), *B* ($t = 89.5\text{ s}$, $\delta_m = 3.29\text{ mm}$), *C* ($t = 1240\text{ s}$, $\delta_m = 2.32\text{ mm}$), *D* ($t = 2352\text{ s}$, $\delta_m = 8.32\text{ mm}$).

(a)

(b)

Figure 8.

A CdSe QD grid at the apex of (a) an undeformed membrane and (b) a membrane deformed to an average area strain of $\epsilon_{avg} = 1.41$, giving an apex strain of, $\epsilon_0 = 1.58$. The membrane was a blend membrane consisting of 90 wt% triblock copolymer, 10 wt% diblock copolymer spuncast to a thickness of $\sim 1.0\mu m$.

Figure 9.

(a) Surface area strain plotted versus time for the non-contact inflation of a 90 wt% triblock copolymer, 10 wt% diblock copolymer membrane spuncast to a thickness of $\sim 1.0\mu\text{m}$. The sum of the profile residuals are also plotted. (b) Area modulus fit plotted versus time for this experiment.

Figure 10.

Non-contact inflation results for a blend membrane consisting of 90 wt% triblock copolymer, 10 wt% diblock copolymer, spuncast to a thickness of $\sim 1.0\mu\text{m}$, $\epsilon_{avg} = 1.92$, $t = 2382s$, $Eh = 0.389\text{N/m}$ (a) Best-fit membrane profile given by Long *et al.* plotted over the experimental image. (b) Comparison of experimental and model profile, (c) Calculated principal tensions for the non-contact profile.

Figure 11.

(a) Membrane apex tension, given by analysis for a non-contact inflation experiment, plotted as a function of ϵ_0 . (b) A comparison of ϵ_0 given by the analysis and that measured experimentally using a nanoparticle grid for a non-contact inflation experiment. The membrane consisted of 90 wt% triblock copolymer, 10 wt% diblock copolymer spuncast to a thickness of $\sim 1.0\mu m$.

Figure 12.

(a) Area modulus fits from Long's model for the deformation of an air pressurized acrylic copolymer membrane (a 90 wt% triblock copolymer, 10 wt% diblock copolymer membrane spuncast to a thickness of $\sim 1.0\mu\text{m}$) into contact with a submerged PDMS substrate (top), the fit residuals (bottom). Region *I* is non-contact inflation, region *II* is contact inflation, region *III* is the "hold in contact" period, region *IV* is withdrawal. (b) Model profile fits plotted over experimental images.

Figure 13. Principal tensions at the contact line plotted as a function of normalized contact radius for the air pressurized acrylic copolymer membrane-PDMS described above. Models fits were not obtained for $a/a_{\max} < 0.975$.

Figure 14.

(a) (top) Area modulus fits from Long *et al.*'s model for a fluid deformed copolymer membrane brought into contact with a PDMS substrate in air (displacement controlled experiment). The membrane consisted of 90 wt% triblock copolymer, 10 wt% diblock copolymer spuncast to a thickness of $1.0\mu\text{m}$. A stepping motor velocity of $0.80\mu\text{m}/\text{min}$ was used. The sum of the residuals for the profile fit is also included (bottom). (b) Model profile fits plotted over experimental images.

Figure 15.

Comparison of experimental and model profiles corresponding to image D from Figure 14: $t = 2573s$, $a/a_{max} = 0.46$, $Eh = 0.685 N/m$.

Figure 16. Comparison of T_{ξ} at the contact line given by Long *et al.*'s model and that calculated from Eq. 16 using the analytical balance data.

Figure 17.

(a) The magnitude of the 3 terms in Eq.7 vs. normalized contact radius for the displacement controlled experiment discussed in section 4, ($1\mu\text{m}$ thick blend membrane, PDMS substrate, $0.80\mu\text{m}/\text{min}$ stepper motor velocity). The lower branch of data corresponds to increasing contact area as the membrane is brought into contact, while the upper branch corresponds to decreasing contact area during withdrawal. (b) Contact line strain as a function of normalized contact radius, for three different displacement controlled peel tests: $1\mu\text{m}$ thick blend membrane, PDMS substrate; $1\mu\text{m}$ thick triblock membrane, PDMS substrate; $1\mu\text{m}$ thick triblock membrane, PDMS-UVO substrate.

Figure 18.

Peel energy vs. normalized contact radius, for the adhesive contact between: a 1 μ m thick blend membrane and PDMS substrate; a 1 μ m thick triblock membrane and PDMS substrate; a 1 μ m thick triblock membrane, and PDMS-UVO substrate. Stepping motor velocity = 0.80 μ m/min. Bottom arrow indicates advancing contact, top arrow indicates receding portion.

Figure 19.

Peel energy, $\mathcal{G}_e^*$, dependence on crack velocity for multiple membrane contact experiments. Black symbols correspond to experiment data sets with $1\mu\text{m}$ thick blend membranes in adhesive contact with an untreated PDMS substrate (stepper motor velocities for these experiments ranged from $0.25 - 1.65\mu\text{m}/\text{min}$). A linear fit to these data sets is provided (dashed line) using the equation $\mathcal{G}_e^*(\text{J}/\text{m}^2) = c_1 + c_2(V(\mu\text{m}/\text{s}))$ with $c_1 = 0.132$ and $c_2 = 0.003539$. The blue data points correspond to membrane contact experiments with blend membranes of thickness $2\mu\text{m}$ (), $2.8\mu\text{m}$ (+), and $4.6\mu\text{m}$ (Δ), in adhesive contact with an untreated PDMS substrate (stepper motor velocity = $0.80\mu\text{m}/\text{min}$). Red data points correspond to membrane contact experiments with $1\mu\text{m}$ thick triblock membranes in adhesive contact with PDMS-UVO (stepper motor velocity = $0.80\mu\text{m}/\text{min}$).