Exploiting Wrinkle Formation

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Wrinkle formation due to age or stretched skin is seen by many as a nuisance to be avoided, often at great financial expense, rather than as a natural phenomenon to be exploited. Skin wrinkling is just one of many natural processes that involve the formation of wrinkles. For example, plums or apples can break as they become ed or dehydrated, fingerprint patterns are a form of wrinkles that appear as early as 10 weeks into a pregnancy, and Earth’s crust wrinkles in response to plate tectonics (1).

Wrinkles also form on much smaller length scales, for example, on the nanometer to micrometer scale in polymer films. These exquisite patterns have been exploited in the self-assembly of new structures and materials (2), have helped to explain fundamental physical phenomena (3), and have led to the characterization of physical properties (4). On page 650 of this issue, Huang et al. (5) exploit wrinkled formation of an ultrathin film on a fluid surface to determine film thickness and elasticity.

Wrinkles form when an applied compressive force acts on a rigid skin that rests on a softer foundation. For example, many fruits have a thin outer skin that surrounds a soft, hydrated interior. When the fruit ages, water is lost from the interior, and the volume of the fruit decreases. Consequently, there is too much skin, which shrinks and forms wrinkles. Prunes (dried plums) provide an excellent demonstration of this phenomenon (see the photo). Wrinkling also occurs in a thin film on a thick elastic substrate when it is subjected to a uniaxial compressive strain parallel to the interface (see the figure, next page).

Huang et al. explored the wrinkling patterns formed under the capillary force exerted by a drop of water placed on a freely floating polymer film. They then used the wrinkling characteristics to develop a simple method to determine film thickness and elasticity. The work represents an exciting leap forward, because the wrinkling of films under capillary forces is relatively unexplored. Moreover, the authors show that the film’s properties can be elucidated directly on a fluid surface, using no more than a dish of fluid and a low-magnification microscope.

Huang et al. induced wrinkle formation by placing a drop of water on a freely floating polymer film. The resulting wrinkles, observed with a low-magnification microscope, had two characteristic features: the number of wrinkles that emanated from the central load point and their length. These two parameters depend both on the surface tension and radius of the water drop and on the elastic properties of the film.

To investigate the effect of each of these systematically, Huang et al. placed water drops of incrementally increasing mass on films of varying thickness and recorded the number and length of the wrinkles formed. As the mass of the drop— and hence its radius—increased, both the number and the length of the wrinkles increased. In addition, as the film became

References

A simple method allows the elasticity and thickness of thin polymer films to be determined.
How thin films wrinkle. Wrinkle formation of a thin film in response to a uniaxial compressive strain, $e$, parallel to the interface. Similar wrinkles form in the experiments of Huang et al., but in their case, wrinkle patterns radiate from the center of the load.

...thicker, the number of wrinkles decreased, whereas their length increased. The authors used these results to develop two scaling relationships (one for the length and one for the number of wrinkles), adapting arguments made by Cerda and Mahadevan (6, 7). Combination of these two scaling relationships shows that if the length and number of wrinkles are known from experimental measurement, the elasticity and thickness of the film under study can be determined by a simple calculation.

To validate their method, Huang et al. monitored wrinkle formation in polystyrene films that contained different amounts of plasticizer and thus had different elastic properties. Their elasticity data are equivalent to, and in some cases have higher precision than, previously reported data obtained with sophisticated, time-consuming, and expensive techniques, such as stress-induced buckling and nano-indentation (8). The authors also show that their calculated film thicknesses are comparable with those obtained from their x-ray reflectivity measurements.

Wrinkle formation, therefore, need not always be regarded as a nuisance. Invaluable information concerning the elasticity and thickness of ultrathin films can be determined simply by measuring the number and length of the wrinkles formed in response to a capillary force. The method developed by Huang et al. is not only simple; in contrast to existing techniques, it also allows both elasticity and film thickness to be determined in one easy, quick experiment. Moreover, measurements can be made directly at a fluid surface. The latter not only eliminates the introduction of artifacts but also opens up the possibility of studying dynamical relaxation processes in thin films, a matter of crucial importance for advancing material design and understanding the viscoelastic behavior of numerous biological and soft materials.

References
different core block chemistry. The key point for choosing the different chemistries of the two hydrophobic blocks is that the two blocks experience a high degree of mutual immiscibility.

In the current experiment, polystyrene (PS) and poly(2,3,4,5,6-pentfluorostyrene) (PPFS) were employed as the different, third hydrophobic blocks in the two triblock copolymers (PAA_{94}-b-PM_{A103}-b-PS_{117} and PAA_{94}-b-PM_{A99}-b-PPFS_{100}) (29). Equal molar amounts of the two triblock copolymers with different respective third blocks were dissolved in pure THF. EDDA was then added to reach a final 1:1 molar ratio of amine groups to acid groups. The diamines underwent complexation with the PAA blocks, thereby forming aggregates with PAA-diamine cores. Notably, these aggregates contained each of the triblock copolymers with both PS and PPFS hydrophobic blocks because of the simple trapping of unlike hydrophobic blocks in the same aggregate by PAA-diamine complexation. Next, introduction of water into the THF solution to a final ratio of THF-water = 1:2 provided for the formation of cylindrical micelles. However, the existence of the original mixed triblock copolymer aggregates, as a result of PAA and diamine complexation, forced the local co-assembly of unlike third hydrophobic blocks into the same micelle core. In addition, the lack of chain exchange in solution that disallows global chain migration and maintains nonequilibrated micelle structures, combined with the fact that the PAA chains in the corona of the newly formed micelles were still complexed with diamines and were not freely mobile within the micelle, guarantee the stability of the mixed-core micelle. The immiscibility of the two different hydrophobic blocks, PS and PPFS, eventually resulted in internal phase separation on the nanoscale, producing multicompartiment micelles. The images shown in Fig. 4, A to D were taken after 4 days of aging a solution of mixed hydrophobic core cylinders. Internal phase separation is clearly indicated by the strong undulations along the cylinder surfaces and the TEM contrast variation along the cylinders. The larger, darker, and more spherical regions within the cylinders are hypothesized to be regions that are concentrated in PAA_{94} regions within the cylinders are hypothesized to be regions that are concentrated in PAA_{94} regions within the cylinders. The larger, darker, and more spherical regions within the cylinders are hypothesized to be regions that are concentrated in PAA_{94} regions within the cylinders. The larger, darker, and more spherical regions within the cylinders are hypothesized to be regions that are concentrated in PAA_{94} regions within the cylinders. The larger, darker, and more spherical regions within the cylinders are hypothesized to be regions that are concentrated in PAA_{94} regions within the cylinders.

Clearly, the undulations shown here are not exclusively correlated with the spherical end caps and are obvious throughout the length of the cylinders. Safran et al. have demonstrated that the curvature energy of a cylinder with undulations could be lower than that of a nonundulating cylinder (31). However, the undulations observed here, although locally induced by unfavorable energetic interactions between PPFS and PS, are only possible kinetically because of the forced mixing of unlike hydrophobic core blocks as a result of PAA complexing with diamines and a specific solvent-mixing pathway.

Both the multicompartiment cylinders with phase-separated cores and the cylindrical nanostructures with alternating layers of chemistry perpendicular to the cylinder axis are results of a solution assembly strategy to create structures with increased complexity with standard linear block copolymer architectures and chemistries. The key parameters are the combination of charged block interactions with multivalent counterions to influence both intra- and intermicellar interactions and solvent mixing to control the assembly pathways.

References and Notes

Capillary Wrinkling of Floating Thin Polymer Films
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A freely floating polymer film, tens of nanometers in thickness, wrinkles under the capillary force exerted by a drop of water placed on its surface. The wrinkling pattern is characterized by the number and length of the wrinkles. The dependence of the number of wrinkles on the elastic properties of the film and on the capillary force exerted by the drop confirms recent theoretical predictions on the selection of a pattern with a well-defined length scale in the wrinkling instability. We combined scaling relations that were developed for the length of the wrinkles with those for the number of wrinkles to construct a metrology for measuring the elasticity and thickness of ultrathin films that relies on no more than a dish of fluid and a low-magnification microscope. We validated this method on polymer films modified by plasticizer. The relaxation of the wrinkles affords a simple method to study the viscoelastic response of ultrathin films.

Thin sheets are much more easily bent than stretched by external forces. Even under purely planar tension, a sheet will often deform out of plane to form wrinkles. This is an everyday phenomenon that can be seen on our skin as it is stretched by smiling, scars, or age;
on the film of cream that floats on warm milk; or on the skin of fruit as it dries.

This familiar instability occurs because the elastic energy required to stretch a sheet is reduced by the out-of-plane bending that accompanies wrinkling. Cerda and Mahadevan (1, 2) considered a situation in which a rectangular elastic sheet is clamped at its ends and stretched. Beyond a critical strain, the sheet wrinkles. Minimization of the total elastic energy leads to scaling relationships between the amplitude and wavelength of the wrinkles. Their arguments have been applied to a variety of contexts, including the mechanics of artificial skins (3, 4) and surgical scars (5).

We report on a study of wrinkling of films under capillary forces, which has thus far remained relatively unexplored. Because thin films are often immersed in fluid environments, both in biological and in synthetic soft materials, the elastic deformation of films under surface tension is relatively commonplace. Thin polymer films form an ideal experimental setting in which to explore wrinkling phenomena: We study films with very high aspect ratios (the ratio of diameter D to thickness h is D/h = 5 × 10^5), which can be treated accurately in the framework of two-dimensional elasticity.

We used films of polystyrene (PS; atactic, number-average molecular weight M_n = 91,000, weight-average molecular weight M_w = 95,500, radius of gyration R_g = 10 nm) spin-coated onto glass substrates. The film thickness h was varied from 31 to 233 nm, as measured by x-ray reflectivity with a precision of ±0.5 nm (6, 7). A circle of diameter D = 22.8 mm was scribed onto the film with a sharp edge. When the substrate was dipped into a petri dish of distilled, deionized water, a circular piece of the PS film detached from the substrate. Because PS is hydrophobic, the film floated to the surface of the water where it was stretched flat by the surface tension of the air-water interface at its perimeter.

Wrinkles were induced in the stretched, floating film by placing a drop of water in the center of the film (Fig. 1), by placing a solid disk in the center of the film (fig. S1A), or by poking the film with a sharp point (fig. S1B) to produce a fixed out-of-plane displacement. All these methods of loading lead to quantitatively similar wrinkling patterns, radiating from the center of the load. We emphasize a crucial difference between loading with a solid and a fluid: The wrinkling induced in Fig. 1 is primarily due not to the weight of the drop, but to the capillary force exerted on the film by the surface tension at the air-water-PS contact line. The radial stress σ_r induced at the edge of the drop is dominated by the surface tension, which for the conditions of Fig. 1 is about 100 times as great as the radial stress developed due to the weight of the drop (mg/2a), where m is the mass of the drop and a its radius. Indeed, a solid object of weight and contact area comparable to those of the drops shown in Fig. 1 would produce no discernible wrinkling. The contact angle of the drop on PS is 88° ± 2°, and thus the geometry of the drop on the film is approximately that of a hemisphere on a flat surface (with perhaps some deformation of the film close to the contact line itself). In view of this attractively simple geometry and the degree of experimental control afforded by loading with a fluid, we focus on wrinkling induced by fluid capillarity as in Fig. 1.

We observe the wrinkling pattern using a digital camera mounted on a low-magnification microscope (Fig. 1). Two obvious quantitative descriptors of the wrinkling patterns are the number of wrinkles N and the length of the wrinkle L as measured from the edge of the droplet. N is determined by counting. Because the terminus of the wrinkle is quite sharply defined and not sensitive to lighting and optical contrast, we are also able to measure L directly from the image. The radius of the circle in which the entire wrinkle pattern is inscribed (see top left of Fig. 1) is determined with a precision of ±3%.

The central question in understanding this wrinkling pattern is, how are (N, L) determined by the elasticity of the sheet (thickness h, Young’s modulus E, and Poisson ratio λ) and the parameters of the loading (surface tension γ and radius of the drop a)? To study systematically the effect of loading and elasticity, we placed water drops at the center of the film using a micropipette, increasing the mass of the drop in increments of 0.2 mg. As the radius of the drop was increased, both L and N increased.

We first focus on N, which is found to increase as N ∝ a/√h. However, as is evident in Fig. 1, N is smaller in thicker films. The combined dependence of N on a and h is correctly captured by the scaling N ∝ a^2h^3/4, as shown in Fig. 2. To understand this scaling, the arguments of Cerda and Mahadevan (2) may be adapted to a radial geometry (5, 8). Because the number of wrinkles remains constant at all radial distances r from the center of the pattern, the wavelength of wrinkles varies according to λ = 2π/r.

![Fig. 1. Four PS films of diameter D = 22.8 mm and of varying thicknesses float-](image)

![Fig. 2. The number of wrinkles N as a function of a scaling variable, a^2h^3/4. Data for different film thicknesses h (indicated by symbols in the legend) collapse onto a single line (the solid line is a fit: N = 2.50 × 10^3 a^2h^3/4). The extent of reproducibility is indicated by the open and solid inverted triangles, which are taken for two films of the same nominal thickness.](image)

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The length of the tension, which is not captured by this argument. The data in Fig. 3A clearly show a dependence on thickness $h$, which is not captured by this argument. The dependence on $a$ and $h$ is reasonably well described by the purely empirical power-law scaling shown in Fig. 3B. $L \sim ah^{1/2}$ (as shown in the inset to the figure), an unconstrained fit to a power-law yields a slightly better fit of $L \sim ah^{0.58}$. This scaling is dimensionally incomplete and an additional factor of $(length)^{-1/2}$ needs to be taken into account. In terms of the available physical variables, the only possibility is $(E/\gamma)^{1/2}$, leading to

$$L = C_L \left( \frac{E}{\gamma} \right)^{1/2} ah^{1/2}$$

where $C_L$ is a constant. From the fit shown in Fig. 3B, we obtain $C_L = 0.031$. $E$ and $h$ appear in Eq. 3 in the combination $Eh$, which is the stretching modulus of the sheet. This indicates that the length is defined purely by in-plane stresses. However, an attempt to write the radial stresses in a manner that is consistent with Eq. 3 yields an answer for $\sigma_0(a)$ that is independent of surface tension, which is implausible. Thus, the dependence of $L$ on $h$ and $a$ is adequately constrained by the experimental data and is well described by Eq. 3 but does not yet have a definitive explanation.

A measurement of $N$ and $L$ allows a determination of both $E$ and $h$ for a film, based on Eqs. 2 and 3. As a demonstration of this technique, we vary the elastic modulus of PS by adding to it varying amounts of di-octylphthalate, a plasticizer. As can be seen in Fig. 4A, we find good agreement with published data (12) obtained by other techniques. As a further test of our technique, we note that accompanying the large variation (greater than 300%) in Young’s modulus, there is also a subtle change (of about 10%) in the thickness of the film as a function of the mass fraction, $x$, of plasticizer. The determination of thickness by means of Eqs. 2 and 3 yields a value that is in very close agreement.

This gives $L \sim a(F/aT)^{1/2}$. In our situation $F = 2\pi r$ and $\tau = \gamma$, thus yielding a linear dependence $L \sim a$. However, the data in Fig. 3A clearly show a dependence on thickness $h$, which is not captured by this argument. The dependence on $a$ and $h$ is reasonably well described by the purely empirical power-law scaling shown in Fig. 3B. $L \sim ah^{1/2}$ (as shown in the inset to the figure), an unconstrained fit to a power-law yields a slightly better fit of $L \sim ah^{0.58}$. This scaling is dimensionally incomplete and an additional factor of $(length)^{-1/2}$ needs to be taken into account. In terms of the available physical variables, the only possibility is $(E/\gamma)^{1/2}$, leading to

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The Source of Saturn’s G Ring

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The origin of Saturn’s narrow G ring has been unclear. We show that it contains a bright arc located 167,495.6 ± 1.3 km from Saturn’s center. This longitudinally localized material is trapped in a 7:6 corotation eccentricity resonance with the satellite Mimas. The cameras aboard the Cassini spacecraft mainly observe small (1 to 10 micrometers) dust grains in this region, but a sharp decrease in the flux of energetic electrons measured near this arc requires that it also contain larger (centimeter- to meter-sized) bodies whose total mass is equivalent to that of a ~100-meter-wide ice-rich moonlet. Collisions into these bodies may generate dust, which subsequently drifts outward to populate the rest of the G ring. Thus, the entire G ring could be derived from an arc of debris held in a resonance with Mimas.

The G ring is unique among Saturn’s major rings in that, before the arrival of the Cassini spacecraft, there was no obvious explanation for its location. The dust-sized particles that dominate this ring’s optical properties should originate quickly in Saturn’s magnetosphere, yet there was no direct evidence for larger source bodies that could replenish the dust and no clear explanation for the concentration of such bodies in this one region (I–5). Unlike the E and F rings, which are closely associated with satellites that could either directly supply material to the ring (Enceladus) or potentially confine the ring particles into a narrow region (Prometheus and Pandora), the G ring is located 168,000 km from Saturn’s center, over 15,000 km from the nearest known satellite. However, using data from the remote-sensing and in situ instruments onboard

References and Notes
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