SOFT JANUS, WRINKLES AND ALL

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DOI: 10.1051/epn/2016103

Right now you are probably sitting on a comfy cushion. This is most likely filled with polyurethane (PU) foam. PUs are very long molecules made up of many repeating units. If the repeating units are prepolymers – intermediate-mass building blocks – with more than two reactive end groups, a three-dimensional network will form – a rubber, or elastomer, which can behave elastically depending on the degree of network cross-linking.

What has all this to do with wrinkles? More than 15 years ago, one of our collaborators' postdocs had produced some polyurethane/polybutadiene diol (PU/PBDO) films – made up of "soft" PU prepolymer stars and "hard" polybutadiene diol linear segments - as part of his research project. These films had been stored in a box near a window. The films were very clear, with a faint yellowish tinge. Then one day, while on a visit to this collaborator's lab, one of us (MHG) casually took a film out of the box and stretched it with her fingers. Now if you do this with a piece of common clear plastic film, say polyethylene, it will turn whitish. If care is taken not to stretch it beyond the elastic regime, then this whitishness will disappear when the strain is removed.

But the PU/PBDO film would do nothing of the sort. Instead, it would remain fairly clear on stretching, but become translucent when released. A detailed examination of the film surface revealed a texture of bands, arranged *perpendicular* to the direction of stretching, whose origin was a mystery. Reproducing this effect in the lab took many months of effort and many false starts, until it was realised that the crucial ingredient was that the films had been stored *by a window*, hence it was essential to irradiate them with ultraviolet (UV) light in order to produce a higher density of crosslinks at the film surface.

Then again, if you were not involved in the above story, why should you care about wrinkles? It turns out that they are ubiquitous in nature, occurring not just in the skins of elderly humans and many animals, such as elephants, rhinoceroses and reptiles, but also in pumpkins, nuts and dehydrated fruits, as well as in single-cell organisms. These patterns evolved by natural selection over millions of years, have practical functions and can also confer a survival advantage. For example, wrinkles and folds play an important role in facilitating nutrient absorption in intestines. And they are invaluable when attempting to improve or correct nature, *e.g.*, by aiding cell adhesion at the interfaces of biomaterials and biological systems.

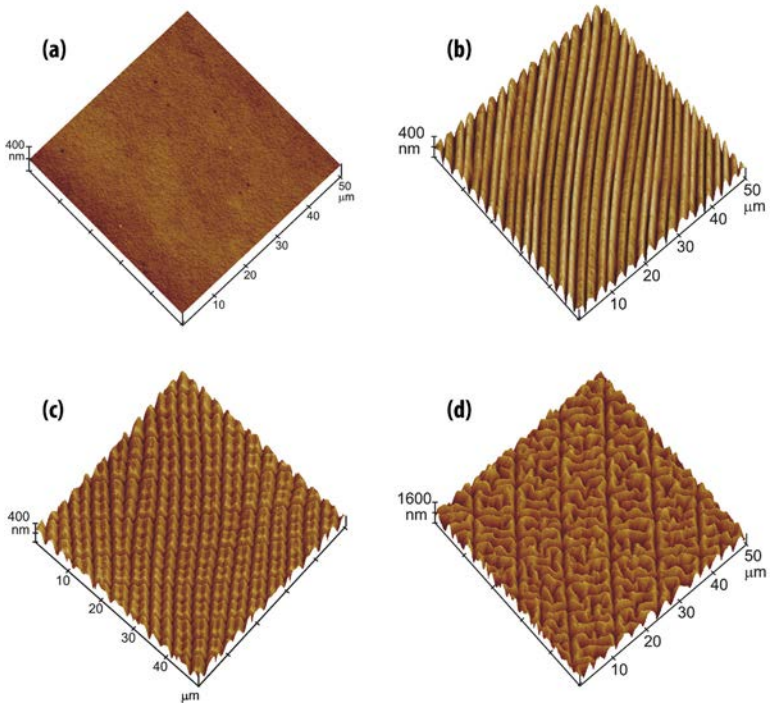
Before we proceed, a disclaimer is in order: this article is framed in the language of PU/PBDO elastomers because that is what we had on the bench at the time, and have expertise in. But qualitatively the same effects can be obtained with any other network-forming polymer.

◂ Wrinkled dried berries of *Bryonia alba*

Films

So how does one make these peculiar films? PU prepolymer and PBDO react in the presence of a specific catalyst. Then the reacting mixture is poured on a treated glass plate and spread with a casting knife moving at a controlled speed, typically 5 mm/s. The resulting film, of thickness in the region of tens of microns, is then cured, first in an oven, then in air. Finally, the film is UV-irradiated for three days. Of course, things are more complicated than this, *e.g.*, the film composition has to be just right. For full details, see [1].

The film as made is unimpressive: even AFM cannot see anything unusual (see figure 1a). But stretch it by some 30% along some direction, then let go: now AFM will reveal a beautiful pattern of one-dimensional (1d) wrinkles, almost defect-free, with wavelengths in the micron range and amplitudes of tens of nanometres (see figure 1b). And this is not all: stretch the film again, by about the same amount, perpendicular to the original deformation, and you will see a beautiful checkerboard pattern appear that results from the superposition of two 1d wrinkle waves (see figure 1c). Even more intriguingly, either of these waves can be erased by again pulling along the direction perpendicular to it. Or, if you wait long enough – a few months should suffice - the whole texture just fades away and the films go back to their unwrinkled state. (If you are in a hurry to get rid of your wrinkles, just heat your films gently.) Thus the films behave elastically on short timescales, but as liquids over longer periods. In other words, they are *viscoelastic* – as, indeed, is much of soft matter. There is, however, a way to preserve the wrinkles for posterity: just swell the films in an appropriate solvent (toluene works best), and the resulting permanent



▲ **FIG. 1: AFM images of a polyurethane/polybutadiene diol (PU/PBDO) film. (a) Immediately after UV irradiation and before any mechanical stress has been applied: the film is smooth, (b) Stretching the film along one direction induces a beautifully regular one-dimensional wrinkling. (c) Further stretching along a second direction perpendicular to the first induces a two-dimensional texture resulting from the superposition of two one-dimensional waves of wrinkling. (d) Swelling the film in toluene imprints the texture permanently. (Adapted from [2]. © EDP Sciences / Società Italiana di Fisica / Springer-Verlag 2007, reproduced with kind permission of The European Physical Journal (EPJ).)**

deformation due to the large internal strains will imprint the texture permanently (see figure 1d).

Most importantly, it is only the UV-irradiated side of the films that wrinkles. We have thus created *Janus films* – named after the Roman god of gates, doors and passages, often depicted as having two faces: one looking into the past, one into the future (see figure 2). A Janus object likewise possesses two sides with distinct compositions or textures. Everything Janus is currently a hot research topic, on account of their many applications, as we shall see later. Methods for fabricating Janus objects typically involve depositing films (*e.g.*, metal) on soft substrates. In our case, however, no such complicated steps are necessary: both wrinkly (looking into the past, in our analogy) and smooth (looking into the future) faces are the same material, and adhere to each other no matter what.

But first: how do our films get their wrinkles? The mechanism was actually worked out by Bowden and co-workers many years ago [3]. Each film consists of a stiff skin and a soft(er) bulk. The skin results from the more extensive cross-linking of the PU due to UV irradiation. When the film is stretched, both skin and substrate deform; however, the skin will deform plastically more than the substrate. So when stress is removed, the substrate will want to go back to its original (pre-deformation) dimensions, whereas the skin is now bigger than it was before. The result is a net compressive stress acting on the skin (due to the bulk) and a net extensional stress acting on the bulk (due to the skin). In other words, the skin behaves as an elastic plate subjected to in-plane compression, hence it will buckle. The wrinkle wavelength λ will thus be determined by the competition between: the bending stiffness of thin stiff skin (which penalises short wavelengths); and the bulk elastic energy of the soft core (which penalises long wavelengths). This yields that the flat state becomes linearly unstable with respect to a wrinkled state of wavelength given by

$$\lambda \sim h(E_{SS}/E_{SC})^{1/3} \qquad (1)$$

where E_{ss} and E_{sc} are the Young's moduli of the stiff skin and the soft core, respectively, and h is the stiff skin thickness, assumed to be much smaller than that of the substrate. As might be expected, λ scales with h, the only relevant length scale in the problem.

Spheres

Now Janus films are interesting, but other geometries may be more convenient for applications. In particular, Janus *particles*, with two sides of distinct compositions or textures, have many potential uses: electronic paper, where one needs to switch between black and white states [4]; optical, chemical or biological biosensors, where the two hemispheres will respond differently to stimuli [5]; anisotropic building blocks for supra-assemblies, allowing a greater variety of novel structures to be built [6]; functional surfactants, where each hemisphere likes or dislikes some other component [7]; or self-motile colloidal particles (swimmers), propelled by the different ways in which either hemisphere interacts with the surrounding medium [8].

We have fabricated Janus spheres, where one hemisphere is wrinkled and the other smooth [9]. The chemistry is the same as for films, but now, rather than cast onto a glass plate, the elastomer solution is dripped into a stirred silicon oil bath, the stirring speed of which is adjusted to yield the desired range of sphere diameters, from millimetres to tenths of a micron. The spheres are then deposited on a cellulose film and UV-irradiated. Clearly we cannot deform a sphere as we do a film, *i.e.*, by direct application of a uniaxial stress. Instead, a high degree of deformation can be achieved by first swelling, and then de-swelling our spheres in toluene (figure 3a). On swelling, both the inner (softer) core and the outer (stiffer) skin deform by the same amount. The outer surface remains smooth. However, upon de-swelling the elastomer network will contract, owing to the loss of solvent and sol fraction (unreacted prepolymer blocks). The inner core has a lower cross-linking density and will recover its natural dimensions, whereas the stiff skin, being more densely cross-linked, will not. The consequent size mismatch leads to a buildup of internal stress, which, as in the case of films, triggers the buckling instability of

the skin. The result is spheres with one smooth and one wrinkly hemisphere (see figure 3b).

Now in addition to the stiff skin thickness, there is one other length scale in the problem: the particle radius R. Put differently, the wavelength λ of linear instability will depend on the dimensionless ratio h/R. Figure 3c shows the wrinkle wavelength vs the co-latitude θ, where θ=0° corresponds to the "North Pole" (defined as the point where the incident UV light was perpendicular to the sphere) and θ=90° to the "equator". Clearly the thickness of the stiff skin (shown in the inset) decreases from the North Pole to the equator and this has a marked effect on λ, as does varying the sphere radius.

Our attempts at generalising equation (1) to a hemispherical shell on a spherical substrate were not successful, but we did manage to derive an analytical result for a cylindrical geometry:

$$\lambda/R \sim (h/R)^{3/4} \qquad (2)$$

valid for $R/h < 50$ (above this value one essentially recovers equation (1)), whereas a fit to our experimental data gave an exponent of 0.82 instead [9]. This is in reasonable agreement with numerical results by Cao *et al.* [10] for micron-sized particles consisting of a closed silica shell on a silver substrate, which suggest an exponent close to 0.8.

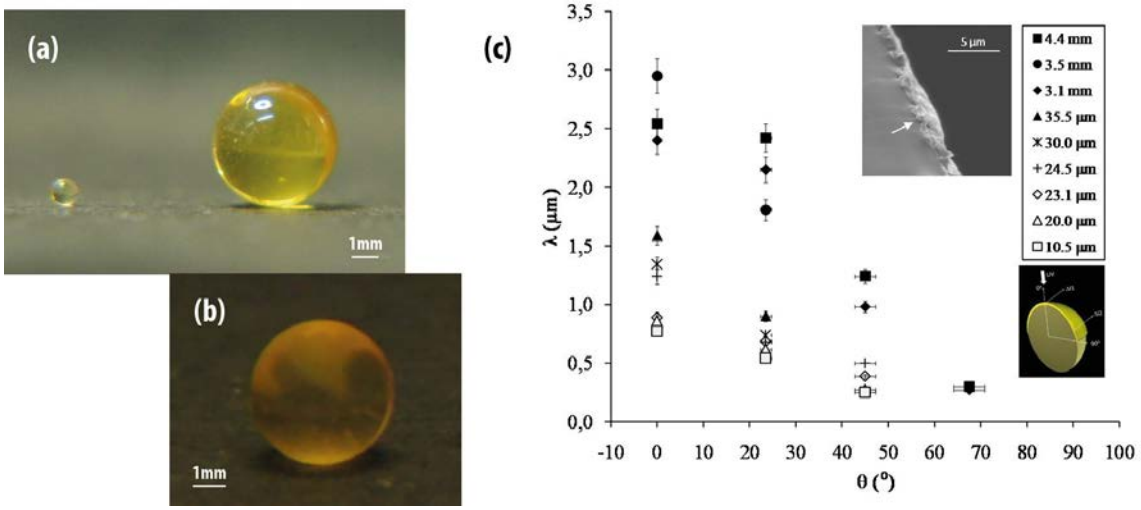
Fibres

If a theory for the spherical geometry seems difficult, what are self-respecting theorists to do? Ask your experimental co-workers to fabricate a system you *can* model – in our case a cylinder. And the experimentalists amongst us were kind enough to oblige: soon we had lots of data on long cylinders – PU/PBDO fibres [11]. These are made by a technique known as electrospinning: a syringe is filled with the reacting PU/PBDO mixture and a voltage is set up between the needle and a target – a rotating frame mounted some distance from the syringe. As the still-liquid elastomer exits the needle, it is accelerated by the voltage towards the target as a long thin fibre. The set of fibres on the target is known as a non-woven mat.

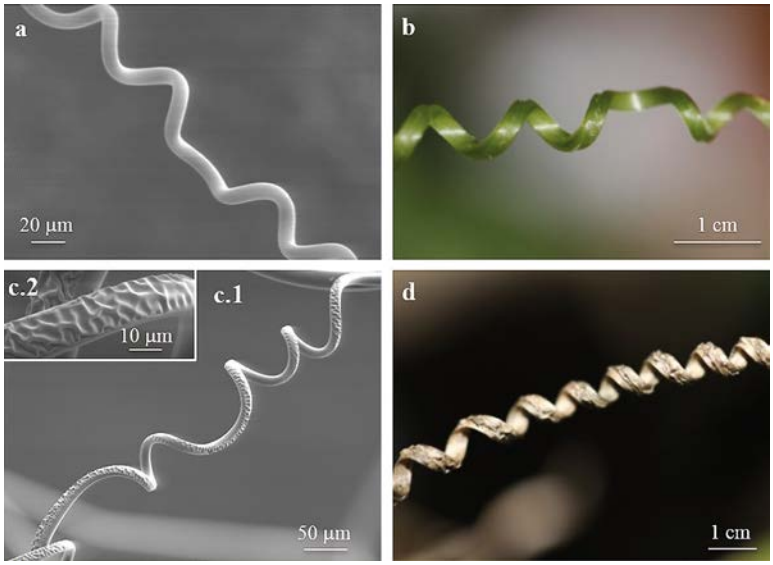
◂ FIG. 2: The Roman god Janus (Fubar Obfusco/ Public Domain.)

The fibres are then UV-irradiated on one side and swollen in toluene while still mounted on the target, *i.e.*, under tension. They are now anisotropic – the irradiated side has a stiff skin while the unirradiated side does not. This, together with solvent evaporation, again causes a size mismatch between skin and core. On removal from the target, the fibres immediately start curling into helices, like the ribbon on a Christmas present – but, surprisingly, the stiff skin remains smooth! Then at some critical radius the curling stops: the helix radius no longer changes and the stiff skin wrinkles instead.

Again, our simple model allows us to describe the crossover between the curling and wrinkling regimes. Both curling and wrinkling are governed by the interplay of bending the skin and dilating the core. The elastic energy of the curled, non-wrinkled state is proportional to ε^2, the square of the skin-core size mismatch, whereas the elastic energy of the wrinkled state grows linearly with ε. Thus, as the fibre dries, ε increases and the fibre curls, without wrinkling, with a radius that is proportional to ε^{-1}. Then at some critical mismatch, $\varepsilon_c \sim (E_{SC}/E_{SS})^{2/3}$, it becomes energetically favourable to stop curling and start wrinkling, with a wavelength given by equation (1).



◂ FIG. 3: (a) A PU/PBDO sphere, before (left) and after (right) swelling in toluene. (b) Janus sphere with one smooth (shiny) and one wrinkly (cloudy) hemisphere. (c) Dependence of λ, the wrinkle wavelength of linear instability, on the skin thickness and sphere diameter. (Adapted from [9]. © 2011, American Chemical Society, reproduced with permission.)



▲ FIG. 4: Electrospun PU/PBDO fibres mimic plant tendrils. A smooth fibre (a) mimics a young tendril (b). An asymmetrically wrinkled fibre (c.1) mimics an old tendril (d). (c.2) shows the detail of the wrinkled fibre in (c.1). Notice the wrinkling is on the outside of the helix, consistent with the assumption that the stiff skin contracts less than the soft core on drying. (From [11]. © WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, reproduced with permission.)

Remarkably, the same qualitative behaviour is seen in the tendrils of climbing plants as they age and dry, albeit on a vastly different length scale: first they curl, then they wrinkle (see figure 4).

Outlook

Ours is a very simple method to fabricate Janus planar films, spherical particles and cylindrical fibres from a single elastomeric material. Janus particles and fibres with diameters ranging from tenths of a µm to a few mm can be produced using current chemicals and techniques. Remarkably, Janus fibres exhibit a crossover between curling and wrinkling regimes when they dry, which can be described by a simple elastic model. This latter result opens up new perspectives on biomimetic materials, as functionalities can be added by having "young" (smooth, small-surface area) and "old" (wrinkled, large-surface area) regions co-exist in the same material. For example, a fibre-based micromanipulator could conceivably be constructed, where a micro- or nano-sized object would be grabbed and carried by an array or wrinkled fibres, then released at a very precise location simply by adjusting the pattern [12].

About the authors

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