Stretchable and ultraflexible organic electronics

Darren J. Lipomi and Zhenan Bao, Guest Editors

Stretchable and ultraflexible electronic devices have a broad range of potential uses, from robust devices for energy storage and conversion to biomedical devices that make conformal interfaces with the skin and internal organs. Organics have long been associated with mechanical compliance, which enables inexpensive manufacturing via roll-to-roll printing. This article provides an overview of the use of organic electronic materials, including π-conjugated polymers and small molecules, in highly deformable devices. It begins with a comparison of devices based on organic devices to those based on inorganic composites. The thin-film nature of organic semiconductor devices has also led to the development of several techniques for metrology that can be applied specifically to brittle organic thin films. The article concludes with a brief discussion of the applications of stretchable and ultraflexible organic electronic devices and a prescriptive outlook for successful collaborative work in this exciting, interdisciplinary field.

Plastic electronics: Back to basics

Five years ago, *MRS Bulletin* published a theme issue on the then—and still—burgeoning field of stretchable and flexible electronics.[1] The authors in that issue explored the mechanics of stretchable thin films,[2] approaches to generating stretchable devices from otherwise rigid materials,[3] and a range of stretchable device components, from batteries to electronic eye cameras.[4] The topics in that issue reflected the state of the art in the field then, which was dominated by devices based on inorganic materials (e.g., metallic films and semiconductor nanoribbons).

A complementary approach to extreme deformability is based on organic conductors and semiconductors.[5] While the conductivity and transport properties of inorganic materials are superior to those of organics, the advantages of these molecular materials remain—oxide-free interfaces, fabrication by printing in a roll-to-roll manner, low cost, tailorability by synthesis, and intrinsic mechanical compliance.[5] Deformability was one of the original goals of organic electronics,[6] but some of the best performing materials today remain stiff, and they crack at relatively low strains. Organic devices can be rendered stretchable in many of the same ways as can devices based on inorganic thin films (e.g., using wavy, fractal, or relief features that direct strain away from the sensitive components).[7] Other approaches that are applicable only to organics, however, give them a distinct advantage, such as the formation of fibers to form elastic mats and the synthesis of materials whose molecular structure or solid-state packing structure permits extreme deformation.[8]

A suite of tools incorporating metrology, synthesis, and fabrication has recently emerged whose goal is to achieve the original dream of organic electronics—to combine state-of-the-art electronic performance with high deformability. This research is, at present, somewhat distinct from efforts in the field to understand and to improve the electronic properties of organic semiconductors, though ultimately, the results of both spheres of inquiry must be merged. The authors of the articles in this issue of *MRS Bulletin* have made key contributions to developing stretchable new materials or stretchable forms of old ones, new techniques for measuring the mechanical properties of fragile thin films, and new devices that exhibit unprecedented deformability.

New materials and stretchable forms of old ones

Stretchable electronics had its beginnings in the 1990s with the work of Wagner, Suo, and others, who examined the mechanics of materials—principally metals—on flexible and stretchable substrates.[9] These materials adopted buckled, wavy, or fractured morphologies that accommodated tensile strains while retaining electronic functionality.[10] In an example of applying this approach to organic electronic materials, we have made stretchable organic solar cells by buckling the devices on elastic substrates.[11] Bettinger and co-workers used a similar approach by producing the first stretchable organic

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transistor (**Figure 1**a).[12] Kaltenbrunner, Bauer, Someya, and co-workers increased the conformability and stretchability of devices by fabricating their devices on ultrathin plastic foils (Figure 1b), noting that the bulk of a "thin-film" electronic device is embodied in its substrate.[13] This approach has been applied successfully to solar cells,[14] light-emitting devices,[15] and pressure sensors.[16] Another strategy is to deposit high-aspect-ratio organic nanostructures on (or in) an elastomeric matrix.[16] This approach has worked for nanowires of regioregular poly(3-hexylthiophene) (P3HT) to yield all-nanofiber transistors (Figure 1c).[17] Bao et al. found the nanoconfinement effect to improve the stretchability of polymer semiconductors through lowering its modulus due to increased polymer chain dynamics.[18] Organic semiconductor films can remain functional in thin-film transistors even if they contain a large density of cracks (as long as the film retains an uninterrupted pathway for charge carriers).[19]

A new strategy relies on the intrinsic stretchability of the organic material. This approach, called "intrinsically"[20] or "molecularly"[5] stretchable, does not require materials to be processed into buckles or nanowires (Figure 1d).[21] Scientifically, this approach requires circumventing the apparent incompatibility
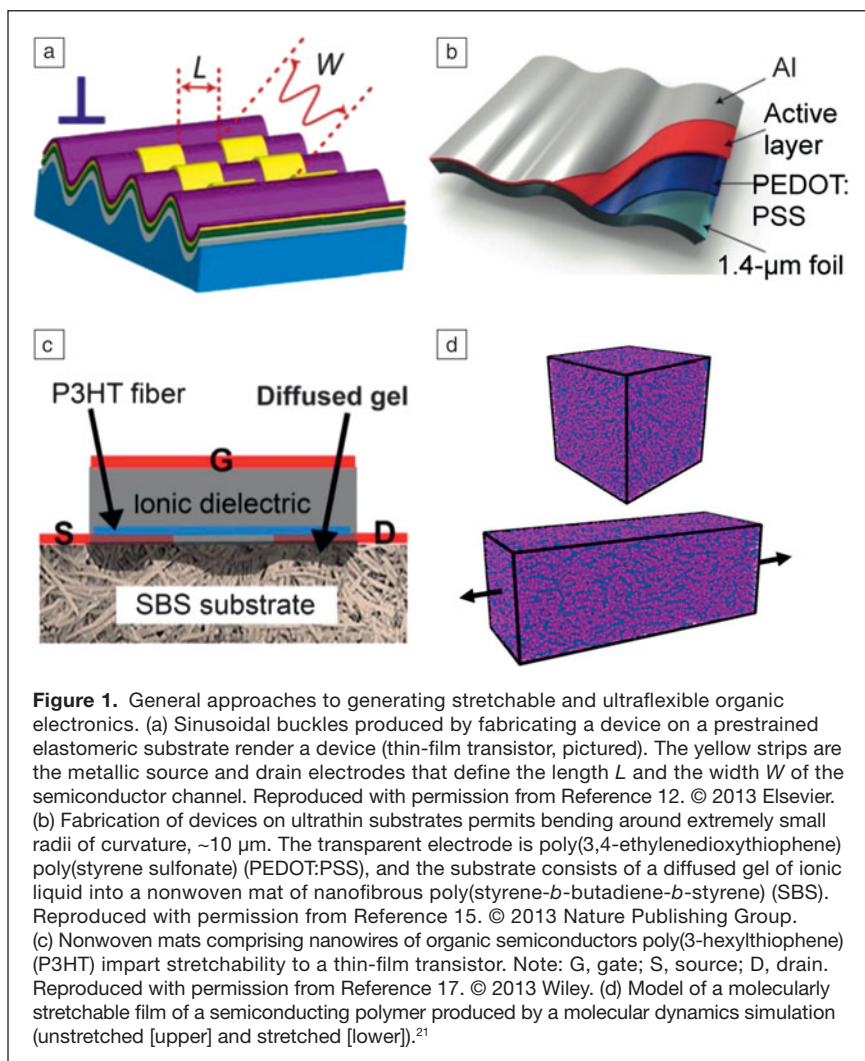
of charge transport with deformability. That is, the stiff, π-conjugated backbones and highly aggregated microstructures of organic semiconductors tend to be good for charge transport, but bad for mechanical deformability. Our groups and several of the groups represented in the articles in this issue have investigated the effects of molecular structure, molecular weight, additives, microstructural details, molecular recognition, and other phenomena, on the mechanical properties of organic semiconductors, and the ways in which intrinsic stretchability can be combined with electronic performance.[22,23]
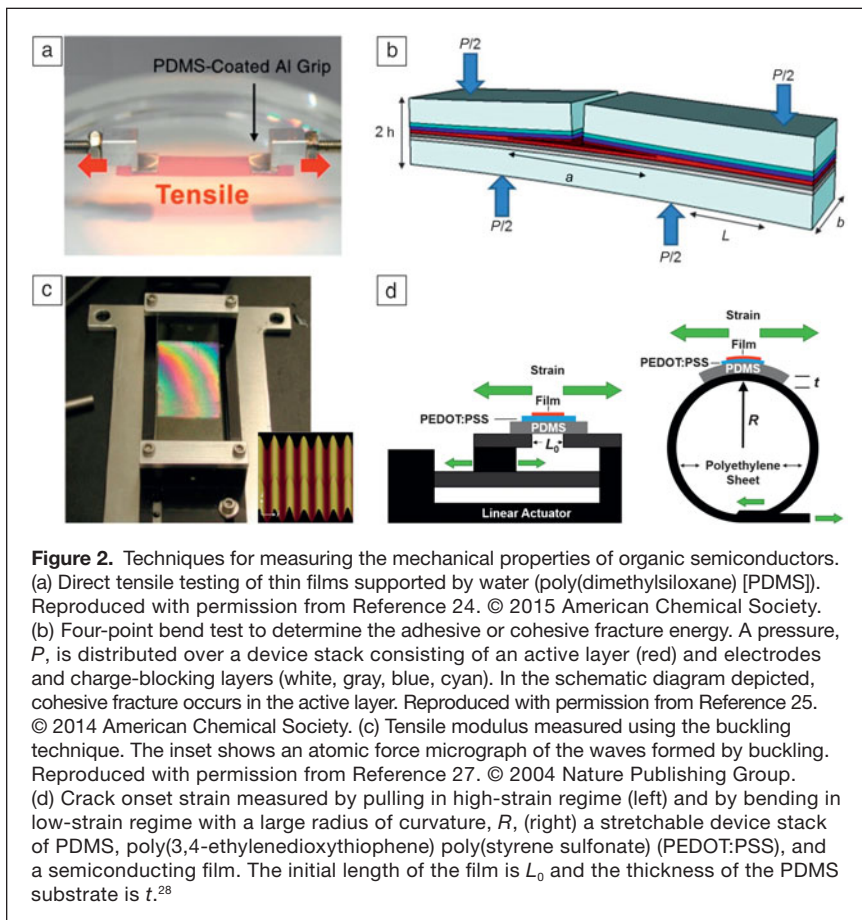
Metrology

Approaches to measuring the mechanical properties of organic semiconductors are subject to two constraints. First, little material is typically produced by a laboratory-scale synthesis. Second, these materials are generally processed into thin films. Traditional pull testing is difficult or impossible for materials produced by syntheses that can yield less than 100 mg of material. The stress–strain behavior can be measured directly for some materials using a highly sensitive technique developed by Kim and co-workers in which the pull test is carried out with the film supported by water (**Figure 2**a).[24] Dauskardt and co-workers have developed the four-point bend test (Figure 2b) and double-cantilever beam test for determining the cohesive and adhesive fracture energies of semiconducting polymer films.[25]

Several techniques have been developed to reconstruct the stress–strain response of thin films by assaying their behavior when strained on elastomeric substrates.[26] The mechanical buckling metrology, as depicted in Figure 2c,[27] is a well-known system to derive the elastic modulus of a thin film based on its buckling pattern on an elastic substrate under small compressive strains. Basically, the modulus increases with the cube of λ_b/d_f, where λ_b is the buckling wavelength and d_f is the thickness of the film.[27] The yield point can be measured by cyclically straining a thin film by incrementally increasing displacements until buckles appear; this point corresponds to where the film has deformed plastically.[26] The crack onset strain of a thin film on an elastic substrate is generally taken to be the strain at fracture, however, as a composite system, it is affected by the adhesion of the film to the substrate (better adhesion leads to larger crack onset strains). Figure 2d[28] shows the experimental configurations of measuring the crack onset strain in the high-strain regime using a linear actuator (left) and in the low-strain regime by bending with a large radius of curvature (right).[29] The results of these film-on-elastomer techniques can be taken together to estimate the stress–strain behavior.[26]

Figure 1. General approaches to generating stretchable and ultraflexible organic electronics. (a) Sinusoidal buckles produced by fabricating a device on a prestrained elastomeric substrate render a device (thin-film transistor, pictured). The yellow strips are the metallic source and drain electrodes that define the length *L* and the width *W* of the semiconductor channel. Reproduced with permission from Reference 12. © 2013 Elsevier. (b) Fabrication of devices on ultrathin substrates permits bending around extremely small radii of curvature, ~10 µm. The transparent electrode is poly(3,4-ethylenedioxythiophene) poly(styrene sulfonate) (PEDOT:PSS), and the substrate consists of a diffused gel of ionic liquid into a nonwoven mat of nanofibrous poly(styrene-*b*-butadiene-*b*-styrene) (SBS). Reproduced with permission from Reference 15. © 2013 Nature Publishing Group. (c) Nonwoven mats comprising nanowires of organic semiconductors poly(3-hexylthiophene) (P3HT) impart stretchability to a thin-film transistor. Note: G, gate; S, source; D, drain. Reproduced with permission from Reference 17. © 2013 Wiley. (d) Model of a molecularly stretchable film of a semiconducting polymer produced by a molecular dynamics simulation (unstretched [upper] and stretched [lower]).[21]

Figure 2. Techniques for measuring the mechanical properties of organic semiconductors. (a) Direct tensile testing of thin films supported by water (poly(dimethylsiloxane) [PDMS]). Reproduced with permission from Reference 24. © 2015 American Chemical Society. (b) Four-point bend test to determine the adhesive or cohesive fracture energy. A pressure, *P*, is distributed over a device stack consisting of an active layer (red) and electrodes and charge-blocking layers (white, gray, blue, cyan). In the schematic diagram depicted, cohesive fracture occurs in the active layer. Reproduced with permission from Reference 25. © 2014 American Chemical Society. (c) Tensile modulus measured using the buckling technique. The inset shows an atomic force micrograph of the waves formed by buckling. Reproduced with permission from Reference 27. © 2004 Nature Publishing Group. (d) Crack onset strain measured by pulling in high-strain regime (left) and by bending in low-strain regime with a large radius of curvature, *R*, (right) a stretchable device stack of PDMS, poly(3,4-ethylenedioxythiophene) poly(styrene sulfonate) (PEDOT:PSS), and a semiconducting film. The initial length of the film is L_0 and the thickness of the PDMS substrate is *t*.[28]

Mechanical properties of organic semiconductors

The mechanical properties of the organics are critical to the stability of the devices in use. For conjugated polymers, increasing molecular weight tends to increase the cohesive energy, toughness, and crack-onset strain.[25] Side chains in conjugated polymers decrease the modulus and brittleness by reducing the glass-transition temperature.[30] Branched side chains have a similar effect, but side chains that are far enough apart to interdigitate produce stiff crystallites.[31] Fused rings (e.g., thienothiophene) tend to produce stiffer thin films than isolated rings (e.g., bithiophene).[31]

The solid-state packing structure, however, is often a stronger predictor of mechanical properties than is the flexibility of an isolated molecule.[32] Small-molecule or polymeric additives (i.e., to increase the efficiency of solar cells) tend to behave as plasticizers, which is an attractive route to achieving high performance and good mechanical compliance.[33] Small-molecule semiconductors have reduced toughness compared to semiconducting polymers, but some specimens may be extended—without cracking—over a large enough range to enable applications that are truly stretchable.[28] Prediction of the mechanical properties of conjugated polymers has recently become the target of computational scientists.[34] Atomistic molecular dynamics simulations of

polymer:fullerene bulk heterojunction solar cells have been used to predict the cohesive fracture energy.[33] In a recent contribution by Root et al., coarse-grained molecular dynamics simulations correctly predicted many key properties of P3HT, including the tensile modulus, strain alignment, Poisson's ratio, and glass-transition temperature.[21]

Applications of stretchable and ultraflexible devices

The Lipomi and Kim groups[35] have reported several intrinsically stretchable solar cells, including wearable[36] and biaxially stretchable ones.[37] O'Connor et al. combined thin substrates with the selection of the most deformable active materials to produce wearable solar cells that could undergo repetitive bending strains with radii of curvature ≥100 µm (**Figure 3**a).[36] Stretchable and ultraflexible thin-film transistors have been made by a variety of techniques. For example, Wu et al. have used the buckling technique to generate microscale wrinkles in the active materials that can accommodate strain.[12] Kaltenbrunner et al. have fabricated "imperceptible" organic electronic devices by fabricating them on ultrathin plastic foils.[13] Chortos et al. have used intentionally cracked (but electrically contiguous) semiconduc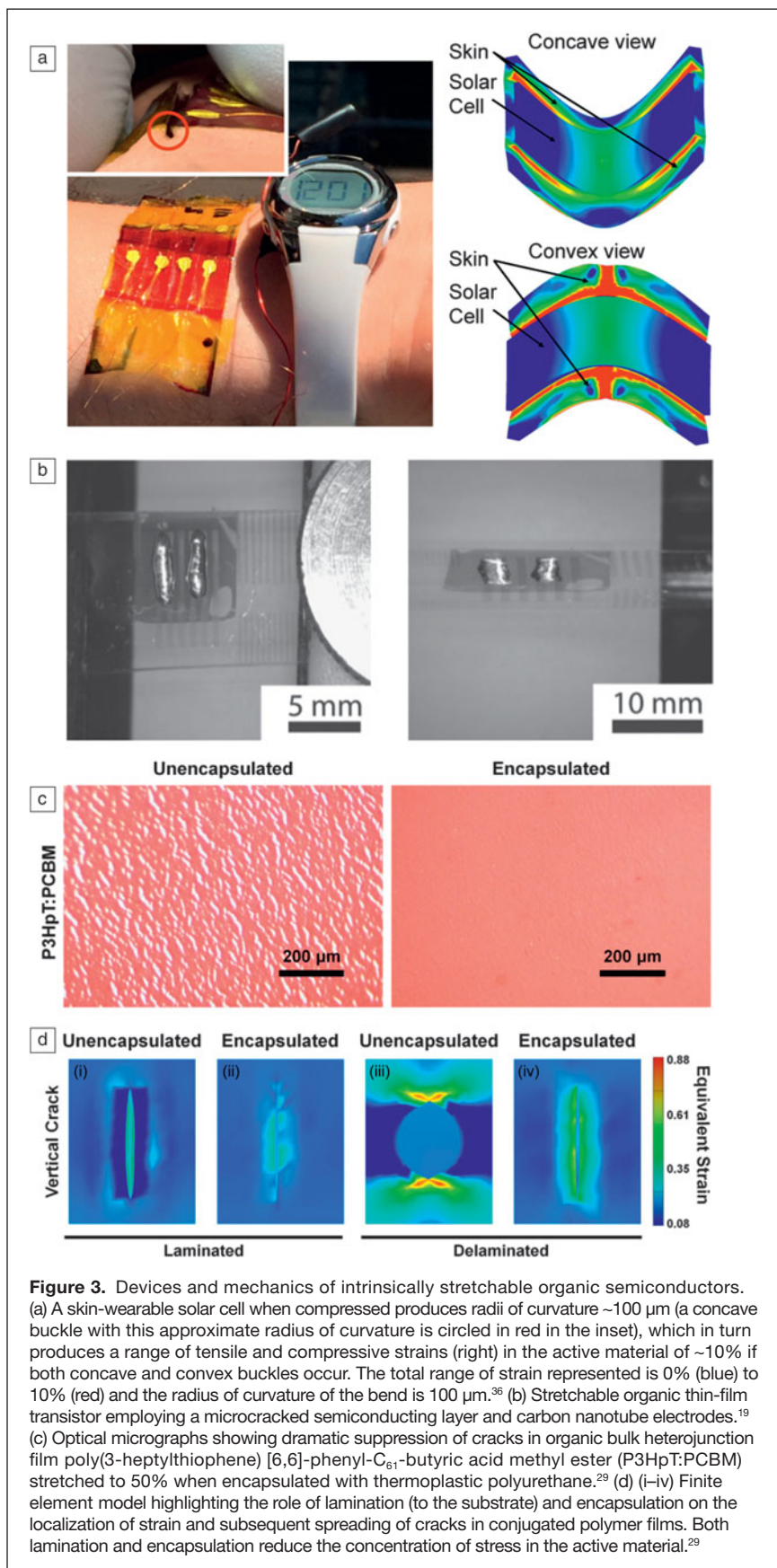tor films[19] (Figure 3b), and Lee et al. used another approach in which the semiconducting channel comprises a network of nanofibers in a stretchable matrix.[8]

We note the importance of encapsulation for improving the stability of flexible and stretchable devices. In the case of flexible applications, use of encapsulation allows the researcher to put the most sensitive components in the mechanically neutral plane; in the case of stretchable applications, encapsulation redistributes strain evenly across the active materials such that strain is not concentrated at thin areas and defects, which are ordinarily the sites where cracks initiate (Figure 3c–d).[29]

In this Issue

The work described in this theme issue is a comprehensive examination of the state of the art in highly deformable organic electronic materials and devices. The articles cover all important areas, including the design of materials, microstructural characterization, mechanical properties, and applications in devices. Thiyagarajan et al. describe several strategies for achieving stretchable active layers in polymeric semiconductors. In their article, Qi et al. cover an oft-overlooked aspect of stretchable devices—the substrate. O'Connor et al. describe the microstructural parameters that influence the stiffness and brittleness of materials in work related to the mechanical properties of materials. Kim et al. cover the mechanical behavior as it relates to reliability. Someya et al.

Figure 3. Devices and mechanics of intrinsically stretchable organic semiconductors. (a) A skin-wearable solar cell when compressed produces radii of curvature ~100 μm (a concave buckle with this approximate radius of curvature is circled in red in the inset), which in turn produces a range of tensile and compressive strains (right) in the active material of ~10% if both concave and convex buckles occur. The total range of strain represented is 0% (blue) to 10% (red) and the radius of curvature of the bend is 100 μm.[36] (b) Stretchable organic thin-film transistor employing a microcracked semiconducting layer and carbon nanotube electrodes.[19] (c) Optical micrographs showing dramatic suppression of cracks in organic bulk heterojunction film poly(3-heptylthiophene) [6,6]-phenyl-C_{61}-butyric acid methyl ester (P3HpT:PCBM) stretched to 50% when encapsulated with thermoplastic polyurethane.[29] (d) (i–iv) Finite element model highlighting the role of lamination (to the substrate) and encapsulation on the localization of strain and subsequent spreading of cracks in conjugated polymer films. Both lamination and encapsulation reduce the concentration of stress in the active material.[29]

describe the use of ultrathin substrates to achieve unprecedented levels of flexibility and "mechanical imperceptibility" on the device side. Liang et al. describe specific applications of stretchable organic semiconductors in thin-film transistors. Li et al. describe work on stretchable sensors and actuators for soft robotics.

Conclusion

The future of stretchable and ultraflexible organic electronic devices is promising. The field has benefitted from a highly collaborative approach, in which synthetic chemists have interacted synergistically with materials scientists and chemical, mechanical, electrical, and biomedical engineers. New materials and metrologies are being developed to overcome the challenges of minute quantities of materials measured in thin-film form. Given the interdisciplinary of the field, it can benefit from open sourcing, of the type recently described by Bauer in a complete description of an apparatus for biaxial stretching.[38] In this spirit of collaboration, the field is overcoming the apparent incompatibilities between charge transport and deformability, and applications in energy[39] and the health sciences are at hand.[40]

Acknowledgments

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