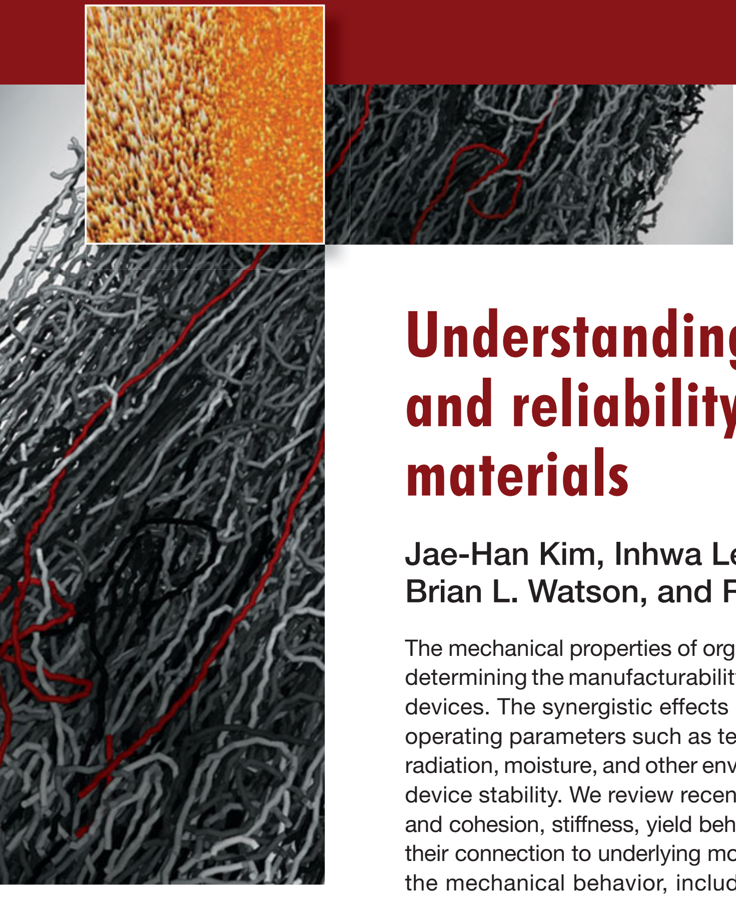

Understanding mechanical behavior and reliability of organic electronic materials

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The mechanical properties of organic electronic materials and interfaces play a central role in determining the manufacturability and reliability of flexible and stretchable organic electronic devices. The synergistic effects of mechanical stress and deformation, together with other operating parameters such as temperature and temperature cycling, and exposure to solar radiation, moisture, and other environmental species are particularly important for longer-term device stability. We review recent studies of basic mechanical properties such as adhesion and cohesion, stiffness, yield behavior, and ductility of organic semiconducting materials, and their connection to underlying molecular structure. We highlight thin-film metrologies to probe the mechanical behavior, including when subjected to simulated operational conditions. We also report on strategies for improving reliability through interface engineering and tailoring material chemistry and molecular structure. These studies provide insights into how these metrologies and metrics inform the development of materials and devices for improved reliability.

Introduction

Stretchable and flexible electronic devices require both structural and active electronic materials that are compliant and able to withstand mechanical deformation without damage. Often, it is desirable that the active electronic materials also act as structural elements—resistant to damage processes such as buckling and fracture without the need for supporting structures. Engineering reliable, flexible, and stretchable devices requires characterizing thermomechanical properties, including strength, stiffness, and ductility of the constituent materials. In addition, the fracture energy, G_c (J/m^2), quantifies the adhesion of interfaces or cohesion of constituent layers and is one of the most fundamental metrics of reliability. Organic electronic materials have G_c values that are often much lower than those of conventional engineering materials, and strategies for improvements are required for thermomechanically reliable technologies.[1]

Characterizing salient mechanical properties of organic charge-transport layers and semiconducting materials used in organic logic devices, displays, and organic or even recent perovskite photovoltaic solar cells have provided essential lessons for the development of mechanically reliable, electronically active, and flexible technologies.

Mechanical properties important for reliability

Adhesive or cohesive failure may result from residual or applied mechanical stresses introduced during device processing, handling, packaging, and operation.[2,3] Mechanical stresses provide the driving force for damage and can vary markedly with thermal cycling or device application, particularly for stretchable and wearable devices subject to significant deformation from physiological motion. The driving force for failure processes like film cracking or interface debonding can be quantified in terms of the strain-energy release rate, G (J/m^2), which is a function of the previously discussed mechanical stresses. Fracture occurs when $G \geq G_c$.

G_c values of representative organic electronic materials can be accurately measured and recently characterized ranges

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are summarized in **Figure 1**. Measuring G_c does not require any information about the mechanical properties or stresses in the layers themselves, which are often unknown or difficult to characterize.[1,2,4]

Complementary thin-film techniques can be used to elucidate other fundamental mechanical properties useful for understanding mechanical failure. Buckling techniques,[5] crack onset strain measurements,[6] and tensile testing[7] provide insight into the stiffness, yielding, and ductility of materials. More complex viscoelastic properties can be characterized using dynamic mechanical analysis techniques,[4,8] and while important, are not addressed in this article.

Mechanical properties are needed for understanding mechanical stability and provide the basis for reliable thermomechanical design and lifetime prediction. For organic semiconducting materials, however, these properties and their connection to underlying molecular structure are often unknown. In addition, the synergistic effects of mechanical stress along with temperature and temperature cycling, moisture and other environmental species, and damaging solar radiation are just as important.[9–12] These variables accelerate damage processes that result in the commonly observed loss of cohesion of layers or adhesion of interfaces, leading to degradation of performance and device failure.

Adhesion and cohesion

We first provide an overview of the typical G_c values for cohesion and adhesion of organic electronic material layers and interfaces that, as already noted, are often much lower than conventional engineering materials (Figure 1).[1,10,13,14] G_c at the most fundamental level involves the energy needed to cause bond breakage that is related to the bond type and density, and by other energy dissipation processes involving, for example, molecular deformation and flow in a localized fracture process zone.[1] In solution-processed molecular materials, such as 2,2′,7,7′-tetrakis[*N*,*N*-di(4-methoxyphenyl)amino]-9,9′-spirobifluorene (spiro-OMeTAD) and C_{60} fullerene layers, the intermolecular forces are weak, and very low fracture energies (~0.1– 0.5 J/m^2) are a result of the absence of stronger covalent or ionic bonds.[14] Other classes of molecular materials (e.g., rubrene, pentacenes, diindenoperylenes, perylene diimides, and tetracyanoquinodimethane) utilized in organic electronic devices have entirely uncharacterized fracture properties and related thermomechanical reliability, although G_c measurements in our lab suggest similarly low values for 6,13-bis(triisopropylsilylethynyl)pentacene (TIPS-pentacene) layers.

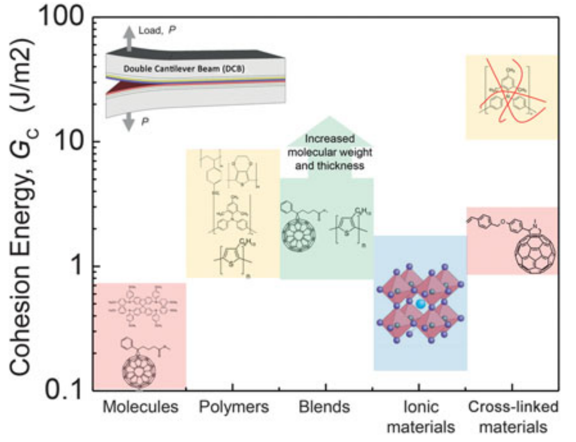

Figure 1. A comparison of G_c values for a wide range of active materials in organic electronic devices.[1,10,13,14] The inset shows the double cantilever beam specimen method used to obtain the data in the plot.

In polymeric semiconducting materials, such as poly(3-hexylthiophene) (P3HT) and poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (PTAA), higher G_c values (~2.5–8 J/m^2) result from increasing degrees of polymer–chain interactions and entanglement, requiring that covalent bonds be broken during fracture. Chain entanglement is strongly influenced by the molecular weight (MW) and provides a further mechanism for the dissipation of energy by viscoelastic deformation related to chain pullout in a fracture process zone localized at the crack tip.[4] Complex composite polymers such as poly(3,4-ethylenedioxythiophene) poly(styrene sulfonate) (PEDOT:PSS) feature entanglements and further ionic interactions that contribute to G_c, but also make the material susceptible to so-called “moisture-assisted” decohesion or debonding, as the synergistic effects of water molecules that weaken the ionic interactions together with mechanical stress lead to a time-dependent fracture process at values of $G < G_c$.[11]

Blends of polymers with small molecules such as bulk heterojunction (BHJ) solar cells present an interesting case study. In these systems, the G_c of the polymer may be significantly compromised through the addition of fullerene material (e.g., [6,6]-phenyl-C_{61}-butyric acid methyl ester [PCBM]) as the extent of polymer chain interactions is reduced.[10] Interestingly, the polymer acts as a solvent for these molecules, allowing for their diffusion and aggregation at surfaces with favorable energies and resulting in fullerene crystal formation. In organic photovoltaic (OPV) devices, this presents a particular challenge for mechanical stability since the weakly interacting fullerene crystal domains compromise both adhesion and cohesion.[10,15]

Ionic hybrid perovskite materials that feature prominently in current literature are formed by crystallization of ionic species from solution and develop their cohesion as solvent molecules leave. Their solubility, however, indicates that their cohesion is low and can be easily overcome by solvent interactions, unlike materials held together by stronger polar-covalent or covalent bonds, which do not easily dissolve. Accordingly, these brittle, ionic materials offer little resistance to fracture and have extremely low G_c values (~0.3–1.5 J/m^2).[13] Additionally, nanoparticulate oxides such as ZnO used as *n*-type semiconducting materials rely on interparticulate interactions for their cohesion, resulting in fracture well below (~0.7 J/m^2) those expected for the brittle fracture of bulk ZnO.[14]

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Molecular cross-linking strategies that increase molecular interactions with strong covalent bonds can be employed to significantly increase G_c values for organic electronic materials, and they will be discussed later.

Other salient mechanical properties

Buckling-based metrologies derive the elastic modulus of polymeric thin films from the buckling wavelength of the films on flexible substrates such as poly(dimethylsiloxane) (PDMS), which acts as a source of compressive strain.[5] Introducing fullerene (PCBM) into polymer blends increases the elastic modulus of the BHJ films due to a filler effect.[16–18] Conjugated polymers with longer or branched side chains have the opposite effect.[18,19] Additives such as 1,8-diiodooctane (DIO), low-molecular-weight PDMS and the fluorosurfactant Zonyl FS-300 in polymers act as plasticizers that also decrease the elastic modulus of the films.[18,20]

Measuring the "crack onset strain" of organic semiconductor layers on flexible substrates has been widely adopted as a method to evaluate the ductility of thin films.[6] Ductile films have a high crack onset strain and tend to be more robust, while brittle films crack even under small tensile strain.[19] An increase in side-chain length and addition of polymer additives such as fluorosurfactant that decrease the elastic modulus tend to increase the ductility of the films and can be used to achieve good mechanical resilience of OPVs.[18,20] In order to quantify the importance of elastic modulus (stiffness) and crack onset strain (ductility) on electronic devices, the effects of mechanical strains and fatigue on photovoltaic properties have been investigated on a PDMS substrate.[18,21]

Direct tensile testing of organic semiconductors, including conjugated polymers and BHJ films, has proven difficult due to the combination of their ultrathin and fragile characteristics. To overcome these limitations, a new tensile testing method was recently developed in which films are floated on water, enabling tensile testing of a variety of materials from metals to organic semiconductors.[7,22] This involves attaching a PDMS-coated Al grip to the film surface using van der Waals adhesion in order to manipulate the ultrathin films. The high surface tension of water supports the films, and the low viscosity of water enables frictionless sliding. By adopting this method, the intrinsic mechanical properties of semiconducting polymers such as P3HT have been directly measured on the water surface without requiring complex calculations to account for any substrate effects.

To float the P3HT thin film on the water surface, deionized (DI) water was used to dissolve the underlying PEDOT:PSS layer on which the P3HT was deposited, releasing the film from the substrate. During tensile testing, load and strain data are measured and the elastic modulus and elongation at break can be obtained from the stress–strain curves.[22]

This technique has enabled characterization of the stress–strain behavior of OPV thin films, including P3HT and other polymer and BHJ active layers. Properties such as the regioregularity (RR) of conjugated polymers strongly influence their mechanical behavior.[22] For example, the tensile modulus of P3HT was reduced from 287 to 13 MPa with decreasing RR from 98% to 64% and a significant increase in the elongation at break from 0.6% to 5.3%. These effects were attributed to the degree of polymer crystallinity, strongly influenced by the regioregularity of P3HT.[22] Highly crystalline 98% RR-P3HT films were much stiffer and more brittle than less crystalline films with lower RR-P3HT.

This method was also used to elucidate the mechanical properties of all-polymer donor–acceptor layers and polymer-fullerene BHJ layers used in organic solar cells.[23] The tensile modulus of a poly[[*N*,*N*′-bis(2-hexyldecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-5,5′-thiophene] (P(NDI2HD-T))-based all-polymer active layer was measured to be only 0.43 GPa, while the modulus of a PCBM-based BHJ layer utilizing the same donor polymer was 4× larger at 1.76 GPa. Moreover, the all-polymer active layer showed a significantly improved elongation (stretchability) of 7.16% compared to that of BHJ films, which was measured as ~0.12%. Similarly, ductile crack growth of the all-polymer active layer at ~7% elongation highlights the difference in ductility of the all-polymer active layer in comparison to the brittle BHJ films, which exhibited fracture at very low tensile strain. The superior mechanical properties of all-polymer active layers reveal the mechanical fragility of PCBM-polymer blends, highlighting the potential benefits of all-polymer systems for future mechanically robust devices.

Influence of operating conditions

Mechanical reliability and resulting operational lifetimes of organic electronic devices are influenced by the complex synergy of "stressing" parameters, such as cyclic mechanical flexing and stretching, operating temperatures, thermal cycling, moisture ingress, and damaging solar radiation.[12,24,25] These variables accelerate damage processes and must be included in a comprehensive analysis of thermomechanical reliability.

The synergistic effects of multiple stressing parameters provide particular challenges for organic materials, which are often more sensitive compared to more stable inorganic engineering materials. These differences highlight an emerging area of research that will require significant efforts to characterize fundamental damage processes, develop quantitative predictive models, and improve accelerated testing protocols to enable reliable flexible organic devices. Here, we review recent studies that provide some indication of this important area of device reliability.

Mechanical strain and thermal cycling

The action of alternating (or cyclic) mechanical strains and thermal cycling can result in the rearrangement of polymer networks and several forms of damage, such as strain localization, crazing, cohesive cracking, and interface separation. Damage accumulates and progresses on a cycle-by-cycle basis akin to well-known mechanical fatigue in structural materials.

In polymers, cyclic straining can also dissipate heat that produces rearrangements in the molecular structure and marked changes in mechanical properties, including chain scission and reduction of the load-bearing capacity.[24] Damage often develops faster (in less time) compared to monotonic loads or constant temperatures and is particularly relevant when assessing the mechanical integrity of flexible devices.

Applying the mechanical testing metrologies already described can provide valuable insights into the influence of alternating mechanical or thermal cycling, but improved testing techniques and analysis are urgently required. The influence of 10s to 1000s of cycles are often currently reported, however, the effects of ~10^5 or more cycles are generally required for engineering reliable devices.

The effects of alternating loading on the structure and ductility of thin semiconducting poly(3-heptylthiophene) (P3HpT) films can be revealed by observing damage (in the form of cracks) using optical microscopy (**Figure 2**a).[24] Films that had not undergone cyclic straining exhibited pinhole fracture at ~90% strain, just below the strain at which the PDMS substrate failed. Conversely, films that had been cyclically strained for 10,000 cycles demonstrated brittle failure, and as the cyclic strain amplitude was increased, so did the brittleness of the resulting films.

Surprisingly, this damage mechanism was not observed in thermally cycled OPVs, and mechanical stability was increased without significant effect on the device performance. Thermal cycling of P3HT:PCBM devices from –40°C to 85°C showed increasing G_c values through the first 200 thermal cycles, similar to the influence of annealing after device fabrication.[12] A kinetic model was developed to predict the increase in G_c as a result of thermal cycling based on integrating the isothermal annealing data over the temperature profile of a thermal cycle (Figure 2b). This allowed for an equivalence between annealing and thermal cycling, where an effective annealing time was determined during thermal cycling. The model successfully predicted the effects of thermal cycling on G_c for various cycle numbers and could be generalized to other temperature ranges. Although no evidence of a cycle-by-cycle damage accumulation mechanism was observed, there is likely to be a more pronounced effect over the course of thousands of cycles, which would be more representative of the operational lifetime of a device.

Environmental species

Moisture and other environmental species such as oxygen and radicals are ubiquitously present in the operating environments of stretchable and flexible devices.[26] Here, we focus on water, a protic solvent and a nucleophile that acts to solvate ionic species and hydrolyze chemical bonds, including carboxylic acid esters, silicates, and imines. The synergistic effects

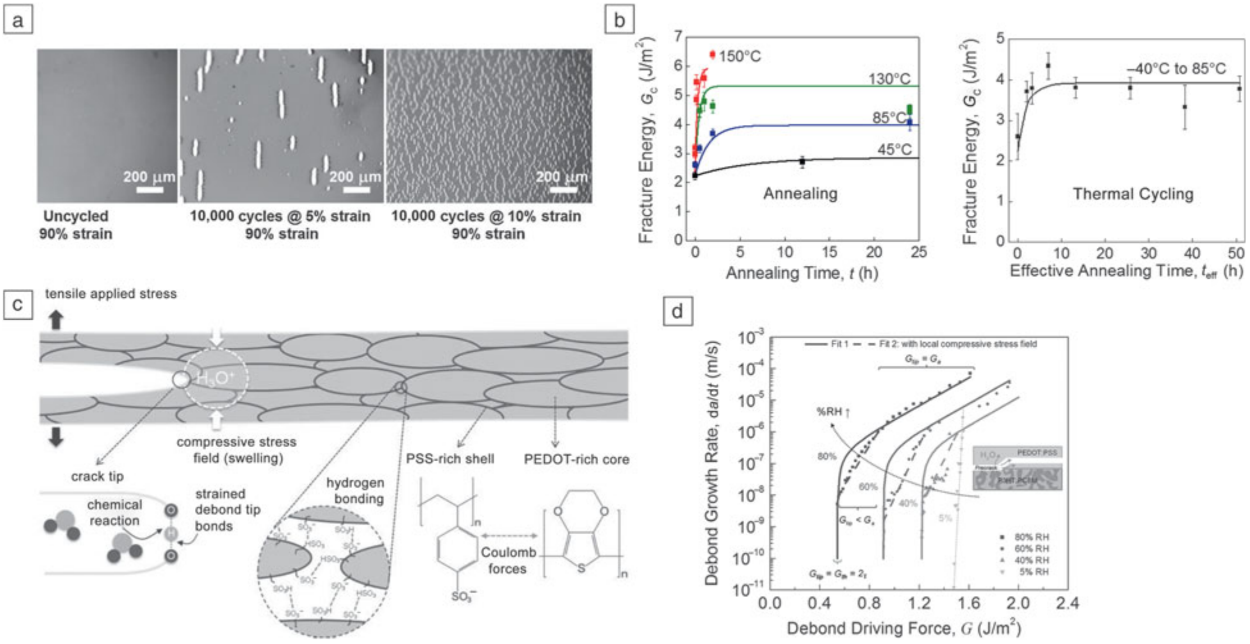

Figure 2. Effects of environmental stressors on organic electronic device materials. (a) Micrographs of cracking in poly(3-heptylthiophene) (P3HpT) films under different strain cycling conditions at 90% strain (highest strain before failure of the substrates) showing the synergistic effects of strain and cycling on crack density in films. Reproduced with permission from Reference 24. © 2016 Elsevier. (b) Measured G_c as a function of annealing time modeled at different temperatures. The isothermal curves are integrated over the temperature profile of a thermal cycle and used to accurately predict effects of thermal cycling on G_c.[12] (c) Illustration of a poly(3,4-ethylenedioxythiophene) poly(styrene sulfonate) (PEDOT:PSS) layer consisting of grains with a PEDOT-rich core and PSS-rich shell, showing the decohesion mechanism enabled by a stress-dependent chemical reaction between the water molecules and strained hydrogen bonds at the debond tip.[11] (d) Debond growth rate curves at a constant temperature and varying moisture content (RH). The applied driving force at the debond tip, G_{tip}; the applied debond driving force, G_a; the threshold driving force, G_{th}; and the intrinsic resistance to bond rupture in the reactive environment, 2γ.[11]

of water and mechanical stress can result in a time-dependent cracking process in which interfaces debond or layers decohere at values of $G < G_c$. The mechanical stress in such kinetic decohesion processes results in strained atomic bonds or molecular interactions at the crack tip. This amplifies the solvating or hydrolyzing effects of the water molecules, highlighting the synergistic effects of these two stressing parameters in device structures.[27,28]

Decohesion kinetics are studied by measuring the decohesion rate, $\mathrm{d}a/\mathrm{d}t$ (m/s), in terms of the applied driving force, G, to produce a $\mathrm{d}a/\mathrm{d}t$ versus G curve, where a is the length of the advancing crack. The threshold value, G_{TH}, represents the lowest decohesion driving force at which the process occurs and is a particularly important indicator of material reliability in the presence of a given environmental species.[2]

As an example, moisture plays a significant role in increasing the decohesion rate of the BHJ and charge-transport layers such as PEDOT:PSS.[11] Since PEDOT:PSS is water soluble and highly hygroscopic, the hydrogen bonds holding the individual grains together are susceptible to moisture-assisted decohesion (Figure 2c). When decohesion rates are measured in humid environments, increasing the humidity markedly increases the decohesion rate, or alternatively considered, shifts the entire $\mathrm{d}a/\mathrm{d}t$ versus G curves to lower G values with correspondingly lower values of G_{th} (Figure 2d). The insidious nature of this time-dependent process is evident by noting that decohesion occurs at G values much lower than G_c for PEDOT:PSS. Similar degradation mechanisms have been reported for many polymer and glassy materials and should certainly be anticipated for other organic electronic polymer molecular complexes.

UV exposure

Organic materials are particularly susceptible to photochemical degradation when exposed to UV light. For example, the solar spectrum induces degradation in the form of discoloration along with embrittlement through changes in mechanical properties. However, the underlying degradation mechanisms and their effect on long-term reliability are not well known and provide particular challenges for the reliability of organic electronic devices.

To demonstrate the complex behavior, we present the results of a recent study of both indoor and outdoor UV exposure on the adhesion and cohesion of a highly transparent silicone adhesive to an antireflective Al_2O_3 layer.[29] Surprisingly, during the initial periods of photodegradation under simulated indoor UV exposure, the silicone was found to fail adhesively at the silicone/Al_2O_3 interface and the adhesion energy was found to systematically increase by two orders of magnitude from 6 to >100 J/m^2 (**Figure 3**). With further exposure, however, the failure became cohesive in the silicone with a gradual decrease in G_c values.

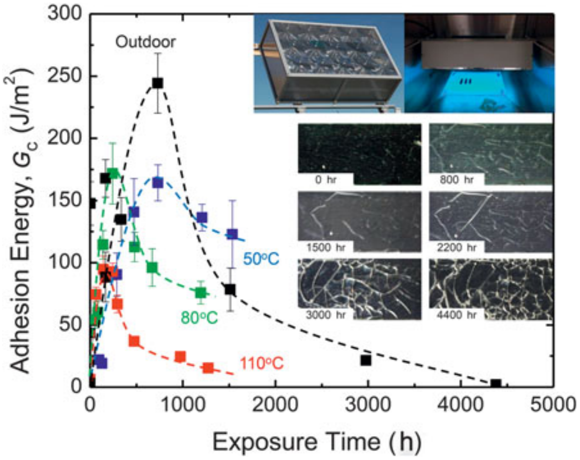

Figure 3. The synergistic influence of concentrated outdoor sunlight exposure or laboratory UV exposure with temperature on the adhesion of a highly transparent silicone adhesive layer to an antireflective Al_2O_3 layer. Initially, the layered structure failed adhesively. With increasing exposure, adhesion increased until failure occurred cohesively; at which point UV exposure resulted in further embrittlement of the silicone adhesive. Insets (moving clockwise from top left show) the outdoor concentrator optics allowing for exposure with 1100× solar concentration onto a 1 cm^2 target (black curve), UV exposure of silicone specimens under investigation in an indoor environmental chamber at 50°C, 80°C, or 110°C at 10% relative humidity (blue, green, and red curves, respectively), and specimens aged under the outdoor concentrator showing formation and growth of cracks through 4400 h of concentrated solar irradiation, similar to those observed for specimens aged in laboratory conditions.[29]

The underlying degradation process was shown to be associated with a photochemical oxidization reaction in which carbon side groups in the silicone molecular structure are cleaved, which then allows a cross-linking reaction to produce additional silicon to oxygen bonds. Both the increase in adhesion with initial exposure followed by the decrease in cohesion could be explained in terms of the increased cross-link density of the silicone. A mechanics model incorporating the photochemical cross-linking reaction was developed to explain the trends.[29] Exposure to outdoor concentrated solar flux produced exactly the same behavior (Figure 3), and models from the short-term indoor exposures could be used to rationalize the outdoor exposure results, providing confidence in the models and suggesting strategies that could be used for organic electronic device reliability predictions.

Strategies for improving mechanical reliability

We discuss here an incomplete list of strategies that can be employed to increase thermomechanical reliability of organic electronic devices by drawing from several examples from our studies. The strategies generally involve manipulating materials chemistry, molecular structure, and interface structure to improve salient mechanical properties.

We note that improvements in mechanical properties must be undertaken with careful consideration of device electrical and optoelectronic properties, since these could have deleterious effects on device performance.[4,10] Our recent studies on the mechanical integrity of organic and perovskite solar cells show stark trends where G_c values appear to scale inversely with power-conversion efficiency.[13] This points to the development of materials and devices that were optimized only for efficiency with no consideration for mechanical reliability. Future materials and device development must be undertaken where both device performance and thermomechanical reliability are considered.

Molecular weight

The molecular weight of semiconducting polymers has been correlated to the mobility of charge carriers in field-effect transistors, their surface morphology, and gelation rates in solution.[30–33] Additionally, the MW of P3HT can significantly influence the cohesive fracture energy of OPV BHJ layers.[4,34] In general, increasing the MW increases intermolecular bonding and chain entanglement, allowing for a greater degree of plastic deformation before cohesive failure (**Figure 4**a–b). G_c increases as a result because chain entanglement leads to increased friction during chain pullout,[35] and more interchain π-π stacking increases the number of van der Waals bonds needed to be broken for chain disentanglement. This effect is shown in Figure 4a, where atomic force microscope images of the fractured surface show increased roughness due to increased plasticity at the crack tip when higher MW P3HT is used.

Plastic deformation also explains the increase in G_c observed with increasing thickness in OPV layers made with ≥53 kDa P3HT. With increased BHJ layer thickness, the plastic zone surrounding the BHJ crack tip can extend out to a larger volume before being constrained by the stiff top and bottom substrates, thus dissipating more energy. This presents significant opportunities that may enable large-scale manufacturing, as studies have shown that device technologies with relatively low G_c values (<5 J/m^2) become difficult to produce, with mechanical failures decreasing the manufacturing yield.[1,2]

Molecular cross-linking

Increasing the molecular interactions of the generally weakly interacting molecular networks of organic electronic materials with covalent cross-links or even van der Waals bonds provides the opportunity to increase mechanical properties, including the elastic stiffness, strength, and cohesion. For solution-processed materials, cross-linking also increases solvent resistance, enabling new device architectures with the ability to use more solvents to deposit subsequent device layers.

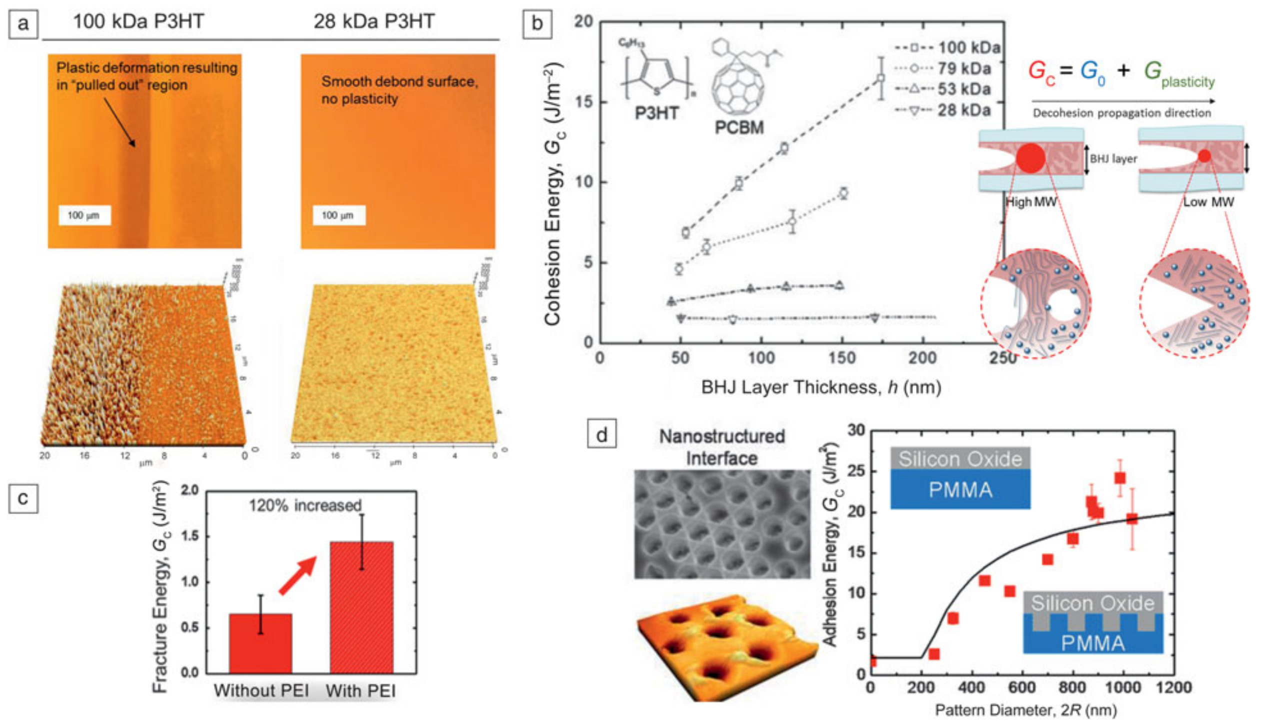

Figure 4. Strategies to improve the fracture energy G_c of organic electronic materials. (a) Atomic force microscope images of fractured poly(3-hexylthiophene) [6,6]-phenyl-C$_{61}$-butyric acid methyl ester (P3HT:PCBM) surfaces showing an increase in roughness with increasing molecular weight. (b) Measured G_c of P3HT:PCBM for various molecular weights and bulk heterojunction (BHJ) layer thicknesses, showing a strong dependence of cohesion on both of these variables. Inset schematic shows the larger plastic zone at the crack tip generated for the higher-molecular-weight (MW) BHJ layer. G_c is the sum of the intrinsic energy required to debond the interface, G_0, and the energy contributed to the plasticity, $G_{plasticity}$.[4] (c) Fracture energies measured at the interface between perovskite and spiro-OMeTAD layers with and without polyethyleneimine (PEI) specimens.[37] (d) Adhesion promotion of an oxide–polymer interface by nanopatterning of SiO$_2$ on poly(methyl methacrylate) (PMMA), showing the effect of varying feature diameter (2R) on adhesion energy, which increases G_c due to a larger fraction of pillars pulled out.[38]

An example is provided by 1-(*p*-phenoxy-*p*-methylvinylbenzene)-indolino[2,3][60]fullerene ($MPMIC_{60}$) (**Figure 5**), which was developed as a replacement for fragile molecular fullerene materials such as C_{60} and PCBM, some of the weakest organic electronic materials we have ever characterized (Figure 1).[14] $MPMIC_{60}$ features a flexible aromatic substituent intended to increase van der Waals bonding between molecules in the solid state (Figure 5a). In addition, the styrene portion of this substituent imbues $MPMIC_{60}$ with cross-linking chemical reactivity. Thermal activation results in the transformation of $MPMIC_{60}$ into a cross-linked film, resistant even to submersion in 1,2-dichlorobenzene (Figure 5b). G_c of $MPMIC_{60}$ was increased tenfold in comparison to PCBM and fourteenfold over C_{60} (Figure 5c). Perovskite solar cells constructed in *n–i–p* architectures using $MPMIC_{60}$ also exhibited improved photovoltaic performance compared to those made with PCBM, which was etched by solvents used in the deposition of subsequent layers. Furthermore, mechanical failure was mitigated in the fullerene layer of perovskite cells using $MPMIC_{60}$, which also exhibited increased short-circuit current (J_{SC}) and open-circuit voltage (V_{OC}) in comparison to C_{60} control devices (Figure 5d).[14]

Similarly, recent work developing a covalent cross-linking strategy for poly(triarylamine) (PTAA), which usually shows G_c values below ~2.5 J/m^2 and adhesion energy values to perovskite layers as low as ~0.3 J/m^2, enabled the formation of solvent-resistant hole-transporting composites exhibiting G_c ~ 25 J/m^2. Additionally, the cross-linker was found to promote adhesion to the perovskite layer and the resulting solvent-resistance-enabled fabrication of inverted *p–i–n* solar cells with markedly increased efficiency, above 17%. The cross-linked PTAA forms a more robust film that enhances stability during device processing, becoming a sputter buffer layer with resilience to harsh plasma and oxidizing conditions that cause standard PTAA-based devices to completely degrade.

Interfacial intermixing and chemistry

Interfaces in organic electronic devices are often the source of mechanical weakness, and strategies to increase interfacial adhesion through changes in interfacial chemistry are important. Many adhesion-promoting chemistries exist for polymer materials, but few can be employed without disrupting device performance through unintended changes to electronic band alignment and charge transport across the interface. Increased adhesion must also be accomplished in combination with increased cohesion to the generally weak organic electronic adjacent layers, and special challenges exist when increasing adhesion to inorganic layers such as perovskites.

Two examples can be given where significant increases in adhesion have been achieved by manipulating interfacial chemistry for polymer/polymer and polymer/inorganic interfaces. Hydrophilic PEDOT:PSS and hydrophobic BHJ layers have a weak polymer/polymer interface. Annealing at elevated temperatures allowed for the formation of a molecularly intermixed zone between P3HT:PCBM and PEDOT:PSS, the thickness of which is dependent on the annealing conditions.[36] The zone initially forms as mobile P3HT chains diffuse into the PEDOT:PSS during annealing and reorient. The composition of the layer changes as interdiffusion occurs, which initially contains PCBM for low temperature or short annealing times, and then PCBM migrates out toward the bottom of the BHJ with higher temperature and duration. G_c increases with annealing time and temperature as the intermixed zone expands (Figure 2b), which increases long-range chain–chain interactions, polymer entanglements, and electrostatic bonds.[35,36] These results suggest thermal annealing after the fabrication of devices could be used to improve adhesive properties and long-term stability.

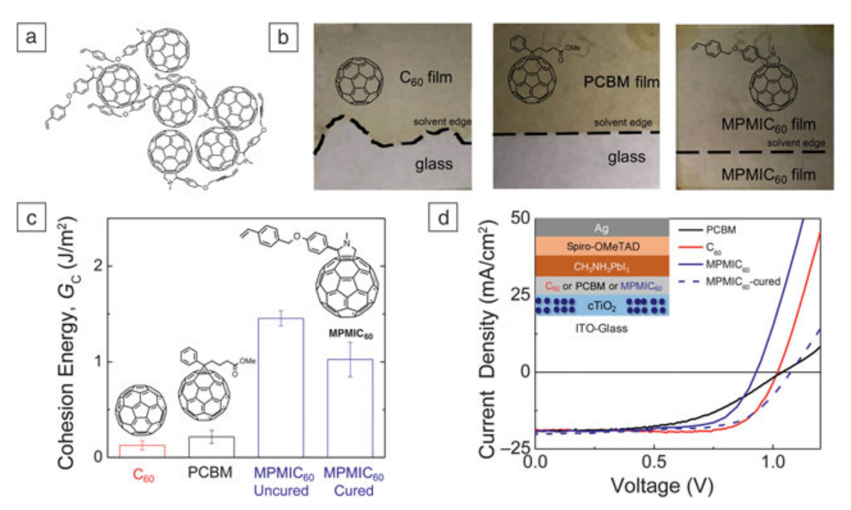

Figure 5. Improvements via cross-linking. (a) The flexible substituent of 1-(*p*-phenoxy-(*p*-methylvinylbenzene)-indolino[2,3][60]fullerene ($MPMIC_{60}$) is designed to increase van der Waals interactions in the solid state. (b) Cured films of $MPMIC_{60}$, [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM), and C_{60} fullerenes after dipping in 1,2-dichlorobenzene. The reactive styrene units of $MPMIC_{60}$ enable transformation of $MPMIC_{60}$ into a film resistant to dissolution. (c) $MPMIC_{60}$ shows marked improvements in cohesion energy over C_{60} and PCBM fullerene in both cured and uncured states. (d) Perovskite solar cells utilizing $MPMIC_{60}$ exhibited increased open-circuit voltage (V_{OC}) and short-circuit current (J_{SC}) over C_{60} controls.[14] Note: spiro-OMeTAD, spirobifluorene; ITO, indium tin oxide.

Another example involves the weak polymer/inorganic interface formed between spiro-OMeTAD and $CH_3NH_3PbI_3$ layers in perovskite solar cells. The application of polyethyleneimine (PEI) at the interface was shown to increase adhesion by 120% from 0.6 ± 0.2 J/m^2 to 1.4 ± 0.3 J/m^2 by forming chemical bonding across the interface (Figure 4c).[37] Nuclear magnetic resonance (NMR) analysis and contact-angle measurements revealed that PEI increased intermolecular interactions such as $N–H_{PEI}\cdots O_{spiro\text{-}OMeTAD}$ and further improved wettability of the spiro-OMeTAD precursor solution to the perovskite film. Additionally, PEI reduced moisture ingress into the perovskite layer under high-humidity conditions. PEI therefore represents an effective interfacial compatibilizer with amine groups, interacting with both perovskite and spiro-OMeTAD layers to increase adhesion.

Nanopatterned interfaces

Modifying the interfacial structure, including increasing interfacial roughness or creating interfacial features, has long been recognized as a strategy to increase adhesion. A recent study used optically transparent organic and oxide layers as barrier layers in flexible organic electronic devices. Interfacial nanostructures in the form of ordered SiO_2 pillars with diameters ($2R$) varying from 0 nm (planar interface) to ~1000 nm at selected feature depths (h) from 0 nm to 1100 nm were fabricated at an interface between poly(methyl methacrylate) (PMMA) and SiO_2.[38] The adhesion energy was demonstrated to be a strong function of the feature size and aspect ratio and could be used to increase the adhesion by an order of magnitude from ~2 J/m^2 (planar interface) to ~24 J/m^2 for the nanostructured interface (Figure 4d). Furthermore, UV aging studies demonstrated that the patterned interface was more resistant to photodegradation and maintained a higher adhesion than its planar counterpart for all durations of UVA and UVB exposure.

Concluding remarks

Thermomechanical reliability, including the synergistic effects of "stressing" parameters involving not only mechanical stresses and strains imposed on flexible and stretchable organic electronic devices but also environmental parameters like moisture and UV exposure, are important considerations for reliable technologies. We have reviewed mechanical testing techniques for elucidating salient thermomechanical properties and provided an indication of the generally mechanically fragile nature of many of the relevant organic electronic materials. Several important lessons for understanding factors that contribute to mechanical failure were provided, and strategies to enhance thermomechanical properties were discussed. For flexible and stretchable organic devices to be a technological success, improved mechanical properties and thermomechanical reliability analysis cannot be an afterthought to device operating performance, but must be addressed in the development of robust and efficient devices.

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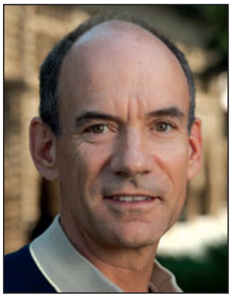

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The general chair is Debdeep Jena of Cornell University, technical program chair is Aaron Franklin of Duke University, and technical program vice chair is Deji Akinwande of The University of Texas at Austin.

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