

## Research Highlight: Electronics That Can Self-Repair

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**Background:** Imagine how wonderful it would be if your smart phone screen could fix itself if you dropped it! While shattered glass and smartphones are well beyond the context of this article, the general concept of the research is indeed self-healing electronics, which are devices that can repair themselves if scratched, cut, or punctured. Research on this cutting-edge technology was described in a recent *Science* publication ([DOI: 10.1126/science.adh0619](https://doi.org/10.1126/science.adh0619)) and featured on the NSF Foundation News Discovery Files Podcast (<https://www.youtube.com/watch?v=r7VQugRhFaU>), which brought it to the attention of the nano@stanford newsletter staff. Our team was intrigued to learn more, so we interviewed one of the paper's authors, Dr. Samuel Root.



*Dr. Samuel Root (left) and Dr. Lukas Michalek (right) at a recent marathon in San Francisco*

Root grew up in Long Island, NY and during high school he landed a job in flexographic printing - a way to rapidly print on a variety of materials, like plastic and paper. This work experience motivated him to pursue a B.S. in chemical engineering at the University of Rochester. He loved his college organic chemistry classes and was enthralled by the complex geometry of organic molecules, in particular polymers. Polymers are enormous molecules made up of smaller, customized molecular units which are attached to each other through chemical bonds to form flexible chains and networks with unique and useful material properties. As an analogy, a polymer would be like a completed LEGO® set made up of interconnected LEGO® blocks. One important nuance is that polymers are not rigid like LEGOs®, but are flexible assemblies of molecular building blocks. Some examples of well-known polymers include DNA, styrofoam, and rubber. Sam's interest in polymers, coupled with his background in flexographic printing, led him to take on an undergraduate research project in soft lithography. After graduating from Rochester, Root pursued a Ph.D. in chemical engineering at the University of California, San Diego, being lured by the warm weather and beautiful beaches of Southern California, as well as the opportunity to further explore his love for polymers. For the next four years, Root researched the mechanical properties of semiconducting polymers under the tutelage of Professor Darren Lipomi. After UCSD, Sam's academic journey brought him back to the northeast where he spent several years as a postdoctoral fellow at Harvard University in Professor George Whitesides' lab. In 2021, Root returned to California and joined Stanford Professor Zhenan Bao's lab to apply his experience with polymer composites to self-healing electronics. Root likes to run and was delighted to find that the Bao group has its own running club, "The Running Baos", created by fellow Bao group member, Dr. Lukas Michalek! This extracurricular community building truly helped create an effective team, and sparked research collaborations between Root and Lukas, who are both coauthors on the self-healing electronics *Science* paper. This nano@stanford newsletter article provides a high-level summary of their research, written for our diverse audience who have a wide range of technical backgrounds. If you want to learn more, you can read all the details in their *Science* paper: ([DOI: 10.1126/science.adh0619](https://doi.org/10.1126/science.adh0619)).

**Sam's Research:** One of the "magic ingredients" that makes self-healing electronics possible is a special type of material called a dynamic polymer. Dynamic polymers have a unique kind of chemical bond, called a dynamic bond, that can be reversibly broken and reassembled under specific conditions, such as exposure to high temperatures or ultraviolet light. Along with these dynamic polymers, the other important ingredients for self-healing electronics are nano-micro-scale conductive and insulative additives which are incorporated into the polymers to impart desired electrical, magnetic, or mechanical properties - kind of like adding

raisins, nuts, and chocolate chips into an otherwise bland cookie. When these extra “goodies” are added to a polymer, the new material is called a polymer composite.

Complex electronic devices may require stacks of many thin ( $<100\mu\text{m}$ ), distinct layers of these polymer composite materials, with each layer having a specific chemistry and electrical functionality. The challenge with developing multilayer devices that can self-heal has been that the layers frequently don’t line up correctly during self-healing, and this misalignment causes the devices to not work as well after self-repair. To address this obstacle, Sam, Lukas, Dr. Chris Cooper, and other researchers at Stanford designed polymer composites that can both self-heal and realign themselves into discrete layers when damaged. How is this possible? It’s not sorcery or witchcraft, but creative and intentional materials engineering. As a proof of concept, the team started with two classes of “immiscible” polymers: polydimethylsiloxane (**PDMS**, used commercially in contact lenses and shampoos) and polypropylene glycol (**PPG**, used to make paintballs) (Figure 1). Immiscible just means that these two polymers partition into separate zones, or “phases”, when they are mixed, much like how water and oil don’t mix well. This predisposition to separate would minimize intermixing between adjacent PDMS and PPG layers and facilitate multilayer realignment. The researchers additionally chemically modified the PDMS and PPG to incorporate those special dynamic bonds, described previously, to enable strong interfacial adhesion between layers and self-healing.

The team performed several types of measurements at the Stanford Nano Shared Facilities (e.g., rheometry, differential scanning calorimetry (DSC) and atomic force microscopy (**AFM**)) to thoroughly understand the self-healing behavior and other properties of modified PDMS and PPG. In one such experiment, the intermixing between two adjoining layers of modified PDMS and PPG were studied by imaging the interfacial stiffness with an advanced type of AFM measurement called Peak Force Quantitative Nanomechanical Mapping (**PFQNM**). Atomic force microscopes are instruments that monitor the movement of a nanometer-sized probe to sense various properties on a sample surface. This sensing can be performed on an array of tens- to hundreds- of thousands of data points to produce a map of that property across a surface at the nanoscale. For PFQNM, the force between the AFM probe and the surface is measured. By fitting this force data to theoretical models, it’s possible to generate maps of specific mechanical properties, such as Young’s modulus. On a macroscope scale, a modulus measurement would be kind of like if you pressed your finger on a brick compared to jello. The brick would “feel” hard, while the jello would be soft and squishy.

The research team prepared three samples for PFQNM by pressing together sheets of modified PDMS and PPG at different temperatures. Figure 2b shows side-view PFQNM modulus images of this layered PDMS/PPG structure. In these images, the softer material (modified PDMS - or “PDMS-HB”) is shown on a false-color scale to be gray, modified PPG (or “PPG-HB”) is shown as pink, and the intermixed region has an intermediate stiffness value and is depicted in white. The images show a direct relationship between the width of the intermixed region and heat-pressing temperature. Next, these samples were annealed (e.g., further heat-treated at 70°C for 24 hours and slowly cooled). After annealing, all of the films had intermixed regions with similar widths which suggested that the widths could be controlled by the annealing conditions. Additional experiments (i.e., by X-ray photoelectron spectroscopy (XPS), not shown) and computer simulations, in collaboration with Stanford Professor Qin’s research group, demonstrated that the intermixed region was thinner when the polymers were more immiscible, which could be controlled by the polymer chemistry and temperature. The authors hypothesized that minimizing the amount of interfacial mixing would favor autonomous realignment of layers during healing. To test this theory, they prepared a sample consisting of alternating 3-15 $\mu$ m-thick layers of modified PDMS and PPG and then cut through this stack to create obvious damage and misaligned layers (Figure 3). They then heat-treated the damaged sample and saw sharp interfaces reform between the layers demonstrating successful self-healing and realignment.

Finally, Root and his co-authors showed that self-healing and layer realignment could be a reality for actual working devices including a pressure-sensitive capacitor, a magnetically assembled soft robot, and an underwater LED circuit. This device work was possible, in-part, because of *cross-departmental collaborations* among Stanford research groups. For example, Professor Renee Zhao’s group lent their expertise on magnetic particles and robotics. In the case of the pressure-sensitive capacitor, optically visible damage and misalignment was observed to self-heal upon heat treatment (Figure 4b). Most importantly, the self-healed capacitor was able to work as well as it had before being damaged (Figure 4c). The authors concluded that deliberate material engineering of polymers with immiscible backbones and dynamic bonds can enable self-healing and autonomous interfacial realignment for robust, next-generation, soft electronic devices.

**What’s Next?** Root is excited to begin his new faculty position in Macromolecular Science & Engineering at Case Western Reserve University in November 2024. Although he’s moving on from Stanford, Root sees great promise for self-healing, realigning electronics. From a commercialization and manufacturing perspective, the technology is quite scalable. The team purposely selected polymers that are synthesized using low-cost, commercially



available reagents and that have simple (single-step) polymerization reactions. Root forecasts that future research in the Bao group will explore other polymer systems with different chemistries and therefore different immiscibility. In particular, these new polymers may have useful attributes for sustainable manufacturing and waste-free processing. His long-term vision is to use the multilayer self-healing polymer systems for electronics that are intended to be damaged. For example, self-healing electronics would be invaluable as artificial skin for surgical simulations during medical training and surgical tool evaluations.

We asked Root if he had any advice to pass on to early-career graduate students. He says that it's rare for things to go as expected in research. You should try your ideas but be flexible and keep your mind open to other directions. It will be exciting to see what the future holds for self-healing, realigning electronics and for Dr. Samuel Root!

## References

C. B. Cooper, S. E. Root, L. Michalek, S. Wu, J. Lai, M. Khatib, S. Oyakhire, R. Zhao, J. Qin, Z. Bao., "Autonomous Alignment and Healing in Multilayer Soft Electronics Using Immiscible Dynamic Polymers." *Science* 380:6648, (June 2, 2023): 935-941. DOI: 10.1126/science.adh0619

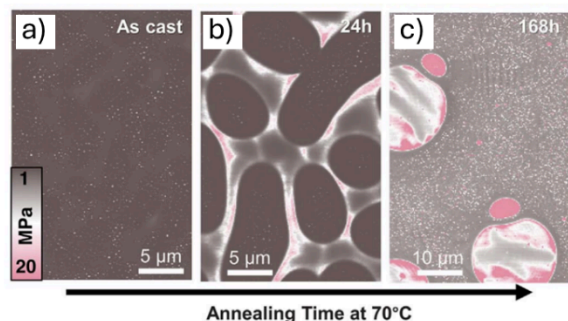


Figure 1. PFQNM modulus images, on a false-color scale, of a thin film comprised of mixture of two polymers (i.e., PDMS-HB and PPG-HB): (a) immediately after depositing the mixture onto a flat surface, (b) after annealing at 70°C for 24 hours, and (c) after annealing at 70°C for 168 hours. PDMS-HB has a lower modulus and is shown as dark gray. Zones containing the higher modulus polymer, PPG-HB, are shown as pink. The images indicate that the two polymers separated into discrete zones and became immiscible upon heating.

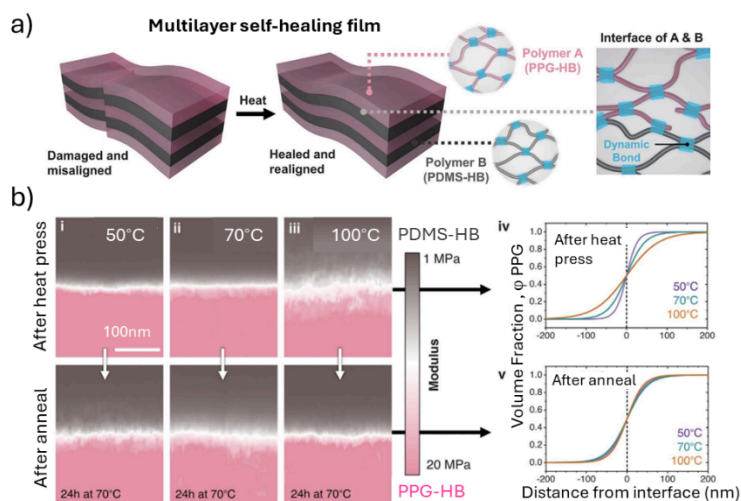


Figure 2. (a) Schematic showing surface-tension mediated realignment and healing of a fractured multilayer polymer system. (b) PFQNM characterization of across a modified PDMS-PPG interface. (i – iii) Modulus images at different heat press temperatures before (top) and after (bottom) annealing. The images are displayed in a false-color scale with pink being a high modulus, correlating with modified PPG and gray being a high low modulus and modified PDMS. (iv, v) Fitted interfacial profiles obtained from the PFQNM modulus images.

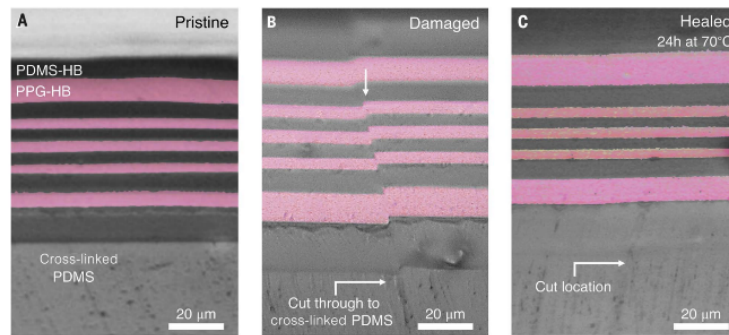


Figure 3. Optical images in side-view of (a) the original multilayer polymer structure, (b) the same sample after being damaged and misaligned, (c) the healed and realigned structure after heating. The modified PPG was stained to appear pink, for optical contrast to guide the eye.

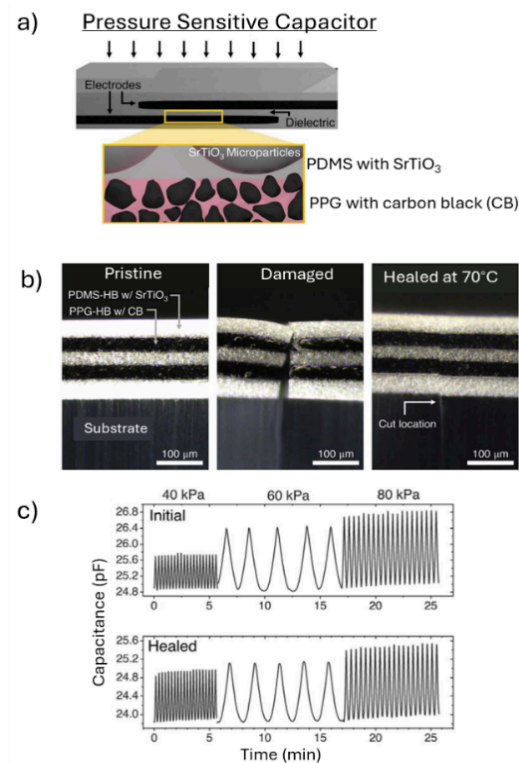


Figure 4. Self-healing and autonomous realignment of functional layers in a pressure sensitive capacitor. (a) Schematic of the device. (b) Optical images, in side-view, of the device before damage, after damage, and after healing. (c) Initial and healed pressure-sensing performance as a time series. Capacitance was monitored while cyclically applying pressures from 0-80 kPa.