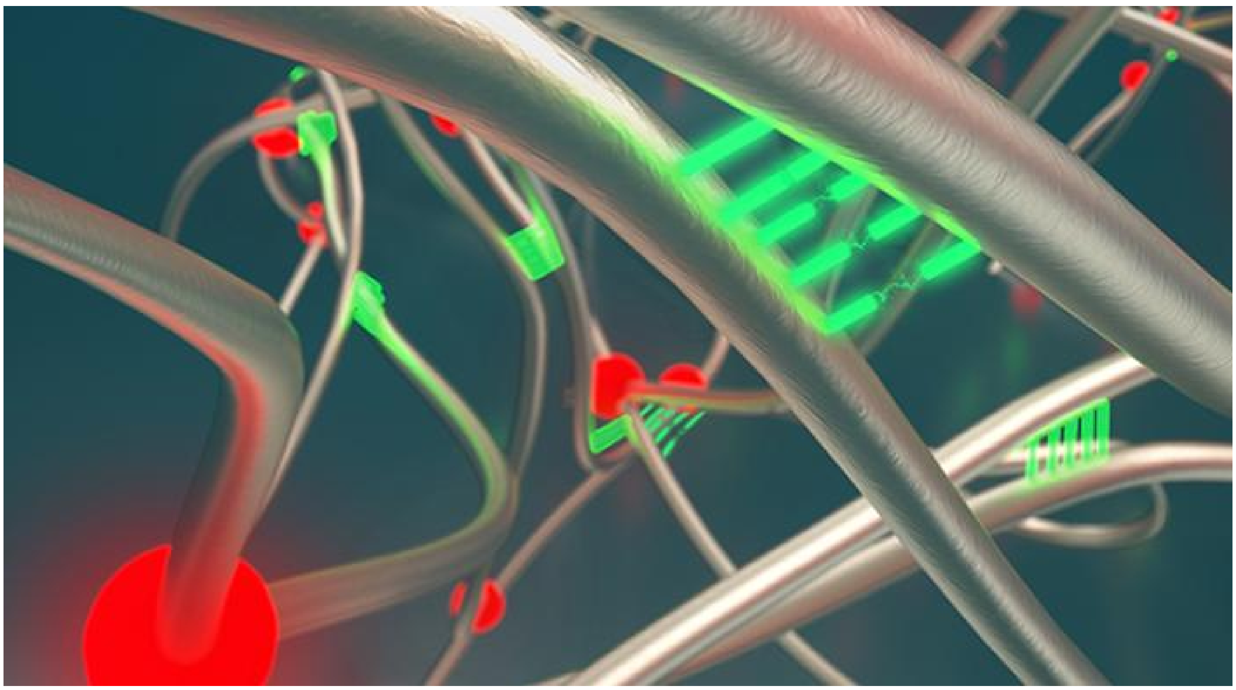
Researchers develop tough, self-healing rubber

August 15 2017, by Leah Burrows



Self-healing rubber links permanent covalent bonds (red) with reversible hydrogen bonds (green). Credit: Peter and Ryan Allen/Harvard SEAS

Imagine a tire that could heal after being punctured or a rubber band that never snapped.

Researchers from the Harvard John A. Paulson School of Engineering and Applied Sciences (SEAS) have developed a new type of rubber that is as tough as natural rubber but can also self-heal.

The research is published in *Advanced Materials*.

Self-healing materials aren't new—researchers at SEAS have developed self-healing hydrogels, which rely on water to incorporate reversible bonds that can promote healing. However, engineering self-healing properties in dry materials—such as rubber—has proven more challenging. That is because rubber is made of polymers often connected by permanent, covalent bonds. While these bonds are incredibly strong, they will never reconnect once broken.

In order to make a rubber self-healable, the team needed to make the bonds connecting the polymers reversible, so that the bonds could break and reform.

"Previous research used reversible hydrogen bonds to connect polymers to form a rubber but reversible bonds are intrinsically weaker than covalent bonds," said Li-Heng Cai, a postdoctoral fellow at SEAS and corresponding author of the paper. "This raised the question, can we make something tough but can still self-heal?"

Cai, along with Jinrong Wu, a visiting professor from Sichuan University, China, and senior author David A. Weitz, Mallinckrodt Professor of Physics and Applied Physics, developed a hybrid rubber with both covalent and reversible bonds.

The concept of mixing both covalent and reversible bonds to make a tough, self-healing rubber was proposed in theory by Cai but never shown experimentally because covalent and reversible bonds don't like to mix.

"These two types of bonds are intrinsically immiscible, like oil and water," said Cai.

So, the researchers developed a molecular rope to tie these two types of bonds together. This rope, called randomly branched polymers, allows two previously unmixable bonds to be mixed homogeneously on a molecular scale. In doing so, they were able to create a transparent, tough, self-healing rubber.

Typical rubber tends to crack at certain stress point when force is applied. When stretched, hybrid rubber develops so-called crazes throughout the material, a feature similar to cracks but connected by fibrous strands. These crazes redistribute the stress, so there is no localized point of stress that can cause catastrophic failure. When the stress is released, the material snaps back to its original form and the crazes heal.

Harvard's Office of Technology Development has filed a patent application for the technology and is actively seeking commercialization opportunities.

The self-healing ability is appealing for a wide variety of rubber products.

"Imagine that we could use this material as one of the components to make a rubber tire," said Wu. "If you have a cut through the tire, this tire wouldn't have to be replaced right away. Instead, it would self-heal while driving enough to give you leeway to avoid dramatic damage."

"There is still a lot more to do," said Weitz. "For materials science, it is not fully understood why this hybrid rubber exhibits crazes when stretched. For engineering, the applications of the hybrid rubber that take advantage of its exceptional combination of optical transparency, toughness, and self-healing ability remain to be explored. Moreover, the concept of using molecular design to mix covalent and reversible bonds to create a homogenous hybrid elastomer is quite general and should enable development of tough, self-healing polymers of practical usage."

More information: Jinrong Wu et al. Tough Self-Healing Elastomers by Molecular Enforced Integration of Covalent and Reversible Networks, *Advanced Materials* (2017). DOI: 10.1002/adma.201702616

Provided by Harvard University