Bond breaking

Making supramolecular polymers tougher

Researchers from the Adolphe Merkle Institute's Polymer Chemistry and Materials group have developed a new approach to toughen supramolecular polymers and have demonstrated the usefulness of such materials as adhesives that enable bonding and debonding on demand when heated or exposed to intense UV light.

Unlike conventional polymers, which consist of long, chain-like molecules with thousands of atoms, supramolecular polymers are composed of smaller molecules that are equipped with "sticky" binding motifs. These moieties bind to one another and assemble the building blocks into polymer-like structures. Because the interactions between the binding sites are reversible, supramolecular polymers can be readily disassembled into their building blocks by applying an external stimulus, such as heat, intense light, or a chemical. This transforms the originally solid material into a low-viscosity liquid that flows more easily than a conventional polymer. When the stimulus is removed, the supramolecular material re-assembles and the original properties are restored. The ability to disassemble supramolecular polymers offers many attractive opportunities: it facilitates processing and recycling such materials, renders them easily healable, and allows creating adhesives that can be (de)bonded on command. But the downside of these materials is that their mechanical properties are typically inferior to those of conventional polymers. This includes being too brittle or lacking sufficient stiffness.

Addressing this issue, AMI researchers have been investigating a previously little explored family of glass-forming supramolecular polymers. These materials consist of disordered networks that are formed by the association of building blocks that contain three or more supramolecular binding motifs. "The supramolecular glasses that our group recently developed were probably the stiffest supramolecular polymers known so far, but they were also very brittle and broke when experiencing the slightest forces," explains PhD student Diana Hohl. "We were therefore interested in finding ways to toughen them in order to create materials with more useful properties."

Hohl and her colleagues found that supramolecular glasses can be made less brittle by the formation of blends with a second component involving a rubbery phase. This approach enabled the researchers to adjust the material's properties by simply varying the ratio of the two supramolecular building blocks, and made it possible to tune both toughness and stiffness. The new materials could serve, for example, as reversible adhesives.

"A good adhesive needs to form a strong bond. For easy and efficient debonding (and bonding), low-melt viscosity is a beneficial characteristic," says Hohl. "Because the supramolecular polymers that we developed contain a large number of reversible bonds formed by the sticky binding motifs, they form liquids with a relatively low-viscosity when heated, but the original properties are retained when cooled. In the context of adhesion, this means that we can easily de-bond molecules by simply heating them above a certain temperature, while the adhesive bond is restored upon cooling back to room temperature."

According to Hohl, the new blends have improved properties when compared with other supramolecular adhesives previously investigated by the Polymer group. But she adds that there is plenty of room for improvement. "We observed that the blends slowly separate into the two components when melted, so they are not the best candidates for multiple bonding and debonding scenarios," she says, adding that "both thermal stability and adhesive strength leave room for further improvement."

The two-component approach should allow for the tailoring of the mechanical properties of supramolecular glasses over a considerable range. For the AMI researchers, this technique should also be applicable to other systems, giving rise to new functional materials with tunable property combinations.

Reference

Hohl, D.K., Ferahian, A.-C., Montero de Espinosa, L., Weder, C. Toughening of Glassy Supramolecular Polymer Networks, *ACS Macro Letters*, **2019**, 8 (11), 1484–1490.