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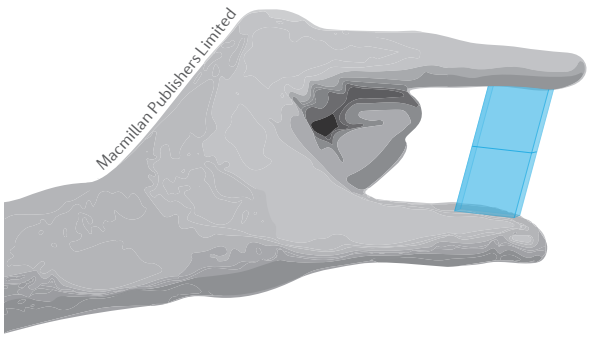
POLYMERS

Sticking together under pressure

> It remains a great challenge to design a polymer with both mechanical robustness and a healing ability at ambient temperatures

Polymers that are both mechanically robust and self-healable are desirable for use in numerous applications, yet these two properties are typically mutually exclusive. Now, writing in *Science*, Takuzo Aida and colleagues report a family of mechanically robust polymers that can self-heal by simply compressing the two fractured surfaces together without the need for melting upon heating, and without any loss of mechanical strength.

"Among the different approaches to engineering healable materials, the use of reversible weak non-covalent interactions is one of the simplest and most effective strategies," says Yu Yanagisawa, first author of the paper. In particular, the reorganization of dynamic hydrogen-bond interactions within low-molecular-weight polymers can be exploited to yield materials that can heal under mild conditions, but such materials are usually soft and thus have a limited range of applications. By contrast, the extent of chain entanglement within typical high-molecular-weight polymers imparts mechanical robustness but necessitates heating to high temperatures to repair the fractured polymer. "It remains a great challenge to design a polymer with both mechanical robustness and a healing ability at ambient temperatures," states Aida. $TUEG_3$ — the best-performing polymer identified by Aida and colleagues — is a relatively rare example of such a material.



$TUEG_3$ is a transparent, non-crystalline, low-molecular-weight polymer comprising thiourea units linked through triethylene glycol spacers. Thiourea is both a good hydrogen-bond acceptor and donor, leading to a high degree of hydrogen-bond cross-linking between the polymer chains of $TUEG_3$ and thus imparting the desired rigidity. Moreover, in a series of healing tests, the researchers showed that samples of $TUEG_3$ that are first fractured and then repaired by compressing the two fractured surfaces together recover their original mechanical strength, a process that takes less than 6 hours at 24 °C and less than 1 hour at 28–36 °C. Importantly, the fracture–healing cycle is repeatable without any appreciable decrease in the mechanical strength of the polymer.

"We conducted a systematic study of the chemical structures together with their dynamic mechanical properties and healable temperature windows, which are often missing from reports despite their importance," explains Yanagisawa. Using this approach, the researchers elucidated the mechanisms and structural elements that underpin the observed behaviour of $TUEG_3$ and established that both the thiourea unit and triethylene glycol spacer have a vital role. First, replacing the thiourea unit with urea — which forms more linear and ordered hydrogen-bond networks — leads to a semicrystalline and brittle material. Thus, the density and ordering of the hydrogen-bonded networks need to be carefully balanced. Second, despite having a low molecular weight, the diffusion dynamics of the polymer chains in $TUEG_3$ are very slow, indicating that the rapid healing is not driven by polymer-chain diffusion. Instead, the researchers propose that it is the dynamic exchange of the hydrogen-bonded thiourea pairs that enables $TUEG_3$ to heal on compression, with the triethylene glycol spacer lowering the activation energy for the slippage of the polymer chains by providing intermediary hydrogen-bond acceptor sites.

Overall, this work provides the blueprint for the design of highly robust, self-healable polymers that have diverse potential applications, ranging from lenses for vehicle taillights to frames for glasses. With regard to $TUEG_3$, "its self-healing is a property that distinguishes it from the typical mechanically robust polymer already on the market, but another big breakthrough to further enhance the mechanical robustness and weather resistance, for example, is required before it can be used in real-world applications," concludes Aida.

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ORIGINAL ARTICLE Yanagisawa, Y *et al.* Mechanically robust, readily repairable polymers via tailored noncovalent cross-linking. *Science* **359**, 72–76 (2018)