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Polymeric Materials

A Self-Healing Elastomer

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hydrogen bonds · materials science · mechanical properties · rubber · self-healing

For centuries, mankind has been fascinated by living nature's faculty to spontaneously repair damage. Perhaps the most striking example in the human body can be found in skin—minor cuts and bruises are healed completely, whereas more severe injuries lead to scars. In either case the operational capability of the system is largely restored. In other creatures, repair can be even more spectacular, for example the Cnidarian hydra can regenerate its whole organism from separated cells. In classical mythology the Hydra of Lerna was invented as a paragon of self-healing. Imparting self-healing properties to nonliving systems is enormously attractive: just imagine the reduction in costs and risks that self-healing crockery, paints, or aerospace materials would bring about!

If artificial self-healing materials remained a pipe dream for centuries, the hope that they might one day become a practical reality has been considerably fuelled over the last decade. In addition to self-healing composites, concrete, ceramics, and fabrics, self-healing polymers have recently enjoyed increasing attention. More than half of all publications on self-healing polymers are no more than five years old, and several review articles and a book on this topic have appeared recently.[1]

Polymeric materials exist in two fundamentally different varieties. In thermosets, covalent crosslinks form a permanent network, which prevents viscous flow in these materials. The equilibrium shape of objects made from thermosets is fixed and can only be changed by machining. Thermoplastics are materials without such permanent crosslinks; they can be given any shape by processing (molding, extrusion) at elevated temperatures. Nowadays, both thermosets and thermoplastics are used in a variety of high-performance applications for which self-healing properties are especially desirable when they perform functions in inaccessible places, or when the surface appearance of the material is paramount.

Self-healing in polymers requires restoration of mechanical properties by bonding across interfaces created by fracture, cracking, or cutting. Healing is especially challenging in thermosets, where the confinements imposed by crosslinks prevent polymer chains to bond surfaces together by the formation of entanglements across the interface. Two main approaches—"reversible-covalent" and "composite"—for self-healing in thermosets have emerged. In the first approach, also referred to as "self-mending", covalent bonds are reshuffled upon application of an external stimulus such as light or heat: cracks in the material will be bridged by newly formed bonds, for example, in a reversible Diels–Alder reaction described by the research group of Fred Wudl (Figure 1 a).[2] Obviously, there is considerable potential for reversible (but strong) noncovalent bonds to be used in such a scheme, and efforts to employ hydrogen bonds for this purpose[1a] are under investigation. In the second approach, pioneered by White, Sottos, and co-workers,[3] microcapsules containing unreacted monomer are embedded in a thermoset material. When a crack appears, the skin of the capsules ruptures; the monomer is released and cured by a catalyst dispersed in the matrix (Figure 1 b). Since no external stimulus is required to initiate healing, this kind of self-healing is referred to as "autonomous".

Self-healing in thermoplastic materials is intrinsically easier than in thermosets, because heating results in chain mobility, which may give rise to the formation of entanglements across interfaces. Thus, in contrast to thermosets, interfaces in thermoplastics can be welded together without an external material that acts as a glue. In some cases the heat required to create mobility can even be provided by the impact of the object that damages the material itself. This process is known as "ballistic impact self-repair".[4]

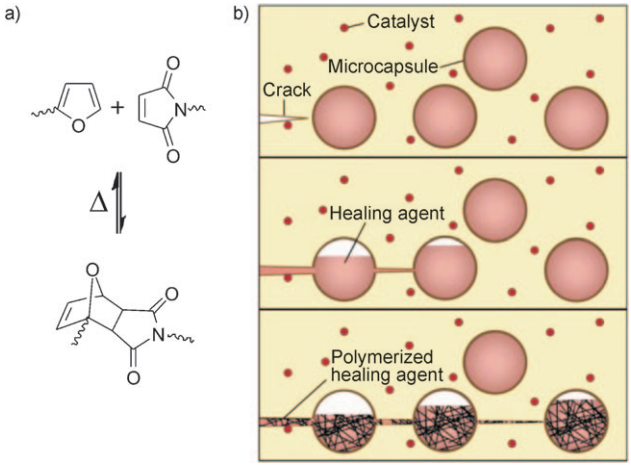

Figure 1. Examples of the two principal approaches in self-healing thermosets explored hitherto: a) reversible covalent bonds,[2] and b) microcapsules with reactive monomer embedded in a thermoset matrix.[3] Wavy lines represent covalently attached polymer chains.

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Thermoplastic elastomers form an economically important class of thermoplasts that show elastic (rubberlike) behavior and essentially no viscous flow at operating temperatures because the chains form physical crosslinks in crystalline or glassy regions with low mobility. Self-repair without healing agents or external stimuli requires high chain mobility and therefore seems to be in direct contradiction with the fixation needed to form a permanent network in thermoplastic elastomers. Yet this combination of elastic and self-healing properties is exactly what has been reported earlier this year.[5] Leibler and co-workers demonstrate the spontaneous and essentially complete restoration of the mechanical properties of a thermoplastic elastomer by simply bringing together fractured surfaces. The system is characterized by indefinitely repeatable healing that occurs with low cost and easy processability and thus potential industrial applicability, with thermoplastic behavior in the melt and presumably with low toxicity. This rare combination of properties constitutes a breakthrough in the world of self-healing materials and explains the considerable attention this publication has received in the scientific world,[6] popular science magazines,[7] and in the international press.

Leibler's system consists of just a few surprisingly simple components. Dimer and trimer fatty acids—produced from vegetable oils, a renewable source—are reacted with diethylene triamine and subsequently with urea (Figure 2). This reaction yields a transparent glassy material with a glass transition temperature of 28 °C. A supramolecular network is formed in this mixture of a large number of di- and trifuctional building blocks with various strongly hydrogen-bonding urea and amide molecules. Crystallization is prevented by the presence of a multitude of different species, which warrants rubbery properties at higher temperatures. The temperature-dependent strength of the hydrogen-bonding units results in a strong decrease of the viscosity of the material at high temperatures, thus the material can easily be melt-processed into any shape. The glass transition temperature was lowered by adding dodecane (11 % by weight) as a plasticizer, making the material a thermoplastic elastomer. Tensile tests showed elongations at break of more than 500 %, characteristic of a soft rubber.

Rheological measurements in shear mode gave insight into the nature of the rubbery behavior and revealed characteristic lifetimes of several weeks (3×10^6 s) for the network. This is necessary for the material to exhibit low creep: indeed, when the material was subjected to constant stresses for several hours causing initial strains of 144 % and 32 %, the material showed little and no creep, respectively. Moreover, creep proved to be almost entirely recoverable, which means that the specimen slowly regains its original shape. This important prerequisite for a useful rubbery material is satisfactorily met by Leibler's material. Although most traditional rubbers show essentially zero creep, the low but significant creep observed here is not a decisive argument: if appropriate operating conditions are found, the material is expected to perform to full satisfaction.

Certainly the most stunning property of this material is its self-healing behavior. If a sample is cut or ripped into two parts, the fragments can recover their original strength when the cut surfaces are merely brought into contact and pressed against each other. While adhesion is almost immediately sufficient for the pieces to sustain their own weight, the bonding increases gradually over time to reach the initial strength after only three hours.

How do Leibler and co-workers manage to avoid compromising self-healing with excessive creep? The key to understanding self-healing in this material was shown to lie in the dynamics and the density of strongly associating hydrogen-bonding groups. When the elastomer fails by rupture, these hydrogen bonds, rather than covalent bonds, are broken, which results in a high density of non-associated groups at the interface. The non-associated hydrogen bonds remain in their free state for a significant time, waiting to find a new partner when brought into contact with another freshly cut surface. Naturally, the free hydrogen-bonding units at the surface tend to seek new partners within the same piece if no second surface is available. Thus, when broken pieces were kept apart for 6 or 18 h and pressed against each other, the

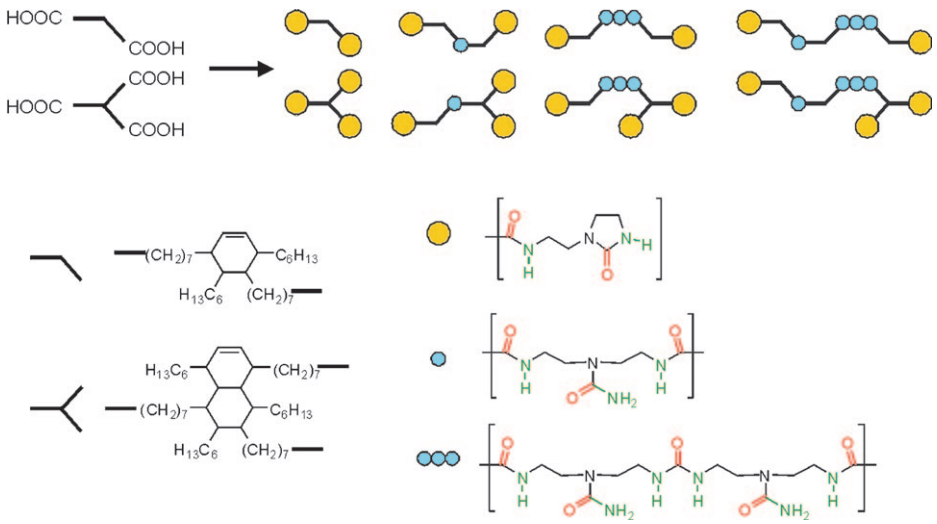

Figure 2. Schematic representation and molecular structures of the materials used in Leibler's self-healing rubber.

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mending process was considerably less efficient and required longer healing times. Relatively fast recombination of a high density of groups at the surface gives rise to a unique repair mechanism that does not rely on reptation of complete polymer chains to recover mechanical strength, but instead connects chains that are already part of the networks on each side of the interface. In that sense, the mechanism is conceptually related to the "reversible-covalent" approach described by Wudl.

Time-resolved FTIR spectroscopy was used as an elegant method to gain direct evidence of the breakage and reassociation of the hydrogen bonds. With this technique, vibrational bands of free and bound N–H bonds can be observed directly. An intact sample was heated to 125 °C for 10 minutes in order to break the hydrogen bonds and quench-cooled to room temperature. Subsequently, reassociation was followed over time, revealing characteristic lifetimes of about 10^4 s for the free N–H groups. The timescale, about 300 times shorter than the mechanical relaxation time of the rubber network, appears to be the key to the uncommon self-healing behavior of the material. However, one of the most intriguing questions that remain to be answered is the detailed architecture that produces the strongly disparate characteristic times for network relaxation and hydrogen-bond reassociation.

Leibler and co-workers emphasize that their general design leaves room for variation and optimization: by using other associating groups, the materials can potentially be tuned for specific tasks. Leibler is currently investigating the scope for industrial production and commercialization of these materials together with the company Arkema.

Leibler's work represents a fundamentally new approach to the construction of supramolecular polymers. An attractive feature of the material is the large-scale availability and low cost of all starting materials, and the easy processability of the polymer produced. The authors' choice not to strive to obtain a material with a single component, but to use a random mixture of compounds would seem complete anathema to many chemists. Yet this choice is the key to their success; less complex mixtures of strongly associating molecules would lead to crystallinity, and thus purportedly preclude any dynamic, self-healing properties.[8]

Leibler anticipates application of these materials in stockings, children's toys, and self-healing seals. Among synthetic chemists, who has never complained about the fact that a hermetic rubber seal is not airtight after repeated puncturing with a needle?

The modular nature of Leibler's concept has the potential to give rise to sundry variations. We thus anticipate that in the long term, useful, large-scale applications will emerge from this seminal contribution to the fields of polymer and supramolecular chemistry.

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