Reports from Other Journals

Nature: Self-Healing Polymers and Other Improved Materials

by Sabine Heinhorst and Gordon Cannon

For this column, we have chosen articles that explore ways to mimic and improve materials and processes found in nature. Some of the work has progressed toward industrial applications (e.g. using biocatalysts for selective organic syntheses), whereas other approaches (e.g. designing self-healing material) are still in their infancy but show remarkable promise for future success.

Nature, February 15, 2001

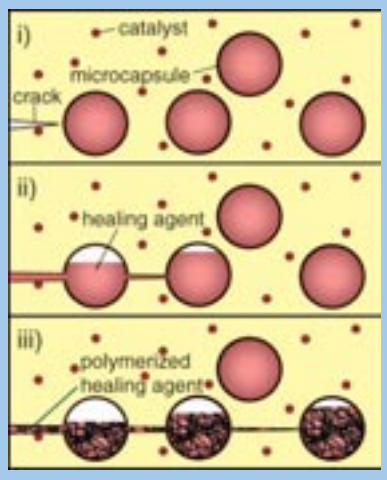
Self-healing, a complex process that is a hallmark of living tissues, has so far largely eluded incorporation in man-made materials. White and coworkers seem to have come closer to reaching that goal in their work (**2001**, *409*, February 15, 794–797; News and Views article by R. P. Wool, pp 773–774). The interdisciplinary team from the University of Illinois at Urbana-Champaign developed a polymer composite that has the ability to self-heal microcracks. Such microscopic lesions, which often remain undetected and can have potentially catastrophic consequences for the performance of the material, tend to form in polymer composite as a result of mechanical stress. The researchers included a living polymerization (ROMP) catalyst (ruthenium-based Grubbs' catalyst) and urea-formaldehyde microencapsulated dicyclopentadiene monomers in the composite. Mechanically induced microcracks propagate toward and rupture the capsules. The monomeric healing agent is released, fills the crack by capillary action, and polymerizes upon contact with the catalyst. The authors report that the repaired polymer material regained 75% of its original strength. Potential future applications of self-healing man-made materials can be envisioned for situations in which the material is not readily accessible for conventional repairs, such as in deep space exploration or as part of artificial organ implants.

Nature, March 29, 2001

The review article on spider silk by Vollrath and Knight (**2001**, *410*, March 29, 541–548) relates the molecular structure of the constituent proteins and the method of fiber formation to the final material's superior mechanical properties (extensibility, strength). Silk fibers of different morphology are produced in various silk glands of the spider by intricate spinning processes that generate composite materials ideally suited for the various tasks they have to fulfill (e.g. dragline vs. prey catching portions of the web). The authors explain the truly remarkable spinning technology of the spider that allows the silk proteins to be maintained as highly concentrated, aqueous liquid crystalline solutions that are extended in the glands' ducts and eventually phase separate and crystallize into silk fibers—all that under ambient temperature and pressure. The article's scope ranges from molecular biology to process engineering of silk production; it is a great basic reference for a research paper. Probably of greater significance, it clearly illustrates how long years of basic research in biology, chemistry, and physics have generated the solid basis of knowledge that makes it possible for engineers and polymer scientists to develop biomimetic materials with potentially superior properties.

Nature, January 11, 2001

A collection of reviews published in the January 11 issue of *Nature* covers various aspects of the use of biological cata-



Scott White, University of Illinois at Urbana-Champaign

Left: The autonomic-healing concept. A microencapsulated healing agent is embedded in a structural composite matrix containing a catalyst capable of polymerizing the healing agent. i: Cracks form in the matrix wherever damage occurs; ii: the crack ruptures the microcapsules, releasing the healing agent into the crack plane through capillary action; iii: the healing agent contacts the catalyst, triggering polymerization that bonds the crack faces closed.

Right: Demonstration of the autonomic-healing process. A crack, propagating from the bottom of the page, ruptures embedded microcapsules releasing red-dyed healing agent. The black particles are embedded catalyst. As healing agent contacts the catalyst, polymerization is triggered, bonding the crack faces closed.

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lysts in industrial processes (**2001,** *409*, January 11). We can briefly discuss only two of these articles here but encourage you to look up the excellent remaining reviews on modular enzymes (pp 247–252), on rational design and *in vitro* "evolution" of enzymes with new or improved properties (pp 253–257), and on current and future trends in industrial applications of biocatalysis (pp 258–268). Koeller and Wong from the Scripps Research Institute (pp 232–240) review the exploitation of enzyme stereospecificity for enantiomer-specific syntheses from racemic precursors. To improve product yield beyond the theoretically possible 50%, racemization catalysts are frequently added that convert the remaining enantiomer to enzyme substrate during catalysis. To adapt cofactor-requiring enzymes to industrial synthetic processes, the cofactor has to be regenerated to drive the reaction to completion. These non-protein compounds are generally present in catalytic amounts, participate in the reaction, and are chemically altered during the catalytic process. With few exceptions, the problem can be solved for most cofactors, such as ATP, NAD(P), and acetyl CoA. The authors further discuss various examples of industrial processes that are either purely enzymatic or involve a combination of conventional chemical and biocatalytic synthesis, and point out ongoing research efforts geared toward improving the performance of enzymes in chemical syntheses. Since many synthetic compounds such as polymers are commonly believed to be insoluble in water, they would not lend themselves to enzymatic synthesis.

The article by Klibanov from the Massachusetts Institute of Technology (pp 241–246) dispels that myth and summarizes the state-of-the-art of enzyme catalysis in organic solvents. Enzymes dissolved in water are conformationally very flexible, a property that is necessary for and greatly enhances their catalytic efficiency. Consequently, in mixtures of organic solvents and water, the proteins denature and become non-functional. In pure organic solvents, on the other hand, the conformational rigidity of the enzymes prevents their denaturation and allows them to maintain their catalytic activity. Interestingly, the catalytic state of the enzyme in the organic solvent is greatly influenced by its "history" in the aqueous medium from which it was obtained. Binding of a ligand during lyophilization or crystallization tends to lock the enzyme into a particular conformation that can greatly influence its catalytic performance (efficiency, specificity) in the organic solvent after removal of the ligand. Likewise, the pH of the aqueous medium determines the ionization state of the protein and, therefore, its enzymatic activity in the non-aqueous solvent.

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