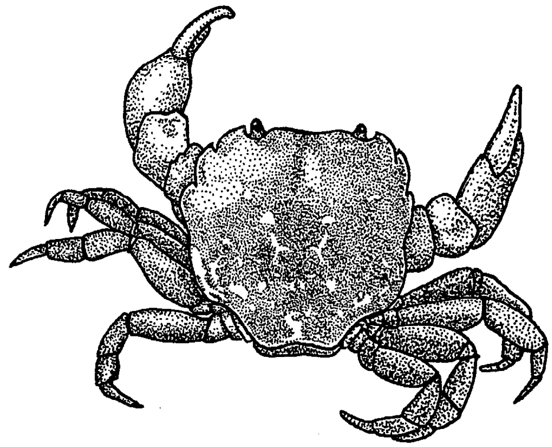

CASHING IN ON CHITIN

The stuff in your dinner crab is full of surprises

The blue crab scuttling in the marsh, the lobster crawling along the ocean floor, the shrimp swimming deep in the ocean: Thoughts of these usually go hand in hand with images of spice seasonings, melted butter, and cocktail sauce. But little do most people realize when they throw away a pile of shells after the feast that those shells contain a compound that may be worth its weight in gold.

Called chitin (pronounced kite-in), this versatile compound may someday be used to reduce calories by binding fats in foods or to replace some plastic products harmful to the environment. And that's just a small sampling of what chitin can do. Chitin's properties also make it useful for burn dressings, surgical sutures, blood coagulants, cattle feed, fungicides, and drinking water purifiers, just, to name a few. Chitin's magic lies in its makeup. Chemically, it is a biopolymer, a large molecule made up of many repeating sugar units. In itself, this isn't unusual. Other biopolymers, such as cellulose and starch, have similar chemical structures. What's unusual about chitin is that side chains on the sugar units give the compound a net positive charge. The charge, in turn, gives chitin the ability to bind to other compounds such as metal ions in drinking water and to interact with proteins and lipids in food products.

Chitin, which makes up at least 25 percent of shell waste, is ubiquitous worldwide, second in abundance only to the biopolymer cellulose. Besides serving as the tough and flexible glue that holds together the shells of lobsters and crabs, chitin makes up the outer skeletons of the spiders in your attic, the beetles in your backyard, and the mosquitoes on your porch. Chitin, which is both non-toxic and biodegradable, even occurs in your mushroom salad, where it is found in the cell walls of your favorite fungus.

This versatile compound was first investigated in 1811. Subsequent research showed that chitin could be treated chemically to produce a derivative

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called chitosan — a compound with properties even more diverse than that of the parent chitin. In the years following this discovery, some interesting applications were found for chitin and chitosan. During World War II, for example, chitosan was used as a glue to hold together the skeletons of a wooden British bomber, the Mosquito. All in all, though, the attention chitin compounds were paid did not match what some chitin enthusiasts thought they deserved. That situation changed when, in the mid-1970s, environmental regulations were passed to limit dumping of untreated shellfish wastes in coastal waters. In a trash-to-treasure story, technologies for processing chitin and chitosan from shellfish waste were hailed as a relatively cheap and environmentally safe way to dispose of the thousands of tons produced annually. The resulting potential from an abundant, readily available supply of chitin led scientists and manufacturers to explore its use in myriad products. Yet experts say chitin is still grossly under-utilized — the 2,000 to 3,000 tons of chitin processed annually worldwide represent only a tiny fraction of the total resource.

With so much naturally occurring raw material available, why hasn't the manufacture of chitin products burgeoned into a multimillion-dollar industry? "Although chitin is an extremely promising technology, there are several factors limiting its success," says Ray Pariser, researcher at the Massachusetts Institute of Technology Sea Grant College Program. Problems include securing Food and Drug Administration approval, ensuring both chemical uniformity and a constant source of chitin for distribution, and breaking into existing markets. "Most of the applications for which chitin can be used are being partially addressed by synthetic products, especially plastics," Pariser says. "It's difficult to replace current products that are well established. "Although replacing these synthetic products would be costly, chitin and chitosan would be superior substitutes — their performance would be the same or better and they have the advantage of being biodegradable.

Another barrier to the acceptance of chitin and chitosan is a lack of staunch federal support. Although funds have been made available through the National Oceanic and Atmospheric Administration's Sea Grant Program, the federal government has not widely supported chitin research and the development of chitin products. In Japan, where the Ministry of Health cleared the way for commercial marketing of chitin products by approving it as an ingredient for hair and skin-care products and for artificial skin, 600 to 700 metric tons of chitin are used annually. In addition, more than 19 Japanese universities and institutes, many funded by the government, are active in basic chitin research, and 36 companies are interested in its commercial aspects. On the other hand, while the United States has successfully conducted research on chitin and chitosan for an equal number of years, federal approval for chitin-derived products has been slow. Some biomedical products that were first developed in the United States are already in use in other countries, yet are still awaiting approval here. As a result, Protan Laboratories in Washington is the only commercial producer of chitin in this country.

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The ray of hope for chitin and chitosan research has been the National Sea Grant College Program. "Sea Grant did an absolutely extraordinary job," Pariser says. "They picked this out 17 years ago." As of last December, the National Sea Grant College Program had supported 18 projects on chitin and chitosan at universities in Washington, Delaware, Alaska, California, Louisiana, Massachusetts, and Rhode Island. Sea Grant's investment since 1971 has been about $1.57 million; this was matched at Sea Grant universities by an additional $940,000. The support has spawned major advancements in the understanding of chitin and chitosan, and has helped spur the development of a new industry. A 1987 forecast estimates that chitin processing and the manufacture of chitin-based products could have an annual market value of $335 million dollars in the United States.

Currently, Sea Grant is funding three projects. At the University of Delaware, John Castle is studying biopolymers from marine resources including chitin. Washington State University's Lee Hadwiger is looking at the mode of gene activation in crab chitosan, and at the University of Washington, G. Graham Allan is focusing on chitin delivery systems for medicine. "We have been the major supporter of the academic research for several years and we still have a strong commitment to by-product development in the seafood industry," says David Attaway, associate program director of seafood science for the National Sea Grant College Program.

Securing increased federal support isn't the only hurdle for those hoping to realize chitin's full potential. The industry faces another problem: inconsistency both in quality, which varies according to the source of chitin, and in quantity, which fluctuates seasonally with the shellfish catch. While chitin processors work on ways to iron out these bugs, chitin disciples push on: About a dozen chitin and chitosan companies are trying to carve themselves a niche in the United States. "Although the future of chitin is uncertain," Pariser says, "there are plenty of needs it can fulfill, providing that some of these obstacles are overcome."

Pariser has recently completed work on the Chitin Sourcebook: A Guide to the Chitin Research Literature. The book, co-authored by Don Lombardi and supported by MIT Sea Grant, was published in January by J. Wiley and Sons. Written for industrial product managers and researchers, it contains the titles of about 500 books, patents, and research publications. "The Chitin Sourcebook is hopefully valuable for somebody who wants to get a serious introduction to the applications, uses, chemistry, and production methods of chitin," says Pariser, who worked on the text for five years. "It is not meant for the layman, really. For the technically educated, it should provide an invaluable, quick reference to the literature."

In addition to authoring the book, in 1985 Pariser and a partner founded the Chitin Co. in Cambridge, Mass. The company's goal is to develop applications for chitin and its derivatives. It is currently producing a chitosan-based system for purifying drinking water. In some communities, such as Boston, the lead in antiquated plumbing systems can result in unacceptably

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high levels of this toxic metal in drinking water. "Our claim is that we can remove lead in a way that nobody else can," says Pariser. "No other product, natural or otherwise, can even come close to the results we get." Current regulations require that the lead content in drinking water be no more than 10 parts per billion at the point of use. Pariser maintains that with the addition of a chitosan derivative from the Chitin Co., existing charcoal filters can be enhanced to keep lead levels well below current requirements. "What we are doing is adding a chitin derivative that is uniquely qualified for capturing heavy metals such as lead, mercury, cadmium, copper, and zinc." Prototypes will filter 500 gallons of water before needing replacement — enough to satisfy a family of four for about six months.

The Chitin Co. is also exploring methods to synthesize chitin biologically. Of particular interest are microorganisms used in fermentation processes. According to Pariser these microorganisms are full of chitin, "but once they have done their job, they are usually burned because nobody knows what to do with them." Pariser predicts that harvesting these micro-organisms would be an economical, speedy, and efficient way to supply more than enough chitin to support the burgeoning industry.

Besides Pariser' s research, several other Sea Grant efforts are trying to capitalize on chitin's use. Some examples:

- **Seed treatment.** Researchers at Washington State University began focusing on chitosan's applications to agriculture in 1969 when chitosan's inhibitory effects on some plant pathogens were discovered. Sea Grant researcher Lee Hadwiger treated winter wheat seeds with chitosan to strengthen them against pathogenic fungi and found a 10 percent boost in crop yield. It appears the treated plants somehow cause chitosan to build up prematurely in the fungi, which causes the pathogen to go into a dormant stage. "We don't eradicate a fungus, we probably just slow it down," he says. Hadwiger adds that researchers aren't yet sure why fungi react this way and that not all fungi are vulnerable to chitosan. In particular, those that naturally contain large amounts of chitosan are not as susceptible to the compound. Hadwiger's efforts have helped obtain U.S. Environmental Protection Agency approval of a chitosan-based seed treatment that is currently being marketed by Bentech Laboratories Inc. in Oregon and costs about $2 an acre. Hadwiger estimates that such a treatment could result in an additional yield of $18 per acre.

  Hadwiger believes chitosan and its parent compound, chitin, are multi-faceted compounds that hold many unrevealed promises. "I think it's just a matter of doing the right chemistry to make the right derivatives," he says.

- **Animal feed.** In another agricultural application, chitin has proven to be a valuable additive to animal feed. Whey, a by-product of cheese manufacture, is difficult for animals to digest because of its high lactose content. As a result, millions of pounds of this high-protein by-product

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are discarded each year. Researchers at the University of Delaware found, however, that when chitin is added to whey, it supports the growth of microorganisms that break down lactose and allow animals to digest it. Sea Grant researcher John Zikakis found that when he added 2 percent chitin and 20 percent whey to a commercial chick feed, the animals grew faster and contained less fat than chicks fed with the unsupplemented commercial product.

- **Surgical sutures.** At the University of Delaware, researchers have shown that chitin's special properties make it an ideal material for surgical sutures. Sea Grant researcher Paul Austin first became interested in chitin in 1936 when he reviewed results of X-ray studies that demonstrated the compound's fiber-forming properties. If a solvent could be found to dissolve chitin, Austin reasoned that the compound could be extruded and strengthened. With colleagues at the College of Marine Studies, he found such a solvent, then searched for ways to use the new material. Because of chitin's wound-healing properties, a natural medical application arose: surgical sutures. And because chitin is a natural product, the sutures had the added advantages of being non-allergenic, absorbable, and resistant to alkaline conditions — particularly attractive features for use in the urinary tract and pancreas. The use of chitin also avoids the scar formation sometimes associated with healing. "There is none of that," Austin says. "It reduces reddening, it reduces pain."

The University of Delaware patented Austin's fiber-forming process, and it was recently licensed by Unitika Ltd., a major fiber producer and hospital supply company in Japan. "They've carried it forward. The material is now commercial," says Austin. "It's being produced and sold in Japan, but not yet as sutures." Instead, Unitika is using the fiber process to make a nonwoven fabric out of chitin for covering wounds in burn therapy and skin grafting.

Although the patent's license is non-exclusive, no one in the United States has licensed it, Austin says, mostly because developing the technology and getting FDA approval is an expensive and lengthy process. The Japanese success may help develop interest in this country.

Austin and his colleagues plan to continue their research, possibly looking at the chitin in squid or studying the properties of chitin in other solvents. "Once you get into chitin," says Austin, "you find it's a very big field."

In all, chitin researchers believe that the future holds many promises for this marvelous compound, which is so abundant in the underwater world and elsewhere in nature. Whether used to stitch and heal in medicine, applied as a fungus fighter to crops, or used to purify drinking water, chitin and chitosan have already proven their worth. Says Pariser: "I am convinced that sooner or later this will be a very important industry."

• Karen Hartley is Communications Manager for MIT Sea Grant.

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From contacts to sutures, chitin's magic works in many ways

Chitin and its derivative. chitosan are extremely versatile. The following are just a few applications for the second-most-abundant biopolymer in the world:

- Contact lenses. Chitosan and derivatives can be molded into hard or soft lenses. The technique was developed and patented by Sea Grant researcher G. Graham Allan at the University of Washington. Both Revlon and Johnson & Johnson have licensed the technique and are working on commercial products. Revlon is developing a disposable contact lens based on chitosan while Johnson & Johnson is apparently concentrating on a non-optical eye bandage application.
- Wound care. Chitin surgical sutures dissolve in the body and are non-allergenic. Chitin wound dressings form a protective water-absorbent layer and promote healing. Both products which have certain advantages over existing materials have already been approved for sale in Japan.
- Anti-cholesterol food additives. Researchers have found that when chitin or its derivatives are added to foods they bind fats (including cholesterol) in the small intestine then pass with them through the body unmetabolized and unabsorbed. The result is that chitin is what some industry insiders call a negative caloric food additive. Researchers are also working on chitin-based anti-cholesterol drugs.
- Drug delivery systems. Because chitin is indigestible and binds easily with a variety of substances, it is a good candidate for carrying and slowly releasing long-acting drugs.
- Animal feed. A nutritional additive has been developed by adding chitin and whey a by-product of the cheese industry to commercial feed mixtures. Chitin supports the growth of micro-organisms which produce enzymes animals need to digest the high-lactose whey. Tons of whey that were once discarded can now be used to boost growth rates in chicks and other farm stock.
- Fungicide. Applied to crops. chitosan stimulates a disease-resistant response and seems to make pathogenic fungi less potent. Coating seeds with chitosan increases the yield of wheat barley oats and peas. The U.S. Environmental Protection Agency recently approved seed coating for commercial use.
- Textiles paper and plastic substitutes. Chitin and chitosan's abilities to form fibers may prove useful to the textile industry. These polymers might also be used in the paper industry as strengtheners and in the food industry as biodegradable plastic wrap substitutes.
- Wastewater treatment. Because of its positive electrical charge chitin can effectively bind with and remove undesirable constituents of wastewater. The Japanese use the compound extensively for sludge treatment. Chitin derivatives are also good for cleaning up toxic organic compounds such as PCBs. In nontoxic effluents chitosan may be used to attract and concentrate desirable compounds such as proteins resulting in a high-protein additive for animal feed.
- Hair and skin-care products. A number of chitin derivatives are useful emulsifiers moisturizers and emollients. Of particular interest to the cosmetic industry is the ability of these compounds to form clear films that are useful for hair sprays and setting gels.
- Water purification. Researchers are working to improve existing charcoal filters by adding a chitosan derivative that removes lead and other heavy metals from the drinking water.

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