The MIT/Marine Industry Collegium

Opportunity Brief

CHITIN AND CHITIN DERIVATIVES

A Project of the

MIT Sea Grant Program

The MIT/Marine Industry Collegium

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MASSACHUSETTS INSTITUTE OF TECHNOLOGY
Sea Grant Program

ADMINISTRATIVE STATEMENT

In 1975 the MIT Sea Grant Program formed the MIT/Marine Industry Collegium, a working partnership between MIT Sea Grant and U.S. Industry to promote the commercial development and application of new marine technologies. In seeking to meet this objective, the Collegium acts as an information resource for industrial members, conducts meetings, workshops, and special programs, and publishes information on new ocean-related business opportunities.

The principal publications of the Collegium are Opportunity Briefs. These 15-25 page papers deal with specific business opportunities growing out of Sea Grant or other MIT sponsored marine research. Opportunity Briefs describe a new technology or process, outline economic and marketing implications, review technical requirements, and consider environmental, regulatory, and political factors. Briefs are a joint effort of subject experts, the MIT Sea Grant Marine Industry Advisory Service and Collegium members. The briefs remain anonymous to give greater freedom in the expression of opinions and in speculation about particular future opportunities.

The five Opportunity Briefs prepared during the Collegium's 1975-1976 year were:

Chitin and Chitin Derivatives

Offshore Mining of Sand and Gravel

Telemanipulators for Underwater Tasks

Advances in Underwater Welding

Untethered Robot Submersible Instrumentation Systems

Each of these Briefs was first issued to Collegium members in draft form. Following this, we held meetings to explore the topic in more depth and to discuss further directions with representatives of interested companies. The Brief in its edited form incorporates many of the comments and suggestions that we received from members through correspondence, phone conversations, and Collegium meetings.

If you would like to receive any of our other Opportunity Briefs, or wish to pursue further any of the topics covered, please contact the Marine Industry Advisory Service, MIT Sea Grant Program, Room 1-215, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139.

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Director

August 15, 1976

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1.0 A BUSINESS PERSPECTIVE

Chitin and its derivatives are potentially profitable by-products that can be recovered from shellfish processing wastes. Opportunities for the commercial use of chitin exist in the paper-making, pharmaceutical, food processing, agricultural, waste treatment and monitoring, and adhesives industries, among others.

Industrial possibilities for utilizing chitin and its major derivative, chitosan, have been known for some time. Chitin's potential is of renewed importance now because:

a) recent research and small-scale production of chitin and chitosan, efforts sponsored in part by the National Sea Grant Program, have expanded the number and variety of potential industrial applications;

b) increasing prices of petrochemicals have made reassessment of certain applications for chitin derivatives appropriate;

c) environmental problems and costs associated with the disposal of shellfish processing wastes have increased; and

d) these factors have led to the recent establishment of two domestic commercial sources and at least one foreign source of chitin and chitosan.

The last consideration reflects an important breakthrough: to date there have been almost no actual industrial applications, a consequence partly due to the lack of reliable supply. In turn, because of the absence of known markets for the raw material, processors have been reluctant to invest in the "refining" equipment needed to supply chitin and chitosan to industrial users.

In this brief, we address primarily the business opportunities related to the potential industrial applications of chitin derivatives. Only secondarily do we address the business of supplying chitin and chitosan, by indicating to the potential user the approximate annual supply and prices of these materials. A detailed Marine Industry Business Strategies (MARIBUS) study conducted by M.I.T.'s Center for Policy Alternatives was directed toward business strategies for supplying and marketing chitin, as well as toward identifying the largest, most profitable applications.

The results of this study, which has been carried out with the cooperation and support of several industrial members of the M.I.T./Marine Industry Collegium, will be available from the M.I.T. Sea Grant Program in the early fall of 1976.

2.0 OVERVIEW

Chitin is a chemical relative of cellulose, the organic material that gives plants their form and rigidity; chitin performs a similar function in the exoskeleton of invertebrates. Chitin is a very tough, rather inert chemical that is slow to decompose. A few species of micro-organisms and animals manufacture an enzyme capable of breaking down chitin into sugar. Almost all of the creatures belonging to the huge group of animals called arthropods (insects, crabs, shrimps, spiders, lobsters) contain chitin in their protective outer shells.* Great numbers of these animals live on this globe, having colonized land, sea, and air space; since all of them have a chitinous shell, the amount of chitin present on earth at any one time is measured in hundreds of millions of tons. However, commercially significant concentrations are available today only through shellfish processors.

Although the gross structure and some of the physical and chemical properties of chitin have been known for more than one hundred years, there are several good reasons for our present renewed attention to this material.

2.1 Expansion of applications. The number and variety of potential markets for chitin - and especially its simple derivative, chitosan - have expanded dramatically. Research indicates that these chemicals have a broad range of potentially interesting applications in pharmaceuticals; in food packaging, food composition, and food processing; in the manufacture and improvement of pulp and paper; in the treatment of radioactive wastes; in the recovery and monitoring of trace metals in water; in the purification of agricultural waste

* Fungi also contain chitin as a structural stiffener.

streams; in the manufacture of specialized adhesives, films; and in ion exchange and chelating processes.

2.2 A substitute for petroleum derivatives. Chitin and chitosan could replace a limited quantity of petroleum derivatives in the manufacture of certain items now made from petrochemicals. The increasing cost of petroleum supplies, and their potential periodic shortage or unavailability, make chitin - a renewable chemical resource - a possible alternative to petroleum for use in manufacturing some types of plastics or adhesives for certain special applications.

2.3 Environmental concerns. Shellfish processors are no longer able to dump extracted carcasses into waters adjacent to their plants without risking federal restraining actions and serious penalties under various environmental laws and regulations. Motivation therefore exists for the shellfish industry to support and/or initiate enterprises that would upgrade the crustacean wastes to a valuable commodity and permit the processors to avoid the financial burden of legal waste disposal.

Some shellfish processing facilities are able to sell the waste products at nominal prices (perhaps $20/ton), thus avoiding the environmental issues and adding to profit. Nonetheless, the possibility of adding value and profit by further processing the waste products into chitin or chitosan should appeal to processors.

2.4 Increased sources of supply. In the last few years, the U.S. shellfish industry has increased considerably in volume, thus increasing the amount of chitin that can be easily collected. There are other potentially large sources of chitin in currently unutilized species of coastal and pelagic crustaceans. The possibility of obtaining chitin and chitosan from other arthropods, mollusks, and fungi is being considered in an effort to broaden the raw material base even more.

These considerations have recently encouraged entrepreneurial efforts in chitin-related ventures that are still in the early stages of development. The Food, Chemical & Research Laboratory (FCRL) in Seattle, Washington, and the Marine Commodities International Corporation in Brownsville, Texas, have started to process shellfish wastes to extract chitin and manufacture chitosan. Both installations are operating on a pilot plant scale. The Kyowa Oil and Fat Company of Japan - a large supplier of fine chemicals - has also started chitosan production and application on an undetermined scale. These companies are the commercial sources of chitin and chitosan that are known to us today.

3.0 PROPERTIES OF CHITIN AND CHITOSAN

Purified chitin is a white solid that is insoluble in water, dilute acids, cold alkalis, and organic solvents. It is composed of long chains of N-acetylglucosamine, and is a crystalline fibrillar substance. It has been extensively studied by many scientists.

One of the most interesting derivatives of chitin is chitosan, a modified carbohydrate polymer that is obtained by deacetylating chitin. Deacetylation removes the acetyl radical ($-COCH_3$) from the amino group (-NH-) of most of the glucose rings to which it is attached. This process is performed by subjecting the purified chitin to strong caustic soda and heat. Sodium acetate is obtained as one of the by-products of this process.

Chitosan is a white, odorless substance, insoluble in water and most common organic solvents; it is soluble without degradation in formic and acetic acids. There is some degradation when chitosan is dissolved in nitric or hydrochloric acids at below pH 2. Chitosan is quite insoluble in sodium hydroxide, sodium carbonate, and other bases. It has a certain degree of crystallinity, is more rigid than cellulose, which it closely resembles in steric configuration, and does not undergo thermal decomposition up to 150° C. Its average molecular weight is dependent on the conditions of preparation which generally induce the degree of polymerization, but can be as high as 120,000. Further technical data are available from the commercial suppliers, and from Sea Grant institutions and researchers cited in Sections 7 and 8.

4.0 BUSINESS OPPORTUNITIES AND INDUSTRIAL APPLICATIONS

As mentioned earlier, chitin chemically resembles cellulose, a similarity perhaps appropriately noted in a marketing context. Cellulose, in the form of wood, cardboard, or paper, has a large number of markets. The conceiveable markets for chitin also seem as diverse, when one considers the implications of research results defining some of its properties. Some of the applications proposed below are based on field-tested uses. Others are more speculative, but are primarily based on known properties of chitin or chitosan.

In the adhesives industry, chitin/chitosan can be utilized because of its special binding properties:

-in the manufacture of plywood;

-for laminating paper, wood blocks, safety glass, and plastic to fiberglass;

-for bonding paper to: regenerated cellulose
wood
cloth
leather
glass;

-for bonding wood to: cork
leather
glass
rubber
rayon
canvas;

-for bonding leather to: leather

cork

regenerated cellulose.

<u>In the paper industry</u>, because of the polymer's stereochemistry and the many positive charges chitosan carries allowing it to bind with cellulose, chitosan may:

- reduce the cost of paper manufacture by replacing some chemical pulp with chitosan;
- improve the "pick resistance" of paper;
- improve the wet and dry strength of paper;
- impart water resistance to finished paper;
- be used as a surface sizing on paper to impart oil and water resistance.

<u>In the natural or synthetic fiber industry</u>, chitin derivatives may be utilized:

- as a semipermanent finish on wool to improve laundering properties and aid in retaining shape and reducing shrinkage of textiles;
- as an antistatic coating for synthetic fibers;
- as a contributor of semipermanent fullness and stiffness to cotton fabrics;
- as an agent to improve the dyeing characteristics of cellulose fibers and films;
- as a lubricating and sizing agent in the manufacture of fiberglass;
- as an agent to impart radically increased strength to synthetic fibers.

In the pharmaceutical industry, chitin/chitosan can be utilized:

- in wound dressings;
- in biomedical applications such as temporary wound covers;
- as a surgical suture with properties that accelerate wound healing;

In the food industry, chitin/chitosan can be utilized because of its positively charged character:

- for the recovery and reuse of undegraded proteins from animal slaughtering wastes and brewery wastes;
- for the recovery and reuse of suspended protein from shellfish and finfish processing;
- for the recovery and reuse of products from cheese whey in dairies.

In waste management industries, chitin/chitosan can be utilized because of its binding properties, especially for transition metal ions:

- for the treatment of nuclear power plant waste;
- for rapid determination of nuclear power plant pollution resulting from leaks or other minor accidents;
- for the removal of mercury from industrial effluents;
- for use in domestic sewage treatment plants.

In mineral resource processing industries, chitin/chitosan can be utilized:

- for the recovery of silver;
- for the recovery of mineral resources of the sea;
- as an oil drilling mud additive.

Finally, because of chitosan's extreme affinity for binding transition metal ions, instrumentation could be developed for measuring and monitoring very low concentrations of various metals in bodies of water.

5.0 SUPPLY OF RAW MATERIAL

Although chitin can be extracted from locusts, cockroaches, squid, and many types of fungi and molds, at present the most concentrated source of this material is shellfish processing wastes such as crab, shrimp, and lobster carcasses. The gross amount of chitin that could be obtained per year depends upon the total amount of the shellfish processing wastes available and also the amount of chitin obtainable from each species comprising the total. Furthermore, prompt collection of wastes can be justified only in geographic areas where there are substantial concentrations of shellfish processing facilities. Finally, unless the total selling price of chitin/chitosan and of the other by-products from processing shellfish is high enough, wide-scale collection of these materials will not take place. Thus, the relationship between the "potentially available supply" and the "economically available supply" is exceedingly complex. The study by the M.I.T. Center for Policy Alternatives (see p. 2) includes careful studies of the question of economically available supplies of shellfish wastes based on transportation costs, seasonality, minimum economically viable processing plants, and related factors.

Very rough estimates of potentially available supplies can be made in the manner illustrated below, but the serious reader is referred to the Maribus Study (see p. 15) for a more detailed consideration of the question.

In 1973, U.S. landings of crab, lobster, and shrimp amounted to 293, 29, and 372 million pounds respectively, for a total of about 700 million pounds. If we assume that 50% of this total was processed, then 350 million pounds of shellfish were available. The weight of the shellfish processing wastes is about 60% of the total weight of shellfish processed, or approximately 210 million pounds. The potential amount of chitin available from these wastes would be about 20 million pounds.

To demonstrate the impact that the chitosan now producible in the U.S. could have upon one segment of the country's industry, the following figures may be interesting as order-of-magnitude indicators: 4 million pounds of chitosan (20% of the potentially available 20 million pounds), if used to coagulate proteinaceous and other organic matter from food processing and brewery operations, could result in the recovery of about 250 million pounds (dry weight) annually of usable wastes. The recovered material, presently discarded in this country, seems quite suitable as feed for livestock, although the U.S. Food and Drug Administration has not yet approved such use.

There are yet other chitin sources to be considered. Shrimpers, for instance, behead the shrimp at sea to prevent the secretion of an enzyme that discolors the rest of the animal. Forty percent of the shrimp's weight is in the head alone. If the heads presently discarded at sea were included in the landed harvest, the annual volume of available chitin might increase by about 50%. Moreover shrimpers, lobstermen, and crabbers usually throw unmarketable crustacean species overboard. An assured market for these species would encourage fishermen to harvest these animals and further increase the availability of chitin.

While the present amount of raw material is small in comparison with an optimistic appraisal of market opportunities, it is sufficient for early business development. Furthermore, the amount of chitin available can be expanded greatly through worldwide efforts and/or use of other natural chitin sources, such as fungi, insects, and other arthropods.

6.0 PRODUCTION OF CHITIN AND CHITOSAN

Preparation of pure chitin and chitosan from raw seafood wastes is relatively simple, and the process has been known for a long time and a large number of patents - perhaps 80 to 100 - have been granted over the years. Many of these patents have lapsed.

Since the principles involved in the extraction and purification of chitin and the manufacture of chitosan are well described in the technical literature, it is possible for anyone to produce both chitin and chitosan without using existing patents. Patents and patent applications concerning uses for chitin/chitosan have expanded recently. Large numbers of U.S. and foreign patents currently exist and more are being filed.

The purification process used by the FCRL for the manufacture of chitin and chitosan involves a step in which the proteinaceous components of the shellfish carcass are removed by alkali treatment, and the organic moiety of the raw material extracted by acid treatment; chitosan is obtained by deacetylation of the purified chitin.

Commercial plants recover pure chitin, chitosan, a denatured protein fraction, minerals, and some of the chemicals used for the process. The process seems clean and profitable since some of the by-products such as protein are saleable, and the others seem benign and easily disposed of.

Selling prices of chitosan are reported to be between \$4 and \$8 a pound, depending upon the purity of the product and the quantity ordered. We understand that under large-scale conditions, chitosan may possibly be obtainable for \$1 to \$2 a pound.

7.0 ONGOING RESEARCH AND DEVELOPMENT ACTIVITIES

A number of M.I.T./Marine Industry Collegium members and other industrial companies are undertaking proprietary research that cannot be reported here, but in parallel a number of Sea Grant institutions are continuing projects funded by the National Sea Grant Program, by the institutions themselves and by corporations. Activities of which we are aware are outlined below.

7.1 In depth study at M.I.T. on chitin business strategies. The Marine Industries Business Strategy Program (Maribus) of the M.I.T. Sea Grant Program's Marine Industry Advisory Service has undertaken a more detailed study of chitin/chitosan business opportunities. Among the topics studied were: the supply of chitin-containing resources and their geographical distribution; production and processing costs; the by-products of chitin extraction and of the manufacture of chitosan, and the markets for the by-products; market displacement of presently utilized polymers by chitin/chitosan; basic chemistry of chitin/chitosan and chemical and physical modifications; and analysis of the largest, most profitable markets for chitin-derived products.

The Maribus study is being carried out by the Center for Policy Alternatives at M.I.T. The results of this study, which has been carried out with the cooperation and support of several industrial members of the M.I.T./Marine Industry Collegium, will be available from the M.I.T. Sea Grant Program in the early fall of 1976.

7.2 Ongoing research at Sea Grant Institutions. The National Sea Grant Program has sponsored chitin/chitosan research at several Sea Grant institutions. Publications relating to the research can be obtained through the directors of the Sea Grant programs at the respective institutions or from the principal investigators. We have given below brief descriptions from recent proposals or correspondence as synopses of current activities at the University of Delaware, the University of Georgia, M.I.T., and the University of Washington.

7.21 University of Delaware. The principal investigator for chitin research at the University of Delaware is: Dr. Paul R. Austin, Adjunct Professor, College of Marine Studies, University of Delaware, Newark, DE 19711. The current research is described as:

"Continuing effort on the utilization of chitin is aimed at (1) search for better solvents to improve technology for preparing high-strength filaments for test as surgical sutures, (2) chitin specifications requisite for wound-healing acceleration and other applications, and (3) supportive information pertinent to patent applications filed on chitin complexes with organic compounds and chitin as a filler and filter for tobacco."

7.22 University of Georgia. The University of Georgia Sea Grant Program has supported chitin research aimed at processing and application. The principal investigator has been Professor Wayne Bough, Marine Ext. Services, P.O. Box 517, Brunswick, GA 31520.

The application areas have primarily focused on use of chitosan as coagulent for recovery of food waste products. In November, 1975, Professor Bough wrote to us as follows:

"My previous Sea Grant project, 1973-1975, entitled 'Recovery and Utilization of By-Products from Shellfish Processing Wastes', was concerned with demonstrating uses of chitosan and its effectiveness for treatment of food processing wastes. Chitosan was shown to be effective for coagulation of suspended solids in processing wastes from vegetable, seafood, meat packing, egg breaking, cheese, and poultry plants as well as activated sludge suspensions, which result from biological treatment of waste water. Coagulated solids were recovered with and without the aid of chitosan. Further studies on activated sludge solids coagulated with chitosan are planned."

"The main emphasis of my current project is on optimizing the chitosan manufacturing process. We have developed methods for determining the molecular weight distribution of chitosan preparations by High Pressure Liquid Chromatography. These results are currently being prepared for publication. These methods have been applied to commercial samples made by Food, Chemical, and Research Laboratories, Inc. and by Marine Commodities International."

7.23 Massachusetts Institute of Technology. M.I.T. has had two separate research activities concerning chitin/chitosan, the previously referenced Maribus study that will be available from the M.I.T. Sea Grant Program in the early fall of 1976, and the continuing research of Professor Benjamin L. Averbach. Professor Averbach is a member of the Department of Materials Science and Engineering, M.I.T., 77 Massachusetts Avenue, Cambridge, MA 02139. Professor Averbach's present work is outlined as follows:

"The principal objective of this project is to characterize chitin in sufficient detail so that it can be specified as an industrial chemical for specific applications. In the first phase of the work, data on polymer chain length, molecular weight, crystal and amorphous structures, viscosity, surface tension, optical absorption, electrical properties, density and chemical composition will be obtained and incorporated in an informational brochure on the general properties of chitin and chitosan. In the second phase, which will be concurrent with the first, we will prepare small batches of chitin and chitosan with variations in molecular weight, chain length, mineral content and structure in order to show how the behavior of chitosan varies with the molecular structure and to indicate how these factors can be controlled by the processing. In the third phase we will investigate the requirements for certain classes of applications such as film formation, ion exchange membranes, coagulation, and adhesion and chelation in an attempt to determine which properties are important in each case."

"At the successful conclusion of this project it will be possible for a user of chitin derivatives to specify a material in sufficient detail to meet the needs for a specific application and for a producer to meet these requirements by controlled adjustments in the processing procedures."

7.24 University of Washington. Dr. G. Graham Allan is a pioneer in the field of chitin research and has been instrumental in rekindling interest in chitin/chitosan in America. His address is University of Washington/University of Puget Sound, Seattle, Washington 98196. The current objectives of the chitin program at the University of Washington are as follows:

"The long-range objective is evaluation of those Northwest marine organisms which could be collected, cultivated, or cultured as sources of polymers usable as fibers or film-formers by the pulp and paper, textile, plastics, or food industries.

"Specific objectives for 1976: 1) continue 1975 development of use of chitosan in nonwovens, in the pulp and paper industry, with particular emphasis on extending previous machine trial results on its performance in strengthening groundwork paper and improving printability; 2) establish merit of *Cyclotella cryptica* as source of mineral-free chitin, 3) study new, more economical methods for the isolation of chitosan, 4) study mechanical and optical properties of sheet structures based on or containing chitin; 5) examine enzymes isolable from shellfish wastes; 6) continue to do structural studies on polymers from unicellular algae and diatoms which have promise for utilization; 7) investigate means of increasing the yield of isolable and potentially useful polysaccharides from unicellular algae, in order to make their production economically feasible."

7.3 The First International Conference on Chitin/Chitosan. The expansion of commercial and academic interest in chitin/chitosan have resulted in an extensive literature dispersed throughout diverse trade journals, and in a need for getting research and product development persons from academics and industry together. Very favorable response to a preliminary announcement has led to firm plans to convene the First International Conference on Chitin/Chitosan in the greater Boston area in April, 1977. The conference will be jointly sponsored by the Massachusetts Science and Technology Foundation and the Sea Grant Program of M.I.T.

The chairman of the Conference will be Professor R. A. A. Muzzarelli of the Universita Degli Studi Di Ancona, Italy. For further information contact:

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8.0 ADDITIONAL READINGS

A large body of technical literature exists on chitin and chitosan; a few references of particular interest are:

Muzzarelli, R. A. A. Natural Chelating Polymers. International Series of Monographs in Analytical Chemistry, Vol. 55. New York: Pergamon Press, 1973.

Muzzarelli, R. A. A. Chitin Chemistry and Applications. New York: Pergamon Press, to be published in 1976.

Pariser, E. R., and S. Bock. Chitin and Chitin Derivatives, An Annotated Bibliography of Publications from 1965-1971. MITSG 73-2* Cambridge: M.I.T., 1973.

Rudall, K. M., and W. Kenchington, "The Chitin System," Biological Review 49:597 - 636, 1973.

Tracey, M. V. "Chitin," Review of Pure Applied Chemistry 7:1-1-14 (Royal Australian Chemical Institute), 1957.

As noted in Section 7, research projects sponsored by the National Sea Grant Program have been and are being carried out at the University of Delaware, University of Georgia, M.I.T., and the University of Washington. For reports on past and current Sea Grant research, contact us or the relevant institutions directly.

* an M.I.T. Sea Grant publication available through our office.