APPLICATION OF CHITIN-CHITOSAN FROM MARINE
BY-PRODUCTS IN THAILAND

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ABSTRACT

Thailand is one of the major producers and exporters of shrimp and other marine products worldwide. Over 600,000 metric tons of marine products containing chitinous materials, shrimp, crab and squid, are produced yearly, which resulted in abundant amount of raw materials for the production of chitin-chitosan. Chitin-chitosan industry in Thailand has grown considerably in the past decade. However, from 2004-2007, the number of companies producing and applying chitin-chitosan has slowly declined due to low local consumption and limited market of chitin-chitosan. This was caused mainly by the lack of intensive research and proper product development. The local consumption then increased dramatically in these last few years. There are over 20 companies nationwide, producing chitin-chitosan and chitin-chitosan related products mainly for agricultural applications. The application of chitin-chitosan for increasing resistance and production of crops has been the major contributors for this significant increase in the local consumption. Chitin-chitosan has been used as foliage spray to induce disease resistance and increase quality and production of orchid, and other ornamental plants. It was applied in crops such as rice, palm, corn, cassava and many tropical fruits with success. It has also been incorporated into animal feed for fish and shrimps as well as poultry, cattle and porcine. However, careful and extensive studies must be performed to establish the proper usage of chitin-chitosan and its related product. The use of chitin-chitosan can elicit proper response when the proper molecular form, chain length and percent degree of deacetylation, and program are applied. Chitin-chitosan can also be applied and used in many other applications such as textile, cosmetics, medicine, composites and nanomaterials, and food and neuropeptide products. Food and neuropeptide has been one of the major applications of chitin-chitosan, since it is the major source of amino sugar, N-acetyl-D-glucosamine and D-glucosamine.

To further promote the development of chitin-chitosan industry, research activities on the applications of chitin-chitosan and marketing of chitin-chitosan related products are crucial.

\textbf{Key words:} Chitin-chitosan, Thailand, marine products

INTRODUCTION

Chitin/chitosan is one of the most abundant bio-renewable resources. It is the major waste product of marine and fishery industry especially from the expansion of shrimp and crab industry of the world. Thailand is one of the world major exporters of shrimp and processed marine products. One of the major wastes from these industries is chitinous materials such as shrimp and crab shells and squid pens. These wastes were normally discarded, used as fertilizer, or use for flavor and aroma extractions. However, there are remarkable advances in the field of chitin/chitosan in the past decade and these materials can be of great value for the fishery industry. Chitin/chitosan can be applied and used with such a vast application. Furthermore the production of such materials are not complicated and can be manufacture anywhere where there is a good source of chitinous materials. Thailand is one of the major producer and exporter of shrimp and other marine products worldwide. Over 600,000 metric
tons marine products containing chitinous materials, shrimp, crab and squid, are produced yearly, which resulted in abundant amount of raw materials for the production of chitin-chitosan.

Chitin/chitosan is a naturally occurring biopolymer. It was found to be one of the world’s most abundant biopolymer next to only cellulose. Despite the highly abundant of this biopolymer, is found only in a small group of living organisms, arthropods, some mollusk, and yeast and fungi. Chitin is a homopolymer of N-acetyl-D-glucosamine linked together by beta 1, 4 linkages. Structurally it is very similar to cellulose. Chitosan is a derivative of chitin from a deacetylation process of the acetamido group of chitin to an amino group. This process in industry is normally a heterogeneous process in nature, where solid chitin is soaked in alkaline solution to remove the acetyl group. The result of this process, if the reaction is completed, is poly-D-glucosamine or chitosan. However, this deacetylation process does not occur homogeneously and normally some N-acetyl-D-glucosamine residues are left over.

The polymer will be considered as chitosan when the percent degree of deacetylation (%DD) of chitin exceeds 50%. However, for commercially available chitosan the %DD is normally above 80%, due to the fact that the heterogeneously deacetylated materials with lower than 80%DD does not completely solublize in weak organic acid, an important characteristic of chitosan. On the other hand, if chitin has been deacetylated via a homogeneous reaction, lower %DD chitosan that completely solubilized in weak acids can be achieved. The important characteristic of chitosan that separates it from chitin, mentioned earlier, is the ability of this derivative to be completely solubilized in weak organic acids such as formic acid, acetic acid, lactic acid, and citric acid. This property has been use as a crucial parameter for chitin/chitosan production and trading. Therefore chitosan is a derivative of chitin where the %DD exceeds 50% and is completely soluble in weak organic acid solution.

**SOURCES OF CHITIN/CHITOSAN**

The major source of chitin for industry is from shrimp shells, crab shells and squid pen. Each source has different chitin content and the source of shells for chitin/chitosan production should be carefully selected. Dried shrimp shells contain approximately 25-40 % chitin, where as dried crab shells contain 15-20% chitin. Squid pen although contains high content of chitin but it is harder to collect and has much lower availability. Other sources of chitinous materials such as other mollusk have even lower chitin content, and it is not economically viable for large scale production. Therefore the major source of chitin/chitosan production in the world is currently from crab and shrimp shells.

Chitin found in nature is normally packed into an orderly crystalline structure which made it strong and able to serve the exoskeleton purpose of the shells of arthropods. Chitin exists in three structural forms called alpha-, beta- and gamma-chitin. The packing and orientation of the chitin strands are different in each of the different types. Alpha-chitin, found in shrimp and crab shell, has anti parallel chitin stands that are packed tightly with both inter and intramolecular hydrogen bonding with makes it the strongest structure in all the three chitin structures found. Beta-chitin, found in squid pens, has parallel chitin strands that are pack looser and lack the intermolecular hydrogen bonding making it weaker. Gamma chitin found in the stomach lining of some mollusk, have a randomly orientated chitin stand. Of these three structural types alpha- and beta- chitin are the most abundant. The structure of chitin will determine the properties and characteristic of the chitosan produced from each type of chitin.

For the production of chitin/chitosan the shells must be used immediately or as soon as it came out of the process line. The high activity of microbes in the shells will rapidly reduce the chitin content within the shells. If the shells are not to be processed right away freezing or drying the shells can help preserve the shells for later chitin/chitosan production.

The selection of shell also plays an important factor in the success of chitin/chitosan production. For instance, the head carapace of shrimps contains much fat and protein and should not be used for chitin/chitosan production. The shell on the back to the tail portion of shrimp is ideal for chitin/chitosan production. An ideal raw material of shells for chitin/chitosan production should be uniform in size and thickness and has low fat and lipid content.
PRODUCTION CHITIN CHITOSAN

The production of chitin and chitosan from chitinous materials are rather uncomplicated and simple chemicals such as HCl and NaOH are used. The process in the production of chitin is divided into two major steps (1) demineralization step by low concentration HCl (1-2 N) and (2) deproteinization step by low concentration NaOH (1-2 N). These two steps are crucial for the elimination of calcium carbonate and other minerals as well as proteins which are present in the shells. To get the best extraction results, the sequence of these two treatment steps vary depending on the raw material used. For crab shells, demineralization by acid treatment must precede the deproteinization step. For shrimp shells, on the other hand, the extraction steps must start with deproteinization step then followed by demineralization step. The waste from each of the extraction steps can be combined and neutralized. White precipitation of mineral and protein and NaCl solution is the by product of chitin production. The NaCl solution is normally treated and let it overflow back into the ocean. The white protein and mineral cake is either used in animal feed or fertilizer.

Chitin Production

Chitin can be dried and sold as it is or can be further converted to chitosan by a deacetylation process in strong base (40-50% NaOH). Normally, chitin will be soaked in 40-50% NaOH with or without heat for varying amounts of time depending on the specification of chitosan needed. The major cost in the chitin/chitosan production is water. Clean and deionized water must be used for chitin and chitosan production, respectively. Since chitosan has very high affinity to divalent cations and impurities in the water, care must be taken to make sure impurities are not present in chitosan product.

The treatment of the strong base use in the deacetylation is one of the major impediments for chitosan production. Some portion of the base can be used for protein extraction but the amount base used in chitosan production is much more than that can be used for protein extraction. Regeneration of NaOH solution for repetitive use would be the most efficient choice of practice.

Once chitosan in produce it must be analyzed for %DD, molecular weight, ash content, moisture content, protein content, heavy metals and microbial contaminations. There are no international specifications for chitin/chitosan. The specification is normally set by the buyers and agreed between the supplier and buyer. In Thailand the ministry of industry has issued a standard for food grade and industrial grade chitin/chitosan, which can be acquired upon request.

The price of chitin/chitosan are hundreds of time higher than the price of shell wastes. Shrimp shell waste cost from 2-5 baht/kg (0.05-0.15 USD/kg) can be value added to 120-200
when precessed into chitin and 1000-5000 baht/kg (30-150 USD/kg) when processed into chitosan.

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**APPLICATIONS OF CHITIN CHITOSAN**

Research and development in the field of chitin/chitosan and its application increased dramatically in recent years. This spurs up the development of new products and application of chitin/chitosan in various fields. Chitin/chitosan has been successfully applied and used in pharmaceutical and medicine, food and feed, agriculture, materials and textiles, and in the new emerging field of nanotechnology.

**Pharmaceutical and Medicine**

Chitin/chitosan is the major source of amino sugar, $\text{N}$-acetyl-$\text{D}$-glucosamine and $\text{D}$glucosamine found in nature. United States FDA has approved only the hydrolysis product of chitin/chitosan to be the source of $\text{N}$-acetyl-$\text{D}$-glucosamine and $\text{D}$-glucosamine for human consumption. These simple amino sugars have been use for the treatment of osteoarthritis in human as well as joints in animals. Chitin/chitosan is being studied and applied for drugs formulation as a mean of control release. It is applied as an adjuvant in vaccines with success. Chitosan coated wound dressing was also explored since chitosan has antimicrobial activity and can accelerate the healing process. Bio-matrix for tissue engineering using chitosan and composite of other inert material with chitosan was also constructed and has been shown to have great potentials for further development.

**Agriculture**

In Thailand chitin/chitosan has been used as foliage spray to induce disease resistance and increase quality and production of orchid, and other ornamental plants. It was researched and applied in crops such as rice, palm, corn, cassava and many tropical fruits with success. Chitin/chitosan has been incorporated into animal feed for fish and shrimps as feed coating as well as supplemented in the drinking water of poultry, cattle and porcine. However, the mechanism and how chitin/chitosan works in these applications remains unclear. Careful and extensive research must be performed to establish the proper usage of chitin-chitosan and its
related product. The use of chitin-chitosan can elicit proper response when the proper molecular form, chain length and percent degree of deacetylation, and program are applied.

**Polymer and Textile**
Chitin-chitosan can also be applied and use in many other applications such as textile. Due to its antimicrobial property, chitin/chitosan when processed in to film or wet spin into fibers can be incorporated into both woven and non-woven fabric and can control the odor and prevent microbial growth.

**Food and Nutraceutical Products**
Food and nutraceutical has been one of the major applications of chitin-chitosan, since it is the major source of amino sugar, N-acetyl-D-glucosamine and D-glucosamine. Chitosan can also act as a thickening agent, and recent studies has shown that chitosan can interact with proteins to change the interaction of protein resulted in improvement of texture of the product, as well as water retention of food products.

When chitosan is added into some food product it can also act as a food preservative and inhibit microbial growth.

**CONCLUSION**

The fishery waste from shrimp, crab and squid processing which contains chitinous material can be processed in to chitin/chitosan with high value added. Chitin/chitosan can be applied and used in various applications from textile, cosmetics, medicine, composites and nanomaterials, and food and nutraceutical products. To further promote the development of chitin-chitosan industry, extensive research activities on the applications of chitin-chitosan and marketing of chitin-chitosan related products are crucial.
REFERENCES