APPLICATIONS *of* CHITIN *and* CHITOSAN

Edited by

MATTHEUS F. A. GOOSEN

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Preface

The main driving force behind the development of new applications for chitin and its derivative chitosan lies with the fact that these polysaccharides represent a renewable source of natural biodegradable polymers. Since chitin is the second most abundant natural polymer, academic and industrial scientists are faced with a great challenge to find new and practical applications for this material. This book is intended to fill this need. It will provide an examination of the state of the art. New applications, as well as potential products, will be examined.

The book is divided into six parts. For people who are new to the field, two special background/overview chapters, dealing with applications, structures, and properties of chitin and chitosan, are provided at the beginning of the book. This is followed by five specific application sections covering structure and properties, food and agriculture, medicine and biotechnology, textiles and polymers, and wastewater treatment.

The intended audience for this book includes industrial personnel involved in bioprocessing, as well as bioengineering students, specialists in the biomedical and biopharmaceutical industry, biochemists, food engineers, environmentalists, and microbiologists and biologists who wish to specialize in chitosan technology.

Our book will differ from competing volumes by dealing almost exclusively with applications. Previous books devoted less than 30% of their available space to commercial/medical uses.

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PART I

OVERVIEW

CHAPTER 1

Applications and Properties of Chitosan

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INTRODUCTION

Chitosan is a polysaccharide obtained by deacetylating chitin, which is the major constituent of the exoskeleton of crustaceous water animals. This biopolymer was traditionally used in the Orient for the treatment of abrasions and in America for the healing of machete gashes [1]. A recent analysis of the varnish on one of Antonio Stradivarius's violins showed the presence of a chitinous material [2]. Chitosan was reportedly first discovered by Rouget in 1859 [3] when he boiled chitin in a concentrated potassium hydroxide solution. This resulted in the deacetylation of chitin. Fundamental research on chitosan did not start in earnest until about a century later. In 1934, two patents, one for producing chitosan from chitin and the other for making films and fibers from chitosan, were obtained by Rigby [4,5]. In the same year, the first X-ray pattern of a well-oriented fiber made from chitosan was published by Clark and Smith [6]. Since then, knowledge about chitosan has been greatly advanced by the work of such pioneers as Muzzarelli [3].

The main driving force in the development of new applications for

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chitosan lies in the fact that the polysaccharide is not only naturally abundant, but it is also nontoxic and biodegradable. Unlike oil and coal, chitosan is a naturally regenerating resource (e.g., crab and shrimp shells) that can be further enhanced by artificial culturing. It was reported that chitosan and chitin are contained in cell walls of fungi [7,8]. Chitin, however, is more widely distributed in nature than chitosan and can be found in mushrooms, yeasts, and the hard outer shells of insects and crustaceans. It was reported, for example, that about 50–80% of the organic compounds in the shells of crustacea and the cuticles of insects consists of chitin [3]. At present, most chitosan in practical and commercial use comes from the production of deacetylated chitin with the shells of crab, shrimp, and krill (the major waste by-product of the shellfish-processing industry) being the most available sources of chitosan [9,10].

One of the most useful properties of chitosan is for chelation. Chitosan can selectively bind desired materials such as cholesterol, fats, metal ions, proteins, and tumor cells. Chelation has been applied to areas of food preparation, health care, water improvement, and pharmaceutics. Chitosan has also shown affinity for proteins, such as wheat germ agglutinin [11] and trypsin [12]. Other properties that make chitosan very useful include inhibition of tumor cells [13], antifungal effects [14], acceleration of wound healing [15,16], stimulation of the immune system [17–19], and acceleration of plant germination [20].

Chitosan is a good cationic polymer for membrane formation. In early research it was shown that membranes formed from the polymer could be exploited for water clarification, filtration, fruit coating, surgical dressing, and controlled release. In 1978, for example, Hirano showed that *N*-acetyl chitosan membranes were ideal for controlled agrochemical release [21]. Later, he found that a semipermeable membrane with a molecular weight cutoff ranging from 2,900 to 13,000 could be formed [22] from chitosan. In 1984, Rha et al. first documented a procedure for preparing chitosan capsules for cell encapsulation [23]. The chitosan-alginate capsules had a liquid alginate core. Since then, several other studies have been reported on the use of chitosan copolymers for immobilization of hybridoma cells and plant cells [24,25]. However, the apparent poor biocompatibility of chitosan with hybridoma and insect cells was indicated by Smith et al. [26] and McKnight et al. [27].

This chapter focuses on various applications of chitosan, as well as current research on its physicochemical properties. Application areas that are covered include water treatment, pharmaceutics, biotechnology, food processing, and membranes.

PHYSICOCHEMICAL PROPERTIES OF CHITOSAN

Chitosan is a collective name given to a group of polymers deacetylated from chitin. The difference between chitin and chitosan lies in the degree of deacetylation. Generally, the reaction of deacetylating chitin in an alkaline solution cannot reach completion even under harsh treatment. The degree of deacetylation usually ranges from 70% to 95%, depending on the method used. These methods have been thoroughly reviewed by Muzzarelli [28]. The technique of Horowitz, for example, treating chitin with solid potassium hydroxide for 30 minutes at 180°C, results in the highest removal (95%) of acetyl groups. Recently, Kobayashi et al. [29] published a procedure for preparing chitosan from mycelia of absidia strains. A chitosan product with 79–91% deacetylation and 1,200,000 molecular weight was obtained. Most publications use the term chitosan when the degree of deacetylation is more than 70%.

Up to now, only a few studies on the molecular conformation of chitosan have been reported. There is still no one simple model describing chitosan, in spite of the fact that several models have been published for chitin, α-chitin [30] and β-chitin [31]. The α-chitin, for example, is tightly arranged in an antiparallel fashion, whereas β-chitin is in a parallel form. An analysis of the diffraction spectra of chitin and chitosan revealed a structural resemblance between the two polymers [28]. It has been suggested that the conformation of chitosan was similar to that of α-chitin [32].

Commercial chitosan is mainly produced by deacetylating chitin obtained from seashell materials. The quality and properties of chitosan products, such as purity, viscosity, deacetylation, molecular weight, and polymorphous structure, may vary widely because many factors in the manufacturing process can influence the characteristics of the final product. Kurita et al. [33], for example, found that the adsorption ability of chitosan for metal ions depended on the hydrolysis process. A homogeneous hydrolysis process could give a chitosan product with a higher adsorption rate than the one prepared by a heterogeneous process with the same degree of deacetylation. Furthermore, Bough et al. [34] investigated the influence of other manufacturing variables. They found that the highest viscosity and highest molecular weight chitosan product could be prepared by grinding the dry shrimp hulls to 1 mm prior to treatment, using alkali deproteination, purging nitrogen into the reaction vessel, and increasing the deacetylation time.

The degree of deacetylation is one of the more important chemical characteristics of chitosan. This determines the content of free amino