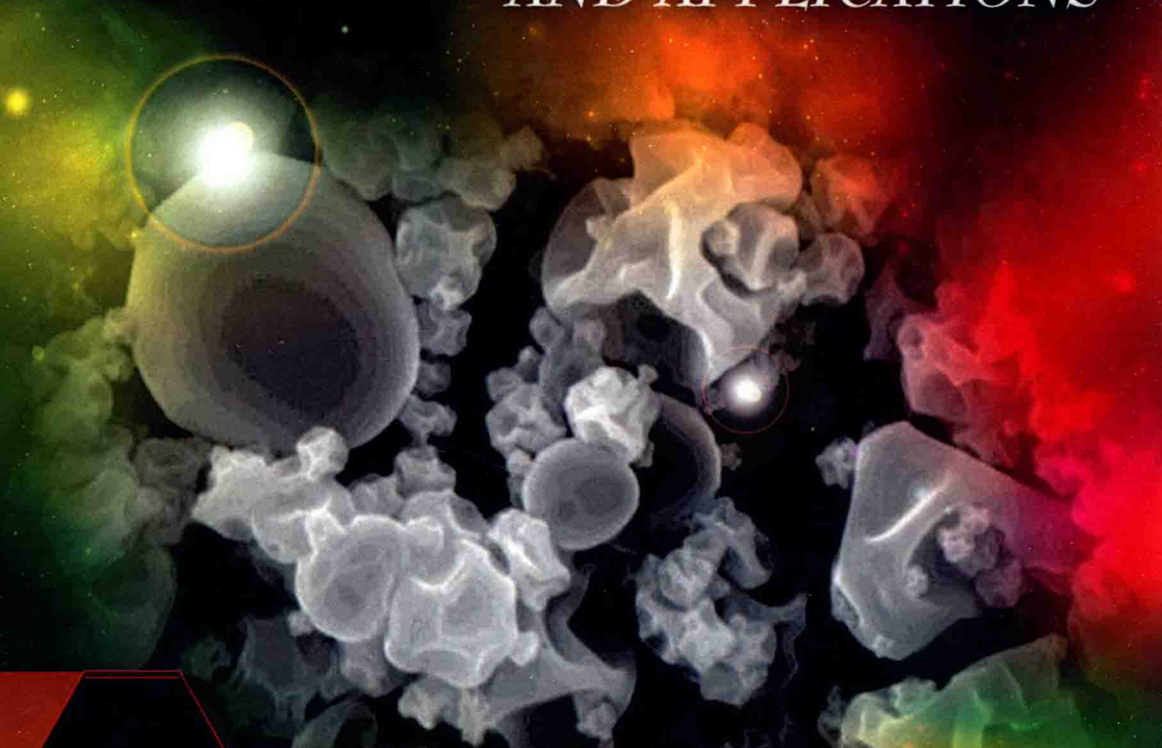
Handbook of Carbohydrate Polymers

Development, Properties and Applications



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Ryouichi Ito • Youta Matsuo
Editors

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HANDBOOK OF CARBOHYDRATE POLYMERS: DEVELOPMENT, PROPERTIES AND APPLICATIONS

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AND

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PREFACE

Carbohydrates play an important role in many biological and biochemical processes, including the fertilization, cell differentiation and maturation, protein folding and degradation. Carbohydrate polymers covers the study and exploitation of carbohydrate polymers which have current or potential industrial application in areas such as food, textiles, paper, wood, adhesives, biodegradables, biorefining, pharmaceuticals, and oil recovery. This book focuses on recent developments on carbohydrate-binding module (CBM) applications in the biomedical, biological and biotechnological fields. Furthermore, polysaccharides are complex carbohydrates that are made up chains of monosaccharide units linked by glycosidic bonds. This book reviews the literature on fibers spun from several polysaccharides and fiber spinning techniques, including both conventional fiber spinning methods and electrospinning. Resulting fiber properties and prospective applications are discussed. This book also reviews research on polysaccharide film-formation and characteristics, analyzed mechanical and barrier properties of polysaccharide-based films, summarizes applications of polysaccharide films in food products and makes conclusions as to the status of polysaccharide films and their future developmental direction. Other chapters in this book examine the pathways leading to the production of bioactive oligosaccharides that have biotechnological applications. The current progress in the development of marine carbohydrates into nutraceuticals and their applications are explored as well.

Chapter 1 - Polysaccharides are complex carbohydrates made of chains of monosaccharide units linked by glycosidic bonds. Some polysaccharides, e.g. cellulose and chitin, are naturally occurring fibrous materials developed during cellular growth, while other polysaccharides are not capable of forming elongated structures *in vivo* because of their molecular structure or physicochemical environments. A variety of polysaccharides have been artificially spun into fibers, for instance, cellulose and its derivatives, chitin and chitosan, alginate, hyaluronic acid, pullulan, and dextran, as well as polysaccharide blends or blends with other materials. Ideal substitutes for synthetic fibers derived from fossil fuels, polysaccharides are renewable and exhibit biodegradability and biocompatibility, and often preferred to protein fibers (silks) in terms of their abundance and economics. This chapter reviews the literature on fibers spun from several polysaccharides and fiber spinning techniques, including both conventional fiber spinning methods and electrospinning. Resulting fiber properties and prospective applications are discussed.

Chapter 2 - Starch-based biodegradable materials are considered one of the most promising candidates to replace certain types of conventional plastics. Starch is relatively cheap and available from a broad range of plants. However, the use of starch for packaging materials is restricted because of its sensitivity to water and inferior mechanical properties. The unique properties of nano-structured substances have opened windows of opportunity for the creation of high performance materials with a critical impact on starch-based materials. This chapter presents a review of ongoing research and development activities in our lab and in the wider scientific community related to starch-clay nanocomposites. As a valuable way to further enhance properties of these nanocomposites, blends involving biodegradable polymers such as poly (vinyl alcohol) are also discussed. Melt intercalation, using extrusion processing, has proved to be an efficient way for preparation of starch-based nanocomposites with improved thermal, mechanical, and barrier properties. The chapter also elaborates the mechanisms of clay exfoliation and dispersion in the starch matrix, which are based on both chemistry and processing effects. Improved interfacial compatibility of the multiphase system (starch, biodegradable polymer, plasticizers, nanofiller, etc.), as well optimized processing parameters, can lead to the design of nanocomposites with enhanced properties. A special emphasis is also given to an overview of mathematic models for some critical nanocomposite properties, such as barrier and mechanical properties. The establishment of a mathematic model provides guidelines for tailoring clay modification, clay dispersion and processing parameters for fabricating starch-based nanocomposites with unique properties.

Chapter 3 - Chitosan, the only alkaline polysaccharide of β-1,4 linked N-acetyl-glucosamine and glucosamine,could be hydrolyzed by many non-specific enzymes such as cellulase, protease, and lipase, especially cellulase, which show high activity on chitosan. The hydrolytic mechanisms of these non-specific enzymes have been received growing attentions.

The focus of this chapter was the characterizations and hydrolyzing mechanism of the non-specific enzymes toward chitosan choosing the three typical non- specific enzymes: cellulase, lipase and papain as objects. The enzymatic characteristics, purification, product analysis, glycoside bond cleavage, active sites and gene cloning of these enzymes to expatiate their non-specific hydrolysis mechanism were studied. From these, we obtained two bifunctional enzymes with chitosanolytic activity from commercial cellulase and lipase,respectively,and one chitosanase from papain.The three purified enzymes were the main reasons for the non-specific chitosanolytic hydrolysis of cellulase,lipase and papain, respectively. Moreover, It is identified that the bifunctional enzyme with chitosanolytic and cellulolytic activity(CCBE) from cellulase (*T.viride*) is identified as a cellobiohydrolase I with exo-β-D-glucosaminidase activity belonging to glycosyl hydrolysase 7 family.The enzmye with chitinase and chitosanase activity (CNBE)from lipase (*A. oryzae*) is the exo-β-D -glucosaminidase with N-acetyl-chitobiosidase activity belonging to glycosyl hydrolysase 18 family. Both of the two enzymes are novel and first reported in chitosanase families. Besides, the active sites and gene expression analysis of CCBE indicated that their dual activities originated from two distinct catalytic domains; while the two active sites overlapped partially.

Chapter 4 - In the first part the preparation of CD polymers is described and examples of CD polymers useful as drug carriers are shown. It is pointed out that CD polymer nanoparticles are promising for application in various biomedical and biotechnological applications, *e.g.* in drug delivery or enzyme immobilization. A special attention was paid to removal of organic dyes from industrial wastewaters by β-CD polymers, having in view the wide use of dyes in textile and cosmetic plants.

The preparation of β-CD copolymers with carbon nanotubes is described in the aspect of their application for removal of *p*-nitrophenol and trichloroethylene from water. It was pointed out that ceramic membranes impregnated with crosslinked silylated CD polymers are promising for removal of polycyclic aromatic hydrocarbons from water. In recent years the importance of imprinted CD polymers is growing; as an example of their application the recognition of oligopeptide structures is presented.

Membranes based on CD polymers are often used today in separation processes; an increasing attention is paid now especially to chiral separation processes. In this aspect the use of chitosan/CD composite membranes in chiral separation of tryptophan was described. In the final part the selected examples of supramolecular architectures based on CD polymers are presented having in view the rapid development of supramolecular chemistry.

Chapter 5 - Moisture, oxygen, carbon dioxide, lipid, flavor and/or aroma transfer between food components or between foods and their surrounding environment can provoke deterioration of food texture, flavour, color, aroma or nutritional values which results in food quality loss. Regulating the mass transfer in food systems by edible films and coatings can increase food-product shelf life and food quality. Besides their barrier properties, edible films and coatings can act as carriers for functional food additives, antioxidants, antimicrobial agents and nutrients; and due to their biodegradability nature, could have an impact on overall packaging requirements.

Edible films and coatings are produced from edible biopolymers and food-grade additives. Film-forming biopolymers can be proteins, polysaccharides (carbohydrates and gums) or lipids. Plasticizers and other additives are combined with the film-forming biopolymers to modify the physical properties or functionality of films. The composition of the film must be chosen according to specific food applications, the type of food products and the major mechanisms of quality deterioration.

Polysaccharide films and coatings are used to extend the shelf life of fruits, vegetables, seafood, meats and confectionary products by preventing dehydration, oxidation rancidity, surface browning and oil diffusion; and in some specific cases can improve the physicochemical, nutritional and sensorial properties of the products. The common polysaccharides used for edible films are: starches and their derivatives; cellulose and its derivatives; seaweed extracts; gums; pectins and chitosan.

The objectives of this chapter are to (a) review research on polysaccharide film-formation and characteristics, (b) analyze mechanical and barrier properties (water vapour permeability, gas permeabilities and volatile permeability) of polysaccharide-based films, (c) summarize applications of polysaccharide films in food products, and (d) make conclusions as to the status of polysaccharide films and their future developmental direction.

Chapter 6 - Carbohydrate-active enzymes (CAZymes) are associated to the synthesis and breakdown of complex carbohydrates and glycoconjugates. CAZymes, beside the catalytic domain (CD), usually present a substrate-binding module named carbohydrate-binding module (CBM), which has independent fold and function. Nearly 7% of the CAZymes contain at least one CBM module. Presently, 58 CBMs families are described in the CAZy database (http://www.cazy.org/), presenting considerable heterogeneity in binding specificity, towards crystalline, amorphous and soluble polysaccharides, both between and within the families. CBMs are known to potentiate the activity of many enzymes, by targeting and promoting a prolonged interaction with the substrate. Since CBMs are functional and structurally independent of the other protein modules, several applications have been described using CBMs obtained by enzyme proteolysis or by DNA recombinant technology.

The present revision focus on recent developments on CBMs applications in the biomedical, biological and biotechnological fields.

Chapter 7 - Natural cellulose fibers are high-molecular polymers that are strongly susceptible to microbial degradation. Fungal and bacterial attack on the fibers cause depolymerization of cellulose macromolecules, which is reflected in decreased molecular weight and strength, increased solubility and a changed crystallinity. Although biodegradable textile fibers are classified as environmentally-friendly materials, the biodegradation process that occurs when the textile product is still in use could cause serious functional, aesthetic and hygienic problems because of textile deterioration, staining, discoloration and odor. To protect the cellulose against biodegradation, chemical modification is of great importance. In this research, therefore, fibers were chemically modified by the use of an antimicrobial finish on the basis of AgCl (AG) in combination with a reactive organic-inorganic binder (RB), water and oil repellent finishes on the basis of fluoroalkylfunctional siloxane (FAS), perfluorooctyltriethoxysilane (PFOTES) in combination with di-ureapropyltriethoxysilane [bis(aminopropyl)terminated-polydimethylsiloxane (1000) (PDMSU) and aminopropyl-perfluoroisooctyl polyhedral oligomeric silsesquioxane ($AP_2PF_2IO_4$ POSS), as well as with an easy-care and durable press finish on the basis of imidasolidinone (DMeDHEU). Moreover, it was expected that these finishes would provide the active or passive antimicrobial properties of the modified fibers. Biodegradation of the finished cellulose fibers was carried out by the soil burial test according to SIST EN ISO 11721-2:2003. The chemical and functional properties of the fibers were determined by means of DP, SEM, AFM, FT-IR, XPS, ICP-MS, appropriate microbiological tests and static contact angle measurements of different liquids on the fiber surface. It can be seen from the study that AgCl embedded in RB imparts active antibacterial and antifungal properties to the coated fibers resulting in excellent microbial reduction and, consequently, strong inhibition of biodegradation. The presence of FAS, PFOTES-PDMSU and $AP_2PF_2IO_4$ POSS coatings, which cause an increase in fiber hydrophobicity, as well as a high drop in surface free energy, results in decreased adhesion of microorganisms and impaired conditions of their growth. In the modification process of cellulose fibers by DMeDHEU, the formation of covalent bonds between the finish and the cellulose macromolecules strengthens the less ordered amorphous regions, resulting in a decrease of fiber swelling. This inhibits the penetration of microorganisms into the fibers, where biodegradation takes place. By applying a combination of FAS and DMeDHEU finishes, a synergistic action of the components is obtained in the coating. In this case, the protective properties of the coating against biodegradation are much higher than those obtained by single component finishing.

Chapter 8 - Oligosaccharides present specific physicochemical and biological properties that can be exploited for specific applications in foods and pharmacology. They can be produced through a number of different physical, chemical and enzymatic catalysed reactions from their parent polysaccharides as well as through transglycosylation reactions. This chapter examines the pathways leading to the production of bioactive oligosaccharides that have biotechnological applications. These carbohydrate oligomers constitute a nutritional type of "*fiber*" that benefits the growth of bifidobacteria and lactobacilli in the colon promoting human health and well-being. The use of oligosaccharides to modify biological responses was recently reported, and this has included their effects as anti-inflammatory and anti-cholesterolaemic stimulating compounds. An overview of nutraceutical and biological functions of these carbohydrate fragments mainly for human health is also reported.

Chapter 9 - Native cellulose is a structural material that is biosynthesized as microfibrils by a number of living organisms ranging from higher and lower plants, to some ameobae, sea animals, bacteria and fungi.-Depending on their origin, individual cellulose microfibrils have diameters from 2 to 20 nm, while their length can reach several tens of microns. The chemical modification of cellulose microfibrils is investigated for preparing new bio-based materials with end-use properties in the fields of adhesion, textile, detergent, paint, cosmetic, medicine, food, etc. Among the possible chemical modifications, the selective oxidation of the primary alcohol group of polysaccharides has been studied for more than a half-century. Recently, a method for selectively oxidizing primary alcohol groups of polysaccharides has been described in literature without degradation of products. The technique is based on a reaction catalyzed by 2,2,6,6-tetramethyl-1-piperidine oxoammonium radical (TEMPO) in presence of NaOBr, generated *in situ* by NaOCl and NaBr, the catalyst being regenerated during the reaction. The chemical modification is a way to modify and introduce specific functionalities leading to the development of new biopolymers in macromolecular prodrug carrier, bio-based composites, nanocomposites, for example. The polymer must be biodegradable and / or biocompatible and must contain appropriate functional sites for chemical conjugation. Despites on large interest on natural and synthetic biodegradable polymers investigated, important efforts are continuing to search for new systems, notably on cellulose.

In this report, the amidation of cellulose materials previously modified by carboxylation reaction is realized from the selection of some amines (cyclic and linear structures). The carboxylation is resulted from the TEMPO mediated oxidation of cellulose, leading to partially or totally oxidized cellulose, in presence of carbodiimide which is known to increase the reactivity of carboxyl groups toward amidation but used rarely for polysaccharides holding carboxyl moieties. Few reports were found in the literature on the use of carbodiimide in the preparation of cellulose conjugates with amines in order to develop new modified cellulose materials. The goals of this report are to develop ways of preparing the cellulose conjugates which can be water-soluble materials or water-insoluble materials, to identify linkage with carboxylated cellulose materials through amide bonds and to understand the obtained results following by FT-IR, NMR spectroscopies (at liquid and solid states) and electron paramagnetic resonance spectroscopy. The carboxyl groups content of oxidized cellulose materials after carboxylation and after amidation reactions are equally determined by titration curves of conductimetry and elemental analysis.

Chapter 10 - Several points concerning the presence in red seaweeds of galactans with cooccurrence of carrageenan and agaran structures (DL-hybrid galactans) are addressed:

a. Analysis of D- and L-galactose enantiomers and their methylated and cyclic derivatives. Spectroscopic, enzymatic and chemical methodologies.
b. Systems of galactans, in which the presence of D- and L-galactose has been determined (DL-galactan systems).
c. The possible deviant structures of carrageenans and agarans in DL-hybrid galactans.
d. The isolation of "pure" carrageenans and agarans from DL-galactan systems.
e. The formation of molecular complexes between carrageenans, agarans and carrageenans/agarans.
f. DL-hybrid galactans or molecular complexes: Evidences in favor of each hypothesis.

Chapter 11 - In the past half century, synthetic petroleum-based polymers have been widely used in a variety of packaging materials but have become a major source of waste disposal problems due to their poor biodegradability. With the increasing demand by consumers for high-quality foods and concerns about limited natural resources and the environment, the use of renewable resources to produce edible and biodegradable packaging materials that can improve product quality and reduce waste disposal problems are being explored. Biopolymer-based edible films and coatings are intended to function as barriers against moisture, oxygen, flavor, aroma and oil, as well as carriers of additives thereby improving food quality and enhancing the shelf life of food products.

Water-soluble polysaccharides are commonly used in food related applications as thickeners due to their increase in viscosity when hydrated. Polysaccharides can also constitute edible films, an important quality since these polymers are of natural origin and come from renewable sources and are biodegradable as well. Though it is recognized that polysaccharide edible films are not good barriers against water vapour, they can find interesting applications as food interfaces, as carriers of active compounds or preservatives, constituting delivery systems with local activity.

The present chapter deals with the study of edible films based on deacylated and/or acylated forms of gellan gum to support L-(+)-ascorbic acid (AA) in view of natural antioxidant protection of foods, by leveraging its activity as a vitamin in the human metabolism. Kinetics of AA-destruction and subsequent non enzymatic browning development were studied in the films stored at constant temperature (25°C) and relative humidity (33.3, 57.7 or 75.2%) and their relationship with the microstructure, at the macromolecular and molecular levels, was also analyzed with the purpose of ensuring a better AA retention as well as lower browning rate as a consequence of controlled water mobility in the polymeric networks.

Chapter 12 - Microencapsulation by coacervation is a common method for microcapsules production. It can be achieved by employing different methods, where the most common one is formation of an insoluble complex of two oppositely charged polymers and its subsequent deposition at surface of dispersed particles (e.g. emulsified oil droplets). In this way, microcapsules with coacervate shell are formed. Composition and microstructure of the coacervate shell are key to determine properties and application of microcapsules.

In this chapter, novel method for microencapsulation by coacervation is presented. The method employs polymer-polymer incompatibility taking place in a ternary system composed of sodium carboxymethyl cellulose (NaCMC), hydroxypropylmethyl cellulose (HPMC), and sodium dodecylsulfate (SDS). In the ternary system, various interactions between HPMC-NaCMC, HPMC-SDS and NaCMC-(HPMC-SDS) take place. The interactions were investigated by carrying out detailed conductometric, tensiometric, turbidimetric, viscosimetric, and rheological study. The interactions may result in coacervate formation as a result of incompatibility between NaCMC molecules and HPMC/SDS complex, where the ternary system phase separates in HPMC/SDS complex rich coacervate and NaCMC rich equilibrium solution. By tuning the interactions in the ternary system coacervate of controlled rheological properties was obtained. Thus obtained coacervate was deposited at the surface of dispersed oil droplets in emulsion, and oil-content microcapsules with a coacervate shell of different properties were obtained. Formation mechanism and stability of the coacervate shell, as well as stability of emulsions depend on HPMC-NaCMC-SDS interaction. Emulsions stabilized with coacervate of different properties were spray dried and powder of microcapsules was obtained. Dispersion properties of microcapsules, and microencapsulation efficiency were investigated and found to depend on both properties of deposited coacervate and the encapsulated oil type.

Chapter 13 - Natural polysaccharides are produced by animals, plants or microorganisms; a large variety of chemical structures is found and as a consequence a large variety of physical properties is available. This chapter focuses on water soluble polysaccharides from different origins; their chemical structures are given as well as their macromolecular characteristics. The selected polysaccharides presented in the following are: alginates from seaweeds, gellan and xanthan from bacteria, galactomannans from seeds, chitin and chitosan from crustaceous shells.

Galactomannans, xanthan and chitosans are thickening linear polysaccharides; the first one is neutral, xanthan is an anionic polysaccharide and chitosan is a cationic polymer in acidic conditions. The main physical properties of these different polysaccharides in dependence with the experimental conditions (temperature, ionic concentrations, nature of counterions…) are described. Considering alginates and gellan, a specific behaviour is observed: physical gelation for which the mechanisms of gelation are discussed in relation with thermodynamic conditions.

The main applications of these different polysaccharides are described in different domains.

At the end, mixtures of two of these polymers are considered: polyelectrolyte complexes formed between alginate and chitosan; cooperative interaction between galactomannans and xanthan. These mixtures open the way to new applications.

Chapter 14 - Nutraceuticals are food or food ingredient that provides medical or health benefits. Carbohydrates are one of the most abundant bioactive substances in the marine organisms. Many marine organisms produce carbohydrates with diverse applications due to biofunctional properties. A great deal of research has been conducted in order to assess the possible use of these marine carbohydrates. The marine carbohydrates including glucosamine glycon, chitin, chitosan, fucoidan, carageenan and alginic acid have a host of bioactivities such as antioxidative, antibacterial, antiviral, antitumor, immunostimulatory and anticoagulant. Moreover, these carbohydrates have many beneficial effects and hence could be developed into potential nutraceuticals. This review describes the current progress in the development of marine carbohydrates into nutraceuticals and their applications.

Chapter 15 - The present chapter intends to focus mainly on applications of various carbohydrate polymers such as aloe vera, chitosan, guar gum, starch etc. to design controlled delivery formulations for release of a variety of bioactive agents such as low and high molecular weights drugs and pharmaceutical compounds, agrochemicals such as pesticides, insecticides etc. The chapter also presents a critical review of various studies carried out over recent past particularly in the fields of controlled release technologies using carbohydrate polymers as carriers. A mention of the current state-of-the-art of carbohydrate polymers in biomedical, pharmaceutical and agricultural fields has also been presented.

Chapter 16 - Chitin, the second most abundant structural biopolymer, has a complicated, multi-level supermolecular construction. All chitins are developed from superfine fibrils having diameters in the nano to micro scales, and each nanofibril contains ordered nanocrystallites inserted into low-ordered non crystalline domains. Acid hydrolysis can be used to dissolve away regions of the marginal domains so that the water-insoluble, highly crystalline residue can be converted into a stable suspension by vigorous mechanical shearing action. Highly crystalline chitin nanofibrils, otherwise called 'whiskers', exhibit enormous surface improvement that allows them to impart strength to several materials such as poly(caprolactone), soy proteins, natural rubber, poly(vinyl alcohol), chitosan, and silk fibroin. Apart from their ability to improve mechanical integrity, chitin nanofibrils may interact well with enzymes, platelets, growth factors, and other cell compounds existing in living tissues. Thus, the wound recovery ability and the ability to induce the formation of granulation tissues are obtained so that the applicability of chitin nanofibrils in medical areas is supported. In this chapter, the structural building principles and nanofibril structure of chitin from various sources and the methods of preparation of nanofibrillated chitin are discussed. Biological activities, as well as attempts to modify chitin nanofibril, are subsequently described.

Chapter 17 - In the course of the work on value addition of Indian seaweeds in the laboratory, modifications of seaweed polysaccharides by various methods such as grafting of these carbohydrate polymers with different substrates, blending and cross linking were embarked upon. This has resulted in hydrogel materials exhibiting improved properties and functions. In this article, our earlier works on modification of seaweeds using grafting as well as cross linking with non-toxic genipin, the naturally occurring cross linker, will be discussed including those recently carried out with the polysaccharides of the seaweed species *Chetomorpha antennina*, *Chamaedoris auriculata*, *Grateloupia indica* and *Sargassum wightii* of Indian waters. Galactans, arabinogalatan, rhamno-galacto-ribo-arabinan, polyuronates and other heteropolymers as well as polysaccharide blends were cross linked with genipin in a water-based eco-friendly process yielding new polymeric hydrogel materials. Galactan-polyuronic acid blend was grafted with a polymeric substrate to yield a robust hydrogel. It appears that the genipin cross linked polymeric products with improved properties are best prepared with homopolymers, the heteropolymers are comparatively less amicable to this modification strategy, which produces remarkably improved functional effects. Polysaccharide blends are also a good starting material of choice for the modification work. The cross linking reaction brings about a significant makeover in the chiroptical properties of the polysaccharides. The modified products exhibited considerable thermal stability and pH-responsiveness in aqueous media. All these new properties predispose these modified products to potential applications in various domains including ingestible and non-ingestible ones.

Chapter 18 - During the last quinquennium, chitosan has suddenly gained importance as a plasmid vector to be used in gene therapy in alternative to unsafe viral vectors. The main characteristics that qualify chitosan for this role are its spontaneous reactivity with DNA and oligonucleotides in general, the protection of DNA against enzymatic destruction by nucleases, the slow release of DNA, the capacity to penetrate into tissues by opening tight junctions of cells, besides its full biocompatibility with human cells and its safe assimilation in the body. The chitosan chemistry has been refined in order to impart to chitosan better solubility in physiological media, by acting on its cationicity and hydrophilicity / hydrophobicity, or combining it with poly(ethyleneimine), polyethylene glycol and derivatives, or conjugating it with cell-specific ligands. The transfection efficacy of said modified chitosans was greatly improved compared to plain chitosan. In order to understand the fate of internalized vector-DNA complexes within cells, fluorophores including the green fluorescent protein have been conjugated with DNA or with chitosan. After the exceptionally good performances of chitosans as functional wound dressing materials and drug carriers, it appears that the involvement of chitins and chitosans in gene therapy will develop into an additional exceptional achievement for this class of polysaccharides.

Chapter 19 - Extreme environments, generally characterized by atypical temperatures, pH, pressure, salinity, toxicity and radiation levels, are inhabited by various microorganisms specifically adapted to these particular conditions. These microorganisms, called *extremophiles*, are of significant biotechnological importance as their enzymes (extremozymes) and biopolymers possess unique properties that offer insights into their biology and evolution. The enthusiastic search for novel extremophiles has largely been stimulated by the uniqueness of their survival mechanisms. This uniqueness can be transformed into valuable applications ranging from wastewater treatment to the diagnosis of infectious and genetic diseases. One adaptation strategy of particular importance to extremophiles is the production of extracellular polymeric substances (EPSs) that envelop the cell as a barrier protecting them against environmental extremes such as desiccation, temperature, pressure, salinity, acidity, heavy metals, and radiation. Due to their many interesting physicochemical and rheological properties, these biopolymers possess novel functionality that is generally superior to petrochemical-derived polymers in aspects that embrace biodegradability, and environmental and human compatibility. Consequently, biopolymers of extremophiles are widely used in foods, cosmetics, pharmaceutical products, textiles, detergents, adhesives, oil-recovery from wells, brewing and waste treatment processes. This chapter presents a brief overview of life under extreme environmental conditions. This is followed by a discussion of extremophilic microorganisms and their adaptation mechanisms, and specifically focuses on the production of EPSs and their ecological and physiological functions. The application areas of industrially important EPSs from various extremophilic producer strains are also mentioned.

Chapter 20 - Naturally occurring polysaccharides are of interest in pharmaceutical and cosmetic applications due to their biodegradability, biocompatibility and non-toxicity. Among these polysaccharides, alginate, a linear polysaccharide that is extracted from marine brown algae, is widely used as a particulate carrier for encapsulation, controlled release and delivery of a variety of bioactive compounds to target organs. Due to its bioadhesive, anionic and colloidal properties, alginate can interact with divalent cations or cationic polymers to form hydrogel micro- or nanoparticles that have specificity for mucosal tissues. A particular area of interest is the use of alginate as a shell or matrix material for encapsulation of essential oils. These oils have therapeutic properties that include antibacterial, antifungal, antiviral, antioxidant, and insect-repellent effects, but are insoluble in water, volatile and unstable in certain environments. This has limited development of new formulations and encapsulation of the oil in carriers is required to overcome these problems. Size reduction of the carriers to the nanometer scale greatly improves the efficacy of the delivery system and may allow targeting of the pharmacological activity of the oil to specific organs. This review focuses on an overview of alginate and essential oils, the preparation of alginate matrices from large to nanometer scale, and encapsulation of essential oils in these matrices. The prospects for development of improved alginate nanoparticles as delivery systems for essential oils are discussed at the end of the chapter.

Chapter 21 - Wastes from the food processing industry have some common characteristics such as large amounts of organic materials: proteins, carbohydrates and lipids. The great production of processed vegetable products is generating an increase of the amount of wastes which represent a valuable source of by products such as carbohydrate polymers.

Utilization of by-products may contribute to the efficiency of the processing and also to the sustainability of the environment. Fruits and vegetables are important sources of dietary fiber although their content is lower than the one of cereals. The cell wall matrix is the major fiber source in this type of foods and these fibers are rich in pectins. The carbohydrate composition, molecular weight and physiological properties of these fibers might be influenced by conditions of extraction as well as sources, location and many other environmental factors.

The object of this research was the study of products enriched in carbohydrate polymers and obtained from quince (*Cydonia oblonga* Miller) or red beet (*Beta vulgaris* L. var. *conditiva*). Different methods of obtention which involved dehydration, acid and/or ethanol treatment were assayed and yield, chemical composition, molecular weight, physiological and technological properties of isolated products were stated.

Chapter 22 - In recent years, interesting works have been focused on the amino polysaccharide chitosan-based microspheres. The chitosan microspheres have been applied in diversified fields, such as food processing, water treatment and biological fields. To bring new or improved properties, the chemical modification of chitosan-based microspheres is of rapidly growing interest. After chemical modification, chitosan-based microspheres can be used as functional materials with modified properties, such as adsorption resins, magnetic resins and nanocomposites, for specific end use in food industry. This paper presents a review of the developments in the preparation and applications of chitosan-based microspheres. The main objective of this review is to provide recent information and to show the development trend about chitosan-based microspheres.

Chapter 23 – This chapter reviews the synthesis of amylose-grafted polymeric materials with well-defined structures by chemoenzymatic method, which is the combination of following chemical with enzymatic reactions. As a chemical reaction for the present chemoenzymatic method, introduction of a maltooligosaccharide as a primer, which is an initiating point for the amylose-forming polymerization, to polymer backbones or polymerizable groups is carried out to produce maltooligosaccharide-grafted polymeric materials or macromonomers having maltooligosaccharide components. As an enzymatic reaction, formation of amylose is performed by phosphorylase-catalyzed enzymatic polymerization using α-D-glucose-1-phosphate as a monomer. This enzymatic polymerization is initiated from a meltooligosaccharide as a primer and the propagation proceeds by the reversible reaction to produce amylose. The main-chain backbones of the amylose-grafted polymeric materials describing in this chapter are polystyrene and polyacetylene as organic synthetic polymers, polydimethylsiloxane and silica gel as inorganic materials, and chitin, chitosan, cellulose, and polypeptide as biopolymers.

Chapter 24 - Polysaccharides are one of essential biomacromolecules in nature, which play important roles in life activities. Some of them exhibit various biological activities or have special functions. Moreover, polysaccharides contain reactive groups, such as hydroxyl, amino and carboxylic acid groups. Thus, they may react with some compounds to produce polysaccharide derivatives. Amphiphilic polysaccharide derivatives can self-assemble into stable micelles in aqueous solution, promising as a new carrier for the controlled release of drugs. In order to overcome various barriers which hinder drug delivery, the drug molecules may be conjugated with polysaccharide chains through chemical bonds to form prodrugs. The parent drug can be released through an enzymatic or chemical transformation during the metabolizing process. This article reviews the investigations of bioactive and functional polysaccharides, amphiphlic polysaccharide derivatives and polysaccharide-based prodrugs for biomedical applications.

Chapter 25 - Maize bran and nejayote (a maize processing waste water) generated from tortilla-making industries in Mexico were investigated as source of water soluble feruloylated arabinoxylans. The tortilla industry is important in Mexico since half of the total volume of consumed food is maize. Therefore, maize residues are potential source of these added-value biomolecules as hydrocolloids for the food industry, considering the volume they represent. Both by-products were treated for these polysaccharides extraction. Because of their different nature, the polymers extracted from each byproduct showed different composition, physico-chemical and functional properties. Feruloylated arabinoxylans from maize bran (FAXMB) presented an arabinoxylan content of 74% (w/w), a ferulic acid content of 0.34 μg/mg FAXMB, an arabinose to xylose ratio (A/X) of 0.85, an intrinsic viscosity [η] of 208 mL/g and a molecular weight (Mw) of 190 kDa. Gels were obtained from this FAXMB by laccase covalent cross-linking of ferulic acid leading to the formation of diferulic (di-FA) and triferulic (tri-FA) acid. Gels elasticity increased from 9 to 14 Pa as the FAXMB concentration changed from 2.5 to 3.5 % (w/v), while the di-FA and tri-FA contents remained constant (0.030 and 0.015 μg/mg FAXMB, respectively). On the other hand, feruloylated arabinoxylans extracted from nejayote (FAXN) showed a ferulic acid content of 0.23 μg/mg, an A/X ratio of 0.65, an [η] of 183 mL/g and a Mw of 60 kDa. Gels were obtained from 4% (w/v) FAXN solution, while no gelation was observed at lower concentrations. Gels elasticity increased from 2 to 4 Pa, as the FAXN concentration increased from 4 to 8 % (w/v), while no change in the di-FA and tri-FA contents was registered (0.020 and 0.010 μg/mg FAXN, respectively). The entrapment of insulin or β-lactoglobulin at 0.1% (w/v) in gels at 3.5 % (w/v) in FAXMB was investigated as well. Insulin and β-lacto-globulin did not modify either the gel elasticity or the cross-links content. Protein release rate from gels was dependent upon their molecular weight. The apparent diffusion coefficient was 0.95×10^{-7} and 0.74×10^{-7} cm^2/s for insulin (5 kDa) and β-lactoglobulin (18 kDa), respectively. The results suggest that FAXMB gels can be potential candidates for the controlled release of proteins. Furthermore, recovery of these gums from low-value maize by-products could represent a commercial advantage in comparison to other gums commonly used.

Chapter 26 - There are a number of reports on the use of polarized light to cure severe burns, heal wounds, and treat eczema psoriasis. Illumination with polarized light increases immunological response in peripheral blood. Amazing applications of polarized light have been recently extended to technically important transformations of polysaccharides.

Visible light, particularly linearly polarized visible light (LPVL), has been found useful in transformations of polysaccharides, starches of various botanical origin, such as xylan, chitin, chitosan, and cellulose. There are two features of the application of that source of energy. Thus, on illumination of aqueous suspension of polysaccharides with LPVL the side chains of branched polysaccharides have initially been split, however, on prolonged illumination repolymerization of the split side chains into linear polysaccharide took place. Response of the polysaccharide to the illumination with LPVL depended on crystallinity of the polysaccharides. The effect of the illumination has been stronger in highly crystalline polysaccharide networks.

Illumination of polysaccharides with red and green LPVL showed certain differences in the action of those wavelengths. Green light stimulated depolymerization of the polysaccharide to a higher degree with no effect on repolymerization of split fragments whereas red light was slightly more efficient in repolymerization than in depolymerization. LPVL has been capable of stimulation of hydrolases and cyclases providing acceleration of the enzymatic hydrolysis of amylopectin, chitin, chitosan, xylan and cellulose with relevant enzymes and higher yield of the products of hydrolysis. Depending on polysaccharide and relevant enzyme used, effect of the stimulation with white non-polarized light could be observed but effect of such illumination was always much weaker compared to the effect of LPVL. Illumination of cyclase with LPVL resulted in production α-, β- and γ-cyclodextrins with higher yield and different proportion of three products compared to these available from the process run without stimulation of the enzyme with LPVL.

Stimulation of enzymes with LPVL presents an essential potential in practical applications. It is beneficial to perform such 1 -2 hour stimulation in a small reaction vessel followed by the application of the enzyme into bioreactor without any further illumination.

Chapter 27 - It is directly observed a variety of morphologies of the cereal starch nano-structural units after the heating gelatinization by using atomic force microscope in the atmosphere. According to the observation results, nano-structural units of starch grains can be classified into spherical, ball chain, branched, cyclic, rod-shaped form and so on. On this basis, the authors observed the starch nano-structural units of high-pressure gelatinization, and compared the topology structure differences of cereal starch nano-structural units under different conditions of gelatinization in nano-scaled.

The results showed: cereal starch nano-structural units is intermediates which are composed of natural starch granules, and their topology morphology is not the simple "chain" connections of glucose 1-4 and 1-6 glycosidic bond speculated by classic study, they have more complex composition ways, structural level. Cereal starch of High-pressure gelatinization compared with that heating gelatinization, have different nano-structure patterns; and the same germplasm starch also have different nano-structure patterns after different pressure treatment; therefore, it can be made different gelatinization characteristics of starch nano-materials by different gelatinization methods.

Chapter 28 - Polysaccharides are being used in food and allied industries as texture improving agents, stabilizers, for the preparation of the edible films etc. Plant and seaweed derived polysaccharides suffer lack of assured supply and variations in quality. Microbial exopolysaccharides (EPS) provide a valid alternative. An EPS producing lactic acid bacterium was isolated from cabbage and identified as *Lactobacillus* sp. CFR-2180. Production of 22 g/L of EPS in 24 h at 30°C was noticed. The EPS had 65% total carbohydrates, 0.7% protein, 10% uronic acid and 2.0% moisture. Analysis by gas chromatography revealed that the EPS is a heteropolysaccharide with the presence of mannose, galactose and glucose in a ratio of 1:7:5, respectively. Gel permeation chromatography and HPLC analysis of the EPS indicated presence of multiple peaks with molecular weight ranging from 1.8×10^4 to 2.5×10^6 Da., confirming the heterogeneity of the EPS. The results of the preliminary characterization of the EPS indicated that it is a new EPS that has not been reported earlier.

Chapter 29 - The article presents an overview of the latest advances in investigations about the development of polysaccharide-based intelligent antitumor drug delivery. Biodegradable, non-toxic and stimuli sensitivity nature of many kinds of polysaccharide encourages its potential use as a carrier for drug delivery system. Besides, it is reported to possess many biological activities, such as antiviral, antitumor, antimicrobial and anticoagulant activities. The innovative idea of incorporating polysaccharide to "intelligent delivery" had motivated the development of nano drug carriers with a triggered release in response to specific external or internal stimuli. Especially, acidic changes are characteristic signals for treating solid-tumors, since the relatively acidic extracellular pH is a distinguishing phenotype of solid tumors from surrounding normal tissues, and more acidic conditions are also encountered in endosomes once the micelle or nanoparticle enters the cells via endocytosis pathways. Base on this idea, quite a few intelligent polysaccharides based polymeric nanocarriers have been exploited to date. This paper summarized innovative ideas polysaccharide-based intelligent antitumor drug delivery, such as chitosan based pH-sensitive micelle systems loaded Paclitaxel, chitosan-alginate multilayer microcapsules as drug delivery vehicle, cholesteryl-bearing pullulans nanogels trapping hydrophobic molecules (antitumor drugs), etc. The paper also contained its developments in the past few decades. Meanwhile, it highlights recent progress of pH sensitive nanosystems developed in our research group mainly about preparation, characterization and biological evaluating of chitosan and dextran based super pH sensitive nanoparticles loading antitumor drugs and introduced previous misdirections and the existing research directions. This article also pointed out prior errors and problems facing in the experiments, one step further investigated the trends in this field.

Chapter 30 - At present, with the rapid development of starch industries, there is a need to expand the breeds of starch, to look for excellent starch resources to meet application requirements in different fields. The mesoscopic scale and form of starch directly effect food quality, color and biological titer. For example, the amylopectin starch structure of cereal starch determines the nature of the material, and also the strength, flexibility and scope of use of starch environmental protection material. Research on all kinds of topology structures such as the column, chain, and ring of starch nano-structural units, obtain the relationship between cereal food quality and the form of starch nano-structural units, provide micro-scale reference for selecting high-quality breeding; in this indicator, successfully developing specialty corn and wheat germplasm, it was found that high-branched-chain corn and wheat products triggered a sense of unique food, having a quality specificity mechanism such as food rheology and so on.

Waxy wheat, a new breed of wheat varieties, is about to realize commercial cultivation. Its starch can be applied to industrial production, and industrial application must understand the physical properties. Compared with traditional wheat, the research on waxy wheat is just in the initial stage. Only part of the nature of waxy wheat starch is studied, but there is no further research on the structure and application of starch. The study, through system and in-depth researching on a variety of physical and chemical properties and nano-structure units, comparing the similarities and differences with common wheat starch, waxy corn starch and other commonly used industrial starch, provides a theoretical foundation for waxy wheat starch applications in industry. The results show that in the physical properties, the waxy wheat starch has low gelatinization onset temperature, a large gelatinization range and low gelatinization endothermic enthalpy change; there are a high peak viscosity, a moderate low viscosity and cold plastic viscosity, the larger collapse of the value and high viscosity of the anti-aging properties in gelatinization processing; the gel surface formatted is brittle, easily broken, the smaller internal hardness, the smaller adhesion and good flexibility. If played by external force, it is easier to restore to the original shape. After the gelatinization of its starch, it has higher transparency, water-holding capacity and moderate apparent viscosity, and antifreeze-thaw stability, viscosity shear stability and viscosity stability is the very best. In general, a variety of physical and chemical characteristics of the waxy wheat starch are similar to that of potato starch.

The research on Waxy starch is helpful to the huge macromolecular level, providing references for the application and selection of food ingredients and starch materials, guiding the effective application of starch resources, resolving the scientific questions, for example, whether this reflects the starch grain varieties characteristics, genetic characteristics and nutritional characteristics, material characteristics and so on.

Chapter 31 - Zein is the major storage protein of maize, which is widely used environmentally for packing-materials in food engineering. In this paper, nano-structures of waxy maize zeins were investigated in virtue of atomic force microscopy (AFM), and morphological properties of nano-particles composing waxy maize zein film were analyzed.

Chapter 32 - Mushrooms along with other fungi belong to the Myceteae Kingdom. Mushrooms have a very diverse structural morphology that they exist as aerial fleshy fruiting bodies, vegetative filamentous mycelia and underground nonfleshy sclerotia. The differentiation of all these structures involve very complicated fungal morphogenesis and metamorphosis that are related to cell wall synthesis and metabolism (Bartnicki-Garcia, 1999; De Groot et al., 2005). With such unique characteristic, mushrooms become a rich source of carbohydrate polymers that are derived from fungal cell wall formed at different morphological stages (Zhang et al., 2007). Unlike carbohydrate polymers obtained from cell wall of higher plants, mushroom carbohydrate polymers are mainly non-starch polysaccharides with beta-glucan-chitin complex and mannoproteins (Bartnicki-Garcia, 1970). Very large structural variations and content of these mushroom carbohydrate polymers exist among the different developmental stages of the mushrooms (Zhang et al., 2007). Mushroom carbohydrate polymers have been known for their bioactive functions such as immunopotentiating, antitumor, antioxidant activities of which their mechanisms are not fully understood (Wasser, 2002; Cheung, 2008; Ooi, 2008). Recently, there is a growing popularity of developing mushroom carbohydrate polymers as functional foods (Chang, 2008). The success of such application requires active research.

Chapter 33 - In this chapter selected examples of metal ion separations with polymeric macrocycles such as crown ethers, calixarenes, resorcinarenes, calixcrowns and cyclodextrins, reported in recent literature, are presented. Particularly, the use of those polymers in separation processes such as ion flotation, solvent extraction as well as transport across liquid and polymer membranes is shown. First, selected examples of crown ether polymers variety cross-linked as metal ion carriers are described, then selectivity species by donor sites bonding and coordination are characterized.

Selected calixarene and calixcrown polymers as ligands of metal ions are described showing their possible applications, especially in the aspect of the separation of toxic metals ions.

. Other macrocyclic compounds such as cyclodextrins (CD) can be also polymerized and then used as ion carriers for transport of metal ions from aqueous solutions. The hydrophobic CD polymers have been used as ion carriers for separation of transition metal cations from dilute aqueous solutions by transport across polymer inclusion membranes. Recent developments of the CD polymers application in sorption processes of heavy metal ion from aqueous solution will be also presented in this chapter. It is also shown that hydrophilic, water