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# Chitin and Chitosan

## PART II. APPLICATIONS OF CHITOSAN*)

**Summary** — A review covering 131 refs. shows the applications of chitosan, *i.e.*, in water treatment, pulp and paper, medical and pharmaceutical materials, cosmetics, biotechnology, agriculture, food and feed additives, textile and membranes. Attention was focused on use of chitosan in papermaking. Commercial chitosan was described, with its various application forms [microcrystalline (MCCh), beads and membranes, chitosan fibres and textile containing chitosan].
**Key words:** chitosan, application, useful forms.

Commercial chitosan is available as flakes [2], powder [3] as well as processed products like films or membranes [4—6], beads or microcapsules [7—9], fibres [10—12] and as well as a new form of this biopolymer, *i.e.* microcrystalline chitosan (MCCh) [13—15]. Applications of chitosan and its derivatives are presented in Table 1 [16—71].

**Table 1. Applications of chitosan**

| Fields of application | Examples |
|---|---|
| Water treatment | Removal of metal ions, pesticides, phenols, radioisotopes [7, 16—19], flocculant/coagulant, protein [20], dyes [21], amino acids [22], filtration [23], |
| Pulp and paper | Surface treatment [24], photographic paper [24], carbonless copy paper [26], purification of water wastes, wet-strength improve agent and chitosan-coated papers [27] |
| Medical and pharmaceutical materials | Bandages, sponges [28—80], blood cholesterol control [31, 32], tumor inhibition [33, 34], membranes [35], dental/plague inhibition [36], skin burns/artificial skin [37], contact lens [38], control release drugs [39, 40], bone disease treatment [41], surgical sutures [42] |
| Cosmetics | Make-up powder [43], nail polish [44], moisturizers, fixtures [44], bath lotion [44, 45], face, hand and body creams [44, 45], toothpaste [45], foam enhancing [45] |
| Biotechnology | Enzyme immobilization [4, 22, 46—49] protein separation [50], chromatography, cell recovery [51], cell immobilization [52], electrodes and sensors [53, 54] |
| Agriculture | Seed and fruit coating [16, 55, 56], leaf coating [55, 57], hydroponics/fertilizers [58], controlled agrochemical release [59], fertilizers and fungicides [60] |
| Food and feed additives | Removal of dyes, solid, acids [61, 62] preservatives and antioxidants [63], color stabilization [64], clarification and de-acidification of fruits and beverages, reduction of lipid adsorption, natural flavor extender, texture-controlling agent, emulsifying, thickening and stabilizing agent, livestock and fish-feed additive, dietary fibres [16, 42, 65] |
| Textile | Sanitary fibrous materials, surgical threads, textile material |
| Membranes | Reverse osmosis [69], permeability control [70], solvent separation [5, 71] |

### COMMERCIAL CHITOSAN

Commercial chitosan is usually offered as flakes or powder. Products of various companies differ in purity, granulation, color, *DD*, average molecular weight, and solubility.

This product may contain insoluble, highly *N*-acetylated fractions, which derive from the core of the particles due to the heterogeneous deacetylation. GlcNAc in the acid-soluble fractions is randomly distributed, whereas the insoluble fractions contain relatively long blocks of *N*-acetylated units [72].

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*) Part 1 — see [1].

The Protan Lab. Inc. (USA) offers premium industrial grade of chitosan with prices ranging from 16 to 25 USD/kg, whereas industrial grade is available from 15 to 20 USD/kg [73]. Heppe GmbH (Germany) offers technical chitosan with various physicochemical properties at price not lower than 5 USD/kg [74]. The Silver Sea Marine Products (India) offers industrial grade chitosan at a price higher than 30 USD/kg [75], and Japanese companies at prices not lower than 30—40 USD/kg [76], whereas the Sea Fisheries Institute, Gdynia (Poland) offers krill chitosan from small-scale production at prices not lower than 70—100 USD/kg [77]. The potential markets for chitin and chitosan are Japan, USA, UK, France and Germany. The market in the year 2000 was projected to be worth 2 billion USD. Japan is considerably advanced in the technology and commercialization of chitosan — the market in this country absorbs about 600—700 tons chitosan per year [78].

Specific properties of the commercial chitosan flakes distributed by Heppe GmbH (Germany) are shown in Table 2.

**Table 2. Typical properties of commercial chitosan manufactured by Heppe GmbH (Germany) [12]**

| Degree of deacetylation, % | 75—80 | 80—85 | 85—90 | 80—85 | 85—90 | 85—90 | > 90 | 85—90 | < 85 |
|---|---|---|---|---|---|---|---|---|---|
| Viscosity, cps | 200—300 | 500—600 | 500—600 | 800—1000 | 600—800 | 400—600 | 150—200 | 200—300 | 100—150 |
| Water content, % | < 10 | < 10 | < 10 | < 10 | < 10 | < 10 | < 10 | < 10 | — |
| Ash content, % | < 0.5 | < 0.5 | < 0.5 | < 0.5 | < 0.5 | 0.5—1 | 0.5—1 | < 1 | 1 |
| Color [Gardner] | — | — | < 2 | < 2 | — | — | < 2 | < 2 | — |
| Heavy metals, ppm | < 30 | < 10 | < 10 | < 10 | < 10 | < 10 | < 20 | < 20 | — |
| Calcium, % | <1 | < 1 | < 0.5 | < 0.5 | < 0.5 | 0.5—1 | 0.5—1 | 0.5—1 | — |
| Protein, % | 1.0—2.0 | < 0.5 | < 1 | 0.5—1 | 0.5—1 | < 1 | 0.5—1 | 0.5—1 | — |

## CHITOSAN BEADS

Chitosan beads are usually prepared by dropping high-viscosity chitosan salt solutions (acetate, maleate, citrate, chloride, *etc.*) into a basic solution with slow agitation [79, 80]. The diameters of drops as well as the stream of solution control diameter of the beads. Chemical and mechanical behavior of beads (solubility, mechanical resistance, and sorption behavior) are enhanced by crosslinking with bifunctional compounds [81], such as glutaraldehyde [9, 52, 82, 83], glyoxal [83], terephthaloyl chloride [84], hexamethylene diisocyanate [84].

The beads may be applied to the recovery of liquid wastes, heavy metal ions [16, 61], as chromatographic support [85] or for immobilization processes [46]. Interesting forms of chitosan beads manifesting a magnetic behavior [86] are prepared by the addition of iron oxide (magnetite) before bead formation. Such beads are more easily recovered from fermentation baths and may be used again by means of multiple treatments.

The preparation of cross-linked chitosan microspheres coated with anionic polysaccharides or lipids for drug delivery systems has been reported [87]. The idea of the layer coating using chitosan and its anionic derivatives was applied for preparation of polyelectrolyte micro- and nanoencapsules [88]. Encapsulation may be useful for preparation of drug with controlled release and as a protein carrier or for the preparation of non-viral vectors [89].

## CHITOSAN FIBRES AND TEXTILE CONTAINING CHITOSAN

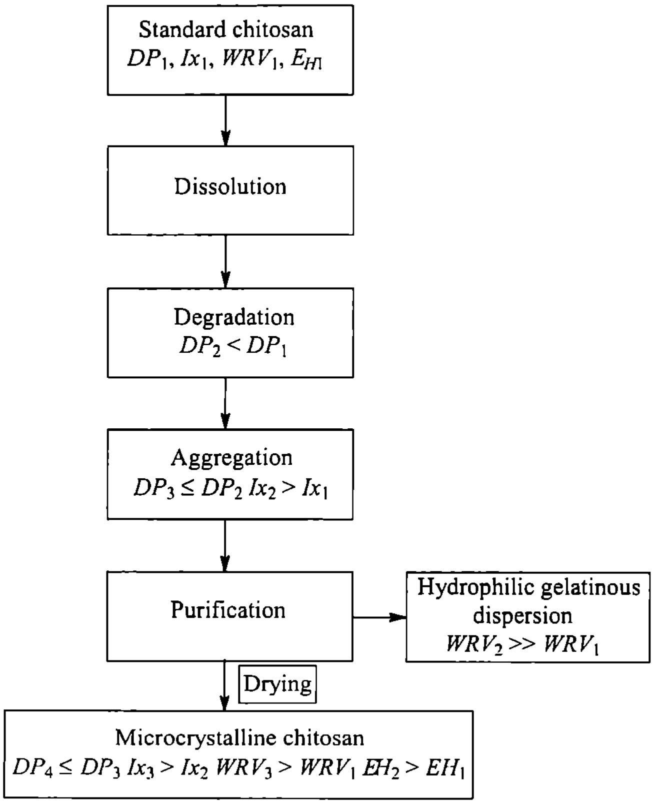
Chitosan fibres are prepared according to several methods [66—68], but most frequently an acetic acid solution of chitosan for the spinning process is used. Mechanical behavior of fibres is improved by cross-links with the bifunctional compounds, similar as for films and beads. Prepared fibres showed better ability to use most commercial conventional chitosan, continuous or staple forms, controlled biodegradability and bioactivity, and were prepared by relatively simple technology. However, fibres containing chitosan are usually friable [11]. The application of special additives both to the spinning solution and coagulation bath allows to controll a modification of the supermolecular structure of chitosan and, consequently, to modify the biodegradability and bioactivity of fibres [90].

The possibility to coat textile fibres (natural or man-made) with chitosan by means of impregnation improves the mechanical properties of such treated textiles; their staining behavior, water resistance, electroconductivity, and adds bioactive, as well as bacteriostatic behavior [12]. The impregnation of textiles may be processed by spraying, foularding or the introduction of chitosan (in the form of xanthate salts or solid microparticles) to viscose [90].

Use of microcrystalline chitosan (MCCh) gel-like dispersion gives many advantages, such as reduction of the textile coating procedure, absence of chitosan regeneration processes, and reduced liquid wastes after impregnation using chitosan solution [12]. It was reported [88] that the adhesion of chitosan to wool fibre is weaker than to cellulose fibres. This phenomenon depends mainly on the ionic interaction between carboxyl groups of wool and amine groups of chitosan as well as on hydrogen linkages. However, chitosan dissolution in the dye-bath has been found during the process of dyeing. The reaction of hydroxyl groups of chitosan with reactive dyestuff in alkaline medium yields a stable coloration of the impregnated textile. The increase in dyeing intensity of the fabric after impregnation with MCCh gel-like dispersion was noted.

## MICROCRYSTALLINE CHITOSAN (MCCh)

Microcrystalline chitosan is a newly available form of the product, existing as gelatinous water dispersion or powder [14, 15, 91]. It is prepared by the precipitation of polymer from an acidic aqueous solution into a sodium hydroxide solution as a coagulation agent (Scheme 1.).



*Scheme 1. Preparation of microcrystalline chitosan [14] (DP — degree of polymerization; WRV — water retention value; $I_x$ — index of crystallinity; $E_H$ — energy of hydrogen bonds detected by FTIR [92].*

The gelatinous dispersion, with much higher WRV coefficient and higher crystallinity than initial chitosan is a consequence of this process. In principle, there is some similarity to the production of microcrystalline cellulose (MCC) from diluted viscose. However, the formation of MCC by coagulation of cellulose xanthate and regeneration of cellulose is only to some extent comparable to the phenomena, which takes place during MCCh aggregation. The process of MCCh preparation by the coagulation under alkaline conditions involves a number of phenomena, such as neutralization, coagulation, and aggregation of polymer chains. These processes lead to the specific behavior of the product and are mainly responsible for its molecular and supermolecular structure differing from the raw substrate. It may be assumed that the properties of MCCh depend on several parameters of the preparation process, such as properties, origin, conditions of the degradation process, conditions prevailing during aggregation procedures, parameters of drying, as well as the presence of electrolytes [12].

Several useful properties of MCCh are unique and partially resulting from the standard chitosan used for its manufacture, such as:

— high water retention behavior (WRV ranged from 500 to 5 000%),

— high adhesiveness,

— ability to form powerful hydrogen bonds,

— chelating and sorption properties,

— direct film-forming behavior (film preparation directly from aqueous dispersion of MCCh),

— high stability of aqueous dispersion,

— controlled biodegradability, higher susceptibility to hydrolytic degradation,

— non-toxicity,

— good miscibility,

— high tolerance for solvent exchange,

— high chemical reactivity, bioactivity, including bacteriostatic properties, and biocompatibility [11].

The most important and extraordinary property of MCCh seems to be its direct film-forming behavior just from aqueous dispersion [93]. Films obtained in this process show excellent adhesion to different types of surface, good elasticity, and water-resistance [92, 94]. Microcrystalline chitosan, especially in the form of gel-like dispersion, can be effectively applied as an auxiliary agent with bioactive action to modify cosmetics: shampoo, liquid soap or bath foam. It was applied as a thickener and viscosity regulator, softener, stabilizer, skin and/or hair-protecting agent, bioactive agent with fungi- and bacteriostatic properties, and as a controlled release carrier [13].

The drawback of standard chitosan application as a binding agent for non-wovens (see section on fibre coating applications) is necessity to carry out the conversion of chitosan polymer salts containing water by treatment with alkali. The use of MCCh solves this dilemma, and with its direct film-forming behavior enhances the properties of non-wovens [93]. The direct introduction of MCCh to viscose has solved the problem of controlled bioactivity of the modified viscose fibres [12]. Special properties of such fibres make them suitable for fabrics and non-wovens in standard applications as well as in special uses in medical, pharmaceutical or cosmetic products.

At pH = 7.0, standard chitosan is relatively low effective for the chelation of metal ions, sorption of dyes and pigments and ion exchange, but the application of MCCh shows an increase in the range of pH in which MCCh is a sufficient chelating agent. It was found that MCCh is effectively combined with metal ions in media beyond pH=6.5 and remains effective at lower pH, similarly to a standard chitosan [95].

Enhanced sorption behavior of MCCh permits to incorporate bioactive compounds into the chitosan structure, as well as to prepare suitable controlled release (CR) forms, playing an important function in medical and pharmaceutical applications.

The different forms of CR agents showed specific release efficiencies depending on the conditions applied during production [14]. Introduction of Lewis-acid type bioactive compounds proceeds by a solvent exchange process involved in the incorporation of these compounds into the chitosan structure, as well as by forming powerful bonds with the polymer.

The high affinity of MCCh for the bonding of protein has been applied in the preparation of a MCCh complex with casein or keratin using various MCCh:protein ratios. These complexes, especially with casein, show an increase in sorption of water and improvement of direct-film behavior. The above properties have been led to application in preparation of films and as a modifier for improving wet-strength of paper sheets [27, 96].

## CHITOSAN FILMS

An aqueous solution of chitosan salts very easily forms transparent films, which may be regenerated to chitosan films by treatment with an alkali solution. Such films show high water absorbance, biocompatibility and permeability to oxygen, biodegradability, controlled release behavior, high reactivity, electrochemical properties, high strength and elasticity [97]. However, flexible and transparent films are about as water permeable as cellophane films, whereas their conductivity is similar to that of organic crystals. The possibility to form the films directly on the skin makes it applicable in treating wounds and burns [98]. The change in the behavior of films by the introduction of bioactive components enhances its application as a useful material in medical agent preparations, characterized by higher durability and susceptibility to degradation by human enzymes. The crosslinking properties of chitosan film are used for improvement the film behavior and for the introduction of modifying agents. However, such modification causes an increase in permeability and a decrease in mechanical properties, especially elasticity [99, 100]. Water vapor transmission rate of calcium chloride cross-linked films containing glutamate and alginate linearly decreases with the increase in concentration of crosslinking agents [101]. Muzzarelli [4] prepared chitosan films containing collagen or gelatin, increasing their elasticity by treatment with tyrosinase in the presence of phenol. In addition, crosslinking with poly(glutamic acid) to increase the polyionic behavior as well as water sorption parameters was examined [102]. The chitosan-cellulose composite films based on blends of microfibril cellulose and chitosan show a high dry and wet tensile strength, completely decompose in soil or seawater, and manifest relatively high biodegradability by *Pseudomonas* sp. H-14 producing cellulase [103]. This type of combined film can be used as a rolled composite film, binder film for dry non-woven fabrics, biodegradable foams, and in medical material such as wound dressings.

The use of *N,O*-carboxymethylchitin films to preserve fruits over prolong periods has been applied in Canada and USA because of higher film permeability to oxygen and water, depromoting fungal growth [104, 105]. Many authors announced the preparation of chitosan laminated films with various polysaccharides such as: pectin [106], methylcellulose [107] or blends with viscose rayon [108].

MCCh is distinguished by its film-forming behavior directly from its aqueous dispersion, making the preparation process of film more direct, faster, and cheaper, finding important use in medicine. The film formed from MCCh gel-like dispersion maintains the behavior of MCCh [11].

Application of a plasticizing agent, which interferes with the hydrogen bonds between the polymer chains stimulates formation of MCCh films. This phenomenon increases the flexibility of the chains and facilitates their relocation. Improvement in the degree of chain ordering and the hydrogen linkages between the plasticizer and biopolymer hydroxyl group during removal of water results from the tight packing of the macromolecules [109]. The addition of low molecular weight compounds, *i.e.* glycerol, causes augmentation of the elastic behavior of formed films; however their crystallization at low temperature is one of the disadvantages of glycerol, limiting the application of plasticized chitosan films at low temperature.

The structure of films formed from chitosan significantly differs depending on their origin. The existence of more ordered areas and amorphous regions was confirmed. Films with low degree of crystallinity formed from high-molecular polymers show better mechanical durability.

## CHITOSAN IN PAPERMAKING

The use of chitosan and its derivatives to improve so-called wet-strength of paper sheets is more specific type of application.

Standard paper is held together by hydrogen bonds [24, 110, 111]. The bonds must span the range between separate segments of fibres that together make the interfibre bonding area. Although several water molecules may or may not be an integral part of the interfibre linkage, it is certain that presence of larger quantities of water has a disruptive effect on paper cohesion. This could be explained by the fact that excess water can disrupt the existing interfibre linkages. Hydrogen bonding sites on the fibre surface are then fully occupied by water molecules, which are in turn hydrogen bonded to such a large excess of free water that the fibres can now be regarded as linked by a macroscopic fluid bridge. The weakness of this bridge is manifested by the so-called wet strength of paper [112].

A number of polymeric materials have been developed in attempt to improve this parameter. These include urea- as well as melamine-formaldehyde condensates, epoxy-containing polyamides, cationic polyacrylamides, and polyethyleneimines. Polyethyleneimines (PEI) [113] are the most extensively investigated wet strength agent. These high molecular weight molecules are globular polyamines containing primary, secondary and tertiary amino groups. However, they do not show film-forming behavior and exhibit little tensile strength in bulk. Cellulose pulp containing many acidic sites due to the oxidation of this polymer or to the presence of lignin or hemicellulosic residues can be efficient in forming ionic bonds and hydrogen linkages with the basic polyethyleneimine. It is assumed that an excess of water will not rupture these ionic bonds. In addition, covalent bonds between aldehyde and amino groups may be formed by Schiff's bases, leading to amide groups derived ammonium salts at high temperature [95]. Other derivatives, as aldehydes, formaldehyde, glyoxal, and polyacrolein impart wet strength obviously due to the formation of acetal linkages. The application of small bifunctional compounds, *e.g.* toluene diisocyanate, causes the formation of carbamate linkages on exposure to the alcoholic hydroxyl group of the cellulose fiber surface [114]. Other derivatives used to improve the mechanical properties of paper are shown in Table 3.

Moreover, the addition of a polycationic substance results in bridging flocculation of anionic cellulose fibres, which are separated by shearing forces to obtain the bridge stabilized system. If additional anionic agent is added (*i.e.* first or second generation colloidal silica system), the particles are flocculated again improving fibre and filler retention, giving better dehydration rate and mechanical strength of paper [115].

A potential additive should meet the following conditions:

— be soluble in an aqueous solution for easy application within a conventional papermaking system,

— be substitute of a cellulose with regard to efficiency of retention,

— be compatible regiospecificially with cellulose surface and not cause disruption of conventional hydrogen linkages,

— have large enough molecular weight to give facilitate creation of interfibre bonds,

— be film-forming to offer cohesive resistance to rupture,

— contain a functional group capable for ionic or covalent reaction with cellulose pulp during the formation of paper,

— be linear to allow accessibility to all functional groups,

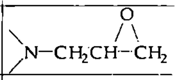
— not contain any potential chromophoric groups which later impart color to the sheet,

— be non-toxic and biodegradable in order to facilitate compliance with environmental regulations,

— not create problems in the repulping and recycling of paper [113].

Chitosan meets all of the above-mentioned conditions. The use of chitosan in the papermaking industry was first reported in 1936 [113], and several authors have continued to pay attention to this area [113, 117—119]. The use of chitosan as a binding agent of fibre strands of microbially produced cellulose is another interesting application. The cellulose has been synthesized by certain

**Table 3.** The chemistry of wet strength treatment for paper [116]

| Treatment | Nature of crosslinking group | Structure of crosslinking group |
|---|---|---|
| Heat | Hydroxyl<br>Carboxyl | $-CH_2OH$<br>$-COOH$ |
| Parchmentizing ($H_2SO_4$) | Hydroxyl<br>Carboxyl | $-CH_2OH$<br>$-COOH$ |
| Urea-formaldehyde resin | Methylolamide | $-NHCH_2OH$ |
| Melamine-formaldehyde resin | Methylolamine | $-NHCH_2OH$ |
| Glycidylated polyaminoamide | Glycidylamine |  |
| Polyethyleneimine | *p*-, *s*-, *t*-amine | $R_2N$, $R_2NH$, $RNH_2$ |
| Cationic polyacrylamide | Amine | $-NH_2$ |
| Protein | Amine<br>Carboxyl | $-NH_2$<br>$-COOH$ |
| Carboxyled polymers | Carboxyl | $-COOH$ |
| Formaldehyde | Aldehyde | HCHO |
| Glyoxal | Aldehyde | CHOCHO |
| Polyacrolein | Aldehyde | -CHO |
| Dialdehyde stretch | Aldehyde | -CHO |
| Diisocyanates | Isocyanate | -NCO |
| Inorganic hydroxides | Inorganic hydroxyl | $-M(OH)_n$ |
| Neoprene latex | Chlorine | =CHCl |

strains of microorganisms of the genus *Acetobacter* and the effective binding of fibres or fragments of material by chitosan resulted in improving wet and dry tensile strength of bonded material [120]. Presence of chitosan within the paper coating results in an improved friction of paper [121]. The effect of chitosan acetate and hydrochloride and water-soluble chitin addition to pulp suspension subjected to sizing with alkylketene dimmers (AKD) in alkaline papermaking process were studied [121]. Chitosan salts show the most significant effect on sizing and AKD retention. Increase in cationic surface charges of AKD emulsion particles by chitosan molecules may result in higher retention of AKD. Chitosan as 1 wt. % aqueous solution in acetic acid was used in the past as a surface treatment of various papers such as newsprint, printings, maps, *etc.* [123] to increase their breaking strength, burst resistance, and folding endurance without any effect on brightness [124]. Chitosan is a compatible binder with paper pulp and looks to be superior for polyacrylamides as a film former. It is also useful as a filler in the preparation of coatings for lithographic paper plates, which accept and hold water and ink [125]. Clays coated with chitosan have been used in paper manufacturing to increase printing capacity. Softwood bleached kraft pulp slurries have been mixed with chitosan salts and epoxidized polyamides to prepare paper with good dry and wet strength. Chitosan is also used as a flexibilizer of paper sheets applied for the production of packing materials [126] comprising core layers of paper or paperboard or a polymer [127]. A barrier layer of polyvinyl alcohol and/or chitosan is placed between the core layer and outer layer, preferably containing plastic polyethylene.

The special quality of moisture holding with cationic behavior of this biopolymer increases the yield of anionic paint sprayed during electrostatic painting of wood-based materials. In addition, chitosan painted on plywood reacts with formaldehyde released from the glueline to form Schiff's bases [128]. Chitosan is capable to increase the number of interfibre bonds because of its chemical similarity to cellulose. Chitosan can form low energy hydrogen bonds not only between hydroxyl groups, but also between hydroxyl groups and amino groups or between amino groups. This allows to use of non-ionic fibre surfaces efficiently [129]. The idea of microcrystalline chitosan use as a binder for paper is based on its three main attributes, *i.e.*:

— direct film-forming behavior,

— highly adhesive behavior,

— possibility of modification by compounds, which increase biodegradability, bioactivity, biocompatibility, *etc.* [11].

The above behaviors, in connection with special properties of microcrystalline chitosan such as bioactivity, controlled biodegradation or biocompatibility, have created a modern binding agent for paper and non-wovens made of different types of fibres or their blends *e.g.* polyester, polyamide, polyacrylonitryle, cotton, wool, or viscose fibres. The useful properties of MCCh were applied in preparation of paper sheets by means of direct introduction of MCCh with or without protein or by precipitation of MCCh. Application of MCCh as a paper additive at 0.5 to 10 wt. %, also in a presence of protein, resulted in preparation of paper sheets exhibiting improved mechanical properties, especially high relative humidity. Paper sheets containing MCCh with or without protein can be used to prepare unique packing materials showing very good mechanical properties, controlled biodegradability and possible bioactivity [27].

An alternative method of the preparation of paper sheets by the addition of chitosan and its blends with polyvinyl alcohol (PVA) and starch was proposed by Mucha *et al.* [130, 131]. Paper sheets have been prepared by coating formed blotters or by introduction into cellulose pulp 1—10 wt. % of polymeric composition. The product obtained shows remarkably increased breaking strength, when relatively low quantities of PVA were used. Also, better mechanical strength is obtained, if blotters were coated by chitosan salt with or without PVA as compared with the introduction of chitosan salt before sheet formation.

Chitosan in a variety of forms has been applied in the purification of pulp and paper industrial wastewater for removal of lignin, giving yields not less than 90% for removal of black liquor coloring and 70% for the decrease in total organic carbon (TOC) [132].

## CONCLUSIONS

There is an increasing interest in the application of chitosan and chitin in a wide range of the technologies, taking advantage of their special properties such as: biocompatibility, biodegradability, reactivity, non-toxicity, adsorption properties, *etc.* Production costs of chitin and its derivatives continue to be the prime factor limiting more widespread applications of these substances.

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