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Hitozan – vsestransko uporaben biopolimer

Pregledni znanstveni članek

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Izvleček

Hitozan je skupno ime za veliko skupino hitinov, deacetiliranih do različnih stopenj. Sestavljen je pretežno iz 2-amino-2-deoksi-D-glukopiranoznih enot, povezanih z ß-1,4-vezjo. V preteklih tridesetih letih je doživel nesluten razvoj in se uspešno uveljavil na najrazličnejših področjih našega bivanja. Hitozan in njegovi derivati se že s pridom uporabljajo pri čiščenju voda, v farmaciji, medicini, kmetijstvu in prehrambni industriji ter ne nazadnje tudi v tekstilni industriji. Zaradi svojega naravnega izvora in dostopnosti ter kemične strukture, ugodne za nadaljnje modifikacije, pa je to biopolimer, ki nedvomno še vedno ogromno obeta.

Ključne besede: hitin, hitozan, biopolimeri, tekstilna vlakna, plemenitenje, medicinske tekstilije, medicina, farmacija, prehrana, ekologija.

1 Uvod

Zaradi porasta bakterijskih nalezljivih bolezni in bolnišničnih okužb potekajo v zadnjem desetletju intenzivne raziskave z namenom poiskati nove materiale in obdelave, ki bi zagotavljale trajne biološko aktivne učinke ob popolni varnosti za človeka kot potrošnika. Zato je opaziti močen trend iskanja in razvijanja tehnologij, ki temeljijo na uporabi alternativnih naravnih materialov[1–5]. Med naravnimi sredstvi s protimikrobnim delovanjem vsekakor prednjači hitozan. Hitozan je naraven proizvod, pridobljen iz hitina, celulozi podobnega ogljikovega hidrata, ki je osnovna sestavina ogrodja rakov, školjk in drugih lupinarjev. Hitin je polisaharid, sestavljen iz 2-acetamino-2-deoksi-ß-D-glukoznih enot, povezanih z ß-1,4-vezjo. Poleg celuloze je drugi najbolj razširjeni biopo-

Chitosan – a universally applicable biopolymer

Review

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Abstract

Chitosan is a common name for a large group of chitins with different degrees of deacetylation, primarily composed of 2-amino-2deoksi-D-glycol pyranose units, connected with ß [1-4] linkages. In the last 30 years, chitosan has become increasingly used for many applications in our daily lives. Chitosan and its derivates are already being used in water cleaning, pharmacy, medicine, agriculture, food provisions, and the textile industry. Chitosan's natural origin, accessibility, and chemical structure, make it a biopolymer with a favourable future for further modification and application in other areas of industry and commerce.

Key words: chitin, chitosan, biopolymers, textile fibres, textile finishing, medical textiles, medicine, pharmacology, nutrition, ecology.

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Table 1: The content of chitin in some of the organisms [7]. [a] wet body weight; [b] dry body weight; [c] on the weight of the organic part of the cuticle; [d] total dry weight of the cuticle; [e] dry weight of the cell wall

Type	Content of chitin [%]	Type	Content of chitin [%]
CRAYFISH		MOLLUSCA	
Crabs	72.1[c]	Clamshell	6.1
Crayfish	69.1[c]	Oyster shell	3.6
Alaskan shrimp	28.0[d]	Squid (*skeleton*)	41.0
Lobster	60–75[c]		
INSECTS		FUNGI	
Cockroaches (*blatela*)	18.4[d]	*aspergillus niger*	42.0[e]
Beetles	27–35[c]	*penicillium notatum*	18.5[e]
Flies (*true flies*)	54.8[c]	*penicillium crysogenum*	20.1[e]
Silk worm (*bombyx*)	44.2[c]	*mucor rouxii*	44.5[a]
		Fungi (*lactarius vellereus*)	19.0[b]

1 Introduction

The past decade has seen intense research with the goal of finding new materials and treatments that are both permanent and safe for human consumption. Further, these investigations have been especially motivated by the increasing incapability of contemporary methods to treat bacterial contagious diseases and infections in hospitals. All of these factors have directed the search and development of technologies based on alternative natural materials [1–5]. Among the many contemporarily investigated natural materials with antimicrobial features, chitosan is has the most promise. Chitosan is a natural product derived from chitin, a carbohydrate

limer na zemlji [6]. Hitozan je skupno ime za veliko skupino hitinov, deacetiliranih do različnih stopenj. Sestavljen je pretežno iz 2-amino-2-deoksi-D-glukopiranoznih enot, povezanih z ß-1,4-vezjo (slika 1).

V naravi najdemo hitin pretežno v živalskih organizmih kakor tudi v manj razvitih vrstah praživali. V rastlinskih vrstah je hitin zaslediti predvsem v celični steni gliv in plesni, ki za prehranjevanje potrebujejo dušik. Hitinske strukture izvirajo v glavnem iz ektoderma večceličnih živali in oblikujejo značilno zunanje ogrodje nevretenčarjev, medtem ko kolagenske strukture izvirajo v glavnem iz mezoderma celic. Hitin sestavlja več kot 50 % vse organske substance hitinskih struktur. Višje vsebnosti hitina so bile odkrite le v členonožcih, ki so sposobni hitin delno sintetizirati. Raki, mehkužci, žuželke in glive proizvedejo letno okoli 100 milijard ton hitina [8], enega izmed najslabše izkoriščanih virov biomase na zemlji. Vsebnost hitina v posameznih organizmih je predstavljena v

Table 2: The approximate composition of crayfish skeletons' offal in percent /% according to the dry weight [9]

The source of chitin	Proteins	Chitin	Ashes	Fats
Crabs (*Collinectes sapidus*)	25.1	13.5	58.6	2.1
Crabs (*Chinoecetes opilio*)	29.2	26.6	40.6	1.3
Crayfish (*Pandalus borealis*)	41.9	17.0	34.2	5.2
Crayfish (*Cragon cragon*)	40.6	17.8	27.5	9.9
Crayfish (*Penaeus monodon*)	47.4	40.4	23.0	1.3
Lobsters (*Procamborus clarkii*)	29.8	13.2	46.6	5.6
Common snipe	61.6	33.0	29.4	1.4

similar to cellulose, which is the base component of the skeletons of crayfish, mussels, and other shellfish. Chitin is a polysaccharide, composed of combined 2-acetamino-2-deoksi-ß-D-glucosic units, and connected with ß-1,4 linkages. It is the second most common biopolymer on earth, besides cellulose [6].

Chitosan is a common name for a large group of chitins with different degrees of deacetylation, primarily composed of 2-amino-2deoksi-D-glycol pyranose units and connected with ß (1–4) linkages (Figure 1).

In nature, chitin is primarily found in animal organisms, but also appears in less developed species of protozoa. Chitin is also present in vegetal species, primarily in the cell walls of fungi and moulds, whose nutritional cycle requires nitrogen. Chitin structures are derived primarily from the ectoderm of multicellular animals, and compose the typical outside skeleton of invertebrates. Collagen structures originate primarily from mesoderm cells. Chitin constitutes more than 50% of all organic substances in chitin structures. Higher levels of chitin are found only in arthropoda, which are particularly well adapted for chitin synthesis. Crayfish, molluscs, insects, and fungi produce around 100 milliard tons of chitin per year [8], which is one of the weakest exploited sources of biomass on earth. The content of chitin in various organisms is presented in Table 1. The approximate dry weight percent composition of crayfish skeletons' offal is presented in Table 2.

In 1811, a French professor of natural science, Henri Braconnot, discovered that, by treating fungi with hot alkaline substances (1–6 n KOH) a higher quantity of albumin and a mysterious compound containing nitrogen could be produced [10]. He named this compound "fungin" and found it was highly resistant to alkaline substances. In 1825, Odier published the results of his research about insect exoskeletons, wherein he reported that he found a new nitrogen containing substance, which he named "chitin," after the Greek term for a cover or circumference (shell).

In 1859, Rouget succeeded in dissolving chitin with a chemical and heat treatment. In this process, he derived the chitosan, which was so-named in 1894 (Hoppe-Seyler). During his re-

preglednici 1, približna sestava odpadkov ogrodij rakov v deležih glede na suho težo pa v preglednici 2.

Leta 1811 je francoski profesor naravoslovja, Henri Braconnot, ugotovil, da se pri obdelavi gob z vročimi alkalijami (1–6n KOH) poleg večje količine beljakovin pojavlja tudi spojina, ki vsebuje dušik[10]. To proti alkalijam odporno substanco je poimenoval „fungin". Leta 1825 je Odier objavil izsledke svojega raziskovalnega dela na eksoskeletu žuželk, v katerih poroča, da je našel novo snov, ki vsebuje dušik, in jo po grškem izrazu za ovojnico oz. opno, obod (lupino) poimenoval „chitin".

Leta 1859 je Rougetu s kemičnimi in toplotnimi obdelavami uspelo raztopiti hitin in na ta način derivatizirati hitozan, ki je dobil svoje ime šele leta 1894 (Hoppe-Seyler). Leta 1930 je Rammelberg pri svojem raziskovalnem delu ugotovil, da sta substanci, dobljeni iz gliv in oklepov rakovic, identični s hitinom. Pozneje sta Purchase in Braum z različnimi načini hidrolize hitina dokazala, da je hitin glukozni amin, leta 1948 pa je Mitsusshima patentiral proizvodnjo glukoznega amina iz oklepov rakovic. V 50. letih prejšnjega stoletja je rentgenska analiza omogočila natančno raziskavo hitina v glivah. Nove tehnologije in razvoj analiznih metod pa so omogočili zanesljivejše študije o hitinu in celulozi v celičnih stenah. V 50. letih prejšnjega stoletja, 140 let po prvih izsledkih profesorja Braconnota, so izšle tudi prve knjige o hitinu [11, 12].

2 Hitin

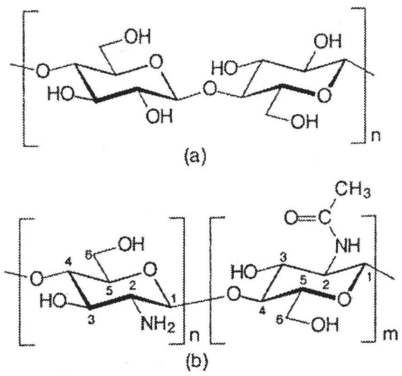

Figure 1: Chemical structures of cellulose (a), chitin and chitosan (b) – chitin mainly consists of monomers in the form of "m" (N-acetyl form), while chitosan, according to the degree of deacetylation, consists mainly of monomers in the "n" form (amine form)[13].

Hitin ima podobno strukturo kot celuloza, le da ima na glukozidnem C2-atomu namesto hidroksilne acetamidno skupino (slika 1). Molekulska masa, čistost in kristalina struktura hitina so v glavnem odvisne od njegovega izvora[14]. V odvisnosti od izvora in od pogojev izolacije hitina je le-ta acetiliran do različnih stopenj. V naravnem hitinu je najmanj eden od šestih ostankov N-acetil-D-glukoznega amina deacetiliran. Podobno je s povprečno dolžino

search in 1939, Rammelberg discovered that the substances that compose fungi and crab skeletons are identical to chitin. Using different methods of chitin hydrolysis, Purchase and Braum later proved that chitin from crab skeletons is a glucose amine. In the 1950s, X-ray diffraction enabled more precise research of chitin in fungi. New technologies and the development of better analytic methods have enabled more precise studies of chitin in cell walls. The first books about chitin were published in the 1950s, 140 years after the initial discovery by professor Braconnot [11, 12].

2 Chitin

Chitin has a structure similar to cellulose, with only one significant difference. Chitin has an acetamide group on the glycol wall C2 atom and not the hydroxyl group, as depicted in Figure 1. The molecular mass, purity, and crystalline structure of chitosan depends on its source [14]. According to the source and the condition of chitin isolation, chitin is acetylated to different degrees. In natural chitin, at least one of the six N-acetyl-D-glucose amine units is deacetylated. Similarly, the average length of macromolecules in chitin is also dependent on its source. The average macromolecule length of crab chitin is 5000 to 8000 monomer units of N-acetyl-D-glucose amine, while fungi chitin is composed of only about 100 units [9]. The length of the molecules decreases in the protein removal process in hot solutions of alkaline substances.

Chitin synthesis in organisms is occurs by the joining of macromolecules by hydrogen linkages between the amine group (–NH) of one molecule and carbonyl group (–C=O) of another. The hydrogen bonds are responsible for the formation of a fibrillar structure and the origin of two polymorphic forms, α and β chitin (Figure 2). α chitin is found in organisms of arthropoda, primarily crayfish. Neighbouring macromolecules are antiparallel and consist of an orthorhombic crystalline cell. In β chitin, synthesized primarily by sea algae (diatomea), macromolecules are in a parallel arrangement and compose a monoclinic crystalline cell. In the past, there have been reports of third polymorphic form of chitin, a γ shape, which pre-

makromolekul v hitinu, ki močno variira in je tudi odvisna predvsem od izvora hitina. Makromolekule hitina rakovic so v povprečju sestavljene iz 5000 do 8000 monomernih enot N-acetil-D-glukoznega amina, v hitinu plesni ali gliv pa le iz okrog 100 enot [9]. Dolžina molekul se med postopkom odstranjevanja proteinov v vročih raztopinah alkalij znatno zniža.

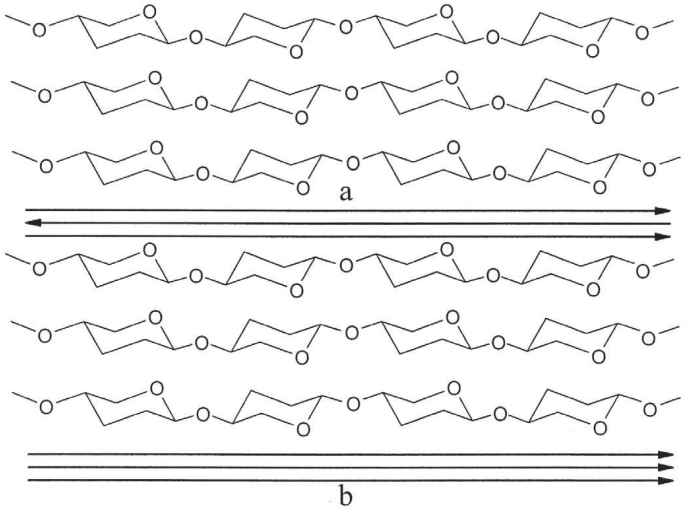

Figure 2: Antiparallel (a) and parallel (b) arrangements of macromolecules of α- and β-chitin [8]

Sintezi znotraj organizmov sledi združevanje makromolekul, ki se med seboj povezujejo z vodikovimi vezmi med aminsko (–NH) skupino ene molekule in karbonilno (–C=O) skupino druge. Vodikove vezi so odgovorne za tvorbo fibrilarne strukture in nastanek dveh polimorfnih oblik, α- in β-hitina (slika 2). α-hitin najdemo v organizmih členonožcev, predvsem rakov, v njem so sosednje makromolekule razporejene antiparalelno in tvorijo ortorombično kristalino celico. β-hitin ima paralelno povezane makromolekule, ki oblikujejo monoklinsko kristalino celico, sintetizirajo pa ga predvsem morske alge (diatomeje). V preteklosti so poročali tudi o tretji polimorfni obliki hitina, o γ-obliki, ki naj bi imela po dve paralelno povezani makromolekuli in eno antiparalelno povezano makromolekulo. Vendar pa prisotnost te oblike ni bila natančneje analizirana in zato ni jasno, ali gre morda le za napake α- oz. β-oblike [8].

Najstabilnejša polimorfna oblika je α-oblika. β-hitin pa lahko ireverzibilno pretvorimo v α-obliko z obdelavo z litijevim tioizocianatom [9]. Vsebnost ene in druge oblike hitina v oklepu oz. skeletu določa njegovo trdnost, prožnost in prepustnost. V α-obliki je količina vodikovih povezav zaradi pravilnosti strukture večja, kar pomeni, da ta struktura v vodi manj nabreka in je slabo prepustna. ß-hitin ima manj medmolekulskih povezav, zaradi česar v vodi bolj nabreka. V splošnem hitin zaradi velike gostote medmolekulskih vodikovih vezi v trdnem stanju ne kaže točke taljenja in je v vodi ter razredčenih raztopinah kislin in baz popolnoma netopen.

V celicah gliv je hitin obdan z ß-glukanom, kar tvori, skupaj z dru-

sumably consists of two paralleled and one anti paralleled bounded molecule. This polymorph has never been closely researched, and so it is uncertain if this polymorph is real, or is actually just a mistaken α or β form [8].

α-chitin is the most stable polymorphic form, while β-chitin can be irreversibly transformed into the α-form with a lithium tio-izocianat treatment [9]. The content both polymorphs of chitin in a shell or skeleton dictates its solidness, elasticity, and permeability. In the α form, the quantity of hydrogen bonds is higher owing to a higher level of structural regularity, a lower permeability, and a strong resistance to swelling in water. ß chitin has a lower content of linkages between molecules, and as such, swells more in water. Generally speaking, because of the high density of hydrogen linkages between molecules in the solid phase, chitin does not show any signs of dissolving in water and dilution in acids and bases.

In fungi cells, chitin is covered with ß-glycol, which together with other polysaccharides and proteins form insoluble complexes in alkaline structures. In crayfish and insects, chitin is bounded into a glycoprotein framework, where it forms complexes with proteins. These complexes are imbued with mineral salts, wax, carotenoids, lipoproteins, and others, which affect their solidness, elasticity, hardness, and permeability. The most important influence on the hardiness of these structures is calcium carbonate and to a lesser degree the calcium phosphate content. In some species of molluscs, the hardiness of chitin structures is enhanced by the inclusion of silicates and iron oxide.

2.1.1 Chitin production

For the chitin production, there are a variety of raw materials available, such as shells of crabs shrimps and prawns (α-chitin), or skeletons of squids (β-chitin). In nature, chitin is covalently bound to other components, and therefore the procedure for its separation from others material is challenging (Figure 3) [8, 15].

This separation involves the removal of proteins with the help of sodium hydroxide or with digestion using proteolitic enzymes such as papain, pepsin and trypsin. Minerals such as calcium carbonate and calcium phosphate can be

gimi polisaharidi in proteini, v alkalijah netopne komplekse. V rakih in žuželkah je hitin povezan v glukoproteinsko ogrodje, v katerem tvori komplekse s proteini. Ti kompleksi so prepojeni z mineralnimi solmi, voski, karotenoidi, lipoproteini itd., kar vpliva na njihovo trdnost, elastičnost, trdoto in prepustnost. Na trdoto teh struktur ima močen vpliv predvsem vsebnost kalcijevega karbonata ali – v manjši meri – fosfata. Pri nekaterih vrstah mehkužcev trdoto hitinskih struktur povečuje vsebnost silikatov ali celo železovih oksidov.

2.1 Pridobivanje hitina

Za pridobivanje hitina so na voljo surovine, kot so npr. lupine rakovic in garnel (α-hitin) ter lignjev in kozic (β-hitin). Ker je hitin v naravi (kovalentno) vezan na druge sestavine, je postopek njegovega izločevanja iz hitinastega materiala dokaj zahteven (slika 3) [8, 15].

Obsega odstranjevanje proteinov s pomočjo natrijevega hidroksida ali pa s presnovo s proteolitskimi encimi, kot so papain, pepsin in tripsin. Minerale, kot so kalcijev karbonat in kalcijev fosfat, je mogoče izločiti s klorovodikovo kislino, pigmente (melanin in karotenoide) pa z obdelavo v 0,02 % raztopini kalijevega permanganata pri povišani temperaturi (T = 60 °C), z vodikovim peroksidom ali pa z natrijevim kloratom (I) [8, 16].

2.2 Hitozan

2.2.1. Pridobivanje hitozana

Razlika med hitinom in hitozanom je odvisna od stopnje deacetiliranja. Shematičen prikaz postopkov pridobivanja hitina in hitozana iz oklepov rakov in rakovic je na sliki 3.

Ime hitozan se navadno uporablja za produkte, pri katerih je stopnja deacetiliranja višja od 70 %. Reakcija deacetiliranja hitina v vročih raztopinah alkalij tudi pri najostrejših pogojih po navadi doseže le 95 % stopnjo. Metode deacetiliranja hitina je natančno opisal že Muzzarelli [17]. Danes se za deacetiliranje hitina uporabljajo različne kombinacije koncentracij raztopin natrijevega ali kalijevega hidroksida (30 do 60 %), temperatur (80 do 140 °C) in časov (do 10 ur) [18]. Vsi našteti parametri morajo biti strogo nadzorovani, saj je od tega odvisna stopnja deacetiliranja, pa tudi molekulska masa produkta, njena porazdelitev in razporeditev deacetiliranih skupin vzdolž polisaharidne verige.

Muzzarelli in sodelavci [20] so predstavili alternativno metodo, ki zagotavlja skoraj popolno deacetiliranje hitina. Metoda predvideva predhodno 24-urno inkubacijo hitina v 50 % raztopini NaOH pri temperaturi 4 °C, nato njegovo ločevanje od topila in mešanje z 10 % raztopino NaOH. Temu sledi segrevanje na 230 °C in zatem naglo znižanje tlaka. Stopnja deacetiliranja ter spremembe v velikosti in razporeditvi molekulskih mas bistveno vplivajo na lastnosti hitozana, kot so na primer topnost v razredčenih kislinah, viskoznost raztopin in biološka aktivnost, ki so izrednega pomena za

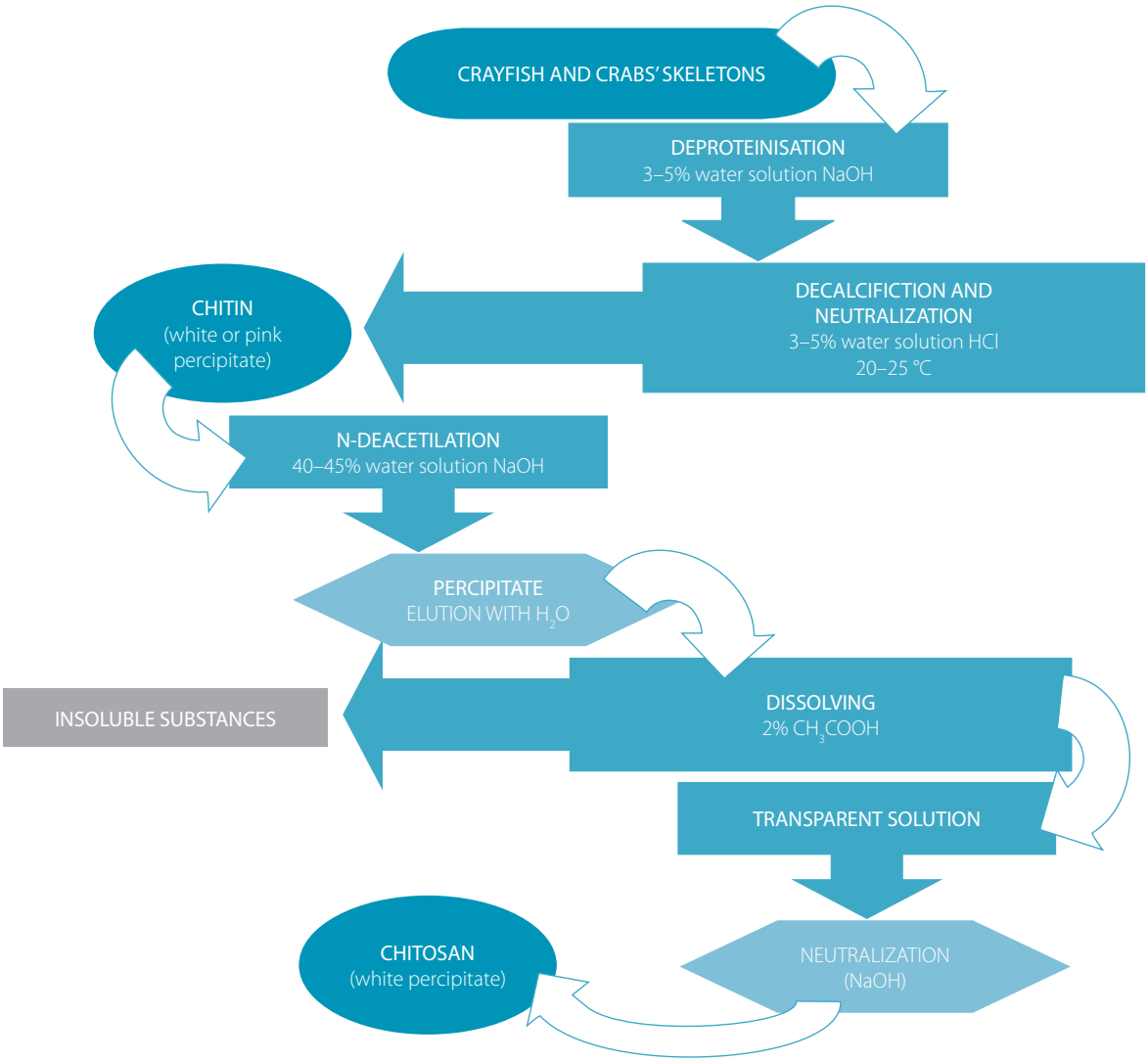

Figure 3: Methods of chitin and chitosan acquisition from the skeletons of arthropods [9, 19]

separated with hydrochloric acid, while pigments (melanin and carotenoids) can be separated with a treatment in 0,02% solution of potassium permanganate (VII) at a higher temperature (T = 60 °C), with hydrogen peroxide or sodium chlorate (I) [8, 16].

2.2 Chitosan

2.2.1 Chitosan production

The difference between chitin and chitosan depends on the degree of deacetylation. Schematic presentation of the chitin and chitosan manufacture procedures from crayfish and crab skeletons is presented in Figure 3.

The name chitosan is normally used for products with a degree of deacetylation higher than

njegovo uporabnost. Vse to kaže na nujnost standardizacije metod in postopkov kakor tudi produktov na tem področju. Zaradi neekoloških postopkov pridobivanja hitozana se vedno več pozornosti namenja nizkomolekularnemu hitozanu, pridobljenemu iz nekaterih gliv, ki je uporaben predvsem v medicinske namene [9, 21].

2.2.2 Fizikalne in kemijske lastnosti hitozana

Kemični strukturi hitina in hitozana sta si precej podobni. Oba polimera vsebujeta reaktivne hidroksilne skupine, vendar je hitozan po navadi manj kristalin kot hitin, zaradi česar je tudi bolj občutljiv za reagente in topila. Za raztapljanje hitina obstaja relativno malo topil, medtem ko skoraj vse vodne raztopine kislin raztapljajo hitozan. Za raztapljanje hitozana se najpogosteje uporabljata metanojska in etanojska kislina. Podobno kot to velja za celulozo, tudi hitin in hitozan nimata tališča, saj se pri segrevanju razgradita še pred točko tališča [8, 15, 22, 23].

70%. The reaction of deacetylation of chitin in hot alkaline solutions usually reaches only a deacetylation degree of 95% even at the most rigorous conditions. Deacetylation of chitin has been discussed in detail by Muzzarelli [17]. Today, the combinations of solution concentrations of sodium and potassium hydroxide (from 30 to 60%), temperatures (from 80 to 140 °C), and time (up to 10 hours) are used for the deacetylation of chitin [18]. All the listed parameters must be closely controlled, since the degree of deacetylation strongly depends on these parameters, also from the molecular masses and their distribution, and the distribution of deacetylated groups along the polysaccharide chain.

Muzzarelli and coworkers [20] have presented an alternative method, which assures an almost complete deacetylation of chitin. The method includes a previous incubation period, lasting 24 hours, of chitin in a 50% sodium hydroxide solution at 4 °C, after that its separation from the solvent and mixing with a 10% NaOH solution, following by heating to 230 °C and a quick lowering of the pressure. The degree of deacetylation and the differences in the size and arrangement of molecular masses have essential influences on the chitosan properties, such as the dissolution properties in diluted acids, viscosity of the solutions, and the biological activity, which are of great importance for its applicability. Standardisation of chitosan manufacturing methods and procedures are a necessity. Owing to unfavourable ecological aspects of chitosan production, more attention is being focused on the usage of low molecular chitosan, derived from fungi, which is used primarily for medical purposes [9, 21].

2.2.2 Physical and chemical properties of chitosan

The chemical structures of chitin and chitosan are very similar. Both polymers include reactive hydroxyl groups. The degree of crystallinity of chitosan is usually lower compared to chitin, which makes it more sensitive to reagents and solvents. There are few solvents that dissolve chitin, while water solutions of acids dissolve chitosan readily. Formic and acetic acid are used to dissolve of chitosan. Similar to cellulose,

Hitin in hitozan sta šibki kislini in zato sta podvržena reakcijam nevtralizacije v alkalnih medijih. Prosti elektronski pari na primarni aminski skupini povzročajo, da je hitozan potencialni nukleofil, ki zlahka reagira z večino aldehidov in tvori imine. Molekule hitozana so močno pozitivno polarne, zato privlačijo negativno nabite molekule.

Čeprav večina reakcij s hitinom in hitozanom poteka predvsem na aminskih skupinah, pa je mogoče tudi, da se hidroksilne skupine selektivno preoblikujejo. Hidroksilna skupina na C6-atomu je bolj reaktivna od tiste na C3-atomu [8].

Molekulska masa naravnega hitina je navadno višja od enega milijona, medtem ko imajo proizvodi iz komercialnega hitozana molekulsko maso med 100 000 in 1 200 000. Med postopkom pridobivanja hitozana ostri pogoji po navadi vodijo do degradacije produktov. Po metodi deacetiliranja po Horowitzu [15], ki predvideva 30-minutno obdelavo hitina pri 180 °C, je sicer mogoče dobiti hitozan s stopnjo deacetiliranja 95 %, vendar pa je povprečna dolžina verig takšnega hitozana le dvajset enot. Na splošno lahko dejavniki, kot so prisotnost kisika, visoka temperatura in strižne obremenitve, povzročijo nadaljnjo degradacijo hitozanskega produkta.

Na topnost hitozana v vodnih raztopinah vpliva predvsem stopnja deacetiliranja, saj je hitozan s 40 % stopnjo deacetiliranja topen v vodnih raztopinah tudi do pH 9, medtem ko je pri 85 % stopnji deacetiliranja topen le do pH 6,5. Primerne so tudi nekatere razredčene anorganske kisline, kot so dušikova, klorovodikova, perklorova in fosforna kislina, vendar le v primeru dovajanja energije v obliki daljšega predhodnega mešanja in segrevanja. Obstaja možnost, da se v dušikovi kislini po raztapljanju polimera pojavi oborina v obliki gela bele barve [15, 19].

Na viskoznost raztopin hitozana vpliva več dejavnikov, kot so stopnja deacetiliranja polimera, povprečje in razporeditev molekulskih mas, koncentracija, ionska moč, pH-vrednost in temperatura. Sprememba pH-vrednosti raztopine polimera pa različno vpliva na viskoznost raztopine v odvisnosti od uporabljene kisline. Viskoznost raztopine hitozana v kislem mediju etanojske kisline se po navadi zvišuje z znižanjem pH-vrednosti raztopine, medtem ko se viskoznost raztopin v klorovodikovi kislini z znižanjem pH znižuje [15, 22].

V primerih, ko so kisline kot substance nezaželene v proizvodih, npr. v kozmetičnih preparatih, zdravilih in hrani, je vodotopnost hitozana nujna lastnost. Dokazano je bilo, da je hitozan, ki ima stopnjo deacetiliranja 50 % in je pridobljen s homogenim postopkom, vodotopen [15]. Raziskovalci so analizirali tudi druge metode za povečanje topnosti hitozana v vodi. Kushino in Asano sta razvila postopek za pripravo vodotopne hitozanske soli [19]. Ta predvideva raztapljanje hitozana v vodi, uravnavanje koncentracije raztopine na 10 %, izparevanje in sušenje pri temperaturi 175 °C. Alternativo za izboljšanje vodotopnosti hitozana predstavljajo različne kemijske modifikacije njegove molekulske strukture.

chitin and chitosan do not have a melting point, since the process of heating them causes them to decompose before melting [8, 15, 22, 23].

Chitin and chitosan are weak acids, and as such, are subject to neutralization reactions in alkaline media. Owing to free electron pairs on the primary amine group, chitosan is a potential nucleophilic, which easily reacts with most aldehydes to form imines. The molecules of chitosan have a high positive polarity and attract negative molecules.

Although most reactions with chitin and chi-

2.2.3 Uporaba hitozana in njegovih derivatov

Od odkritja hitina pa vse do danes se je uporaba hitina in hitozana razširila skoraj na vsa področja raziskav [15]. Iz hitozana je mogoče s kemičnimi modifikacijami pridobiti širok spekter derivatov, ki so uporabni v najrazličnejše namene (slika 4).

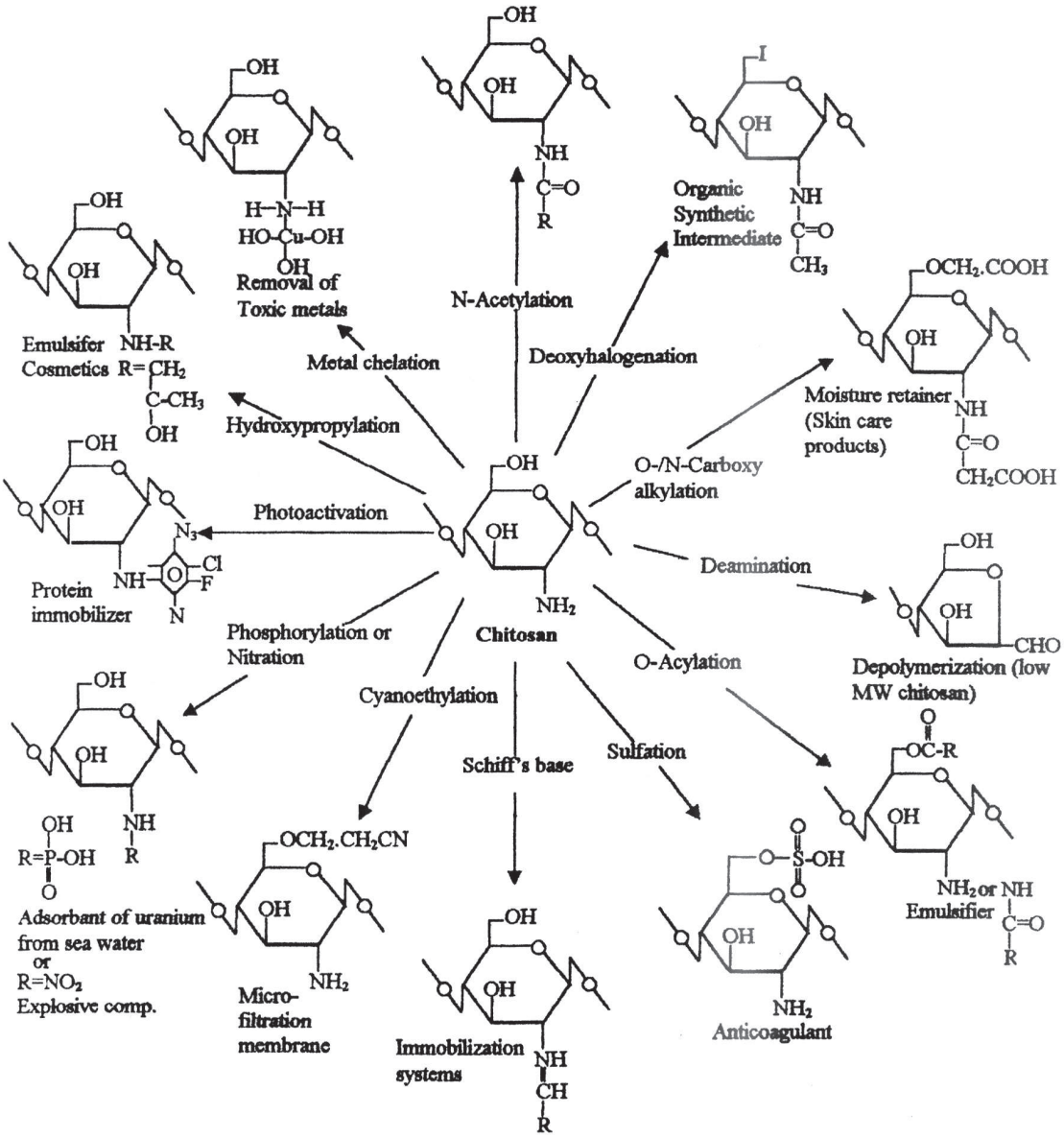

Figure 4: Chitosan derivates [8, 16]

Pri nekaterih izmed teh so odkrili biološko pomembne značilnosti, kot so imunsko specifične, protikoagulacijske, spermicidne, fungistatične, bakteriostatične lastnosti, pa tudi flokulacijske lastnosti [8, 15, 19, 24–30], kar pomeni, da je hitozan uporaben tako na ekološkem (čiščenje odpadnih voda) kakor tudi na prehrambnem, medicinskem in farmacevtskem področju. Na sliki 4 so prikazane možnosti pridobivanja derivatov hitozana in možnosti njihove uporabe.

tosan occur primarily on amino groups, there is also the possibility of selective substitution of the hydroxyl groups. The hydroxyl group on the C6 atom is more reactive than the group on the C3 atom [8].

The molecular mass of natural chitin is usually higher than one million, while the products of commercial chitosan have a molecular mass between 100000 and 1200000. During the production of chitosan, rough conditions usually lead to degradation of products. According to the Horowitz method of deacetylation [15], which assumes a 30 minutes treatment of chitosan at 180 °C, it is possible to manufacture chitosan with a 95% degree of deacetylation, but such chitosan only has an average chain length of about twenty units. Generally speaking, factors, such as the presence of oxygen, high temperature, and shear stress can cause a further degradation of the chitosan product.

The degree of deacetylation has a significant affect on chitosan dissolution in water media, since the chitosan with a 40% degree of deacetylation can be dissolved in water solutions with the pH up to 9, while chitosan with an 85% degree of deacetylation can only be dissolved in solutions of pH 6,5. Ethanoic and methanoic acids are two of the most commonly used acids for dissolving chitosan. Some diluted inorganic acids are also suitable, such as nitric acid, hydrochloric acid, perchloric, acid and phosphoric acid, but only in the case of supplying enough energy in the form of a longer period of mixing and heating. In the case of chitosan dissolution in a solution of water and nitric acid, there is a risk of solid precipitations in the form of a white colour gel [15, 19].

There are many factors that affect the viscosity of chitosan solutions, such as the degree of deacetylation, average molecular masses, concentration, ionic strength, pH value, and temperature. The change in the pH value of the polymer solution differently influences the viscosity of the solution depending on the acid used. The viscosity of the chitosan solution in an acidic medium of ethanoic acid generally increases with the decrease of solution pH, while the viscosity of HCl solutions decreases with decreasing pH [15, 22].

In cases where acids as are not welcome in

Kakovost in lastnosti hitozanskih produktov, kot so čistost, viskoznost, stopnja deacetiliranja, molekulska masa in polimorfna struktura, so zelo spremenljive. Nanje vplivajo pogoji obdelave, predvsem temperatura, pH, koncentracija hitozana, čas trajanja postopka ipd.

Medicina, farmacija in biotehnologija

V zadnjem desetletju farmacevtska industrija podrobno raziskuje možnosti uporabe hitozana na medicinskem področju [31–35]. V obliki raztopine ali gela je uporaben kot bakteriostatično ali fungistatično sredstvo, s katerim je mogoče obdelovati tudi različne trdne površine (tekstilije, folije, membrane). V obliki gela in suspenzije lahko uporabimo hitozan kot t. i. dostavni sistem, to je kot nosilec za počasno in kontrolirano oddajanje zdravil, kar omogočajo prav osnovne značilnosti hitozana kot polikationa [36]. Zdravilna substanca je bodisi fizikalno bodisi kovalentno vezana na aminsko skupino hitozana, velja pa, da se s hitozanske matrice ob stiku s telesnimi tekočinami sprosti [37]. Razvijajo se številni dostavni sistemi s hitozanom, najpogosteje pa hitozan sestavlja mikro- in nanodelce ter liposome, pri čemer se s pridom izkoriščajo bioadhezivne lastnosti hitozana kakor tudi njegova sposobnost, da poveča absorpcijo učinkovin skozi različne sluznice [38]. Hitozan in nekateri njegovi derivati, kot so kvarternizirani N-metil hitozan klorid ali glutamat in mono-N-karboksimetil hitozan, namreč učinkovito povečajo prepustnost različnih sluznic [37, 38]. Hitozan ima majhno peroralno toksičnost, ki je odvisna predvsem od njegove stopnje deacetiliranja, molekulske mase, čistosti in načina aplikacije. Za humano uporabo se priporoča le hitozan najvišje stopnje čistote [38].

Hitozanske membrane lahko uporabljamo kot umetne membrane ledvic, ker jih odlikujejo dobre mehanske lastnosti, poleg tega pa prepuščajo sečnino in kreatinin. Ker ne prepuščajo serumskih proteinov, imajo edinstveno prednost zaščite pred toksičnimi kovinami v krvnem obtoku, kar pa ni odlika drugih membran [32].

Hitozan ima dobre bioadhezivne lastnosti, ki so predvsem posledica tvorbe vodikovih in ionskih vezi med pozitivno nabitimi aminoskupinami polimera in negativno nabito sialično kislino, prisotno v glikoproteinih na površini sluznice. Tiohitozani pa omogočajo še močnejšo bioadhezijo, in sicer zaradi tvorbe kovalentne vezi tiolnih skupin polimera s površinskimi glikoproteini [39].

Pri hitozanu, pridobljenem po postopku sulfoniranja, so odkrili, da ima 15 do 45 % protikoagulacijskih sposobnosti heparina in vitro [8]. Uvajanje uronskih karboksilnih skupin povečuje protikoagulacijsko delovanje hitozana. Dokazano je, da hitozan zavira rast rakavih celic, kot tudi, da krepi imunski sistem. Slednje lahko s pridom uporabimo pri zdravljenju sepse in drugih virusnih boleznih. Uporaba hitozana se je pokazala kot ustrezna in učinkovita za ustavljanje krvavitev ob težkih pogojih nestrjevanja krvi in pri presajanju organov, saj lahko med tem posegom pacienti izgubijo veliko krvi [31, 40–42].

products, such as in cosmetic preparations, drugs, and food, the water solubility of chitosan is of significant importance. It has been demonstrated that chitosan with a 50% degree of deacetylation and produced by a homogeneous procedure is water soluble [15]. Researchers have also analysed other methods for increasing the water solubility of chitosan. Kushino and Asano have developed a procedure for the preparation of water soluble chitosan salt [19]. This method involves the dissolution of chitosan in water, adjusting of solution concentration to 10%, and evaporating and drying at 175 °C. The ability to tune the water solubility of chitosan represents different possibilities for its chemical modification.

2.2.3 Applications of chitosan and its derivates

Since the discovery of chitin, the use of chitin and chitosan has expanded into many research fields [15]. The flexibility in the chemical modification of chitosan and its derivatives permit their application into a variety of areas. (Figure 4).

Important characteristics have been discovered in these chitosan derivatives, such as immunoadjuvant, antithrombogenic, spermicidal, fungistatic, and bacteriostatic. These derivatives has exhibit flocculation characteristics [8, 15, 19, 24–30], meaning they can be used in different spheres, e. g. ecological (waste water cleaning), food and nutrition, medical areas, and in the pharmaceutical industry. In Figure 4 different chitosan derivatives are presented with their potential applications.

The characteristics of chitosan products such as purity, viscosity, deacetylation degree, molecular mass, and polymorphic structure can vary from one product to another. These factors are influenced by the treatment conditions, almost importantly, temperature, pH, chitosan concentration, and treatment time.

Medicine, pharmacy and biotechnology

In the last decade, the pharmaceutical industry has researched chitosan for its potential use in the medical area [31–35]. In the form of a solution or gel, it can be used as a bacteriostatic or fungistatic product, applicable for solid materi-

Celice in encime zlahka ujamemo v ionotrofičen gel hitozana, ki ga dobimo z mešanjem raztopine hitozana z raztopino anionskih polimerov (natrijev alginat, karagen ali pektin) [8].

Na trgu je trenutno vrsta preparatov iz hitozana za zniževanje telesne teže, katerih delovanje naj bi temeljilo na izsledkih raziskav, ki potrjujejo, da vsakodnevno peroralno jemanje hitozana zniža nivo plazemskega holesterola in trigliceridov ter poveča izločanje žolčnih kislin in maščob z blatom. Vendar pa so si rezultati raziskav mnogokrat nasprotujoči, saj naj bi na drugi strani z raziskavami na podganah ugotovili, da takšna dolgotrajna uporaba hitozana povzroči pomanjkanje lipidotopnih vitaminov v plazmi, zaostajanje v rasti, zmanjšanje mineralne gostote krvi, kar lahko posredno vodi do osteoporoze, in spremembe črevesne flore, te pa lahko povzročijo razrast odpornih patogenov [38].

Hitozan nudi v medicini in farmaciji naslednje uporabne možnosti: uporablja se kot sredstvo za lajšanje bolečin, primeren je za zdravljenje kostnih bolezni, za ločevanje proteinov, za zaščito zob, za izdelavo kontaktnih leč itd. [8, 13, 15, 31, 40–43]. Uporabo hitina in hitozana na področju oskrbe ran in opeklin ter izdelave povojev, sterilnih gaz in higienskih medicinskih oblačil pa je predstavljena v sklopu medicinskih tekstilij.

Kmetijstvo in prehrana

Na področju kmetijstva je hitozan še vedno premalo uporabljan naravni polimer. Hitozan inhibira rast fitopatogenih gliv in bakterij ter vzpodbuja odpornost rastlin proti glivičnim in virusnim infekcijam. Raziskave na Washington State University so pokazale, da je pšenično zrno, prevlečeno s tankim hitozanskim filmom, bolj odporno proti škodljivcem. V tem primeru vpliva hitozan na selektivno sintezo najmanj dvajsetih vrst proteinov, kar ima za posledico povečanje encimske aktivnosti substanc. Te delujejo proti plesnim, kot so: fitoaleksin, pisatin in hidrolitični encimi hitinaze ter glukanaze. Hitozan se uporablja tudi pri nadzorovanju dodajanja pesticidov in herbicidov. Uporaba hitinaste biomase v prsti vzpodbuja rast naravnih mikrobov, ki učinkovito ščitijo določene vrste pridelkov [8, 43].

Hitozan ponuja torej tudi na področju kmetijstva in prehrane široke možnosti uporabe, kot so npr. obdelava semen in listov, biostimulacija rasti rastlin, izdelava gnojil, zaščita rastlin in pridelkov pred bakterijami in virusi, biopredelava pri proizvodnji obogatenih prehrambnih proizvodov, konzerviranje, različni dodatki k dietetični hrani, tvorba naravno razgradljivih tankih filmskih oblog, uporaba odpadnega materiala, ki nastane pri predelavi hrane in pri bistrenju ter zmanjševanju kislosti sadnih sokov, itd. [8, 41, 43, 44, 45].

Osebna higiena, kozmetika

Depolimeriziran hitozan in karboksimetil hitin se uporabljata kot aktivni sestavini v šamponih, regeneratorjih in lasnih oblogah, ker so njune vodne raztopine viskozne, tvorijo tanek film in ohranjajo vlago ter tako mehčajo lase in kožo [8, 41, 43].

als treatment (textile, foil, membranes). In the form of a gel or a suspension, chitosan can be used as a system for a slow and controlled delivery of a medicine, which is possible due to the fact that chitosan acts as a polycation [36]. The medicinal substance could be physically or covalently bonded to the amino group of chitosan, and slowly released from chitosan matrices in the contact with body fluids [37]. Many delivery systems using chitosan are presently being developed, wherein the bio-adhesive characteristics and the ability of increasing the absorption of active substances through mucous membranes of chitosan is being used for micro- and nano- capsules, and as liposomes [38]. Chitosan and some of its derivates, like quarternized N-methyl chitosan chloride or glutamate and mono-N-carboxymethyl chitosan, successfully increase the permeability of different mucous membranes [37, 38]. Chitosan has a low peroral toxicity, which mostly depends of its deacetylation degree, the molecular mass, purity, and method of application. Chitosan with the highest degree of purity is recommended for human use [38].

Chitosan membranes can be used as artificial membranes for kidneys, due to their good mechanical characteristics and the fact that they permeate urea and creatinine. Since they are not permeable to serum proteins, they have a unique advantage of protecting from toxic metals in blood circulation, which is not a characteristic of other membranes [32].

Chitosan has good bio-adhesive characteristics, due to the formation of hydrogen and ionic bonds between positively charged amino groups of the polymer and negatively charged sialic acid, found in glycoproteins on the mucous membrane surface. Tio-chitosans allow an even greater bio adhesion, due to the formation of covalent bonds between polymer tio- groups and the surface glycoproteins [39].

Sulfated chitosan has been found to have 15 to 45% of the anticoagulation capability of heparin in vitro [8]. The introduction of uronic carboxyl groups increases the anticoagulation activity of the chitosan. It has also been proven that chitosan inhibits the growth of cancer cells and strengthens the immune system, important for the medical treatment of sepsis and other

Hitozan se na kozmetičnem področju uporablja v naslednjih proizvodih: pudrih, lakih za nohte, pa tudi v odstranjevalcih lakov za nohte, ličilih za ustnice, tekočih milih za prhanje, kremah za obraz, roke in telo, zobnih pastah itd. [8, 41–44].

Ekologija

Hitozan je dobro koagulacijsko sredstvo in flokulant, kar je posledica visoke vsebnosti aminskih skupin, ki lahko reagirajo z negativno nabitimi substancami, kot so proteini, trdni delci, barvila in polimeri. Že tri desetletja se uporablja pri detoksifikaciji vode. Ob dodatku vode hitozan absorbira maščobe, olja, težke kovine in druge potencialne toksične snovi. Dušik, prisoten v aminski skupini molekule hitozana, reagira kot donor elektronov in je domnevno odgovoren za selektivno tvorbo kelatov s kovinskimi ioni [15, 18]. Prosta aminska skupina hitozana je v primerjavi z acetilno skupino hitina primernejša za vezavo kovinskih ionov. Višja ko je vsebnost prostih aminskih skupin v hitozanu, višja je stopnja adsorpcije kovinskih ionov. Adsorpcijska sposobnost hitozana je odvisna tudi od faktorjev, kot so stopnja kristalinosti, stopnja deacetiliranja in hidrofilnost [46]. Sposobnost hitozana za adsorpcijo kovinskih ionov je odvisna tudi od postopka hidrolize. Homogeni postopek hidrolize vodi do hitozanskega produkta z višjo sposobnostjo adsorpcije kot heterogeni postopek pri enaki stopnji deacetiliranja hitozana [15, 22]. Ugotovljeno je bilo, da se vzorci s stopnjo deacetiliranja 55 %, pripravljeni po homogenem postopku, odlikujejo z najboljšo sposobnostjo adsorpcije. Ti vzorci so amorfni in so zelo dobro topni v vodi. Adsorpcijo kovin je mogoče izboljšati z zamreženjem, nadzorovanim N-deacetiliranjem in tvorbo kompleksov z drugimi polimeri, kot je npr. glukan. Kompleks hitozana in glukana se ponaša z mnogo večjo sposobnostjo tvorbe kelatov kot pa sam hitozan, saj veže mnoge kovinske ione iz vode, med drugim tudi Cr, Co, Ni, Cu, Cd in Pb.

Hitozanski prah in suhi zaščitni filmi so pri adsorpciji kovinskih ionov v primerjavi z raztopinami bolj uporabni, ker sprostijo večino aminskih skupin nad pKa. Agencija za varovanje okolja Združenih držav – USEPA (United States Environmental Protection Agency) je za prečiščevanje pitne vode dovolila uporabo hitozana do maksimalne stopnje 10 mg/l. Karboksimetil hitozan in zamrežen hitozan sta se posebej izkazala pri odstranjevanju Pb^{2+}, Cu^{2-} in Cd^{2+} iz pitne vode. Prav tako pa je hitozan izredno uspešen pri prečiščevanju polikloriranih bifenilov iz kontaminirane vode in je pri tem celo bolj učinkovit kot aktivno oglje [8, 15, 43, 44]. Uporablja se tudi za odstranjevanje barvil, filtriranje, koaguliranje, flokuliranje, adsorbcijo pesticidov itd. [8, 15, 41, 44, 47–48].

Tekstilstvo

Zaradi edinstvenih lastnosti, kot so biorazgradljivost, netoksičnost, kationska narava in antimikrobiološka aktivnost, je hitozan primeren za številne tekstilne aplikacije. Uporabo hitozana na tekstilnem področju lahko razdelimo v dve veliki skupini, in sicer na uporabo

viral diseases. Unmodified chitosan has proven to be a suitable and effective agent for bleeding control under difficult conditions of anticoagulation and in the transplantation of organs, where patients can lose significant amounts of blood during surgery [31, 40–42].

The immobilization of cells and enzymes is a method that limits the cells and enzymes in a specific phase, separated from the phase of accumulation, and as such, enables an exchange between these two phases. The cells and enzymes can easily be seized into an ionotrophic gel of chitosan, which is acquired when mixing the solution of chitosan with the solution of anionic polymers (sodium alginate, carrageen or pectin) [8].

Contemporarily, we can find many preparations of chitosan on the market specifically targeted to weight loss. The activity of these preparations is supposed to be founded in research results, which apparently have proven that a daily peroral use of chitosan lowers the degree of plasmatic cholesterol and triglycerides, and increases the secretion of bile acids and fat with excrement. However the results of these researchers are often contradictory, since other researchers have found out that a longer use of chitosan causes insufficiency of lipid soluble vitamins in the plasma, the lagging in growth, and the decreasing of mineral density of blood, which can lead to osteoporosis and the change of intestinal flora, and subsequent growth of resistant pathogens [38].

In medicine and pharmacy, chitosan is also used as a pain-killer, treat bone diseases, to separate proteins, to protect teeth, and in the contact lenses production [8, 13, 15, 31, 40–43]. We will present the use of chitin and chitosan in the area of wound and burn treatment, production of bandages, sterile gauzes, hygiene, and medical clothes in the unit discussing medical textiles.

Agriculture and nutrition

In the field of agriculture, chitosan as a natural polymer remains underused. Chitosan inhibits the growth of fitopathogenic fungi and bacteria and also increases the resistance of plants to fungi and virus infections. Researchers at Washington State University have dem-

hitozana in njegovih derivatov za obdelavo vlaknatih materialov, bodisi v klasičnih ali alternativnih plemenitilnih postopkih, ter na izdelavo hitinskih in hitozanskih vlaken.

J. G. Domszy je s sodelavci ugotovil, da se adsorpcija hitozana na celulozna vlakna izboljšuje z zniževanjem molekulske mase in stopnje N-acetiliranja. Povečano adsorpcijo so zaznali tudi pri obdelavi pri višji temperaturi. Velik vpliv na adsorpcijo imata pH in koncentracija raztopine hitozana [22, 23]. Afiniteta hitozana do bombaža je posledica podobne strukture bombaža in hitozana, glavna povezava v tem primeru pa so van der Waalsove sile. Druga možnost vezanja hitozana na celulozo je zamreženje med reduciranim celuloznim koncem (–CO–H) in aminoskupinami hitozana ob prisotnosti Schiffove baze. Pomembno vlogo pa imajo tudi vodikove vezi.

Hitozan absorbira anionska barvila, kot so direktna, kisla in reaktivna z elektrostatično privlačnostjo, ki jo povzroča kationska narava hitozana v kislih medijih. Ugotovili so, da lahko uporaba hitozana izboljša obarvljivost nezrelih bombažnih vlaken. Z raztopino hitozana v razredčeni ocetni kislini so obdelovali bombažna vlakna po različnih postopkih impregnacije in izčrpavanja. Predobdelave bombaža s hitozanom so izboljšale sposobnost izčrpavanja direktnih barvil in omogočile obarvanje nezrelih vlaken do enakih globin kot pri zrelih vlaknih [49]. Pri barvanju z reaktivnimi barvili postopek ni bil uspešen. Najbolj efektivna glede na količino hitozana, vezanega na bombažno vlakno po spiranju, je bila aplikacija hitozana po impregnaciji in sušenju, vendar pa med sušenjem prihaja do migracije hitozana in zaradi tega do neenakomernega obarvanja.

Pri spiranju tkanine, obdelane s hitozanom in barvane z direktnimi barvili, se opazi največja izguba barve pri prvem spiranju, izguba se stabilizira po približno 15. spiranju, vendar pa imajo v tej fazi s hitozanom obdelani vzorci vrednosti K/S še vedno večje, in to za okrog 35 %, v primerjavi s tistimi vzorci, ki niso bili predobdelani s hitozanom. Predlaga se, da bi s takšnimi predobdelavami zmanjšali porabo barvil in s tem tudi vsebnost barvil v odpadnih vodah, pa tudi porabo elektrolitov do 50 % [49].

Poleg zgoraj omenjenih klasičnih tekstilnih aplikacij podajajo razni viri še vrsto drugih možnih aplikacij hitozana na področju klasičnega plemenitenja tekstilij, in sicer se uporablja še kot sredstvo za apretiranje bombažnih tkanin proti mečkanju [4, 50–51], sredstvo za doseganje deodorantskih učinkov [52], mikrokristalini hitozan za najrazličnejše aplikacije [53], sredstvo za prekrivanje nopkov in nepravilnosti na tkaninah in pleteninah [54], sredstvo za obdelavo volnenih tkanin za nižjo polstivost [55] oz. boljšo obarvljivost [26], gostilo pri pigmentnem tisku [57].

Medicinske tekstilije so postale v zadnjih nekaj desetletjih izredno pomembno in hitro rastoče področje tehničnih tekstilij [1]. Biološko aktivnost površin medicinskih tekstilij dosegamo na različne načine: s kemično modifikacijo vlaknotvornega materiala, z dodajanjem bioaktivne substance v izpredilno maso, z naknadno

onstrated that wheat grain, covered with a thin chitosan layer, is more resistant against pests. In this case, chitosan influences the selective synthesis of at least 20 kinds of proteins, leading to an increased enzymatic activity of substances. These are active against moulds, such as fitoalexine, pisatin, and hydrolytic enzymes of chitinase and glucanase. Chitosan is also used for controlling the addition of pesticides and herbicides. The use of chitin biomass in humus stimulates the growth of natural microbes, which can effectively protect harvests [8, 43].

It this way, chitosan has a variety of applications in the field of agriculture and nutrition, such as the treatment of seed and leaves, bio stimulation of the plants' growth, the making of manure, protection of plants and harvests against bacteria and viruses, bioprocessing in the production of fortifying nutritional products, preservation, extras additives to dieting products, the production of biodegradable thin layers, the reuse of waste material from food production, and the clarification or reduction of sourness in fruit juices. [8, 41, 43, 44, 45].

Personal hygiene, cosmetics

Depolymerised chitosan and carboxymethyl chitin are used as active components in shampoos, regenerators, and hair compresses. Their water solutions are viscous and form a thin layer that retains moisture to soften hair and skin [8, 41, 43].

In the cosmetics area, chitosan is used in powders, nail polishes, nail polish removers, lipsticks, shower gels, face creams, body and hand creams, and toothpastes. [8, 41–44].

Ecology

Chitosan is a good coagulation and flocculation, agent owing to the high content of amino groups, which can react with negative charged substances, such as proteins, solid particles, pigments and polymers. For the last three decades it has been used for the detoxification of water. Chitosan absorbs fats, oils, hard metals, and other potentially toxic substances in water. Nitrogen present in the amino group of the chitosan molecule reacts as a donor of electrons and is responsible for the selective formation of chelates with metal ions [15, 18]. The free ami-

obdelavo vlaken z bioaktivnimi komponentami, z nanosom nanoslojev itd. [2].

Tekstilne materiale, uporabne na medicinskem in zdravstvenem področju, delimo v dve osnovni skupini, in sicer glede na to, ali se uporabljajo znotraj organskih tkiv (interni: kirurške niti in različni vsadki) ali na njihovi površini (eksterni: gaze, povoji, kirurška pregrinjala, plenice, tamponi itd.). Ne glede na področje uporabe pa morajo biti osnovne bioaktivne lastnosti medicinskih tekstilij v prvi vrsti protimikrobne [1–5].

Z odkritjem mehanizma delovanja protimikrobnih sredstev na osnovi kvarternih amonijevih soli sta se začela hiter razvoj in uporaba različnih vrst protimikrobnih sredstev na tekstilnih izdelkih. Med najvažnejša protimikrobna sredstva, uporabna na tekstilnih materialih, štejemo organske spojine, ki vsebujejo kovine, fenole, kvarterne amonijeve soli in različne silikone. Našteta sredstva pa imajo tudi številne negativne vplive na človeški organizem, zato trenutne raziskave na tem področju potekajo v smeri odkritja oz. razvoja substance, ki bo v vseh pogledih človeku nenevarna in bo hkrati uporabna za aplikacijo na tekstilnih materialih. V zadnjih nekaj letih se zato kot protimikrobno sredstvo vedno bolj uveljavlja hitozan [8, 13, 15, 58].

Protimikrobno delovanje hitozana pripisujejo predvsem aminskim skupinam, ki v razredčenih kislinah tvorijo amonijeve soli. Nastale soli vplivajo na prepustnost celične membrane, kar ovira potek normalnega metabolizma mikroorganizmov in vodi do smrti celic [5, 25, 26, 59].

Različni literarni viri navajajo, da je protimikrobna aktivnost hitozana odvisna od njegove molekulske mase, stopnje deacetiliranja, koncentracije, vrste mikroorganizmov.

Vplivi molekulske mase, stopnje deacetiliranja in vrste bakterij na učinkovitost hitozana so bili relativno dobro raziskani. Shin je s sodelavci [60, 61] raziskoval učinkovitost treh različnih vrst hitozana z različno molekulsko maso (1800, 100 000, 210 000) in stopnjo deacetiliranja od 86 % do 89 % v prisotnosti petih vrst bakterij. Po obdelavi bombažnih vlaken s hitozanom je bilo ugotovljeno, da ima hitozan z višjo molekulsko maso višjo efektivno sposobnost zadrževanja rasti bakterij kot hitozan z nizko molekulsko maso. Ta ugotovitev pa vzporedno velja tudi za koncentracijo raztopin hitozana. Vlakna, obdelana z 1 % raztopino hitozana, imajo 90 % sposobnost redukcije bakterij, medtem ko ima vlakno, obdelano z 0,1 % raztopino hitozana, le okoli 75 % sposobnost redukcije bakterij. V isti raziskavi so ugotovili tudi, da ima hitozan z višjo molekulsko maso tendenco manjšega absorbiranja v notranjost vlakna, kar pomeni, da je v večji količini na površini tekstilije, iz tega pa sledi, da so aminske skupine veliko bolj dostopne in reakcijsko sposobne.

Protimikrobno delovanje hitozana je močno odvisno tudi od kislin, uporabljenih za pripravo raztopin [4]. Pri uporabi etanojske kisline se z višanjem koncentracije hitozana poveča tudi protimikrobno delovanje, vendar pa se mehanske lastnosti vla-

no group of chitosan readily reacts with metal ions compared to the acetyl group, which is also part of chitosan molecule. The higher the density of free amino groups in chitosan, the higher the degree of metal ion adsorption. The adsorption ability of chitosan is dependent on factors such as the degree of crystallization, the degree of deacetylation, and hydrophilicity [46]. The ability of chitosan to adsorb metal ions also depends on hydrolysis. Homogeneous hydrolysis leads to a chitosan product with a higher absorption capability compared to heterogeneous hydrolysis of chitosan with the same degree of deacetylation [15, 22]. Samples with the 55% degree of deacetylation, prepared using homogeneous hydrolysis, have the best ability for metal ion adsorption. These samples are amorphous and can be easily dissolved in water. Metal absorption can be improved by crosslinking N-deacetylation with other polymers such as glycan. The complex of chitosan and glycan has a much greater ability of producing chelates in comparison to the pure chitosan, because it binds many metal ions from the water, including Cr, Co, Ni, Cu, Cd, and Pb.

Chitosan powder and dry protective layers are more useful for metal ion adsorption, compared to solutions, because they free almost all amino groups above pKa. The United State Environmental Protection Agency (USEPA) permits a maximum of 10 mg/L of chitosan in cleaning the drinking water. Carboxymethyl chitosan and crosslinked chitosan have proven to be successful in removing of Pb^{2+}, Cu^{2-}, and Cd^{2+} ions from drinking water. Further, chitosan is finding more success in cleaning polychlorinated biphenyl from contaminated water, and is even more effective than the active charcoal [8, 15, 43, 44]. Chitosan is also used to remove pigments, in filtration, coagulation, flocculation, and in the adsorption of pesticides. [8, 15, 41, 44, 47–48].

Textiles

Due to the unique biodegradability, nontoxicity, cationic nature, and antimicrobial activity characteristics of chitosan, it is suitable for many textile applications. The use of chitosan in the textile area can be divided into two groups: the use of chitosan and its derivates for

ken slabšajo. V tem primeru se je kot alternativa izkazala citronska kislina.

Uporaba hitozana kot protimikrobnega sredstva za obdelavo netkanih tekstilij iz polipropilena za kirurška pregrinjala je bila raziskana v odvisnosti od vrste bolnišničnih bakterij [25]. Tako obdelane tekstilije so učinkovale zavirajoče na gramnegativne in grampozitivne bakterije, medtem ko so bile uporabne lastnosti teh tekstilij nekoliko poslabšane: večja togost, manjša pretržna trdnost in prepustnost zraka.

Razviti so bili tudi številni derivati hitozana, za katere je bilo dokazano izboljšano protimikrobno delovanje v primerjavi z izhodnim hitozanom, ko so bili aplicirani na tekstilijah. Eden takšnih je NMA-HTCC (O-akrilamidometil-N-[(2-hidroksi-3-trimetilamonijev)propil] hitozan), ki v 1 % koncentraciji nanesen na bombažni tkanini omogoča 100 % redukcijo bakterij Staphilococcus aureus oz. 99 % redukcijo po petdesetih zaporednih pranjih [62].

Hitozanske mikrokapsule, sestavljene iz jeder iz poli-n-butilakrilata (PBA) in hitozanskega ovoja, nanesene na bombažno tkanino po postopku impregniranja, omogočajo 99 % bakterijsko redukcijo [63]. Mikrokapsule imajo ozko porazdelitev velikosti s srednjim premerom okrog 300 nm in visok pozitiven površinski naboj.

Izredno pomembno področje uporabe hitozana in hitina je vsekakor področje oskrbe ran in opeklin, saj tovrstni izdelki s svojim pozitivnim površinskim nabojem ugodno vplivajo na koagulativne lastnosti krvi in tako na hitrejše celjenje ran [64]. Hitozan in hitin v obliki vlaken imata dodatne prednosti, saj imajo vlakna poleg velike površine tudi specifične mehanske lastnosti in so tako uporabna tudi kot nosilni materiali v obližih za rane [65]. Na trgu so danes že dobro uveljavljeni številni izdelki za oskrbo ran iz hitina in hitozana, predvsem japonskih proizvajalcev. Podjetje Eisai Co. je proizvajalec izdelkov iz hitina v obliki gobic ali z nosilnimi netkanimi PET-tekstilijami, obdelanimi s hitinom, znanih pod imenom Chitopac C®. Japonsko podjetje Unitika Co. proizvaja obliže iz netkanih materialov, izdelanih iz hitinskih vlaken. Ameriški 3M se ukvarja s proizvodnjo hitozanskega gela Tegasorb® in hidrokoloida Tegaderm® za zdravljenje obširnih notranjih ran [64]. Univerzitetni medicinski center v Washingtonu je proizvajalec hitozanskih obližev, namenjenih regeneraciji kože po resnih drugo- ali tretjestopenjskih opeklinah. Drugi izdelki, ki vsebujejo hitin in hitozan in ki delujejo kot bioaktivni tekstilni materiali, so znani pod naslednjimi imeni: Syvek patch, RDH (Marine Polymer Technologies), Clo-Sur PAD (Medtronic-Scion), Chito-Seal (Abbott), M-Patch in Trauma DEX (Medafor) [66].

Hitozanska vlakna pa se uporabljajo tudi na področju tkivnega inženiringa. Tekstilno tehniko priprave cevastih ogrodij iz hitozanskih vlaken za vzgojo tkiv je predstavil Wang s sodelavci [67]. Cevasta tvorba iz hitozanskih vlaken je bila pripravljena na pletilnem stroju tako, da ima dvofazno strukturo sten, vlaknato notranjo površino in polprepustni zunanji sloj ter je primerna za vzgojo tkiv cevastih oblik.

the treatment of fibrous materials in classical or alternative finishing procedures and the production of chitin and chitosan fibres.

J. G. Domszy and his co-workers discovered that the absorption of chitosan on cellulosic fibres improves with decreasing of molecular mass and the degree of N-acetylation. They also observed a higher absorption in higher temperature treatments. The pH value and concentration of chitosan solutions significantly impact absorption [22, 23]. The affinity of chitosan towards cotton is the result of the similar structure of cotton and chitosan, wherein the main linkages are Van der Waals forces. The other possibility of chitosan binding on cellulose is the crosslinking and the formation of a Schiff's base between the cellulose reductive end (–CO–H) and the amino groups of chitosan. Hydrogen bonds also have an important role.

Chitosan can easily absorb anionic (direct, acid and reactive) dyes with electrostatic attractive forces, which is a result of the cationic nature of chitosan in an acidic environment. It has been observed that chitosan improves the dyeability of immature cotton fibres. Cotton fibres have been treated with a chitosan solution in diluted acetic acid solution for different impregnation and exhaustion finishing procedures. Previous treatments of cotton with chitosan have improved direct dyes absorption and have enabled the dyeing of immature fibres to the same depth as the mature fibres [49]. For dyeing with reactive dyes, the treatment has not successful. The most effective regarding adsorbed chitosan quantity on cotton fibres after washing procedure was the application of chitosan in impregnation and drying, however during drying essential migration of chitosan occurs, which causes an unequal dyeing.

During the rinsing of the fabrics treated with chitosan and dyed with direct dyes, it is observed that the greatest loss of the colour occurs after the first rinsing, which is later stabilised after about the fifteenth rinsing. Samples treated with chitosan have K/S values 35% higher compared to untreated samples. It is proposed that dye consumption could be lowered using chitosan treatments, which correspondingly lowers the amounts of dye in waste water, and decreases the consumption of electrolytes by 50% [49].

4 Zaključek

Hitozan je v preteklih tridesetih letih doživel nesluten razvoj in se uspešno uveljavil na različnih področjih našega bivanja.
Je najpomembnejši derivat hitina, ki je za razliko od slednjega topen v raztopinah kislin in pod posebnimi pogoji celo v nevtralnem pH mediju. Najpomembnejša prednost hitozana pred drugimi podobnimi polisaharidi je njegova molekulska struktura, ki omogoča celo paleto modifikacij in s tem pridobivanje številnih derivatov. Z uvedbo specifičnih funkcionalnih skupin v molekulo hitozana je mogoče oblikovati njegove derivate za najrazličnejše namene in uporabo v prehrani, kozmetiki, farmaciji, medicini, ekologiji in seveda tudi v tekstilstvu. Prav na področju pridobivanja derivatov hitozana je bilo predlaganih veliko različnih metod in tehnik kemijskih sintez, od katerih pa jih je relativno majhno število razvitih do industrijskega nivoja. Kljub temu, ali morda prav zaradi tega pa je hitozan biopolimer, ki še nedvomno ogromno obeta.

5 Literatura

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In addition to the aforementioned classical textile applications, chitosan can be used in finishing processes, like the durable press treatments of cotton fabrics [4, 50–51], and imbuing fabrics with deodorant effects [52]. Further, microcrystalline chitosan can be used for [53], covering defects and irregularities on woven and knitted goods [54], the treatment of wool against felt [55], improving the dyeability of wool [26], and as thickeners in pigment printing [57].

In previous decades, medical textiles have become an important and fast growing field of technical textiles [1]. The biological activity of medical textile surfaces can be achieved by the chemical modification of the fibrous material, the addition of bioactive substances into the spinning mass, subsequent treatments of fibres with bioactive components, and with nanolayers. [2].

Textile materials used in the medical field or health service are divided into two basic groups, according their use inside (internal: sutures and various implants) or outside organic tissues (external: gauzes, bandages, surgical masks, gowns and coverings, nappies, tampons, and so on). Irrespective of the use, medical textiles need to have basic bioactive resistance against microbes [1–5].

The discovery of the mechanism of anti-microbial activity on the basis of ammonia salts initiated a fast development and use of different kinds of anti-microbial treatments of textile materials. The most important anti-microbial agents used in textile materials are organic compounds containing metals, phenols, ammonia salts, and different silicones. These agents are often dangerous to humans, which has directed researchers to develop substances which would not be dangerous for humans, but at the same time still be applicable as bioactive textile materials. Chitosan is a material that potentially realizes both human safety and textile anti-microbial bioactivity [8, 13, 15, 58].

The anti-microbial activity of chitosan is assigned to the amino groups, which in acidic media form ammonium salts. Formed salts have an effect on the permeability of the cell membranes, which hinders the course of the normal metabolism of microorganisms and leads to the death of cells [5, 25, 26, 59].

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Different literature sources allege that the anti-microbial activity of chitosan depends on its molecular mass, concentration, and the degree of deacetylation, as well as the type of micro-organism.

The influence of molecular mass, the degree of deacetylation, and the type of bacteria on the efficiency of chitosan have been well researched. Shin and co-workers [60, 61] have investigated the effectiveness of three different kinds of chitosan with different molecular masses (1800, 100 000, 210 000) and the degree of deacetylation from 86% to 89%, in the presence of five types of bacteria. After the treatment of cotton fibres with chitosan, it was observed that chitosan with a higher molecular mass had a higher effective ability of bacterial reduction than chitosan with a lower molecular mass. These findings are similarly true for comparable concentrations of chitosan solutions. Fibres treated with 1% solution of chitosan reduce bacteria growth by 90%, while fibres treated with 0.1% solution of chitosan reduce bacterial growth by 75%. In the same research, it has also been stated that chitosan with a higher molecular mass has a tendency to be adsorbed on the textile surface and only slightly penetrates into the fibres. In such a way, the chitosan amino groups are more accessible and able to react.

The anti-microbial activity of chitosan depends on which acids are used for the chitosan solution preparation [4]. In the case of using ethanoic acid, an increase of the chitosan amount adsorbed on the textile surface is expected to increase anti-microbial activity. On the other hand, the mechanical characteristics of such fibres decrease. In this case, citric acid has been presented as an alternative.

The use of chitosan as an anti-microbial agent for the treatment of polypropylene nonwovens for surgical covers was researched with different types of hospital bacteria [25]. Textiles treated in such a way are effective against gram-negative and gram-positive bacteria. Unfortunately, the treatment leads to a higher stiffness, a lower breaking strength, and air permeability of the treated materials.

Many derivatives of chitosan have been developed that have a better anti-microbial activity in comparison with source chitosans. One

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such derivative is the NMA-HTCC (O-akrylamidomethyl-N-[(2-hydroxy-3-threemethylammonium) propyl] chitosan), which if applied at 1% concentration to the cotton fabric enables a 100% reduction of Staphilococcus aureus, or a 99% reduction of the same type bacteria after 50 consecutive washing processes [62].

Chitosan microcapsules made of poly-n-butyl acrylat (PBA) cores and chitosan shells, applied on cotton fabric using the impregnation procedure, enable a 99% reduction of bacteria [63]. Microcapsules have a narrow size distribution with a central diameter of about 300 nm and a highly positive surface charge.

A very important field of chitosan and chitin application is wound and burn management. Chitosan and chitin positive surface charge favourably affects the coagulative characteristics of blood and in this way stimulates a faster healing of wounds [64].

Chitosan and chitin in the fibre form have additional advantages, since the fibres, besides having larger surfaces, have specific mechanical characteristics and are useful as carrying materials in wound dressings [65]. Contemporarily, numerous wound and burn management products are available, primarily from Japanese producers. The company Eisai Co is the producer of chitin products in the form of sponges or PET nonwovens treated with chitin, known under the name of Chitopac C®. The Japanese company Unitika Co produces wound dressings from nowovens, made from chitin fibres. The American 3M produces the chitosan gel Tegasorb® and hydrocolloid Tegaderm® for treatment of extensive inner wounds [64]. The University of Washington Medical centre is the producer of chitosan dressings, used for the skin regeneration after serious second- and third-degree burns. Other products, which include chitin and chitosan, and act as bioactive textile materials, are known under the following names: Syvek patch, RDH (Marine Polymer Technologies), Clo-Sur PAD (Medtronic-Scion), Chito-Seal (Abbot), and M-Patch in Trauma DEX (Medafor) [66].

Chitosan fibres are also used in the field of tissue engineering. The textile technique of preparing tube-shaped scaffolds of chitosan fibres for tissue engineering has been introduced by

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Wang and co-workers [67]. The tube-shaped forms from chitosan fibres have been prepared on a knitting machine in such a way that they have a two-phase wall structure: a fibrous inner surface and semi-permeable outer layer, which are suitable for the growing of tube shaped tissues.

4 Conclusion

In the last 30 years, the application of chitosan in our daily lives has seen significant development. Chitosan is the most important derivative of chitin, and is soluble in acidic water media and even in neutral pH media. The most important advantage of chitosan in comparison to other polysaccharides is its molecular structure, which enables a wide variety of chemical modifications, and in this vein, permits the possibility of numerous derivatives for various fields of application, such as: food, cosmetics, pharmacy, ecology, and textiles. In the field of chitosan derivatisation, many new methods and techniques have been proposed and introduced, from which, however, relatively few have been developed for the industrial level.

Chitosan, as a natural biopolymer, has significant potential, which raises our expectations for future research and development.

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