23st Conference
of Polisch Chitin Society

„NEW ASPECTS ON CHEMISTRY AND APPLICATION OF CHITIN AND ITS DERIVATIVES"

Wałbrzych, September 20-22nd 2017

Polish Chitin Society

XXIII Conference

„New aspects on chemistry and application of chitin and its derivatives”

Conference place: Wałbrzych, Książ Castle, „Przy Oślej Bramie” Hotel

Scientific Committee: Prof. Małgorzata JAWORSKA, Ph.D.,D.Sc. – chairman

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Co-organizers: Institute of Biopolimers and Chemical Fibres, Lodz, Poland

We would like to inform that the organization of the XXIII Conference on “New Aspects on Chemistry and Applications of Chitin and its Derivatives” is funded under contract 652/P-DUN/2017 from the resources of Ministry of Science and Higher Education allocatied for activities which disseminate the science.

Ministry of Science
and Higher Education
Republic of Poland

XXIII Konferencja Polskiego Towarzystwa Chitynowego

„NOWE ASPEKTY W CHEMII I ZASTOSOWANIU CHITYNY I JEJ POCHODNYCH"

Wałbrzych, 20-22 września 2017 r.

Polskie Towarzystwo Chitynowe

XXIII Konferencja

„Nowe aspekty w chemii i zastosowaniu chityny i jej pochodnych"

Miejsce Konferencji: Wałbrzych, Zamelk Książ , Hotel „Przy Oślej Bramie"

Komitet Naukowy: Prof. ndz. dr hab. inż. Małgorzata JAWORSKA – przewodnicząca

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Prof. dr hab. inż. Mirosława EL FRAY
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Współorganizatorzy: Instytut Biopolimerów i Włókien Chemicznych, Łódź

Organizacja XXIII Konferencji Naukowej "Nowe aspekty w chemii i zastosowaniu chityny i jej pochodnych" - zadanie finansowane w ramach umowy 652/P-DUN/2017 ze środków Ministra Nauki i Szkolnictwa Wyższego przeznaczonych na działalność upowszechniającą naukę.

Ministerstwo Nauki
i Szkolnictwa Wyższego

Honorable quests,

We meet for 23st time on Conference „New Aspects in Chemistry and Applications of Chitin and Its Derivatives”.
I do hope that our meeting will contribute as previously to the progress of Polish chitin and chitosan science.

I wish the fruitful debate to all participants of 23st Conference.

On behalf of the Polish Chitin Society

Prof. Małgorzata Jaworska

The President

Wałbrzych, September 20-22nd 2017

Szanowni Państwo,

Po raz dwudziesty trzeci spotykamy się na Konferencji pt. „Nowe aspekty w chemii i zastosowaniu chityny i jej pochodnych".
Mam nadzieję, że tak jak poprzednio nasze spotkanie przyczyni się do rozwoju polskiej nauki w dziedzinie chityny i chitozanu.

Życzę wszystkim uczestnikom XXIII Konferencji owocnych obrad.

W imieniu Zarządu PTChit

Prof. nzw. dr hab. inż. Małgorzata Jaworska

Prezes

Wałbrzych, 20-22 września 2017 r.

SCHEDULE OF CONFERENCE

September 20th 2017 - Wednesday

16^{00}- 18^{00}	**Registration**
18^{00}- 22^{00}	**Welcome reception**
	Dinner

September 21st 2017 – Thursday

8^{30}-8^{45}		**Openning ceremony** **Prof. Małgorzata M. Jaworska, Ph.D.,D.Sc.**
8^{45}-9^{15}		**Prof Henryk Struszczyk prize-giving ceremony**
Session A		**Physico-chemical session**
Chairman		**Prof. Maria Mucha, Ph.D.,D.Sc.**
A 1	**9^{15}-9^{35}**	**Svetlana Bratskaya**, Alexander Mironenko,Yuliya Privar, Evgeniy Modin, Alexander Pestov, Anatoliy Mirochnik - „Luminescent hybrid materials based on chitosan and it's derivatives"
A 2	**9^{35}-9^{55}**	**Hermann Ehrlich –** "Sponge chitin: 10 years after discovery"
A 3	**9^{55}-10^{10}**	**Magdalena Gierszewska**, Ewelina Chrzanowska, Ewa Olewnik-Kruszkowska – „Modified chitosan/montmorillonite nanocomposite films: preparation and characterization"
A 4	**10^{10}-10^{25}**	**Agata Goszczyńska**, Agata Niemczyk, Agnieszka Piegat- „Chemoselective acylation of chitosan – problems and challeng"
A 5	**10^{25}-10^{40}**	**Katarzyna Lewandowska – "**Studies on the mineralization process of chitosan materials in the sbf solutions"
10^{40}-11^{00}		**Coffee/tea break**

September 21st 2017 – Thursday

Session B1		**Poster Session**
SP 1	**11^{00}- 11^{45}**	**Dorota Biniaś**, Włodzimierz Biniaś, Jarosław Janicki – „The obtaining of biomaterials from chitin"
SP 2		**Ewelina Chrzanowska**, Magdalena Gierszewska, Ewa Olewnik-Kruszkowska, Wojciech Kujawski – „Pervaporation of alcohol/water mixtures through modified nanocomposite chitosan membranes"
SP 3		**Renata Czechowska-Biskup,** Radosław A. Wach, Piotr Ulański, Janusz M. Rosiak – „Procedure optimization for determination of molecular weight of chitosan by viscometry"
SP 4		**Urszula Filipkowska**, Tomasz Jóźwiak, Paula Szymczyk, Natalia Niedźwiecka – „The influence of the chitin amination on the effectiveness of rb5 and ry84 dye sorption"
SP 5		**Maciej Galiński**, Izabela Stępniak – „Preparation and characterization of chitosan-based membranes with copper nanoparticles"

SP 6		**Małgorzata Gnus**, Gabriela Dudek, Roman Turczyn – „Chitosan based mmms for pervaporative separation of ethyl alcohol"
SP 7		**Bożena Grimling**, Maria Szcześniak, Jan Meler, Martyna Kocoń, Bożena Karolewicz, Adrianna Złocińska, Agata Górniak – „ Investigation of physicochemical properties of dental hydrogels with clotrimazole based chitosan"
SP 8		**Aleksandra Grząbka-Zasadzińska**, Sławomir Borsiak – „Nanometric cellulose modified with ionic liquid as a filler for chitosan biocomposites"
SP 9		**Aleksandra Grząbka-Zasadzińska**, Sławomir Borysiak – „Chitosan composites filled with modified nanometric cellulose"
SP 10		**Tomasz Jóźwiak**, Urszula Filipkowska, Paula Szymczyk, Małgorzata Kuczajowska-Zadrożna, Artur Mielcarek – „The influence of the deacetylation degree of chitosan in the form of flakes on the effectiveness of nitrates v sorption from aqueous solutions"
SP 11		**Barbara Kochańska,** Mirela Łukaszewska, Jolanta Sochocińska – „Determination of hydrolytic activity of saliva using chitosan ascorbate as a substrate"
SP 12		Ewa Kopania, Radosław Dziuba, **Danuta Ciechańska**, Ruslan Monich, Teresa Doroszewska, Dorota Bobrecka-Jamro- „Development of innovative biodegradable soybean seed coating based on biopolymers from renevable raw materials for better tolerance of plants to adverse enviromental conditions"
11^{45} -13^{00}		**General Assemble of the Polish Chitin Society**
13^{00}-14^{00}		**Lunch break**
14^{10}-17^{30}		**Guided tour of Książ Castle** *"The Princess Daisy route"*
20^{00}- 01^{00}		**Conference dinner**

September 22th 2017 – Friday

Session B2		**Poster Session**
SP 13	9^{00}- 9^{45}	**Katarzyna Małolepsza-Jarmołowska –** „Pharmaceutical assessment of gynecological powders with a sodium alginate containing lactic acid complexed with chitosan"
SP 14		**Katarzyna Małolepsza-Jarmołowska** – „The effect of a carboxymethylcellulose sodium salt on the properties of hydrophilic powders containing lactic acid complexed with chitosan"
SP 15		**Ewelina Ortyl**, Sonia Zielińska, Aleksandra Korbut, Jacek Pigłowski –„Photochromic chitosan films obtained by chemical modification with azobenzene dyes"
SP 16		**Katarzyna Struszczyk-Świta,** Michał Benedykt Kaczmarek, Mirosława Szczęsna-Antczak, Tadeusz Antczak – „Waste fungal biomass from biotech industries as a source of chitosan"
SP 17		**Maria Szcześniak**, Bożena Grimling, Jan Meler, Bożena Karolewicz, Katarzyna Więckowska – „Application of chitosan in the formulation of dermatological hydrogels prepared on the basis of macromolecular compounds"
SP 18		**Jan Meler**, Bożena Grimling, Maria Szcześniak, Bożena Karolewicz, Paweł Biernat – "The study of adsorption of vitamin C on the chitosan in an in vitro model"
SP 19		**Paula Szymczyk,** Urszula Filipkowska, Tomasz Jóźwiak – „The influence of chitosan flakes deacetylation degree on orthophosphate sorption efficiency from aqueous solutions"
SP 20		**Marcin Wysokowski**, Iaroslav Petrenko, Sabine Kaiser, Teofil Jesionowski, Hermann Ehrlich – „Extreme biomimetics: development of geo$_2$-chitin nanocomposites with enhanced photoluminescent properties"
SP 21		**Adam Zając**, Lucyna Dymińska, Jadwiga Lorenc, Jerzy Hanuza – „The spectroscopic properties of new chitosan-keratin-fibroin biocomposites"
SP 22		Klaudia Brodaczewska, Sylwia Szkudlarek, Katarzyna Donskow-Łysoniewska, **Maria Doligalska** -„Activation of JAWSII Cells by Chitosan of Different Molecular Weight"
SP 23		**Maria Wiśniewska-Wrona,** Mirosława El Fray - „Selected physico-chemical, functional and biological properties of polymeric biocomposites"
SP 24		**Maria Szymonowicz**, Bogusława Żywicka, Maciej Dobrzynski, Kamila Kołodziejczyk, Mariusz Korczynski , Zbigniew Rybak – „Studies of biomaterial biocompatibility"

September 22th 2017 – Friday

Session C		**Medical Session**
Chairman		**Prof. Barbara Kochańska, Ph.D.,D.Sc.**
C 1	**9^{45}- 10^{05}**	Maria Ina and **Samuel M. Hudson –** „The synthesis of an iodoacetyl chitosan derivative and rheological studies of its behavior when in blood"
C 2	**10^{05}- 10^{20}**	**Radosław A. Wach**, Karol K. Kłosiński, Małgorzata K. Girek, Renata Czechowska-Biskup, Paweł B. Szymański, Zbigniew Pasieka –„Synthesis and potential cytotoxicity evaluation of carboxymethyl chitosan hydrogels"
C 3	**10^{20} – 10^{35}**	**Agata Przekora**, Aleksandra Benko, Marta Błażewicz, Grażyna Ginalska – „Hybrid matrix made from mixing chitosan with β-1,3-glucan – a promising base for biomaterial fabrication"
10^{35}-11^{00}		**Coffee/tea break**

September 22th 2017– Friday

Session D		**Biotechnological Session**
Chairman		**Prof. Maria Doligalska, Ph.D.,D.Sc.**
D 1	**11^{00}-11^{15}**	**Michał Benedykt Kaczmarek,** Katarzyna Struszczyk-Świta, Mirosława Szczęsna-Antczak, Maurycy Daroch, Tadeusz Antczak – „Synthesis of a policistronic system enabling efficient modification of chitin and its derivatives"
D 2	**11^{15}–11^{30}**	**Monika Figiela,** Izabela Stępniak – „Synthesis of cuo-chitosan nanocomposites and their application for nonenzymatic glucose detection"
D 3	**11^{30}–11^{45}**	**Agata Gozdecka**, Agnieszka Ewa Wiącek, Małgorzata Jurak – „The effect of tio$_2$ addition on the chitosan-based imitation skin composites"

September 22th 2017– Friday

Session E		**Pharmaceutical Session**
Chairman		**Katarzyna Małolepsza-Jarmołowska, Ph.D.,D.Sc.**
E 1	**11^{45}-12^{00}**	**Agnieszka Piegat**, Martyna Giergiel, Agata Niemczyk, Agata Goszczyńska – „Chitosan-based drug delivery systems - preparation and physicochemical properties"
E 2	**12^{00}-12^{15}**	**Anna Ilnicka,** Jerzy P. Łukaszewicz – „Carbon materials obtained from chitosan containing nitrogen and titanium heteroatoms"
	12^{15}-12^{30}	**Closing of the conference**
	12^{45}-13^{45}	**Lunch**

PHYSICO-CHEMICAL SESSION

Svetlana Bratskaya[1], Alexander Mironenko[1],Yuliya Privar[1], Evgeniy Modin[1], Alexander Pestov[2], Anatoliy Mirochnik[1]

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LUMINESCENT HYBRID MATERIALS BASED ON CHITOSAN AND IT'S DERIVATIVES

In contrast to well-explored topic of plasmonic metal nanoparticles formation in solutions of biopolymers, interest to synthesis and application of biopolymer based materials with luminescent properties has grown significantly only in the last decade. High potential of chitosan and it's derivatives in this field is determined by several factors: i) good complexing properties allowing binding of ions of f- and d-metals – precursors of luminescent semiconductor and metal nanoparticles, ii) exceptional film-forming properties allowing fabrication of luminescent coatings, iii) hydrophilicity and biocompatibility, which are required for biomedical applications and sensing various organic and inorganic substances in the environment. Here we report on fabrication of luminescent film sensors and quantum dots (QD) based on chitosan and its derivatives.

Despite significant progress in the synthesis of nanomaterials by conjugation of quantum dots (QDs) and biological molecules, in most cases QDs are synthesized “ex situ” by the traditional organometallic method using organic solvents. An alternative to this approach is the synthesis of QDs directly in the biopolymer matrix in aqueous solution. Since one of the essential aspects in QDs biomedical application is the toxicity of "traditional" materials based on cadmium sulfides and selenides, an increasing interest is directed toward the use of cadmium-free particles, e.g. zinc sulfide. In this work water-soluble chelating chitosan derivatives carrying carboxyethyl and imidazolyl functionalities have been used for the synthesis of ZnS and ZnS/MnS QDs in aqueous media. Effect of chitosan substitution degree and metal:ligand ratio on stability and optical properties of QDs has been investigated.

Another type of fabricated luminescent hybrid materials is chitosan coatings doped with optically active compounds – organic indicators and lanthanide ions. Thin chitosan coatings co-doped with Eu^{3+}

and bromothymol blue has been developed for detection of methylamine. Doping chitosan coatings with luminophore indicator - 2-(benzoylamino)-3-[4-(dimethylamino)phenyl]-acrylic acid (LCF) allowed detection of Cu(II) in the aqueous solutions due to formation of strong-luminescent dimeric form from weak-luminescent LCF molecules in the presence of Cu(II) ions.

Acknowledgements:

Financial supports from Russian Foundation of Basic Research for the synthesis and characterization of chitosan-based QDs (project 17-03-00919) and from FEBRAS Program for Basic Research "Far East" for fabrication of chitosan-based luminescent sensors (project 0265-2015-0038) is gratefully acknowledged.

Hermann Ehrlich

Institute of Experimental Physics, Technische Universität Bergakademie Freiberg, Leipziger Str. 23, 09596 Freiberg, Germany

SPONGE CHITIN: 10 YEARS AFTER DISCOVERY

Chitin has been known to be part of the skeletal structure of various invertebrates for many years. Odier (1823) demonstrated that the exoskeleton of insects is composed of chitin. Diverse chitin-based structures are found in at least 19 animal phyla, however chitin in sponges (Porifera) was discovered only in 2007, probably, because previously, the presence of chitin in some sponge macerates was ascribed to "contamination" by a variety of microinvertebrates harbored by the sponges. Now, it is well established that alpha-chitin-based scaffolds are an integral part of skeletal elements of a number of marine as well as of fresh water sponges. Recently, we reported the discovery of 505-million-year-old chitin, found in exceptionally well-preserved *Vauxia gracilenta* sponges from the Middle Cambrian Burgess Shale. This finding indicates that, given the right fossilization conditions, chitin is stable for much longer than previously suspected. During the last decade, we succeed in development of novel methods for the production two or three-dimensional cleaned chitin skeleton of dictyoceratid sponges and use thereof. The extraordinary biocompatibility and mechanical properties of chitinous scaffolds from marine sponges endows these structures with unique properties that render them ideal for diverse biomedical uses. The obtained experimental results suggest that chitin from the marine demosponges is a promising, highly biocompatible biomaterial for stem cell-based tissue-engineering applications.

Also, the biomimetic potential of chitin-based composite biomaterials of poriferan origin is under investigation now. Recently, for the first time, we proposed sponge chitin as thermostable template for development of new generation of biocomposites using "extreme biomimetic conditions" via hydrothermal synthesis route.

Magdalena Gierszewska*, Ewelina Chrzanowska, Ewa Olewnik-Kruszkowska

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MODIFIED CHITOSAN/MONTMORILLONITE NANOCOMPOSITE FILMS: PREPARATION AND CHARACTERIZATION

During last decades, biopolymers, due to their excellent biocompatibility, biodegradability and non-toxicity, have been widely used in various fields of human life [1]. Chitosan is one of the most abundant biopolymer obtained from chitin in a deacetylation process. Chitosan is a linear polysaccharide composed of β-(1→4)-2-amino-2-deoxy-D-glucopyranose and β-(1→4)-2-acetamido-2-deoxy-D-glucopyranose. It can also be presented as a homopolymer of β-(1→4)-2-amino-2-deoxy-D-glucopyranose. Due to its unique polycationic nature it is an object of a research in medical and pharmaceutical fields, as well as a membrane for different separation techniques [2]. Unfortunately pure chitosan in different forms (beads, films, membranes etc.) is characterized by a relatively low mechanical strength in both dry and swollen state.

In order to obtain superior stability of chitosan-based films, the addition of a natural multilayer silicate known as montmorillonite (MMT) clay is used. MMT significantly enhances the chemical and/or mechanical stability of chitosan in comparison with the pure polymer [3]. In some cases highly hydrophilic poly(vinyl alcohol) (PVA), biodegradable synthetic polymer, can also be used to enhance hydrophilic properties of new membrane.

A series of novel chitosan-montmorillonite nanocomposite films crosslinked with glutaraldehyde (Ch/MMT/GA) (*Fig. 1a*) as well as chitosan/MMT/poly(vinyl alcohol) nanocomposite membranes (Ch/PVA/MMT) (*Fig. 1b*) were obtained by dissolution and solvent evaporation technique. To confirm the chemical structure of prepared membranes Fourier transform infrared spectroscopy (FTIR) was applied. The surface morphology of investigated composite films was studied by scanning electron microscopy (SEM) and atomic force microscopy (AFM). Changes in surface hydrophilicity were characterized by contact angle measurements. The results showed that MMT is uniformly dispersed in the

Ch/GA and Ch/PVA matrix. SEM and AFM micrographs revealed that obtained membranes are dense and non-porous with low surface roughness.

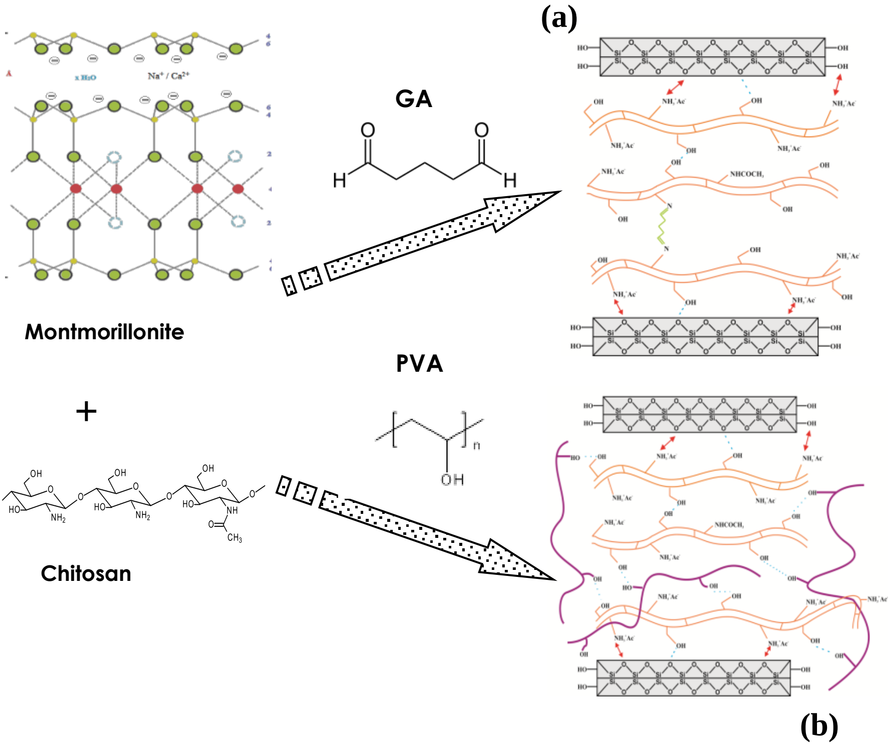

Fig. 1. Chemical structure of chitosan-montmorillonite nanocomposite membranes (a) crosslinked with glutaraldehyde and (b) modified with poly(vinyl alcohol).

References:

[1] A. Kumari, S. K. Yadav, S. C.Yadav, *Biodegradable polymeric nanoparticles based drug delivery systems*, Colloid. Surf. B: Biointerfaces 75 (2010) 1–18. [2] R. Jayakumar, D. Menon, K. Manzoor, S. V. Nair, H. Tamura, *Biomedical applications of chitin and chitosan based nanomaterials—A short review*, Carbohyd. Polym. 82 (2010) 227–232. [3] S. Bensalem, B. Hamdi, S. Del Confetto, M. Iguer-Ouada, A. Chamayou, H. Balard, R. Calvet, *Characterization of chitosan/montmorillonite bionanocomposites by inverse gas chromatography*, Colloid. Surf. A: Physicochem. Eng. Asp. 516 (2017) 336–344.

Agata Goszczyńska, Agata Niemczyk, Agnieszka Piegat
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CHEMOSELECTIVE ACYLATION OF CHITOSAN – PROBLEMS AND CHALLENGES

Chitosan, among the others polysaccharides, is considered as an attractive material for chemical modification. The main reason for this is the presence in its structure different functional groups, i.e. acetamide, primary and secondary hydroxyl and the most reactive amine. Therefore, in the literature, can be found an enormous number of publications showing diverse chitosan derivatives [1]. However, in the case of highly selective chemical modification, with well-defined product structure, the number of publications decrease and reveal different difficulties. The main disadvantage of chitosan, independently of its deacetylation degree or molecular mass, is the solubility limitation. Despite the water solubility of some kinds of chitosan (such as oligochitosans or salts) is considered as a significant improvement, it has to be emphasized that it is still an aqueous environment, which is not favorite in the reactions with hydrophobic compounds such as fatty acids. The chemoselective acylation of chitosan with multiple reactive sites is a long-standing problem, especially when the reaction with hydroxyl groups of chitosan is planned. Stronger nucleophilic character of amino group cause necessity of protection of this group which involves the use of additional blocking reagents or special reaction conditions. Additionally, statistical character of grafting reactions of polysaccharides, which might lead to non-uniform derivatives has to be also taken into account [2].

Therefore, in our work, the influence of different reaction conditions such as type of solvent, coupling agent, additives, pH of reaction medium and methods of product isolation on the chitosan-fatty acid product was investigated. The Infrared Spectroscopy (IR) and Proton Nuclear Magnetic Resonance Spectroscopy (^{1}H NMR) were used to establish the structure of the reaction products. The degree and substitution position were determined and correlated with the product structure. The change of reaction solvent, presence of chloride anions in the reaction mixture as well as pH variation allows to manipulate of the ratio of amino and hydroxyl groups substitution. The combination of a coupling agent and additive i.e. carbodiimide EDC with *N*-hydroxysuccinimide influences the substitution, particularly increasing the substitution degree. Also, it is worth to emphasize that the method of product isolation – precipitation or lyophilization also has a significant impact on the final product.

References:

[1] I. Aranaz, R. Harris, A. Heras, Chitosan amphiphilic derivatives. Chemistry and applications, Curr. Org. Chem. 14 (2010) 308–330

[2] B. Focher, A. Massoli, G. Torri, A. Gervasini, F. Morazzoni, High molecular weight chitosan 6-0-sulfate. Synthesis, ESR and NMR characterization, Macromol. Chem. 187 (1986) 2609–2620

Acknowledgements:

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STUDIES ON THE MINERALIZATION PROCESS OF CHITOSAN MATERIALS IN THE SBF SOLUTIONS

The purpose of the present work was the preparation and evaluation of the physico–chemical properties of new composites of biopolymers and inorganic additives. The morphology and structure of thin films containing chitosan (Ch) with montmorillonite (MMT) or nanoclays after surface modification were characterized by scanning electron microscopy (SEM), atomic force microscopy (AFM), thermogravimetric analysis (TGA) and attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR). Thin films of chitosan sample and composition of chitosan with montmorillonite or nanoclays have been formed by casting methods from acetic acid solutions and have been soaked in a SBF (simulated body fluid) solution at 37°C for 2 weeks. The samples before and after soaking were compared. The obtained results showed growth of new phases containing calcium in all prepared films. The largest increase was observed for the Ch/nanoclay composite films.

POSTER SESSION

Dorota Biniaś, Włodzimierz Biniaś, Jarosław Janicki

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THE OBTAINING OF BIOMATERIALS FROM CHITIN

Chitin is a natural polysaccharide with a high degree of orderliness that significantly impedes the solubility of this biopolymer in common organic solvents, making it difficult to use.

Preliminary studies have provided a chitin solution from which fibrous biomaterials or microparticles can be obtained. The properties, including its form, depend to a large extent on the composition of the dissolution mixture and on the environment of its coagulation.

As a solvent, a controlled-substance mixture is used that is strongly active against hydrogen bonds that maintain the native chitin structure and affect its solubility. An important factor affecting the form of chitin regenerated from the solution is the composition and parameters of the coagulating bath. Coagulation bath specifically affects the rebuilding of hydrogen bonds responsible for the physicochemical properties of the products.

Ewelina Chrzanowska, Magdalena Gierszewska*, Ewa Olewnik-Kruszkowska, Wojciech Kujawski

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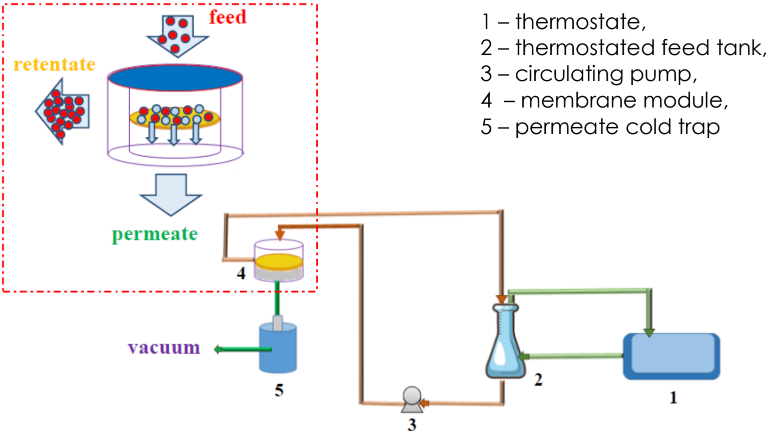
PERVAPORATION OF ALCOHOL/WATER MIXTURES THROUGH MODIFIED NANOCOMPOSITE CHITOSAN MEMBRANES

Increasing environmental pollution had limited the development of synthetic materials and turned people's attention into bio-based materials. Among bio-based polymers like cellulose, starch, etc. chitosan and its derivatives are widely favored because of their good film-forming properties, biocompatibility, biodegradability and antibacterial properties [1]. Moreover chitosan, cationic biopolymer, is highly bioactive, exhibits nontoxicity and antimicrobial activity. These properties combined with its ability to form films, allow usage of this polysaccharide in different industrial areas. Till today chitosan found a wide variety of applications, in tissue engineering (bone substitutes and artificial skin), drug and gene delivery systems, in agriculture, pharmaceutical, food packing etc [2]. Materials based on chitosan can be formed into gels, sponges, nanocomposites, scaffolds, powders, beads and films. These can be also based on various blends of chitosan with natural polymers, synthetic polymers or clay minerals. The combination of chitosan with clay minerals provides a further opportunity to develop new functional biomaterials.

Membranes based on pure chitosan and on chitosan blended with other polymers or fillers can be easily prepared by casting of its solution/dispersion and solvent evaporation. Taking into consideration that chitosan has in its structure amino and hydroxyl functional groups, membranes based on this polymer are highly hydrophilic and can find the application in the dehydration of organic solvents [3].

In the present study the chemical and physical characteristics of chitosan and chitosan/montmorillonite membranes crosslinked with glutaraldehyde (Ch/GA and Ch/MMT/GA) as well as chitosan/MMT/poly(vinyl alcohol) nanocomposite membranes (Ch/PVA/MMT) are discussed. Hydrophilic nature of chitosan and poly(vinyl alcohol) constitute theirs potential in the selective separation of water from alcohol. For this reason, the permeation and separation characteristics of two component water/ethanol and water/isopropanol mixtures of different composition through Ch/GA Ch/MMT/GA and Ch/PVA/MMT membranes in vacuum pervaporation process were investigated (Fig. 1). All pervaporation experiments were performed at 30°C.



1 – thermostate,
2 – thermostated feed tank,
3 – circulating pump,
4 – membrane module,
5 – permeate cold trap

Fig. 1. Pervaporation setup ring

It was found that nanocomposite Ch/PVA/MMT membranes exhibit better separation properties in comparison with Ch/GA and Ch/GA/MMT membranes in dewatering of ethanol and isopropanol mixtures.

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PROCEDURE OPTIMIZATION FOR DETERMINATION OF MOLECULAR WEIGHT OF CHITOSAN BY VISCOMETRY

Application of chitosan usually depends on its degree of deacetylation (DD) and molecular weight. Many studies on chitosan indicate that low-molecular-weight chitosans have much better biological activity than high-molecular-weight polymer. Low-molecular-weight chitosan, in the order of several dozen or so kDa, exhibits better antibiotic and antifungal effects. Moreover, it stimulates plant growth and acts as agent stimulating the plant resistance to pathogens.

Many research centers in countries that produce chitosan carry out extensive researches on various types of chitosan, also on oligochitosan. To characterize and compare such materials precisely, it is important to identify two key parameters of this polymer, i.e. the average molecular weight and degree of deacetylation. Methods of DD determination, including FTIR and UV-Vis spectroscopies, NMR spectroscopy, and a few titration approaches were compared in our previous report [1]. Precise determination of molecular weight requires sophisticated and expensive equipment, such as GPC or laser-light scattering, nevertheless one can obtain a good approximation using popular and low-cost method of viscometry to determine the viscosity-average molecular mass. Unfortunately, the commonly used molecular weight determination procedures are best suited for high- to medium-molecular-weight chitosans [2]. In this work we test the molecular weight determination procedures for their suitability for low-molecular-weight chitosans evaluation.

In the first stage, viscometry measurements using standard procedures have been performed on high-molecular-weight chitosan, and then the same operations were applied to chitosans of relatively low molecular weights, (from 600 kDa to 30 kDa). The obtained results show that viscometric method of determination of viscosity average molecular weight can be used for chitosans with molecular weight down to 30 kDa, if the initial polymer concentration is adjusted to provide sufficiently high relative viscosity.

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THE INFLUENCE OF THE CHITIN AMINATION ON THE EFFECTIVENESS OF RB5 AND RY84 DYE SORPTION

Chitin is regarded as a material of high potential with the possibility of structure change in order to achieve desirable properties [Pillai C.K.S. et al. 2009]. The literature describes various ways of chitin modification aiming at the improvement of its properties as well as creating new, better products. The physical parameters such as the size of the main surface, diameter of pores as well as chemical parameters such as addition of amino groups might get changed.

The purpose of this processes is the improvement of sorption properties as well as the increase of mechanical durability and resistance to acidic environment. The modifications are carried out using physical or chemical methods. Physical methods include obtaining chitosan in different forms, such as powder, nanoparticles, gel beads, membranes, sponges, 'honeycomb' structures and various types of fiber [Guibal E. 2004]. The ultrasound modification of chitin leads to the increase in the porosity of material, enables easier flow of the substance and as a consequence increases the amount of places to bond the dye. The adsorbent has the same functional groups as before the modification, but has bigger surface and amorphic structure.

The chemical processes rely on the crosslinking of the polymer structure with croslinking agents such as glutaraldehyde, oxidized β-cylkodekstrine, diglycidyl ether of ethylene glycol or epichlorohydrine [Lee S.T. et al. 2001].

Chitosan as a product of N-deacetylation of chitin can also be a subject to various types of modifications and crosslinking. The modification of chitosan is easier due to the presence of free amino groups in its molecular structure, which increases its reactivity [Struszczyk M.H. 2002].

Dyes are chemical compounds having the ability to intensively absorb electromagnetic radiation in the visibility range, close to ultraviolet and infrared. They transform the absorbed energy and forward it to other materials. Dyes have diverse and complex chemical structure, what causes differences in their physicochemical and usable properties.

In the cellulose and textile industry reactive (helactine) dyes appear to be the most useful, their advantage is their durability and high quality of colour of dyed material. This group contains anionic dyes, their characteristic feature is the presence of azo groups in the molecular structure (-N=N-). Anionic dyes are firstly adsorbed on cellulose and then react with cellulose fiber. The reaction occurs through the creation of covalent bonds between the molecules of dye and fibers. However present in the colouring bath hydroxyl ions in the alkaline environment compete with the cellulose bed. The result of that is the presence of 10÷50% of initial dye concentration in the wastewater [Al-Degs Y. et al. 2000].

The aim of the work was the determination of the effectiveness of reactive dyes Reactive Black 5 and Reactive Yellow 84 removal from aqueous solutions by sorption, with the use of two sorbents: chitin and chitin subjected to ammonification.

Higher effectiveness of adsorption was obtained with the use of aminated chitin. The adsorption capacity has increased 1,6 – times in case of RB5, and 1,25 – times in case of RY84 in relation to adsorption capacity of chitin not subjected to modification.

In the research it was stated that the adsorption process of two tested dyes was more effective on ammonificated chitin. The reason for that was the addition of amino groups to the structure of chitin molecule. The adsorption of dyes was best described with the double Langmuir model. Both tested dyes Reactive Black 5 and Reactive Yellow 84 were sorbed in two active sites: on acetamide group and on the attached amino group on the chitin molecule.

During the Reactive Yellow 84 dye sorption on unmodified chitin different mechanism was observed. The dye was sorbed on the acetamide group and the single Langmuir model was better to describe obtained experimental data.

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PREPARATION AND CHARACTERIZATION OF CHITOSAN-BASED MEMBRANES WITH COPPER NANOPARTICLES

Metal nanoparticles (NPs) or nanocrystals are the particles of the size below ca. 100 nm at least one dimension. Such small-sized particles of different shapes demonstrate the unique properties of the obtained materials [1]. In addition, the properties of the NPs strongly depend on methods and conditions of the preparations. The growing interest of potential NP's application appeared in hundreds scientific publications per year. From the wide range of possible applications the most cited are: catalysis, electronics, photography, biomedical, imaging, water treatment, stimuli–response polymers or sensing [2,3].

The potential applications for copper nanoparticles (Cu-NPs) include catalysis, medicine, electronic, and sensing.

By the use of specific conditions, such as capping agents, polymer (biopolymer) or surfactant solutions, it is possible to control structure of the final materials. One of the methods is incorporating the biopolymer (such as chitosan) with amino- and hydroxyl- groups to coordinate copper ions and to take control of the nucleation process [4,5].

Here we present results of the preparation chitosan-based membranes decorated by the copper nanoparticles. Cu-NPs were synthesized in hydrogel obtained from the acetic solution of commercial chitosan (CS) and copper sulfate by regulation of pH and following reduction by hydrazine. The particle growing process was stopped by the immersed in liquid nitrogen. The membranes of foam-like structures with Cu-NPs were obtained by the freeze-drying method. Structure and morphology of the CS-Cu-NPs composites were studied by SEM and XRD techniques.

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CHITOSAN BASED MMMs FOR PERVAPORATIVE SEPARATION OF ETHYL ALCOHOL

A promising type of membrane material emerging potential for future applications is mixed matrix materials (MMMs) composed of homogeneously interpenetrating polymeric phase and inorganic particle matrices which could be attractive alternative to conventional organic or inorganic membrane materials. Compared to pristine polymeric membranes, MMMs are characterized by significant improvement in separation properties with tiny loss of membrane flexibility. Furthermore, they are significantly cheaper than ceramics membranes.

It has been shown that the inorganic filler plays indeed, an important role in the improvement of the membrane performance. Inorganic materials are characterised by high thermal and chemical stability, while organic materials possess properties such as flexibility, ductility, and malleability. Therefore, combining polymer and inorganic substance in a hybrid membrane results in favourable selectivity and permeability, consequently gaining more and more importance. In general, the resulting membranes show improved chemical, mechanical, and thermal stability and hydrophilic–hydrophobic balance.

Composite chitosan membranes filled with various amount of iron ferroferric oxides (Fe_3O_4) and cross-linked by epichlorohydrin were prepared. Dehydration of ethanol by means of pervaporation was conducted. Based on the pervaporation results of evaluated total flux and GC analysis of the permeate composition, as well as independently carried out vapour permeation experiments, the transport characteristic of investigated membranes was evaluated, both for mixture and pure components.

The influence of iron(II,III) oxide content on the membrane transport properties were discussed. After addition of magnetite oxide nanoparticles to the polymer matrix diffusion coefficient of water increased above 11 times, while for ethanol approximately two times decreases in diffusion coefficient was observed. Permeation coefficients of both components remain on constant levels, what means, that filler influences most of all the separation factor of MMMs membranes. The best separation performance was obtained for membranes with 15 wt.% of iron(II,III) oxide content, for which PSI value was equal to 295.3 $g \cdot m^{-2} \cdot h^{-1} \cdot \mu m^{-1}$, in contrast to 106.6 $g \cdot m^{-2} \cdot h^{-1} \cdot \mu m^{-1}$ of the pristine epichlorochydrin crosslinked chitosan membrane.

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INVESTIGATION OF PHYSICOCHEMICAL PROPERTIES OF DENTAL HYDROGELS WITH CLOTRIMAZOLE BASED CHITOSAN

The work involves the development of dental gel composition obtained on the basis of the incorporated clotrimazole on chitosan in order to improve the drug solubility.

Solid dispersions were prepared by using two methods: grinding and kneading methods. Solid dispersions were in different weight ratios of drug to polymer. Solid dispersions of the best parameters were introduced into the gels and the texture, spread and viscosity were investigated to determine the best hydrogel mucosal system for oral infections

Texture testing was performed using the texturometer. Results of hydrogels texture study were compared to sample H0 chitosan-free system with a hardness of 131.0 g, a consistency of 485.7 g·s and a cohesion of 98.94 g. The hardness of hydrogel H 5+5 containing 1% of polymer was 206.41 g and was the lowest value among chitosan systems. The tenacity of this hydrogel was 693.51 g·s and the cohesion of 170.32 g. The highest values of all texture parameters were achieved for sample H 2+8 hydrogel containing 4% chitosan in its composition. Its hardness was 355.38g, tenacity of 1165.70 g·s and cohesion of 306.86 g. The hardness of the gels increased with the increase in chitosan content in the system. The difference between the values of this parameter for subsequent hydrogels was an average of 70 g. Similar dependence also concerned cohesion. Consistency increased on average by 200 g·s in order from hydrogel samples of the smallest to the highest chitosan content. The presence of chitosan influenced the hardness and coherence of the system.

The gel spread capability was measured using an extensometer. This testifies to the spread of the system. The wheel surface area for hydrogel without the addition of chitosan was 19.24 cm^2 with a maximum load of 1200 g. The surface area of the wheel at the highest load decreased as the percentage of chitosan in the system increased. The wheel surfaces for subsequent H 5+5, H 3+7 and H 2+8 hydrogels were 18.10 cm^2, 15.55 cm^2 and 13.20 cm^2 for the final load. The above analysis indicates that the best spread among natural polymer systems was obtained for hydrogel, in which the ratio of drug to chitosan was 5:5.

Based on the rheological properties of the gels, it has been found that these are highly viscous systems. The viscosity was affected by the presence of carbopol, chitosan and pH of the environment.

Hydrogel H 2+8 with 4% chitosan has the highest shear stress of 10766.66 N/m^2 and the highest viscosity of 224.31 Pa·s at the highest rotation speed of the cone. The viscosity of the hydrogels increased with increasing chitosan, but decreased with the increasing shear rate of the system. Tested gels are non-Newtonian, pseudoplastic systems.

The addition of clotrimazole gels based on chitosan affects the profitably on the rheological properties which facilitatesthe preparation, squeezing from a tube and spread on the mucosa.

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NANOMETRIC CELLULOSE MODIFIED WITH IONIC LIQUID AS A FILLER FOR CHITOSAN BIOCOMPOSITES

Cellulose is a ubiquitous polymer of natural origin that has four principal allomorphs called cellulose I, II, III and IV. The crystal structure of native cellulose I can be converted into cellulose II (process called mercerization), what causes a conversion of chain crystal structure [1]. Cellulose II manifests different nucleating abilities than native cellulose. Polymorphic structure of cellulose may also influence the formation of nanosized cellulose and the determination of the particle size distribution. Nanometric cellulose is a smart, green nanomaterial derived from natural resource that exhibits some unique properties e.g. high aspect ratio, specific strength, optical properties, surface area, biodegradability, and non-toxicity [2]. The most common production method of nanometric cellulose is an acid hydrolysis. This method has many drawbacks, including difficulties in controlling the progress of the reaction [3, 4] or quite intensive formation of sulfate ester groups at the surface of nanocellulose [5] that influences interactions at the nanometric cellulose/polymer matrix interface. Not without significance is the necessity of use concentrated, toxic reagents and separation of nanoparticles from such solutions. Hence, ionic liquids can be used as an alternative hydrolyzing agent.

Due to its some remarkable biological properties chitosan is currently very eagerly used for forming composites. The presence of reactive amino and hydroxyl groups enables its chemical modifications but is also responsible for its poor solubility in organic solvents [6]. Due to their chemical compatibility, nanometric cellulose and chitosan can be combined without any extra modifications, but the lack of proper distribution of nanofiller in chitosan matrix is still an issue. Surface modification of nanometric cellulose limits its aggregation and is known to help to overcome such problems.

This work is a continuation of our studies on chitosan/nanometric cellulose composites. The main goal of this research was to evaluate the influence of crystallographic form of nanocellulose produced with ionic liquid on thermal and mechanical properties of chitosan-based composites. Nanometric celluloses were obtained with ionic liquid as hydrolyzing agent. Subsequently, such nanometric fillers were used to prepare chitosan composites. In result, the influence of cellulose polymorphism on mechanical properties of such composites was defined. Especially much emphasis was put on the relationship between the polymorphic form of cellulose and the particle sizes of nanometric cellulose.

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CHITOSAN COMPOSITES FILLED WITH MODIFIED NANOMETRIC CELLULOSE

Nanocrystalline cellulose, a nanometric filler with great mechanical properties, can be successfully applied as a reinforcement for numerous biodegradable matrices, e.g. thermoplastic starch, polylactide or chitosan [1, 2]. Chemical structure of chitosan is analogous to cellulose but in cellulose, in position C2, there are hydroxyl group, whereas in case of chitosan there are amine groups [3]. This structural similarity of cellulose and chitosan facilitates the formation of chitosan/nanometric cellulose composites. Although these strong chitosan/cellulose interactions are important to obtain an appropriate percolation of the nanofiller in polymer matrix, they are also responsible for formation of undesirable agglomerates [4]. These cause a lowering of mechanical properties of composites. Therefore, a chemical modification of filler is believed to be an effective way to conquer this issue. One of the most common method for modification of nanometric cellulose is its esterification with carboxylic acid anhydrites, acid chlorides or dicarboxylic acids. It was proved that modification of nanometric cellulose with acid chlorides causes a better dispersion of filler in polymer matrix [5]. The application of dicarboxylic acids as coupling agents for bacterial nanocellulose and poly(vinyl alcohol) composites was also found to enhance its mechanical properties, as well as to limit water absorption [6]. On the other hand, it was showed that the dicarboxylic acid chain length has an influence on adsorption of TiO_2 nanoparticles, self-cleaning properties and washing durability on cotton fabrics [7].

In this research nanometric celluloses of two polymorphic forms (CNC I and CNC II), produced using the enzymes coming from bacteria, were chemically modified with pimelic acid. Wide angle X-ray scattering (WAXS) and infrared spectroscopy (FTIR) methods were used to confirm, respectively, supermolecular and chemical structures of cellulosic materials. After characterization, both modified and unmodified, nanometric celluloses were used as fillers for chitosan matrix. The obtained chitosan/nanometric cellulose composites were subjected to tensile tests. Based on the resultant tensile curves, the mechanical parameters were calculated. All the tested composites were characterized with good mechanical properties. However, in terms of Young's modulus and tensile strength enhancement, addition of 1% of modified CNC I turned out to be optimal. Chemical modification of nanometric cellulose with pimelic acid was found to be effective only for materials with polymorphic form characteristic for cellulose I.

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THE INFLUENCE OF THE DEACETYLATION DEGREE OF CHITOSAN IN THE FORM OF FLAKES ON THE EFFECTIVENESS OF NITRATES V SORPTION FROM AQUEOUS SOLUTIONS

The post-production wastewater from the fertilizer, explosives or metalworking industry due to the high concentration of nitrates V belong to particularly problematic. Nitrates which enter the natural environment might cause eutrophication of rivers and lakes. Another problem is also the possibility of nitrates V entering the drinking water tanks or ground water. The consumption of water contaminated with nitrates V might lead to the creation of nitrosoamines, detrimental to the human organism, and be the reason of digestive system cancer as well as the formation of methaemoglobinaemia. It is particularly important to use effective technologies of wastewater treatment before returning them to the environment.

Treatment of wastewater containing excessive load of N-NO_3 in conventional, biological wastewater treatment plants might lead to their incorrect functioning and is usually ineffective. Chemical methods of nitrates V removal from aqueous solutions such as electrodialysis, electrocoagulation and electroreduction are usually more effective than biological methods but require bigger amount of energy as well as expensive installation. Among physical methods, most efficient technology of N-NO_3 removal from aqueous solutions is reversed osmosis. However, among drawbacks of this method are: huge loss of water, high cost of membranes and problems with their regeneration or later management. The alternative method of nitrates V removal from aqueous solution is sorption. This method is commonly considered as safe for the environment. The process is easy to carry out and cost is usually limited only to the price of the sorbent. The most common are sorbents based on active carbon. They are characterised by quite good efficiency but are rather expensive, what forces to use cheaper or more efficient alternatives.

In order to effectively bond nitrates, the sorbent should have basic character. In theory, positively charged surface of the sorbent electrostatically attract the anions of nitrates V what would significantly improve the effectiveness of sorption. The material, which has basic character and proved to be of good use with nitrates V removal from aqueous solutions is chitosan. Chitosan is a polysaccharide, the derivative of chitin, which is one of the most common biopolymers in nature. It might be obtained in greater amounts from the waste obtained from the crustacean processing industry. Because of that chitosan is considered as widely available and cheap material.

High effectiveness on anion bonding on chitosan comes from the presence of primary amine groups, which are able to protonate, being the main sorption centres. The amount of $-NH_2$ groups depend on the degree of deacetylation of chitosan. Theoretically the degree of deacetylation of chitosan might have a huge influence on the sorption effectiveness of anionic pollution. It seems as of high importance to carry out the research upon the dependence between the degree of deacetylation of chitosan and its sorption abilities.

In the work the influence of chitosan deacetylation degree on the effectiveness of nitrates V sorption from aqueous solutions was examined. For the research purpose chitosan from the crab shells in the form of flakes in the degree of deacetylation of DD=75%, DD=85% and DD=90% was used. The research was divided into two parts. In the first step the influence of pH (pH range 2-11) on the sorption effectiveness of NO_3^- on tested chitosan sorbents was examined. After determining the optimal pH of sorption, the experiment upon sorption capacity in time of 5/ 15/ 30 and 60 min. was carried out. The experimental data was described with Freundlich and Langmuir isotherms.

The sorption effectiveness of nitrates V on chitosan sorbents was the highest at the pH of 4. Sorption at the pH 2-3 resulted in the dissolving of the sorbent. In the research upon the determination of sorption capacity, the best fit to the experimental data showed the Langmuir model. The effectiveness of sorption of nitrates on tested sorbents depended on the degree of deacetylation of chitosan and increased according to DD=75% < DD=85% < DD=90%. The obtained sorption capacity of tested chitosan flakes regardless of the degree of deacetylation was the highest after 30 min of sorption. After 60 min of sorption, the obtained sorption capacity of tested chitosan sorbents was lower than after first 30 minutes. This proves the desorption of nitrates, presumably caused by the change of pH in the system.

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DETERMINATION OF HYDROLYTIC ACTIVITY OF SALIVA USING CHITOSAN ASCORBATE AS A SUBSTRATE

The aim of this study was to determine of N-acetyl-D-glucosamine concentrations in saliva during incubation with and without chitosan ascorbate (ChA).

In this study were used sterile chitosan ascorbate in the form of powder. Chitosan was obtained from krill chitin and deacetylation degree was equal 60%. The ratio of ascorbic to chitosan was equal 1. The samples of saliva were taken from 30 healthy volunteers aged from 25 to 62 years. Unstimulated mixed saliva was collected under standardized conditions: saliva collection (7 ml) was performed in the morning (9.30 – 10.00) two hours after breakfast. The samples of saliva were used to the preparation of 30 separate experimental kits. Each of them was made up of 3 different incubation mixtures: mixture A (pH 5.9) consisted of 3 ml of fresh, non-centrifuged saliva + 1 ml of buffer solution (0.6 M sodium citrate, 1.2 M Na_2HPO_4, pH 5.1); mixture B (pH 5.8) consisted of 3 ml of fresh, non-centrifuged saliva + 20 mg chitosan ascorbate + 1 ml of buffer solution (0.6 M sodium citrate, 1.2 M Na_2HPO_4, pH 5.1); mixture C (pH 5.8) consisted of 20 mg chitosan ascorbate + 1 ml of buffer solution (0.6 M sodium citrate, 1.2 M Na_2HPO_4, pH 5.1) + 3 ml of bidistilled water. The incubation of all mixtures was carried out simultaneously at 37^0 C in a water bath under constant shaking for 26 hrs. Each sample was analysed to detect N-acetyl-D-glucosamine according to the modified method of Reissig et al. (J. Biol. Chem., 1955, 217, 959 – 966) for N-acetyl-aminosugars determination. N-acetyl-D-glucosamine concentration was determined in each mixture before incubation and after 1, 8, 20, 24 and 26 hrs of incubation. Absorbance was measured at 544 nm by Beckmann spectrophotometer. This study was supported by the MUG (St-31).

Values of N-acetyl-D-glucosamine in saliva without ChA before incubation were between 0 and 6.8 μg/ml with mean 4.5±1.6 μg/ml (mixture A and B). Significant increase of N-acetyl-D-glucosamine concentration in saliva was observed directly after the addition of ChA. Values of N-acetyl-D-glucosamine directly after the addition of ChA were between 2.3 and 13.5 μg/ml with mean 6.1±3.2 μg/ml (mixture B). Significant increase of N-acetyl-D-glucosamine concentration in mixture B was observed moreover after 8 hrs (9.6±3.5 μg/ml), 20 hrs (17.6±8.6 μg/ml) and 24 hrs of incubation (23.9±6.5μg/ml). In the case when an experimental mixture contained saliva only (mixture A) significant increase concentration of N-acetyl-D-glucosamine was observed only after 1 hrs of incubation (5.5±1.9 μg/ml). The concentrations of N-acetyl-D-glucosamine in mixture A after 8, 20, 24 and 26 hrs of incubation were similar (5.4±2.5 μg/ml, 5.9±3.4 μg/ml, 5.5±1.9 μg/ml and 5.5±1.9 μg/ml). In the case when an experimental mixture contained ChA only (mixture C) the initial concentration of N-acetyl-D-glucosamine was low (3.4±2.4 μg/ml). Significant increase concentration of N-acetyl-D-glucosamine was observed after 20 (6.3±3.4 μg/ml) and 24 hrs of incubation (7.5±4.4 μg/ml).

Conclusion: The unstimulated whole saliva showed the hydrolytic activity in the presence of the chitosan ascorbate as a substrate. The significant increase of N-acetyl-D-glucosamine concentration was observed directly after the addition of ChA to saliva and after 8, 20 and 24 hrs of saliva incubation with ChA.

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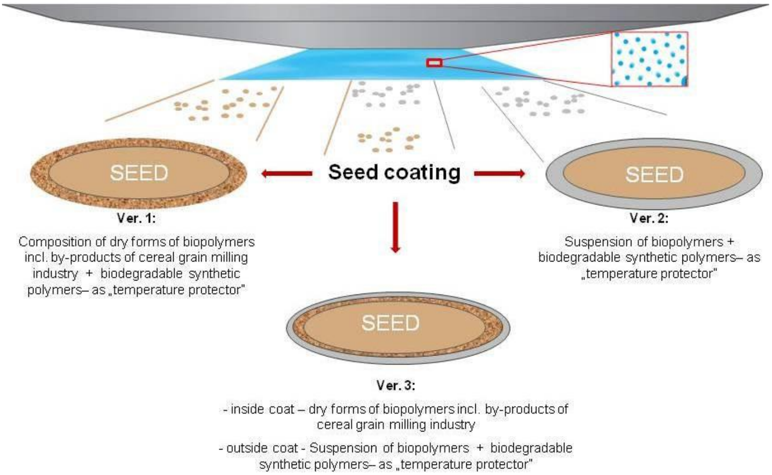
DEVELOPMENT OF INNOVATIVE BIODEGRADABLE SOYBEAN SEED COATING BASED ON BIOPOLYMERS FROM RENEVABLE RAW MATERIALS FOR BETTER TOLERANCE OF PLANTS TO ADVERSE ENVIROMENTAL CONDITIONS

Soybean - a plant valued in many parts of the world, is sometimes called the "meat of the fields", " the yellow jewel," or even "the queen of all plants". This unusual plant combines the nutritional value similar to meat with a wealth of plant micro- and macroelements. Therefore soybean is a versatile plant whose components are used in food industry, as well as in medical nutrition, feeds, technical products. Important consumer role play: soy oil, soy milk, tofu, okara - textured soy protein (TSP) and others. Around the world soybeans are mainly used for oil processing, soymeal cake - for feeding purposes as a valuable high protein feed supplements. Food industry widely uses defatted soybean flour for making bread, cereals and confectionery. Soy oil is also used in production of paints and soaps. Soy protein isolates are used in textile industry, perfumery, pharmaceutical, paper and other technical fields. Due to the growing popularity of vegetarian and vegan diets in Poland it is also growing demand for GMO free soybeans for food purposes. At the moment, the cultivation area of soybean in Poland is not limited, but needs special cultivars - due to the climatic and geographical conditions only soybeans grown or tested locally can be cultivated in Poland. Soybean is a short day plant with high thermal requirements, therefore most of the foreign soybean cultivars will not mature in Poland.

The aim of the project is to develop biodegradable and environmentally friendly seed coating, based on renewable biopolymers compositions, protecting soybean seeds against adverse weather conditions and diseases caused by soilborne pathogenic fungi. To prepare a polymer composition for seed coating will be used selected natural polymers characterized by a high bioactivity and a qualified seed material. The study on the impact of seed coat on microbial environment will be made in the project. The project is consistent with I.14. Area of III BIOSTRATEG programme. Project subject is a combination of all aspects: technological, raw materials and waste recycle (from renewable raw materials and wastes to soil-friendly biodegradable bioproducts), product and technology eco-innovations, optimization of crops and environmental safety, resources-efficiency by maximizing the potential of seeds in different and variable weather conditions (temperature, humidity, bacteria) using modern measurement techniques for assessing the environmental performance of developed technological solutions in terms of Life Cycle Assessment of developed bioproducts. Potential customers for coated soybean seeds are organic and conventional farms.



Consortium implementing the project

Leader of the consortium: Institute of Biopolymers and Chemical Fibres, Łódź. Partners: Scientific Research Center of Soya Development „AgeSoya" Sp. z o.o., Huta Krzeszewska; Institute of Soil Science and Plant Cultivation – State Research Institute, Puławy; University of Rzeszów, Rzeszów.

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PHARMACEUTICAL ASSESSMENT OF GYNECOLOGICAL POWDERS WITH A SODIUM ALGINATE CONTAINING LACTIC ACID COMPLEXED WITH CHITOSAN

Treatment of vagina inflammatory condition is usually long and difficult because of its frequent relapse. The condition is recognized increasingly more often due to improved diagnostic methods. Traditional therapeutic schemes recommended by world treatment centres and health organizations do not bring satisfactory results. Insufficient duration of the drug's contact with vaginal mucosa does not provide adequate pH the physiological biocenosis of the organ [1, 2].

The use of hydrophilic base for lactic acid complexed with alkaline polymers enabled production of powders passing under natural conditions in the gels with rheological properties of vaginal mucus. The gel remains at the site of application and provides adequate environmental pH. The research is continuing on optimization of the powders composition in order to improve their adhesion properties and thus increase the efficacy of the therapy. Gynecological powders are designed to correct abnormal pH environment of the vagina and the achievement to the physiological state.

The aim of this study was to investigate the influence of sodium alginate on the physico-chemical properties of powders for gynecological purposes.

By adopting the above-mentioned assumptions tested impact of sodium alginate in the properties of the powders. The study was used prepared formulations with different pH and rheological properties. In the constructed for this purpose the device simulating the conditions in the vagina, the adhesion test and movement the gel on the mucosa of the organ were performed. The powders passing in the gels were examined for their properties. As a result of *in vitro* studies it was found that the gels obtained from the powders are maintained at the application site.

The powders after application to the apparatus passes in the gels and cover the surface. The test shows thixotropical properties of gels. On the basis of studies, the dynamic viscosity of the gels obtained from powders was defined. The range of pH of the gels allows the selection of the optimum formulation.

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THE EFFECT OF A CARBOXYMETHYLCELLULOSE SODIUM SALT ON THE PROPERTIES OF HYDROPHILIC POWDERS CONTAINING LACTIC ACID COMPLEXED WITH CHITOSAN

Modalities of treatment inflammatory conditions in the vagina are based on antibiotic and chemical therapy, which destroys the physiological conditions in the vaginal environment. Commonly applied drug forms tend to leave the vagina when the patient assumes a vertical position [1, 2].

The using of hydrophil base as a vehicle for the complexes we were able to produce of powders passing under natural conditions in the gels with the rheological properties of the vaginal mucus. Thus formed gels does not flow out. The gels uniformly covers the mucous membrane and remains there during the daily activities of the patient. In the effect the normal physiological pH is restored, what enables the reconstruction of natural bacterial flora. The effect was achieved thanks to high adhesive properties and the ability of the gel to spread, what provides prolonged action of the preparation.

The aim of the study was to investigate optimization of pharmaceutical properties of hydrophilic powders containing lactic acid complexed with chitosan.

In implementing the assumptions tested influence of carboxymethylcellulose sodium salt on the properties of the powders. The formulations were prepared with varying pH and rheological properties.

The device simulating the conditions in the vagina, studied the adhesion and movement of the gel on the mucosa of the organ. The powders which passes in the gels were examined for their properties.

In vitro studies have demonstrated that the gels obtained from the powders are maintained at the application site. The powders after application to the apparatus passes in the gels and cover the surface.

As a result of studies, obtained the value of dynamic viscosity of the gels obtained from powders. The test shows thixotropical properties of gels. The range of pH of the gels allows the selection of the optimum formulation.

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PHOTOCHROMIC CHITOSAN FILMS OBTAINED BY CHEMICAL MODIFICATION WITH AZOBENZENE DYES

Chitosan is natural polymer, which has a number of unique properties such as biocompatibility, biodegradablity, nontoxity, antimicrobal activity and film-forming ability. Due to these properties chitosan has wide application in various areas, such food industry, pharmaceutics, cosmetics, medicine, agriculture.

In this work we report on preparation of the photochromic chitosan film by chemical modification of chitosan films with azobenzene dyes. In the first step chitosan or chitosan modified by 4-hydroxybenzaldehyde was used to form films onto the glass substrate by casting method. In the next step the surface of the films was modified by chemical reaction with azobenzene dyes: 4-[4-(dimethylamino) phenylazo]benzaldehyde and 4-(dimethylamino)azobenzene-4’-sulfonyl (dabsyl chloride), respectively. The obtained materials were characterized by UV-VIS spectroscopy and ellipsometry to characterize photochromic properties of new derivatives and their response to the light stimulation.

The presented method of preparations of photosensitive chitosan films eliminates the disadvantages of the limited solubility of chitosan in organic solvents. Prepared materials show interesting properties and extend the field of potential applications of chitosan.

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WASTE FUNGAL BIOMASS FROM BIOTECH INDUSTRIES AS A SOURCE OF CHITOSAN

More than 60% biotech industries use fungi in different processes such as brewing and baking, as well in foods, antibiotics and pharmaceuticals, organic acids and enzymes production. Thousands of tons of waste fungal biomass is produced every year and is subjected to land filling or incineration for easy disposal [1].

The fungal strain of *Mucor circinelloides* IBT-83 is known as a producer of membrane-bound lipase which can be used in many different hydrolysis and ester synthesis processes [2-7]. This strain can also be a source of high amount of oils [7] as well as chitin, chitosan, chitin- and chitosanolytic enzymes [8-10]. Crude preparation of the latter enzymes (defatted and dried mycelium) can be applied in chitosan hydrolysis, yielding functional, biologically active chitosan oligomers [8]. The method of obtaining a partially purified *M. circinelloides* IBT-83 intracellular proteins preparation containing both chitosanase and lipase was described in [10]. It was proved that after the culture conditions optimal for efficient production of both enzymes, from 15 to 20 g of crude enzymes preparation (d.m.), and from 30 to 60 g of fungal oils, as a side product, can be obtained [7].

M. circinelloides produces oils and accumulates them inside the mycelium, both *de novo* (when sugars are the only carbon sources) and *ex novo* (when lipids, e.g. oils, are the carbon source). This fungus can therefore be used to obtain oil in cultures on various food industry wastes, e.g. to obtain oil - as raw material for biodiesel production [11]. This would involve leaving large amounts of spent defatted biomass, which could be a source of valuable substances, such as chitosan.

Chitosan is presently extremely valuable biopolymer which has a wide range of applications. It was found that mycelium of the strain of *M. circinelloides* IBT-83 contains chitosan. The biopolymer contents varied from 5 to 9% of cell walls, that gives the possibility of "eco-friendly" development of waste biomass remaining after separation of lipids, by recovery of this value-added product.

It has been found that the yield of chitosan separated from spent *M. circinelloides* mycelium was equal to 0.64 - 0.92 g/dm^3 of culture medium. Initial dewatering of mycelium by freeze-drying had a positive effect on chitosan separation from the waste biomass. The water contained in fungal mycelium obtained after the culture adversely affects the lipids extraction and the separation of chitosan. Our studies revealed that the mixture of hexane:isopropanol in a ratio of 3:2 v/v was the best for fungal oils extraction (the amounts of oils has reached 58 g per 100 g d.m. of initial biomass). Extraction of lipids with the mixture of these solvents in combination with pre-lyophilization of waste biomass also gave the highest efficiency of chitosan separation, up to 92 mg per 1 g d.m. of defatted biomass (the presence of the biopolymer was confirmed by FTIR analysis).

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APPLICATION OF CHITOSAN IN THE FORMULATION OF DERMATOLOGICAL HYDROGELS PREPARED ON THE BASIS OF MACROMOLECULAR COMPOUNDS

Chitosan is a natural polysaccharide and has many beneficial properties such as biocompatibility, biodegradability. This allows it to be used in medicine, among others, as a component of dressings and drug carriers. Currently, a new generation of dressings are used, e.g hydrogels. They are characterized by the ability to absorb large amounts of exudate, maintain proper moisture in the wound, facilitate the process of natural autolysis.

The effect of chitosan concentration on the properties of dermatological preparations prepared with 2% methylcellulose and 10% PVP was studied. As the chitosan, propylene glycol-1,2 and glycerol increased, the hardness, consistency and cohesiveness of the hydrophilic gels increased, while the dissipation capacity the decreased. Gels based on methylcellulose and chitosan, compared to formulations containing PVP, have a higher rate of loss of volatile compounds, for 1,2-propylene glycol formulation and texture parameters. The tested hydrogels have good rheological properties, allowing extrusion from the tube and spread on the skin.

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THE STUDY OF ADSORPTION OF VITAMIN C ON THE CHITOSAN IN AN IN VITRO MODEL

In medical practice for the treatment of obesity-affected diseases, polymers based on the reduction of bioavailability of lipids are used. These measures swells in the gastrointestinal tract increases the adsorption surface that has the ability to adsorb 5 times more fat in relation to its own weight.

Vitamins and other remedies are also used during weight loss treatments.

The aim of our study was to determine the ability to bind vitamin C by chitosans, depending on the variables of physical-chemical conditions, in the model of the gastrointestinal tract.

The phenomenon of adsorption of vitamin C was studied using a dynamic model biopharmaceutical simulating in vivo conditions. The amount of adsorbed vitamin c by chitosan was calculated from the difference in vitamin C concentrations before and after sorption. Results of quantitative determination of bound vitamin were used to calculate mean percent of adsorbed dose.

The results show that vitamin C is adsorbed by chitosan in the pH ranges used. The binding capacity depends on the pH of the environment, the viscosity and the concentration of vitamin c administered, as well as the type of chitosan and the substances present in the gastrointestinal tract. The average value of adsorption of vitamin C to chitosan, depending on the pH of the environment, ranged from 45 to 98%. The highest adsorption amounts are noted above pH 6.4 (chitosan at this pH is in the form of precipitated gel-emulsion-forming polymer).

In summary, it can be stated that dietary supplementation with chitosan-containing supplements reduces the amount of vitamin c administered and has a large impact on its bioavailability.

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THE INFLUENCE OF CHITOSAN FLAKES DEACETYLATION DEGREE ON ORTHOPHOSPHATE SORPTION EFFICIENCY FROM AQUEOUS SOLUTIONS

Phosphorus (P) is an essential nutrient for the plant and microbe growth, however in excessive amount it is considered as the main factor leading to the eutrophication of water tanks. The source of phosphorus in the aquatic environment might be natural as well as due to anthropogenic processes. The emission of biogenic components to surface waters as a result of weathering or precipitation is a natural and inevitable process. The biggest and most dangerous source of biogenic substances is human activity. From industries, agriculture, households and as a result of the drop of treated wastewater, significant amounts of phosphorus enter the natural environment. Because of the contamination of water tanks, climate changes and rising human needs, water resources across the world are in danger. Considering restricted access to high quality water, treatment and re-use of treated wastewater became a very important aspect.

There are many physicochemical and biological methods of phosphorus removal from wastewater. Precipitation of phosphorus compounds with iron or aluminium salts is considered as the most effective. This method is expensive and leads to the salinification of water and formation of excessive amounts of sludge. Because of that cheap and effective methods of phosphates removal from post-production wastewater are still being sought, one of them being the process of sorption. Sorption is considered as one of the easiest and safest methods of wastewater treatment. The costs of this method depend mostly on the price and efficiency of the sorbent. Until now the most used sorbent was active carbon, but its use is noneconomic because of high costs of production and regeneration. Good alternative for sorbents based on active carbon is chitosan. Chitosan is a deacetylated form of chitin, which is the most common biopolymer in nature. Chitosan sorbents, due to the presence of amine groups, are particularly effective on anionic pollution. However the degree of deacetylation of chitosan has big effect on effectiveness of such pollution removal. Along with the increase of the deacetylation degree there is an increase in the free amine groups, which are the main centres of sorption.

The main purpose of the research in the presented work was to evaluate the influence of deacetylation degree of chitosan in the form of flakes on the effectiveness of orthophosphates removal from aqueous solutions with the use of sorption process. The research was carried out in two stages. The first step was to determine pH in which the sorption process run the most effectively (from the range 2-11 pH). The experiments were carried out at the concentration of 1 mg $P\text{-}PO_4/dm^3$. The highest effectiveness of orthophosphates removal on chitosan regardless of its deacetylation degree was obtained at the pH 4. At the pH 2 and 3 chitosan flakes dissolved.

The second step of the research was to determine the maximum sorption capacity of chitosan sorbents. The initial concentrations of the solution were 1 mg/dm^3, 2 mg/dm^3, 3 mg/dm^3, 4 mg/dm^3, 5 mg/dm^3, 6 mg/dm^3, 8 mg/dm^3, 10 mg/dm^3, 15 mg/dm^3 and 20 mg/dm^3. The samples in the amount of 10 cm^3 were taken after 5 min, 15 min, 30, min and 60 min in order to mark the concentration of the remaining sorbent. Based on the obtained results it was stated that along with the increase of chitosan deacetylation degree there is an increase in its sorption ability towards orthophosphates. After 60 minutes the desorption process has begun, probably caused by the increase in the pH in the solution. Because of the ability of sample neutralisation by chitosan and connected with it risk of desorption, the time of the contact of the sorbent with wastewater cannot be longer than 60 minutes.

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EXTREME BIOMIMETICS: DEVELOPMENT OF GEO$_2$-CHITIN NANOCOMPOSITES WITH ENHANCED PHOTOLUMINESCENT PROPERTIES

This work presents utilization a chitinous template of poriferan origin in the synthesis of nanostructured biocomposites, accordingly to *Extreme Biomimetic* concept [1,2]. The specific thermal stability of the nanostructured chitinous template allowed for the hydrothermal synthesis a novel germanium oxide−chitin composite with a defined nanoscale structure. Using a variety of modern analytical techniques including: FTIR, Raman, energy dispersive X-ray (EDX), near-edge X-ray absorption fine structure (NEXAFS), and photoluminescence (PL) spectroscopy, EDS-mapping, selected area for the electron diffraction pattern (SAEDP), and transmission electron microscopy (TEM), it has been proven that selected scaffold of poriferan origin induces the growth of GeO_2 nanocrystals with a narrow (150–300 nm) size distribution and predominantly hexagonal phase, demonstrating the chitin template's control over the crystal morphology. The obtained GeO_2–chitin nanocomposite possesses several specific physical properties, such as a striking enhancement in photoluminescence exceeding values previously reported in GeO_2-based biomaterials. This study demonstrates the potential of *Extreme Biomimetics* for developing new-generation nanostructured materials [2].

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THE SPECTROSCOPIC PROPERTIES OF NEW CHITOSAN-KERATIN-FIBROIN BIOCOMPOSITES

New hybrid materials were obtained by applying a suitable chitosan cross-linking mixture (organic acids, phytates, fibroin and keratin). The conducted studies–characterized the synergistic mechanisms of ionic crosslinking of chitosan gels and the effect of selected phytate salts on spontaneous formation of gels and fibrillar fibroin.

The obtained materials have been studied by infrared and Raman spectroscopy methods, including the use of a confocal Raman microscope for mapping their surface. IR spectra were recorded in the range 50 – 4000 cm^{-1} and Raman spectra in the range 80 – 4000 cm^{-1}. These methods are very sensitive to the presence of structural changes in the material and changes in its chemical composition. In addition, they register the presence of various functional groups in the composition of the composite. They play a special role in determination of the way of linking biopolymers with a component bonding them in the form of composite by a system of chemical bonds, ionic interactions, and hydrogen bridges.

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ACTIVATION OF JAWSII CELLS BY CHITOSAN OF DIFFERENT MOLECULAR WEIGHT

Due to physical and chemical properties of polysaccharide biomaterials, many of these substances are suitable for therapeutic purposes. However, before these compounds can find full use as implants, drug carriers or vaccine adjuvants, their immunogenic properties need to be characterized. Depending on their structure these substances may induce or modulate the immune response because are recognizable by cell receptors.

Chitosan is believed to be bioactive and biodegradable. The polymer in vivo is eventually broken down and its chains with low degrees of acetylation may remain active in the body for several months; the length of the released chains will influence the degree to which chitosan may differentially affect the outcome of the immune response. To better understand the mode by which chitosan influences the immune system, more research is needed into the immune reactivity induced by the primary given structure of the polymer and by the chains released during its biodegradation. Therefore we evaluated the immune activation upon different molecular weight chitosan treatment an immortal dendritic cells (DC) line termed JAWS II derived from bone marrow DC of a C57BL/6 p53-knockout mouse. Three types of chitosan were used for in vitro studies: oligosaccharides (2-6 sugar residues, COS), low molecular weight (Mw = 50-190 kDa; LMW) and high molecular weight (Mw = 190-375 kDa, HMW).

Chitosan was non- toxic to immature dendritic JAWS II cells; It was independent of the mass of chitosan and its concentration and even with a very high concentration of polymer (40 µg/ml), no reduced cell viability was observed in the culture. Chitosan HMW, at low concentrations (0.125-2.5 µg/ml), showed a slight positive effect on these cells. However, cytometric analysis showed that the HMW and LMW polymers reduced the percentage of living cells by 20%. in the culture. Both the percentage of necrotic cells and the early stage of apoptosis have increased simultaneously. In contrast, COS, did not affect cell viability.

The level of cell activation in culture was determined on the basis of changes in the expression of cell markers: MHC II, CD80, CD40 and CD86 were determined by flow cytometry. The percentage of JAWS II cells with MHC II expression increased upon HMW chitosan treatment and LPS, which was used as a positive control. Significantly, LMW chitosan and COS doubled the number of MHC II positive cells. Elevated CD86 expression did not depend on the molecular weight of the polymer but CD80 and CD40 expression variably responded to HMW, LMW and COS polymers; LMW and COS chitosan decreased the percentage of CD80 positive cells. In case of CD40 receptor, HMW chitosan decreased the percentage of CD40 positive cells, in contrast to increasing CD positive cells in response to LMW and COS chitosan.

JAWS II dendritic cells in response to LPS increased the production of MCP-1, IL-1β, IL-6 and IL-12. COS reduced the production of IL-10. LMW and HMW significantly increased the production of MCP-1 chemokines. The secretion of IL-12 was elevated by LMW, but HMW slightly activated cells to IL-6 and IL-10 production.

The chitosan solvent, adipic acid, had no effect on cell viability, cytokine production and cell receptor expression in JAWSII cells in vitro.

We conclude that DC of JAWS II cell line can reflect a difference in the activation of immune cells after exposition to chitosan of different size and molecular weight.

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SELECTED PHYSICO-CHEMICAL, FUNCTIONAL AND BIOLOGICAL PROPERTIES OF POLYMERIC BIOCOMPOSITES

Bedsore is a damage of the skin and the deeper underlying tissues that occur due to prolonged compression and friction, or the action of both these factors at the same time. This process leads to tissue necrosis, particularly in areas where the bones directly compress the soft tissue and inhibit or restrict the circulation of the blood [1].

Bed healing is a complex process that leads to regeneration of connective tissue, vascular and epidermis. It has been shown that wounds heal two times faster in a humid environment and that the temperature and oxygen concentration have a significant effect on the wound healing rate. This particular microclimate can be created using multi-functional dressings based on natural polysaccharide polymers.

Polyaminosaccharides, in particular chitosan and alginate, due to the specific biological properties related to the ability to accelerate the granulation and wound epithelization, bioactivity, biocompatibility, biodegradability, high antimicrobial activity are convenient materials for the construction of wound dressings for the treatment of hard-to-heal wounds, especially bedsores [2]. The biopolymers used for dressing construction are designed to ensure their biodegradation and partial resorption at the wound area.

The paper presents studies related to the preparation and evaluation of physicochemical, functional and biological properties of polymer composite materials based on chitosan and sodium alginate in a form of monolayer film acting as a carrier for the anti-inflammatory drug (zinc sulphate). The amount of active substance was determined based on the dose recommended in the Polish Pharmacopoeia (FP VIII, 2008) for preparations for external use [3]. Zinc acts as an immunostimulant, stimulates tissue renewal, protein synthesis, and accelerates wound healing and bedsores, in addition, the zinc compounds exhibit antiseptic, dehumidifying and anti-inflammatory effects [4]. Using the of thermal and thermomechanical analysis (DSC, DMTA), infrared spectrophotometric method (FTIR) and nuclear magnetic resonance (NMR), the influence of the variable content of chitosan and alginate and addition of active substance on the chemical and phase structure of the polymer biocomposites was investigated. Biological studies of selected biocomposites based on direct cytotoxic effect on mouse fibroblasts NCTC clone 929 and evaluation of antimicrobial activity against Gram (-) bacteria *Escherichia coli* and Gram (+) *Staphylococcus aureus* have also been carried out. It has been found that the quantitative composition of biocomposites and the addition of the active substance in the form of zinc sulphate have a significant effect on the biocomposite properties (absorbency and sorption).

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STUDIES OF BIOMATERIAL BIOCOMPATIBILITY

Biomaterial is any substance other than a medicament or a combination of synthetic and natural substances that can be used at any time to supplement or replace an organ or its parts, or to take over its biological functions temporarily or permanently in a specific application, in accordance with its dedication. However, if a substance can be considered biomaterial and approved for medical use, it has to undergo a number of studies. It should be demonstrated that the material is biocompatible, biologically inert. Biocompatibility is the interaction between the implant and the biological environment as a result of which the aim resulting from the dedication of the biomaterial is met.

Demand for biomaterials continues to grow, among others, due to the prolonged life expectancy and the expectation of continuous improvement in quality, and, at the same time, a limited number of organs for transplantation. The scope of biomaterial use is wide. Due to the requirements of modern medicine, it is necessary to use the latest materials and advanced technologies for their production.

The demands placed on biomaterials include sterility, chemical and physical biocompatibility, biofunctionality. Chemical biocompatibility depends on the chemical structure and the shape of the implant, surface morphology, surface energy. The implant response to physical stimuli is the same as the replaced tissue and depends on: the physical properties of the implant i.e. strength, elasticity, resistance to brittle fracture. Newly designed and manufactured biomaterial should be biocompatible, without the effect of tissue irritancy and without causing allergic or immunological reactions. Material that can be considered as a biomaterial and will be approved for medical applications should go through a series of studies.

Biological research aims at determining the suitability and safety of biomaterial use in medicine. The guidelines for the selection of test methods for biomaterial evaluation are contained in ISO 10993:1-14 [1].The standard provides unified research procedures. Biological studies of the material are multi-stage. From *in vitro* studies to *in vivo* studies. The choice of research methodology depends on the intended use, the dedication of the product. Studies selected on the basis of the type and timing of contact with the organism are always performed in the following order: physicochemical, mechanical, biological *in vitro, in vivo*, experimental on animals and clinical. In vitro studies include cytotoxicity, genotoxicity, and blood contact in which cell lines, tissues, and bacteria are used. In *vivo* studies are investigations of irritant, allergic, acute and chronic toxicity, and implantation studies including local tissue reaction, toxicokinetic, and carcinogenic studies. Experimental studies on animals are performed in units included in the list of entities authorized to conduct experiments on animals of the Ministry of Science and Higher Education. These tests are performed by qualified individuals with individual permits for research and approval by the Local Ethical Commission or the National Ethical Committee for Experiments on Animals. In animal studies, the 3R rule, replacing, reducing, refining should be applied. Replacement is a replacement with experience *in vitro*. Reduction means reduction of the number of animals while refinement is the improvement of research methods to reduce the suffering of animals in the experiment [2, 3].

Biocompatibility studies, biomaterial interaction with blood are an integral and inseparable part of complex evaluation *in vitro* and *in vivo* of biomaterials [4]. Verifying biocompatibility with blood shows whether and to what extent the material affects haemocompatibility affects the cells and blood proteins. Studies are concerned with haemolytic effects, coagulologic activation, evaluation of coagulation and fibrinolytic system. Studies are conducted on the degree of activation, aggregation and adhesion, platelets, erythrocytes, leucocytes and diagnostics of blood parameters as well as studies on morphological and functional changes after the temporary contact of the biomaterial with blood [5,6].

There is a set of mechanisms in the organism that keep circulating blood in a fluid state and leading to stoppage of bleeding after discontinuation of the vessel. The effectiveness of haemostatic mechanisms depends on the correct course of coagulation and fibrinolysis processes, the smooth adhesion and platelet aggregation and other haemostatic functions of these cells and the condition of the vessels. A well-functioning haemostatic system may not be sufficient to stop the loss of blood. Therefore, a number of measures for non-traumatic haemorrhage stoppage, locally haemostatic, convenient and easy to use, which, in addition to basic protective functions, accelerate the haemostatic process, healing and regeneration of damaged tissues have been introduced for medical use.

At the Institute of Biopolymers and Chemical Fibres in Łódź studies have been conducted for several years on the use of biopolymers for dressings, for the medicine, pharmaceutical and veterinary industries [7,8]. In the Department of Experimental Surgery and Biomaterials Research Wroclaw Medical University evaluation of the haemostasis and haemostatic properties of chitosan-alginate dressings in the form of sponges and model of dressings in powder form, made from chitosan/alginate Na-Ca complex and /or chitosan/alginate Na-Ca/CMC complex in the form of micro- and nanofibrids [9-11] The developed technology of obtaining materials in the form of powder is dedicated in the first phase of the local haemostatic process to provide first aid and to supply post-traumatic wounds. The beneficial feature is their biodegradation during wound healing, which reduces the damage to fresh tissue during the process of removing it from the wound.

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MEDICAL SESSION

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THE SYNTHESIS OF AN IODOACETYL CHITOSAN DERIVATIVE AND RHEOLOGICAL STUDIES OF ITS BEHAVIOR WHEN IN BLOOD

A variety of advanced hemostats have been brought to market, where most of products work simply by absorbing the blood at the site of the wound rather than by actively coagulating the blood. In this study, a new hemostatic system that causes a induced blood clots formation via simultaneous gelation of blood proteins and agglutination of the various suspended cells, transforming a liquid blood into an elastic gel, selectively at the site of injury.

The key chemistry of this study relies on the formation of covalent crosslinks between a hemostat matrix and sulfhydryl compounds in the blood. A Chitosan-iodoacetic acid derivative was successfully prepared by substituting amino groups of chitosan at its C-2 position with iodoacetic acid which is an irreversible inhibitor of all cysteine peptidases to interact with the free thiol group of cysteine. A series of rheological experiments were carried out on the mixture of 2 wt % chitosan-iodoacetic acid/acetic acid solution and sodium citrated blood in order to investigate the rheological properties of the mixture. The steady shear measurement revealed that the viscosity of the blood increased by nearly a million-fold higher after being mixed with the derivative solution. Moreover, changing the ratio of the derivative content to the blood content demonstrated that chitosan-iodoacetic acid enables the blood to change to a gel, right upon the mixing.

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SYNTHESIS AND POTENTIAL CYTOTOXICITY EVALUATION OF CARBOXYMETHYL CHITOSAN HYDROGELS

The aim of the research was to employ radiation processing in order to produce flexible hydrogels of uniform structure, characterization of their swelling properties and cytocompatibility for potential application as hydrogel wound dressings.

A semisynthetic polymer of carboxymethyl chitosan (CMCS) is the main component of the hydrogels. Despite that the CMCS undergoes partial crosslinking upon irradiation with high dose rate, it was irradiated in aqueous solution in the presence of a macromonomer of poly(ethylene glycol)diacrylate (PEGDA) as a crosslinker. 12 different compositions, i.e. CMCS at 6 concentrations ranging from 3% to 20% and two PEGDA concentrations of 3% and 5% were irradiated with an electron beam. The obtained hydrogels were subjected to sol-gel analysis to determine the amount of the insoluble fraction (GF) and the equilibrium degree of swelling (EDS). The maximum GF was in the range of 50% to 100% and raised with an increase of PEGDA/polysaccharide ratio. Gels were characterized by high capacity of water absorption, ranging from ca. 15 to approx. 200 g of water per g of gel. The EDS was higher for lower content of the crosslinker, and decreased with delivered dose, which is associated with higher crosslinking density.

The gels are foreseen to be used in contact with the tissue, particularly damaged skin, thus initial biocompatibility evaluation, of cytotoxicity testing, was conducted. The in vitro XTT cell viability assay was employed in order to determine potential toxicity towards murine fibroblasts (L929 cell line) being in contact with hydrogels of selected 8 compositions. Analyzed hydrogels showed no significant cytotoxicity. The crosslinking agent was responsible for undesired effect, of moderate reduction in cell viability, particularly due to presence of unreacted terminal double bonds in its structure. Thus, low amount of PEGDA in the hydrogel is fundamental for biological safety of the biomaterial. Increasing PEGDA concentration, or the polysaccharide to macromonomer ratio will results, at a specific irradiation dose, in greater number of retained double bonds. When designing a medical hydrogel product one should select a composition with lower concentration of the macromonomer and apply relatively high irradiation dose in order to exhaust virtually all reactive double bonds of PEGDA, preferably in crosslinking reactions. Due to addition of synthetic component of PEGDA, the hydrogels are not fully biodegradable. Therefore, the produced construct may be considered in wound care applications, as a dressing.

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HYBRID MATRIX MADE FROM MIXING CHITOSAN WITH B-1,3-GLUCAN – A PROMISING BASE FOR BIOMATERIAL FABRICATION

Scaffolds for bone tissue engineering applications are often composite materials made of polymeric matrix – which mimics organic part of the bone, and bioceramics in the form of hydroxyapatite or tricalcium phosphate ceramics (α-TCP and β-TCP). Biological properties of chitosan – like non-cytotoxicity, rapid biodegradation, and stimulation of osteoblast adhesion due to its structural similarity to glycosaminoglycans of bone extracellular matrix (ECM) – make this polysaccharide commonly used for biomaterials' fabrication [1]. The β-1,3-D-glucan (curdlan), which is a linear homopolymer of D-glucose produced by bacteria *Alcaligenes faecalis*, is another biopolymer with wide biological activity spectrum and huge potential in biomedical applications [2]. The aim of this work was to prepare hybrid chitosan/β-1,3-glucan matrix with improved biological properties compared to pure chitosan matrix. It should be noted that unlike composite material wherein all components are simply mixed, hybrid materials reveal chemical interactions between their constituents. As a consequence, resultant hybrid material possesses different properties compared to its individual components.

In this study, 2 different polysaccharide matrices were prepared: pure chitosan matrix (chit) and chitosan/β-1,3-glucan matrix (chit/glu). Then, physicochemical properties like wettability, surface energy and surface chemical properties of the matrices were compared. Moreover, FTIR-ATR analysis was performed to demonstrate chemical interactions between chitosan and glucan units. Finally, prepared matrices were used as a base for fabrication of 2 biomaterials: chitosan/hydroxyapatite (chit/HA) and chitosan/β-1,3-glucan/hydroxyapatite (chit/glu/HA).

Biocompatibility of fabricated composite materials was compared via evaluation of their protein adsorption ability, analysis of osteoblast adhesion and proliferation on their surfaces as well as via determination of proinflammatory cytokine production by inflammatory cells and osteoblasts upon culture on biomaterials.

Presented studies proved that addition of β-1,3-glucan to chitosan matrix leads to formation of the specific hybrid chitosan/β-1,3-glucan matrix as chemical interactions between the $–NH_2$ group and probably also C=O···HN specie of chitosan and the -OH group of β-1,3-glucan were demonstrated by FTIR-ATR analysis. Both matrices (chit and chit/glu) showed relatively high water contact angle ($\theta > 100^\circ$) and rather hydrophobic character. However, chit/glu/HA biomaterial revealed enhanced serum protein adsorption followed by better osteoblast adhesion, spreading, and proliferation compared to the material comprising pure chitosan matrix (chit/HA) [3]. Moreover, chit/glu/HA scaffold was demonstrated to adsorb lower amount of fibrinogen than chit/HA material, which is key protein responsible for stimulation of macrophage adhesion as well as induction of inflammatory response. The chit/glu/HA material was also found to induce augmented TNF-a production (but not IL-6) by human osteoblasts [4] and to enhance osteogenic differentiation through TNF-a-mediated mechanism. [5].

Based on obtained results, it may implied that chit/glu/HA scaffold made of hybrid chitosan/β-1,3-glucan matrix, not only carries reduced risk of biomaterial-induced inflammatory response, but also may accelerate bone regeneration process. Thus, chitosan/β-1,3-glucan matrix possesses improved biocompatibility compared to pure chitosan matrix and is very promising base for biomaterial fabrication for regenerative medicine applications.

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BIOTECHNOLOGICAL SESSION

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SYNTHESIS OF A POLICISTRONIC SYSTEM ENABLING EFFICIENT MODIFICATION OF CHITIN AND ITS DERIVATIVES

Chitosan, the N-deacetylated derivative of chitin, is characterised by good solubility in acidic solutions and a range of unique properties, therefore it is widely used in numerous industries[1]. Additionally, in the recent years, there has been much interest in the products of chitin and/or chitosan hydrolysis, especially chitooligosaccharides (COS). These linear oligosaccharides are soluble in solutions with neutral pH. Due to their low molecular weight and decreased viscosity they can be successfully applied, for example, as carriers for gene transfection and drug delivery matrices[2]. At present, chitosan and COS are obtained as a results of the thermo-chemical and/or physical processes which are environment unfriendly and very difficult to control[3].

We are conducting a research project aimed the creation of first, polycistronic, eukaryotic system enabling simultaneous expression of three genes coding chitin- and chitosanolytic enzymes which are crucial for efficient modification of chitin and its derivatives. We have heterologously expressed two isoforms of chitin deacetylase from *Mucor circinelloides* IBT-83[4]. Activity of both chitin deacetylase isoforms were confirmed after expression in methylotrophic yeast *Pichia pastoris*. After biochemical characterisation, the genes of these enzymes and other carefully selected genes comprising multienzymatic complex were codon-optimized and synthesized to match the codon usage bias of Pichia pastoris. Potentially genes coding chitin deacetylase, chitinase and chitosanase will be involved in this construct. The functioning of this multi-gene system will be based on conservative, viral 2A self-processing sequences enabling polycistronic expression under the control of one promoter[5]. We believe that this approach will significantly reduce the cost of producing enzyme preparations, making biotechnological methods competitive to conventional physical and chemical processes. In addition, the interaction of all enzymes in one reaction mixture can significantly increase the yield of the production of defined chitin derivatives.

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SYNTHESIS OF CUO-CHITOSAN NANOCOMPOSITES AND THEIR APPLICATION FOR NONENZYMATIC GLUCOSE DETECTION

Glucose is a very important source of energy in human metabolism. However, blood glucose concentration is strictly defined and should be regulated by the body. For that reason, monitoring and control glucose levels is a very important element in preventing diabetes. Conventionally, glucose concentration in blood was monitored by electrochemical readout systems. Most of these systems are based on enzymatic methods, which using the glucose oxidase (GOx) or glucose dehydrogenase (GDH) immobilized onto an electrode. Electrochemical glucose sensors based on GOx have been widely investigated owing to their high sensitivity, specificity and low detection limit [1]. Generally, enzyme-based electrode involve complicated and multi-step immobilization procedures. The activity of enzymes is completely dependent on temperature, pH, humidity and toxic chemicals due to the nature of enzymes. On the other hence, the development of efficient nonenzymatic glucose sensor with desirable properties (high stability, sensitivity and reproducibility) draws high interest. Sensors without enzymes are based on the current response of glucose oxidation directly on the electrode surface.

Up to now, many materials display electroactivity for glucose detection and they areuesed to preparation of electrochemical nonenzymatic glucose sensor. Noble metals (Pt, Pd, Au), transition metals (Cu, Ni, Mn) and metal alloys have been extensively investigated in the sensors development. There are several metal oxides (NiO, ZnO, CuO) are used in sensors for glucose detection. Metal oxide-based nanomaterials are often employed in sensor technology due to their surface reactivity and electrocatalytic activity, low cost, ease of synthesis and stability. The CuO is a promising material for application in nonezymatic glucose sensor due to non-toxicity, low cost, ease of production. Copper oxide has received great attention because of their redox pair (Cu(II)Cu(III)) is an effective electron mediator in the electrocatalytic oxidation of glucose.

Glucose electrooxidation performance depends on unique structure of modified electrode. The control of materials morphology is one of the most important issues in the synthesis of materials with the definded properties. During the past few years, a variety of CuO nanostructures have been prepared, for example nanowires, nanospheres, nanorods, nanofibers, nanoplatelets which show different sensitivity and selectivity. Therefore, it is significant to synthesize novel size and form of CuO nanoparticles and further improved in order to its application in glucose detection.

Chitosan is N-deacetylated product of chitin. The amino groups of chitosan are responsible of the original properties of this biopolimer. One of properties of chitosan is its ability to coordinate the metal ions. These interaction chitosan- metal ions can be used for the synthesis of new materials.

In this work we present a nonenzymatic glucose biosensor using a glassy carbon electrode modified by CuO-chitosan (CuO-CS) nanocomposite, which was obtained by hydrothermal method. The electrochemical characteristics of the CuO-CS modified electrodes have been performed using cyclic voltammetry (CV) and chronoamperometry technique.

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THE EFFECT OF TiO_2 ADDITION ON THE CHITOSAN-BASED IMITATION SKIN COMPOSITES

Chitosan (Ch), natural polymer is characterized by many useful properties such as biocompatibility, non-toxicity, biodegradability or controlled bioactivity, which makes it a well-studied substance for many years. Ch is a desirable substrate also in the medical industry due to its high reactivity, the ability to mix with various substances and antimicrobial activity. High bioadhesiveness of Ch is due to the fact that, as positively charged and soluble in acidic and natural solutions, it easily attaches to negatively charged surfaces such as membranes. On the other hand, titanium dioxide is the most common and the most durable of all titanium oxides. Characterized by amphoteric properties, but more acidic than alkaline, the pH of its aqueous dispersion is similar to that of the skin. It also has a high resistance and is non-toxic. Chitosan, in addition to biomedical and immunological activity, also has protective functions that delay product aging and water loss, whereas TiO_2 improves chitosan thermal stability and oxidation resistance.

Due to the unique physicochemical and antibacterial nature, both compounds may form part of the so-skin substitutes. So far used imitation skin composites are mainly hydrophilic which has undoubted advantages and disadvantages. Such composites are successfully prepared on a hydrophobic substrate capable of containing skin-friendly polymers or natural substances (hyaluronic acid, HA), but they are also an excellent environment for the development of bacteria and fungi. As a result, they can have a negative impact on human cells, so the full characterization of the interactions of their components with cell membranes is an important step in understanding the processes occurring in the human body. The main components of the membranes are phospholipids (PC). The amphiphilic character of PC makes it possible to test their properties in the interfacial areas. Particularly frequently used membrane model system is the Langmuir monolayer (L) formed on the water-air interface. The nature of the obtained surfaces can be controlled by appropriate selection of parameters such as pH, ionic strength or addition of stabilizer.

The aim of the study was to obtain the physicochemical characteristics of imitation skin composed of TiO_2, chitosan and hyaluronic acid and to estimate the effect of these components on properties of the model membrane. These objectives were achieved through the study of changes in the surface pressure – area per molecule isotherms, compression modulus and morphology of the DPPC monolayers on various subphases, and then after deposition onto the glass plates, the wettability and surface free energy of the examined systems and their topography were determined.

Saturated phospholipid, DPPC (dipalmitoylphosphatidylcholine) as typical component of eukaryotic cell membranes, was used to prepare the model Langmuir monolayers. The zwitterionic DPPC possesses a negatively charged phosphate group and a positively charged ammonium group saving uncharged monolayer at the pH studied. The components of subphase, i.e. Ch, TiO_2, HA, were found to interact with DPPC causing changes in the monolayer molecular organization by perturbation of chain packing. Expansions of the monolayers were associated with insertion of the subphase components to the monolayer mainly due to hydrophobic interactions and hydrogen bonding. On the other hand, phosphate groups of DPPC can form covalent bonds with the surface hydroxyl groups of TiO_2. These interactions play an important role in the cell membrane disturbing activity of Ch, TiO_2, and HA. Taking into account these results a possible mechanism of the interactions between the components of subphase and the floating DPPC monolayer was proposed.

After formation of the artificial skin composites on glass the surface wetting parameters were determined by measuring the contact angles of three test liquids (water, formamide and diiodomethane) with strictly defined surface free energy components and also the contact angles of *SBF* (simulated body fluid). The obtained results were interpreted in relation to the energy parameters and topography of the examined surfaces. Variable wettability can be a convenient parameter to inform about the properties of artificial skin. The rational combination of applied research techniques allowed for the full characterization of functional chitosan-oxide materials. The obtained composites with optimal physicochemical characteristics can be identified as a good candidate to use in the controlled release of active ingredients as well as in the production of antimicrobial films. Getting more profound insight into the interactions between model membrane and components of imitation skin can make the subsequent biological effects more predictable.

PHARMACEUTICAL SESSION

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CHITOSAN-BASED DRUG DELIVERY SYSTEMS - PREPARATION AND PHYSICOCHEMICAL PROPERTIES

Drug encapsulation into polymeric micelles depends on two primary factors: chemical nature of the drug, and features of amphiphilic material. These properties and specific interactions between the active substance and the vehicle are responsible for the overall metabolic cycle of the drug delivery system i.e.: stability, susceptibility to breakdown/degradation, the rate and place of the drug release, solubilization capacity, preservation of drug activity etc. [1].

Following our previous experience with chitosan and chitosan-fatty acid micelles formation [2], as a next sept this work presents the encapsulation of the selected drugs in the chitosan based new micellar systems. Various drugs, differ in water solubility, namely: α-tocopherol, ibuprofen and amoxiciline were selected for the study. Drug concentration, molecular mass of the chitosan, and mixing methods were examined in order to optimize the encapsulation process. The ionic gelation method with sodium tripolyphosphate (TPP) as crosslinking agent and Tween 80 as surfactant were used in order to encapsulated the α-tocopherol inside the chitosan micelles. Morover the O/W emulsification process was applied for all of the drugs encapsulation in chitosan-fatty acid derivative. The characterization of the micelles was performed using a dynamic light scattering technique including measurements of the hydrodynamic radius (R_h) and Zeta potential of the obtained micelles. The stability studies were carried out in the diverse storage conditions. The critical micelle concentration was evaluated by the UV-Vis technique, using the hydrophobic dye solubilization method with 1,6-diphenyl-1,3,5-hexatriene (DPH) as indicator.

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CARBON MATERIALS OBTAINED FROM CHITOSAN CONTAINING NITROGEN AND TITANIUM HETEROATOMS

Recently, the development of research on carbon materials obtained from natural precursors is observed. Particular attention is given to carbon materials containing heteroatom functional groups in the form of carbon-nitrogen bonds [1]. Another example is to carry out modifications aimed at obtaining TiO_2-containing carbon materials [2]. Therefore, carbons containing both nitrogen and TiO_2 seem to be a good solution considering their potential applications [3]. The use of these types of materials can lead to improved conductivity and at the same time, have a positive effect on the activity and stability of the electrodes in electrochemical devices.

In these research a series of new carbon materials containing nitrogen and TiO_2 ($N\text{-}C/TiO_2$) were obtained. Carbonaceous materials containing heteroatoms were prepared using proposed procedures using chitosan-activator (Na_2CO_3 and $CaCO_3$) system and the addition of crystalline forms of TiO_2, i.e. rutile and anatase. Carbonization of the obtained chitosan-based masses were carried out under inert atmosphere using the following heat-treatment temperatures of 700, 800 and 900°C. The influence of process temperatures and the ratio of used reagents on the obtained of $N\text{-}C/TiO_2$ structure were investigated. To determine morphological properties, scanning electron microscope analysis and X-ray diffraction analysis were performed. Surface parameters were also determined using analysis of low temperature adsorption of nitrogen analysis and elemental composition of the obtained materials.

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Annual, published in September, 30th
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3. Results and Discussion: The Results section should describe the outcome of the study. Data should be presented as concisely as possible, if appropriate in the form of tables or figures, although very large tables should be avoided.

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4. Conclusions: should contain summary of the most important findings

5. Acknowledgements: *should be printed in italic.*

Citation

Cite references in the text by numbers in square brackets, e.g. This result was presented in [2, 5, 13].

6. Reference list: The list of references should only include works cited in the text and that have been published or accepted for publication. Personal communications and unpublished works should only be mentioned in the text. Do not use footnotes or endnotes as a substitute for a reference list.

Reference list entries should be in the order of appearance in the text and each should contain the full title of the cited paper. Papers should contain **DOI** identification when applicable.

[1] Smith J, Jones M, Houghton L; (1999) Future of health insurance. N Engl J Med 965, 325–329.

[2] Slifka MK, Whitton JL; (2000) Clinical implications of dysregulated cytokine production. J Mol Med. Doi:10.1007/s001090000086

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[4] Brown B, Aaron M; (2001) The politics of nature. In: Smith J (ed), The rise of modern genomics, 3rd edn. Wiley, New York, 230-236.

[5] Wolfrom ML, Szarek WA; (1972) Halogen Derivatives. In: Pigman W, Horton D (eds), The Carbohydrates, Chemistry and Biochemistry, Vol. 1A, 2nd ed, Academic Press, New York, 239-251.

All documents should contain a DOI number if possible

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Formula charts and Schemes: Particular attention should be paid to current conventions for drawing sugar ring structures (tapered thickening of forward edges, etc.). Structural formulas should be grouped for insertion in the text at appropriate points. Such groups need not have a caption, but those showing reaction sequences (i.e. containing arrows) may be designated Scheme 1, Scheme 2, etc. In charts and schemes formula numbers must follow in sequence across the page, except where a single structure with R groups represents two or more compounds. The sequence then follows the listing below the structure, which should be in "tabular" format.

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