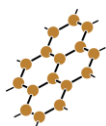




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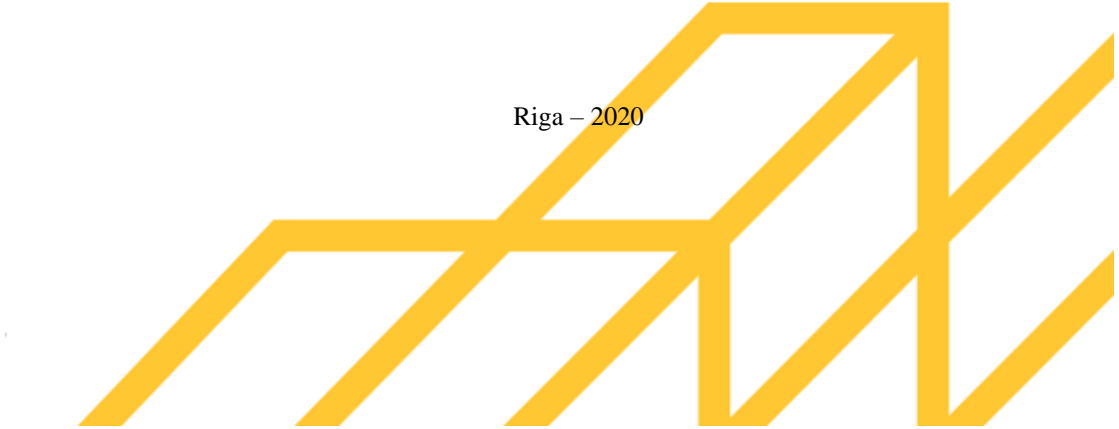
**"MATERIALS SCIENCE AND APPLIED CHEMISTRY
2020"**



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Invited lecture

How to quantify 200 metabolite with one LC-MS/MS method?

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The central carbon metabolism including glycolysis, the pentose phosphate pathway and the TCA-cycle is essential for all biological systems. The measurements of metabolites involved in these pathways, known as metabolomics, can provide valuable insights about cell biology for various life science applications including biomedical research. However, the chromatographic separation of these, mostly polar compounds (e.g. amino acids, carboxylic acids, cofactors, nucleotides, sugars and sugar-phosphates), is still a challenging task. It has been shown that ion pair- reverse phase chromatographic separation is a suitable technique to tackle this challenge.

We took advantage of the Agilent metabolomics dynamic MRM database and method to establish a robust workflow for quantification of almost 200 metabolites. This LC-MS/MS based method employs ion pair- reverse phase chromatographic separation using tributylamine as an ion-pair reagent. In order to ensure high repeatability, back flushing of the column using a 6port/2-position divert valve is applied for cleaning purposes. For the metabolite detection, a dynamic MRM method is employed. It should be pointed out that methods can be freely modified and all parameters are accessible.

Our main aim was to establish a workflow for absolute quantification using an external calibration and internal standardization. First, we comprehensively revised the provided MRM method, optimized and implemented detection settings for additional 10 metabolites. Furthermore, MRM transitions for more than 70 isotopically labelled metabolites were implemented into the method. For this purpose, the U13C labelled yeast extract combined with isotopically labelled metabolite standard substances was used. Afterwards, the influence of ISTD concentration in samples on method performance was evaluated and optimized for various samples types. For external calibration, we established a library of 190 metabolite standard substances. These were used to comprehensively assess LOD, linear range, dynamic range, and calibration range for each metabolite. Based on the obtained results we prepared customized metabolite standard mix for 10-point calibration curves. The established workflow has been successfully applied for the metabolite quantification in several sample types including cell extracts, tissue and plasma samples.

Oral communications

Sol-gel coating processing optimization for knitwear and yarns

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The pretreatment, coloring and finishing are the main stages in textile processing and production. Finishing stage is the final process in textile manufacturing, where most of finishes are applied to knitwear, woven and nonwoven products,¹ to add additional value and properties. This study focuses on finishing stage mainly involving textile and yarn modification with sol gel method. The commercial availability of organic and inorganic precursors for sol gel method makes it a well-established technology, and it can be used to obtain additional properties or to improve existing ones.

Modification was carried out onto a single jersey plain woven sock (76% cotton/22% polyamide/2% elastane) with the following pretreatment – processed in acetone and water solution (1l water- 70 % acetone). Before treatment was carried out to reduce the waxes present on the product after industrial knitting. The 2² factorial design was followed through the process of modification. Dipping time and % mass concentration of modifier- zinc acetate dehydrate was varied. Changes in textile mass, linear and horizontal density as well as air permeability was assessed. Additional modification of pure polyamide textile and 100% cotton yarns was carried out - optimizing sol-gel coating process by changing solution to sample wight proportion ratio and after consolidation time. A sequential technology scheme for thread modification was developed and performed.

Table 1

Weight changes after modification and washing

ZAD wt. % & dipping time	Weight before modification, g	Weight after modification, g	Weight after modification and washing, g	Changes after modification and washing, %
ZAD_5%_60min	19.38	22.21	20.40	8.1
ZAD_5%_30min	19.79	22.92	20.90	8.9
ZAD_7,5%_60min	19.72	21.74	20.67	4.9
ZAD_7,5%_30min	19.10	21.12	20.10	4.8

Acknowledgements

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Integration of electrically conductive yarns into fabric by weaving

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In this work, the suitability of different electrically conductive yarns for their integration into the non-conductive fabric by weaving is considered and the conductive properties of the yarns after washing are tested.

In the production of electrically conductive textiles, it is necessary to choose appropriate electrically conductive yarns that would be able to provide the functions of both contact electrodes and conductive tracks. In order to be used in weaving conductive yarns must meet a number of requirements: the yarn must be flexible so that it can bend between the warps or wefts without affecting the overall structure of the fabric; the yarn must be strong when used in the direction of the warp, where tension is high and where abrasion are possible; the yarn must retain its conductive properties even after repeated washing; after washing, in the case of shrinkage of the base fabric, electrically conductive yarn must be fit into its structure without slipping out of the fabric.

Four different types of conductive yarns were selected for the experiment - silver-coated polyamide yarns and multifilament stainless steel yarn. The yarns were woven into the non-conductive fabric in different ways, both as a single yarn and as forming wider strips. Washing (15 cycles) was performed in accordance with the standard with a special detergent intended for washing steel and silver-containing textiles. After washing, the fabric shrank in both directions. The silver-coated polyamide yarn (Shieldex 235dtx x 4) shrank along with the non-conductive fabric (see Figure 1, b) and the surface of the fabric was smooth. This type of yarn is suitable for weaving.

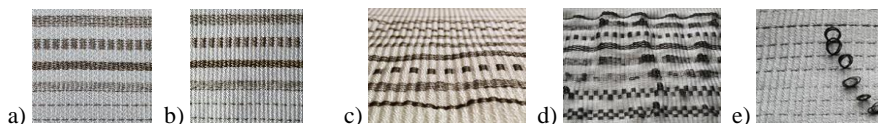


Figure 1. Conductive yarns in woven structure before and after washing: silver-coated polyamide yarn Shieldex 235dtx x 4 (a, b) and stainless steel yarn Thermotex N-30 (c,d,e).

The stainless steel yarn did not shrink, but formed loops on the surface of the fabric, as well as the entire fabric wrinkled (see Figure 1, d,e). Consequently, this yarn is not suitable for weaving into fabrics that shrink under the washing effect.

Measurements of electrical resistances showed that the electrically conductive yarns tightly integrated into the fabric structure slightly reduce the electrical conductivity under the influence of washing. The coarser the yarns or the more yarns put together, the lower the electrical resistance and the smaller the change in resistance due to washing.

Acknowledgments

This work has been supported by the doctoral studies grant of Riga Technical University (Nr.34-14000 DOK.MLKF/19).

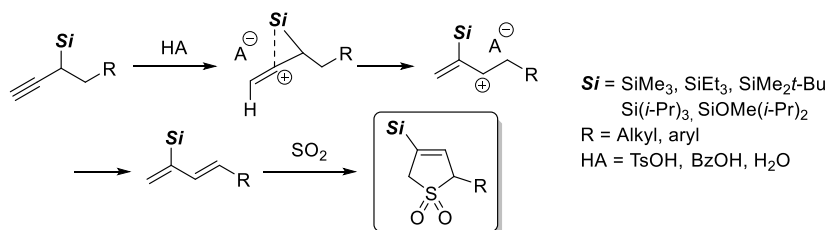
Use of propargylsilanes in tandem transformation for the synthesis of silyl sulfolenes

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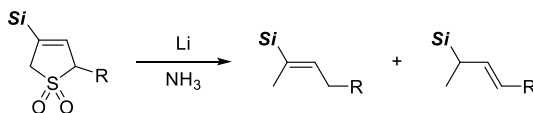
Stabilizing properties of silicon in reactions of vinyl, allyl, allenyl and propargyl silanes, that proceeds via β -silyl carbenium ion, is commonly known as β -silicon effect. Mechanistic insights show two possible pathways of stabilization – vertical (e.g. hyperconjugation) or non-vertical (e.g. formation of silonium ion).¹ Formation of closed silonium ion with combination of other stabilizing effects explains why many reactions involving β -silyl carbenium ion tend to undergo 1,2-silyl shift.

Previously we have reported the use of propargylsilanes in the synthesis of silyl dienes and indenenes by the catalytic amounts of strong Brønsted acids (TfOH, Tf₂NH, Tf₃CH) that involves 1,2-silyl shift.² Herein we report the use of liquid sulfur dioxide for this transformation as highly polar and Lewis acidic reaction media which offers possibility to use weaker acids (e.g. BzOH, TsOH). Moreover, in a tandem cheletropic addition process silyl sulfolenes are obtained from the in situ formed dienes.



Scheme 1. Synthesis of silylsulfolenes from propargylsilanes.

Herein we also demonstrate possible reductive cleavage of “SO₂” moiety by Birch reduction conditions.



Scheme 2. Reductive cleavage of C-S bonds.

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Lignocellulose based aerogel preparation from wood and hemp waste materials

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Term cryogel is used for aerogels prepared by freeze drying process. Aerogels are low density and highly porous solid-state structure, consisting of nano-dimensional materials. Highly porous and exclusive structure of aerogel has various properties such as low thermal conductivity, high sound absorption capacity, low dielectric constant, super absorption activity and, they are super lightweight. Thermal and acoustic insulators, flexible energy storage devices, drugs, and catalyst carrier as well as template for other functional materials are a few possible application areas where the unique combination of aerogel properties can come in hand. Cellulose is biodegradable, abundant and renewable resource material for preparation of composites and cellulosic aerogels.¹ Cellulosic composites and aerogels gathered great interest in research field for the past decade, but not much research is done to reproduce wood like structure aerogels or composites and is relatively unstudied area.

Current work involves aerogel preparation approaches and research routes. Herein, we report the manufacturing and characterization of nanofibrilated lignocellulose cryogels obtained from different lignocellulose sources. Nanofibrils were obtained from several lignocellulose waste sources – wood flour and hemp fibers via microfluidization process; while the cryogels were prepared by freeze drying technology. Several lignocellulose component concentrations from 0.2% till 3% have been chosen to prepare cryogels. Five runs were processed through microfluidizer apparatus for each cellulose-water suspension. Applied pressure for the first pass was 10 000 psi and then increased to 30 000 psi for the 2-5 pass. FTIR analysis was performed to control molecular interaction between lignocellulose nanoparticles. XRD was used compare fiber crystallinity. SEM was used to study structure; TGA - for thermal stability analysis. Compression test for mechanical properties.

Acknowledgements

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Development of fibrin matrices for controlled drug delivery

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Commercially available fibrin matrices take advantage of a simplified method for fibrinogen activation, bypassing the clotting cascade.¹ Vancomycin hydrochloride (V-HCl), a glycopeptide bactericidal antibiotic, has been used in medicine for over 40 years.² Poly (lactic-co-glycolic acid) (PLGA) is a biodegradable, bioresorbable polymer, widely used for drug formulations and medical purposes since it is nontoxic and well tolerated by the human body.³ The aim of this study was to develop fibrin matrices from commercially available raw materials for controlled V-HCl delivery.

Blank PLGA and loaded with V-HCL microcapsules were prepared by w/o/w method. Fibrin matrices were prepared from fibrinogen (from Bovine plasma) and thrombin (from Bovine plasma), using the two-syringe method. Thrombin was first mixed with 40 mM CaCl₂ solution and then mixed with fibrinogen, to obtain a homogenous mass. The synthesized samples were characterized by FT-IR, SEM, XRD.

Fig. 1A shows the morphological features of PLGA drug loaded microcapsules in SEM. The microcapsules were on average size of 50 µm with small bead formations on the surface. The particles were spherical, with a smooth surface of polymer layers. Less CaCl₂ solution in the fibrin matrix sample (see Fig.1B) provides a more cross-linked sample and prevents it from losing shape over time. For inhibition, drug release kinetics from samples with V-HCl non-encapsulated were tested. Fig. 1C shows distribution of V-HCl encapsulated in PLGA microcapsules and embedded in fibrin matrix showed longer drug release than non-encapsulated V-HCl in the fibrin matrix sample formulation. V-HCl release was evaluated for 13 days; burst release was observed after 312 h, and by the end of the assay, only 49.4% of the encapsulated vancomycin had been released from sample. In the same time, if V-HCl is not encapsulated, it shows release of 77% in the first 13 days.

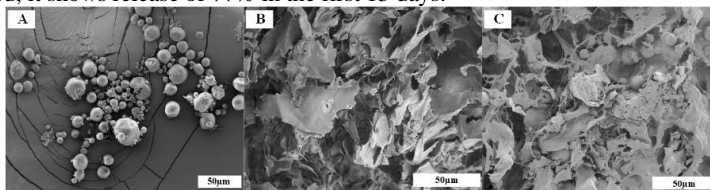


Figure 1. PLGA microcapsules (A); Developed fibrin matrix (B); V-HCl / PLGA within developed fibrin matrix (C).

Acknowledgements

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The effect of crosslinking on the electro-thermal properties of carbon black and ethylene-vinyl acetate composites

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Self-regulating heating polymer materials are promising in fields where flexible and safe temperature control is needed without the possibility of overheating. Self-regulating heating materials have positive temperature coefficient of resistivity (PTC) and in case of polymer composites resistivity increases nonlinearly vs temperature due to existence of tunnelling currents between adjacent conductive filler particles.¹

The aim of our research is to investigate cross-linked and non-crosslinked ethylene-vinyl acetate (EVA) and highly structured carbon black (CB) composites and their electro-thermal properties depending on concentration of CB and crosslinking degree of polymer matrix.

The samples were prepared by dispersing EVA (VA content 40%) in chloroform and adding a mixture of CB ultrasonicated in chloroform (10–30 phr). For crosslinked samples different amounts of dicumyl-peroxide (DCP) are added 1–3 phr. The entire mixture is left in the fume hood overnight for the solvent to evaporate. Next the polymer – CB composite is pressed into a rectangular form by applying heat and pressure – for noncross-linked EVA-CB 170°C for 15 minutes at 4,35 MPa pressure, but for crosslinked EVA-CB-DCP 150°C for 30 minutes at 1,45 MPa pressure. Lastly, silver glue electrodes are painted on opposite ends of the sample resulting in 100 mm long, 69 mm wide and 1.4 mm thick samples (the space between electrodes is 80 mm).

Electro-thermal properties of samples were investigated, particularly the electrical resistance dependence on temperature in universal heating oven (external heating) and by applying a voltage of 5V (internal heating due to Joule heat). The PTC effect in polymer composites is caused due to the expansion of the matrix and subsequent reduction of tunnelling currents in the electroconductive channels because the filler particles move away from each other. Investigation of CB concentration influence on EVA-CB composites showed a lower equilibrium temperature and resistivity for lower filler loads. 30 phr EVA-CB-DCP samples showed that by increasing the concentration of DCP, the equilibrium temperature decreases, while the overall resistivity increases. Samples with 2 phr DCP showed better results than samples with 1 and 3 phr DCP because this cross-linking degree probably provides a dynamic balance between the formation and collapse of electroconductive channels in the sample.

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An adaptive smart window device based on the photochromic effect and capable of electricity generation

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In today's world, an ever-growing concern is energy consumption. One of the biggest consumers of power are HVAC systems, used to control the climate in high rise buildings. To combat these smart windows can be exploited to decrease the amount of heat coming into the room through the window in terms of infrared radiation. However, the vast majority of smart windows are electrochromic devices, where DC current is used to change the transmittance. Another possibility are photochromic coatings, that, sadly, do not provide much possibility for transmittance manipulation and have slow recovery.

We propose a new concept for photochromic devices. Previously, we have shown, that titanium dioxide nanoparticles exhibit photochromism due to photodoping in hole scavenging media, when irradiated with UV light.¹ The response to UV light can be tuned either by doping or changing the hole scavenging media.² By incorporating these particles into a thin film, it is possible to combine the photochromism of TiO₂ with the photovoltaic properties of TiO₂ based DSSCs.

Acknowledgements

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The mechanism of contact-electrification on polydimethylsiloxane surface

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Contact-electrification is a process in which a static, electric charge is created on surfaces by contacting and separating two material surfaces. The main mechanism of contact electrification is mass transfer - with the increase of material softness, the larger charge will be formed on the surface^{1,2}. Polydimethylsiloxane (PDMS) is an inexpensive, easy-to-prepare polymer with an easily variable hardness that allows the efficient study of contact electrification.

Solutions of PDMS samples of different hardness (elastomer: crosslinking agent 5:1, 10:1, 15:1, 20:1, 25:1, 30:1 wt %) were spin-coated on a PET / ITO electrode (2.5×2.5 cm). The samples were cross-linked for 20 minutes at 80 °C. Each sample consist of three layers. Samples were tested against an ITO / PET sample on a glass substrate (2.5×2.5 cm). The samples were connected in the electrical circuit with an Instron dynamic tester, a Keithley electrometer, and a Picoscope 6000 series oscilloscope. The short-circuit current and the voltage on 1 G Ω electrical resistance were measured. By integrating the obtained current peaks, the surface charge density for each sample was obtained. Using this value, prepared samples were compared and conclusions were made about charge formation depending on the hardness of PDMS samples.

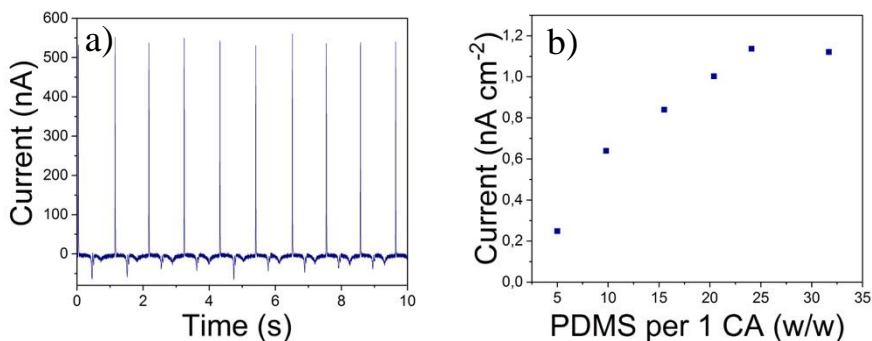


Figure 1. a) Instantaneous current dependence of time for PDMS 20:1 sample; b) Current density dependence of sample hardness for PDMS 20:1 sample.

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Development and biomimetic characterization of bilayer scaffolds based on gellan gum and bioactive glass for osteochondral tissue engineering

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In regeneration of bone tissue, ideally, an implant and cell carrier should be three-dimensional characterized by high porosity and a network of interconnected pores. Furthermore, these implants have to exhibit certain mechanical characteristics that correspond to characteristics of the implantation site.¹ Articular cartilage is an avascular, soft tissue exposed to dynamic compression under in vivo conditions. Hydrogels were extensively investigated in the development of scaffolds for cartilage tissue engineering due to high-water content and properties similar to soft tissues. Osteochondral implants need to exhibit properties of both aforementioned tissues, *i.e.* to be composed of a highly porous bone layer and a viscoelastic cartilage layer on top. A special challenge is to obtain a thin, well integrated interfacial zone between the layers. In this study, two-phase scaffolds based on gellan gum (GG) and bioactive glass (BAG) were synthesized and examined as potential osteochondral implants. The osteo-inductive GG-BAG layer composed of 2 % w/w GG hydrogel with 2 % w/w nanoparticulate BAG was produced by lyophilization in order to obtain open porosity in axial and radial directions. The chondral layer was obtained by pouring a 2 % w/w GG solution over the frozen macroporous GG-BAG layer at -25°C so as to achieve adequate integration of layers in the intermediate zone. The obtained scaffolds were characterized under physiologically relevant conditions in a biomimetic bioreactor with specially designed chambers to provide supply of two media relevant for chondral and bone tissues. In this study, constant flow of simulated body fluid (SBF) was supplied countercurrently at the flowrate of 1.1 mL/min during 14 days of the experiment. In addition, dynamic compression (compression rate of 337.5 $\mu\text{m/s}$, 5% deformation of the chondral layer, 1 h/day) was applied from day 7 until day 14. Scaffolds in SBF under static conditions served as a control. The initial scaffolds and scaffolds sampled in the end of the experiment were characterized regarding mechanical properties in the biomimetic bioreactor, as well as morphology and hydroxyapatite (HAp) formation by using scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS). It has been shown that all of the samples retained integrity while the formation of HAp was uniform throughout the osteo-layer of the scaffolds studied in the bioreactor. Moreover, HAp formation and, thus, bioactivity was significantly higher under biomimetic conditions as compared to static controls.

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Effect of the reinforced plastic clamp fitting on the bending strength of the spruce T-type loose tenon joints

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This article presents the bending strength¹ and flexural properties of the glued T-type spruce loose tenon construction joints with and without reinforced plastic clamp fitting. Construction joints are design according to Eurocode 5.² The samples are made from European spruce (*Picea abies* Karst.) C24 class construction material³ with relative wood moisture 18% and relative wood density 410 kg/m³. Samples are assembled with water/high temperature resistant polyurethane adhesive⁴ and polyvinyl acetate dispersion adhesive. The total number of samples are 48. The sample width is 95mm and thickness is 45mm. Samples were subjected to moisture, weight controls and 48h stored in the climate chamber¹ before practical bending load test. T-type loose tenon joint construction samples with reinforced plastic clamp fittings glued with polyurethane adhesive under bending load are 2,6% stronger and 13,8% less flexural then without reinforced plastic clamping fittings. T-type loose tenon joint construction samples with reinforced plastic clamp fittings glued with polyvinyl acetate dispersion adhesive under bending load are 9,7% weaker and 20% less flexural then without reinforced plastic clamping fittings. The accuracy of the developed bending strength, deformability and elasticity modulus of the examined construction joints was verified positively both by experimental studies and numerical calculations.

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Polymer based triboelectric nanogenerators: how to choose the right materials?

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Triboelectric nanogenerator (TEG) devices have potential to satisfy growing energy needs in portable electronics and sensors providing a clean alternative to conventional batteries.¹ They are produced from cheap, lightweight, flexible, widely used polymer materials. Key feature of TEG devices is surface charge formation from contact electrification. For charge formation three mechanisms are considered – electron transfer,² ion transfer,³ and material transfer.⁴ Among these the scission of covalent bonds accompanied with material transfer is the most reasonable, therefore, physicochemical properties of polymer must play a crucial part.

In our work we show that polymer contact electrification magnitude can be predicted using the respective cohesive energy density (CED) of polymer (Figure 1). Polymer materials are ranked from the lowest CED to highest (left to right). Results indicate that CED allows to confidently predict whether positive or negative charge forms on the polymer. This allows selection of the most suitable materials as the building blocks for efficient TEG devices.

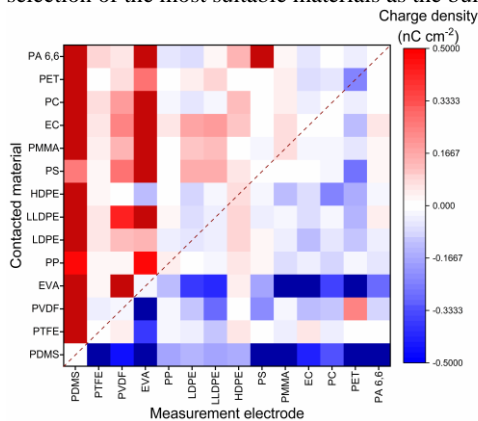


Figure 1. Charge density map of 14 mutually contacted polymer materials.

Acknowledgements

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Method for evaluation anthropometric fit and ergonomics of clothing

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The motivation for the study is based in the industry, where departments requiring special-purpose (functional) clothing often encounter problems in procurement of uniforms - most often in aspects of fit, lack of information and data or their shortcomings. Often, the officials responsible for the supply are not sufficiently informed about the fit aspects of the uniforms and their assessment. Industry standards¹⁻³ highlight the needs for anthropometric fit and ergonomics assessment, but this study shows that they allegedly outline issues but do not support the decision-making. Apparent a set of practicable principles is needed, promoting the parties' understanding of the fit parameters and the evaluation and decision-making process.

Development of the method was achieved through a series of tasks: aspects of clothing design were identified; the components of the concept of fit were summarized; methods for assessing the fit and ergonomics of clothing were studied, including standardized; practical principles for algorithm development were selected; the method was developed and validated. Approbation of the method was performed for the analysis of duty uniforms of the State Fire and Rescue Service of Latvia. A pre-study, wearer research and ergonomics tests have been implemented in the approbation; a questionnaire was developed to clarify the subjective evaluation of end-wearers. In total 59 firefighters participated in the validation experiments.

The developed method allows to identify shortcomings in the anthropometric fit and ergonomics of clothing, as well as promotes the objectivity of users' decision-making in the evaluation of clothing. The principles developed contribute to raising awareness among users (wearers, supply services) in assessing the conformity of clothing. The results obtained can be practically realized in the improvement of supply processes, and algorithm variations can be used in the evaluation of a different assortment of clothing (it is repeatable and adaptable).

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Synthesis and characterization of amorphous calcium phosphate

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Amorphous calcium phosphate (ACP) expected to become a widely used biomaterial for its excellent properties. Compared to other calcium phosphate materials, it is highly soluble, has good remineralization abilities, bioactivity, and biodegradation properties. It is known that the properties of crystalline calcium phosphates depend on Ca/P molar ratio. The aim of the study was to synthesize ACP with Ca/P molar ratio higher than 1.5 and to investigate the influence of Ca/P molar ratio on the properties of products.

ACP was synthesized from calcium oxide and orthophosphoric acid with different initial Ca/P molar ratio (1.5, 1.58 and 1.67) via re-precipitation method.¹ The initial suspension was dissolved in hydrochloric acid to obtain calcium and phosphate ion rich solution. By rapid adding of strong base to the ion rich solution, the ACP precipitation occurred. The synthesis was done at end pH 9.5 and 11.5. Obtained precipitation were centrifuged, washed with deionized water, and lyophilized. Further ACP was calcinated at 1100 °C to determine Ca/P molar ratio. Phase compositions were detected using x-ray diffraction analysis (XRD) and Rietveld analysis. Product was characterized with Fourier transform infrared spectroscopy (FT-IR), BET method and gas pycnometry. Thermal stability of ACP was detected by thermogravimetric (TGA) and differential thermal analysis (DTA). Phase stability at room temperature of dried samples was studied with XRD.

ACP was successfully prepared at all different synthesis parameters. The structure that is characteristic to amorphous state was observed in XRD patterns and FT-IR spectra. The product contains carbonate ions and has SSA in range from 103 to 139 m²/g. The density of ACP powder is in range from 2.44 to 2.60 g/cm³ and calculated from BET particle size is in range from 17 to 23 nm. The correlation between synthesis parameters (pH and initial Ca/P molar ratio) and ACP microstructure parameters was not observed.

After calcination of ACP, formation of β -tricalcium phosphate (β -TCP) or biphasic mixture of β -TCP/hydroxyapatite was observed. The Ca/P molar ratio of the products was in range from 1.50 to 1.55. The obtained ACPs with different Ca/P molar ratios are structurally stable in dried state up to 9 months in room temperature.

Acknowledgements

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Laser technology for controlling the spectral sensitivity of the GeSn IR photodiode

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Lasers are highly versatile in material processing and have wide range of applications. In this study a new approach is proposed – to use temperature gradient field induced by powerful pulsed laser radiation with the aim to redistribute Sn impurity atoms in the Ge host material of epitaxial germanium-tin (GeSn) solutions, grown by molecular beam epitaxy method (MBE) on silicon substrates for full compatibility with silicon electronics. In this way, the control of the spectral sensitivity of the GeSn IR photodiode in the mid-infrared region was performed. We focused on the photodiodes prepared by using 200 nm thick Ge_{1-x}Sn_x (x = 0.05) epitaxial layers on Ge/n-Si substrate with aluminum contacts (Fig. 1a). Photodiodes were formed on non-irradiated and Nd:YAG laser irradiated layers. The samples were irradiated by pulsed Nd:YAG laser with 136.7-462.6 MW/cm² intensity. The photodiodes were characterized by using short laser pulses with the wavelength in 2.0-2.6 μm range (Fig. 1b). The laser-irradiated diode was found more sensitive in the long wavelength due to laser-induced Sn atoms redistribution providing formation of graded bandgap structure.

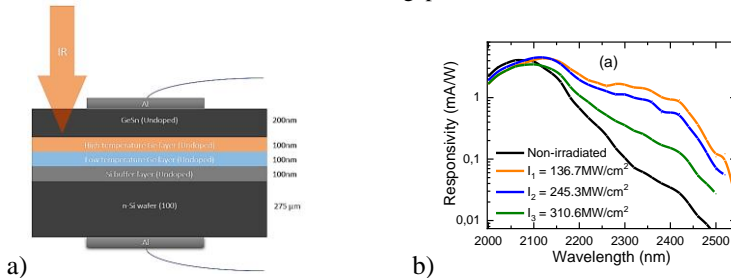


Figure 1. (a) Schematic structure of the GeSn photodiode. (b) Responsivity spectral dependences of the photodiodes with different laser irradiation.

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Synthesis of A-D-A type chromophores containing 5,11-dihydroindolo[3,2-*b*]carbazole donor core

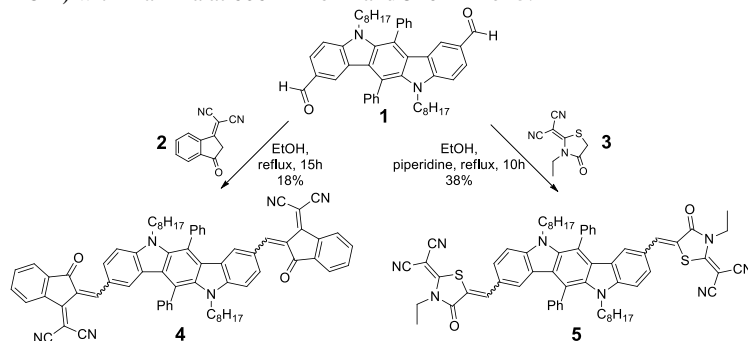
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Polymer/fullerene bulk heterojunction (BHJ) cells have been one of the most promising technologies in the organic photovoltaic (OPV) field. However, the intrinsic problems associated with low absorption of light of fullerene acceptor materials limit the maximum attainable efficiency of OPV cells. Recently, rapid progress has been achieved in the development of the substitutes for fullerenes. Low-molecular weight acceptors with rod-shaped A-D-A configuration have drawn substantial interest as replacements of fullerenes.¹

In this report we present two novel organic dyes (**4** and **5**) containing 5,11-dihydroindolo[3,2-*b*]carbazole as electron donor core. The dialdehyde **1** was used as the substrate for the synthesis of compounds **4** and **5**. Simple materials, such as indole, benzaldehyde and 1-iodooctane were used in the synthesis of **1** utilizing procedures known in literature.^{2,3} The Knoevenagel condensation of compound **1** with active methylene group containing compounds **2** and **3** was performed with poor yields due to the low solubility of the mono-condensation intermediate in the ethanol. Additionally, decomposition of the starting material was observed after long reaction times.

The products **4** and **5** are highly soluble in nonpolar solvents like DCM. Thin, amorphous films of the materials could be easily prepared from solutions in chloroform via spin-coating method. The dyes exhibit intensive absorption bands ($\epsilon_{max} \approx 77000 \text{ M}^{-1}\cdot\text{cm}^{-1}$, solutions of DCM) with maxima at 606 nm for **4** and 510 nm for **5**.



Acknowledgements

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Individualization of tight-fitting sportswear

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The aim of this research is to develop a methodology for individual design of tight-fitting sportswear. Performance of the athlete is mostly affected by his physical fitness, experience and emotional readiness for the upcoming task; however, sports equipment that includes sportswear is equally important to provide and possibly enhance performance and augment body functioning.¹ In sports where every hundredth of a second matters, aerodynamic drag and the associated energy losses are very important. When designing such functional clothing several essential parameters must be taken into account, including the speed, posture, morphology of the fabric surface (surface roughness, texture), air permeability, elasticity, constructive solutions such as the location of seams and fasteners and clothing fit.² The aim is to reduce aerodynamic drag and thus increase speed.

As the research focus group professional athletes engaged in luge had been chosen. Given the fact that professional athletes tend to have wide variety of body morphology depending the specifics of the sport and may not fit into standard measurement systems and size charts provided by the producer, nevertheless in order to maintain the performance level ergonomic and anthropometric clothing fit is of essence.^{1,2}

One way to enhance speed with clothing is to modify the surface structure by material choice and construction strategy to reduce the drag between the body and the environment. Research shows that less elastic knitted fabrics could provide aerodynamic benefits by reducing resistance at higher speeds, while more elastic fabrics can provide aerodynamic benefits by reducing resistance at lower speeds.³ For luge sport it would be recommended to use less elastic fabric with relief at the macro structure and a certain filament tuft direction. Moreover, tight-fitting garments could be used to streamline the body shape to improve the aerodynamics, although the amount and placement of the compression is to be taken into account, since it could cause restriction of movement and discomfort.

Acknowledgements

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Optimal use of industrial hemp for PLA biocomposite and LLDPE composite reinforcement

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This study investigated the optimal use of industrial hemp fibers for polylactide (PLA) biocomposite and linear low density polyethylene (LLDPE) composite reinforcement. In these samples both low-grade fiber, waste and high-quality hemp fiber are used.

To optimize the use of hemp fiber in both the biocomposite and the fossil-based polymer matrix composite, the first phase of the technology envisages the use of high-quality hemp fibers in the production of the PLA biocomposite. This process also produces a by-product (hemp waste). Further, in the second stage, the technology envisages the use of hemp waste in the production of LLDPE (semi-fossil) composite. PLA and hemp fiber biocomposites have high mechanical properties, which allow reducing the amount of materials in the product. Also, low-grade fiber composites show remarkable mechanical properties.

The advantage of extracting hemp fibers is that it is possible to use all parts of the plant at the same time for the production of different products – hemp seeds, their shells, hemp shives, thus maximizing the value-added of this resource, that conforms to the concept of sustainable development and circular economy principles. Also, it improves the ecological assessment (Life Cycle Assessment) of the product and reduces the environmental impact.

Annually renewable hemp fiber resource has the potential to create new products and develop the renewable material industry in EU. Considering the Europe Green Deal guidelines,¹ it is important for the manufacturer to provide a sustainable, economically justified and environmentally friendly material (switch to recyclable materials till 2021, switch to recycled, reusable or alternative materials till 2025).

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Biological nitrogen removal from pharmaceutical wastewater

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Pharmaceutical wastewater typically consists of organically bonded nitrogen compounds – including heterocyclic nitrogen compounds, amines, amides, residues of active pharmaceutical ingredients, and organic solvents - acetonitrile, dimethylformamide, *N*-methylpyrrolidone and even pyridine. These compounds are biological resistant and/or toxic therefore activated sludge microorganisms cannot use them directly as a nutrient source in a bioavailable form.

Pharmaceutical enterprises greatly differ each from other with biogenic (nutrient) substances level and type in wastewater. Nutrient balance is one of the key requirements for effective biological wastewater treatment. Pharmaceutical products are typically produced in multi-stage batch processes that create complex waste streams with variable chemical composition and nutrient ratio. In case of JSC “Grindeks” COD/N ratio typically varies in the range 25-45 leading to fluctuations in process parameters.

The wastewater monitoring data of pharmaceutical company JSC “Grindeks” indicate, that about 55% of organically bonded nitrogen in pharmaceutical wastewater is directly utilized by heterotrophic bacteria, 10-20% of organic nitrogen compounds are persistent and non-biodegradable while remaining part of organic N is converted and involved in nitrification-denitrification process. Previous research shows that bioaugmentation with selective strains of microorganisms or co-metabolic biodegradation could be applied to enhance the biodegradation of recalcitrant organic nitrogen compounds in pharmaceutical effluents¹.

The pivotal role of the biological nitrogen removal process plays chemical structure of dissolved nitrogen compounds, environmental and physicochemical factors such as pH, temperature, dissolved oxygen concentration, however salinity levels also reduce microbial diversity and inhibit nitrification performance.

Acknowledgements

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Liposomes as vancomycin hydrochloride delivery system

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Liposomes (LIP) are unique drug delivery systems due to their ability to encapsulate both hydrophilic and hydrophobic drugs, as well as they improve the disadvantages of free drug administration.¹ However, LIP have a significant disadvantage - low encapsulation efficiency. Currently, researches are focused on increasing the LIP encapsulation efficiency by studying the effect of LIP preparation methods, composition and encapsulating drug type.² The aim of our study was to evaluate the effect of 1,2-distearoyl-sn-glycero-3-phosphocholine (DSPC) and cholesterol (Chol)-containing LIP on the vancomycin hydrochloride (VANKA) encapsulation efficiency.

LIP and VANKA-LIP were synthesized using the thin film hydration method and 3 dehydration-rehydration (d-r) cycles. 3 LIP compositions were used for both LIP and VANKA-LIP samples, where lipid bilayer consisted of DSPC:Chol in ratios (n/n) of 2:1, 3:1 and 4:1. The lipids were dissolved in chloroform, which was evaporated using nitrogen gas and vacuum drying. The dry lipid film was gradually hydrated with 5 ml of deionized water or VANKA solution ($c=250 \mu\text{g/ml}$) and treated in an ultrasonic bath.

The results of this study show that regardless of the composition of the LIP, the shape of the obtained LIP is spherical, they are agglomerated, and their size distribution is non-uniform as can be seen in Figure 1. TEM image shows LIP sizes in the range of 0.1 - 0.5 μm , but the light microscopy image proves the presence of large size LIP in the range of 1.0 – 3.0 μm . Lipid composition and the number of d-r cycles do not affect the size of LIP, but it does affect the VANKA encapsulation efficiency. By increasing the number of d-r cycles, the amount of VANKA encapsulated in LIP increases, which after the third d-r cycle for DSPC:Chol 2:1, 3:1 and 4:1 LIP are $56.44 \pm 0.02\%$, $48.63 \pm 0.01\%$ and $48.77 \pm 0.02\%$ respectively. The highest drug encapsulation efficiency is for the LIP composition of DSPC:Chol 2:1, because it contains the highest amount of Chol, which improves the stability of the lipid bilayer.³

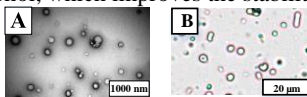


Figure 1. Liposome micrographs: A – TEM; B – light microscopy

Acknowledgements

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Hyaluronic acid based composites for local drug delivery

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Site specific drug delivery systems (DDS) are often developed to overcome high drug dosages, side effects and even toxicity of conventional ones (e.g. injections or oral ingestions). Creating smart drug delivery vehicles with greater efficiency it is possible to predict the therapeutic response as well as ensure controlled and prolonged drug release periods.¹ Post-traumatic and post-operative tissue damage often carries potential infection risks, usually precluded through local antibiotic therapy. Microencapsulation of gentamicin sulphate (GENTA) could overcome possible infections due its wide range of antibacterial spectrum.² Effective strategy to provide an optimal drug release rate and ensure the necessary therapeutic levels over the certain period of time is to load the microencapsulated active substances into the hydrogel matrix.³ DDS made of hyaluronic acid (HA) and ϵ -poly(-L-lysine) (ϵ -PL) have shown high biocompatibility and increased antibacterial activity.⁴ Thus, the aim of the current study was to prepare HA/ ϵ -PL composites for controlled drug delivery and to analyze the active substance release profiles. For this purpose, GENTA was microencapsulated in poly-L-lactic acid (PLA) matrix and prepared vehicles were incorporated in HS/ ϵ -PL hydrogels.

HA/ ϵ -PL GENTA loaded hydrogels and HA/ ϵ -LL hydrogels loaded with GENTA/PLA microcapsules were prepared with solid to liquid phase ratio 1:5 and 2:5 (mass:volume). GENTA containing microcapsules were prepared by water-in oil-in water (W1/O/W2) double emulsion technique. GENTA release kinetics from modified HA/ ϵ -PL hydrogels were studied using Ultra Performance Liquid Chromatography equipped with Evaporative Light Scattering Detector (UPLC-ELSD) at $\lambda=650$ nm, using Aquity UPLC BEH C18 column.

Analyzing drug release profiles from HA/ ϵ -PL hydrogels loaded with GENTA/PLA microcapsules (Fig.1), it was observed that within the first 24 h already $78 \pm 3\%$ (HA/ ϵ -PL 1:5 mass:volume) and $59 \pm 7\%$ (HA/ ϵ -PL 2:5 mass:volume) of GENTA was released, while rest of the drug was transferred into the dissolution medium within next 144 h. If GENTA was directly incorporated into the HA/ ϵ -PL hydrogel matrix, total drug release was already observed after 24 h.

During the research it was established that HA/ ϵ -PL modification with GENTA loaded PLA microcapsules prolonged the total drug release up to one week.

Acknowledgements

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Injectable, porous, osteoinductive calcium phosphate cements

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Due to continuous growth of the global population, more active lifestyles of people, increase in life expectancy as well as large defects generated by trauma, pathological conditions or tumour resection, more frequent and complicated orthopaedic problems occur¹ and the need for bone grafts increases. Calcium phosphate cements (CPCs) have gained attention as very suitable biomaterials with a great potential in bone regeneration due to their similarity to bone mineral chemical structure, ability of self-setting in vivo and resorbability by organism.² Despite the variety of research and number of products in the market there are still properties to be improved in order to obtain porous injectable osteoinductive calcium phosphate cement, suitable for clinical use. This study focuses on the latest trends and suggestions to develop the material with desirable properties.

Phase separation is an essential factor to be improved to obtain injectable material; several methods have been proposed.

Osteoinductive bone substitutes promoting rapid resorption of the cement together with balanced rate of new bone formation could form a solution of bad mechanical performance of CPCs.

Osteoinductivity of CPC could be attained even without the addition of different supplements.

Less complex composition of CPC would potentially reduce the price of the final product and make it more widely available on the market.

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Synthesis of 1,4-dihydropyridine derivatives with spontaneous and stimulated emission properties

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Several 2-(1-benzyl-2-(styryl)-6-methylpyridin-4(1*H*)-ylidene) fragment containing glassy organic compounds (see Fig. 1) have been synthesized and investigated as potential solution-processable light-emitting materials.

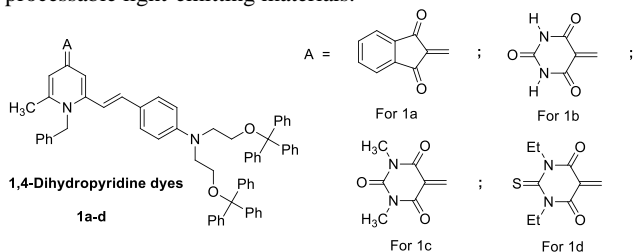


Figure 1. Synthesized 1,4-dihydropyridine derivatives.

Absorption bands of compounds 1a-d in the solutions of dichloromethane are in the range from 350 nm to 500 nm with photoluminescence from 500 nm to 650 nm. Thermal stabilities of synthesized 1,4-dihydropyridine compounds 1a-d are higher than 260°C with glass transition temperatures are above 100°C. The incorporation of various electron acceptor fragments within the 1,4-dihydropyridine fragment containing molecules only slightly influenced absorption and photoluminescence band shifts in comparison to the respective 4*H*-pyran-4-ylidene derivatives.¹

Based on these compounds, neat spin-cast films were obtained and their spontaneous and stimulated emission properties were investigated. Synthesized compounds 1a-d show stimulated emission (ASE) with λ_{\max} in the range from 603 nm to 615 nm with ASE threshold energies as low as 46 $\mu\text{J}/\text{cm}^2$ in thin films. Investigated 1,4-dihydropyridine derivatives show perspective for further research as solution-processable components for light-emission and light-amplification studies in new photonics materials.

Acknowledgements

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Posters

Effects of clays on CO₂ hydrogenation at low pressure over CuO/SBA-15 catalysts

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In recent years, with the rapid increase of CO₂ emissions, the global warming caused by the greenhouse effect is becoming increasingly prominent, and severely affects the ecological balance on the earth.¹ Therefore, the capture and practical use of CO₂ have become a hot

research topic in the world.² Synthesizing highly value-added industrial products such as methanol through the catalytic CO₂ hydrogenation is a very economical and effective way to reduce CO₂ emissions, since methanol not only is a clean, renewable fuel but also can be used as an intermediate to produce valuable chemicals.¹

Over the past several decades, numerous efforts have been made to developing effective catalysts for CO₂ hydrogenation to methanol. Among these, the Cu/ZnO based catalysts were highly active for methanol synthesis.^{1,2} More studies have shown that SBA-15 has good application prospects as catalyst carrier material because of its flexible pore structure and large specific surface area.³ It was proved that the addition of metal oxide promoters could change the structure or properties of the catalyst and improves the dispersion of reduced copper and the size of copper micro crystals, which was beneficial to methanol synthesis. In this study, CuO/SBA-15 catalyst was prepared with impregnation post synthesis method and when mixed with two types of clays – kaolin and hectorite. The obtained catalysts were characterized using XRD analysis, N₂ adsorption-desorption analysis and SEM-EDX analysis. The effects of clay as promoter was studied on CO₂ hydrogenation reaction at 20 bar 250°C with H₂/CO₂ molar ratio 3:1.

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Chemical engineering for improvement efficiency of microwave energy usage in processing of plant biomass

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Plant biomass which is renewed in the result of photosynthesis plays the key role in realization of bioeconomy strategy accepted by modern society. Plant biomass has an enormous potential for production of energy carriers and chemicals able substitute partly or completely the analogous products obtained to-day from fossil sources. The different technologies of biomass thermal conversion need in the development of effective techniques for external supply of heat energy. High polydispersity, heterogeneity and low thermal conductivity of plant biomass often makes convective/conductive heating too expensive operation.

It is known numerous advantages of microwave application in various chemical processes established in laboratory scale experiments. It has been found that microwave radiation exposure allows to significantly accelerate many chemical reactions, to carry out rapid heating of liquid and solid materials, to decrease significantly the energy consumption and to reduce the harmful emission into atmosphere. However, the efficient industrial application of microwave energy is limited. This is mainly due to the lack of appropriate equipment, in particular, waveguides capable of summing the microwave energy of some generators over a small surface area, as well as providing protection of magnetrons from heat, pressure, and aggressive atmosphere in the reaction chamber. Finally, the measuring equipment must operate in an electromagnetic field.

The aim of the present work was the development of constructions which meet the above mentioned requirements. A round coaxial wave guide equipped with placed radially three magnetrons with power 1.2 kW per each, choke flange junction, protective module and pressurized reaction chamber were designed and manufactured in the Latvian State Institute of Wood Chemistry for innovative microwave assisted extraction of high value added biologically active products and fractionation of plant biomass. The tests of waveguide have shown that the efficiency of summing energy of three magnetrons was closed to 100% at heating efficiency 52-55 % that correspond to specification of commercial microwave ovens. The designed waveguide allows to operate at temperature up to 250°C and pressure up to 10 bars. The extraction set up equipped with above mentioned wave guide and reaction chamber have demonstrated the stability and safety operation of transmitting block and accurate automatic control of temperature and pressure inside of reaction chamber in the presence of strong electromagnetic field.

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Impact of hyaluronic acid content on hyaluronic acid/ ϵ -polylysine hydrogels properties

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Hyaluronic acid (HA) is a polysaccharide which is the major component of an extracellular matrix. It is widely used to make hydrogels for tissue regeneration due to its biocompatibility, biodegradability and hydrophilic nature. HA demonstrates an anionic charge, thus it is able to form hydrogen bonds with water molecules through the carboxyl and acetamido groups¹. ϵ -Poly-L-lysine (ϵ -PL) is a natural polypeptide mainly used in the food industry due to its antibacterial characteristics, but in recent years it has also found the applications in the biomedicine field because of its water-soluble, nontoxic and biodegradable aspects². Thus the main objective of the current research was to prepare HA/ ϵ -PL hydrogels with different HA content and characterize them towards the swelling behavior and gel fraction.

HA/ ϵ -PL hydrogels with different HA content (from HA/ ϵ -PL ratio 10:90wt% to HA/ ϵ -PL ratio 90:10wt%) were physically crosslinked and characterized. Swelling behavior of prepared hydrogels were evaluated in 20 ml deionized water at 37 °C for 3 months. Gel fraction was determined by measuring insoluble part of lyophilized composites after immersing them in deionized water for 48 hours at 37 °C.

Obtained results indicated that increasing the HA content in the prepared compositions, the gel fraction values increased from 24.7% \pm 0.5% - 77.6% \pm 2.1% (HA/ ϵ -PL ratio 20:80wt% – 70:30wt%), revealing the affirmative effect of HA content in composites on crosslinking reaction. The swelling equilibrium of compositions with HA content up to 90wt% was reached within 168 h and was in the range from 191.8% \pm 2.3% (HA/ ϵ -PL ratio 40:60wt%) up to 267.9% \pm 11.3% (HA/ ϵ -PL ratio 80:20). Compositions containing 10 - 30wt% hyaluronic acid was stable in aqueous media only for 1 h, reaching the swelling degree of 194.5% \pm 21.9%, followed by rapid disintegration of samples in the next 24 h. It was found that HA content less than 40wt% influenced the insoluble part of composites and after 48 h already 70% of sample was dissolved, indicating that at least 40wt% of HA is necessary for the stable HA/ ϵ -PL hydrogel preparation.

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Heat treatment effect on a hypereutectic Al alloy obtained by selective laser melting

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In the search for more efficient processes and materials, additive manufacturing processes are great candidates. These technologies offer better production speed and flexibility and different properties from those obtained by well-known industrial processes. Therefore, it is necessary to know the microstructure and the mechanical properties evolution of these materials in greater detail. In this research, the annealing heat treatment effect at different temperatures (between 200 °C and 550 °C) with a holding time of 1 h is studied. The tensile test measurements indicated that for anneals below 400 °C, the material registers a strength decrease accompanied by an improvement in the extension of the homogeneous deformation zone concerning the as-printed material. After the heat treatments and employing digital image correlation (DIC), it was found that the deformation fields were more homogeneous than in the printing condition where there were multiple strain concentration points.

Use of disperse dyes for dyeing of recycled polyethylene terephthalate fibers

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Population, economic growth, and industrialization in the world cause an increase in the amount of waste. Waste policies should be developed, and waste management studies should be carried out, especially in the environment causing landfill problems.¹ Recycled polyethylene terephthalate (r PET) is the widely recycled plastic employed for new textile production in the world. It reduces environmental impact and lowers cost of the production.¹ For the traditional dyeing of polyethylene terephthalate (PET), commercial disperse dyes are generally used.² Disperse dyes today constitute the second largest sector in the dyeing industry and it is closely related to the growth of PET using.³ The disperse dyes are sparingly soluble in water and must be dispersed with the aid of a surfactant in the dyebath.³ It is essential to apply a dispersing agent in dyebath to improve dye aqueous solubility; retains dye in consistent dispersion throughout dyeing by enclosing single dye particle with a protective film.⁴

In this study color properties following the ISO 105-JO3:2009 standard of r PET fibers with linear density 6 den dyed with disperse dyes Itospense: Red, Blue and Yellow with concentration 3 wt.% in dyebath are studied as well as the influence of intensifier salicylic acid (concentration 4, 6, 8, 10 g/L) is examined. The optimal concentration of dyebath is recommended. For Blue dyed samples determination of color fastness to washing using adapted ISO 105-C10:2006 standard is applied.

It is found that it is possible to dye uniformly the r-PET fibers with disperse dyes Itospense in the presence of an intensifier salicylic acid. The salicylic acid concentration improves dyeing results, but the recommended concentration differs for each dye.

The optimal concentration of dye bath is:

Red 3% - 10 g/L; Blue 3% - 8 g/L; Yellow 3% - 4-6 g/L.

The increasing of salicylic acid concentration above mentioned does not improve the staining results and would not be useful. The minor changes in color parameters occur in the test of color fastness to washing for tested blue dyed samples.

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The influence of the solvents on the antioxidant properties of the birch outer bark extract in cosmetic emulsions

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The chemical composition of the birch outer bark comprises different classes of natural compounds – essential oils, saponins, tannins, hydrocarbons, carbohydrates, flavonoids, coumarins, carotenoids, terpenoids, etc. The major outer bark extract components among these groups being valuable phenolic compounds and derivatives of the lupane-type pentacyclic triterpenoids like betulin, lupeol and betulinic acid.¹

The cosmetic and dermatological importance of plants phenolic compounds is mainly based on antioxidant action. The application of antioxidants in cosmetics reduces oxidative damage, constituting a good alternative in therapy and prevention of premature aging. It also provides photoprotective action and helps on the treatment of sensitive or sun-stressed skin by anti-inflammatory activity. The antioxidant compounds are also applied to prevent or reduce oxidative deterioration of active constituents of the cosmetic and to avoid oxidation of oily substances present in the formulation.² Birch outer bark extracts show a significant amount of antioxidant activity, despite the fact that they contain phenolic compounds in small amounts.³

The goal of this study is to evaluate the influence of the solvents used in birch outer bark extraction on the antioxidant properties of the dry extracts used in cosmetic product emulsions. Extracts obtained in ethanol, 2-propanol, 1-butanol, and ethyl acetate as well as one purified in ethanol at its boiling point by means of recrystallization were chosen for this study. The extracts were dried and milled to pass through 125 µm sieve and then used as antioxidant additives to cosmetic water-oil type emulsion, which were added in 30 and 60 mg/g concentrations. The oxidative stability was tested in “Mikrolab Aarhus ML Oxipres” apparatus. The cosmetic product sample was tested in an oxygen atmosphere under pressure at 120°C in a continuous regime for 18 hours. The highest stability was measured in the cosmetic sample, which had raw birch outer bark extract obtained in 2-propanol. At the additive concentration 60 mg/g, the protection factor is 20.6 times better than a blank sample. In addition, 2-propanol, among other solvents used, is better solvent for birch outer bark phenolic compounds, which content reached 3.58 wt%. It could be concluded that raw birch outer bark extracts act as an excellent antioxidant additive in cosmetic creams.

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A novel approach for the synthesis of nanocrystalline TiO₂ and its phase transformation in the presence of gadolinium

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Due to its optical, thermal, photocatalytic and electrophysical properties, nanocrystalline titanium oxide (TiO₂) is widely used in various fields.¹

In the present work, a series of pure and Gd-modified (0.5, 5, 50 mol%) TiO₂ nanocrystalline powders were prepared by a novel approach for the synthesis – extraction-pyrolytic method (EPM). Method consists of two general steps: metal containing extracts (precursors) production by liquid-liquid extraction using valeric acid as extractant and thermal treatment (pyrolysis). Thermal behavior of the produced precursors was studied by thermogravimetric analysis (TGA) and high temperature differential scanning colometry (HDSC). The phase composition of produced materials was determined by X-ray diffraction method (XRD). Investigations on polymorphic transformations of anatase to rutile were performed for both pure and Gd-modified TiO₂ powders produced at pyrolysis temperatures (T_{pyr}) 450 °C – 850 °C. The mass fractions of anatase phase and rutile phase in produced materials were determined by Spurr and Myers method.²

With reference to the HDSC-TGA data minimal pyrolysis temperature for unmodified TiO₂ powders production is 450 °C. Formation of low crystallinity TiO₂ with crystal structure of anatase was confirmed also by XRD. Polymorphic transformation of anatase to rutile begins at 550 °C, and at 750 °C complete anatase-rutile phase transformation occurs. Established that increasing the T_{pyr} leads to increase in the average crystallite size of anatase phase and rutile phase from 9 nm to 30 nm and from 30 nm to 52 nm, respectively.

Modifying TiO₂ powders with 0.5 mol% of gadolinium shifts beginning of anatase to rutile phase transformation to 650 °C. Wherein increasing gadolinium content to 5 mol% results the formation of pure anatase phase powder even at 750 °C. In both cases anatase phase is still presented at T_{pyr}=850 °C, moreover, in 5 mol% Gd-modified sample formation of Gd₂Ti₂O₇ phase occurs. This is consistent to the XRD analysis results of 50 mol% Gd-modified samples – Gd₂Ti₂O₇ formation begins at 800 °C.

Photocatalytic activity of produced powders was studied by photocatalytic degradation of methylene blue (MB). Established that the best photocatalytic performance demonstrates 0.5 mol% Gd-modified TiO₂ produced at 650 °C (degradation degree of MB solution 90%).

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Kinetic model of the 1,2-propanediol oxidation reaction in the presence of 3wt%Pd/Al₂O₃ catalyst

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More recently, lactic acid has been used mainly for production of pharmaceuticals, cosmetics, textiles, leather or food. However, lactic acid has now become an important monomer with an annual production of over 120,000 tons for the production of biodegradable and non-toxic polylactic acid and lactic acid ester.¹ Nowadays, researchers are paying more and more attention to finding the cheapest and most environmentally friendly methods for production of lactic acid. The most promising method is the catalytic oxidation of 1,2-propanediol (1,2-PDO). In our previous work² activity and selectivity of different novel Pd and Pt containing catalysts, synthesized by two different ways were studied in 1,2-PDO oxidation to lactic acid in alkaline water solutions both under atmospheric oxygen pressure and at $p(\text{O}_2) = 6$ bar. In this work, we studied activity and selectivity of a commercially available 3wt%Pd/Al₂O₃ catalyst in 1,2-PDO oxidation in alkaline water solutions. A power function-type reaction kinetic model was used to evaluate oxidation kinetics of 1,2-PDO over the 3wt%Pd/Al₂O₃ catalyst.

It was found that 3wt%Pd/Al₂O₃ catalyst is active in an alkaline water solution. Influence of 1,2-PDO concentration, $n(1,2\text{-PDO})/n(\text{Pd})$, $p(\text{O}_2)$, NaOH initial concentration and reaction temperature in 1,2-PDO oxidation was studied. Lactic acid was obtained as the main oxidation product; by-products were also formed: pyruvic and acetic acids. Using the obtained experimental data, partial kinetic orders of the reaction with respect to 1,2-propanediol, $c_0(\text{NaOH})$, $p(\text{O}_2)$, $n(1,2\text{-PDO})/n(\text{Pd})$ were determined and an experimental kinetic model of the catalytic oxidation reaction was obtained:

$$r = k \cdot c(1,2\text{-PDO}) \cdot c_0^{0.5}(\text{NaOH}) \cdot p^{-0.8}(\text{O}_2) \cdot (n(1,2\text{-PDO})/n(\text{Pd}))^{-1.4},$$

where $k = f(T)$.

Activation energy of the process was calculated and was found to be about 53 ± 5 kJ/mol.

The best result (100 % 1,2-PDO conversion and 88 % selectivity for lactic acid) was achieved using the 3wt%Pd/Al₂O₃ catalyst with the following oxidation parameters: $c_0(1,2\text{-PDO}) = 0.3$ mol/L, $n(1,2\text{-PDO})/n(\text{Pd}) = 500$ mol/mol, $p(\text{O}_2) = 2$ bar, $c_0(\text{NaOH}) = 1.5$ mol/L, $t = 60$ °C.

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Optimization of main synthetic medium component concentration relations for *Kluyveromyces marxianus* biomass production

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2-Phenylethanol (2-PE) is a colorless, liquid, aromatic alcohol. The distinctive feature of this chemical is its rose scent, which makes it widely applied in cosmetics and fragrances, and as a flavoring agent in the food industry.¹ Commercial 2-PE is mainly synthesized via three petrochemical routes (Friedel–Crafts, Raney nickel and via the transformation of chlorobenzene), which implies the use of catalysts that are corrosive and toxic to human beings, animals and the environment. Natural 2-PE is expensive and cannot meet the market demand due to its relative low content in plants.

An alternative method of 2-PE production is its biosynthesis from L-phenylalanine by the yeast *Kluyveromyces marxianus*. The application of yeast for the biosynthesis of 2-phenylethanol is more environmentally friendly, as in comparison to traditional chemical methods, during biosynthesis no carcinogens or harmful by-products are produced. Biosynthesized 2-PE can be considered a high added-value product of natural origin, and its price on the market today is estimated at around 1000 USD per kilogram.

In order to achieve higher productivity of 2-phenylethanol during biosynthesis, a high concentration of biomass in the culture medium is required, which can be achieved only by running the cultivation in the fed-batch mode. Although, a serious problem of fed-batch cultivations is the increase in osmotic stress, which is induced by accumulation of unconsumed feeding solution components in the growth medium. The latter can drastically influence the biosynthesis productivity and final biomass yield.

The aim of the present study was to find out the optimal composition of the synthetic growth medium and feeding solution, in respect to the main biomass components: carbon, nitrogen and phosphorous (C:N:P) to achieve the maximum *K. marxianus* biomass yield and 2-PE productivity.

To find out specific carbon, nitrogen and phosphorous consumption rates, *K. marxianus* microcultivation (96 well microplate) experiment was set up. The results obtained from the microcultivation experiment were implemented when formulating feed media for the fed batch experiment in the 5 L laboratory bioreactor. The obtained results indicate that the optimal molar relations of analyzed components C:N:P is respectively 1:0.039:0.006. After medium and feeding solution composition optimization no significant growth medium component accumulation was observed during the fed-batch process in bioreactor cultivations.

Acknowledgements: This research was funded by a Bio-economic grant “MarksKultOpt” from the Latvian State Institute of Wood Chemistry.

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Synthesis and structure investigation of benzimidazole-based 1,2- and 1,4-quinone derivatives

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Quinone derivatives can enhance the efficiencies of energy-harvesting and energy-storage systems because of their unique electrochemical properties and cost-effectiveness.¹ Studies on the relationship between quinone's molecular structure and its electrochemical behavior may provide further insights for the chemical engineering of quinone molecules. For example, chemical and electrochemical stability or solubility of small organic compounds can be controlled through hydrogen intermolecular bonding² or bonding between the organic ligands and metal ions.³

In this work structures of benzimidazole-based 1,2- and 1,4-quinone derivatives (**1-5**) were investigated using single crystal X-ray crystallography data (Fig. 1). The treatment of 6,7-dichloropyrido[1,2-*a*]benzimidazole-8,9-dione with malononitrile or barbituric acid in the presence of triethylamine led to compound **1** or **2** as triethylammonium salts. Compounds **3-5** were obtained previously.^{4,5}

Analysis of X-ray crystallography data (bond lengths and bond angles) of quinone derivatives **1-5** showed that compound **2** exist as 1,2-quinone, compound **5** - as 1,4-quinone, but in the case of compounds **1**, **3** and **4** the resonance quinone methide or quinone imine forms with charge distribution make a significant contribution to the real structure, as evidenced by bond delocalization. As a result, the structure of the compounds **1-5** molecule can be theoretically divided into two parts: the heterocyclic part (colored in blue) and a system of a conjugated double bonds (colored in red) (Fig. 1). Analysis of bond lengths and angles in heterocyclic part of the compounds **1-5** revealed that they were unaffected by changing from 1,2- to 1,4-quinone structure. In case of compounds **1-4**, the substituent at C(6)-position mostly influences the conjugated system of double bonds and determines the form of the derivative – 1,2-quinone or 1,4-quinone methide/quinone imine.

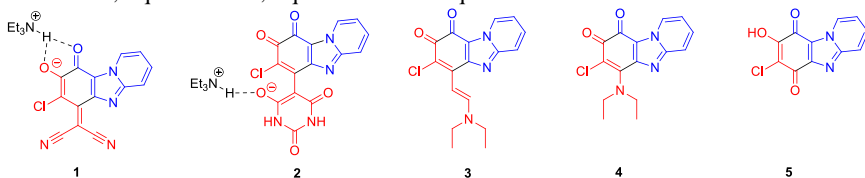


Figure 1. Structures of benzimidazole-based 1,2- and 1,4-quinone derivatives **1-5**.

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Method development for leachable furfural determination in wood-based panels by HPLC-UV system

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Analytical method has been developed and validated to determine the free or leachable furfural concentration in wood-based panel materials. In this work wood-based panel acetone extracts were analyzed with GC-FID system, but water and acetonitrile extracts were analyzed with HPLC-UV system. After the GC data in acetone extracts furfural concentration was below method limit of detection. HPLC-UV data showed that in acetonitrile extracts furfural concentration is also below methods limit of detection. In water extracts furfural concentration was possible to determine and it varies from 0.003 mg·mL⁻¹ to 0.30 mg·mL⁻¹ depending on the sample. As no separate validation guidelines have been developed for samples from biomass, the analytical parameters of the furfural detection method developed in this work have been selected and definitely based on guidelines for the validation of pharmaceutical preparations and pesticide detection methods.¹⁻⁴ Compliance with analytical parameters was determined by the validation requirements for pesticide residue detection methods.¹

In this work method for determination of free furfural in wood-based panel samples was developed. Method was partially validated with accordance to SANTE/SANCO guidelines, and it can be concluded that HPLC-UV is suitable and fast method for furfural determination in wood-based panel water extracts. Developed method passes all set acceptance criteria with linear range from 0.001 to 0.012 mg·mL⁻¹. The limit of detection was 0.0012 mg·mL⁻¹ and limit of quantification was 0.004 mg·mL⁻¹. Method repeatability was determined to be 2 %, but system repeatability was 2.2 %. The recovery at all levels were above 99 %. This shows no interference from sample matrix.

Acknowledgments

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Formation of anisotropic tribological properties on the steel surface by laser radiation

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Laser-induced periodic surface structures (LIPSS) can be formed on different materials such as metals, semiconductors, and dielectrics. Our preliminary study has shown that it is possible to obtain surfaces with wettability angle anisotropy by the formation of LIPSS on the steel [1]. The aim of this study is to develop laser technology to form the metal surface with controlled anisotropic tribological properties. To achieve this aim, the surface of cylindrical shape steel samples were irradiated by Nd:YAG laser in order to obtain LIPSS perpendicular and parallel to motion direction (Fig.1.a,b). The samples were treated with following laser parameters: $\lambda = 1064$ nm, $W = 41$ mJ, $\tau = 6$ ns, hatch spacing 0.4 mm, rotating speed 1 mm/s.

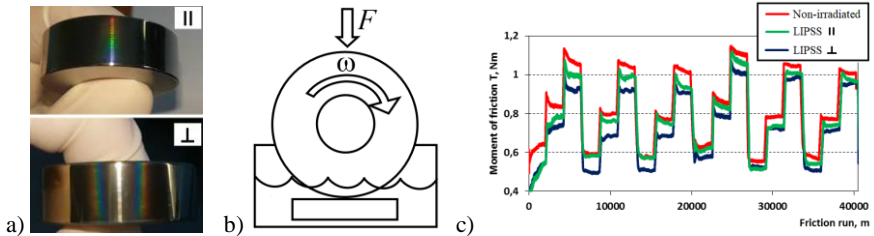


Figure 1. a) Image of cylindrical shape steel samples irradiated by Nd:YAG laser with surface structures parallel and perpendicular to motion direction; b) scheme of tribotest, and c) diagram of friction moment for non-irradiated and irradiated samples.

The experiments confirmed that morphological changes induced on the steel surface by laser radiation (perpendicularly LIPSS samples) leads to decreased moment of friction (Fig.1.c) by more than 10 % in comparison with non-irradiated. During the tribotest time the difference in friction moment between parallelly and perpendicularly irradiated samples was about 12 % in the first part of test and drop to about 5 % from half time of run. Perpendicularly irradiated samples show the best results.

Acknowledgements

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HBsAg production in methanol controlled *P. pastoris* GS115 MutS bioreactor process

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Hepatitis B virus is encompassed by an outer envelope made of lipids and three envelope proteins, which, expressed in the artificial production systems, have the ability to self-assemble into non-infectious hepatitis B surface antigen virus-like particles (HBsAg VLPs) that can serve as delivery platforms for vaccines.¹ In order to generate immunogenic recombinant HBsAg VLPs, eukaryotic expression hosts such as yeasts or mammalian cells are usually employed.² Production and purification of HBsAg VLPs in yeast *Pichia pastoris* is well-documented and has several advantages from the perspective of vaccine production – strong and tightly regulated AOX1 promoter, scalability, the ability to reach high cell densities in inexpensive media, high recombinant protein productivity, correct disulfide bond folding and the absence of toxins, pyrogens and viral inclusions when producing recombinant proteins.³

Despite the high protein productivity, the optimization of *P. pastoris* cultivation is still imperative due to strain- and product-specific challenges. Generally, process engineering strategies include the optimization of fermentation conditions, such as temperature, pH, dissolved oxygen level (DO) and substrate (methanol) feed rate and concentration. Finally, product purification is of the utmost importance, since, in the case of HBsAg, the VLPs are formed during downstream processing.⁴

In this work we investigated two different *Pichia pastoris* cultivation strategies for HBsAg VLP production in a laboratory scale bioreactor and the influence of process parameters (temperature, substrate concentration, dissolved oxygen level) and purification strategy on product yield.

Employing a cultivation protocol presented by Gurramkonda *et al.*³ with an increased methanol concentration controlled at 6 g/l and a reduced DO level below 10%, resulted in a final dry cell biomass concentration of 140 g/l. A novel and rapid purification method was developed including steps of ammonium sulfate precipitation, size-exclusion chromatography and hydrophobic interaction chromatography which resulted in 186 mg/l (1.3 mg/g dry cells) purified HBsAg VLPs.

Acknowledgements

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Peat processing processes to highly added products

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About 3% of the Earth's land surface is peat, and it is environmentally friendly and a slowly regenerating renewable organic matter. On average, peat regenerated around 1 mm per year. Peat has the largest natural carbon stock on earth. There are more than 3 million km² of untouched peat bogs worldwide, which is more than 550Gt of carbon, making up 42% of all soil carbon. Unused peat bogs absorb up to 0.37Gt of CO₂ per year. We need determine the best way of peat processing, which will be high grinding degree, sustainability, energy, and cost efficiency.

It is known that naturally occurring peat is a polydisperse heterogeneous three-phase elastoplastic body. By varying the dispersion of peat by mechanical and chemical action may be to some extent affect the physical and mechanical properties of the finished product. Depending on the purpose and principle of operation, there are grinding machines which: crushing (compression of a piece), fracture (bending), splitting (equivalent to stretching), abrasion and impact. Also interesting is chemical-physical milling processes like ultracavitation, hydro-cavitation, and electro discharge. In this work is obtain main directions of peat milling processes for production optimization include preference and disadvantages of each method. Here we report on the characterization of the processes of mechanical grinding and physical chemical grinding.

Influence of extracts from bark of deciduous trees on the activity of the amyolytic enzyme – alpha-amylase

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At present, enzymatic therapy is the main component of treatment for salivary and pancreatic insufficiency. The normal functioning of these glands ensures efficient digestion and absorption of essential nutrients. Constant stress, unhealthy ecosystem, bad habits and inability to eat properly are the main factors in the development of the above-mentioned diseases. Diseases of the salivary glands are quite widespread and require special attention. A change in the composition of saliva occurs with the development of viral, bacterial, oncological and other diseases, which in turn is accompanied by a change in the activity of saliva enzymes. The amyolytic enzymes containing in saliva carry out the initial stage of the digestion process - the breakdown of complex carbohydrates. The entire digestive process will depend on how quickly and efficiently the breakdown of complex carbohydrates occurs.

Currently, in clinical practice, many synthetic drugs are used, characterized by various combinations of components and enzymatic activity. However, the risk of side effects and the cost of these synthetic drugs are higher than for herbal ones. Many natural compounds, in particular, polyphenols and their glycosides, can control amylase activity and glucose absorption in the small intestine. In wood processing, branches, greens, and bark are waste and do not find a useful application. However, these parts of wood contain many valuable biologically active components, e.g. proanthocyanidins, that can effectively influence the activity of α -amylase. The advantage of using these activators as therapeutic agents in the treatment of the digestive system lies in their availability and a simple method of isolation by extraction.

Proanthocyanidins are of the greatest interest in the world due to their antioxidant, antimutagenic, anticarcinogenic, anti-inflammatory, and antiviral properties and almost complete absence of toxicity.

The present study was aimed at the obtaining of the proanthocyanidins-rich extracts from bark of deciduous trees aspen (*Populus tremula*) and black alder (*Alnus incana*), which are widespread in the Baltic region, the characterization of the extracts, as well as the study of the biological activity of the extracts by ABTS⁺, DPPH tests and the assessment of the influence of the extracts on the activity of the alpha-amylase by in vitro tests.

In vitro tests of the extracts biological activity were performed at Riga Stradins University based on European standards protocols. The tests results have shown that the extracts of aspen and alder bark may be beneficial for the human health as they promote alpha-amylase activation.

Acknowledgements

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Wood and wood bark extracts as natural sunscreen ingredients for cosmetic products

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Moderate sun exposure has several beneficial effects, including vitamin D production, antimicrobial activity, and improved cardiovascular health. However, prolonged exposure to ultraviolet (UV) rays poses a potential health risks, in addition to sunburns of the skin, it is skin aging and facilitation of the development of skin cancer. Therefore, UV protection against harmful UVA and UVB rays is becoming an important function of many cosmetic products.

At the moment, there is a huge number of sunscreens on the market that contain synthetic aromatic compounds as UV-absorbers, which have certain limitations from an environmental point of view and due to the individual reactions of the human body. These compounds include benzophenone derivatives, dibenzoyl methane derivatives, *para*-aminobenzoate derivatives, cinnamate derivatives, *etc.* Despite the high degree of protection from harmful UV rays, these compounds cause irritation, skin allergies, and, penetrating the skin, can cause the formation of free radicals and have many toxic effects. The risk of side effects in the presence of these compounds, which are often in a combined form, is very high, so it is essentially necessary to find an alternative to these synthetic aromatic compounds. Polyphenols, low and high molecular weight secondary metabolites synthesized in plants to protect plants from various environmental stresses, are valuable biologically active compounds with many useful biological properties. Polyphenols can absorb UV radiation in varying degrees due their molecular structure. In addition to limiting harmful UV radiation sequences in the human body, the antioxidant, antimicrobial and anti-inflammatory activity typical for polyphenols improves the properties of cosmetic sunscreens.

The investigated extracts were obtained from the bark of Latvian pine (*Pinus Sylvestris*), black alder (*Alnus incana*) and willow (*Salix caprea*) by extraction with an aqueous/ethanol solution. The aim of this work was to study composition of the extracts using liquid chromatography methods UHPLC-ESI-MS/MS, their antioxidant activity by ABTS⁺, DPPH tests, and to assess their effectiveness as natural sunscreen ingredients for cosmetic creams. For evaluation of the level of UV protection, the "Star Rating" approach developed by Diffey / Boots in 2011 was applied.

The results of the study showed that the cream containing 5% and 10% (w.w.) extract rich in pinosylvin had SPF about 5 and 9, respectively. Cream transmittance curve profile is comparable with transmittance spectrum of commercial sunscreen "DZINTARS", SPF10. Extracts obtained from the bark of deciduous trees reduce the transmittance in UVB region to a much lesser extent in comparison with extract rich in pinosylvin. In UVA region their action may be slightly greater.

Acknowledgements

This research was funded by a Bio-economic grant "LignoBark" from the Latvian State Institute of Wood Chemistry and ERDF project no. 1.1.1.1/18/A/182. "Innovative green extraction process, using water, with elaboration of microwave hybrid reactor and mechano-chemical biomass pretreatment, creating a new biorefinery cluster oriented to phytochemicals and biomaterials production from underexploited tree biomass".

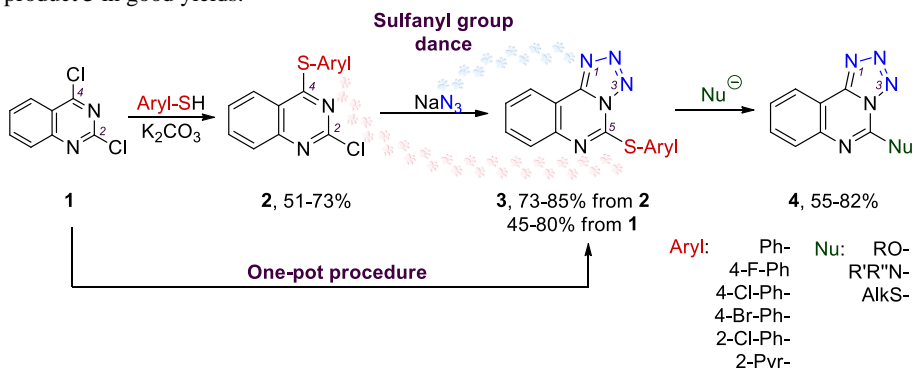
Application of arylsulfanyl group dance in the synthesis of novel tetrazoloquinazolines

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Quinazoline core has already been proven to be important molecular scaffold in anticancer drugs such as erlotinib, gefitinib, lapatinib and afatinib.¹ Using both leaving group capability of arylsulfanyl group and azidoazomethine-tetrazole tautomeric equilibrium, novel tetrazoloquinazoline derivatives can be acquired as potential drug candidates.

Using C4-selective S_NAr reaction of commercially available 2,4-dichloroquinazoline **1** with thiols, several 4-arylthio-2-chloroquinazoline derivatives **2** were obtained in good yields (Scheme 1). Then the azide group was introduced to the quinazoline core, which resulted in an unusual sulfanyl group dance around the quinazoline core and products **3** were obtained in good to excellent yields. This transformation from **1** to **3** can also be easily carried out as a one-pot reaction, if kinetic rates of all competing steps are taken into account, leading to product **3** in good yields.



Scheme 1. Synthesis of 5-substituted tetrazolo[1,5-c]quinazolines.

Due to electron-withdrawing nature of tetrazole ring, arylsulfanyl group can then be easily substituted with different nucleophiles, leading to a previously inaccessible and unknown variety of 5-substituted tetrazolo[1,5-c]quinazolines **4** in good yields. A few analogs of this class have already been proven to have effective anti-cancer properties.²

Acknowledgements

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Optimization of exposed concrete pigmented with Fe_xO_y

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As demands on pigmented concrete has grown in the industry section great deal of attention has been allocated to explore physical and chemical properties of exposed pigmented concrete worldwide. The applicability, consistence and increase of resistance to external influences have eminently increased the importance of concrete in the construction industry.¹

Significant amount of iron oxide based concrete mix designs were constructed and compared for compressive strength development during time in different conditions. Changing variables were temperature and humidity. As compressive strength is defined in all construction specification it plays major role in building industry.



Figure 1. Different pigmented mix designs.

During curing exposed pigmented concrete, a precipitation migration was determined also called efflorescence. These precipitations may be different type but it trends to migrate to the surface of concrete leaving white spotty discolorations.² A different curing course has been proposed to avoid migration of precipitation to the surface and avoid exposed surface of concrete to be mottled.

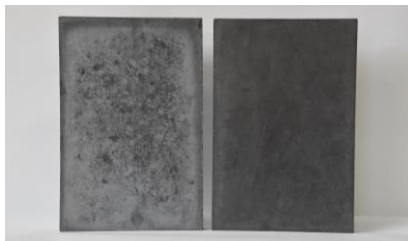


Figure 2. Limestone efflorescence migration on surface of exposed pigmented concrete

Acknowledgements

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Rheological properties of wood plastic composites based on polypropylene and plywood sanding dust

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Wood fiber composites based on polyethylene and polypropylene have gained increasing interest over the past three decades in the scientific community and industry. A lot of different, popular products produced from WPCs are wood sawn timber such as facade, terrace boards and garden furniture. WPC products are used also in car industry. Different processing methods, like extrusion and injection molding, for manufacturing of these products are used. Due to the WPCs are processed from polymer melt condition, important role play the rheological properties of the WPCs melts. One of the main methods of the rheological investigations is capillary rheometry at different shear deformation rates, for example from 10-20 s⁻¹ up to 10.000-15.000 s⁻¹. Rheological properties of the industrially produced WPCs based on polypropylene and birch plywood sanding dust (PSD) have been studied in our previous works.¹ In this work once more five systems based on polypropylene+40wt.% PSD with different additives rheological properties, melt flow index (MFI) and thermal stability were investigated. The obtained results of MFI measurements show that numerical values of the MFI are very similar for all five investigated composites and change only in limits from 1.52 g/10min. up to 1.66 g/10 min. That is normal situation because all tested composites contain equal amount of PSD (40 wt.%) what mainly influence viscosity and fluidity of composites. That confirms the value of MFI of the pure PP (3.0 g/10min.) which differs nearly two times comparing with filled composites. Nevertheless, the decreasing of MFI of the WPC is not so critical, and all investigated composites can to process by traditional polymer processing methods for example like extrusion. The investigations of rheological properties of polymer composite melts at the temperatures 190, 200 and 215°C and in the wide shear rate interval. (shear rate interval 20-8000 1/s) which partially coincide with the temperatures and shear rates of the processing of WPC based on polypropylene (200-215°C and shear rates 100-2000 1/s). Basing on these data we can predict how could behave composites during the real processing processes. Fluidity curves, dependences of shear viscosity-shear rate and fluidity index-shear rate indicate on the character of the typical pseudo-plastic liquids for what viscosity is not only depend on the temperature and the shear rate and shear stress, but also decreases with the increase of the shear deformation rate. Besides the shear viscosity depending on the composite composition and conditions of experiments can decrease up to 10 times with the increase of the shear rate up to 8.000-10.000 1/s. TGA measurements show that all systems have quite good thermal stability at tested temperature 215°C during 2h. The weight losses values were from 2.43 up to 5.29 %.

Acknowledgements

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Formate esters containing biodiesel – diesel mixed fuels

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The blends of varying proportions of biodiesel (FAME) containing formate esters of glycerol and 93.0 wt.% fatty acid methyl esters, obtained in an interesterification reaction with methyl formate without further purification¹, and winter diesel fuel, were prepared, analyzed and compared with winter diesel fuel. The obtained results showed that blends comprising up to 20 vol.% of FAME fulfill the requirements of the standard LVS EN 590 concerning such characteristics as cold flow properties, viscosity, density, and carbon residue. The increase of FAME content worsens the cold flow properties; however, the mixed fuel with 20 vol.% or lower FAME content, according to the cloud point and cold filter plugging point values, remains in the same severe climate "Class 0" group as winter fuel. The carbon residue of mixed fuels raises with increasing FAME content but stay low and do not exceed the limits of standard for mixtures with FAME percentage up to 20 vol.%. The comparison of mixed fuels containing 20 vol.% of FAME and the same amount of neat biodiesel (99.6 wt.% of fatty acid methyl esters) shows that the difference is negligible. The obtained results have indicated a good potential of FAME obtained in the interesterification reaction with methyl formate without further purification as a diesel fuel additive for up to 20 vol.%.

Acknowledgements

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Photopolymerization of epoxidized soybean oil acrylate / lignocellulose biocomposites

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Biopolymer popularity in photopolymer mixtures are growing every year, because of their ability to be produced from renewable sources-natural oils, that we use in everyday applications. To use natural oils in photopolymer mixtures they need to be chemically modified and that process allows to fine tune polymer properties. In many cases polymer mixture needs to be further improved and modified with addition of fillers, improving mechanical properties, polymerization characteristics and lowering shrinkage. Epoxidized soybean oil acrylate (AESO) is one of more often used bio oligomer in photopolymerization, that is modified with additional monomers and lignocellulose fillers.¹ Trimethylbenzoyl diphenylphosphine oxide (TPO) was used as photoinitiator.² Research goal is to create AESO mixture in tandem with different type and amount of lignocellulose nanofillers and polymerize them under UV light. Determine how does filler type and concentration (5, 10, 20, 30 wt%) changes composite properties. The gel fraction and density measurements, thermogravimetric and dynamic mechanical analysis were carried out on composite samples. FT-IR spectra was collected from samples with different irradiation times, and optimal irradiation time was determined for each mixture. In this study analyzing 30 wt% CNC content composite storage modulus at 40 °C was 405% higher than plain photopolymer. NFC and HC composites similarly increased mechanical properties. Composite density increased as filler amount increases, up to 1.10 g/cm³, from empty photopolymer 1.06 g/cm³. In this study, thermal and mechanical properties were investigated. It was determined that lignocellulose as filler in photopolymer composite can increase material mechanical, physical and thermal properties. It was found that while concentration of filler increases, storage modulus of composite increases significantly. With this method needed photopolymer amount can be reduced significantly, while improving composite characteristics.

Acknowledgement

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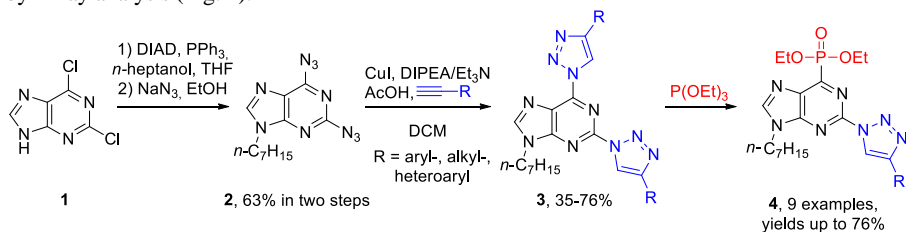
Synthesis of 2-triazolyl purine C6 phosphonates in S_NAr -Arbuzov reaction

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Purines and their derivatives show wide spectra of biological activities. They are widely used as antiviral and anticancer drugs. From the literature it is known that modification with phosphonate¹ and triazolyl² moieties could lead to novel class of biologically active compounds.

To obtain the target phosphonate derivatives, firstly 2,6-diazidopurine **2** was obtained using a sequence of Mitsunobu and S_NAr reactions. Then 2,6-bis-1,2,3-triazolylpurine derivatives **3** were synthesized via copper(I) catalysed azide-alkyne cycloaddition (CuAAC) between diazide **2** and different alkyl/aryl/heteroaryl alkynes. Finally, 2-triazolyl C6 phosphonates **4** were obtained in S_NAr -Arbuzov type reaction between bistriazoles **3** and $P(OEt)_3$, using triazolyl ring at C6 position of purine as a good leaving group³ (Scheme 1). The structure of compound **4** was proved by X-ray analysis (Fig. 1).



Scheme 1. Synthesis of 2-Triazolyl Purine C6 phosphonates **4**.

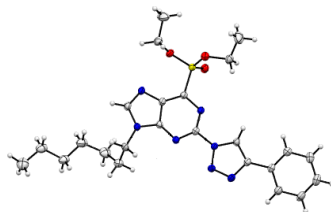


Figure 1. X-ray structure of diethyl (9-heptyl-2-(4-phenyl-1H-1,2,3-triazol-1-yl)-9H-purin-6-yl) phosphonate.

Acknowledgements

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Lichens (*Xanthoria parietina*) – bio-indicators for sulphur and metallic elements for pollution investigation in Riga city

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Lichens are symbiotic organisms consisting of a group of fungi and algae or cyanobacteria. They are the most widely used bio-indicators to describe the state of the environment, especially air quality, to characterize the pollution level in the urban and industrial areas.

Lichens are very sensitive to air pollutants, especially to heavy metallic elements and sulphur dioxide, which inhibit the photosynthetic processes of lichens and damage their membrane cells.¹

Foliose lichens (*Xanthoria parietina*) are one of the most widespread and easily recognizable species that is highly resistant to air pollution and have the highest accumulation capacity of metallic elements, what makes them ideal for use as pollution bio-indicators.²

The aim of the research was to evaluate the content of sulphur and metallic elements in foliose lichens (*Xanthoria parietina*) in the different growing places in the territory of Riga.

Samples were collected from trees about 1-2 meters above the ground. During the research, three different places of Riga were chosen: Freeport of Riga (Kundzinsala), residential area (Sarkandaugava) and Mezaparks. Freeport of Riga and Sarkandaugava are described as areas with a high level of pollution, but Mezaparks was chosen as the closest ecologically cleanest place.

Lichen samples were divided into two groups: washed and unwashed lichens. Sample digestion was performed in a closed microwave energy system in the mixture of HNO₃:H₂O₂ (10:2). Sulphur content was determined turbidimetrically as sulphate ions, but metallic element content was determined using the ICP-MS analysis method.

Lichens (*Xanthoria parietina*) show that the territory of the Freeport of Riga has the higher content of sulphur and metallic elements than Sarkandaugava and Mezaparks. The sulphur content decreases significantly after washing the lichens, and that indicates that the dust contains sulphur-containing compounds. In the Freeport of Riga, there is a greater dispersion of obtained results, which indicates that the given area is a stationary polluted area, and this pollution is caused by coal dust and other dispersed particles.

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Variations of some metallic elements in different parts of lingonberry (*Vaccinium vitis-idaea L.*) and soil

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Lingonberries (*Vaccinium vitis-idaea L.*) are the Ericaceae family plant with red and juicy berries. The geographical distribution of lingonberries in the world ranges from Eurasia (mostly Scandinavia) to North America (USA, Canada). Favorable conditions for the growth of lingonberries are an open, sunny place with podzolic or swamp soil (pH 3.5-6.0). In Latvia, lingonberries are found in dry pine forests, clearings and swamps. Climatic conditions are very favorable for the growth of these plants in Latvia.¹

Various berries, both wild and cultivated, are becoming increasingly popular for use in medicine, food production, pharmacology and cosmetology. In recent years, the use of lingonberries in the production of pharmaceutical products and food supplements has been actively studied, not only lingonberry berries, but also their components (leaves, roots) are analyzed.² Use of lingonberries in pharmacology and food production makes it very important to know the elemental content of these plants.²

The aim of research was to evaluate the content of metallic elements in lingonberries (*Vaccinium vitis-idaea L.*) and soil depending on their place of growth and evaluate the transfer factor values from between different parts of plants (pine roots, leaves, berries).

For the research was selected two different forest areas: Garkalnes pine forest and Vecumu forest. Soil samples were collected at the depth level ~0-10 cm and lingonberries were collected different part of the plants (pine roots, leaves and berries).

Lingonberry pine roots and leaves were digested in the closed microwave energy system in the mixture of conc. HNO₃:H₂O₂ (6:2), but berry samples were digested using the dry digestion method and then dissolved in 2 mol·L⁻¹ HNO₃ solution. 1 mol·L⁻¹ HNO₃ solution was applied for extraction process of soil samples. Metallic element content (Cu, Fe, Zn, Mn, K, Ni, As and Pb) was determined using the ICP-MS analysis method.

Despite the different growing conditions, the content of Fe, Cu, Zn and K are similar in lingonberries in Garkalnes and Vecumu forests, but in soil samples content of these elements is different. Determined content of metallic elements in lingonberries decreases in the following order: K> Mn> Fe> Zn> Cu> Ni> Pb> As. Transfer factor values show that K and Mn accumulate in lingonberry leaves and berries, but other metallic elements are held in lingonberry roots to prevent its toxicity. Forest soil in the analyzed territories are strongly acidic (pH ~3.39-4.50) which promotes migration of Zn and Mn ions from soil to plant and these elements mostly accumulate in lingonberry roots. The content of As and Pb in lingonberries decreases significantly (from 10 to 20 times) in the following order: roots > leaves > berries.

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Influence of crystallite size of nickel and cobalt ferrite on the catalytic intermediate pyrolysis of buckwheat straw by using TGA-FTIR method

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In the past decades, many different techniques (biological and thermochemical pathways) have been developed to convert biomass into fuels or chemicals. Among these techniques, pyrolysis, which can decompose biomass into the bio-oil, biochar, and non-condensable gases at 400-700 °C with the absence of oxygen, has been extensively recognized as a promising technique for converting biomass. The crude bio-oil produced from pyrolysis of biomass contains a large amount of oxygenated compounds, which will cause negative properties such as low stability, high corrosiveness, and low heating value; it is unsuitable for direct use in the existing petroleum-based infrastructure. The crude bio-oil must be upgraded to reduce the undesirable components and increase the content of useful compounds (hydrocarbons).^{1,2}

Catalytic cracking is one method that could remove oxygen from bio-oil in the form of H₂O, CO and CO₂ through deoxygenation without hydrogen supply and at atmospheric pressure. Due to their redox properties and acid-base properties, metal oxides have been widely used in the catalytic pyrolysis of biomass.²

In this study, intermediate pyrolysis of buckwheat straw with or without catalysts was investigated using TGA-FTIR method in order to determine the influence of crystallite size of nickel and cobalt ferrite on the yield of the compounds.

All catalysts showed deoxygenation activity. The addition of catalysts increased the production of volatile matter from 66.5% to 82.1%, 75.1%, 75.0%, and 74.6% under NiFe₂O₄ (crystallite size of 15 nm), NiFe₂O₄ (crystallite size of 45-47 nm), CoFe₂O₄ (crystallite size of 20-22 nm), and CoFe₂O₄ (crystallite size of 52-54 nm). NiFe₂O₄ with crystallite size of 15 nm had a substantial effect on the production of monoaromatic hydrocarbons, whereas the yield of olefins notably increased in the presence of CoFe₂O₄ with crystallite size of 20-22 nm.

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Micromechanical and tribological properties of nanostructured carbonitride coatings deposited by PVD technique

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Nanostructured smart coatings (NSC) based on the TiAlSi-CN composite structure elements were deposited using reactive high-power physical vapor deposition (PVD) technique. The advanced modular deposition system included up to 8 high-power magnetron sputtering devices (MSD) allowing operate them simultaneously and exceed power density of 120 W/cm² within each device erosion zone. The novel designed NSC on bearing steel 100Cr6 substrates demonstrated enhanced mechanical and tribological properties comparably with bearing steel ones required for multifunctional high-tech applications. The deposited NSC containing TiAlSi-CN nanoparticles strengthened by Cr and Nb additives exhibited microhardness as high as 2500 HV values in comparison with 750 HV of 100Cr6 steel substrates. Load-displacement curves obey Meyer's power-law surprisingly well because power-trendline fitted ones by R-squared value of 0.9999 for all the film-samples.

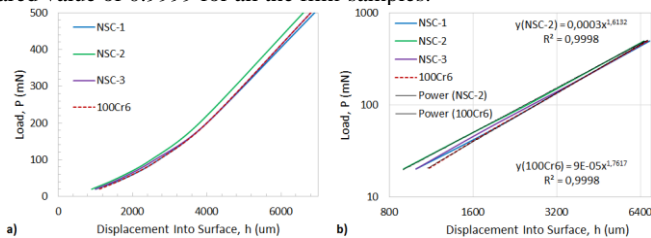


Figure 1. a) Typical micro-indentation response: Load-displacement, P-h, curves of the NSC film-samples in a linear scale plot, b) Typical micro-indentation response: Load-displacement, P-h.

Tribological properties were measured under dry friction conditions between the bearing steel ball of \varnothing 6 mm and the film-samples' flat surface. Coefficient of friction (CoF) ranges between 0.17-0.56 depending on a sample and load. Tribotracks worn under the friction indenter were too shallow to evaluate them by Mitutoyo profilometer SJ-500. Therefore, the wear rate was estimated as ball wear of the friction indenter.

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Synthesis of silicon-containing unsaturated carbohydrates

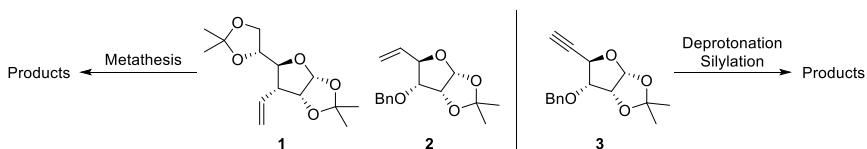
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Carbohydrates are very important building blocks of the biological systems. As the part of a more complex structures, they are responsible for many regulating processes and storage and transcription of the genetic information. Carbohydrate-containing compounds are widely used as antiviral therapeutic agents, of whom many are synthetically modified to improve efficiency. Thus, scientists explore different possible modifications of the carbohydrates to find novel applications.

Silicon-containing carbohydrates potentially can be used for synthetic applications,¹ exhibit a biological activity, and could be used for production of modified silicon-based materials.² Although there is a potential application for these modification, the methods and variety of the compounds is scarce.³ In our research, we have already explored a possibility for C-silylation of C-sp³ carbons in the sugar moieties.⁴ Now, we report results on synthesis of unsaturated Si-containing carbohydrates.

Starting from D-glucose, we synthesized double and triple bond containing sugars that were further used for the introduction of the silicon-bearing fragment. We have utilized a double bond metathesis and a triple bond deprotonation-silylation reactions to yield various unsaturated products (Scheme 1). Additionally, we have demonstrated that the compounds can be selectively hydrogenated to yield fully saturated products.



Scheme 1. A substrate scope and the used methods for the syntheses of the title compounds.

Acknowledgements

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The synthesis of renewable hydrocarbons from different vegetable oils and soapstock by hydrotreatment over high metal loading supported Ni catalyst

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Renewable hydrocarbon production by hydrotreatment of vegetable or animal oils is catalytic process. Different noble Pt, Pd, Rh, Ru and transition Ni, Mo, Co, Cu, Fe etc. metals as promoters or active components in supported catalysts are widely studied subject for their utilization in hydrotreating processes like green diesel production. In the present study the impact of fatty acid content, composition and saturation of sunflower (SO), linseed, (LO) coconut (CO) and rapeseed (RO) and its soapstock derived acid oil (RS) were investigated to evaluate marketable hydrocarbon production with wide range of carbon chain length under relatively gentle hydrotreatment conditions in the presence of commercial Ni65%/SiO₂-Al₂O₃ catalyst.

Commercial Ni65%/SiO₂-Al₂O₃ catalyst has sufficient active metal loading (64.7%) and textural properties (specific surface area 165 m²/g, total pore volume 0.25 ml/g and average pore diameter 6.0 nm) for vegetable oil feedstock conversion into renewable hydrocarbons by catalytic hydrotreatment.

It was observed that high yields of marketable liquid saturated hydrocarbons can be obtained from RO, RS, SO and LO with different saturation in short residence time 15 min at operating temperature 340 °C over commercial Ni65%/SiO₂-Al₂O₃ catalyst. Overall (70.3-71.6%) and dominant hydrocarbon *n*-pentadecane, *n*-hexadecane, *n*-heptadecane and *n*-octadecane (58.8%-60.0%) yields were very close for all three unsaturated vegetable oils - RO, SO and LO. The lowest overall (44.6%) and dominant linear saturated hydrocarbon C15-C18 (7.4%) yield was obtained from CO. Large fraction of short chain fatty acids in CO leads to formation of light hydrocarbons with relatively low molecular weight and boiling point, which cause the loss by volatilization during product extraction procedures from reaction mixture.

The highest overall (78.1%) and dominant linear saturated hydrocarbon C15-C18 (74.2%) yields were achieved from RS. Obviously the present of different contaminates in RS suppress the effect of catalyst on formation of low molecular weight and boiling point hydrocarbons. In result increased yield of liquid hydrocarbons were observed.

Hydrocarbon composition of samples produced from SO, LO and RO are almost identical, due to similar fatty acid chain length. Ni65%/SiO₂-Al₂O₃ mostly produce *n*-heptadecane, when SO, LO, RO and RS were used as feedstock. This means that particular catalyst has high selectivity to hydrocarbons produced by reaction pathways where elimination of carbonyl group takes place.

Acknowledgements

This work has been supported by the European Regional Development Fund within the Activity 1.1.1.2 "Post-doctoral Research Aid" of the Specific Aid Objective 1.1.1 "To increase the research and innovative capacity of scientific institutions of Latvia and the ability to attract external financing, investing in human resources and infrastructure" of the Operational Programme "Growth and Employment" (No. 1.1.1.2/VIAA/1/16/031).

Investigation of furfural formation and mechanical properties of suberinic-acids bonded particleboards depending on their preparation parameters

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Formaldehyde-based synthetic adhesives are widely used today in the production of different kinds of wood based-panels including particleboards (PBs). PBs made from these kinds of adhesives are most commonly used in the furniture products¹ and emit formaldehyde which is carcinogenic to humans.² With an ever-increasing demand for safer and more eco-friendly materials, there has been high research interest in bio-adhesives, particularly in soy-, tannin- and lignin-based.¹ Silver birch (*Betula pendula*) outer bark suberin can also be used as a raw material to make a bio-adhesive for particleboards³ (PBs). However, the adhesive is acidic, which can catalyse furfural (FUR) formation from xylans⁴ in wood particles that are used for the preparation of PBs. FUR being a volatile organic compound can be emitted from the PBs and exposure to it can have harmful effects on humans.

In the scope of this study, the effects on technological parameters (wet adhesive pH: 3, 6 and 9 and hot-pressing temperature (180...230 °C)) were investigated on the FUR formation in PBs. Also, glycerol as an additive to adhesive (5, 10 and 15 wt%) was studied because in the presence of acid catalysts FUR acetalisation with glycerol can occur.⁵ The FUR content was determined with high-performance liquid chromatography-ultraviolet spectroscopy system from the extracts of milled PBs. Mechanical properties (modulus of elasticity, bending strength, and thickness swelling) of the PBs were also studied. When using an adhesive with a pH 6 at hot-pressing temperature 230 °C with no glycerol added, it was possible to obtain PBs that satisfied the requirements of EN 312 P2 (boards for interior fitments). The FUR yield of these boards were more than 6 times lower than for the PBs pressed at 230 °C with a wet pH 3 adhesive. However, the PBs made from pH 3 adhesive showed more water-resistant properties as determined from thickness swelling results.

Acknowledgements

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Effect of ground vulcanizate modification methods on properties of oil-petroleum-resistant rubber

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In this paper, the influence of the modification method applied to ground vulcanizate (GV) on properties of elastomeric compositions based on nitrile rubber is discussed. Modified GV was mixed with the elastomeric composition which is used for the manufacturing of oil-petroleum-resistant rubber products.

The work takes into consideration two types of ground vulcanizates with different chemical nature. The first GV type is rubber crumb produced from end-of-life tires. The second GV type is obtained from wastes of the manufacturing of products based on nitrile rubber. Three methods of the modification are compared in the research: by mechanical activation in a planetary ball mill, swelling in a Polyethylene glycol (PEG-400) medium, and the mechano-chemical modification of GV with PEG-4000.

Properties of magnesium oxychloride and magnesium oxysulphate cement composites

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Today, the construction industry accounts for about 40 % of all energy. Environmental pollution and CO₂ emissions are caused by a number of industrial activities and also building sector. Most of these emissions come from the production process of building materials.¹ Cement is one of the most widely used building materials. Although it has a number of good features, most of the negative aspects must be taken into account. It is important to highlight that cement accounts more than 94 % of CO₂ emissions. The main source of energy consumption is the process of material production.²

The use of ecological building materials is becoming more important in recent years. Magnesium (MgO) based cements can provide environmental benefits because of the low calcination temperatures. There are several types of MgO cements of which the most commonly used are: magnesium phosphate cements, magnesium silicate cements, magnesium oxychloride and oxysulphate cements.³

This paper presents results of an experimental investigation to produce two magnesium-based cements (magnesium oxychloride and magnesium oxysulphate). The physical, mechanical and durability properties of cement composites were determined by comparing the obtained values of density, compressive strength, thermal conductivity and capillary water absorption.



Figure 1. One of the prepared samples during the capillary water absorption test.

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Characterization of woven composite material properties by using an inverse technique based on vibration tests

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Nowadays use of woven composite materials has increased and, due to their high stiffness and low weight properties, these materials are utilized widely in different engineering applications like aircraft, automobile, ship, railway constructions, etc. Unfortunately, not always all necessary material data are available from manufactures for the design and optimisation purposes of advanced lightweight structures. For this reason, a mixed numerical-experimental technique based on vibration tests is modified and applied in the present study to determine the elastic material properties of woven composites.

The non-destructive technique consists of physical experiments, numerical modelling and material identification procedure, where an identification of material properties is performed minimising the error functional between the experimental and numerical parameters of structural responses. The computational effort has been substantially reduced by using non-direct optimisation methodology developed on the planning of experiments and response surface technique.

For the characterisation of woven composite material properties, two carbon fibre panels made of four anisotropic layers with different reinforcement schemes $[0^\circ/90^\circ/0^\circ/90^\circ]$ and $[-45^\circ/45^\circ/-45^\circ/45^\circ]$ have been prepared. The selected thicknesses and reinforcement schemes of specimens have been chosen in relation to the design requirements for a manufacture of power shells widely used in aircraft structures. Samples have been made of CM-PregF-T27 200/1250 CP0041 45 prepreg carbon fibre material by manual layout technology, vacuuming under the polyethylene film and curing in an autoclave at high temperature and pressure.

The plans of experiments with regular distribution of the points of experiments in the domain of factors for both samples have been formulated for 3 design parameters and 20 experiments. Then in each experimental point the finite element vibration analysis based on the first-order shear deformation theory have been carried out in ANSYS for the samples with completely free boundary conditions. Physical experiments have been executed by using non-contact excitation with loudspeaker and optical sensing with POLYTEC scanning laser vibrometer PSV-400-B. During vibration testing, 11 first frequencies have been measured for specimen 1 and 12 first frequencies - for specimen 2. Different order polynomial functions have been estimated in their applicability to approximate accurately the numerical results. The identified elastic material properties have been successfully validated by comparison of numerical and experimental resonant frequencies.

Acknowledgements

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Development of plywood binder by partial replacement of phenol-formaldehyde resins with birch outer bark`s components

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Phenol-formaldehyde resins (PFR) is widespread binding agent for wood gluing due of its water, heat, wear resistance, strength, and chemical stability. It is the second most important wood composite binder with up to 3 million tons/year usage worldwide. The apparent shift in climate has resulted in the pursuit of environmentally friendly bio-based products to reduce the carbon footprint. PFR is a product of condensation reaction of phenol and formaldehyde in an acidic or basic medium. In the scientific literature are many attempts to make PFR more sustainable by using bio-based phenolics in the synthesis instead of petroleum-based phenol.¹ However, it is also important to reduce the content of formaldehyde in the binder, the vapours of which are toxic and even carcinogenic to the human body, so its permitted indoor emissions are internationally strictly regulated.² One of the technically simplest solutions could be the incorporation of other bio-based wood composite binders into the completed PFR, for example, by blending them in certain weight ratios.³ Previous experiments in our laboratory have shown that birch outer bark`s suberinic acids is an effective, ecological, thermosetting binder to produce mechanically durable and moisture-resistant wood composites.⁴

The aim of the study was to adapt the components of birch outer bark for their incorporation into industrial PFR and to find the optimal level of resins replacement by practical experiments. At the same time to keep similar level of the bending strength and moisture resistance (shear strength) of plywood bonded with modified binder compared to pure industrial PFR. During the birch outer bark`s components adaptation experiments, pre-treatment of the birch outer bark, suberin depolymerization medium, pH level of suberinic acids precipitation, moisture content of components and PFR/components dry matter ratios, as well as plywood hot pressing conditions were varied.

As a result, it was found that it was possible to replace up to 30 dry wt% of the PFR with birch outer bark`s components to obtain birch plywood without significant loss of the bending strength and moisture resistance. In this way, it would be possible to significantly reduce the carbon footprint of synthetic PFR binder in the birch plywood industry by using birch processing residues.

Acknowledgements

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Study of chromatographic properties of catecholamines and their acidic metabolites using novel molecularly imprinted polymers as stationary phases

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Quantitative analysis of biologically active compounds such as catecholamines and their acidic metabolites can provide vital information for diagnosis and treatment of various diseases (such as adrenal tumors). However, complicated purification protocols are usually required to isolate the analytes. Molecularly imprinted polymers have attracted considerable attention as a means of selectively separating desired compounds from their matrix (especially from biological fluids). Therefore, we propose a synthetic procedure for new molecularly imprinted sorbent that possesses selective binding sites for both catecholamines and their acidic metabolites. The polymer utilizes non-covalent and semi-covalent imprinting. Sodium (3,4-dimethoxyphenyl)acetate acts as a “dummy template” for acid metabolites. Methylenebisacrylamide, 4-vinylbenzyl-*N,N,N*-trimethylammonium chloride and 3-phenylpropylacrylate were used as the cross-linker, functional monomer and protected functional monomer/template, respectively. Several molecularly imprinted polymers were synthesized by changing the monomer/cross-linker ratio. The binding properties of MIPs were evaluated using chromatographic experiments. The polymers were analyzed using Scanning Electron Microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FTIR). The obtained values for selectivity coefficients and imprinting factors suggest that the MIPs bind with catecholamines much more selectively than with their acidic metabolites (see Figure 1). Therefore, increasing sorption selectivity for these acids is the next goal of our future research. This would make it possible to simultaneously extract catecholamines as well as their acidic metabolites with the help of molecularly imprinted solid-phase extraction.

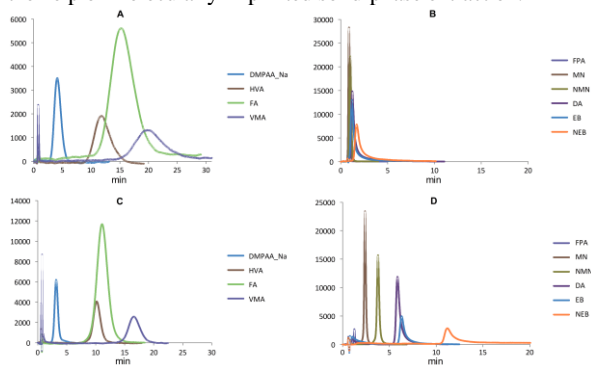


Figure 1. Chromatographic behavior of acids and bases on control (A, B) and MIP (C, D)

Acknowledgements

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Analytical pyrolysis for valorization of herbal pharmaceutical industry wastes excluding necessity of preparative isolation of their components

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Pharmaceutical industry produces large amounts of herbal medicine waste, the mass of which reaches on average 85-90% of the raw materials consumed. The development of an efficient utilization method for these wastes can give both economic and environmental benefits.^{1,2} The residues of medicinal plants can be considered as a renewable source of a number of valuable products of natural origin, including cellulose, hemicellulose, lignin. The residual biologically active substances (target pharmaceuticals) detected in the waste after extraction also can find an application in other areas, e.g. in agriculture.¹ Among analytical methods available for characterization of the composition of lignocellulosic biomass and its fractions, Pyrolysis GC/MS (Py-GC/MS) can be considered as one of the most informative and convenient technique. This analysis quantifies the products formed from the momentary thermal (600°C, some seconds) decomposition of biomass in which the resulting fragments of macromolecules do not have time to enter the secondary reactions.

The objectives of the work were obtaining of information about composition of herbal pharmaceutical industry wastes, revealing structural transformation of components caused by extraction, estimation of the efficiency of extraction of target pharmaceuticals and detection of possible directions for plant residues application. Besides that, application of analytical pyrolysis for analysis of the herbs residues allows to avoid disadvantages that can arise at the preparative isolation of phytomass components, which is commonly used for analysis of the component composition of the residues after extraction. The object of our study were medical herbs (*Aconitum leucostomum*, *Thermopsis alterniflora*, *Glycyrrhiza glabra* and *Vinca erecta*) residues after extraction of targeted pharmaceuticals applied at the Pilot Production Unit of the Institute of the Chemistry of Plant Substances (Uzbekistan). The total capacity of pilot plant is tens of tons of various medicinal herbs annually.

The results revealed that aconite and licorice roots residues after the extraction could be perspective raw material for obtaining of carbohydrates-based products. The periwinkle grass waste is perspective source for obtaining of aromatic and phenolic products. Meal of aconite, thermopsis and periwinkle contained significant amounts of unextracted targeted pharmaceutical compounds owing to the regime of extraction applied at the Pilot Plant, that can open opportunity for their further application.

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Densification of amorphous calcium phosphate: A comparison of cold sintering processes

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The recent surge in interest in the densification of calcium phosphate powders needs consideration of all the influencing factors. Spark plasma sintering with the primary contribution from the spark plasma and cold compaction that densifies from the large compaction pressures were considered. X-ray diffraction and Fourier transform infra-red spectroscopy characterized the powder and tablet to show the retention of the amorphous phase. Density was measured using the Archimedes method and viewed by scanning electron microscopy. The final tablets were indented by nanoindentation to determine the hardness and elastic modulus. Reports on the density showed that the smallest contribution to density arose from vacuum, a marginally higher densification from the spark plasma effect, but the largest densification arose from the use of significantly higher pressures. Nanoindentation showed a small difference in elastic modulus between tablets densified at 25 °C and 200 °C, but a larger difference in the hardness.

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Influence of MeV gamma rays on thermostimulated exoelectron emission from MgO films

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Exoelectron emission is the emission of low-energy electrons (several eV) from a surface depth of less than 10 nm. In the case of thermally stimulated exoelectron emission (TSEE), the energy required for an electron to be emitted from a material is supplied by heating. TSEE has found application in studying the effect of various external factors on electron trapping centers in thin near-surface layers. For example, the number of electrons in the trapping centers can change under the influence of ionizing radiation. This allows the TSEE method to be used for dosimetry of ionizing radiation absorbed by thin surface layers.

In this research, the application of magnesium oxide (MgO) films for TSEE dosimetry was studied. MgO has a wide bandgap of ~7.8 eV and is considered a tissue-equivalent material, since its effective atomic number $Z_{eff}=10.8$ is close to that of tissue (tissue Z_{eff} ranges from ~7 for soft tissue to ~13 for bone).

MgO films were fabricated on a Si/SiO₂ substrate using the extraction-pyrolytic method. The method consisted of the following steps: preparation of a precursor (extract) by extracting magnesium ions from an aqueous solution into caproic acid, deposition of the extract on the substrate by self-spreading, heating from room temperature to 550 °C, and annealing for 15 minutes in the atmospheric air (pyrolysis). X-ray diffraction (XRD) confirmed the formation of the monophasic MgO with a cubic crystal structure and an average crystallite size of 16 nm.

MgO films were irradiated with 6 MeV gamma photons in the dose range 20–100 Gy using a medical linear accelerator. TSEE spectra from the films were measured before and after irradiation. The TSEE intensity and the area under the TSEE spectra for both irradiated and unirradiated films increased after repeated TSEE measurements. However, in the case of gamma-irradiated films, the percentage increase in the area depended on the radiation dose, decreasing linearly with an increase in the radiation dose from 0 to 80 Gy (Fig. 1). The results allowed us to suggest that gamma radiation reduced the density of trapped electrons present in the as-grown MgO films, or created competing electron traps that inhibited TSEE from the films.

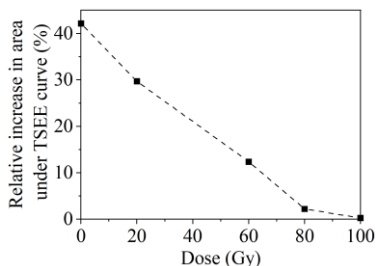


Figure 1. The relative increase in the area under TSEE curves of MgO films depending on dose of gamma radiation.

Acknowledgement

This research was supported by the European Regional Development Fund under the project No. 1.1.1.2/VIAA/1/16/167 “Thin films with embedded nanoparticles for dosimetry of ionizing radiation”.

Effect of the cold sintering process parameters on densification and structure of amorphous calcium phosphate

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Although amorphous calcium phosphate ceramics are of great interest in the field of artificial bone substitute materials, it is still a great challenge to densify amorphous calcium phosphate to high relative density. The main reason that makes its densification difficult is its unique hydrated structure.¹ This structure is irreversibly altered when amorphous calcium phosphate is heated to temperatures above a few hundred degrees Celsius, resulting in its crystallization and transformation to other less bioactive phases.² Therefore, low-temperature sintering techniques have been actively investigated for its densification. Here, for sintering of amorphous calcium phosphate, we used principles of the so-called cold sintering process. We investigated the effect of sintering temperature (room temperature, 100, 120 and 150 °C) and presence or absence of transient liquid (20 wt. % water), while holding the uniaxial pressure applied at 500 MPa, on densification and structure of amorphous calcium phosphate. Relative density of the cold sintered samples that were produced from the dry starting powder at room temperature (the samples retained amorphous calcium phosphate structure) already reached 76.3 (±2.1) %. Neither increased sintering temperature nor the presence of transient liquid significantly affected bulk, true and the resulting relative density values of the samples that retained amorphous calcium phosphate structure. Furthermore, the use of transient liquid led to crystallization of amorphous calcium phosphate at lower sintering temperatures.

Acknowledgements

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Comparison of efficiency of three primary driers during auto-oxidation of alkyd and boiled linseed oil

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Drying oils are a good choice for wood coating, whenever a renewable product is wanted.¹ One of the most common and widely used drying oil is linseed oil. Linseed oil has a high drying power, thanks to the presence of linolenic acid, linoleic acid and oleic acid, which are all unsaturated fatty acids.² Although alkyds have replaced them in the market, drying oils are regaining interest. New formulations, where renewable components are included, are a valid alternative to formulations based exclusively on petrochemical raw materials. The film formation for drying oils and alkyd resins requires the oxygen absorption to start. To accelerate this process it is necessary to use special metal salts, so called driers. In this work, three primary driers, based on cobalt, iron and manganese are compared. The study has been done using FTIR spectroscopy to investigate the rate of drying for each drier, analyzing the specific bands which changed during the film formation. The aim of this work was to check if less toxic Fe and Mn driers can replace Co. The monitoring of the rate of hydroperoxides formation, corresponding to the band at 3450 cm^{-1} (stretching of $-\text{OH}$) shows that with cobalt drier, the film formation is faster than with the other two alternative driers.

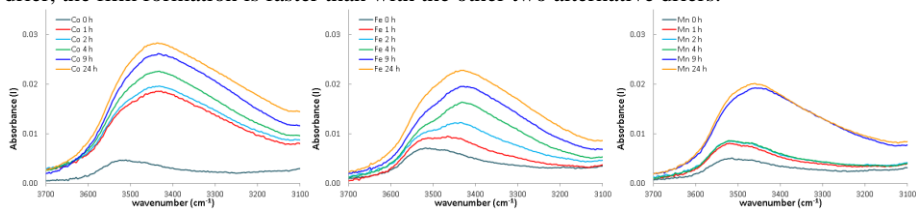


Figure 1 Monitoring of $-\text{OH}$ groups for the three driers during film formation

Results confirm that Co drier has a higher catalytic activity, and already after 1 h (red line), the area of the band is much larger than the area for the other two driers.

Acknowledgements

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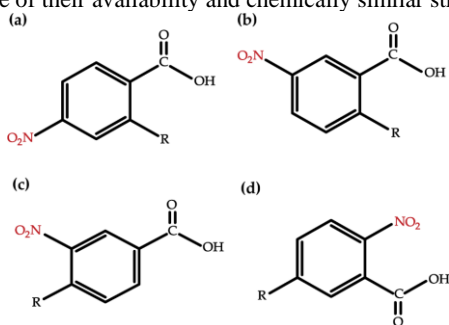
Computational prediction and experimental confirmation of solid solution formation from different nitrobenzoic acid derivatives and their isomers

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Recrystallization from ethanol of mixtures of various nitrobenzoic acid derivatives and their isomers, and as a result preparation of anisolvated crystalline phases, in order to ensure that solid solutions can form between them.¹ Crystalline phases that were obtained during the work were identified using X-ray powder diffraction and thermal analysis methods, in addition using the resulting nuclear magnetic resonance spectrum, obtained information about the ratio of mixtures of various nitrobenzoic acid derivatives and their isomers in crystallization products.^{1,2}

Several nitrobenzoic acid (NBA) derivatives (*-chloro*, *-methyl*, *-hydroxyl*) and their isomers (Fig. 1), such as 2-substituted 4-nitrobenzoic acid (24NBA, Figure 1a), 2-substituted 5-nitrobenzoic acid (25NBA, Figure 1b), 4-substituted 3-nitrobenzoic acid (43NBA, Figure 1c) and 5-substituted 2-nitrobenzoic acid (52NBA, Figure 1d), were selected as model compounds because of their availability and chemically similar structures².



R = halogen atom (-Cl), hydroxyl group (-OH) or methyl group (-CH₃)

Figure 1. Molecular structures of various nitrobenzoic acid derivatives and their isomers

Further, the structural analysis of crystal structures and energetic aspects – intermolecular interaction and crystal lattice energy, are studied and described, for possibility to predict formation of solid solution of the studied compounds.³

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Evaluation of antibacterial properties of chemically cross-linked hydrogels based on ϵ -polylysine and hyaluronic acid

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Introduction: In recent years, fabrication of novel hydrogels with certain multifunctional properties has attracted research interest in different fields of biomedicine. The bacterial infections and antibiotic resistance are becoming a global problem in health care sector, and therefore design and development of hydrogels for tissue engineering with an antibacterial function are a main focus in biomedical research. The aim of this study is to develop and investigate novel antibacterial hydrogels based on natural biopolymers: antibacterial ϵ -polylysine (ϵ -PL) and intrinsic biocompatible hyaluronic acid (HA).

Methods: The hydrogel series based on ϵ -PL and HA (mass ratios of ϵ -PL and HA are 50:50; 60:40; 70:30 and 80:20 wt%) were *in situ* synthesized via chemical cross-linking using 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC) and *N*-hydroxysuccinimide (NHS) crosslinking agents (with molar ratio of EDC:NHS =1:1).¹ The molecular structure, phase composition and morphology of all synthesized hydrogels were evaluated using Fourier transform infrared spectroscopy (FTIR), X-ray powder diffractometry (XRD) and scanning electron microscopy (SEM). The minimal inhibitory concentrations (MIC) of ϵ -PL against Gram+ and Gram- bacteria were determined. The antibacterial activity of the fabricated ϵ -PL-HA hydrogels were tested against *E.coli* and *S.aureus* bacterial cultures.

Results: FTIR spectra indicated interaction between ϵ -PL and HA and successful formation of cross-linked copolymer via amide bond linkage. XRD patterns show diffraction maximum of copolymer amorphous phase without external maximums. SEM micrographs of the lyophilized ϵ -PL-HA hydrogels revealed homogeneous and microporous structure. The obtained hydrogels were successfully sterilized by steam sterilization. The MIC of ϵ -PL against *E.coli* and *S.aureus* were determined to be 25 μ g/ ml.

Discussion & conclusions: In the described study, novel hydrogels based on chemically cross-linked ϵ -polylysine and hyaluronic acid copolymer system were synthesized and investigated. The antibacterial tests indicated inhibition ability against Gram+ and Gram-bacterial cultures. It is concluded that the developed hydrogels can be considered as promising antibacterial biomaterials for tissue engineering.

Acknowledgements

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Purine-phenoxazine and purine-phenothiazine conjugates

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Several reports about fluorescent properties of purine derivatives have been published till now.¹⁻⁴ Such compounds are often used for fluorescent cell labeling, however research into purine photophysical properties for application in materials science is rare. Currently there is only investigation of purine derivatives as fluorescent emitters in OLEDs by Castellano's group^{5,6} and a single publication about development of fluorescent purine derivatives as emitters exhibiting thermally activated delayed fluorescence (TADF).⁷

In this research, phenoxazine and phenothiazine groups were introduced as electron donors in an electron deficient purine system through a meta-connected benzene ring bridge to facilitate thermally activated delayed fluorescence. Mitsunobu reaction and Suzuki-Miyaura coupling afforded the target compounds **1-4** (Figure 1). Photophysical properties of the synthesized purine derivatives were explored and quantum yields in the thin layer film reached up to 8 % and in the PMMA doped thin layer film up to 15 %.

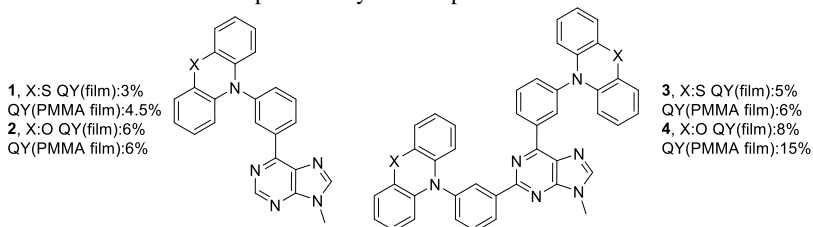


Figure 1. Purine derivatives with phenoxazine and phenothiazine electron donating groups

Acknowledgements

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Influence of crystallization additives on morphology of selected benzoic acids – a molecular dynamics (MD) simulation study

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Two model substances were used in the study – 2,6-dimethoxybenzoic acid (2,6MeOBA) and 3-hydroxybenzoic acid (3OHBA), each having two polymorphic forms, including a form without carboxylic acid homodimers in their crystal structure.¹⁻⁶ For each polymorph 2-3 largest crystal faces were selected for MD simulations and the crystal was cut along these planes by preparing simulation box with these planes facing towards solution. In the performed study it was determined which additives potentially can influence the crystal morphology (based on the selected planes) and possibly also the obtained polymorph achieved by significantly changing crystal growth rate by adsorbing on the surface.⁷⁻⁹ For the study 4-5 additives providing different intermolecular interaction possibilities were selected.

Growth of both explored surfaces of 2,6MeOBA form I are best inhibited by urea in 1,4-dioxane, while in methanol all explored additives act almost equally. All the studied surfaces of form II dissolved, indicating the very low stability of this.

A different effect of urea and *para*-aminobenzoic acid (PABA) on the morphology of 3OHBA form I was found. In 1,4-dioxane different sorption results were observed for both additives. The growth of {011} surface could be inhibited by urea, but the {020} surface by PABA. The simulations showed that urea could not play a decisive role in the discrimination of 3OHBA polymorphic forms, as it was well sorbed on surfaces of both forms. Meanwhile the simulations showed that *trans*-stilbene has the potential to inhibit the formation of {110} surface of 3OHBA form II in methanol due to a strong π - π interactions.

It was also observed that solvent has notable effect on the sorption of additives. The sorption of the studied additives was notably different in 1,4-dioxane, but in the methanol sorption of all additives was rather similar. Based on the results 1,4-dioxane is probably a better solvent for inhibition of growth of surfaces where hydrogen bonds are the dominant type of interactions.

Among the studied additives urea showed the most complete sorption and the longest residence time on surfaces for both substances with the exceptions of some specific planes. Meanwhile, complete and irreversible adsorption on crystal could also indicate on the possibility of formation of a mixed phase (co-crystal) in the presence of these additives.

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Biodegradation studies of poly(butylene succinate)/nanofibrillated cellulose nanocomposites

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Owing to the recent advances in biopolymer field, the production of biocomposites is growing exponentially. Herein we report production and biodegradation studies of poly(butylene succinate) and nanocellulose composites. PBS is emerging biopolyester with properties comparable to polyethylene and polypropylene and compatible with conventional processing technologies.¹ Considering the biodegradable properties of PBS and cellulose,² we designed functional materials for advanced applications and non-toxic disposal routes. We compared conventional solvent casting method with our improved concentrate production and melt processing for enhanced properties. Loadings from 1 to 50 wt.% were prepared and tested under composting conditions (58°C, >50% humidity) to study accelerated disintegration of the prepared samples. Disintegration process was characterized by differential scanning calorimetry (DSC), Fourier Transform Infrared Spectroscopy (FTIR), laboratory scale testing and visual observations.

Disintegration was achieved after two months, confirmed by laboratory scale testing and visual observations. FT-IR indicated cleavage of ester bonds of PBS and glycosidic bonds of NFC and the crystallization and melting peaks were shifted to lower temperatures as observed in DSC scans.

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Influence of leaning materials on the quality of building ceramics

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Research is devoted to the reduction of the quartz effect in the production of building ceramics using Devonian illite containing clays from the Liepa deposit as a basic raw material. Two types red and light of this Devonian clay deposit are used. The main difference between these clays is the grain size distribution. Red clay is less plastic due to the increased content of sand fraction (up to 20 %) in them. At present, corporation Lode uses a mixture of both types of clay to produce full facing bricks. Presence of quartz grains in the clay materials caused formation of cracks in the firing process of ceramic especially during cooling of dense ceramic in the temperature range up to 600 °C.¹ The crack formation is affected by changes in quartz modifications in this temperature range, which is accompanied by changes in the volume of quartz grains and is called the quartz effect.² Traditionally, ground scrap chips are used in the production of ceramics to reduce the plasticity of clays without sand. In the present work the milled waste E-glass of glass fiber factory Valmiera is used as a leaning material in the amount of 5–15 %. Samples are fired at various temperatures in range 950 till 1100 °C. Thermal processes occurred during thermal treatment of dried samples is investigated and analysed by differential thermal analysis using equipment SETARAM SETSYS Evolution -1750. Crystalline phases in the samples are determined by X-ray diffraction (XRD, Rigaku Ultima + Japan) with Cu K_α radiation. Thermal expansion of sample is determined by a horizontal dilatometer (Linseis L67/1600, Selb, Germany) on 20 mm long bars in flowing air at heating rate 10 °C/min in temperature range up to 1100 °C. The magnitude of the quartz effect is calculated from the thermal expansion curves for both dried and fired samples in the temperature range up to 400–600°C. Ceramic properties such as water uptake, apparent porosity, apparent (bulk) density are determined by Archimedes law.

Results obtained show a positive effect of milled E-glass fibre on the decrease of quartz effect in ceramic produced from Liepa clay. The magnitude of quartz effect depends on the amount of glass added and on the firing temperature. Water uptake decreases with increasing amount of glass additive. The magnitude of the quartz effect by addition of glass reduces compared to the addition of the same amount of sand as a leaning material. The use of waste fiber glass in ceramic engineering is the one of the ways for reducing of industrials waste in environment.

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Use of molecular dynamics simulations to investigate the molecular association of dihydroxybenzoic acids in solution

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Molecular dynamics (MD) is a computer simulation method that can depict the motion of the molecular system, and it is very versatile method for the investigation of molecular interactions. MD was developed, for example, to study folding of the proteins, association processes in the solution, water or ingredient residence times at protein sites and for other applications. However, in recent years MD simulations have also become more and more often used for small organic molecules to study similar processes.^{1,2}

Dihydroxybenzoic acids (diOHBA) are six isomeric small organic molecules with mutually different ability to form solvated and polymorphic forms.³⁻⁶ For example, during crystal form screening 2,3-diOHBA did not form neither multiple polymorphs nor solvates while 3,5-diOHBA was on the other end of the spectrum forming multiple solvated forms and even mixed solvates containing both water and organic solvent molecules in the crystal structures.

In the previous computational studies⁷ no distinctive tendencies in solution for formation of carboxyl acid homodimer present in almost all crystal structures was observed. Meanwhile, calculations indicated towards existence of possible stable hydrogen bond associates with solvent molecules. In this study, four diOHBA isomers having different characteristics regarding diversity of the obtainable crystalline phases (2,3-, 2,4-, 3,4- and 3,5-diOHBA) and solvent 2-propanol (IPA) that can act both as hydrogen bond donor and acceptor and during crystal form screening did not form any solvate were used. MD simulations for the selected compound IPA solutions were used to investigate molecular association in given medium in order to understand association processes in solution and rationalize how these processes differed among diOHBA isomers and how association could influence the obtainable crystalline phase. In addition to use of MD simulation, FT-IR spectroscopy was also used to experimentally confirm or deny the formation of associates observed in the simulations.

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Features of the structure formation of diffusion boride layers upon preliminary activation

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A study of the structure formation of diffusion layers obtained by a technology including preliminary surface treatment of steel products and subsequent boriding in powder media has been carried out. The pretreatment consisted of dynamic alloying in the superdeep penetration (SDP) mode with a on SiC powder-based composition.

High-carbon steel U8 (0,8%C) (GOST 1435) was used as a model material. The choice of steel is due to the increased factor of brittleness of diffusion layers and low kinetics of growth of the thermal diffusion layer, which hinders the widespread use of steel with the considered strengthening.¹ The preliminary activation of the U8 steel samples was performed by dynamic alloying in the SDP mode. Dynamic processing in the SDP mode was carried out using a cannon accelerator under the following conditions:² particles velocity ~ 1000 m/s, exposure time -100 μs, workpiece material: U8 carbon steel, impactor material: 50% SiC powder (99% SiC, particle size distribution 63-70 microns), 35% - PA-4 aluminum powder (98% Al, particle size distribution 15-100 microns); 15% - PG10N01 powder (% C 0.6-1.0; Cr 14-20; Ni- base; Si 4.0-4.5; Fe 3.0-7.0; B 2.8-4.5; particle size distribution 40-100 microns). Boriding modes: high-temperature borating - 4 hours at 900-920 °C, low-temperature - 4 hours at 640-650 °C. Diffusion saturation was carried out in a powder medium in containers sealed with a fusible seal.

It was found that in both variants of boriding, upon preliminary activation with the powder composition, the morphology of the thermodiffusion layer changes, which is expressed in a decrease in porosity, in particular in the subboride layer, and in a decrease in the needle-like structure traditional for boriding. As a result of pre-treatment, the thickness of the diffusion layer increases by 20 ... 50%, this is especially noticeable for high-temperature borating. The proportion of the high-boron FeB phase in the layer increases, which indicates an intensification of the diffusion and reaction stages in the metal.

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Characterization of pigments from *Malus domestica* leaves for wool dyeing

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Textiles were dyed with natural dyes from plants, fungi and insects until mid-nineteenth century. Natural dyeing of textiles is a traditional cultural heritage of Latvia. Craftsmen and peasants were used mainly local plants to obtain dyes. The popular dye plants of Latvia summarized in the study of knowledge of plant dyes: *Alnus* L., *Hypericum*, L., *Betula pendula* Roth., *Anthemis tinctoria* L., *Beta esculenta* L., *Allium cepa* L., *Isatis tinctoria* L., *Chamomilla recutita* (L.) Rauschert, *Galium* L., *Quercus robur* L. and *Vaccinium myrtillus* L.¹

Malus domestica is one of the most widely cultivated fruit tree. The chemical composition of apples has been extensively studied, however other parts of the plant have been less examined. The apple leaves are valuable source of quercetin derivatives and dihydrochalcones. Phlorizin and phloretin, which belong to dihydrochalcone class, are major phenolic compounds in the leaves. The dihydrochalcones are used for the identification of *M. domestica*.^{2,3} The apple tree leaves give a different shade of colours: yellow, brown and grey.^{3,4} *Origanum vulgare* in combination with the leaves of *Pirus malus* or *M. domestica* gives red colour.^{5,6}

The study will present results of chemical analysis of mass spectrometry, evaluating the content of pigments in *M. domestica* leaves dyeing solution and in dyed woolen yarn nowadays. The yarn was dyed with fresh leaves of *M. domestica* tree. Before dyeing the yarn was treated with potassium aluminium sulphate mordant. Dyestuffs from the yarn were extracted in compliance with the method of hydrolysis described by Wouters and Verhecken (1989) with some modifications.⁷ The extracts were analysed by ultra performance liquid chromatography coupled with diode array detector and mass spectrometry (UPLC-DAD-MS) for identification of the pigments.

Phytochemical screening of dyeing solution of *M. domestica* leaves showed presence of phloretin, flavanol derivatives (procyanidin B1, epigallocatechin 3-O-p-coumarate, epicatechin), quercetin derivatives (hyperoside, quercetin 3-rhamnoside, isoquercetin) and other compounds.

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Amorphous calcium phosphate with fluoride for dental application

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Amorphous calcium phosphate (ACP) is one of the calcium phosphate (CaP) group materials used for biomedical applications. ACP have been proposed for dental hard tissue remineralization, as coating of metallic bone implants, for self-setting inject-able cements and as fillers in polymetric composites.¹⁻³ Current research is focused on ACP synthesis for dental application. Here we offer to incorporate fluoride into ACP structure. ACP phase provides remineralization ability, while fluoride have scientifically proven anti-caries effect and it can increase mechanical properties of CaP bioceramic.⁴ Preventive dentistry is familiar with ACP materials as additive to dentifrices, varnishes and toothpastes to protect enamel from caries, but our study is aimed to produce material suitable for cold sintering process, thus for the first time it might be possible to obtain bioactive bioceramic as restorative material for dentistry.

Precipitation reaction between CaO and 2M H₃PO₄ was used for synthesis of ACP with fluoride (ACPF). NaF was source of fluoride. Obtained CaP precipitates were dissolved by rapid 3M HCl addition, then solution was stirred for 30 min. Later NaOH was added to induce rapid re-precipitation of ACPF. The product was washed with deionized H₂O, filtered and frozen in liquid N₂ right after the washing procedure. Obtained ACPF was subjected to freeze-drying. XRD, FTIR, BET, pycnometry, EDS were used for characterization of material.

Specific surface area of ACPF was 174.3±2.4 m²/g and the density of the powder – 2.50 g/cm³. Observed bands in FTIR analysis evidenced amorphous ACPF phase, although XRD pattern showed CaP phase with very low crystallinity. EDS confirmed presence of fluoride in the ACPF samples, additionally peaks in the XRD pattern after thermal treatment at 1100 °C indicate formation of crystalline fluoapatite and β-tricalcium phosphate phases.

This study is the first step in the development of a new bioactive bioceramic material. Obtained results are promising for further investigations, because the obtained material has a large surface area, it is amorphous and contains fluoride in the structure.

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Synthesis and spectroscopic characteristics of new ligands based on quinolin-8-ol for preparation of Alq3 type complexes

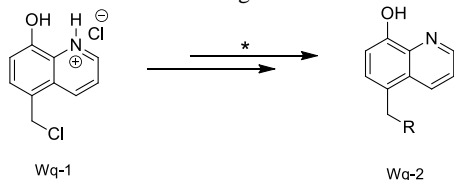
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Tris(8-hydroxyquinolino) aluminum (Alq3) complexes are intensively studied as the light-amplification system components in 4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4*H*-pyran (DCM):tris(8-hydroxyquinolino) aluminum (Alq3) organic solid-state laser applications.¹⁻³ Since the required Alq3 complexes are usually obtained in 8-hydroxyquinoline further reaction with Al³⁺ ion containing reactants, the ligands themselves can be also modified by introducing different substituents and functional groups in their chemical structures by various methods of organic synthesis.^{3,4}

5-(Chloromethyl)-8-hydroxyquinolin-1-ium salt^{3,4} (Wq-1) is one of the most well know intermediates that enables a number of functionalization possibilities in 5-position of the 8-hydroxyquinoline. Compound Wq-1 was also used in our research in order to obtain several 5-functionalized-8-hydroxyquinoline derivatives (see Scheme 1). Synthesis possibilities, reaction conditions and spectroscopic characteristics of several Wq-2 derivatives will be discussed in detail during the conference.



Scheme 1. Synthesis of 5-substituted 8-hydroxyquinoline derivatives Wq-2. Symbol * represents various reaction conditions as well as one or several multi-step procedures. R – substituents having different aliphatic or aromatic structures.

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Influence of the cellulose and soft wood fibres on the impact and tensile properties in polypropylene bio composites

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Nowadays, polymer composites demonstrate a high potential of applications in various industries, such as automotive, civil industry, marine and space owing to high specific strength and stiffness, high fatigue life, reliability, good wear resistance and other physical and mechanical properties. However, the disadvantages of the polymer composites with synthetic fibres (carbon fibres, glass and aramid) are a rather high cost and negative effect on the environment.

Therefore, the polymer composites with natural fibres, called bio-composites, are considered now as an alternative to traditional polymer composites with synthetic fibres in an attempt to decrease the negative influence on the environment. Various types of natural fibres, including cellulose and soft wood fibres, are used for manufacturing of the bio-composites. These materials are described by such advantages as renewability, low density and sometimes bio-degradability making them eco-friendlier. At present, bio-composites are the subject of extensive investigations due to their light weight, low manufacturing and subsequent disposal costs.

The main aim of this research is to investigate an influence of different weight contents of the soft wood fibres (Cordenka) and man-made cellulose fibres (Weho 500) embedded into polypropylene matrix (homopolymer HP400R) on the tensile properties (Young's modulus, tensile strength) and impact properties. Mechanical properties such as elastic modulus, tensile strength, and impact strength of the reinforced composites determined for each weight content of the cellulose fibres and microfiller were used as the design parameters. The problem was solved by planning of the experiments and response surfaces method. The results demonstrated that using two types of fillers enhanced the mechanical properties. The tensile modulus increased by ~114%. The bio-composite with highest weight content of man-made cellulose fibres and lowest content of soft wood microfibrils has maximum tensile strength (more 66 MPa). Cordenka fibres demonstrated a significant influence on impact properties.

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