Riga Technical University 62nd International Scientific Conference

"Materials Science and Applied Chemistry"

Program and Abstracts

October 22, 2021

Program

Plenary Session - https://rtucloud1.zoom.us/j/5204285574

9:50-10:00 Opening ceremony Prof. M. Turks, Dean of Faculty of Materials Science and Applied Chemistry, RTU, Latvia
Awarding of Paul Walden Prize Winner 2021

10:00-10:50 ***Prof. Emiliano Bilotti***, Queen Mary University of London, UK
Multifunctional Polymer (Nano)Composites

10:50-11:10 ***Prof. Māra Jure***, RTU FMSAC, Latvia
Historical Sites of Chemistry in Riga

Oral Presentation Sessions

General Materials Science

11:10-11:25 **Linards Lapčinskis.**
Triboelectrification of nanocomposites using identical polymers with different concentrations of nanoparticle

11:25-11:40 **Osvalds Verners.**
Assessment of improvement of triboelectric contact electrification of polymeric materials by surface functionalization

11:40-11:55 **Raivis Eglītis.**
Photochromic TiO_2 organogels

11:55-12:10 **Mārtiņš Randers.**
Structure and composition of alkali treated illite clay

12:10-12:25 Andris Šutka.
Antibacterial properties of brownmillerite in water disinfection

12:25-12:40 **Agneta Veženkova.**
Injectable, porous, osteoinductive calcium phosphate cements in patent literature

12:40-12:55 **Andris Ozols.**
Polarization microholograms in an azobenzene film

Polymer Materials and Composite Materials

11:10-11:25 **Anda Barkāne.**
Reinforcement efficiency of cellulose nanofibers and nanocrystals in UV-curable vegetable oil polymer matrix

11:25-11:40 **Velta Fridrihsone.**
Modification of cellulose with maleic acid anhydride in an anhydrous environment as additive for paper

11:40-11:55 **Sergejs Beļuns.**
Lignin and Xylan addition to cellulose nanopaper - a sustainable solution to improve properties

11:55-12:10 **Madara Žiganova.**
Plasticization and properties of microbiologically synthesized polyhydroxyalkonate

12:10-12:25 **Artūrs Ķīsis.**
Effect of the polyurethane adhesive and polyvinyl acetate dispersion adhesive on the strength of the construction joints in bending strength

12:25-12:40 **Kristaps Zvirgzds.**
Additives for hemp shive board to decrease water absorption

12:40-12:55 **Laimdota Vilcēna.**
Technology development for betulin integration into nano-fibers web

Chemistry of Organic Compounds

11:10-11:25 **Rūdolfs Beļaunieks.**
Electrophile-induced transformations of propargyl silanes

11:25-11:40 **Kristaps Leškovskis.**
Aromatic substitution of azido-pyridopyrimidines and study of their azide tetrazole equilibrium

11:40-11:55 **Krista Gulbe.**
Sulfur dioxide-promoted glycosylation with glycosyl fluorides

11:55-12:10 **Armands Rudušs.**
The use of thiazoline-based carbenes for a development of metallo-organic thermally activated delayed fluorescence emitters

Clothing and Textile Technologies

11:10-11:25 **Solvita Bilinska.**
Fabric sewability, today's challenges

11:25-11:40 **Ilze Balgale.**
Multilayer woven textile switch array

11:40-11:55 **Liene Siliņa.**
Systematization of anthropometric characteristics of individual athletes

The MSAC poster session will be held virtually.

The posters are available: https://msac.rtu.lv/program-2021-2/ (till October 25, 2021).

Abstracts

XRD investigation of CdS layers on polypropylene film

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Cadmium sulfide (CdS) is an essential semiconductor compound that has applications in solar cells, solid-state gas sensors, field effect transistors, and light-emitting diodes [1]. Its n-type semiconuctivity property is used as a heterojunction partner for n-type materials [2]. CdS films were deposited on stainless steel, soda lime glass, fluorine-doped tin oxide (FTO), and other substrates. Various physical and chemical techniques have been employed for the preparation of CdS thin films.

In this paper, the chemical bath deposition method was chosen due to its simplicity. Polypropylene (PP) film as a cheap, chemically stable, and flexible substrate was chosen for experiment. The hydrophobic PP was pretreated for 25 min at 90 °C with oxidizing solution. Thin layers of CdS were deposited on a PP film (thickness 150 μm) at 80 ° C for 180 min from an aqueous solution containing 1 M $CdSO_4$ and 3 M thiourea. Pretreated PP samples were immersed vertically along the wall of the reactor. At the end of the deposition time, the samples were taken out and then rinsed with distilled water for 30 s to remove the desorbed ions. The results were yellow-colored, uniform, and very well adhered CdS thin layers on PP. The precipitate formed in the reactor was washed, dried, and stored in a desiccator. The aim of this paper is to investigate the composition of CdS/PP and CdS precipitates by XRD.

X-ray diffractogram of CdS precipitates (Fig. 1, a) peaks obtained at 2θ values 24.995, 26.672 and 43.880, which are associated with planes (100), (002), (110), respectively, of hexagonal crystal structure (JCPDS card no.: 80-6) and the corresponding calculated *d* values are 3.5596, 3.3394, 2.0616, respectively.

In the CdS/PP X-ray diffractogram (Fig. 1, b), the peaks are obtained at 2θ value 28.422, plane (101) and *d* value 3.1377 of hexagonal crystal structure (JCPDS card no.: 80–6), 2θ value 36.470, plane (214) and *d* value 3.1377 of orthorhombic crystal structure (JCPDS card no.: 47-1179), respectively.

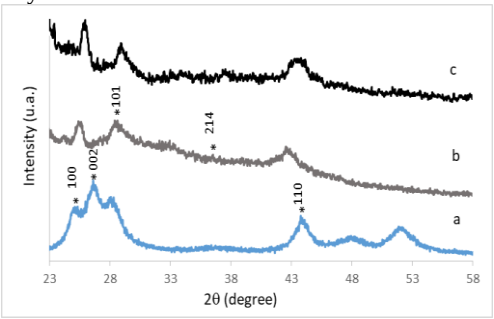

Figure 1. XRD patterns of CdS precipitate (a), CdS/PP composite (b), and pure PP (c)

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Multilayer woven textile switch array

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Today, there is a growing demand for textile systems that can monitor human health or safety. Such systems usually consist of different types of textile sensors. For example, the carpet, made as a large textile sensor, is able to detect human movement in hospitals or nursing homes, providing unobtrusive observation.

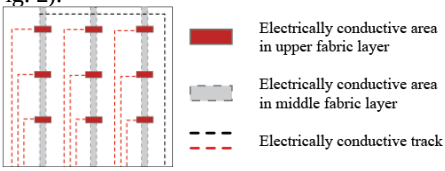
The simplest type of force pressure sensor is an array of pressure switches. With the mapping system, individual points will appear on the computer screen where the contact electrodes are connected as a result of the pressure.

In this work a hollow multilayer woven fabric structure was chosen to make a sample of the textile switch array (see Fig. 1).

Figure 1. Cross-sectional view of the fabric structure.

The experiment showed that the selected materials in the weaving of the samples can ensure the operation of the pressure switch: multifilament polyamide yarn and multi-layer fabric structure ensure fabric shape stability and flexibility - it keeps the fabric layers spaced apart throughout the fabric structure and is flexible enough to allow the top layer to bend and contact the contact surface in the middle layer, as well as be able to return to the previous position after removing the load. Silver-plated multifilament polyamide yarn has the necessary properties to form woven conductive tracks, paths and contact areas: it is flexible (fits well into the fabric structure), strong (can also be used as warp yarn), has a high electrical conductivity and a small change in electrical resistance due to washing.

The set of pressure switches of the fabric sample arranged in the form of a matrix - in rows and columns (Fig. 2).

a) 

b) 

Figure 2. Illustration of arrangement of pressure switches (a) and the fabric sample (b)

Nine separate conductive areas are woven into the top layer of the fabric, and three conductive paths are woven into the middle layer. Each pressure switch operates independently. The structure of the chosen fabric and the materials used ensure the operation of the textile sensor and can be used in further experiments.

Acknowledgments

This work has been supported by the doctoral studies grant of Riga Technical University.

Reinforcement efficiency of cellulose nanofibers and nanocrystal in UV-curable vegetable oil polymer matrix

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Cellulose is known to be the most abundant biopolymer. Meanwhile, vegetable oils have been acknowledged as a perspective renewable feedstock for UV-curable resin development. Cellulose-based nanoparticles, such as nanofibers (CNFs) and nanocrystals (CNCs), for vegetable oil-based resins are an attractive bio-based reinforcement filler. Combination of nanocellulose fillers and vegetable oil-based resins are a perspective approach for UV-curable resin applications.

Current work investigates the efficiency of nanocellulose filler reinforcement by comparing CNFs and CNCs at different loads. Preparation of the reinforced films can be seen in Figure 1. Four steps of film preparation: resin preparation, cellulose separation from water suspension, reinforced resin preparation and resin curing. Efficiency of the reinforcement was determined by evaluation of thermal, thermomechanical performance, and structural properties. Used investigations methods involved UV-VIS, FTIR, TGA, DMA and SEM measurements. Results and calculations showed: CNC has stronger fillers-matrix interaction, while CNF has stronger filler-filler interaction which interferes with matrix interaction.

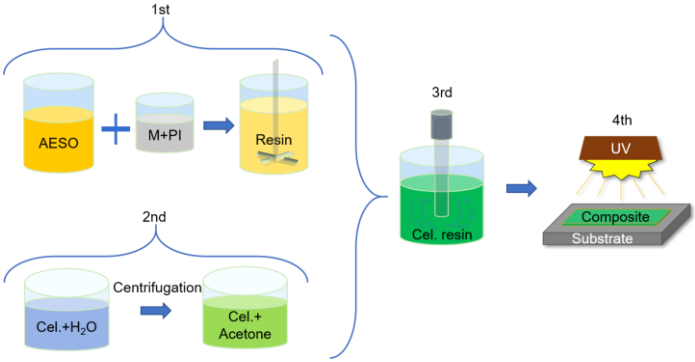

Figure 1. Preparation scheme: acrylate epoxidized soybean oil (AESO), photoinitiator (PI), TMPTA, HDDA (M), and CNCs and CNFs (Cel.).[1]

Acknowledgements
This research was supported by Riga Technical University's Doctoral Grant program.

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Electrophile-Induced Transformations of Propargyl Silanes

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Stabilizing properties of silicon in reactions, 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. 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 [2].

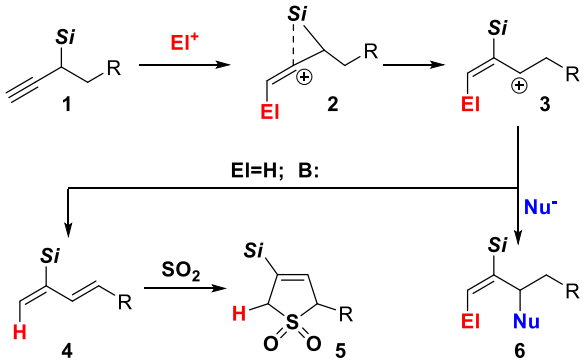

Figure 1. Mechanism and Transformations of Propargyl Silanes

Herein, we report the use of liquid sulfur dioxide for the transformation of propargyl silanes **1** as a 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 **5** are obtained from the *in situ* formed dienes **4** [3].

To expand this concept further, other electrophiles have been used to activate propargyl silane moiety to obtain intermediate **3**. The latter can react with various nucleophiles to obtain compounds **6**.

Acknowledgements

This work was supported by the Latvian Council of Science grant LZP 2018/1-0315 and RTU doctoral student grant.

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Lignin and Xylan addition to cellulose nanopaper - a sustainable solution to improve properties

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As the world has become increasingly reliant on various fossil-based plastic materials, long-term sustainability has become a major problem. To combat rising plastic pollution and reduce fossil carbon dioxide emissions, a shift to bio-based and biodegradable products is required. Cellulose, hemicellulose, and lignin are ubiquitous molecular structures found in renewable forestry and agricultural resources and wastes. As an alternative to commodity plastics, there is considerable interest in translating these available resources into modern functional materials.

Current work involves modified cellulose nanopaper preparation by combining nanocellulose suspension in water with lignin and xylan. Grinding old filter paper, microfluidizing, casting, and water evaporation are all part of the process. According to thermogravimetric analysis, the filter paper is made of highly purified cellulose. The addition of lignin and xylan at various loadings ranging from 1 to 30 wt% shows that characteristics can be fine-tuned to a large extent. Furthermore, the simultaneous addition of lignin and xylan to these nanopapers improves their mechanical qualities significantly. Tensile strength increased by more than 2-fold with the addition of xylan, while elastic modulus increased by up to 3-fold. Due to phase separation and the heterogeneous structure created by these nanopapers, high loadings prove to be detrimental. The usage of lignin and xylan with loadings up to 5% wt% has several benefits because they operate as surface modification agents, affecting the chemistry and bond formation of nanopapers. The use of bio-based and biodegradable components in the manufacture of sustainable products has numerous advantages. When compared to other investigations that use organic solvents, acids, or bases, water suspensions offer a substantial benefit. Thermal characteristics of nanopapers show that these materials have better conductivity and diffusivity than unmodified nanopapers. With the given lignin and xylan natural components derived from biomass waste, it is now possible to create high-performance packaging, filtering, and sensor materials.

Acknowledgements
This research is funded by the Latvian Council of Science, project RealHLC, project No. lzp-2019/1-0390. This research is funded by Riga Technical university PhD grant, R Development of scientific activity in universities, DOK.PMI/20, Performance funding for doctoral grant MLĶF.

Research of electro spun Poly vinyl alcohol fibres mat

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Poly(vinyl alcohol) (PVA) is used as biomedical polymer due to its good chemical and physical properties like water solubility, chemical resistance, high melting point and biological compatibility. The nanoscale fibers are generated by the application of strong electric field on polymer solution or melt. Electrospinning of PVA can be performed from aqueous solutions leading to generation of homogenous nanofiber webs [1, 2].

For the research the Moviol 28-99 PVA (Aldrich, Mw ~ 145000) was used. PVA was dissolved in a distilled water (10 wt. %) and swelled for ~16h. The solution was prepared by using magnetic stirrer at 85°C for 2 hours. The fibers mat was produced at +21.9°C and RH of 28% using Nanospider™ LAB 200 (Elmarco, Czech Republic) with a circular cylinder (Ø2 cm) as the emitting electrode with following parameters - distance between electrodes 15 cm, roller speed - 3 rpm, applied voltage - 65 kV. Cross-linking of the produced PVA fibers mats was performed by thermal treatment for 1 h at 150°C. Thickness (ISO 9863-1:2005) and mechanical properties (ISO 13934-1:2013) in the transverse and machine direction of the samples were tested after equilibrating in a desiccator at RH 52% with use of potassium dichromate and at RH 0% with use calcium chloride. Thermogravimetric analysis (ISO 11358-1:2014), infrared spectroscopy and microscopy of the fibers mats were determined.

Randomly oriented PVA fibers mats with thickness in the range of 4-8 µ were obtained. It was observed that humidity level within the produced fibrous mats equilibrated within ca 300h. Mechanical properties of the obtained PVA fibers mats varied in the range of 4450 – 88 MPa for modulus, 63-21 MPa for ultimate stress and 5-73 % for ultimate strain, generally depending on the thickness and humidity level. It was also observed that thermal stability of the obtained PVA fibers mats was considerably larger than that for uncross-linked samples.

Acknowledgements

The authors thank for support Anna Šutka, leading researcher of Institute of Materials and Surface technologies.

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1,3-Dicarbonyl type antioxidants containing an activity enhancing moiety

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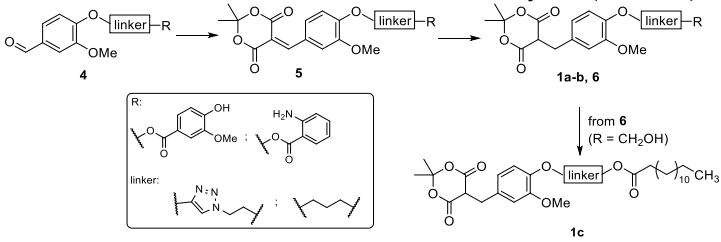
Oxidation processes reduce the shelf-time of various products, e.g. polymers and food. In living organisms, oxidation processes produce reactive oxygen (ROS) and nitrogen (RNS) species, which work as cell signaling molecules in small amounts. However, an overproduction of these molecules can lead to oxidative stress and related health issues, e.g. cancer,[1] Alzheimer's,[2] and Parkinson's[3] disease. Antioxidants can be used to regulate the production of ROS.

Herein, a relatively little studied class of antioxidants – 1,3-dicarbonyl compounds – was further explored. Arylmethyl Meldrum's acid derivatives have shown promising antiradical activity.[4] To increase either their activity or solubility, the structures were modified with amines, long alkyl chains, and phenol type antioxidants. In the case of amine and phenol derivatives, the overall procedure involved the synthesis of an aldehyde **4** containing the desired additional moiety. The aldehyde **4** was subjected to the Knoevenagel condensation with Meldrum's acid. Finally, the resulting arylidene **5** was reduced affording the target compounds **1a-b**. In the case of the alkyl chain containing arylmethyl Meldrum's acid derivative **1c**, the same steps were used to afford an alcohol **6**, which was then esterified with a fatty acid (Scheme 1).



Scheme 1. Synthesis route of compounds **1a-c**.

The DPPH radical scavenging activity at a 100 μM concentration of compounds **1a-c** is at least 70%, the IC_{50} values varied around 60 μM. All synthesized compounds are more active than BHT.

Acknowledgements
The research was financed within the Latvian Council of Science (grant no. LZP-2020/2-0165).

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Acrylated Vegetable Oil Inks for UV Light Assisted 3D Printing

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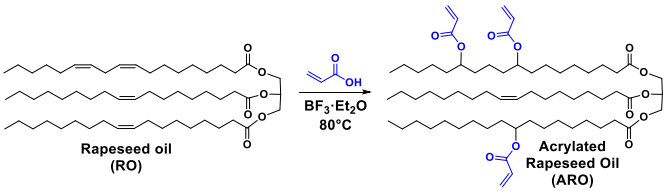
Modified vegetable oils, as a renewable resource, can undergo free radical photopolymerization. Photopolymerization process plays an important role particularly with acrylates. When using UV light, acrylates are among the most reactive monomers.[1,2]

The effect of one-step synthesized acrylated rapeseed oil (ARO) (presented in Scheme 1.)[3] as a petroleum-based monomer replacement for inks used in stereolithography (SLA) 3D printing are discussed. Fig. 1. shows the preparation and application of polymer resin composition. ARO up to 90% together with acrylated epoxidized soybean oil (AESO) were used to obtain UV curable films. ARO affect on the properties of cured films were determined using TGA and DMA as well as FT-IR for evaluation of double bond conversion after curing.

It was observed that adding ARO increased elasticity in obtained UV curable polymer films. Furthermore, polymer composition was optimized to achieve low viscosity. Resin with the shortest curing time was used in SLA 3D printing technology, showing good layer fusion and high resolution.



Scheme 1. One-step synthesis of acrylated rapeseed oil

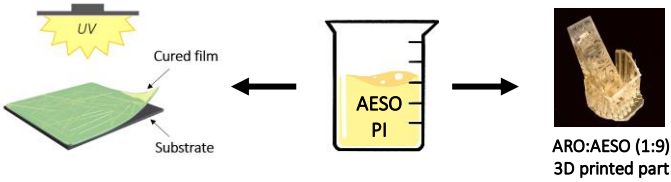


Figure 1. Preparation and application

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Synthesis of C-C linked Triazolylpurines

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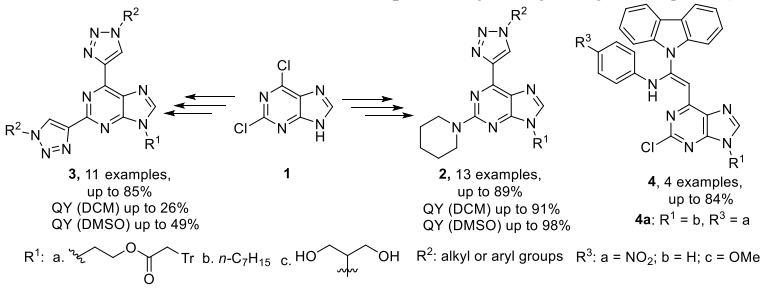
Purine-triazole conjugates belong to the push-pull systems and possess fluorescent properties which can be potentially used in OLED technology and in cell imaging.[1,2]

Target compounds **2-3** were synthesized from 2,6-dichloropurine **1**, using the sequence of Mitsunobu, Sonogashira, CuAAC and S_NAr reactions (Scheme 1). Photophysical properties of target compounds have been studied. Quantum yields reached up to 91% in DCM and 98% in DMSO solutions. In S_NAr reactions with carbazole, the formation of triazole ring opening products **4** was observed and their structure was proven by X-ray analysis (Figure 1).



Scheme 1. General structures of obtained compounds **2-4**.

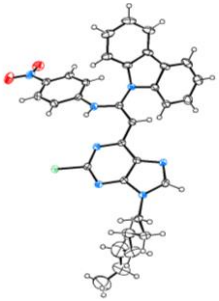


Figure 1. X-ray analysis of compound **4a**.

Acknowledgements

Dr. chem. K. Traskovskis is acknowledged for photophysical measurements. *Dr. phys.* A. Mishnev is acknowledged for X-ray analysis.

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Content of various phenolic compounds in bumblebee honey

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Bumblebee honey is a rarely known food product in society. Bumblebee honey is considered to be more valuable than bee honey. Bumblebees can also collect nectar from plants, from which bees cannot obtain nectar. Bumblebees process nectar into honey in much longer time than bees. Also the obtained amount of bumblebee honey is small. Bumblebee honey is believed to have greater healing effects. It helps to cure health ailments such as indigestion, respiratory diseases (for example, asthma, bronchitis), certain liver diseases, genital problems faster.

One of the indicators of biological activity of honey is the content of phenolic compounds. It would therefore be important to compare these parameters in the bumblebee and bee honey.

The aim of our work was to determine and compare the content of different polyphenolic compounds in bumblebee and bee honey. Some bee honey samples (multifloral and buckwheat) and Bumlebee honey from Russia were selected for analysis. Honey samples were purchased using the link of a Russian company (https://bearhoney.ru). The phenolic compounds in bee honey and bumblebee honey samples were determined by applying the method of high performance liquid chromatography (Schimadzu LC-40 Nexera). Bee honey samples were extracted in methanol, but bumblebee honey samples were extracted in methanol and ethanol.

The results of the analyzes showed that bumblebee honey contained certain phenolic compounds, which were not present in any sample of bee honey. Polyphenols such as caffeic acid and 2-hydroxycinnamic acid were found in bumblebee honey. These polyphenols were not found in bee honey. In turn, the analyzed bee honey samples contained many of determined polyphenolic compounds, which were not found in bumblebee honey. Those were: homovanillic acid; vanillic acid; epicatechin; hydroxycinnamic acid; quercetin; luteolin. The obtained results showed that the content of individual phenolic compounds was higher in bee honey than in bumblebee honey. This could be explained by the fact that bumblebees also visit nectar plants from which bees do not obtain nectar. Bumblebees and bees also have different nectar processing cycles and many other biological - physiological processes. Of course, the region, where honey was harvested, also plays an important role.

Acknowledgements

This work has been supported by the program “Fundamental research activities in Latvia University of Life Sciences and Technologies” (Nr. 3.2.-10/278)

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Cultivation of methanotrophic bacteria using different medium compositions: stimulation of biomass growth rate

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Methane, a potent greenhouse gas, and methanol, commonly called wood alcohol, are considered common by-products of modern industrial processes. However, both mentioned substances can be consumed as substrates by multiple methanotroph bacteria strains. Multiple studies it was shown that methanotrophic biomass obtained during bioreactor cultivations has high contents of unsaturated fatty acids.[1] Moreover, such biomass displayed high potential for accumulation of macronutrients and micronutrients. In this context, methanotrophic bacteria seem to be a pioneering solution and a new perspective, e.g., in supplementing animal diets, or as a new source of substances with a beneficial effect on the development and growth of animals.[2]

The most efficient and cost effective methane and/or methanol bioremediation process using methanotroph biomass is considered to be a cultivation operated in a continuous regime, as usually such microorganisms show low specific substrate consumption rates. However, to achieve the latter, it is necessary to go through batch as well as fed-batch stages in order to reach the required biomass concentrations. In order to reduce time and costs and quickly transfer the process to the continuous mode, it is necessary to accelerate the growth of applied organisms as much as possible during the batch and fed-batch phases. This can be achieved by supplementing the growth medium with various growth factors (vitamins, amino acids etc.), using more bioavailable substrates, and by optimizing the cultivation conditions (for example, by controlling the concentration of the substrate in the medium). Usually, the processes of culturing methanotrophic bacteria are carried out using a fully synthetic mineral medium (Nitrate mineral salts medium (NMS)) without the addition of any growth factors.[3] At the same time, it is argued that the addition of any growth factors does not affect the growth rate of methanotrophic bacteria.

The aim of our research was to study the influence of growth factors such as vitamins, and different nitrogen sources (yeast extract, yeast nitrogen base with/without amino acids and tryptone) on the growth of such methanotrophic bacteria as *M. alcaliphilum*, *M. methanica* and *M. trichosporium*. From the statistical analysis of experimental results, it was observed, that supplementation of the growth medium with complex compounds, e.g. yeast extract or tryptone, seems to promote the growth rate of studied methanotrophic bacteria, when grown on methanol as the main substrate. Furthermore, specific growth rates observed during cultivations in mediums containing vitamins mixture with cobolamin also seem to positively affect the biomass growth rate.

Acknowledgements

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Comparison of ZnO powders synthesized under solvothermal conditions

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Zinc oxide (ZnO) is naturally n-type metal oxide semiconductor with a wide direct band gap of 3.37 eV (at 300 K) and high exciton binding energy of 60 mV, thus the excitons can be observed even at room temperature.[1] ZnO materials are suitable for a wide range of applications like optoelectronic devices and transparent electrodes[2]. The aim of this study was to obtain ZnO nanocrystalline powders with increased photoluminescence band intensity in UV spectral region by Lithium (Li) doping employing solvothermal type synthesis method.

In this work five sets of samples were prepared by microwave assisted solvothermal synthesis method using Li-doping (0, 0.5, 1, 3 and 5 at%).

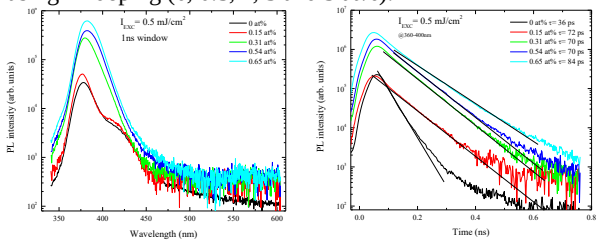

Figure 1. Comparison of undoped and Li doped ZnO sample PL spectrum (a) and PL decay time at 360 to 400 nm emission range (b) at excitation intensity 0.5 mJ/cm^2.

As a result, the photoluminescence (PL) intensity (Fig. 1a) was increased with Li content in ZnO crystals (by an order of magnitude). The decay time of emission at 360-400 nm range (Fig. 1b) increases up to 2 times by increasing Li doping concentration. Increasing the excitation power of the laser increases the carrier lifetime and the obtained photoluminescence response intensity that is observed for all the samples. This elucidates the advance of our method with respect to sol-gel, where the reduction of bandgap emission is observed with Li doping. Our advantage can be explained by the reduction of detrimental to carrier recombination V Zn and V O defect concentrations by Fermi level shift to the bandgap center.

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From blood to regenerative tissue: how autologous platelet-rich fibrin can be used as drug carrier system

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Autologous platelet-rich fibrin (PRF) is a second-generation platelet concentrate derived from centrifuged blood.[1] PRF is a unique system that combines biocompatibility and biodegradability, and contains growth factors and peptides that promote tissue regeneration. Nowadays, this makes PRF the preferred choice for a variety of biomaterials. After centrifugation, PRF still combines not only the autologous growth factors found in the original blood, but also the cells involved in the wound healing process (see Fig.1.).[2,3]

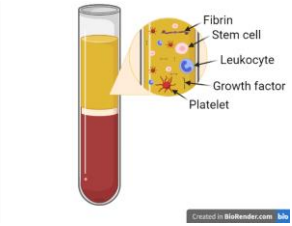

Figure 1. Main elements of PRF.

However, despite these positive properties, PRF does not have particularly pronounced antibacterial properties. As we know, the most common postoperative risk of minor surgeries is infection caused by membrane exposure and colonization of wound bacteria [4,5]. Therefore, many studies combine PRF with drugs to reduce the risk of infections. Unfortunately, these studies show insufficient analysis and lack of data, such as, drug release time and amount. Only an understanding of the ability of these materials to be combined with other biomaterials and drugs will allow us to obtain new biomaterials with the necessary properties for use in many fields of medicine.

Acknowledgements
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Photochromic TiO_2 / PEGDA organogels

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In today's world, energy consumption is becoming an ever increasing concern. One of the culprits of this, especially in modern cities, are heating, ventilation and air conditioning systems used in residential and office buildings. One way to combat this, would be to reduce the amount of indoor lighting, heating and cooling used in buildings. This can be done by employing smart window devices, capable of dynamically modifying the transmitted light. Photochromic smart windows, allow to do this in a passive way, without the need for complimentary equipment. TiO_2 quantum dots (QDs) can be used in photochromic applications as they undergo photodoping when exposed to UV light under anaerobic conditions and in the presence of a hole scavenger.[1] However, colloidal QDs are not suitable for such applications as the colloids are prone to leakage. On the other hand, TiO_2 films need to be at least 8 μm thick in order to fully block transmitted light. Films this thick are difficult to produce and when photodoping, only the upper layers of the film darkens.

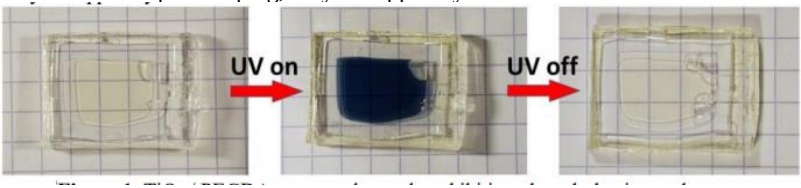

Figure 1. TiO_2 / PEGDA organogel sample exhibiting photodarkening and recovery.

An optimal solution to this would be gels, as this would allow the QDs to be in touch with the hole scavenger throughout the gel volume, while retaining any liquid, thus preventing leakage. In this work, we are presenting transparent TiO_2 QD/polymer gels, with a TiO_2 content of up to 5 volume% and employing polyethylene glycol diacrylate as the polymer linker, DMF as a stabilizer and EtOH as hole scavenger. These gels are capable of total photodarkening upon UV light irradiation and recovery, when not exposed to UV light.

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Acknowledgements
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Modification of cellulose with maleic acid anhydride in an anhydrous environment as additive for paper

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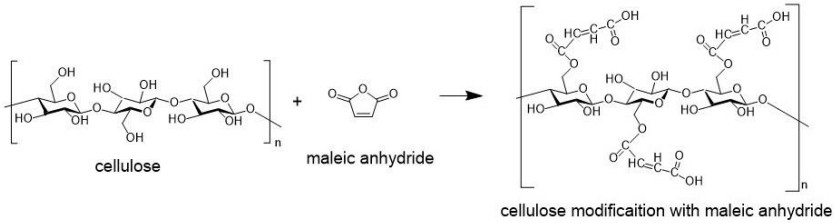
Cellulose, the most abundant organic compound in nature, which has been extensively investigated for decades. Cellulose derivatives represent significant field of value-added products obtained via chemical modification of low-cost, naturally occurring raw biopolymers. Chemical modification of cellulose is well known. It involves esterification, etherification, and oxidation reactions of its hydroxyl groups[1]. Derivatization of cellulose is performed due ability of hydroxyl groups to bond, however, there is still missing information about several possible derivatization pathways, especially using compounds of dicarboxylic acids.

Since starch is structural isomer of cellulose, many authors have investigated its possible reactions with dicarboxylic acid anhydrides (succinic, adipic)[2,3] due to the more easily accessible functional groups if compared with cellulose, which is more difficult to modify glucose chains due to its stiff rod-like conformation, aided by the equatorial conformation of the glucose residues. In general – a polysaccharide can be modified with a substituted cyclic dicarboxylic acid anhydride (represented by maleic anhydride). Patent from Caldwell suggests that product has one substituted hydroxyl group[2] (Scheme 1) .



Scheme 1. Proposed scheme of obtaining ester from cellulose and maleic acid.

In this part of research modification has been performed in non-polar solvent to avoid side reactions of maleic anhydride with other substances containing free hydroxyl groups. Task of the next stage is to add obtained derivative to paper composition and investigate the effect on paper properties.

Acknowledgements
Financial support for this research is from Latvian State Institute of Wood Chemistry Bio-economic grant “CelFun”. Scientific supervisor *Dr. sc. ing.* Inese Filipova.

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o-Quinone derivatives containing functionalized indane fragment: experimental and theoretical studies

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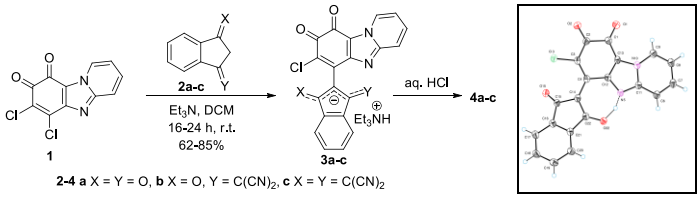
Quinone[1] and indane[2] derivatives are known as chromophores which can form donor–acceptor systems with intramolecular charge transfer. Non-planar compounds with several chromophores within the same molecule would be of interest for the construction of complex molecular functional units.[3] In this work heterocyclic *o*-quinone derivatives **3a-c** connected by single C-C bond with functionalized indane fragments have been synthesized (**Scheme 1**). Reaction with HCl led to the formation of hydrolyzed products **4a-c** since absence of the Et_3NH^+ signals was evidenced in ^1H NMR spectra of these compounds. Compounds **4a,b** could exist in keto and/or enol form, while only keto form is expected for the compound **4c**.



Scheme 1. Synthesis of compounds **3a-c** and **4a-c** and X-ray crystal structure of compound **4a** (enol form).

The UV spectra of derivatives **3a-c** consist of the absorption bands of initial substrates **1** and **2a-c** and new longest wavelength absorption band, which is expected to arise from the interaction between both chromophore units (at 660, 751 and 864 nm in DCM respectively). This interaction disappeared after protonation since the absence of longest wavelength absorption band in UV spectra after acid addition to the solution of compound **3a-c**. According to the DFT calculations interplanar angles between heterocyclic quinone and functionalized indane planes for compound **3a-c** are 60±5° and almost 90° for compounds **4a-c** if protonation occurs at C-2 atom of indane moiety. Compound **4a** in solid state exists in diketo form as shows analysis of IR spectrum, while in solution keto/enol tautomeric equilibrium of indandione fragment was evidenced by ^1H NMR. The crystals of enol form of compound **4a** were obtained and X-ray crystallography confirmed the structure, that was stabilized by strong intramolecular H-bond of OH···N type as well as σ-hole interaction between oxygen of C=O bond in indandione fragment and chlorine atom.

Acknowledgements
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Silk and calcium phosphate based hydrogels for drug delivery

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Bone fragility is expected to increase by 27% by the year 2030 in the six biggest countries in Europe, hence, new materials need to be developed to improve people's quality of life.[1] Silk fibroin (SF) is a protein, which is similar to human bone organic phase.[2] By combining it with calcium phosphates (CaP) a new composite can be made, where. CaP would imitate inorganic phase inside the bone.[3] In future SF/CaP hydrogel drug delivery systems could be made, which can do both – heal and regenerate. CaP was synthesized in situ in SF solution at different pH values and then enzymatically crosslinked with horseradish peroxide (HRP) and hydrogen peroxide (H_2O_2). The obtained SF/CaP composites were analyzed with X-ray diffractor (XRD), Fourier infrared spectroscopy (FT-IR) and Brunauer-Emmett-Teller method (BET). Gel fraction was determined by immersing lyophilized hydrogels in deionized water for 48 hours in 37 °C and stirred at 100 rpm. Swelling of prepared hydrogels was evaluated in 20 mL deionized water at 37 °C for 24 hours at 100 rpm. Obtained composites from pH 6 to 8 consist of brushite and hydroxyapatite (HAp), but from pH 10 to 11 from pure HAp. The specific surface area was similar to pure calcium phosphates and was in the range from 57.78±5.028 m^2/g (pH 6) to 66.97±6.268 m^2/g (pH 8). Our results showed that hydrogels with CaP have better swelling degree and gel fraction than pure SF/HRP/H202 hydrogels. The highest swelling degree 956.32±18.20% and gel fraction 107.30±25.70% was for the hydrogel, which consisted of pure HAp synthesized at pH 10, however hydrogel without CaP swelling degree was 539.53±60.97% and gel fraction 0.9113±0.6261%.

Acknowledgements
This research has received funding from the European Union's Horizon 2020 research and innovation programme under the grant agreement No 857287 and the Latvian Council of Science research project No. lzp-2020/1-0054 "Development of antibacterial autologous fibrin matrices in maxillofacial surgery (MATRI-X)".

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Sulfur Dioxide-Promoted Glycosylation with Glycosyl Fluorides

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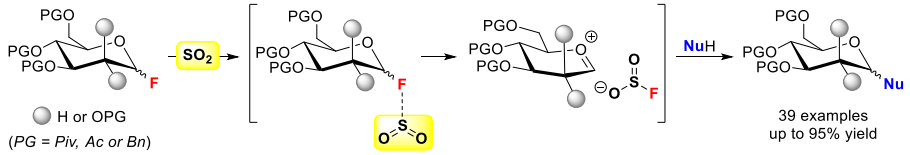
Liquid SO_2 is a polar solvent that possesses Lewis acid properties. It is known to facilitate Lewis acid promoted and/or carbenium ion mediated chemical transformations.[1] Apart from that, SO_2 has an affinity towards fluoride ion that leads to covalent bonding in the form of relatively stable fluorosulfite anion.[2]

Based on the aforementioned physico-chemical properties of SO_2, we have developed sulfur dioxide-promoted glycosylation with glycosyl fluorides as glycosyl donors in liquid SO_2 without an external promoter (Scheme 1).[3] The novel synthetic method was successfully applied for the synthesis of *O*-, *S*- and *C*-glycosides in moderate to excellent yields by employing benzyl- and acyl-protected manno- and glucopyranosyl fluorides, including 2-deoxyglycopyranosyl fluoride. The α/β-selectivity of glycosylation was proposed to be substrate-controlled presenting thermodynamic equilibrium. The formation of fluorosulfite species during the glycosylation in the presence of SO_2 was proved by both ^{19}F NMR spectroscopy and DFT calculations. Additionally, it was demonstrated that saturated solutions of SO_2 in traditional solvents like DCM and toluene retain the promoting effect of SO_2 as a Lewis acid towards glycosylation with glycosyl fluorides. Such a modification of reaction conditions offers more convenient experimental procedure that does not require high-pressure stainless steel equipment.



Scheme 1. Sulfur dioxide-promoted glycosylation with glycosyl fluorides

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Synthesis of ZnO nanoparticles by microwave-assisted method and their photocatalytic properties

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For last decades scientists have been interested in photocatalysts due to their possibilities to degrade organic compounds into less toxic compounds.

In this research ZnO nano and micro particles were obtained in 3 synthesis series. In every series different substance (urea (A series), sodium bicarbonate (B series), sodium carbonate (C series)) was added to zinc nitrate hexahydrate. The temperature was changed in range 100°C to 225°C for each series to determine the best synthesis conditions for microwave - assisted synthesis of ZnO photocatalysts. Microwave-assisted synthesis method was chosen because it is faster than other methods and the process can be made under high pressure conditions, which ensures particles with smaller crystallite sizes and grater specific surface area (BET). After synthesis samples were filtered, grinded and heated at 400°C for 2 hours. Photocatalytic activity of each sample was determined by using spectrophotometric method and degradation of MB (methylene blue) solution for 30min under UV/VIS (300W) irradiation. By evaluating obtained photocatalytic activities results, in **Fig.1** is shown every series most active sample.

The highest result was shown by A series sample, which was obtained at 125°C, B series sample which was obtained at 200°C and C series sample which was obtained at 225°C. They can degrade 92.2%, 98.0% and 98.8% of MB in 30min, respectively. In conclusion the highest photocatalytic activity is shown by C sample. It is determined that sample A average crystallite size is 46nm, B sample-35nm and C sample-24nm, which allows to conclude that sample with the smallest crystallite size has the highest photocatalytic activity. By evaluating specific surface of the samples, it is concluded that C sample has shown the highest specific surface-38.3m^2/g, while A sample and B sample showed 23.9m^2/g and 34.4m^2/g, respectively. By performing XRD analysis it is concluded that every sample contains only ZnO zincite crystalline phase.

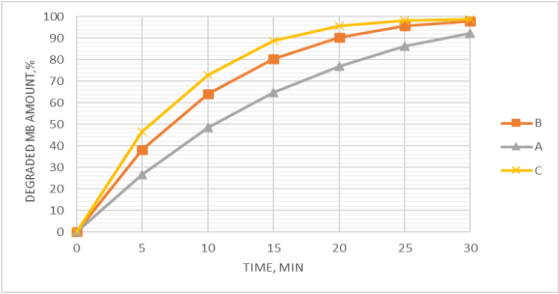

Fig.1 Photocatalytic activities results of most active ZnO samples from each synthesis series depending on raw materials used. (A series-urea, B series-sodium bicarbonate, C series-sodium carbonate).

Bark and shoots of Sea buckthorn cultivars growing in Latvia as a source of natural antioxidants

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The sea buckhorn products produced in Latvia are mainly made from berries. The by-products obtained in berry production, generally leaves, shoots and branches are unutilized. It is already known that these parts are valuable material of biologically active compounds. The aim of this research was to characterize the most important active compounds with emphasis on antioxidants, in shoots and bark of eight different cultivars (Otto, Tatjana, Marija Bruvele, Bot.Ļub., Rumanija, Leikora, Duet, Tarmo) to explore the currently limited knowledge.

The parts of sea buckthorn were collected in Bruwell Ltd., Latvia in two different harvest times, bark in winter (January) and shoots in summer (June). The active compounds were obtained using extraction with distillate water and water/ethanol (50:50, v/v). The individual compounds were identified by LC-UV-TOF/MS. Additionally extracts were characterized in terms of total polyphenols, proanthocyanidins and antioxidant activity (DPPH test).

The extraction yields ranged from 15 to 30% of sea buckthorn biomass. The total polyphenol content was quite similar in shoots of all cultivars and varied from 30 to 50 GSE g /100g. The highest content of polyphenol compounds was in bark of Maria Bruvele cultivar (68 GSE g/100g). The extracts contained proanthocyanidins ranging from 2% to 15%. The highest levels of proanthocyanidins were found in extracts obtained with 50% EtOH from Maria Bruvele bark (15%), Otto's shoots (14%), Maria Bruvele's shoots (13%) and Romania's shoots (13%). The extracts obtained showed high antioxidant activity (0.6 for Otto shoots and Maria Bruvele bark to 1.3 for Leikora shoot extracts, IC_{50} mg/L), which is comparable to Trolox (water soluble vitamin E analogue) antioxidant activity.

Results obtained showed that sea buckthorn shoots and bark grown in Latvia by their chemical composition - total polyphenols and proanthocyanidins and high antioxidant activity- are prospective source of antioxidants, the most richest sources were bark and shoots of Maria Bruvele and Romania.

Acknowledgements
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Application of nanoindentation for testing frozen masses

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In the frozen state, any material changes its properties, some remain harder, others more fragile, others gain or lose a property altogether. Such changes are very significant for materials used in building structures and can change the strength of the whole structure and for materials used in direct contact with humans, such as food or drugs. For the last one these tests are particularly important because frozen medicines are a new, alternative form of drug with a high potential to improve patient consent to take medicine. However, to ensure that such a form is introduced, the right methods must be found not only for preparing and storing the medicinal product to perform its function but also test when it is no longer safe to use. No specific test methodology has been developed for frozen medicinal products at present and testing is performed in the same way as frozen edible masses, in the molten state, freeze drying the product or without considering the effect of temperature at all, which does not provide information on the true structure and properties of the frozen product.

Nanoindentation is a method that mainly provides information on the surface of a material. Using this method, it is possible to determine or calculate properties such as material hardness, elasticity, viscoelasticity and creep. However, what really gives the method its potential and makes it important in the study of frozen masses is the possibility to use the device together with the cold stage, in which a continuous flow of nitrogen gas ensures a constant stable temperature even when used below zero. This allows both the measurement of frozen masses and their change at a temperature below zero and the determination of the conditions under which the material loses its properties.

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Effect of the polyurethane adhesive and polyvinyl acetate dispersion adhesive on the strength of the construction joints in bending strength

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This document presents the bending durability strength[1] and flexural properties of the glued 45° and 60° spruce loose tenon construction joints, 45° and 60° spruce double notched (with and without pins) construction joints, 45° and 60° spruce tenon – mortise construction joints[2] (Fig. 1). Construction joints are design according to Eurocode 5.[3] The samples are made from European spruce (*Picea abies Karst*) C24 class construction timber[4] with relative wood density 410 kg/m^3 and relative wood moisture 13%. Loose tenon and pins are made from European beech (*Fagus Sylvatica*) with relative wood density 740 kg/m^3 and relative wood moisture 13%. Samples are assembled with water/high temperature resistant polyurethane adhesive[5] and polyvinyl acetate dispersion adhesive. The total number of samples is 14. The sample width is 95mm and thickness is 45mm. Samples were subjected to moisture, weight controls and 48h stored in the climate chamber before practical bending durability load test. 45^0 spruce double notched with pins construction joint glued with polyurethane adhesive performed with the highest durability strength (17,3 kN) and highest flexural properties till breaking point (23mm).

The accuracy and durability of the developed bending strength, deformability and elasticity modulus of the examined construction joints was verified positively by experimental studies and SolidWorks mathematical simulations (Fig.1.).

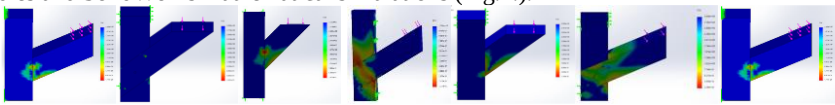

Figure 1. SolidWorks mathematical simulations of maximum durability of the construction joints in bending strength.

Acknowledgements

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Transesterification of esterified extract from rapeseed soapstock

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Advanced biodiesel is economically competitive and sustainable; it could be synthesized from non-edible fatty material sources as vegetable oil refining byproducts. New technologies should be elaborated to obtain high quality biodiesel from such starting materials.[1]

We prepared extract from rapeseed soapstock (SS) rich in free fatty acids (FFA) and glycerides. The resulting extract is subjected to acid catalyzed esterification of FFA with MeOH. Esterified extract with FFA content 0.9–4.5 wt% is obtained depending on the esterification conditions. The allowable FFA in base catalyzed transesterification reaction is reported from <0.5 till <2.0%[2] to <5 wt%.[3] We conduced series of experiments to determine the effect of FFA content in transesterification reaction of esterified extract from rapeseed SS and to find the best catalyst.

Esterified extract contained 43.0% triglicerides (TG), 48.5% FAME and 1.74% FFA. Rapeseed FFA is added till needed amount, reaction conditions: MeOH:TG 6:1, catalyst 15.0 mol% of TG plus equivalent to FFA, time 1 h, and 60 °C temperature. KOH and NaOH are not suitable catalysts for esterified extract (see Table 1), transesterification reaction was not finished, and yield was low. Controls using refined rapeseed oil with added FFA led to complete reaction and good yield. NaOMe led reaction to completeness in all cases, but obtained yield decreased and product washing hardened with increasing FFA content.

In conclusion, NaOMe is suitable to achieve biodiesel with excellent FAME content, when esterified soapstock extract contains up to 4 wt% FFA, but to make process beneficial and achieve better yields, the content of FFA should be as little as possible (preferably ≤1 wt%).

Table 1. Yield (%) and composition (wt%) of transesterification reaction products.

Entry	Catalyst	Added FFA	Yield	MG	DG	TG	FAME	FFA	Sum
1	KOH	2	68.8	1.39	2.80	6.78	82.5	0.25	93.7
2	NaOH	2	78.4	0.96	1.86	6.29	85.1	0.25	94.5
3	NaOMe	1	88.8	0.42	0.16	0.00	96.5	0.12	97.2
4	NaOMe	2	82.6	0.35	0.14	0.00	96.8	0.23	97.5
5	NaOMe	3	75.1	0.29	0.41	0.00	96.5	0.14	97.4
6	NaOMe	4	70.3	0.18	0.58	0.00	96.7	0.22	97.7
7	NaOMe	5	67.9	0.31	0.27	0.00	89.0	0.14	89.7

Acknowledgements
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Triboelectrification of nanocomposites using identical polymers with different concentrations of nanoparticles

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Strong contact electrification has been observed between polymer materials with a significant difference in mechanical hardness or porosity, regardless of their chemical composition.[1] In this study, we investigate triboelectrification in polymer nanocomposites using identical polymer matrixes containing different concentrations of nanoparticles (NPs). When triboelectric layers contain the same particles in the same concentrations, small current and voltage peaks are generated from the triboelectric generator (TEG). In contrast, much higher peaks are produced when the polymer matrix is the same but has different concentrations of filler particles (Figure 1 (a)). Tendency is particularly clearly manifested in the case of EVA polymer and its composites with TiO_2 NPs filler (Figure 1 (b) and (c)).

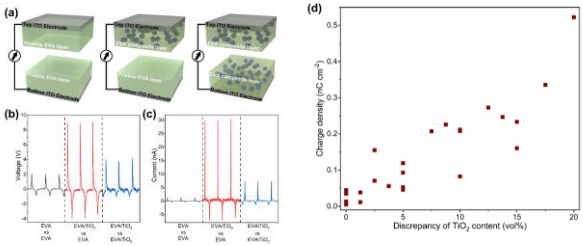

Figure 1. (a) Schematics of three types of TEGs using EVA polymer and/or EVA-based composites. (b) Generated voltage and (c) current peaks by the three TEGs. (d) Increasing the difference between the TiO_2 content in EVA layers leads to increased charge density.

The triboelectric surface charge density on polymer layers increases as the difference in nanoparticle filler concentration between the two layers escalates, even though the polymer is the same (Figure 1 (d)). Effect is observed in tests of various polymer types (EVA, PDMS, PVAc, PU) and filler NPs (TiO_2, WO_3, MnO_2, α-FeO(OH)). Mechanical experiments and finite element analysis simulations confirm that polymeric triboelectrification is related to the surface viscoelastic deformation that occurs during mechanical contact and separation. This supports the heterolytic scission of covalent bonds as an explanation for the triboelectricity.

Acknowledgements
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Azide-tetrazole equilibrium study in 2,4-diazidopyrido[2,3-*d*]pyrimidine

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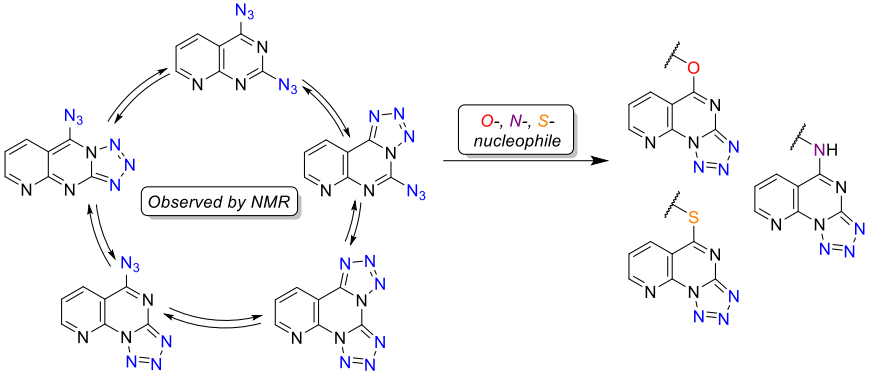
Pyrimidine scaffold is found in many biologically active compounds such as antiviral, antimicrobial and anticancer drugs.[1] Therefore modifications of pyrimidine moiety and new synthesis methods toward modified pyrimidines are continuously developing.

Azido substituted pyrimidines undergo dynamic azido-tetrazolo tautomerism when dissolved in organic solvents. By selection of appropriate solvent the equilibrium can be shifted towards one tautomer. Thus reactivity and product outcome can be changed by switching between different solvents.[2] Herein we examine azido-tetrazolo equilibrium in 2,4-diazidopyrido[2,3-*d*]pyrimidines and reactivity thereof (**Scheme 1**).



Scheme 1. Azido-tetrazolo equilibrium in diazido-pyridopyrimidines and reactivity thereof.

Supervisors: Irina Novosjolova, Māris Turks

Acknowledgements

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Preperation of hybrid materials from Wood char and Tar

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Preparation of tailored carbon materials from biomass and its waste resources by a simple and up-scalable method still is a challenge. From all available biomass waste resources, more than 47 million tons of wood residues is available across the EU each year.

At the same time developers of new innovative wood biorefinery processes meet the problems with obtained by-product valorisation. For example, in thermochemical conversion technologies char and liquid wastes are produced as by-products and used as fuel. In sugar platform technologies, where acids or ferments are applied for hydrolysis, lignin is a by-product of the process, and is considered to be a low added value product and the extent of its further utilization market is far from the desired.

However, due to the many factors influencing the formation of carbon materials, it is rather difficult to define the necessary parameters of their structure and to determine the optimal conditions for obtaining a product with given characteristics. For carbon materials, the role of ultramicro-, supermicro-, micro-, meso- and macropores in the processes of ion diffusion, which is important for capacity and energy density, has not been sufficiently studied. The formation of a porous structure will also occur in different ways under the same activation conditions of the solid ligno-carbohydrate complex of wood in comparison with the liquid aromatic matrix of lignin with a high content of mineral components (e.g., black liquor).

Activated carbon have also shown promising results as electrodes for batteries and supercapacitors, and as catalysts for fuel cells. Supercapacitors, batteries and fuel cells are critical for enabling technologies and are at the centre of vast global research and initiatives to meet the rising global demand for clean, sustainable energy.

The goal of this research is synthesis of carbon materials with high specific surface and adjustable pore distribution using solid (char) and liquid (tar containing lignins and phenols) biorefinery wastes precursors to obtain novel hybrid composite materials for energy devices.

liquid precursor for impregnation of a solid one, as well as increasing the activation temperature pore size increases. It is possible to obtain a hybrid material with a large specific surface area and more than 40% mesopores volume.

Acknowledgements
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Polarization microholograms in an azobenzene film

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Studies of microhologram recording are of interest because holographic disks have much higher information capacity than other optical disks (CD, DVD, Blu Ray). In this work, we have experimentally studied unfocused and focused polarization holographic grating (HG) recording in 1.6 μm thick azobenzene molecular film B11 [5,5,5-triphenylpentyl4-((4-(2-(4-(bis(2-hydroxyethyl)amino)phenyl)-1-cyanovinyl) phenyl)diazenyl)benzoate] on the glass substrate with linear *p-p* and orthogonal circular *L-R* polarizations of recording and readout laser beams. HG periods were 2μm , 6 μm and 10 μm. HG diameters were 1.17mm and 0.14mm for unfocused and focused HG, respectively. Measurement technique of laser beam diameters was developed, especially useful for focused laser beams. The obtained results were compared with analogous measurements for scalar HG in As-S-Se and As_2S_3 films[1,2] .

It was found that HG recording in B11 film is much less efficient with focused laser beams than with unfocused ones. This is not always the case for chalcogenide films [1,2]. Recording with orthogonal circular *L-R* beam polarizations was much more efficient than with linear *p-p* beam polarizations. The maximum diffraction efficiencies of 26% and 10% were obtained for unfocused and focused recording, respectively at the HG period Λ=6 μm with *L-R* recording beam polarizations at 1000J/cm^2 exposure.

Recording efficiency Λ- dependences for unfocused beams at 200 J/cm^2 exposure and at 1000 J/cm^2 exposure were *different* with a maxima at 2 μm and 6μm, respectively. Recording efficiency Λ- dependences for focused beams at 200 J/cm^2 exposure and at 1000 J/cm^2 exposure were *the same* with the maximum at 6μm. Thus focusing equally affected properties of polarization microholograms recorded with different polarizations .

Trans-cis-trans photoisomerization cycles takes place according to the spatial polarization modulation of recording light leading to the inscription of volume birefringence grating (VBG). VBG creates also spatially modulated photoisomerization pressure , which together with electric gradient force results in mass transfer forming surface relief grating (SRG) and/or volume density grating (VDG) . At first, VBG is recorded, and it decays during the readout. The following SRG and VDG grow slower but are stable.

The much less efficient HG recording with focused beams in the B11 film is due to the photoisomerization and mass transfer light intensity dependence. The more efficient *L-R* recording compared to the *p-p* one can be explained by the fact that circular polarizations were addressing more chromophores. The optimal Λ=2 μm at 200 J/cm^2 exposure , evidently, was due to the dominant light electric field gradient force ~1/Λ at the first stage of SRG recording. For exposures>200J/cm^2 the deformation of the sample surface becomes significant and the surface elastic forces also ~1/Λ start to counteract the mass transfer. The tradeoff of all forces forming SRG at 1000 J/cm^2 corresponds to optimal Λ=6 μm. For focused 5 W/cm^2 light recording processes proceed so fast that surface tension effect starts to act immediately, therefore, again the optimal Λ=6 μm.

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Synthesis and physicocemical evaluation of cationic amphiphilic 1,4-dihydropyridine and calixarene derivatives

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The therapeutic potential of numerous drugs has been largely limited by the low bioavailability caused mainly by low aqueous solubility, poor biomembrane permeability, instability in the gastrointestinal tract, and extensive metabolism in the body. To enhance the bioavailability of these drugs, diverse micro-/nano-sized delivery systems such as emulsions, polymeric particles, and vesicular systems have been investigated. The delivery systems improved the bioavailability by enhancing solubility, permeability, and stability of the drugs. Multifunctional nanoparticles with appropriate inherent physicochemical properties and labels would allow us to diagnose diseases and evaluate treatment efficiency, while tracking pharmacokinetics and drug releasing of the particles.

Both apmphiphilic calixarene and 1.4-DHP nanosystems have been studied in gene therapy, but their composite nanoparticles have not been fully explored yet. In order to reduce the lack of available information in this area, cationic amphiphilic 1,4-dihydropyridine, calixarene derivatives and their compositions were obtained. Their formed aggregates in water media physical chemical properties were studied using DLS technique.

Cationic calixarenes are able to form nanoaggregates with cationic amphiphilic 1,4-DHP derivatives, the resulting nanoaggregate ranges were in size from 44-389 nm, which are stable for up to 96 days. Cationic amphiphilic 1,4-dihydropyridine particles are stable and suitable for further research as potential genes therapeutic agents by looking at their ability to form complexes with DNA, cytotoxicity and transfection activity.

Acknowledgements
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Photodegradation stability of poly(butylene succinate-butylene)/CuO nanocomposites

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Biodegradable polymers have gained significant attention because of their potential to reduce environmental pollution. Bio-based poly(butylene succinate) (PBS) is an attractive polymer owing to its high mechanical properties and service temperatures comparable with some polyolefin materials. However, PBS is susceptible to environmental impacts, particularly to ultraviolet (UV) light, that results into the reduced service lifetime and limit its outdoor applications. Metal oxide nanoparticles are known as effective UV-barrier additives for polymers due to their ability of UV absorption, scattering, and reflection.

The current study was aimed is to improve photodegradation stability of PBS by addition of CuO nanoparticles. Nanocomposites (0.5, 1, 3 wt.% CuO) produced by solution casting method were exposed to UV irradiation (4 mW/cm^2) and tested after different time periods: 2, 4, and 7 days. UV ageing of PBS resulted into dramatic decrease of the mechanical properties, progressive weight losses of samples, reduced melting temperatures and crystallinity and increased surface wetting. Nanocomposites demonstrated high photodegradation stability: the higher, the greater content of CuO nanoparticles. The kinetics and nature of chemical decomposition in PBS and nanocomposites were compared by FTIR.

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Structure and Composition of Alkali treated Illite Clay

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Alkaline treatment of clay minerals has been widely studied topic in past decades, due to potential of forming either geopolymers – an alternative to Portland cement with lower environmental impact and higher durability (Khalifa et al., 2020) or zeolites – microporous materials used as ion exchangers, molecular sieves, sorbents and catalysts (Mezni et al., 2011). Most of the research in this area is focused on kaolinite, however studies suggest that illite also has capacity to react with alkaline solutions and form alumosilicates. Structural differences and lower chemical activity of illite requires more intense treatment process, such as using high concentration hydroxides and curing at elevated temperatures.

This study investigates structural changes of illite clay by high concentration alkaline treatment. Source of illite fractioned clay from Kuprava pit (Latvia). Alkaline treatment was done using 6M and 10M NaOH solutions, with following curing process at 120°C and 600°C, and alkaline-hydrothermal method at 180°C for 24h.

Composition of crystalline phase, structure and morphology of raw and synthesized samples are investigated by XRD and SEM.

Figure 1 shows formation crystalline sodium alumosilicates – a form of zeolite for alkali-hydrothermal treated samples, which is also supported by XRD results. Samples cured at 120°C and 600°C show more fused and amorphous structure with lower crystallinity of sodium alumosilicates, suggesting higher degree of geopolymer formation.

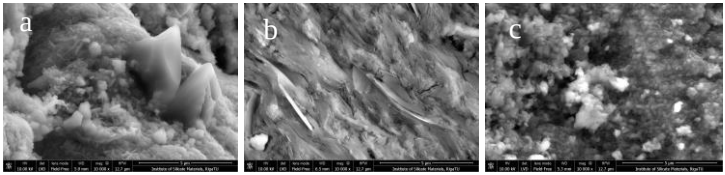

Figure 1. SEM micrographs of alkali treated illite clay. a) alkaline-hydrothermal method; b) 10M NaOH with curing at 600°C; c)10M NaOH with curing at 120°C.

Scientific supervisor: Dr.h.chem., leading researcher *Gaida Maruta Sedmale*

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4-(*N*-Alkylpyridinium)-1,4-Dihydropyridines as Bifunctional Lipid-Like Compounds

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Over the past few decades, scientists around the world have made efforts to expand the discovery and development of a broad range of nanoparticle delivery systems[1]. Synthetic nanoparticle-forming cationic lipid-like compounds have been developed as delivery agents for the transfer of genetic materials, including plasmid DNA (pDNA) molecules, into cells[2,3] and recently also for therapy and diagnostic applications[4]. Previously, our group elaborated and studied multiple liposomes forming cationic 1,4-dihydropyridine (1,4-DHP) amphiphiles, which were capable of transfecting pDNA into different cell lines in vitro[5].

In this work, we have studied in detail the ability to form nanoparticles by cationic 4-(*N*-alkylpyridinium)–1,4-DHP derivatives in aqueous media. Transmission electron microscopy images of nanoparticles of selected compounds have been obtained. We also established the size distribution and the stability of nanoparticles by dynamic light scattering (DLS) measurements. Additionally, critical aggregation concentration has been estimated by the DLS technique. Moreover, the cytotoxicity of 4-(*N*-alkylpyridinium)–1,4-DHPs on HT-1080 and MH-22A cell lines has been evaluated, and an approximate LD_{50} value has been predicted. The hydrophobic interaction between 4-(*N*-alkylpyridinium)–1,4-DHP derivatives and DPPC model membranes has been studied.

The obtained results showed that a variation of alkyl moiety lengths at the quaternised nitrogen atom at position 4 of the 1,4-DHP cycle and the numher of propargyl moiety and position in the 4-(*N*-alkylpyridinium)–1,4-DHP molecule strongly affects the self-assembling properties of compounds and characteristic parameters, and the stability of formed nanoparticles, as well as the toxicity of tested lipid-like 1,4-DHP derivatives.

The results will provide a basis for the further understanding of the structure–activity relationships of these compounds.

Acknowledgment
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The Use of Thiazoline-Based Carbenes for a Development of Metalorganic Thermally Activated Delayed Fluorescence Emitters

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In recent years thermally activated delayed fluorescence (TADF) exhibiting emitters have been explored as potential materials for OLED application.[1] However, long delayed fluorescence lifetime causes severe efficiency roll-off and low external quantum efficiency at high luminance. A new class of photoemitters - linear carbene-metal-amide (CMA) complexes with short radiative lifetimes has recently remerged as alternative to the conventional TADF materials.[2]

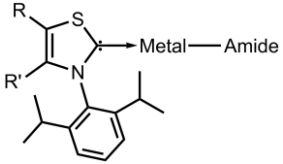

Figure 1. General structure for synthesized thiazoline-based CMA complexes (Metal - group IB coinage metals; R – alkyl-; R' – alkyl- or aryl-).

In our research we have systematically examined various thiazoline-based CMA type group IB metal complexes with different amide ligands (Fig. 1). By carefully tailoring substitution of thiazoline ring and amide ligand highly luminescent complexes were obtained (λ_{max}= 470 .. 510 nm with quantum yield (QY) up to 0.86 in 5 wt % PMMA matrix). Quantum chemical calculations show that complexes exhibit ligand-to-ligand charge-transfer (LLCT) type excitation with HOMO localized on amide fragment and LUMO localized on thiazole ring. HOMO and LUMO orbitals contain a small but not negligible contribution on central Cu atom, which increases transition oscillator strength values. TADF from LLCT excited states was assigned as the main emission mechanism for complexes. A low singlet-triplet energy gap (0.08 eV) enables rapid reverse intersystem crossing leading to radiative rates up to $7 \cdot 10^5$ s^{-1}, essential for highly emissive materials for OLED application.

Acknowledgements
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Removal of Mn(II), Ag(I), Au(III), and Pd(II) from Aqueous Solutions using a Hybrid Liquid Membrane – Electrodialysis Process

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Membrane extraction is a promising technique for removal of valuable and toxic metal ions from dilute industrial solutions.[1] Application of a direct electric field significantly intensifies the transport of ions through the liquid membranes. The aim of the present work is to study the membrane extraction of Mn(II) from H_2SO_4 solutions, Au(III) and Pd(II) from HCl solutions, and Ag(I) from HNO_3 solutions by the liquid membranes containing di(2-ethylhexyl)phosphoric acid (D2EHPA), trialkylbenzylammonium chloride (TABAC) and tri-*n*-octylamine (TOA) under the conditions of galvanostatic electrodialysis.

The experiments were carried out in a horizontal five- or four- compartment electrodialysis cell, containing a liquid membrane, which was arranged between two cellophane films.

The imposition of a direct electric field allows to intensify extraction from the feed solution and to transfer the metal ions into the stripping solution (or catholyte) as well as to obtain cathodic silver coatings from dilute acid solutions.

The increase of the current density results in a rise of the metal ions extraction degree from the feed solution, stripping degree from the liquid membrane and transmembrane flux. A practically complete removal of Mn(II) and Ag(I) from the feed solutions is achieved. The increase of initial metal ion content leads to a rise of the flux as well as deposit mass (Fig. 1).

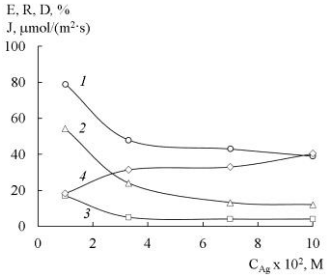

Figure 1. Dependence of extraction degree E (1), back extraction degree R (2), electrodeposition degree D (3) and silver flux J (4) on $AgNO_3$ initial concentration.

Composition of the stripping solution does not exert a considerable influence on the electrodialytic transport of metals. Dilute solutions of HCl, HNO_3, H_2SO_4, $HClO_4$, NH_4OH and H_2O were used as the stripping solutions in the several studied systems. Concentration of D2EHPA in the liquid membrane insignificantly affects the metal ions removal rate. The increase of TOA and TABAC content in organic phase usually leads to a decrease of metal ions transport rate into the liquid membrane and into the stripping solution.

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Modulation of luminescence spectra via solid solution formation of thioxanthone derivatives

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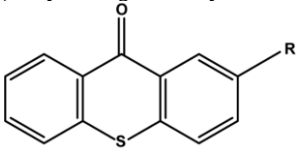
Solid solutions (SS) are single multicomponent solid phases for which the constituent component ratio can vary in continuum. Along with the composition, also properties of solid solutions are modulated. The changes in composition are often accompanied by a continuous change in some physical and/or chemical properties (e.g., density, solubility, melting point), and more complex properties such as non-linear optical properties, solid-state luminescence, and phosphorescence properties, that are composition-dependent.[1, 2]

Several thioxanthone (TXANT) derivatives (Figure 1) were selected as model compounds because of their physico-chemical properties and chemically similar structures, in which the different atom (R) may not significantly affect the dominant intermolecular interactions.[2]



R = **Cl** (TXANT-Cl), **I** (TXANT-I), **Br** (TXANT-Br) or **F** (TXANT-F)

Figure 1. Molecular structure of thioxanthone derivatives

In this study we explore solid solution formation in thioxanthone derivative systems, namely, 2-iodothioxanthone : 2-chlorothioxanthone/2-bromthioxanthone and 2-fluorothioxanthone : 2-chlorothioxanthone/2-bromothioxanthone. Solid solutions have been identified and characterized using powder X-ray diffraction and thermal methods of analysis. Their composition limits are summarized in respective two component phase diagrams. The compounds have been selected based on reported room-temperature solid-state luminescence phenomena. Photoluminescence spectra of all crystalline phases in powder form were recorded to see how they change with respect to those of the pure substances known from the literature. This confirmed that technologically relevant properties can be modulated via solid solution formation and therefore can be modulated in a continuous fashion.[3]

Acknowledgements

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Synthesis and characterization of chemically cross-linked hydrogels based on ε-polylysine and hyaluronic acid

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In recent years, health care sector has been facing with the bacterial infections during post-surgery period and antibiotic resistance, and therefore design and development of such biomaterial class as 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).

The hydrogel series based on ε-PL and HA (mass ratios of ε-PL and HA are 40:60, 50:50; 60:40; 70:30 and 80:20 wt%) were synthesized via EDC/NHS (molar ratio 1:1) mediated cross-linking reaction [1]. The molecular structure and morphology of all synthesized hydrogels were evaluated using Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). Antibacterial efficiency of ε-PL and activity of the fabricated hydrogels were tested against *E.coli* and *S.aureus* bacteria. FTIR spectra indicated changes in absorbance curve due to interaction between ε-PL and HA, resulted in formation of cross-linked copolymer via amide bond linkage. SEM microphotos of the lyophilized ε-PL-HA hydrogels revealed homogeneous and micro-/macro-porous structure. Gel fraction tests indicated the existence of newly formed matrix and insoluble part in synthesized samples on average 55%, in addition, swelling behavior proved of material restructuring property by revealing cross-linked matrix ability for water uptake, increasing self-mass up to 8 times on average. Steam sterilization technique was successfully used for hydrogel sterilization with no structural changes indicated. *In vitro* studies revealed ε-PL and ε-PL-HA hydrogel inhibition ability against *E.coli* and *S.aureus* bacteria.

To sum up the novel hydrogels based on chemically cross-linked ε-polylysine and hyaluronic acid copolymer system were synthesized and investigated. First stage of physicochemical investigation of prepared samples revealed promising tendency. Such results as newly formed amide group absorbance maximums, porous and homogeneous surface morphology, as well as typical gel fraction values and swelling behavior will be used for further material mechanical investigation. The *in vitro* evaluation of antibacterial properties indicated ε-PL antibacterial effect in hydrogel matrix presence against *E.coli* (Gram-) and *S.aureus* (Gram+) bacteria. It is concluded that the developed hydrogels can be considered as promising antibacterial biomaterials and should be used in further investigation processes for potential tissue engineering uses.

Acknowledgements
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Polymorphic outcome control in crystallization and stabilization of metastable forms using surfactants

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Physical properties such as solubility[1] and bioavailability[2] of active pharmaceutical ingredients (API) can significantly depend on the polymorphic form. Many APIs have low solubility in water and use of a metastable polymorphic form can enhance the solubility and bioavailability.[3] However, metastable forms have lower stability and often they can very rapidly transform to a stable form. The use of crystallization additives is one of the empirical methods for stabilizing metastable forms[4,5] and also promoting their nucleation in a crystallization[6].

In this study, 2,6-dimethoxyphenylboronic acid (2,6-MeOPheBA) was used as a model substance to investigate the ability of surfactants as an additive to allow the crystallization of the metastable form. 2,6-MeOPheBA exists as two polymorphs[7] (see Fig.1.).

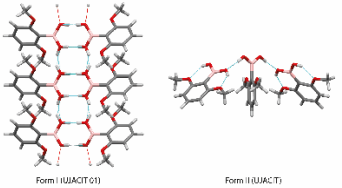

Figure 1. Hydrogen bonding in crystal structures of 2,6-MeOPheBA polymorphs.

In this study both 2,6-MeOPheBA polymorphs were characterized using thermal analysis to determine the relative stability of polymorphs. 2,6-MeOPheBA was crystallized under different conditions by performing evaporation and cooling crystallization from different solvents. Solid forms obtained in the crystallization were characterized with powder X-ray diffraction. After evaluation of the polymorphic outcome in crystallization from pure solvents, toluene was selected for additive (surfactant) screening. Surfactants with divergent intermolecular interaction possibilities were used as additives. Surfactants improving the likelihood for crystallization of the metastable form were studied further under different crystallization conditions. Form I, the stable polymorph, contains boronic acid homodimers, but form II, the metastable polymorph, – hydrogen-bonded catamer synthon. Surfactants Span 20 and OGP promoted crystallization of metastable form and its stabilization in evaporation crystallization. New unstable polymorph III was obtained in presence of Span 20 and OGP. Form III rapidly transforms to form II.

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Synthesis and photophysical properties of metal-amide complexes of *N*-heterocyclic carbenes containing peripheral acceptor groups

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Recently a new class of highly emissive triplet emitters has emerged in the form of carbene-metal-amide complexes, featuring coinage metals (Cu, Ag, Au).[1,2] Due to the combination of strong donor-acceptor coupling and significant spin orbital coupling (SOC) provided by the transition metal, these compounds possess efficient thermally activated delayed fluorescence (TADF) and have found application as emitters in organic light emitting diodes (OLEDs). The general design principles of these materials involve the use of electron donating amide (carbazolides, diphenylamines) and electrophilic carbene. The emission in complexes therefore arise from the charge transfer (CT) process between these groups.

We demonstrate an alternative approach to these emitters. Strong electron accepting groups are introduced in the periphery of the carbene moiety (Figure 1). As a result, CT proceeds not with carbene, but in a through-space fashion between the amide and the peripheral acceptor.

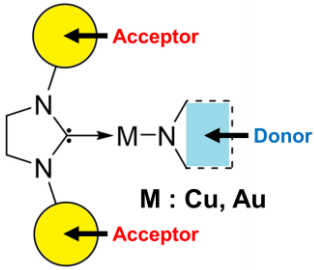

Figure 1. Design principle of the novel emissive carbene-metal-amides.

This difference results in a completely novel photophysical behavior, where compounds possess notably reduced SOC values, but at the time singlet-triplet energy gaps are significantly reduced, in such way aiding the TADF process. With the tuning of energy levels, materials with efficient room temperature phosphorescence can be acquired with the demonstrated molecular design.

Acknowledgements
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Validation of Cannabidiol Determination and Quantification Method for Novel Dug Delivery System Development

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Cannabis is a plant which contains more than 100 different cannabinoid compounds. CBD is the main non-psychoactive component of the cannabis plant.[1,2] CBD has antinausea, antipsychotic, pain-relief, anticonvulsive, sleep improvement, anti-inflammatory, antianxiety, and cancer cell antiproliferative effects.[3] However, the main limitation of CBD is its low absorption capacity in body fluids due to its lipophilic nature.[4] To overcome this limitation, CBD can be incorporated in drug delivery systems.[1] In order to evaluate the efficiency of the drug delivery system, it is necessary to study the release kinetics of the active substance using an appropriate analytical method. Therefore, the aim of this study was to develop an ultra-performance liquid chromatography (UPLC) method for CBD determination as well as to validate the method to verify the suitability of the analytical procedure for CBD quantification.

To prepare solutions in concentration range from 2.4 µg/ml to 100 µg/ml CBD was dissolved in a mixture of mobile phase solutions a - 0.1% formic acid in water and b - 0.1% formic acid in acetonitrile with a volume ratio of a:b 30:70. To analyze the samples photometric detection (λ = 228 nm) and *Waters Acquity UPLC BEH C18, 1.7 µm, 2.1×150 mm* column was used. The mobile phase consisted of a:b (v/v) 25:75. Flow rate was set to 0.2 mL/min, column temperature was 30°C ± 5°C and the injection volume was 3 µL. During the validation of the method, series of standard solutions were prepared and analyzed, and the statistical parameters of the obtained calibration curves were evaluated. The obtained results show that CBD detection limit is DL = 0.500 ± 0.041 µg/ml and quantitation limit is QL = 1.514 ± 0.125 µg/ml. The stability of CBD at 37°C is very low, because the CBD degradation is already observed within the first 24 hours. The precision, intermediate precision and total accuracy of the samples are 99.54 ± 0.06%, 99.72 ± 0.10% and 102.36 ± 3.96%, respectively. Robustness was also assessed for the analytical method. It was determined that small variations in analytical conditions do not significantly change the obtained outcome parameters and do not affect the precision of the UPLC method. It was concluded that the UPLC method is suitable for the determination and quantification of CBD and can be used for the determination of CBD release kinetics from liposomes.

Acknowledgements
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Moisture diffusion into lignin and xylan containing cellulose nanopaper

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The development of high-performance eco-friendly materials is one of the most important factors for sustainable growth of the packaging industry. Owing to their high mechanical properties and biodegradability cellulose-based materials are promising candidates for replacing fossil-based counterparts. However, environmental durability of cellulose materials is a major concern limiting their applications.

The study reports on moisture absorption and its effect on mechanical properties of cellulose nanopaper containing lignin and xylan. Cellulose nanopaper films were produced by casting 1 wt.% nanofibrillated cellulose (NFC) dispersions produced from paper waste. NFC dispersions were modified with different lignin and xylan loading: 1, 2.5, 5, 10, 20, and 30 wt.%. The kinetics of moisture absorption was studied on samples conditioned in desiccators under saturated salt solutions giving different relative humidity levels (RH). Totally, 13 different compositions under 6 different RH are studied. Saturated samples were tested mechanically to assess moisture impact on the elastic and strength characteristics of the nanopaper. Retention of properties was studied on saturated and then dried samples.

Moisture absorption of the nanopaper generally follows the Fick's diffusion law, although a two-stage behavior is observed under high RH. The Fick's and Langmuir models are applied for modelling the weight gain kinetics. The moisture saturation levels increase with water activity levels and sorption isotherms are finely described by BET model. Adding of both lignin and xylan into the cellulose nanopaper resulted into increased water absorption capacity, although to a much higher extent for lignin-based compositions. The diffusivity increased with growing content of lignin, while the opposite effect is noticed for the xylan containing nanopaper. Absorbed moisture resulted into decrease of the elastic modulus and strength of all samples, however noticeable retention in the mechanical properties is obtained after moisture desorption indicating to its plasticization effect. The higher RH (water activity) was applied, the higher the irreversible impact on the structure and mechanical properties of the nanopaper. The obtained results could guide material designers in selecting appropriate biobased sustainable materials with tailored mechanical performance and barrier properties. Additionally, the results will contribute to the effective waste management and conversion of waste to resources that is line with the latest EU activities towards development of circular economy.

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Mechanical properties of sheep wool fibers under environmental impact

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The sheep wool is an eco-friendly, renewable, and totally recyclable material increasingly used in textile, filters, insulation and other building and composite materials. Wool fibers are susceptible to environmental degradation that could shorten their lifetime and limit applications. Thus, assessment of environmental durability of wool fibers is highly important.

This study reports on mechanical properties of Latvian dark-headed sheep wool fibers under humid environment (RH = 97%, 22 °C) and UV irradiation (24 h, 35 °C) impacts. The elastic and strength characteristics of the fibers were evaluated in quasistatic tensile single-fiber tests according to ASTM D3379-75. The average diameter was computed from 5–10-point measurements along each fiber length. The mechanical tests for pristine fibers were performed under different gauge lengths (L_0 = 10, 30, and 50 mm), while the environmental impact was studied for fibers with L_0 = 30 mm. 22-40 tests were done for each group of fibers and the data were treated via the statistical analysis.

The wool fibers are characterized by reasonably high strength and elastic modulus (Figure 1) comparable with other wool and natural fibers. The two-parameters Weibull distribution model was applied for the fibers' strength evaluation. The scale parameter related to the characteristic strength σ_0 reduced with growing L_0 due to the increased number of defects at a longer length of fibers, while no evident trend was noticed for the shape parameter m. The Weibull parameters for pristine fibers (L_0 = 30 mm) are σ_0 = 154.8 MPa and m = 5.6.

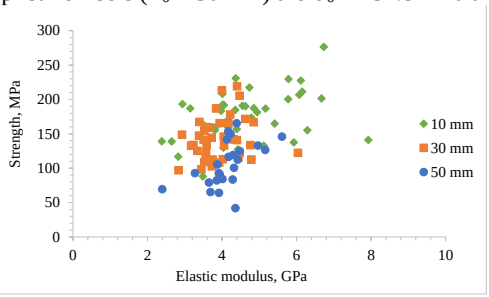

Figure 1. Strength versus elastic modulus of pristine wool fibers for different L_0.

Conditioning under humid environment and UV irradiation resulted into σ_0 decrease for 32% and 38%, respectively. The elastic properties were almost not affected by UV light, while absorbed moisture resulted into fibers' plasticization and decrease of the elastic modulus for 43% and increase of the strain at failure for 16%.

Production and Determination Of C-Phycocyanin

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The microalga *Arthrospira platensis* (trade name *spirulina*) is widely available food and feed supplement. *A.platensis* is an edible cyanobacterium that produce light-harvesting pigments - chlorophyll, carotenoids, and phycobiliproteins. C-phycocyanin (CPC) is a natural blue pigment widely used as a nutritional ingredient, in natural dyes, as fluorescent markers, and in pharmaceuticals as an antioxidant and anti-inflammatory reagent.

Strain, growth parameters, drying regime and other parameters can affect pigment content in algae. So, it is important to develop methods for producing spirulina with high pigment content. However, to purify pigments for accurate qualitative and quantitative analysis there is no universal method for all algae and literature data are contradictory. CPC can be extracted from cyanobacteria by different procedures which combine breakage of the cell walls and extraction of water-soluble phycobiliproteins into aqueous media. Combinations of physical and chemical methods are used for cell breakage. Several factors influence CPC extraction: the most important being the cellular disruption method, type of solvent, biomass-solvent ratio, and type of biomass[1]. The aim of this study was to compare several methods to find most appropriate for extracting c-phycocyanin from *A.platensis*. Freezing and ultrasonication pre-treatment was used. The combination of both was more effective. Ultrasonic probe with 26 Hz was disrupting cells more effective than 40 Hz ultrasonic bath. Sever solvents were compared: 1.5% solution of calcium chloride in water, phosphate buffer solution and deionized water. Absorbance measurements were performed on the clear part of the fugate at 615 and 652 nm. For the extraction of c-phycocyanin the most appropriate solvent is a 1,5% solution of CaCl2 in water, which is 5 and 57 times more effective than phosphate buffered saline or distilled water, respectively**.** Additionally, it was detected that 5 g/L NaCl addition to growth media gives 12% higher CPC content in biomass.

Acknowledgements

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3D bioprinting of inorganic/organic composite systems for bone tissue regeneration: review

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Every year, the number of people suffering from bone diseases and injuries drastically increases due to the accelerating population aging and increased life expectancy. Thereby, bone has been ranked as the second most transplanted tissue after the blood. Three dimensional (3D) printing technologies have opened new opportunities for the production of complex geometric scaffolds for bone defect repair and the possibility to combine various biomaterials, biomolecules and cells. Therefore, increasing efforts have been focused on the development of novel (3D) bioprinted scaffolds for bone tissue regeneration [1]. The main advantages of 3D bioprinted calcium phosphate (CaP)/biopolymer scaffolds are that organic/inorganic composition and ratio can satisfy the requirements for bone tissue engineering. The most used bioinks for 3D bioprining are hydrated 3D networks of biopolymers known as hydrogels. Biopolymers such as alginate, chitosan, collagen and hyaluronic acid exabit better biological performance for cell differentiation and proliferation than synthetic polymers (polylactic acid, polycaprolactone, e.c.). However, synthetic polymers have better mechanical properties and degradation rate than biopolymers [2]. To overcome poor mechanical properties, improve bioactivity, and increase bone tissue regeneration effectiveness, biopolymers can be combined with cell cultures (gEPCs, gBMSCs, nBMSCs, hMSCs, 3T3-E1, MC3T3-E1, e.c.) and CaP (biphasic calcium phosphate, hydroxyapatite and calcium-deficient hydroxyapatite, e.c.) to fabricate 3D bioprinted bone scaffolds. Up to now, the most attention has been paid to the cell-laden CaP/alginate composites for bone tissue regeneration. Despite the intensive studies on alginate application as a bioink, recently, Demirtas et al. [3] proposed cell-laden chitosan/CaP hydrogels. Obtained results demonstrated that the cell proliferation rate in chitosan/CaP hydrogels was significant higher ($p < 0.05$) than in alginate/CaP hydrogels [3]. This study notably reviled that the variety of bioinks might help the researchers to drive 3D printing technologies towards the medical applications. Thus, combinations of different biomaterials and biopolymers are required to develop advanced bioinks for 3D bioprinting in bone tissue engineering applications.

Acknowledgements
The authors acknowledge financial support from the Latvian Council of Science research project No. lzp-2019/1-0005 “Injectable in situ self-crosslinking composite hydrogels for bone tissue regeneration (iBone)” and European Union’s Horizon 2020 research and innovation programme under the grant agreement No 857287.

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Tree barks as a source of natural dyestuffs

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Dyeing textiles with natural dyes is now becoming more relevant in the context of the sustainable development and renewable resources. The number of studies on natural dyes has grown significantly over the last years. These dyes have been used for centuries to produce colours for yarns, textiles and leather. Natural colourants are biodegradable, non-toxic, non-carcinogenic and less allergenic than synthetic dyes [1].

Natural dyestuffs can be found in diverse species of plants: leaves, seeds, flowers, barks, roots, etc. The popular dye trees of Latvia summarized in the listing of plant dyes are: black alder (*Alnus glutinosa*), grey alder (*Alnus incana*), silver birch (*Betula pendula*), juniper (*Juniperus communis*), alder buckthorn (*Frangula alnus*), pedunculate oak (*Quercus robur*), bird cherry (*Padus avium*), aspen (*Populus tremula*), European crab apple (*Malus sylvestris*), ash (*Fraxinus excelsior*) [2, 3]. The first publications about plant dyestuffs, including alders, oaks and birches appeared in the Latvian press at the end of the 19th century. Dyes from tree barks and mordants create a wide colour range from yellow to brown, reddish, grey and black [3- 6].

The study will present the results of chemical analysis of mass spectrometry, evaluating the content of the dyestuffs in *A. glutinosa, A. incana, B. pendula, Q. robur* and *P. avium* barks dyeing solution and in nowadays dyed woollen yarn. The yarn was premordanted with aluminium potassium sulfate and dyed with fresh and dried barks of the trees. The dyestuffs from yarn were extracted using acid (hydrochloric, formic and acetic acid) hydrolysis. The extracts were analysed by ultra performance liquid chromatography coupled with diode array detector and mass spectrometry (UPLC-DAD-MS) for identification of the dyestuffs.

Supervisor: Dr.chem. Liāna Orola

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Injectable, porous, osteoinductive calcium phosphate cements in patent literature

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Scientific publications are not the only source, where to look for new developments in a particular field of interest.

Recent patents with grant date or patent applications with earliest priority date starting from 2017 were chosen, searching in Espacenet by keywords ‘injectable calcium phosphate’, ‘injectable osteoinductive porous calcium phosphate’ and ‘porous calcium phosphate’. Search results were evaluated, and most relevant documents are reviewed in this study.

Effect of nanodisperse powder particles on the formation of single-phase titanium nitride material

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Titanium nitride (TiN) is today widely recognized as one of the most interesting engineering materials of ceramics due to its unique chemical and physical properties. This is due to the high melting temperature (2950 ºC) of TiN, good thermal and electrical conductivity, high hardness, good thermal stability, perfect chemical stability in both acid and alkaline, low friction coefficient, wear resistance and low adhesion to metals, excellent oxidation resistance and beautiful gold color. All this makes it interesting for some possible industrial applications. Due to the strong covalent bond, the very low self-diffusion coefficient for mass transport and the tendency to decompose at high temperatures, titanium nitride is difficult to completely sinter without additives. The reasons why the sintered pure TiN is rarely used are the low consolidation activity of the microcrystalline TiN powders obtained so far, and the brittleness and low mechanical strength of the monolithic material. Newly developed nanocrystalline TiN powders offer a very promising opportunity to produce dense TiN materials at lower temperatures. In addition, nanosized TiN powders can lead to ceramic fine grain microstructures with improved mechanical and tribological properties. The use of nano-sized powders allows the samples to be sinter at a lower temperature (1300 to 1500 ºC).

In this work the effect of TiN particle size on its sintering and properties using nanodispersed (average particle size 40 nm) and micrometric dispersion TiN powders is studied. Sintering was carried out on a SPS machine (Sumitomo) at 1600 ºC with a temperature rise rate of 100 ºC/min. Sintering studies have shown that the density of the sample obtained using mixtures of both powders is higher than in the case of pure raw materials. In addition, samples with 30% by weight of nanopowder have the highest density. In contrast, the hardness of the samples reaches the highest values at 50-80% by weight of the nanopowder. The grain size is also the smallest for samples containing 30-70% by weight of nanopowder.

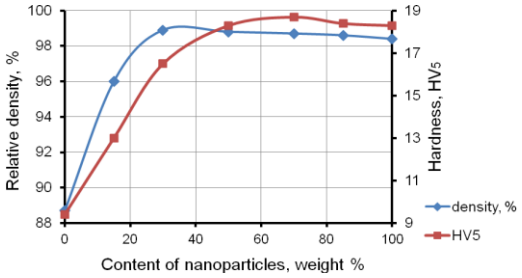

Figure 1. Density and hardness of TiN ceramics depending on nanoparticle content.

An explanation of this phenomenon is offered in this work.

Plasticization and properties of microbiologically synthesized polyhydroxyalconate

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In recent years, numerous research works have focused on valorisation of organic waste for production of biodegradable polymers. Materials derived from renewable sources containing polysaccharides, lipids, and proteins can be consumed by microorganisms, especially by bacteria, in order to obtain monomers such as hydroxyl alkanoic acids, which can be later converted to polymers or copolymers.

In this work, improvement of mechanical properties in biodegradable materials was obtained by incorporation of natural and biodegradable plasticizer triethyl citrate (TEC) into poly(hydroxybutyrate-co-hydroxyvalerate) (PHBV) copolymer. PHBV is a promising bio-based, biodegradable polymer for replacing synthetic polymers, but brittleness limits its application range. Due to PHBV low elongation, the material was plasticized. Production of plasticized PHBV films was performed by two-roll milling followed by compression molding. Plasticization of the copolymer was efficient in improvement of the mechanical properties of the resulting material. It was observed that plasticization by TEC made processing easier as well allowed to reduce processing temperature.

Obtained PHBV compositions were tested to evaluate mechanical, thermal, rheological, and physical properties using tensile testing, differential scanning calorimetry (DSC), thermogravimetric analysis, density analysis, rheometry, melt flow index measurements, water vapor sorption/desorption analysis.

The formulation with 30 weight % of TEC was the most effective demonstrating 49 % increase of ultimate elongation. Concomitant, reduction of elastic modulus and stress were by 83 % and 21 % respectively. DSC analysis showed that by adding plasticizer, the polymer melting point shifted to the direction of lower temperatures. Melt flow index of the plasticized PHBV composites at maximum TEC content was four times higher than for neat PHBV; consequently, viscosity decrease was observed along with rising TEC content.

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Eggshell derived amorphous calcium phosphate and its densification

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Chicken eggshell is a typical example of product-specific waste in the food processing industry. High content of calcium (380 mg of calcium/gram) makes it an attractive precursor material for the synthesis of calcium phosphates that can be used in bone regeneration applications. So far, the use of chicken eggshells for synthesis of amorphous calcium phosphate has received little attention, although the presence of biologically relevant ions (such as Sr^{2+} and Mg^{2+}) in chicken eggshell could allow to obtain amorphous calcium phosphate with high stability. In the present study, we synthesized amorphous calcium phosphate by using eggshells as a source of Ca2+ ions and investigated the possibilities to densify the obtained amorphous calcium phosphate powder. First, eggshells were thermally processed to obtain CaO. Then, CaO suspension in water was prepared to which 4.76 M orthophosphoric acid was added. Afterward, 3 M HCl was added to the synthesis solution to dissolve the precipitates. Finally, 2 M NaOH aqueous solution was rapidly poured into the synthesis media to induce precipitation of the amorphous calcium phosphate. Precipitates were washed with deionized water in a vacuum filter and later lyophilized. Densification of the synthesized powder was done at different pressures (≥500 MPa) by automatic hydraulic laboratory press (pressing die with an inner diameter of 13 mm was used). The synthesized material and the samples made from it were characterized by X-ray diffraction (XRD), as well as their densities were determined. XRD data showed that amorphous calcium phosphate was successfully synthesized (Figure 1.a). After densification the samples retained amorphous calcium phosphate phase. Amorphous calcium phosphate ceramic samples with relative density >75% could be obtained.

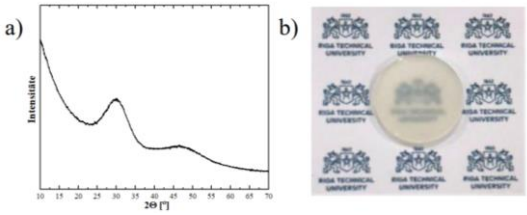

Figure 1. a) XRD pattern for synthesized ACP; b) densified sample.

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The authors acknowledge financial support from the Baltic Research Programme project No. EEA-RESEARCH-85 "Waste-to-resource: eggshells as a source for next generation biomaterials for bone regeneration (EGGSHELL)" under the EEA Grant of Iceland, Liechtenstein and Norway No. EEZ/BPP/VIAA/2021/1.

The application of aromatic interaction promoting groups for modulation of emission properties of heteroleptic iridium (III) complexes.

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Since the first reports two decades ago,[1] iridium(III) complexes have become the leading commercialized material class as the emitters in organic light emitting diode (OLED) technology. Despite the extensive research in alternative structural approaches that avoid the use of the expensive Ir metal, the performance characteristics and longevity of devices are currently unmatched. One of the fundamental drawbacks of the Ir(III) complexes are their susceptibility to the concentration quenching. This limits the attainable complex mass content in the emitting layer of OLEDs and may lead to a reduced device performance due to the phase separation processes in guest-host systems. Recently we have demonstrated that this drawback can be reduced by intramolecular stacking between an inert auxiliary group and the complex core, which provides a buffer layer at the molecular periphery and limits concentration quenching.[2]

In attempt to exploit this principle and potentially acquire vacuum-depositable materials with similar stacking ability, we have synthesized a series of novel Ir(III) complexes and measured their photophysical properties in solutions and films. These compounds feature phenyl or pentafluorophenyl substituents that are expected to take part in aromatic interactions. X-ray structure of one structural example indeed shows a stacking process (Figure 1). In this case stacking proceeds not intramolecularly, but intermolecularly, and a formation of a dimer is observed. This effect is considered as the origin for transformed emissive properties of the compound.

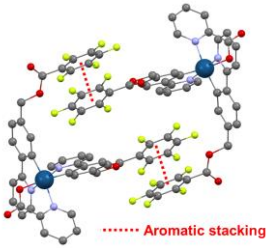

Figure 1. Dimer structure of the synthesized Ir(III) complex.

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Additives for hemp shive boards to decrease water absorption

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In the search for opportunities to create new ecological materials from agricultural production residues, hemp shives have been identified as a valuable resource in achieving this goal[1]. Hemp shives are researched as filler material to produce board materials for building and furniture industry[2]. The article presents research of such hemp shive board interaction with water. A total of 18 different board samples were produced consisting of hemp shives or milled hemp fibres, urea-formaldehyde binder and various colour and antiseptic additives. Samples are made using cold pressing technology by pressing mixture of components to 19 mm thickness and 280-300 kg/m^3 density.

Application of additives were done in two stages by either pre-treating hemp and drying before mixing them into moulding mass or by adding the component during mixing process.

To determine most durable samples water absorption test was performed according to LVS EN 317 standard[3]. 50 x 50 mm board samples were immersed into clean, still water and measurement for thickness and weight were obtained after set amount of time. Period until total structural disintegration was compared between sample groups to determine best hemp and additive combination.

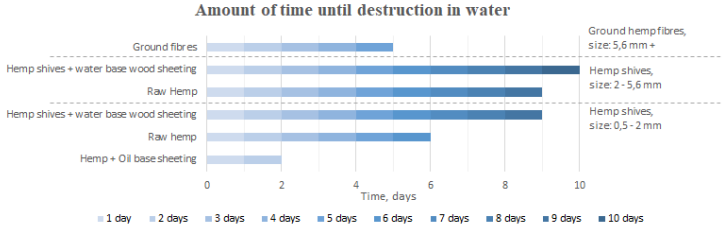

Figure 1. Amount of time until sample destruction in water.

Most water absorption occurs during first 5 minutes of material immersion. After 15 minutes the mass of raw hemp shive material increases 3 times. Samples with additives after same amount of time increase their mass properties only 2 times. Swelling in thickness is reduced by 35% for samples with additives in contrast to raw samples. Also, material structural integrity increases by either using coarse base material or using additives to the mixture (see figure 1). After concluding the tests, it was deemed that separating the process of additive application and using binding agent produces better results but consumes more time. Additionally, additives with colour pigments allows to produce better looking textures which was unintended benefit to material.

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