Riga Technical University

Faculty of Materials Science and Applied Chemistry

64th International Scientific Conference of Riga Technical University

Materials Science and Applied Chemistry

Program and abstracts







Program

9.00–9.10		Opening and welcome addresses Prof. Māris Turks , Riga Technical University, Latvia
9.10-9.30 PL-1	Res.	Chemists, Educated in Riga in the Last 160 Years Walden Medal Awardee Prof. <i>Alīda Zigmunde</i> Riga Technical University, Latvia
9.30-9.50 PL-2		Paradigm Shift in Sintering of Calcium Phosphates and their Composites Walden Medal Awardee Prof. <i>Jānis Ločs</i> Riga Technical University, Latvia
9.50-10.35 PL-3		TKX-50: a New High Explosive Developed at LMU Munich Prof. Thomas M. Klapötke Ludwig Maximilian University of Munich, Germany Baltisch-Deutsches CCHSCHULKONTOR

10.40-11.10

Coffee break



RISEus2 Session: Final RISEus2 Conference (Zunda krastmala 8-108) Session Chair: Prof. Jānis Ločs





Adsorption onto Apatitic Calcium Phosphates for Drug Delivery: toward the Development of Biomaterials with Local Activity

Assoc. prof. *Stéphanie Sarda* Institut National Polytechnique de Toulouse CIRIMAT, France

11.30–11.50 PL-5



The Role of CaP Biomaterials in Maxcilo-Facial Surgery

Dr. rer. nat. **Anja Heselich** Frankfurt Orofacial Regenerative Medicine Laboratory, Goethe University Frankfurt, Germany

11.50–12.10 PL-6



How Bioreactors can be used for Biomaterial Development and Evaluation?

Prof. *Mauro Alini* AO Research Institute Davos, Switzerland

12.10–12.30 PL-7



Cells Compartmentalization to be used in Bone Tissue Engineering

Prof. *João F. Mano* Chemistry Department of the University of Aveiro, Portugal

12.30-13:50

Poster Session (Zunda krastmala 8-107/108)

Materials and Technologies for Cybersecurity Session (Zunda krastmala 8-107) Session Chair: Prof. Sergejs Gaidukovs

11.10–11.30 PL-8



Enhanced Electromagnetic Protection and Cybersecurity through Field-Deployable Innovative Shielding, Monitoring and Data Destruction Technologies

Prof. *Sergejs Gaidukovs* Riga Technical University, Latvia

11.30–11.50 PL-9



High-Performance EMI Shielding Materials and Structures

Miks Bleija, Oskars Platnieks Riga Technical University, Latvia

11.50–12.10 PL-10



Thin sheet material electromagnetic shielding effectiveness testing using 3D printed test setup

Eduards Lobanovs, Gatis Šūpols Institute of Electronics and Computer Science, Latvia

12.10–12.30 PL-11



Indoor Localization Applications for Data Protection

Pēteris Paikens, Krišjānis Nesenbergs, Kirils Solovjovs Institute of Electronics and Computer Science, Latvia

12.30-13:50

Poster Session (Zunda krastmala 8-107/108)

Oral Presentation Session 1: Biomaterials Research (Zunda krastmala 8-108) Session Chairs: Assoc. Prof. Kristaps Kļaviņš, Leading Researcher Jana Vecstaudža

13.50-14:00 OC-1



Development of Nanocomposite Double Network Hydrogel

Abhishek Rajesh Indurkar Riga Technical University, Latvia

14.00-14:10 OC-2



Octacalcium Phosphate and Doxorubicin Hydrochloride: Novel Drug Delivery System for Cancer Treatment

Ilijana Kovrlija Riga Technical University, Latvia

14.10-14:20 OC-3



A Direct and Feasible Method for the Preparation of Octa Calcium Phosphate

Rajan Choudhary Riga Technical University, Latvia





Exploring the mechanism Of PLL/HA Hydrogel Cytotoxicity

Jingzhi Fan Riga Technical University, Latvia

14:30-14:40 OC-5



Highly Porous Hybrid Scaffolds for Local Delivery of non-Antibiotic Antimicrobials

Līga Stīpniece Riga Technical University, Latvia **14:40-14:50** OC-6



Injectable Nanoparticle-Hydrogel Composites for Bone Regeneration

Anna Rubīna Riga Technical University, Latvia

14:50-15:00 OC-7



Exploring Platelet-Rich Fibrin Microstructure and Histology: with and without Hydrogel Carriers

Karina Egle Riga Technical University, Latvia





Calcium Phosphate Bone Cements for Doxorubicin Delivery

Estere Oseļska Riga Technical University, Latvia

15:10-15:20 OC-9



Revealing Physicochemical and Antibacterial Properties of Chemically Coupled ε-Polylysine/Hyaluronic Acid Hydrogels

Artemijs Sceglovs Riga Technical University, Latvia Oral Presentation Session 2 (Zunda krastmala 8-107) Session Chair: Doc. Oskars Platnieks

13.20-13:30 OC-10



High-Voltage Dual-Electrolyte Zn-MnO₂ Battery Enabled by PAM Hydrogels

Ramona Dūrena Riga Technical University, Latvia

13.30-13:40 OC-11



Wood Mimic Compsoites from Cellulose, Hemicellulose and Lignin

Sergejs Beļuns Riga Technical University, Latvia

13.40-13:50 OC-12



Weathering Investigations of Bio-Based Resin 3D Printed Samples

Anda Barkāne Riga Technical University, Latvia

13.50-14:00 OC-13



Lamination of Bio-Based Films xith Sprayed-on Cellulose for Sustainable Packaging

Mārtiņš Nābels-Šneiders, Riga Technical University, Latvia

14:00-14:10 OC-14



Development of Graphene-Containing Kevlar Fabric Coating *via* Liquid Exfoliation of Graphite

Laimdota Vilcēna, Riga Technical University, Latvia

14:10-14:20 OC-15



Research of Soft Ballistic Vests Panels and their Constructive Compliance with Regulatory Documents

Dana Barkāne, Riga Technical University, Latvia

14:20-14:30 OC-16



Use of the Martindale Tester in Determining the Triboelectric Properties of Textile Materials

Evelīna Mileika, Juris Blūms, Riga Technical University, Latvia





NMR Studies of 6-Aminosubstituted Pyrido- and Pyrimido-[1,2-*a*]benzimidazole-8,9-diones

Anastasija Gaile, Riga Technical University, Latvia

14:40-14:50 OC-18



Investigation of the Sulfonyl Group Dance for the Synthesis of 4-Azido-6,7-dimethoxy-2-sulfonylquinazolines

Dāgs Dāvis Līpiņš, Riga Technical University, Latvia

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Plenary lectures



PL-4

Adsorption onto apatitic calcium phosphates for drug delivery: toward the development of biomaterials with local activity

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Calcium phosphates with apatitic structure (or apatites) constitute the mineral part of calcified tissues in vertebrates such as bone. Interfacial properties of apatitic calcium phosphate play an important role in living organisms for biomineralization processes and biomaterials devices. Generally, the adsorption of biomolecules on apatites is considered to electrostatic interactions, but the study of the adsorption of various active molecules such as proteins or bisphosphonates on such surfaces seems to follow a similar pathway. The adsorption process can be generally well described using Langmuir isotherms, and studies of the adsorption reaction reveal, in most cases, an ion exchange mechanism involving the replacement of mineral ions of the apatite surface by molecular ions from the solution. However, the mechanism of adsorption depends on several parameters such as the chemical structure of the biomolecule or the properties of apatitic surface. Considering biomimetic apatite nanocrystals, variations of the adsorption parameters are observed depending on the composition and maturation time of the nanocrystals. Such surface properties can be exploited for the development of drug delivery system using apatite-based multifunctional materials, highlighting the important role of the surface.

The role of CaP biomaterials in maxcilo-facial surgery Anja Heselich

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In oral- and maxillio-facial surgery a broad variety of defects, especially intrabony defects are presented to the surgeon, ranging from small tooth extraction defects to trauma defects and to most challenging tumor defects. Often natural healing, especially in larger defects is not possible, or far too weak to allow for efficient restauration and regeneration. Bone transplants from healthy donor sites to the defect can be an option, however these will then present a secondary defect with a chance for unwanted morbities and for additional burden to the patient. In many cases such an option is not given at all. Bone substitute CaP-based biomaterials offer a highly valuable option for regeneration of such defects, but for efficient application the physico-chemical properties of have to be kept in mind to achieve the right balance for guided bone regeneration.

PL-6

How bioreactors can be used for biomaterial development and evaluation?

Mauro Alini

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Advanced biomaterials and tissue engineered constructs have been developed to improve tissue repair; nevertheless, their clinical translation has been hampered, also by the lack of reliable in vitro models suitable for pre-clinical screening of new implants and compounds mimicking the in vivo situation. Tissue regeneration is strongly influence by the mechanical properties and behavior of biomaterials, which can be completely different when tested in "isolation" or in a biological context. Therefore, it is important to evaluate the performance of such advance biomaterials in in vitro models, which reproduce closely the in vivo tissue status. To such end, we have developed several complex organ models (cartilage, intervertebral disc, bone, etc.) which include, not only the tissue part, but the tissue is cultured within a bioreactor, reproducing loading patterns like the in vivo microenvironment. Here, we will focus on bioreactor systems that transmit a mechanical stimulus, as this is a key parameter in the homeostasis of various musculoskeletal tissues, such as bone, cartilage, tendon, and intervertebral disc. By testing regenerative therapies under conditions that are closer to the ones encountered in vivo, bioreactors can provide a useful screening tool and standardization opportunities for the evaluation of various biomaterials, but as well as cell types, drugs, or tissue engineered products. This will allow to reduce the number of samples for the final in vivo evaluation, allowing the 3R philosophy approach to be implemented.

Cells compartmentalization to be used in bone tissue engineering

João F. Mano

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Bioinspired engineered microenvironments provide cells with a holistic "instructive niche" that offers the adequate entourage for cellular control both in space and time. We have been proposing different strategies of generating microtissues with well defined combinations of cells and biomaterials that could be then assembled into larger constructs for tissue engineering applications. Examples from our group are presented, including: (i) cell-rich systems, either cell-stamps obtained by magnetic force based-tissue engineering; (ii) ultrathin microparticles able to self-assemble with cells to form miniaturised tissues; (iii) cell encapsulation in liquified capsules with thin biomaterials shells for the autonomous development of microtissues. In particular examples on the recreation of adequate ecosystems for cells to develop bone-like engineering microtissues will be highlighted. Such elements can be used as building blocks to be assemble into large constructs to produce macroscopic tissues using bottom-up tissue engineering methodologies.

PL-10

Thin sheet material electromagnetic shielding effectiveness testing using 3D printed test setup

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For material electromagnetic shielding effectiveness (SE) measurements in frequency range from 30MHz to 1.5GHz ASTM D4935-18 standard is used. ASTM D4935-18 standard describes SE measurement methodology for thin sheet materials. The standard SE tester has multiple shortcomings, for example, the cost which arises from the sheer size of material and the amount that needs to be processed as well as the complexity and the unclear characteristics of the design¹.

To overcome the stated shortcoming, we proposed and tested the design of a 3D printed SE tester. SE tester consists of two parts of flanged coaxial line with air dielectric. Signals are fed through N-type female coaxial connector internally after the connector, a transition from Teflon (or polyethylene) dielectric coaxial cable to air dielectric coaxial is formed. To improve the accuracy of material measurement, it is necessary to measure a larger sample area. To achieve this the narrow coaxial gradually changes to a wider one while maintaining impedance of 50 ohms. Coaxial extension determines the highest measured frequency, which is around 1.8 GHz.

R&S ZNB20 vector network analyzer (VNA) (Fig. 1, left side) was used in SE measurement test setup. With its help it is possible to measure the S parameter matrix from which the SE parameters are determined. Multiple types of material shielding properties were tested- globular composites with PBS/PBSA + MWCNT, dispersed composites and nanopapers. Results are shown in Figure 1 (right side). From these SE measurements results the materials combinations will be used to create an electromagnetic shielding enclosure.

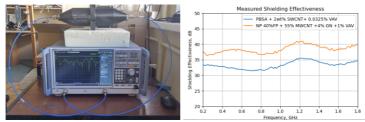


Figure 1. Test setup and SE result of measured materials

Acknowledgements. This work was supported by the Latvian State Research Project no. VPP-AIPP-2021/1-0007 "Enhanced electromagnetic protection and cybersecurity through field-deployable innovative shielding, monitoring and data destruction technologies (EMCFieldShield)".

References

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Oral communications



OC-1 **Development of nanocomposite double network hydrogel**

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This study aimed to overcome the mechanical limitations of single-network hydrogels for bone and tendon regeneration applications by developing a stretchable double network (DN) nanocomposite hydrogel. The hydrogel was created through the combination of gelatin methacrylate (GELMA), polyacrylamide (PAM), Pluronic's P123, and citrate-stabilized amorphous calcium phosphate (ACP_CIT). Crosslinking was achieved using ammonium persulfate and N,N,N',N'-tetramethylethylenediamine. The optimization process involved adjusting the P123 concentration in the PAM-GELMA hydrogel, with the best-performing DN hydrogel containing 7.5 w/v% P123. Subsequently, nanocomposite DN hydrogels were developed by incorporating 0.75 w/v% ACP_CIT, which resulted in improved mechanical properties compared to the pristine DN hydrogel. These enhancements included increased Young's modulus, tensile strength, and elongation at break. Furthermore, the viscoelastic properties of the optimized nanocomposite DN hydrogel showed improved flexibility and resistance to deformation over time. Both hydrogel types were designed to support cell encapsulation, with in vitro analysis confirming their cytocompatibility with MC3T3-E1 cells, suggesting their potential utility in bone tissue engineering.

Acknowledgements. The authors acknowledge financial support from the European Union's Horizon 2020 research and innovation program under grant agreement No. 857287 (BBCE) and 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.

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Octacalcium phosphate and doxorubicin hydrochloride: novel drug delivery system for cancer treatment

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Introduction: Over the past few decades, researchers have delved into the potential of octacalcium phosphate (OCP) as a highly efficient drug delivery system (DDS). The rise in cases of malignant bone tumors, coupled with the demand for fine-tuning localized drug delivery, necessitates that the exploration of innovative DDS options be enriched with fresh combinations. Due to its unique composition featuring interlayered apatite and water levels, OCP offers an elegant avenue for drug integration. Consequently, doxorubicin hydrochloride (DOX) was selected as a model drug for investigation. Despite the growing array of drugs loaded onto OCP, there has been a lack of assessment regarding the *in situ* incorporation of DOX and its aftermath. Hence, the primary objective of this study was to ascertain the feasibility of incorporating DOX into OCP. Furthermore, the study aimed to elucidate the impact of DOX on structural changes of OCP, as well as to determine the kinetics of drug release.

Methods: 100 mg of α -TCP and 1, 5, 10, 20 wt% of DOX were added *in situ* into 50 mL of 0.0016 M H₃PO₄, for 24 h at 22°C, under unremitting stirring. The products were centrifuged and dried overnight (37°C). To corroborate the OCP phase, X-ray powder diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR-ATR) were employed. DOX release profile was determined by infusing the DOX-OCP in phosphate buffered saline (PBS), for 42 days. DOX content in PBS was verified using ultraviolet–visible spectroscopy (UV/VIS) at λ =480 nm.

Results: Phase composition and chemical composition of all DOX-OCPs, was confirmed by the XRD and FTIR. However, above 10 wt% (theoretical loading) of DOX, OCP formation was inhibited. Finally, from used 10 wt% of DOX, only 2 ± 0.6 wt% was incorporated into DOX-OCP, possessing the drug initial burst release in the first 2 h (16±1%), and reaching 38±2% DOX release after 42 days.

Acknowledgments. The authors acknowledge financial support from the European Union's Horizon 2020 research and innovation programme under the grant agreement No. 857287 (BBCE – Baltic Biomaterials Centre of Excellence) and from the EU's Horizon 2020 research and innovation programme under the GA No.860462 (PREMUROSA).

Highly porous hybrid scaffolds for local delivery of non-antibiotic antimicrobials

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Antibiotics are considered the most successful treatment option for bacterial infections. However, their effectiveness is reduced due to antibiotic-resistant pathogens. Thus, the choice of antimicrobials is essential to avoid bacterial resistance. Biomaterials with protection against multidrug-resistant bacteria offer a promising approach to preventing infections. Thus, the aim was to obtain multifunctional scaffolds mimicking the microstructure of trabecular bone for local delivery of non-antibiotic antimicrobials – antibacterial metal ions and bacteriophages and for bone regeneration.

Porous Ag- and Ag-/Ti-containing β-tricalcium phosphate (β-TCP) scaffolds were prepared as follows: (1) porous hydroxyapatite (HAp) scaffolds (substrates) were prepared by polyurethane foam replica method and sintering at 1300°C; (2) Ag- and Ag-/Ti-containing calcium-deficient HAp nanopowders were synthesised by wet chemical precipitation method and coated on the substrates by vacuum-assisted impregnation followed by sintering at 900°C. The Ca-alginate/lytic *S.aureus* bacteriophage coatings were applied on the porous bioceramic scaffolds by vacuum-assisted impregnation. The obtained scaffolds were characterised by XRD, FTIS, SEM, *etc.* Release of the antimicrobials was assessed in TRIS-HCl buffer (pH ~7.4). *In vitro* bioactivity was assessed in SBF. Antibacterial activity against *S.aureus* (ATCC 25923) was determined using the bactericidal assay. The lytic activity of the bacteriophages was determined using the plaque assay. Cytotoxicity using the Balb/c 3T3 and L929 cell lines was assessed. Cell proliferation using the MG-63 osteoblasts was evaluated.

Interconnected porous structure (porosity 92±2%, pores size 50-450 μ m) was observed for the scaffolds without and with coatings. The Ag- and Ag-/Ti- β -TCP scaffolds showed antibacterial activity against *S.aureus* and gradual release of the Ag⁺ ions for up to 28 days. Lytic activity of the *S.aureus* bacteriophages embedded in the Ca-alginate coatings and release of the bacteriophages at >10⁴ PFU/mL titer for up to 72 h was observed. *In vitro* bioactivity, *i.e.*, the ability to induce the formation of the biomimetic apatite layer, cell viability and biocompatibility, was observed for all compositions.

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Injectable nanoparticle-hydrogel composites for bone regeneration

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Osteoporosis leads to bone fractures and irregular bone defects. Current treatments, such as bone grafts and implants, have limitations like availability issues, disease transmission, infection, and brittleness. We need innovative, injectable, antibacterial biomaterials to address osteoporotic bone defects.

The aim of this study was to synthesize and characterize composite hydrogels based ε -polylysine (ε -PL), hyaluronic acid (HA), and strontium substituted hydroxyapatite nanoparticles (Sr-nHAp), and to evaluate, which of the 8 proposed compositions are most suitable for filling osteoporotic bone defects.

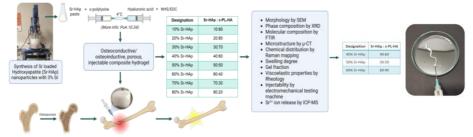


Figure 1. Composite hydrogel synthesis and characterization (made with biorender.com).

Injection force of all 8 composite hydrogel compositions did not exceed 30 N - the accepted limit of manual injectability. However, syneresis of the fabricated composite hydrogels decreases with increasing Sr-HAp concentration. Thus, ϵ -PL-HA/Sr-nHAp composite hydrogels with 60:40, 50:50, 40:60 and 30:70 wt% were further evaluated.

Rheology measurements revealed that all of the selected composite hydrogels are shearthinning but only 3 of them (40, 50 and 60% Sr-HAp) are injectable. From these 3 composite hydrogels Sr^{2+} ions were slowly released over 90 days, reaching a concentration, which can facilitate bone growth.

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Exploring platelet-rich fibrin microstructure and histology: with and without hydrogel carriers

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Platelet-rich fibrin (PRF) is a type of platelet concentrate derived from blood without the need for anticoagulants. It contains essential growth factors that enhance tissue regeneration.¹ Platelets in PRF store growth factors that trigger collagen synthesis, cell division, differentiation, and cell migration to the treated area.² In this study, we investigated the structural changes of PRF depending on its combination with hydrogel carrier containing fucoidan (FU) and chitosan (CS). This allow us to understand the importance of PRF incorporation to slow down its degradation, thus providing a longer-lasting delivery of bioactive molecules. PRF was obtained using a low RCF protocol at 600 rpm for 8 minutes. After centrifugation, PRF was collected and 200 μ L of it was added to the FU_CS hydrogels, while pure PRF matrix was used as a control. The study evaluated the microstructure and histology/immuno-histology of PRF matrices and PRF/FU_CS hydrogels. The histology analysis employed a staining protocol involving hematoxylin and eosin. Additionally, CD31 and CD61 markers were utilized to examine the presence of leukocytes and platelets within the PRF network. In addition, the release of bioactive molecules was evaluated using the ELISA method.

The study found that the surface morphology of PRF exhibits a porous fibrous structure. In the case of PRF incorporated into the FU_CS hydrogel, the PRF effectively occupies the hydrogel's pores, creating a network-like structure. A comparison of PRF and PRF/FU_CS hydrogel samples after 3 and 7 days shows a decrease in the number of cells in the PRF matrix. In addition, histology data showed that PRF is still incorporated into the FU_CS hydrogel structure after 7 days. Immuno-histology showed that leukocytes and platelets had reached the central region of the hydrogel matrix and were relatively evenly distributed in the matrix. The effect of platelets and leukocytes on the fibrin mesh, observed in the fibrin region may mean that various blood cells are able to stay in PRF for at least 7 days, releasing cytokines and intended tissue regeneration.

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Calcium phosphate bone cements for doxorubicin delivery

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Every year the number of patients who suffer from musculoskeletal diseases, especially bone cancer, is rapidly increasing. Long-term treatment is needed, which typically involves a multidisciplinary approach, including a combination of surgical procedures and drug chemotherapy. This often negatively affects the health of patients, causing side effects such as neurological disorders and heart diseases as well as the development of drug resistance.¹ Furthermore, after tumour resection a large void remains at the affected bone site that preferably must be filled with an appropriate biomaterial, such as calcium phosphate bone cements (CPCs), due to their ability to induce bone tissue regeneration and, also, to serve as local drug delivery systems. Thus, the aim of this study was to evaluate the influence of the drug addition and the variation of different solid and liquid phase compositions on the physico-chemical properties of prepared CPCs, as well as on the drug release kinetics.

CPCs were prepared by using α -tricalcium phosphate (α -TCP) as a solid phase (synthesized at different temperatures) and 0.5 M and 1 M sodium salt solutions as the liquid phase. Doxorubicin (DOX) was used as an anticancer agent and its amount loaded in CPCs was estimated as 1.5wt % from the solid phase. Obtained cements were characterized using XRD, BET, SEM, Archimedes method and helium pycnometry. The setting time of the prepared CPCs was measured by Vicat needle. The release kinetics of the DOX were analyzed by UV-VIS at λ =480 nm.

The experimental results indicated that addition of DOX affects the setting time and porosity of CPCs, but does not influence the bone cement density. Moreover, setting time of CPCs was affected by both changes in liquid phase molarity and α -TCP synthesis temperature. It was found that the synthesis temperature of the solid phase also affects the composition of the crystalline phase of developed calcium phosphate bone cements. Obtained results revealed that the release of DOX from the CPCs can be controlled not only by varying the solid phase synthesis temperature, but also by changing the molarity of the liquid phase. Therefore, studies showed that DOX-loaded CPCs are able to gradually release the active substance for more than 60 days.

According to the results, DOX loaded CPCs have a potential to be used as porous injectable biomaterials for bone tissue regeneration and drug delivery, however further studies are required in order to establish their efficiency for bone cancer treatment.

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Revealing physicochemical and antibacterial properties of chemically coupled ε-polylysine/hyaluronic acid hydrogel

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Developing of natural polypeptide-based hydrogels with bacteria-resistant antimicrobial activity is of high demand in biomedical field. According to the recent reports^{1,2} we developed hydrogels based on two chemically coupled naturally-derived polymers: polypeptide - ε -polylysine and polysaccharide - hyaluronic acid with promising physicochemical features, antibacterial activity and cell viability.

Full spectra of hydrogel series with ε -PL to HA mass ratios of 40:60, 50:50; 60:40; 70:30 and 80:20 wt% were prepared according to methodology described in previous report.² Conventional steam sterilisation strategy of 20 min cycle at 121°C was used in current study. Physicochemical features were investigated to characterize prepared hydrogels and describe an impact of steam sterilisation. To evaluate *in vitro* antibacterial efficacy, the fabricated ε -PL/HA hydrogels were investigated against broad spectrum of bacteria strains. For *in vitro* cytotoxicity, ε -PL/HA hydrogels were tested on HDFa and Balb/3T3 cell lines.

FT-IR spectra showed no significant changes (p>0.05) in calculated intensities from normalized data of non-sterilised and sterilised curves. Hydrogels show sufficient water uptake ability, achieving swelling equilibrium within 4 hours. Rheological properties revealed materials shear-thinning properties, as well as matrix recovery feature under stress inducing cycles. Extracted stiffness moduli from amplitude sweeps were in the range from 5 to 15 kPa. Antibacterial tests revealed significant bacteria colony reduction within 24 h against all tested bacteria strains. Finally, cytotoxicity tests demonstrated that ϵ -PL/HA hydrogel compositions with 70:30 and 80:20 wt% mass ratios showed a significant reduction in cell viability.

Obtained results were used to get full picture on newly-developed hydrogels as well as defining criteria to find optimal amino acid-to-polysaccharide mass ratio. It was found that e-PL/HA hydrogels of 50:50 and 60:40 wt% showed the most favourable mechanical properties and biocompatibility for developing multifunctional antibacterial and injectable biomaterials for tissue engineering applications.

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High-voltage zinc-manganese dioxide batteries

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As the world moves towards sustainable power sources and tries to eliminate fossil fuels, the scientific community is paying more attention to various battery technologies.¹ Even though lithium-ion batteries are promising, other options will be required.² One such alternative could be improved Zn-MnO₂ batteries.³

Herein, we present a dual-electrolyte Zn-MnO₂ battery with semi-solid electrolytes. Both electrolytes are polyacrylamide-based hydrogels with immobilized pH since the catholyte is acidic and the anolyte is alkaline. In Figure 1a first 200 charge/discharge cycles are represented and over 40 cycles stabilization of the battery can be seen. Afterwards stabilization, the battery can be cycled with a specific capacity of 25 mAh/g with ~100% Coulumbic efficiency as seen in Figure 1b. This immobilized pH gradient is stable for more than 6 days. By applying this dual-electrolyte, the open circuit potential of the battery increases up to 2.4 V and can be charged/discharged several times.

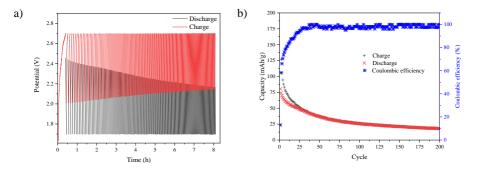


Figure 1. Charge/discharge plot (a) and specific capacity/Coulombic efficiency (b) over 200 cycles.

Acknowledgements. R.D. acknowledges this work has been supported by the European Social Fund within the Project No 8.2.2.0/20/I/008 «Strengthening of PhD students and academic personnel of Riga Technical University and BA School of Business and Finance in the strategic fields of specialization» of the Specific Objective 8.2.2 «To Strengthen Academic Staff of Higher Education Institutions in Strategic Specialization Areas» of the Operational Programme «Growth and Employment».

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Wood mimic composites from cellulose, lignin, and hemicellulose

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The development of sustainable biomimetic materials is imperative in the quest for ecofriendly alternatives to conventional synthetic materials. In this context, wood mimic composites derived from cellulose, hemicellulose, and lignin, the primary components of wood, have garnered significant attention. Cellulose, hemicellulose, and lignin are abundant biopolymers found in plant cell walls, particularly in wood, offering an appealing raw material source for sustainable composites.

The primary focus of this research lies in the extraction and manipulation of cellulose, hemicellulose, and lignin from various biomass sources, such as wood pulp, agricultural residues, and non-wood plants. Subsequently, these biopolymers are combined in controlled ratios to create composites that mimic the structural and mechanical properties of natural wood. Two distinct composite preparation routes were explored: the preparation of wood mimic composite thin films and the preparation of wood mimic lightweight foams. The fabrication process often involved advanced techniques like chemical modification, nanofibrillation, and blending with other biodegradable polymers.

The resulting wood mimic composites exhibit a notable array of properties, including high tensile strength, stiffness, thermal stability, and biodegradability. Moreover, they can be tailored to meet specific application requirements, such as packaging materials, construction components, and sorption or separation materials. Furthermore, the sustainable nature of these composites aligns with the principles of the circular economy and contributes to a reduced carbon footprint. By harnessing the abundant resources of cellulose, hemicellulose, and lignin, this research represents a step forward in the development of environmentally friendly biomaterials, fostering a greener and more sustainable future.

Weathering investigations of bio-based resin 3D printed samples

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Vegetable oil-based resins have been studied to replace petroleum-based resins in UVassisted 3D printing.¹⁻³ However, there have been no efforts in studying their durability to weathering, while coatings have been studied extensively.⁴⁻⁵ This research closes the gap in the bio-based acrylic 3D-printed polymer weathering performance investigation. QUV accelerated weathering was used on 3D-printed vegetable oil-based compositions reinforced with nanofibrillated cellulose (NFC). Discoloration, cracking, FTIR measurements of surface chemical degradation, and mechanical performance were used to characterize materials performance changes during the weathering. NFC reinforcement delays the yellowing and cracking during the weathering. After weathering, increased flexural stress and strain were achieved. Chemical analysis reveals simultaneous photocleavage and additional crosslinking of the macromolecular chains. The glass transition temperature increased during the weathering. NFC introduction in bio-based polymers increased the weathering endurance and mechanical performance. The NFC is compatible with and is a perspective filler for bio-based acrylic resins for 3D printing applications.

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Development of graphene-containing kevlar fabric coating *via* liquid exfoliation of graphite

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Cyrene, an organic biodegradable solvent derived from natural cellulose residues, has been used to create a liquid medium of graphite LPE. It has been established that graphite exfoliation in a single solvent environment at an input graphite concentration of 20 to 25 mg/mL led to the aggregation of exfoliated graphene flakes, the resulting dispersion has weakly bounded to the textile substrate. Addition of the triethanolamine into liquid medium managed to solve 3 problems: a) obtain a stable dispersion of exfoliated graphene flakes, b) provide the ability to regulate the viscosity of the dispersion, c) as a result, it become possible to create a graphene-containing coating on the fibers of para-aramid or cotton fabric.

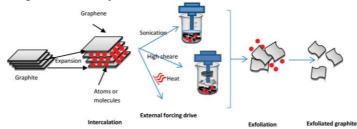


Figure 1. Intercalation and exfoliation process.¹

Looking at various possible options for solving problems, the liquid medium was supplemented with the triethanolamine (TEA), the use of which has not yet been established in combination with polar aprotic solvents. Addition of the triethanolamine into liquid medium managed to solve 3 problems: a) obtain a stable dispersion of exfoliated graphene flakes, b) provide the ability to regulate the viscosity of the dispersion, c) as a result, it become possible to create a graphene-containing coating on the fibres of para-aramid fabric fibres.



Figure 2. Modified para-aramid fabric sample.

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Research of soft ballistic vests panels and their constructive compliance with regulatory documents

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Individual ballistic protection vests (BPV) research is currently being radically updated around the world; as undergarment and outer garment BPV, they are in high demand for both civil and military defence purposes. When designing BPV, including BPV panels, such contradictory tasks as maximum ballistic energy absorption, comfort of the wearer, usability, flexibility of the structure (pattern and design), compliance with regulatory documents and reducing the overall weight of the product have to be solved.

The main functional parts of the BPV are BPV panels and BPV plates which provide protection to the wearer against bullet impacts. An in-depth investigation of the BPV panels construction and assessment of its compliance with the standards of NIJ (National Institute of Justice) Standard-0101.06 "Ballistic Resistance of Body Armor"² was carried out. Although there are a number of regulatory documents that directly address BPV, it is concluded that there is no single methodology for designing BPV panels and BPV for a specific size or range of typical human bodies.

Based on the requirements of standard² for the planar configuration, minimum and maximum size of the BPV panels, and area limit values, two types of BPV panels (outer garment and undergarment) in 16 various sizes (covering body height 160–200 cm, chest circumference 80–140 cm) have been designed.

Considering that the size of the BPV directly affects the mass usability and the physical comfort of the wearer, but the gradation step between the sizes is still quite big—10 cm, further research is planned to solve the adaptability of the sizes for each specific type of figure.



Figure 1. Construction of BPV used for military purposes.¹⁻³

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NMR studies of 6-aminosubstituted pyrido- and pyrimido[1,2-*a*]benzimidazole-8,9-diones

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Quinone-functionalized molecules have a great potential for the construction of organic electrode materials. Additional stabilization of these materials can be provided by the formation of noncovalent interaction network¹ where aminosubstituted quinone derivatives can serve as a platform for investigation. Herein we select pyrido- and pyrimido-[1,2-a]benzimidazole-8,9-diones for modification with primary amines (Fig. 1, a) to explore intra-/intermolecular noncovalent interactions. Obtained compounds showed two notable features in ¹H NMR spectra: low-field signal of NH proton and a broad downfielded signal of the CH₂ group (adjacent to NH) of compounds **3b-g** and **4b** in DMSO-*d*₆ solution (Fig. 1, b).

Chemical shift of NH proton is solvent dependent since it correlated well with β_1 value² (H-bond basicity) of used solvents (DMSO- d_6 , MeCN- d_3 , CDCl₃). Variable temperature studies resulted in linear correlation between NH proton chemical shift of compound **3f** and temperature. Cooling of MeCN- d_3 solution (248 K) of compound **3f** or **3g** revealed the presence of two forms in the solution: with or without intramolecular H-bond.

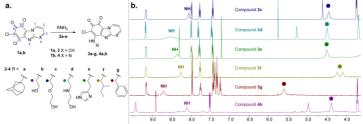


Figure 1. (a) Synthesis of compounds **3a-g** and **4a,b** (b) fragments of ¹H NMR spectra of obtained compounds in DMSO- d_6 solution.

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Investigation of the sulfonyl group dance for the synthesis of 4-azido-6,7-dimethoxy-2sulfonylquinazolines

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Quinazoline derivatives employ a wide range of biological activities. Modified quinazolines are widely used as anticancer, antiviral, and α 1-blocker drugs.¹

We have adapted the sulfonyl group dance, first characterized in the purine class,² to the quinazoline core, and obtained 4-azido-6,7-dimethoxy-2-sulfonylquinazoline derivatives **3** from the commercially available 2,4-dichloro-6,7-dimethoxyquinazoline **1** via two different synthetic pathways (Scheme 1).



Scheme 1. Synthetic approach toward 4-azido-6,7-dimethoxy-2-sulfonylquinazolines 3.

The sulforyl moiety at the C2 position of **4** inverses the reactivity of the quinazoline core in S_NAr reactions, allowing for selective C2 modification, which in literature is mainly done through ring closure reactions (Scheme 2).³



Scheme 2. Synthesis of 4-azido-6,7-dimethoxy-2-aminoquinazoline derivatives 4.

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Obtaining different diameter polystyrene fibres via electrospinning

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The polymer industry is huge, but in comparison very little of polymer waste gets recycled. Considering polystyrene, the percentage of recycling is almost none, so reuse of polystyrene as a functional material is a compelling research topic. The main goal of the project is to develop a triboelectric generator device which consists of recycled polystyrene with different surface properties. As in our previous studies¹ we have shown that charge density of contact separation for the same material, but different surface roughness, surface functionalization or material thickness, in this study we investigate the influence of different electrospun fibre diameters. Herein we present a method to obtain electrospun polystyrene fibres with different fibre diameters. The addition of sodium chloride in the solution for electrospinning aids in generating thinner fibres from more diluted solutions of polystyrene in dimethylformamide and tetrahydrofuran. The SEM images of larger and smaller diameter electrospun fibres is shown in Fig. 1.

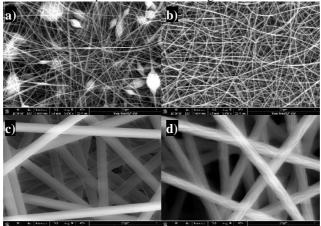


Figure 1. Electrospun polystyrene fibres from 10 wt% solution a) without added sodium chloride, b) with added sodium chloride and from 30 wt% solution c) without added sodium chloride, d) with added sodium chloride.

Acknowledgements. This work is supported by the Latvian Council of Science, project "Development of triboelectric laminates for energy harvesting by recycling waste polystyrene packaging", project No. lzp-2021/1-0603.

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Bio-based polyester blends with clay and chitosan

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The increasing need for alternative materials for packaging is leading to gradual replacement of petroleum-based polymers with more sustainable polymers like bio-based polymers, which can provide the same properties for the final product.¹ More value to bio-based polymers can be added by making composites with other perspective fillers like nanoclay² to improve mechanical and thermal properties and chitosan³ to improve antibacterial properties of the polymer matrix.

The studied bio-based polymer composites consisted from bio-based polyester matrix (NaturePlast) and nanoclay (Nanocor) and chitosan fillers at various wt% concentrations. All composites were prepared by laboratory two roll mills. Samples for physical properties tests were made by compression molding.

Results of mechanical properties revealed that addition of nanoclay filler to the bio-polymer matrix at 1-5 wt% concentration and even chitosan addition at 3-10 wt% increased storage modulus of obtained composites. Similar composites with nanoclay showed higher tear force values in tear tests. Nanoclay and chitosan effect on processing properties showed that both nanoclay and chitosan fillers increase the melt viscosity of bio-based polymer matrix. The obtained results are used for development of anti-bacterial bio-based packaging films.

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Improving the compatibility of vegetable oil resins and cellulose nanocrystal reinforcement

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With the advancements of 3D printing technologies, it is necessary to move towards a more sustainable future and find alternatives for petroleum-based polymers. Cellulose, as the main ingredient of plants, is a sustainable and almost inexhaustible raw material for polymers that can meet the growing demand for environmentally friendly materials.¹ For this purpose, vegetable oil-based acrylates are considered in combination with nanocellulose as a reinforcement. However, there is still room for improvement at the interface between hydrophilic cellulose and hydrophobic polymer matrix.²

In the present work, cellulose nanocrystals (CNC) are modified in an attempt to improve the compatibility between cellulose and the polymer matrix. Seven vegetable oil-based resin formulations suitable for stereolithography (SLA) 3D printing were prepared: with no reinforcement, CNC and five functionalization's of CNC, including acrylation of CNC, graft polymerization with PMMA and a novel approach with suberin fatty acids (SFA) as reinforcement.

The effects of functionalized CNC components on 3D printed sample interface, thermal stability, mechanical properties, and wettability were evaluated in detail. Using SFA functionalized CNC filler for reinforcing polymer matrix enhanced mechanical properties which show great potential for application in 3D printing prototyping.

Enhancing the mechanical properties of a CNC reinforcement polymer matrix with functionalized SFA has considerable promise for use in 3D printing applications. This work emphasizes the numerous opportunities for improving interactions with acrylated vegetable oils utilizing green functionalization of CNC. This creates opportunities for the development of high-performance, eco-friendly UV initiated 3D printing materials.

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PLA-PBS copolymer synthesis

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PLA-PBS copolymer has been proposed as a compatibilizer, plasticizer and nucleating agent for immiscible PLA-PBS polymer blends that would blend the strength of PLA and the plasticity of PBS reducing the brittleness of PLA and increasing the toughness of PBS. Combining two biobased materials into one versatile.^{1,2}

Current work involves PLA-PBS copolymer synthesis approaches and research routes. Herein, we report the synthesis of PLA/PBS with tin ethylhexanoate, titanium butoxide and a combination of both. The synthesis was performed in a one pot synthesis, polymerizing PLA then adding PBS and the other way around. The structure was analyzed and confirmed with NMR. Low molecular mass polymers were produced as determined by their highly viscous liquid state. Chain extension reactions were performed with commercial chain extenders as well as different diisocyanates and a mixture of them producing a variation of polyurethane, polyamide, and polyester copolymers with differing solubilities in convential solvents for PLA/PBS.

The neat copolymer was used as a compatibilizer in neat PLA-PBS polymer mixtures to stabilize the immiscible components and mechanical properties were measured showing an increase in compatibility between PLA-PBS mixtures with copolymer ratio from 2.5-5.0% in 80:20 ratio between PLA:PBS displacing PLA.

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Plant-based meat flavour component (leghemoglobin) production through yeast fed-batch fermentations

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Every year the Earth's population increases rapidly. Therefore, higher demand for resources, especially food production, is beginning to have a severe environmental impact. For example, livestock production causes pollution of soil and water, loss of biodiversity due to extending the agricultural land, soil erosion, as well as greenhouse gas emissions¹.

In recent years environmentally friendly initiatives are gaining popularity and are being taken into account both by the public and by the food industry, for example, vegan and vegetarian diets have become more popular, as the result of environmental and ethical concerns connected to the current meat production systems². The above mentioned problems of traditional meat production systems nowadays drive the development of alternatives to conventional meat, e.g., plant-based meat.

The introduction of hemoglobins or plant leghemoglobins (LegH) is gaining popularity as a sustainable and effective mean of enhancing the taste and aroma of plant-based meat. LegH proteins during cooking create compounds that simulate the characteristic meat taste, thus significantly improving the consumer perception of plant-based meat³. Recent studies have concluded, that economically feasible LegH production can be achieved only by using recombinant microorganism strains and advanced biotechnological methods.

The aim of this study was to develop a suitable medium composition for optimal leghemoglobin production using a recombinant strain of *Komagataella phaffii*. The designed fermentation medium was applied in fed-batch fermentations at lab-scale. A novel model-predictive control (MPC) system was applied to automatically correct and optimize the substrate feeding rate in said fermentations⁴. The developed medium, in contrast to industry accepted formulas, utilizes ammonium salts (rather than ammonium hydroxide), which makes it possible to control the pH and ensure optimal nitrogen levels independently.

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Modification of TiO₂ towards the improvement of its light activated gas sensing properties

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Nowadays more and more emphasis is being put on both environmental and work safety. To achieve this, gas sensors are deployed for the monitoring of air quality for pollutants as well as to detect the leakage of any harmful volatile organic compounds (VOCs). Out of all the gas sensors available, chemoresistive metal oxide semiconductor (MOS) gas sensors are well suited for these use cases due to their combination of long lifetime and stability.¹ One MOS, that has been widely known for its low-cost and low-toxicity, is titanium dioxide (TiO₂). This MOS has been shown to exhibit excellent gas sensor to function. Heating has the downside of being a high-power consumption way of powering the gas sensors, as well as making them prone polymorph changes. Furthermore, heating is also a safety hazard, as it limits the spectra of VOCs that can be sensed with the gas sensor.

In recent years, researchers are putting emphasis on light-activation of these gas sensors, rather than heat. In this case TiO_2 has also been shown previously to be capable of gas sensing even at room temperature and ambient humidity.² However, these sensors showed a slow recovery speed between repeated sensing experiments as well as the ambient humidity range being limited to below 40%, limiting their potential usefulness.

To increase the recovery rate, transition metal doping was employed, to increase the electron concentration achievable in the gas sensors, while also increase the rate of electron scavenging that facilitates the recovery step of the TiO_2 gas sensing mechanism.

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Stimulated UV emission from localized excitons in poly-dispersed ZnO powder

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Modern optoelectronics stimulates the search for new physical principles and approaches to increase the homogeneity of the laser field, which is violated by the negative effect of speckles. The most prospective and reasonable approach to overcome the negative speckles effect is the development of a non-coherent laser. Studies of disordered photonic media (DPM) with strong light scattering and high luminescence efficiency are promising in this direction. One of the suitable DPM is based on the ZnO crystallites.¹ In this work, a comparative analysis of stimulated emission (SE) spectra was carried out depending on the structure type, size of crystallites and their distribution in ZnO powders. Based on the study of photoluminescent (PL) spectra, Raman shift, X-ray diffractograms and SEM, the types of crystalline phases, the sizes of the smallest nanograins and their spatial distribution were determined. It was established that polydisperse nano-micro-crystalline (PNMC) ZnO powder, with crystallite sizes from 50 nm to 2 µm, which, in turn, consist of nanograins with a size of 25 nm. This fact causes the maximum 387 nm UV band in the PL spectrum to be fixed in the entire excitation range. It explains the mechanism of SE by coupled excitons due to the crystalline boundaries preventing the exciton continuum from breaking. The superlinear growth of this band with the simultaneous narrowing of its half-width from 19 to 14 nm indicates an SE with incoherent feedback inherent to random laser² in PNMC powder. The amplification factor was calculated, which was 150 cm⁻¹. Based on the obtained results, it was concluded that the further improvement of incoherent lasers based on ZnO powder involves a transition from 3D to 2D-like systems.3

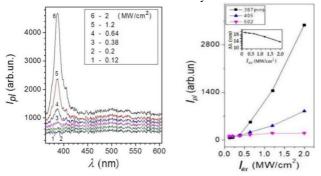


Figure 1. a) Evolution of the PL spectra in the compressed PNMC ZnO powder for different excitation intensities I_{ex} ($\lambda_{ex} = 337$ nm) in the range of 0.12 – 2 (MW/cm²) at room temperature. b) Dependences of the PL spectral bands intensity I_{pl} versus the excitation intensity I_{ex} ($\lambda_{ex} = 337$ nm) for different wavelengths, nm: 387, 405, 502. Insertion: band halfwidth w at 387 nm vs I_{ex} .

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The impact of the various testing methods on the triboelectric properties of modified polystyrene films

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The rapid advancement of the Internet of Things (IoT) is anticipated to drive a rise in the utilization of microelectronic devices. Consequently, there is an increasing demand for ecofriendly energy sources as substitutes for conventional batteries. In recent years, there has been a notable upswing in enthusiasm for polymer-based triboelectric generator (TEG) systems as a viable solution for energizing microdevices. Our objective is to develop a technique for manufacturing triboelectric generators exclusively from a single triboelectric polymer material, as well as establish the best possible testing parameters to obtain the highest and most useful output power. This methodology eliminates the necessity for additional materials and enables the creation of TEG devices using a sole material, namely recycled polystyrene.

Previous studies have demonstrated that enhancing the triboelectric properties of polymer films can be achieved through various surface modifications, encompassing both physical and chemical alterations.^{1,2} Furthermore, when the surface roughness is synchronized with chemical surface functionalization, the power density of the triboelectric generator becomes sufficient to power a compact electronic device.²

First and foremost, in this study, recycled polystyrene films are fabricated, and both their surface physical and chemical engineering are performed. The results show that by aligning both surface engineering methods, the magnitude of the developed triboelectric charge has been amplified nearly tenfold.

Secondly, two different testing equipment was used - dynamic testing machine and highspeed contact-separation system – to test triboelectric generator made of smooth surface PS film modified with VTMS and rough surface PS film modified with APTES. Pneumaticdriven contact-separation provides a higher impact and separation rate, but it comes with the trade-off of limited precision in controlling testing parameters. Results show that best results for energy density can be achieved by using dynamic testing machine, however the use of pneumatic-driven contact-separation device enabled the attainment of power densities significantly higher by an order of magnitude.

Acknowledgements. This work is supported by the Latvian Council of Science, project "Development of triboelectric laminates for energy harvesting by recycling waste polystyrene packaging", project No. lzp-2021/1-0603

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Use of WO₃ as a mediator in hydrogen production *via* decoupled electrolysis

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Hydrogen possesses excellent properties for being used as an intermittent energy storage media or as a syngas. For it to become more accessible and environmentally friendly, electrolysis efficiency and costs must be improved. Only 4% of the world's hydrogen is produced via electrolysis¹.

Here, we demonstrate using WO₃ as a red-ox mediator in decoupled electrolysis. During the intercalation cycle, O_2 is produced on the Pt electrode, and the H⁺ ion intercalates in the WO₃ mediator, forming H_xWO₃. During the intercalation cycle, H_xWO₃ decomposes, and H₂ is released on the Pt electrode to limit gas mixing and exclude the use of polymer membranes². Better materials and production methods are needed to improve decoupled electrolysis efficiency. A way to enhance WO₃ specific capacity is by using lyophilisation and different annealing conditions. Lyophilisation increases WO₃ specific capacity more than two times compared to air-dried samples. Even more, Capacity can be improved by self-doping WO₃ using annealing in an inert atmosphere- N₂. Provided WO₃ samples showed excellent cycle stability of Faradaic efficiency of 98-99% and overall efficiency of 34-58%.

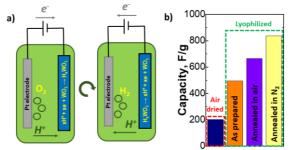


Figure 1. Principle of decoupled electrolysis in acidic media (a) and effect of synthesis parameters on WO_3 specific capacity (b).

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Investigation of by-product of industrial aluminium waste reaction with water

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Aluminium is a versatile material that is being used in a large number of industries, we all have aluminium products near us at all times. Unfortunately, despite conventional assumption, large amount of Al is not recycled rather landfilled; partially due to varying composition and alloying. It is perceived that in the future the purity of Al parts and alloys will pose a substantial problem to true recycling.¹ On the other hand it has been proposed to use aluminum as energy storage material with hydrogen release via metal reaction with water, thus, posing a promising directions of aluminium use to produce hydrogen and heat that can be used for heating and electricity depicted in Fig. 1.^{2,3}

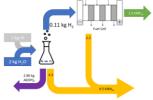


Figure 1. Possible power production form waste aluminium, adapted from Haller et al.²

Then the by-product of the reaction contains aluminium complexes such as aluminium hydroxide, which can be recycled or sold to the aluminium industry. Even though there are many proposed reaction models^{4,5} the investigation of by-product at different low concentration promoter electrolytes have not focused on the quantitative analysis of the by-product. This work aims to quantify the by-product precipitation after industrial waste aluminium shavings reactions with water with various promoters and concentrations.

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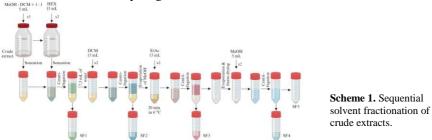
Extraction of marine sponges

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Sponge is an invertebrate, sessile organism that can be widely found in temperate, tropical, and polar habitats and, presently, over 8000 marine sponge species are known.¹ During the past 50 years, more than 9700 chemically diverse novel molecules have been isolated from sponge extracts, representing 30 % of marine molecules discovered to date. Therefore, marine sponges are considered as the most prolific oceanic source of new bioactive substances.²

Extraction of marine sponges. After freeze drying, sponges were grinded and appropriate volume of a methanol/dichloromethane (1:1 v/v) mixture was added (solvent-to-sponge ratio: 20 mL/g). Sponge suspension was then sonicated in ultrasonic bath followed by centrifugation. The supernatant was collected and evaporated to obtain a crude extract. *Sequential solvent fractionation of crude extracts.* Fractionation was carried out according to the scheme 1. The collected fractions were evaporated, redissolved and transferred into glass vials. These were dried to constant mass and dry weight of each fraction was determined.



A total of 44 samples belonging to 13 marine sponge species were extracted and 43 of them were fractionated to obtain 213 fractions. Marine sponge *Axinella verrucosa* showed highest total extraction yield (i.e., 22.74 ± 1.82 %). The lowest yield was 3.25 ± 0.30 %, observed for *Agelas oroides*. Among all analysed sponge samples, the methanol fraction had the highest fraction-to-extract mass ratio, followed by hexane fraction for most species. Ethyl acetate and water fraction showed the lowest fraction-to-extract mass ratios.

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Synthesis methodology and characterization of octacalcium phosphate

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Introduction: The growing occurrence of musculoskeletal disorders and diseases requires the development of innovative materials for bone tissue regeneration. Due to the chemical and structural similarities with the inorganic phase of bone tissue, calcium orthophosphates (CaPs) have been considered as the most reliable and appropriate materials for hard tissue regeneration. Octacalcium phosphate (OCP) is a biodegradable and osteoconductive material that stimulates bone cells and promotes bone regeneration processes.² Because OCP's similarity to hydroxyapatite (HAp) it has a high tendency to transform into it. Moreover, it is presumed to be the precursor of biologically formed apatite.¹ The goal of this study was to obtain a high yield of OCP and to characterize it with a multi-technique approach by XRD, FTIR and SEM, in order to confirm the purity of the obtained phase.²

Methods: To obtain 100 mg of OCP powder, 100 mg of α -TCP were dissolved into 50 mL of 0.0016 M H₃PO₄ solution, with constant stirring at room temperature during the 24 h period. During the synthesis, pH of the reaction medium was monitored. After 24 hours, the collected suspension was centrifuged and dried overnight at 37 °C. Scale-up synthesis were performed by dissolving 1000 mg of α -TCP into 500 mL of 0.0016 M H₃PO₄ solution, with constant stirring at room temperature during the 72 h period. The collected suspension was centrifuged and dried overnight at 37°C. After the synthesis, the obtained powder was characterized by using XRD, FTIR and SEM.

Results: XRD and FTIR confirmed that with the hydrolysis method, both syntheses resulted in OCP crystalline phase – XRD pattern showed a unique low angle maxima at 2θ 4.72 degrees and a doublet at 2θ 9.44 degrees and 9.77 degrees. SEM micrographs revealed plate-like structure corresponding to the OCP morphology (Fig. 1), which was used to distinguish it from HAp's thread like morphology (Fig. 2).



Figure 1. SEM micrographs of OCP phase.

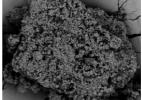


Figure 2. SEM micrographs of HAp phase.

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P-13

Surface modification of activated carbon by oxidation with H₂O₂

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Carbon materials have a widespread application in many fields from electrodes in batteries and capacitors, to adsorbents for environmental remediation, and catalysts in organic chemistry to name a few. Alongside fossil sources like coal this material can also be obtained from a renewable and abundant resource, biomass. Another advantage of this material is the possibility for relatively easy and diverse modification, to change pore volume and surface area, micro-meso pore distribution, elemental composition, graphitic content and surface chemistry.

Carbonization of biomass increases carbon content of the material, making it more stable, conductive, hydrophobic, and gaining other desirable traits. Using activation to increase the porosity of the carbon material leads to further increase in carbon content. However, this increase in carbon content is related to loss of oxygen, which forms the majority of surface groups responsible for such desirable carbon material properties like electrochemical performance and adsorption. One of the methods for carbon modification is oxidation using chemicals like H₂O₂. Oxidation can help reintroduce oxygen back into the carbon materials, thus ensuring oxygen content in the form of active surface groups, resulting in a highly porous and graphitic carbon material that also contains considerable amount of oxygen.

The purpose of this study was to evaluate the role of residence time for oxidation of activated carbon using H_2O_2 . Chemical oxidation of two different activated carbons was performed using 30% H_2O_2 and 5 different residence times. Elemental analysis, FTIR, Boehm titration and thermogravimetric analysis was performed to study the surface chemistry of obtained materials. Changes in morphology after oxidation were evaluated using scanning electron microscopy.

Tribovoltaic performance of TiO₂ thin films: crystallinity, contact metal, and thermoelectric effects

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The Internet of Things (IoT) will connect over 30 billion devices by 2025.¹ These devices require efficient sources of energy, from a combination of energy storage and energy harvesting technologies.² Mechanical energy harvesters have been proposed as ideal candidates to power such IoT devices, harvesting vibrational energy from the urban environment.³ Tribovoltaic (TV) devices are attracting increasing attention as motion-based energy harvesters, due to the high local current densities that can be generated. TV devices are made from solid semiconductor-semiconductor or metal-semiconductor sliding heterojunctions. On sliding, the friction causes the electronic excitations and heating. The induced charges are separated by the built-in electric field and transmitted over the junction. The other driving force for charge separation at the triboelectric interface is thermoelectric power. However, while these tribovoltaic devices are being developed, debate remains surrounding their fundamental mechanism.

Here, we fabricate thin films from one of the world's most common oxides, TiO₂, and compare the tribovoltaic performance under contact with metals (Mg, Ti, Ag, Mo, Zn, W) of varying work functions, contact areas, and applied pressure. The resultant current density shows little correlation to the work function of the contact metal, and a strong correlation to the contact area. Considering other effects at a metal-semiconductor interface, the thermoelectric co-efficient of different metals were calculated, which showed a clear correlation with tribovoltaic current density. On the microscale, molybdenum showed the highest current density of 192 mA cm⁻². This work shows the need to consider a variety of mechanisms to understand the tribovoltaic effect and design future exemplar tribovoltaic devices.

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Development of a graphene-based functional coating for textiles

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The aim of the study is to improve the ballistic properties of para-aramid woven fabrics by applying graphene coatings directly onto the fabric substrates. The improvement of the mechanical properties is achieved by the formation of an ordered layered structure and efficient load transfer between the fabric fibres and the graphene nanosheets.

Dipolar aprotic organic solvents DMAc (N,N-Dimethylacetamide) and Cyrene (Dihydrolevoglucosenone) with added TEA (Triethanolamine) were used to disperse the graphite flakes in a liquid medium, followed by graphite intercalation and nanosheet exfoliation by ultrasonication and sediment removal in a centrifuge. Using two solvents, stable dispersions with isolated nanosheets were obtained and deposited directly onto the fabric substrate using a liquid medium. The parameters for the preparation of the dispersions can be seen in Table 1.

Variant designation	Graphite, wt%	DMAc, wt%	Cyrene, wt%	TEA, wt%	Ultrasonication	Centrifugation
DMAc-TEA1	2*	78	-	20	I 60 min	I 20 min, 272 rad s ⁻¹
DMAc1b-TEA2	25**	60	-	15	II 30 min	II 20 min, 126 rad s ⁻¹
DMAc2b-TEA3	25**	43	-	32	III 30 min	III 20 min, 105 rad s ⁻¹
CIR1-TEA1	2*	-	80	18	I 60 min	I 20 min, 272 rad s ⁻¹
CIR1b-TEA2	25**	-	50	25	II 30 min	II 20 min, 126 rad s ⁻¹
CIR2B-TEA2	25**	-	45	30	III 30 min	III 20 min, 105 rad s ⁻¹

Table 1. Dispersions composition and processing parameters

* Pristine graphite flakes. ** Recovered sediments

To assess the quality of dispersions, particle size and zeta (ζ) potential analyses were carried out to determine their stability using the Anton Paar - Litesizer 500 system.

Coating of the samples was carried out by dipping, rolling and heating. The coating properties and quality were determined using the CIELAB colour space model, which allows the deposition of particles on the fabric substrate to be evaluated, FTIR spectral analysis, friction tests to assess the adhesion of the coating, etc.

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Sustainability and recycling challenges of textile products

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European textile product consumption has the fourth highest environmental and climate impact.¹ Therefore, in 2022, Europe presented its sustainability strategy for the textile industry² to make it greener and more competitive, as well as to achieve sustainable development goals defined in the Paris Agreement,³ looking at the entire life cycle of textiles, thus focusing equally on the environmental, social and economic aspects of sustainability. Significant importance is given to increasing the longevity of textile products and effective textile waste management. Moreover, the proposed revision of the Waste Framework Directive⁴ aims to ensure that used textiles are sorted for reuse and that non-reusable textiles are prioritized for recycling; therefore, promoting textile separate collection and development of sorting, reuse, and recycling sector in the EU and beyond and reducing the negative impact of textiles on the natural resources. However, due to the complex nature of textile products, the lack of quality data and infrastructure, circularity and sustainable textile waste management is still ineffective and, in most cases, economically and environmentally disadvantageous.



Figure 1. Textile waste streams.

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P-17

Thermal modification of wood in nitrogen under pressure

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Several wood thermal modification (TM) processes have been introduced in the European market which primarily differ from each other by the way of oxygen exclusion and the pressure conditions. TM technologies can be divided into 2 major groups: open system and closed system technologies. Open systems are mainly advanced traditional drying ovens. TM of wood is performed by a pyrolysis process at high temperature and normal atmospheric pressure. The largest TM wood plants, incl. International ThermoWood Association preforms treatment in water steam environment at atmospheric pressure. Closed systems modifies wood materials in the process of hydrolysis at high pressure, but at a lower temperature, thus the pressure serves as a temperature substitute. The main advantage of TM treatment in steam at increased pressure compared to treatment at atmospheric pressure is lower maximum treatment temperatures and, consequently, lower energy costs. Another advantage is the shorter total TM time from heating, incineration and cooling of the material to room temperature. In closed system process total time of processing until complete cooling of the material is 22-30 hours. For full process ThermoWood needs up to 70 h. Recently new closed system TM process in nitrogen environment was invented. TM process in nitrogen has more efficient heat transfer capacity and no energy is required to convert water to steam. The treatment is carried out at higher pressures up to 18 bar and the elevated pressure acts as a temperature substitute. As a result, it is possible to reduce the maximum modification temperature and the processing cycle time to 8-12 h. From the point of view of production costs and productivity, the closed type process in nitrogen is a much better technique which needs to be investigated from scientific point of view. In various studies, TM in a nitrogen environment was mostly carried out in small-sized laboratory reactors at maximum temperatures of 160-240°C for 1 to 8 hours with a total processing time of up to 40-50 hours. Information about the maximum pressure during the modification phase is questionable.

In this study silver birch (*Betula pendula*) and scots pine (*Pinus sylvestris*) wood planks (100 x 25 x 1000 mm) were TM in 340L pilot device using different TM parameters: temperature (160-180°C), time at max temperature (30-90 min), initial pressure in autoclave (4-6 bar). TM parameters – energy consumption, pressure, temperature, process time were recorded. To characterize TM process intensity, the mass loss and volumetric changes of wood specimens was determined. Equilibrium moisture content (EMC), anti-swelling efficiency (ASE) and bending strength of TM wood were conducted to assess the effectiveness or drawbacks of the process. The ASE values of TM wood was in wide range 20-64% while EMC was 40-60% lower compared to untreated wood. The bending strength decreased by 10-30% for the most treatments reaching up to 40% at highest TM temperature.

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Development of injectable composite hydrogels containing hydroxyapatite nanoparticles and hyaluronic acid

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Osteoporosis is a degenerative bone disease characterised by progressive loss of bone mass and deterioration of bone's mechanical properties¹. Healing bone defects is a challenge in clinical practice, which requires the development of innovative biomaterials. The aim of this work is to develop injectable bioactive composite hydrogels for osteoporotic bone regeneration based on hydroxyapatite nanoparticles (nHAp) and hyaluronic acid (HA). *In situ* forming HA/nHAp composite hydrogels with HA to nHAp mass ratio of 70:30 wt%, 60:40 wt%, 50:50 wt%, 40:60 wt%, 30:70 wt% were fabricated by covalently cross-linked HA (molar ratio of EDC to NHS was 1:1) and chemically precipitated nHAp. The effect of nHAp phase on the swelling degree, gel fraction, enzymatic and bio-degradation, injectability, viscoelastic properties, morphology, and molecular structure of the hydrogels was investigated.

It was observed that the addition of the nHAp phase to the hydrogel synthesis medium increased the gel fraction from 47 to 75 %, reduced the mass loss after biodegradation from 41 to 23 %, increased the enzymatic degradation time by 5 times, and reduced the swelling degree by 4 times compared to the HA hydrogel. The higher the mass fraction of nHAp in the composite hydrogel, the higher the injection force. All samples showed a good ability to recover viscosity after injection. Future studies will focus on drug release studies and *in vitro* biocompatibility tests of the composite hydrogels.

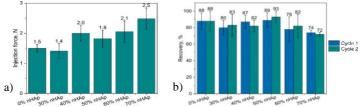


Figure 1. HA/nHAp composite hydrogels a) injectability (16 gauge needle) and b) viscosity recovery after injection (cyclic strain time sweep rheology experiments).

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Gallium containing amorphous calcium phosphate crystallization kinetics in different media

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Amorphous calcium phosphate (ACP) is a metastable phase of any calcium phosphates (CaP) with characteristic short-range order. Due to ACP's unique properties determined by its metastable nature, ACP has enormous potential for application in bone regeneration.¹ ACP tends to spontaneously crystallize in liquid solutions and form a thermodynamically more stable crystalline apatite phase. In addition, it is accompanied by changes in physicochemical properties, which may significantly impact the material's biological properties.² Thus, it is essential to anticipate the stability of ACP in different environments. Additionally, it is important to note that implantation of any biomaterial carries the risk of infection. A promising solution to this problem when applying CaP biomaterials could be the substitution of Ca²⁺ ions with Ga³⁺ ions, which inheres antibacterial properties.³ Consequently, this research aimed to develop a method for obtaining gallium-containing ACP (GaACP) and investigate the influence of Ga³⁺ on the physicochemical properties and stability of ACP in different media.

To obtain GaACP, the conventional precipitation method was used. Under agitation, concentrated NaOH solution was rapidly added to Ca^{2+} , $PO4^{3-}$, and various amounts of Ga^{3+} ions containing solution (2 and 4 wt%). As a result of a rapid pH change, the GaACP precipitated. For implementation of crystallization kinetics experiments, lyophilized ACP and GaACP powders were suspended in the selected media (Dulbecco's Modified Eagle Medium (DMEM), Phosphate Buffered Saline (PBS) and deionized water (DI H₂O) and placed in incubator-shaker at 37°C and 80 rpm. After particular time points (20 min, 40 min, 60 min, 90 min, 4 h, 24 h, 48 h), samples were taken from the incubator-shaker, centrifuged, rinsed with ethanol and DI H₂O, and eventually lyophilized. The stability of the GaACP powders was analysed using X-ray diffraction (XRD) and Fourier-transform infrared spectroscopy (FT-IR).

The XRD and FT-IR results revealed that the GaACP powders are most stable in DI H_2O . Nevertheless, the crystallization process in PBS occurred most promptly compared to other media. Furthermore, the ACP without added Ga showed lower stability in all media compared to the GaACP. A tendency of enhanced stability was observed with increasing Ga concentration in the ACP.

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Micro-computed tomography imaging of acellular or cellular hydrogels and organ-on-a-chip platforms

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Organ-on-chip (OOC) platforms are a cutting-edge approach for studying tissue physiology and disease modeling in a physiologically relevant context. Usually as different tissue mimics within the OOCs hydrogels are used. However, when hydrogel-filled OOCs are imaged using micro-computed tomography, the contrast of the images is low. Therefore, this study aims to screen possible staining agents for x-ray contrast improvement of such hydrogels.

In the study, 10 wt.% Gelatin methacryloyl (GelMA)¹ acellular or cellular hydrogels were used. Cellular hydrogels were with MC3T3-E1 pre-osteoblasts (1x10⁶ cells/mL). Crosslinking was done using UV (λ =365 nm, 5 min, *Irgacure* 2959). Then, the following staining agents were used: lead acetate, phosphotungstic acid, barium chloride, potassium iodide, Lugol's iodine, iron (III) oxide, ammonium monovanadate, ammonium molybdate, and sodium tungstate. Micro-CT imaging was done with μ CT 50 instrument (Scanco Medical, CH).

Results of the study showed increased X-ray contrast for GelMA hydrogels treated with staining agents compared to untreated (Fig. 1). In most cases, uniform staining was obtained.

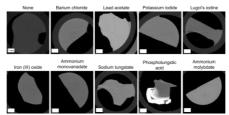


Figure 1. 2D micro-CT image slices show increased X-ray contrast of GelMA hydrogels stained with different staining agents for 24 h (2% w/v).

Overall, our approach successfully demonstrated the capabilities of the non-destructive visualization of hydrogels using micro-CT analysis with varying x-ray contrasting agents. This study paves the way for more comprehensive studies of cell-hydrogel interactions.

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Biomass granulation and pyrolysis process studies

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In Latvia alone 5 million tons of straw are generated annually, which has a negative impact on the environment because straw is a source of CO₂. Recycling is a good solution for reducing the amount of carbon dioxide and expanding the raw material base for new products.¹ In the food industry, 30 % of the waste generated after barley processing is incinerated. Wheat straw, barley straw and barley waste (husks) are good raw materials for the production of biochar.² This type of recycling will allow the already recycled product to be put back into the agricultural cycle.

Wheat straw (WS), barley straw (BS) and barley waste (husks) (BWH) were used as raw materials. In the first stage we studied the properties of raw materials such as moisture, ash content, crude fibre content, Ca, N, Mg, K, F. The material was grounded in two steps, mixed with peat in the proportion of 85% material and 15% peat and granulated using a matrix granulator. Three types of granules with a diameter of 6 mm were obtained. The granules were pyrolysed in Ar at 500 °C, heated at a rate of 5 deg/min and dwell time 1 hour. The main characteristics of the obtained material (biochar) such as yield of the product, strength, called mass per hectolitre. The morphological properties of the granules after pyrolysis were studied by electron spectroscopy. A comparative characterisation of the material obtained was carried out on the basis of the data obtained.

A study was carried out to evaluate the moisture absorption properties of granules in soil. Under laboratory conditions, peat for planting plants was mixed with granules after pyrolysis in proportions 1:4. Water was passed through the layer of the resulting planting mixture and its absorption rate was determined. Granules obtained from barley straw showed the highest degree of moisture absorption. For the biochar obtained from the three raw materials, tests were carried out under real agricultural conditions. We prepared soil for planting plants by mixing granules with peat in proportions 1:4. A sensor placed in the middle of the planting pot was used to record soil moisture change indicators. Lettuce was planted in the pots. The process was monitored for a month by recording sensor readings daily. Comparative characterisation of the results showed that granules obtained from BS and BWH held moisture better. The use of plant waste as a raw material for biochar will not only partially solve the issue of utilisation but also expand the raw material base, reduce the cost of the product and improve the quality of the soil.

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