



**NORDIC
POLYMER
DAYS** **2023**



Nordic Polymer Days 2023

CONTENT

PLENARY LECTURES	3-8
ORAL PRESENTATIONS	9-74
PROCESSING, SIMULATION	10
NANOCOMPOSITES/MATERIALS	15
POLYMER CHEMISTRY	23
BIOPOLYMER PROCESS	40
COMPOSITES/NANOCOMPOSITES	54
ADDITIVE MANUFACTURING	58
RECYCLING	62
POLYMERS FOR ELECTRICAL APPLICATIONS	68
POSTER PRESENTATIONS	74-101
EXHIBITORS AT NORDIC POLYMER DAYS 2023	102

Plenary Lectures



Nordic Polymer Days

Nordic Polymer Days **PLENARY PRESENTATIONS**

MELT EXTRUSION BASED ADDITIVE MANUFACTURING OF DEGRADABLE POLYMERS – PRINTABILITY, SPATIAL STIFFNESS AND SURFACE CHARACTERISTICS Anna Finne-Wistrand	5
THE SUSTAINABLE AGENDA AND CIRCULAR ECONOMY STRATEGY OF THE LEGO GROUP Søren Kristiansen	6
TEXTILE ACTUATORS AND BONE-GROWING MICROBOTS BASED ON ELECTROACTIVE POLYMERS Edwin W.H. Jager	7
DESIGN FOR RECYCLING: SYNTHESIS OF NEW BIOBASED POLYMERS Baozhong Zhang	8

MELT EXTRUSION BASED ADDITIVE MANUFACTURING OF DEGRADABLE POLYMERS – PRINTABILITY, SPATIAL STIFFNESS AND SURFACE CHARACTERISTICS



Anna Finne-Wistrand^{*}

1 KTH Royal Institute of Technology, Department of Fibre and Polymer Technology, School of Engineering Sciences in Chemistry, Biotechnology and Health

* annaf@kth.se

Degradable polymers have been used for a very long time in widely differing types of implants and solved various clinical challenges. Different manufacturing methods have been used and the competence in this area is high, we can in advance have a reliable guess about what will generate a good clinical outcome and what will not.

When additive manufacturing was added to the list of possible manufacturing methods, new opportunities were obtained to tailor three-dimensional matrices, so-called scaffolds. The ability to control each layer, generate for example the possibility to tune mechanical properties as well as the flow through the scaffold, properties that have a great impact on tissue regeneration.

When the application requires the implant to be able to withstand mechanical load without being deformed, polyester based polymers and melt extrusion based additive manufacturing are often used. The challenge when degradable polymers are used is to avoid polymer degradation while printing and it remains challenging to develop a large scaffold structure capable of providing both sufficient external mechanical support and an internal cell-like environment. We have strategically assessed how different copolymers behave during melt extrusion based additive

manufacturing and associated the results to the final properties. By varying the process, polymer composition and design, we are now able to use melt extrusion based additive manufacturing without influencing the molar mass. We have also evaluated the surface characteristics and we can tune the mechanical properties at both the macro- and micro-scales to provide sufficient external mechanical support and obtain a good internal cell-like environment for soft tissue regeneration.

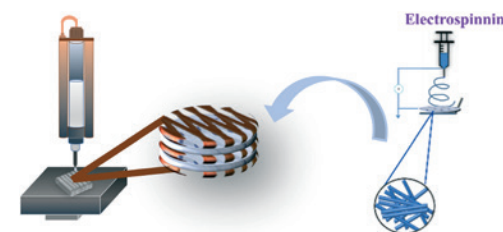


Figure: Additive manufacturing and a modular design strategy improve cell-material interactions.

References:

1. H. Liu, A. Ahlinder, M. A. Yassin, A. Finne-Wistrand, T. C. Gasser. Computational and experimental characterization of 3D-printed PCL structures toward the design of soft biological tissue scaffolds. *Mater. Design*, **2020**, 188, 108488.
2. H. Liu, S. Jain, A. Ahlinder, T. Fuoco, T.C. Gasser, A. Finne-Wistrand. Pliable, Scalable, and Degradable Scaffolds with Varying Spatial Stiffness and Tunable Compressive Modulus Produced by Adopting a Modular Design Strategy at the Macrolevel. *ACS Polym. Au*, **2021**, 1 (2), 107–122.
3. S. Jain, M.A. Yassin, T. Fuoco, S. Mohamed-Ahmed, H. Vindenes, K. Mustafa, A. Finne-Wistrand. Understanding of how the properties of medical grade lactide based copolymer scaffolds influence adipose tissue regeneration: Sterilization and a systematic in vitro assessment, *Mater. Sci. Eng. C.*, **2021**, 124, 112020.

THE SUSTAINABLE AGENDA AND CIRCULAR ECONOMY STRATEGY OF THE LEGO GROUP



Author¹ **Søren Kristiansen**,
Senior Director of Technology,
Materials, The LEGO Group

* soeren.kristiansen@lego.com

Our ambition is to make LEGO® bricks from more sustainable sources by 2030 without compromising on quality or safety. This is a bold ambition, as we need to develop new materials, new technologies, new capabilities and be part of building supply chains. The link between academia and the industry has shown highly important for achieving our goals. The presentation will show the broadness and depth of activities needed to progress on the journey toward our goal.



TEXTILE ACTUATORS AND BONE-GROWING MICROROBOTS BASED ON ELECTROACTIVE POLYMERS



Edwin W.H. Jager*

Linköping University,
Dept. Of Physics,
Chemistry and Biology (IFM)

* edwin.jager@liu.se

Ionic electroactive polymers can be used as actuators from micrometre-sized robots¹ to macroscopic wearables². We are developing bionic devices with a focus on biomedical applications. Traditional microfabrication technology, including photolithography, and novel

additive manufacturing methods such as 3D printing are used to create new soft microrobots comprising conducting polymer microactuators to drive the microrobots.³ We have developed new biohybrid materials based on gels and Plasma Membrane Nanofragments that induced bone formation.⁴ By combining these new biohybrid materials with the CP microactuators we have created microrobotic devices that create their own bone. The same conducting polymers, now shaped as fibres or yarns are used to make macroscopic textile actuators, by merging advanced textile technology with conducting polymer processing.⁵ Using knitting and weaving, we are developing soft textile actuators ("Knitted Muscles") for use in wearable devices such as haptic communication garments and textile exoskeletons.

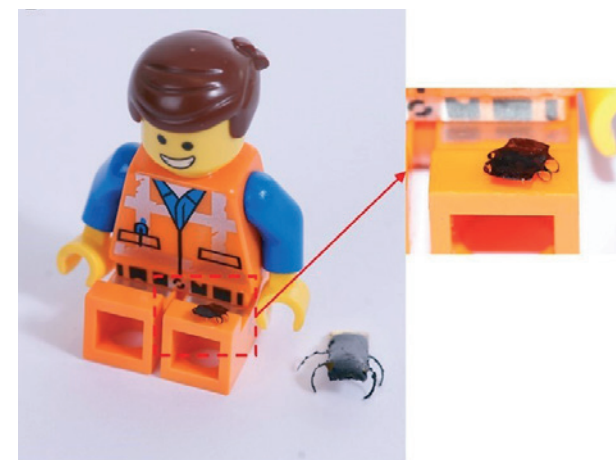


Figure:
Two additively manufactured microrobots driven by electroactive polymers with a with a Lego minifigure.

References:

1. Jager, E. W. H., Inganäs, O., Lundström, I. Microrobots for Micrometer-Size Objects in Aqueous Media: Potential Tools for Single Cell Manipulation. *Science*, **2000**, 288(5475), 2335-2338.
2. Jager, E. W. H., Martinez, J. G., Persson, N. K. (2019). Textile exoskeletons in Electroactive Polymers and Devices EAPAD, Denver, CO, USA, 3-7 March **2019**.
3. Tyagi, M., Spinks, G. M., Jager, E. W. H. 3D Printing Microactuators for Soft Microrobots. *Soft Robotics*, **2021**, 8(1), 19-27.
4. Cao, D., Martinez, J. G., Hara, E. S., Jager, E. W. H. Biohybrid variable stiffness soft actuators that self-create bone. *Advanced Materials*, **2022**34(8), 2107345, <https://doi.org/https://doi.org/10.1002/adma.202107345>
5. Maziz, A., Concas, A., Khaldi, A., Stålhund, J., Persson, N.-K., Jager, E. W. H. Knitting and weaving artificial muscles. *Science Advances*, **2017**, 3(1), e1600327.

DESIGN FOR RECYCLING: SYNTHESIS OF NEW BIOBASED POLYMERS



Baozhong Zhang*

1 Centre for Analysis and Synthesis, Department of Chemistry, Lund University, Sweden

* E-mail address of corresponding author: Baozhong.zhang@chem.lu.se

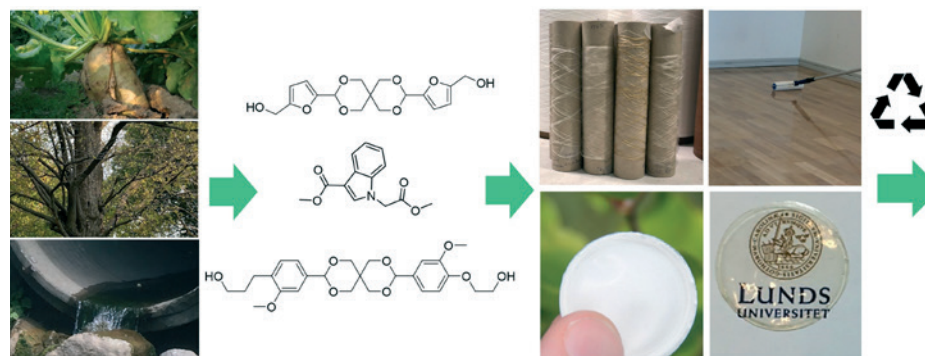


Figure: Recent examples of biobased monomers and polymers in our group.

Biobased polymers are expected to help solve many global environmental challenges, such as greenhouse gas emissions, fossil depletion, plastic pollution etc. Currently there are two important demands/trends in the development of new biobased polymers. On one hand, biobased polymers with enhanced properties have attracted growing attention due to their potential to outperform the low-cost fossil-based polymers. On the other hand, it has become increasingly important

to consider recycling possibilities during the initial phase of designing and synthesizing new biobased polymers.

Here, recent advances in our group in the development of biobased polymers will be presented with the focus on the molecular design and synthesis toward enhancing the materials properties and recyclability. Various monomer structures were designed and synthesized using biobased building blocks

such as sugar, vanillin, indole, etc. Particularly, we have been working on polyesters and polyurethanes with spirocyclic acetal structures (Figure below), which could effectively enhance the thermal properties and enable chemical recycling.^{1,2} Our exploration on the use of indole as a new sustainable aromatic unit for polyester synthesis will also be presented.³ Finally, investigations of the obtained biobased polymers toward coating and textile fibre applications will be presented.

References:

1. Mankar, S. V.; Gonzalez, M. N. G.; Warlin, N.; Valsange, N.; Rehnberg, N.; Lundmark, S.; Jannasch, P.; Zhang, B. Synthesis, life cycle assessment, and polymerization of a vanillin-based spirocyclic diol toward polyesters with increased glass transition temperature. *ACS Sustainable Chem. & Eng.*, **2019**, 7, 19090-19103.
2. Warlin, N.; Gonzalez, M. N. G.; Mankar, S. V.; Valsange, N.; Sayed, M.; Pyo, S. -H.; Rehnberg, N.; Lundmark, S.; Hatti-Kaul, R.; Jannasch, P.; Zhang, B. A rigid spirocyclic diol from fructose-based 5-hydroxymethylfurfural: synthesis, life-cycle assessment, and polymerization for renewable polyesters and poly(urethane-urea)s. *Green Chem.* **2019**, 21, 6667-6684.
3. Wang, P.; Arza, C. R.; Zhang, B. Indole as a new sustainable aromatic unit for high quality biopolyesters. *Polym. Chem.*, **2018**, 9, 4706-4710.

Oral Presentations



Nordic Polymer Days

Nordic Polymer Days 2023 **PROCESSING, SIMULATION**

- NOVEL OPPORTUNITIES TO INVESTIGATE ELONGATIONAL BEHAVIOUR OF POLYMER MELTS AND BIO INKS** 11
Dirk W. Schubert, Alexander M. Bier, Stefan Schrüfer
- PREDICTION AND OPTIMIZATION OF BLUSH DEFECT IN PLASTIC INJECTION MOULDING USING MACHINE LEARNING METHODS** 12
Alireza Mollaei Ardestani, Ghasem Azamirad, Yasin Shokrollahi, Matteo Calaon, Jesper Henri Hattel, Murat Kulahci, Roya Soltani, Guido Tosello.
- PHYSICAL PROPERTIES OF RING-OPENED CELLULOSE DERIVATIVES** 13
Patric Elf, Hüsamettin Deniz Özeren, Per A. Larsson, Anette Larsson, Lars Wågberg, Robin Nilsson, Thanaphon Chaiyupatham, Mikael S. Hedenqvist, Fritjof Nilsson
- SPATIAL RADICAL DISTRIBUTION IN FRACTURED POLYMER GLASSES AND MELTS VISUALIZED USING A PROFLUORESCENT NITROXIDE PROBE** 14
Qian Huang, Ole Hassager, **Jeppe Madsen**

NOVEL OPPORTUNITIES TO INVESTIGATE ELONGATIONAL BEHAVIOUR OF POLYMER MELTS AND BIO INKS

Dirk W. Schubert^{1*}, Alexander M. Bier¹,
 Stefan Schrüfer¹

¹ Institute of Polymer Materials,
 Friedrich-Alexander-University
 Erlangen-Nürnberg

* dirk.schubert@fau.de

Recent experimental developments are shown paving the way for the investigation of elongation in polymer melts up to high elongation rates (100 1/s) which are relevant in industrial processes, like fiber spinning. While on the other hand low viscous pastes or bio-inks can be analyzed by an augmented bio-printer set-up (BERIT), considering the shape of the jet/strut between nozzle and print bed.

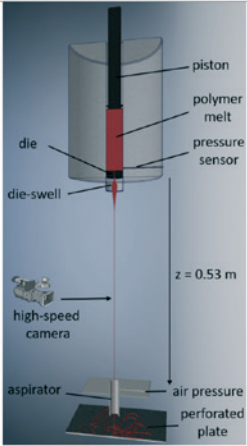
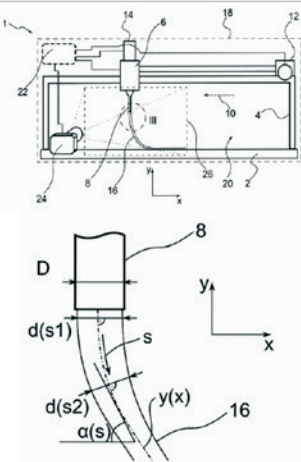
Results from application of the devices are shortly introduced.

Acknowledgement: The author thanks the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) —Projektnummer 326998133—TRR 225

(subproject A07) and German BMBF (Project VISP 03VP06651) for funding this work. Results from application of the devices are shortly introduced.

References:

1. A. Bier, W. Arne, D.W. Schubert, Novel High-Speed Elongation Rheometer Macro. Materials & Eng. 2022, 2100974
2. DE 10 2020 216 545, D.W. Schubert, P. Dalton, S. Schrüfer

Elongation of polymer melts up to high elongation rates (100 1/s)	Elongation of low viscous pastes or bio-inks
	
<p>Trick: Calibration of the force applied by the high speed stretching aspirator. [1]</p>	<p>Trick: Analyzing the trajectory and shape of the jet utilizing appropriate coordinates. [2]</p>

PREDICTION AND OPTIMIZATION OF BLUSH DEFECT IN PLASTIC INJECTION MOULDING USING MACHINE LEARNING METHODS

Alireza Mollaei Ardestani¹,
Ghasem Azamirad^{2*}, Yasin Shokrollahi³,
Matteo Calaon¹, Jesper Henri Hattel¹,
Murat Kulahci⁴, Roya Soltani⁵, Guido Tosello¹.

- 1 Department of Civil and Mechanical Engineering, Technical University of Denmark, 2800 Kgs. Lyngby, Denmark,
- 2 Department of Mechanical Engineering, Yazd University, Yazd, P.O. Box 8915818411, Iran
- 3 Department of Mechanical Engineering, Amirkabir University of Technology, Tehran, P.O. Box 158754413, Iran
- 4 Department of Applied Mathematics and Computer Science, Technical University of Denmark, 2800 Kgs. Lyngby, Denmark
- 5 Yazd Poolica Co., Yazd Industrial zone, Yazd, P.O. Box 8947183963, Iran

* E-mail address of corresponding author:
Azamirad@yazd.ac.ir

Injection molding is one of the most important processes for the mass production of plastic parts. In recent years, many researchers have focused on predicting the occurrence and intensity of defects in injection molded parts, as well as optimization of process parameters to avoid such defects. One of the most frequent defects of manufactured parts is blush, which usually occurs around the gate location. In this study, to identify the effective parameters on blush formation, eight design parameters with effect probability on this defect have been investigated. Using a combination of design of experiments (DOE), finite element analysis (FEA), and ANOVA, the most significant parameters have been identified (runner diameter, holding pressure, flow rate, and melt temperature).

Furthermore, to provide an efficient predictive model, machine learning methods such as basic artificial neural networks, their combination with particle swarm optimization, and genetic algorithm have been applied and their performance analyzed. It was found that the basic artificial neural network (ANN), with an average accuracy error of 1.3%, provides the closest predictions to the FEA results. Additionally, the process parameters were optimized using ANOVA and a genetic algorithm, which resulted in a significant reduction in the blush defect area.

Keywords: plastic injection molding; design of experiments; machine learning; digital twin; process optimization

PHYSICAL PROPERTIES OF RING-OPENED CELLULOSE DERIVATIVES

Patric Elf^{1,3}, Hüsamettin Deniz Özeren⁶, Per A. Larsson^{1,3}, Anette Larsson^{2,4}, Lars Wågberg^{1,3}, Robin Nilsson^{2,4}, Thanaphon Chaiyupatham², Mikael S. Hedenqvist^{1,3}, Fritjof Nilsson^{1,1}

- 1 School of Engineering Sciences in Chemistry, Biotechnology and Health, Fibre and Polymer Technology, KTH Royal Institute of Technology, SE-100 44 Stockholm, Sweden
- 2 Department of Chemistry and Chemical Engineering, Chalmers University of Technology, SE-412 96 Gothenburg, Sweden
- 3 FibRe Centre for Lignocellulose-based Thermoplastics, KTH Royal Institute of Technology, Stockholm, Sweden
- 4 FibRe Centre for Lignocellulose-based Thermoplastics, Chalmers University of Technology, SE-412 96 Gothenburg, Sweden
- 5 FSCN research centre, Mid Sweden University, 85170 Sundsvall, Sweden
- 6 Division of Glycoscience, Department of Chemistry, AlbaNova University Centre, KTH Royal Institute of Technology, SE-106 91 Stockholm, Sweden

* pelf@kth.se

For lignocellulosic materials to be able to compete with today's traditional petroleum-based plastics, it is important that they can be processed in conventional processing equipment, including extruders and injection moulders. There are several possible approaches to accomplish this. Changes in functionality/polarity by ring-opening of glucose units, grafting of chemical groups on the cellulose backbone, addition of lubricants/plasticisers are examples. Modifications can be made on microfibrillar and fibre levels. Modifications/changes can also be achieved on all major constituents; cellulose, hemicellulose and lignin, or other lignocellulose components. An important question is here, which is the most promising way forward? Since there are many possible paths to investigate, a purely experimental approach will be time-consuming and therefore also costly. An efficient prediction tool will here be valuable. With atomistic/meso-scale simulations different molecular and fibre/fibril surface modifications can be rapidly evaluated and assessed whether they will meet the target properties of the material. The effects of lubricants and plasticisers can also be assessed, including also effects of water. Besides the prediction power, these types of simulations can also be used to

determine detailed mechanisms responsible for the properties and help to explain what one observes experimentally. Hence simulations are important complements to experimental work. Here we present the effects of ring-opening cellulose molecules on the physical properties of the cellulose material in both dry and moist conditions.

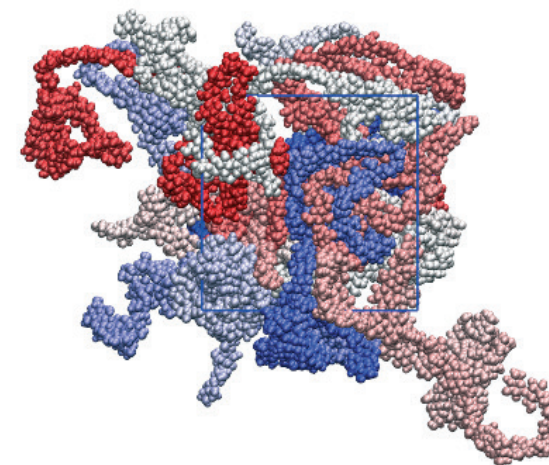


Figure: Equilibrated molecular dynamics simulation box, with polymer chains shown in different colours.

SPATIAL RADICAL DISTRIBUTION IN FRACTURED POLYMER GLASSES AND MELTS VISUALIZED USING A PROFLUORESCENT NITROXIDE PROBE

Qian Huang¹, Ole Hassager², **Jeppe Madsen**^{2*}

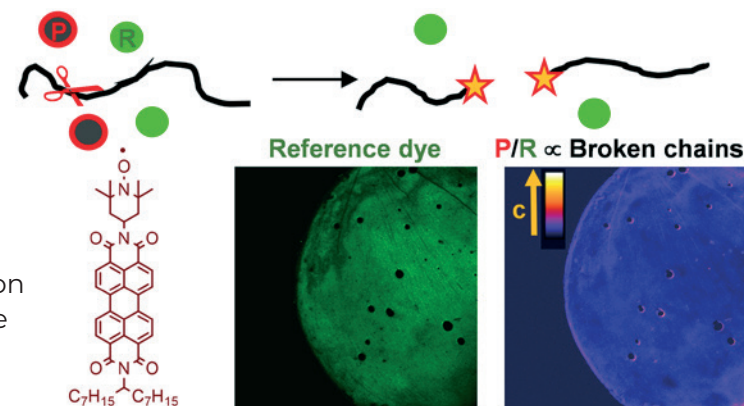
1 State Key Laboratory of Polymer Materials, Engineering, Polymer Research Institute, Sichuan University, 610065 Chengdu, China

2 Danish Polymer Centre, Department of Chemical Engineering, Technical University of Denmark, 2800 Kgs Lyngby, Denmark

* pjma@kt.dtu.dk

The early detection of fracture events in polymers remains relevant, as fracture is detrimental to the structural integrity of polymer specimens. [1] More recently, the molecular mechanism responsible for rupture of polymer melts has gained significant interest. [2] Despite the relevance, literature remains relatively scarce when it comes to methods for sensitive three-dimensional mapping of broken chains around fractures. Mechanically induced chain scission of common plastics typically gener-

Figure 1: Spatial mapping of chain scission using a combination of a radical-reactive dye and a reference dye



ates radicals when chains break. [4] Here we demonstrate three-dimensional mapping of radicals around fractures through the addition of a nitroxide-containing perylene-diimide-based dye (PeNO) and a reference dye (Perylene) to the polymer matrix. The fluorescence intensity of the profluorescent dye is highly sensitive to the radical concentration. When combined with a reference dye it is possible to suppress other contributions to the changes in fluorescence intensity and thereby

estimate radical concentrations through a simple ratiometric treatment of clsm images. The technique is used on incised solid polystyrene films, illustrating how far away from an incision chains scission can be detected. In addition, the technique is used to examine vitrified, ruptured polystyrene melts, illustrating that non-uniform chain scission occurs during melt fracture. [4]

References:

1. Kinloch, A.J.; Young, R. J. Fracture Behaviour of Polymers, Elsevier **1985**
2. Malkin, A.Y.; Petri, C. J. S. Some Conditions for Rupture of Polymer Liquids in Extension. *J. Rheol.* **1997**, 41, 1–25
3. Symons, M. C. R. Formation of Radicals by Mechanical Processes. *Free Radic. Res.* **1988**, 5 (3), 131–139
4. Huang, Q.; Hassager, O.; Madsen, J. Spatial Radical Distribution in Fractured Polymer Glasses and Melts Visualized Using a Profluorescent Nitroxide Probe *Macromolecules* **2022**, 55 (21), 9431–9441

Nordic Polymer Days 2023 **NANOCOMPOSITES/MATERIALS**

NOVEL 2D SILICONE OXIDE NANOPARTICLES USING GRAPHENE OXIDE TEMPLATES

Björn Birdsong, Richard T. Olsson

16

STRETCHABLE, ANTI-LEAKING, AND REVERSIBLE PHOTOCHROMIC HYDROUS TiO₂ GLYCEROL-PDMS ELASTOMER FOR REWRITABLE INFORMATION STORAGE MEDIA WITH MINIMAL RESOLUTION LOSS

Chonghui Li, Liyun Yu, Weizhen Zhao,
Anne Ladegaard Skov

17

THIOLATED CELLULOSE NANOCRYSTALS AS GREEN DEPRESSANTS IN MINERAL PROCESSING

Feliciano Ludovici, Robert Hartmann, Henriikki Liimatainen

18

USING NANOCELLULOSE FOR SELECTIVE MORPHOLOGICAL CONTROL OF BATTERY-RELATED METAL IONS

Billy. W. Hoogendoorn, O. Karlsson, X. Xiao, R. T. Olsson

19

EXCEPTIONALLY SMALL AND TRANSPARENT LIGNIN PARTICLES – SEEING CLEARLY THROUGH LENSES WITH LIGNIN

K. Alexander Henn, Sahar Babaeipour, Paula Nousiainen,
Susanna Forssell, Pekka Oinas, Monika Österberg

20

TEMPORARY ABANDONMENT OF OIL WELLS USING POLYMER-BASED PLUG

Skowyra M.M., Echarri-Giacchi M., Ivanova Y.D.,
Ravnkilde K.M., Frederiksen C.H., Skov A.L.

21

SPONTANEOUS FORMATION OF DISCRETE SILVER NANOPARTICLE PATTERNS IN POLYACRYLAMIDE GELS LOADED WITH LIGNIN NANOPARTICLES

Mohammad Morsali, Seyed Ehsan Hadi,
Ievgen Pylypchuk, Lennart Bergström, Mika Sipponen

22

NOVEL 2D SILICONE OXIDE NANOPARTICLES USING GRAPHENE OXIDE TEMPLATES

Björn Birdsong¹, Richard T. Olsson^{2*}

^{1,2} KTH Royal Institute of Technology,
Stockholm Sweden

* birdsong@kth.se

Oral presentation for: Polymer composites and nanocomposites, Polymerization and advanced polymer synthesis.

Lightweight nanocomposites are promising materials for high-performance areas and advanced applications such as catalysts, water filtration, biomedical applications, electronics and energy storage. Polymer-based composites containing nanoparticles with a two-dimensional (2D) structure have gained special interest due to their improved properties by the high aspect ratio, quantum behaviour, and large surface area of the nanoparticles. Notably, among these 2D materials, graphene has been widely studied for its unique properties, such as its exceptional mechanical strength, high thermal and electrical conductivity, and large surface area. However, its high cost

remains a limiting factor for the large-scale production of lightweight polymer-based composites.

An alternative material to graphene is its precursor, graphene oxide (GO), which has become more popular lately due to its lower cost while sharing similar morphology to graphene. The available functional groups on the surface of GO provide greater opportunities for its use as a template in polymer coatings, allowing for unique coating reactions that are otherwise not possible using graphene. One such polymer coating of interest is silicone oxide, which can provide outstanding and highly sought-after properties such as semi-conductivity, high mechanical strength, chemical inertness, biocompatibility, and temperature resistance for nanomaterials.

In this work, we report synthesis methods for novel 2D silicon oxide nanoparticles that replicate the morphology of GO with great accuracy. The successful coating was achieved using GO as a template, allowing a controlled condensation reaction on the surface and forming a coherent silicone oxide polymeric network. The 2D silicone oxide particles

behaved similarly to the GO template but exceeded the GO template in some respects, including surface area, relative viscosity, and thermal stability. These results indicate that the inherent properties of the synthesized silicone oxide polymer particles are promising for high-performance applications, as mentioned above. Further envisioned new areas can include reusable templates for further polymerizations and coating reactions.

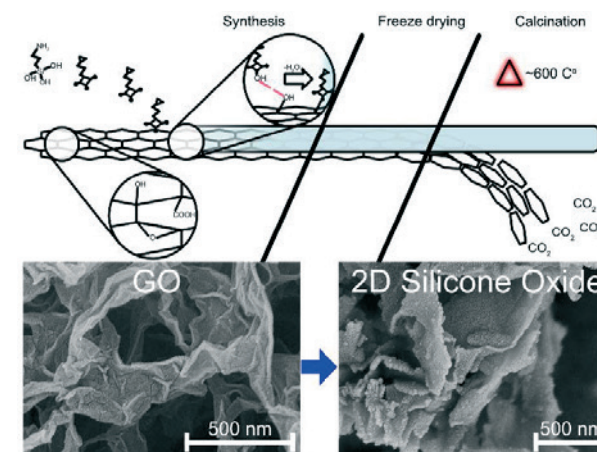


Figure: reaction illustration for the synthesis of 2D Silicone oxide nano-sheets replicating the graphene oxide template.

STRETCHABLE, ANTI-LEAKING, AND REVERSIBLE PHOTOCROMIC HYDROUS TiO₂ GLYCEROL-PDMS ELASTOMER FOR REWRITABLE INFORMATION STORAGE MEDIA WITH MINIMAL RESOLUTION LOSS

Chonghui Li^{1,2}, Liyun Yu¹, Weizhen Zhao², Anne Ladegaard Skov^{1*}

- 1 Danish Polymer Centre, Department of Chemical and Biochemical, Technical University of Denmark, Denmark,
- 2 Beijing Key Laboratory of Ionic Liquids Clean Process, Institute of Process Engineering, Chinese Academy of Sciences, China

* al@kt.dtu.dk chongli@kt.dtu.dk

Photochromic materials are sought-after in the fields of rewritable paper and information storage. In this study, a photoreversible color-switching elastomer was developed by incorporating hydrous titanium oxide (TiO₂) glycerol droplets in poly(dimethylsiloxane). The resulting photochromic elastomer exhibited fast photoresponse, reversible coloring capability and outstanding stretchability. Additionally, the elastomer effectively prevented leakage associated with liquid-state photo-

chromic compounds. The degree of coloration following UV irradiation was modulated by the hydrous TiO₂ content (1-20 wt%), with total color changes (ΔE) ranging from 6.13 to 25.53. High-resolution patterns were rapidly photo-printed onto the PDMS elastomer, which could be erased and rewritten 20 times with minimal degradation in resolution. It is believed that the hydrous TiO₂ glycerol PDMS elastomer could hold great promise for utilization in optical applications.

Figure: Photographs of printing and erasing QR code on the photochromic elastomer. Scale bars, 1 mm.



References:

1. Z. Gao.; L. Liu.; Z. Tian.; Z. Feng.; B. Jiang.; W. Wang. Fast-response flexible photochromic gels for self-erasing rewritable media and colorimetric oxygen indicator applications. *ACS Appl. Mater. Interfaces*, **2018**, 10 (39), 33423-33433.
2. J. Yang.; C. Tang.; H. Sun.; Z. Liu.; Z. Liu.; K. Li.; L. Zhu.; G. Qin.; G. Sun.; Y. Li.; Q. Chen. Tough, transparent, and anti-freezing nanocomposite organohydrogels with photochromic properties. *ACS Appl. Mater. Interfaces*, **2021** 13 (26), 31180-31192.
3. I. S. Zhao.; S. Chu.; O. Y. Yu.; M. L. Mei.; C. H. Chu.; E. C. M. Lo. Effect of silver diamine fluoride and potassium iodide on shear bond strength of glass ionomer cements to caries-affected dentine. *Int. Dent. J.*, **2019**, 69 (5) 341-347.

THIOLATED CELLULOSE NANOCRYSTALS AS GREEN DEPRESSANTS IN MINERAL PROCESSING

Feliciano Ludovici^{1*}, Robert Hartmann²,
Henrikki Liimatainen¹

1 Fiber and Particle Engineering Research Unit,
University of Oulu, P. O. Box 4300,
FI-90014 Oulu, Finland

2 Fraunhofer Center for Chemical-Biotechnological Processes, 06237 Leuna, Germany

* E-mail address of corresponding author:
feliciano.ludovici@oulu.fi

Froth flotation is the most common process in mining industry for the beneficiation of complex sulfide ores. The minerals are separated based on their wettability properties, which are manipulated using a wide variety of both inorganic and organic reagents. Typically, collectors are adsorbed on the mineral surface increasing its hydrophobicity, hence helping its floatability. Contrary, depressants selectively prevent the adsorption of the collector at the mineral/water interface, enhancing the minerals hydrophilicity, therefore helping the selective flotation of a specific mineral. Nowadays, there is an urgency to reduce the environmental impact of petroleum-based mining chemicals, and instead, to engineer efficient and non-toxic alternatives. Cellulose, as ubiquitous and versatile biopol-

ymmer, offers a renewable source to develop advanced, green, and sustainable mining chemicals. In this work, cellulose nanocrystals were successfully functionalized through an aqueous silylation reaction by grafting a thiol functional moiety onto the cellulose surface to enhance its affinity towards sulfide minerals. Microflotation tests were carried out in an in-house built Hallimond tube and the efficiency of the cellulose nanoparticles as depressants was investigated towards chalcopyrite and pyrite minerals. Especially, the role of pH and depressant concentration in flotation recovery was revealed. The results demonstrated that functionalized bio-based nanomaterials can unlock new paths towards more sustainable mineral processing.

USING NANOCELLULOSE FOR SELECTIVE MORPHOLOGICAL CONTROL OF BATTERY-RELATED METAL IONS

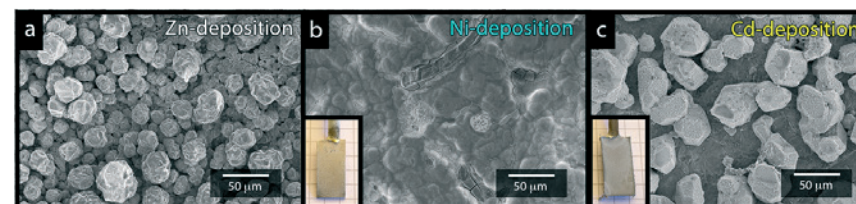
Billy. W. Hoogendoorn¹, O. Karlsson¹,
X. Xiao¹, R. T. Olsson^{1*},

KTH Royal Institute of Technology,
Teknikringen 56, Stockholm, Sweden

* rols@kth.se

Metal recycling is a field of research that is expected to grow extensively within the next decade. The so-called electrification of our society, which includes an exponentially increased use of batteries, will additionally create a steadily growing demand for valuable battery metals. However, current projections estimate that the supply of several essential battery metals will not be met unless new strategies are developed to supply the increased demand [1]. Developing novel recycling strategies of discarded metals, particularly water-based ones, is considered one of the most important endeavours in this aspect. Although these methods, which usually involve the dissolution of metals followed by a

Figure 1: Micrographs showing the morphologies of electrodeposited Zinc (a), Nickel (b), and cadmium (c)



selective separation through chemical precipitation or electrodeposition, are seen as the more environment friendly recycling strategy, a major challenge concerns the ability to achieve a selective separation from solutions that often contain a complex mixture of metal ions and other residues [2].

In this study, the effect of nanocellulose was investigated during the electrodeposition of zinc, cadmium and nickel, with the first one being chosen as a proof of concept and the 2nd and 3rd one being tested due to their use as the fundamental components in nickel/cadmium batteries. The results showed that the incorporation of small amounts (0.5 g/L) of nanocellu-

lose had a significant morphological impact on zinc and cadmium, promoting a considerable formation of easily detachable dendritic structures [3]. However, while this growth was induced for two metals known to share similar characteristics, the same effects were not observed for nickel, which instead consistently formed a homogenous layer, regardless of whether cellulose was present. These results reveal that nanocellulose is strongly capable of inducing morphological effects during electrodeposition. However, this effect is strongly selective depending on the metal being deposited, which highlights cellulose as a promising tool for controlling the deposition kinetics when recovering valuable battery metals.

References:

1. Murdock, B.E., K.E. Toghiani, and N. Tapia-Ruiz, A Perspective on the Sustainability of Cathode Materials used in Lithium-Ion Batteries. *Advanced Energy Materials*, **2021**. 11(39): p. 2102028
2. Su, X., Electrochemical separations for metal recycling. *The Electrochemical Society Interface*, **2020**. 29(3): p. 55.
3. Hoogendoorn, B.W., et al., Cellulose-assisted electrodeposition of zinc for morphological control in battery metal recycling. *Materials Advances*, **2022**. 3(13): p. 5304-5314.

EXCEPTIONALLY SMALL AND TRANSPARENT LIGNIN PARTICLES – SEEING CLEARLY THROUGH LENSES WITH LIGNIN

K. Alexander Henn¹, Sahar Babaeipour²,
 Paula Nousiainen¹, Susanna Forssell²,
 Pekka Oinas², Monika Österberg^{1*}

¹ Aalto University,
 Department of Bioproducts and Biosystems.

² Aalto University, Department of Chemical
 and Metallurgical Engineering.

* monika.osterberg@aalto.fi

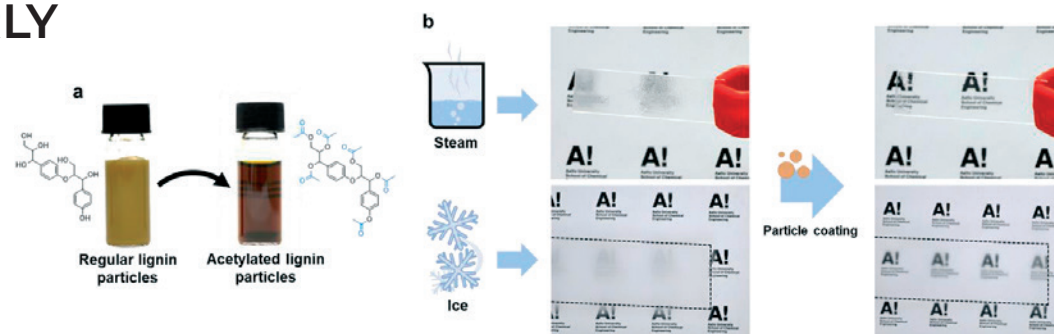


Figure: The preparation of transparent lignin particles via acetylation for transparent coatings. (a) Dispersions of regular lignin particles (\varnothing : 240 nm) and acetylated lignin particles (\varnothing : 70 nm). (b) Fogging and icing on uncoated glass (left) and glass coated with one monolayers of acetylated lignin particles (right).

Lignin nanoparticles have enabled the use of lignin in applications that would have been difficult to envision only ten years ago. [1] Lignin is still underutilized, but if suitable applications are found, lignin could become a much-needed alternative to fossil-based materials. There have recently been studies on the use of lignin particles as protective surface coating for wood and metal, [2] but because of lignin's strong brown colour, lignin particle coatings have been unsuitable for transparent materials, like glass.

Small particle size improves lignin's performance in many applications, but more interestingly; it increases the optical transparency of the particles both in dispersion and in dried form. In this work we pushed the size to the minimum to open yet another field of applications. By replacing lignin's hydroxyl groups with acetyl groups, particles sizes below 100 nm could be reached even at high precipitation concentrations. The particles were indeed transparent and were well suited for optical applications. Glass substrates coated with a monolayer of particles became

excellently resistant against the formation of fog. By using thicker layers it was even possible to control the film's colour through thin film interference, and bright hues of blue, purple and yellow could be achieved. Because traditional acetylation methods are difficult to upscale, we also developed a new quick and direct acetylation method to support the application. With this method the acetylation could be performed quickly with conventional equipment, and the method provided an excellent control over the degree of acetylation.

References:

1. Österberg, M.; Henn, A.; Farooq, M.; Valle-Delgado, J. J. Biobased Nanomaterials - The Role of Interfacial Interactions for Advanced Materials. *Chemical Reviews.*, **2023**
2. Henn, K. A.; Forsman, N.; Zou, T.; Österberg, M. Colloidal Lignin Particles and Epoxies for Bio-Based, Durable, and Multiresistant Nanostructured Coatings. *ACS Appl. Mater. Interfaces*, **2021**, 13 (29), 34793-34806

TEMPORARY ABANDONMENT OF OIL WELLS USING POLYMER-BASED PLUG

Skowyra, M.M.^{1*}, Echarri-Giacchi, M.^{1**}, Ivanova, Y.D.², Ravnkilde, K.M.², Frederiksen, C.H.², Skov, A.L.¹

1 Danish Polymer Centre, DTU Chemical and Biochemical Engineering, Technical University of Denmark (DTU)

2 Danish Offshore Technology Centre, Technical University of Denmark (DTU)

* magsk@dtu.dk,

** maecgi@dtu.dk

Even though the North Sea is one of the world's largest oil and gas exploitation areas, many of the oil wells present there are reaching the end of their productive life. This means that a large number of them are expected to be plugged and abandoned (P&A) in the coming years to ensure that the remaining fluids are contained safely within the well and that

the risk of environmental damage is reduced. Traditionally, cement has been used as the primary material for P&A applications, however, not without limitations such as operational issues, lack of resistance to certain chemicals (H₂S, hydrocarbons, etc.) or tendency to crack. As such, new materials are being developed to address these challenges.

Our novel approach is based on the development of a durable temporary polymer plug with a shelf life of up to 18 months. The goal is to reduce the pressure build-up in the oil well's pipeline and B-section and mitigate the risk for the rig entry prior to abandonment, simultaneously lowering the costs. The polymer's working time at room temperature is sufficiently long to allow for the pumping of the liquid solution down the well. After that, the free-radical cross-linking polymerization process is activated with high temperatures present at those depths, forming a rigid, solid polymer plug with low gas and water permeability.

In addition, the material is designed to be environmentally friendly and able to withstand the extreme conditions of oil wells, such as high pressure and aggressive environments.

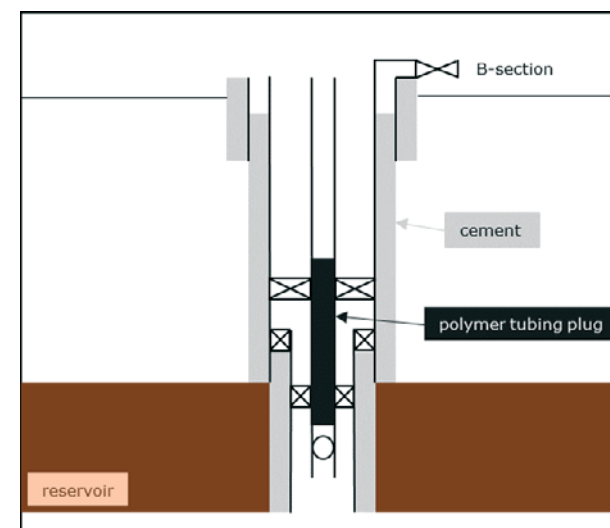


Figure: Schematic of a cross-linked polymer plug inside an oil well.

References:

1. Vrålstad, T.; Saasen, A.; Fjær, E.; Øia, T.; Ytrehus, J. D.; Khalifeh, M. Plug & abandonment of offshore wells: Ensuring long-term well integrity and cost-efficiency. *Journal of Petroleum Science and Engineering*, **2019**, 173, 478-491.

SPONTANEOUS FORMATION OF DISCRETE SILVER NANOPARTICLE PATTERNS IN POLYACRYLAMIDE GELS LOADED WITH LIGNIN NANOPARTICLES

Mohammad Morsali^{1,2}, Seyed Ehsan Hadi^{1,2},
Ievgen Pylypchuk¹, Lennart Bergström^{1,2},
Mika Sipponen^{1,2*}.

1 Department of Materials and Environmental Chemistry, Stockholm University, 106 91 Stockholm, Sweden.

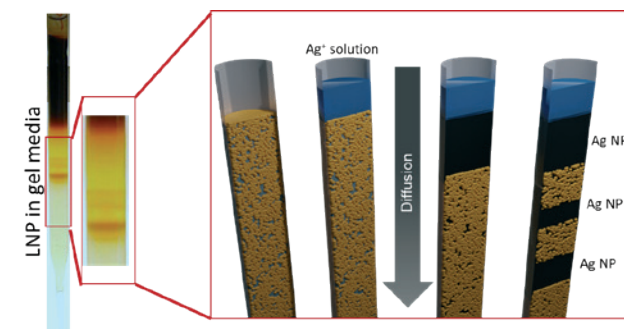
2 Wallenberg Wood Science Center, Department of Materials and Environmental Chemistry, Stockholm University, SE-10691 Stockholm, Sweden.

* mika.sipponen@mmk.su.se, mohammad.morsali@mmk.su.se

Transforming lignin into lignin nanoparticles is a promising strategy to utilize bio-based technical lignin in advanced applications. Colloidally stable lignin nanoparticles can be used in a wide range of applications such as stiffening fillers in polymeric blends, surfactant in Pickering emulsions, and nano-templates

for enzyme immobilization. Recently, we have demonstrated that it is possible to achieve solvent and alkali stable lignin nanoparticles,[1] which broaden their applications towards chemically active components for reduction and self-assembly of metallic ions like silver on the surface of lignin nanoparticles. The behaviour of lignin nanoparticles in reducing silver nanoparticles is intriguing and distinctive with a non-linear kinetics, autocatalytic nucleation and growth mechanism. Coupling autocatalytic reactions with diffusion in a system can result in formation of spatially confined and temporal patterns.² Such pattern forming systems are ubiquitous in nature, and has been classified according to their formation mechanisms such as Turing patterns in organic systems, Belousov-Zhabotinsky (BZ) oscillating reactions and Liesegang patterns in convection-free inorganic reactions. The number of chemistries studied and capable of forming such reaction diffusion systems in the lab are rare and limited. In this work we show the formation of discrete precipitation

patterns of silver nanoparticles as a result of unidirectional diffusion of silver ions across a polyacrylamide gel embedded with stabilized lignin nanoparticles. This system is important not only for deciphering the underlying mechanisms, but also show a great potential towards engineering spontaneous patterning of soft matter.



Formation of discrete patterns of silver nanoparticles in the presence of lignin nanoparticles in polyacrylamide hydrogel.

References:

1. Morsali, M.; Moreno, A.; Loukovitou, A.; Pylypchuk, I.; Sipponen, M. H.; Stabilized Lignin Nanoparticles for Versatile Hybrid and Functional Nanomaterials. *Biomacromolecules*, **2022**, 23, 11, 4597–4606.
2. Morsali, M., Khan, M. T. A., Ashirov, R., Holló, G., Baytekin, H. T., Lagzi, I., & Baytekin, B. Mechanical control of periodic precipitation in stretchable gels to retrieve information on elastic deformation and for the complex patterning of matter. *Adv. Mater.*, **2020**, 32(10), 1905779.

Nordic Polymer Days 2023 **POLYMER CHEMISTRY**

SYNTHESIS AND POST-FUNCTIONALIZATION OF HETEROFUNCTIONAL POLYESTER DENDRIMERS

Arunika Singh, Daniel J. Hutchinson,
Natalia Sanz Del Olmo and Michael Malkoch

25

BIOMIMETIC AND ANTIBACTERIAL GELATIN HYDROGELS WITH MULTIFUNCTIONAL PROPERTIES FOR BIOMEDICAL APPLICATIONS

Hengzhi Ruan, Marko Bek, Santosh Pandit,
Alexandra Aulova, Jian Zhang, Philip Bjellheim,
Martin Lovmar, Ivan Mijakovic, Roland Kádár

26

A THIENOTHIOPHENE MONOMER FOR DIRECT ARYLATION POLYMERISATION

Joost Kimpel, Youngseok Kim, Mariavittoria Craighero,
Renee Kroon, Christian Müller

27

EPOXIDIZED TECHNICAL KRAFT LIGNIN AS RESIN COMPONENT IN HIGH PERFORMANCE HEAVY-DUTY COATINGS

Alessio Truncali, Tejasvi Laxminarayan,
Narayanan Rajagopalan, Claus Erik Weinell,
Søren Kiil, Mats Johansson

28

EMULSION POLYMERIZATION OF ACRYLATE MONOMERS WITH WOODY BIOPOLYMER TOWARDS SUSTAINABLE COATING

Luyao Wang, Qiwen Yong, Patrik Christoffer Eklund,
Martti Toivakka, Xiaoju Wang, **Chunlin Xu**

29

BIO-BASED AROMATIC COATING COMPONENTS FROM LIGNIN

Harald Silau, Antonios Melas, Alicia G. Garcia,
John M. Woodley, Kim Dam-Johansen, Anders E. Daugaard

30

THIN MULTIFUNCTIONAL COATINGS FOR TEXTILES BASED ON LAYER-BY-LAYER APPLICATION OF POLYPHENOLIC HYBRID NANOPARTICLES

Sahar Babaeipour, Paula Nousiainen, Monika Österberg

31

RESPONSIVE POLYCATIONS WITH HYDROPHOBIC COUNTERIONS

Vikram Baddam, Erno Karjalainen, **Heikki Tenhu**

32

CONTENT CONTINUES NEXT PAGE >>

Nordic Polymer Days 2023

POLYMER CHEMISTRY

**POLY(IONIC LIQUID) NANOVESICLES VIA
POLYMERIZATION INDUCED SELF-ASSEMBLY
AND THEIR STABILIZATION OF CU NANOPARTICLES
FOR TAILORED CO₂ ELECTROREDUCTION**

Yonglei Wang, Jian Chang, Jiayin Yuan

33

**POLYMERSOMES COMPRISING
CLEAVABLE BLOCK COPOLYMERS**

Karolis Norinkevicius, Jeppe Madsen, Radosław Górecki,
Torsten H.B. Regueira, Anders E. Daugaard

34

**PET-RAFT MEDIATED RROPISA FOR SYNTHESIS
OF DEGRADABLE POLYMER NANOPARTICLES**

Olivia Wilson, Maryam Mousa, Eva Malmström

35

**ANALYTICAL PYROLYSIS, ANOTHER POWERFUL TOOL
FOR ANALYZING POLYMERS**

Helena Jönsson

36

**SYNTHESIS AND PROPERTIES OF ABA-TRIBLOCK
COPOLYMERS FROM POLYESTER A-BLOCKS AND
EASILY DEGRADABLE POLYACETAL B-BLOCKS**

Karolina Cichoń, Bartłomiej Kost, Malgorzata Basko

37

**CHEMICALLY RECYCLABLE POLYMERS
BASED ON DIOLS DERIVED FROM CITRIC ACID**

Rauno Sedrik, Olivier Bonjour, Siim Laanesoo, Ilme Liblikas,
Toñis Pehk, Patric Jannasch and Lauri Vares

38

**LIGNOCELLULOSE-BASED DICARBOXYLATE
MONOMERS FOR AROMATIC POLYESTERS:
SYNTHESIS, CHARACTERIZATION, AND PROPERTIES**

Nitin Valsange, Niklas Warlin, Smita Mankar,
Nicola Rehnberg, Baozhong Zhang and Patric Jannasch

39

SYNTHESIS AND POST-FUNCTIONALIZATION OF HETEROFUNCTIONAL POLYESTER DENDRIMERS

Arunika Singh, Daniel J. Hutchinson,
Natalia Sanz Del Olmo and Michael Malkoch*

¹Department of Fibre and Polymer Technology,
KTH Royal Institute of Technology,
Stockholm, Sweden

Presenting author: arunika@kth.se,

* Corresponding author: malkoch@kth.se

Dendrimers are highly branched macromolecules with a layered architecture that exhibit unique properties such as monodispersity, and high functional group density¹. Established dendritic platforms such as poly(amido amine) (PAMAM) dendrimers² and bis-MPA polyester dendrimers³, have been extensively

explored in application-driven research due to their commercial availability and simple synthetic modification. While PAMAM dendrimers have an inherent toxicity towards cells due to the large concentration of amine groups, hydroxyl functional bis-MPA dendrimers are known for their biocompatible, non-toxic and biodegradable nature.³

Most dendritic scaffolds exhibit a dormant interior and an active exterior with peripheral groups available for further manipulation. The exterior may be homo- or heterofunctional, with the latter including two or more distinctly different functionalities.⁴ The scope of these dendrimers could be greatly increased by including distinct functionalities into the interior. One such is the recently surfaced multifunc-

tional bis-MPA dendrimers from AB₂C monomers with interior and exterior functionalities⁵.

To expand the library of multifunctional dendrimers, a new AB₂C monomer has been synthesized and used to create polyester dendrimers with heterofunctionality throughout their entire dendritic framework, by employing a divergent growth strategy and anhydride chemistry for esterification reactions.⁶ Furthermore, robust chemistries based on click chemistry concepts will be utilized for the post-functionalization of these distinct functional groups to introduce an array of moieties with selective chemical reactivity and hence maximizing the potential of these polyester heterofunctional dendrimers for diverse applications from a single scaffold⁴.

References:

1. Yang, J.; Jia, C.; Yang, J. Designing Nanoparticle-based Drug Delivery Systems for Precision Medicine. *International Journal of Medical Sciences* 2021, 18 (13), 2943-2949. DOI: 10.7150/ijms.60874.
2. Tomalia, D. A.; Baker, H.; Dewald, J.; Hall, M.; Kallos, G.; Martin, S.; Roeck, J.; Ryder, J.; Smith, P. A New Class of Polymers: Starburst-Dendritic Macromolecules. *Polymer Journal* 1985, 17 (1), 117-132. DOI: 10.1295/polymj.17.117.
3. Carlmark, A.; Malmström, E.; Malkoch, M. Dendritic architectures based on bis-MPA: functional polymeric scaffolds for application-driven research. *Chemical Society Reviews* 2013, 42 (13), 5858. DOI: 10.1039/c3cs60101c.
4. Walter, M. V.; Malkoch, M. Simplifying the synthesis of dendrimers: accelerated approaches. *Chemical Society Reviews* 2012, 41 (13), 4593. DOI: 10.1039/c2cs35062a.
5. García-Gallego, S.; Stenström, P.; Mesa-Antunez, P.; Zhang, Y.; Malkoch, M. Synthesis of Heterofunctional Polyester Dendrimers with Internal and External Functionalities as Versatile Multipurpose Platforms. *Biomacromolecules* 2020, 21 (10), 4273-4279. DOI: 10.1021/acs.biomac.0c01068.
6. Antoni, P.; Hed, Y.; Nordberg, A.; Nyström, D.; Von Holst, H.; Hult, A.; Malkoch, M. Bifunctional Dendrimers: From Robust Synthesis and Accelerated One-Pot Postfunctionalization Strategy to Potential Applications. *Angewandte Chemie International Edition* 2009, 48 (12), 2126-2130. DOI: 10.1002/anie.200804987.

BIOMIMETIC AND ANTIBACTERIAL GELATIN HYDROGELS WITH MULTIFUNCTIONAL PROPERTIES FOR BIOMEDICAL APPLICATIONS

Hengzhi Ruan^{1*}, Marko Bek¹, Santosh Pandit², Alexandra Aulova¹, Jian Zhang², Philip Bjellheim³, Martin Lovmar^{2,3}, Ivan Mijakovic^{2,4*}, Roland Kádár^{1,5*}

1 Department of Industrial and Materials Science, Chalmers University of Technology, 41296 Göteborg, Sweden.

2 Department of Biology and Biological Engineering, Chalmers University of Technology, 41296 Göteborg, Sweden.,

3 Wellspect Healthcare AB, 43121 Mölndal, Sweden.

4 The Novo Nordisk Foundation Center for Biosustainability, Technical University of Denmark, 2800 Kongens Lyngby, Denmark.

5 Wallenberg Wood Science Centre (WWSC), Chalmers University of Technology, 41296 Göteborg, Sweden.

* hengzhi@chalmers.se;
 ivan.mijakovic@chalmers.se;
 roland.kadar@chalmers.se

Gelatin hydrogels have been used in the last decades for different biomedical applications due to the excellent biocompatibility, easy processability, bioactivities to mimic the extracellular matrix (ECM). However, the poor mechanical properties and thermostability limited their potential applications. Herein, a facile and economical approach of introducing dopamine and [2-(methacryloyloxy) ethyl] dimethyl-(3-sulfopropyl) ammonium hydroxide (SBMA) via in situ synthesis into gelatin hydrogels with the existence of ZnSO₄ was applied to overcome these disadvantages. This fabrication method allows the obtaining of gelatin-based hydrogels (GSDZ) with fatigue resistance and mechanical stability from -100 to 80 °C. Moreover, the hydrogels showed adhesive, self-healing, electrical and excellent antibacterial properties leading to their potential use as wearable monitoring sensors and antibacterial coatings. In particular, the hydrogels showed adhesion to various types of surfaces such as paper, skin, wood, plastic, rubber and steel, as well as 99.99% and 100% of antibacterial efficiency against Gram-positive and Gram-negative bacteria respectively, indicating widespread applications in many biomedical areas.

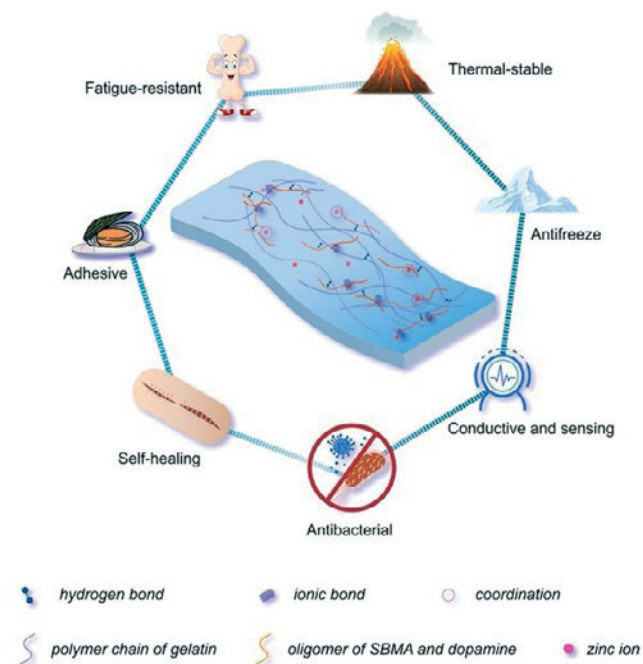


Figure 1: Schematic diagram of GSDZ hydrogels with multiple performances and applications.

A THIENOTHIOPHENE MONOMER FOR DIRECT ARYLATION POLYMERISATION

Joost Kimpel^{1*}, Youngseok Kim¹,
Mariavittoria Craighero¹, Renee Kroon²,
Christian Müller¹

1 Department of Chemistry and Chemical Engineering, Chalmers University of Technology, Göteborg, Sweden

2 Laboratory of Organic Electronics, Department of Science and Technology, Linköping University, Norrköping, Sweden

* kimpel@chalmers.se

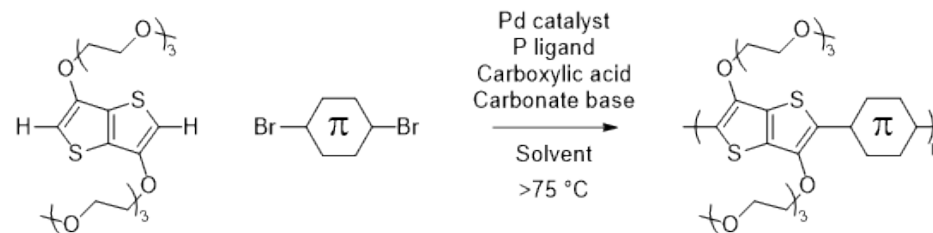
Areas of content: i) Polymerization and Advanced Polymer Synthesis and ii) Polymers for Electrical and Electronic Applications.

Direct arylation polymerisation (DAP) is a condensation polymerisation method using a palladium catalyst and various additives to couple halogenated aromatics and C-H activated aromatics to yield conjugated polymers. The C-H activated aromatics in DAP do not need further functionalisation, leading to better atom economy and less toxic reactive species than alternatives such as in Stille coupling (organotin), Suzuki coupling (organoboron) or Kumada coupling (organomagnesium). However, DAP has several challenges to overcome such as a limited number of suitable monomers that are stable under polymerisation

conditions and the lack of C-H regioselectivity leading to defects in regioregularity.

This work presents the synthesis of conjugated polymers comprised of a 3,6-di(triethyl-ene glycol)thieno[3,2-b]thiophene with various aromatic comonomers through DAP (Figure). The substituted thieno[3,2-b]thiophene monomer possesses only one C-H position which is activated by the adjacent oxygen. This leads to a decrease in defects, whilst increasing reactivity and polymer molecular weights, respectively. This pursuit can be anticipated to lead to higher yields, minimisation of defects, well-defined end-groups, and may facilitate upscaling of the synthesis.

Figure:
Direct arylation polymerisation explored in this work



EPOXIDIZED TECHNICAL KRAFT LIGNIN AS RESIN COMPONENT IN HIGH PERFORMANCE HEAVY-DUTY COATINGS

Alessio Truncali¹, Tejasvi Laxminarayan², Narayanan Rajagopalan², Claus Erik Weinell², Søren Kiil², Mats Johansson^{1*}.

1 KTH Royal Institute of Technology, Department of Fibre and Polymer Technology, Division of Coating Technology, Teknikringen 56-58, SE-100 44 Stockholm, Sweden.

2 Technical University of Denmark (DTU), The Hempel Foundation Coatings Science and Technology Center (CoaST), Department of Chemical and Biochemical Engineering, Building 229, 2800 Kgs. Lyngby, Denmark.

* matskg@kth.se

Unmodified softwood Kraft lignin was epoxidized in order to obtain a renewable solid resin, with the aim to reduce the fossil-based amount of commercial epoxy coatings. The epoxy content in functionalized lignin was analyzed and quantified via spectroscopic analyses (³¹P-NMR, FTIR). A series of formulations, combining petroleum-based (Novolac and Bisphenol F DiGlycidyl ether) with lignin-based epoxy resins, were subsequently prepared and amine cured on steel panels at ambient conditions. FTIR was utilized to confirm the crosslinking reaction. The structural properties of the coatings were investigated in regards to the thermal properties by differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). Anticorrosive and adhesion performances were examined under salt spray and pull-off adhesion test respectively. Hardness pendulum damping and direct impact resistance analyses gave other useful information regarding the mechani-

cal properties of the coatings. In our study, the presence of the lignin-based epoxy resin has generally confirmed an improvement on the desired performances, as well as it has replaced the fossil-based resin up to 50%, paving the way for a future scalable process.

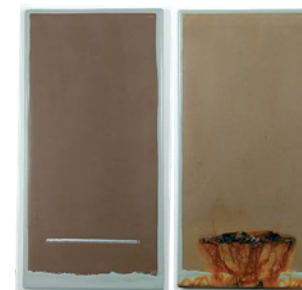


Figure: coating cured on steel panel containing 25% wt. of epoxidized Kraft lignin and 75% wt. of an epoxy Novolac resin, before and after 60 days of salt spray exposure. No corrosion defects have been detected.

References:

1. Over, L.C., Grau E., Grelier, S., Meier, M. A. R., Cramail, H. Synthesis and Characterization of Epoxy Thermosetting Polymers from Glycidylated Organosolv Lignin and Bisphenol A, *Macromolecular Chemistry and Physics*, 2017, 218, 1-11.
2. Gioia, C., Lo Re, G., Lawoko, M., Berglund, L. Tunable Thermosetting Epoxies Based on Fractionated and Well-Characterized Lignins, *J. Am. Chem. Soc.*, 2018, 140, 4054-4061.

EMULSION POLYMERIZATION OF ACRYLATE MONOMERS WITH WOODY BIOPOLYMER TOWARDS SUSTAINABLE COATING

Luyao Wang¹, Qiwen Yong¹, Patrik Christoffer Eklund², Martti Toivakka¹, Xiaoju Wang¹, **Chunlin Xu**^{1*}

¹ Laboratory of Natural Materials Technology, Åbo Akademi University, Turku FI-20500, Finland

² Laboratory of Molecular Science and Engineering, Åbo Akademi University, Turku FI-20500, Finland

* chunlin.xu@abo.fi

Latex colloids have prevailed as ideal materials across a wide range of film and binding applications, ranging from coatings and binders, to structurally colored materials and advanced functional templates. With the continued focus on sustainability and environmental issues, there is a high demand for bio-latex to reduce carbon footprints. In the most recent decade, forest biorefinery concepts have been

developed to provide woody biopolymers that are renewable and sustainable alternatives to the petroleum-based building blocks in latex fabrication.

O-acetyl-galactoglucomannan (GGM), the major hemicellulose derived from softwood, was functionalized with polymerization-active allyl-terminated groups via base-catalyzed etherification. Free-radical emulsion polymerization of butyl acrylate monomer with allylated GGM in aqueous media successfully fabricated bio-latex films with highly transparent, hydrophobic, and flexible characteristics. Notably, the bio-content of GGM-based latex could reach about 99%, which shows a tremendous perspective for sustainable packaging.¹ Also, lignin accounts for more than 30% of dry wood and its macromolecules possess multiple functional groups for accessible functionalization. Intriguingly, lignin functionalized with allyl-terminated groups could conveniently form lignin nanoparticles (LNPs) with durable dispersity and surface-exposed functionality

through self-assembly in a purifying dialysis process. Therefore, we extended the research to core-shell emulsion polymerization of acrylate monomers with the dispersed surface-allylated LNPs (A-LNPs) present as structural templates.² The interfacial-modulating function on the A-LNPs regulated the emulsion polymerization of acrylate monomers and successfully produced a multi-energy dissipative latex film structure containing a lignin-dominating core. Dependent on the surface functionalization degree, the A-LNP-latex film can achieve a high toughness that is 2.9 times higher than the neat polymer film. This class of aqueous bio-latex colloids can retain a high lignin content (20% relative to the total weight of acrylate monomers). As a conclusive remark, we have established facile but high-performance synthesis approaches to integrate such waste-stream biopolymers as woody hemicellulose and lignin in water-borne latex production, which can potentially find industrial use as sustainable solutions for dispersion barrier coating.

References:

1. Yong, Q.; Xu, J.; Wang, L.; Tirri, T.; Gao, H.; Liao, Y.; Toivakka, M.; Xu, C. Synthesis of galactoglucomannan-based latex via emulsion polymerization. *Carbohydrate Polymers*, **2022**, 291, 119565.
2. Wang, L.; Wang, Q.; Rosqvist, E.; Smått, J-H, Yong, Q.; Lassila, L.; Peltonen, J.; Rosenau, T.; Toivakka, M.; Willför, S.; Eklund, P. C.; Xu, C.; Wang, X. Template-directed polymerization of binary acrylate monomers on surface-activated lignin nanoparticles in toughening of bio-latex films. *Small*, **2023**, Accepted, DOI: 10.1002/smll.202207085.

BIO-BASED AROMATIC COATING COMPONENTS FROM LIGNIN

Harald Silau^{1,2}, Antonios Melas^{1,3},
Alicia G. Garcia¹, John M. Woodley⁴,
Kim Dam-Johansen¹, Anders E. Daugaard^{2*}

1 CoaST

2 DPC

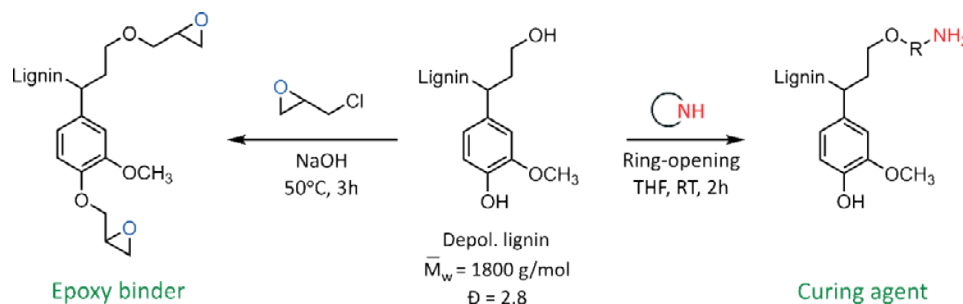
3 CHEC

4 Prosys Department of Chemical
and Biochemical Engineering, DTU

* adt@kt.dtu.dk, hasil@kt.dtu.dk

Coatings are essential in the modern world to protect steel structures from corrosion in applications from construction to transportation. Currently, most coatings components are derived from petrochemical aromatic raw materials, which in the context of a green transition is not sustainable for future generations. A bio-based aromatic and renewable

Scheme 1:
Transformation of
liquid depolymerized
lignin species into
epoxy binders and curing agents
for coating
applications.



material, lignin, has the potential to substitute fossil-based raw materials for coatings as it is an abundant by-product from the pulp and paper industry available at a low cost.

The challenges of lignin utilization comes from its biopolymer nature with high molecular weight and heterogeneity which results in poor solubility and matrix compatibility thus limiting the content that can be incorporated into coatings.¹ Pre-treatment of lignin through sequential solvent fractionation followed by reductive hydrogenolysis can partially break down the lignin structure to obtain liquid

aromatic raw materials with a high degree of hydroxyl functionality.² The reduction in molecular weight and lower steric hindrance results in excellent solubility properties which increase the effectiveness of further chemical transformations of lignin's hydroxyl groups into bio-based coating components such as epoxy binders or curing agents (Scheme 1). The lower molecular weight and liquid nature of the lignin species allow complete curing in thermosetting networks without the need for classic fossil-based coating components and the high aromaticity which lignin provides yields good thermomechanical properties.

References:

- Over, L. C.; Grau, E.; Grelier, S.; Meier, M. A. R.; Cramail, H. Synthesis and Characterization of Epoxy Thermosetting Polymers from Glycidylated Organosolv Lignin and Bisphenol A. *Macromol. Chem. Phys.* **2017**, 218 (4), 1600411
- Silau, H.; Melas, A.; Dam-Johansen, K.; Wu, H.; Daugaard, A. E.; Høj, M. Solvent Fractionation and Depolymerization Provide Liquid Lignin Fractions Exploited as Bio-based Aromatic Building Blocks in Epoxies. *ACS sus. Chem. Eng.*, **2023**, 11 (4), 1591-1597

THIN MULTIFUNCTIONAL COATINGS FOR TEXTILES BASED ON LAYER-BY-LAYER APPLICATION OF POLYPHENOLIC HYBRID NANOPARTICLES

Sahar Babaeipour¹, Paula Nousiainen²,
Monika Österberg^{2*}, etc.

¹ Department of Bioproducts and Biosystems,
School of Chemical Engineering,
Aalto University,
FIN-00076 Espoo, Finland

* paula.nousiainen@aalto.fi

One of the most actively developing areas of implementing modern advances in the textile industry is the creation of antibacterial and water-repellent, breathable coating with low toxicity and simple preparation processes. Such multi-functional materials are in high demand in protective outdoor textiles. Many current methods are based on synthetic, non-degradable, and toxic materials which have detrimental environmental impacts. There are recent examples of breathable and hydrophobic coatings based on natural wax particles. In addition, lignin and its derivatives have intrinsic anti-microbial and UV-blocking characteristics that can be utilized in coatings. However, all these properties are seldom combined in one coating without hampering the sustainability and biodegradability of the material. Herein, bio-based nanoparticles, derived from esterified lignin, and natural waxes were coated onto cotton fabrics to develop multifunctional textile coatings with enhanced hydrophobicity, breathability, self-cleaning, antibacterial, and UV-shielding properties.

The nanoparticles were applied on the cotton surface by layer-by-layer deposition, creating a self-assembled multilayer. The particulate coatings on the cellulosic substrate were comprehensively characterized with respect to layer structure and thickness (scanning electron microscopy and atomic force microscopy) and functionality (wetting, breathability, antimicrobial performance, and UV blocking). We found that already a nanoscale coating rendered the textile hydrophobic and self-cleaning while retaining excellent breathability. The phenolic structures in the coating added antibacterial and UV shielding properties to the material. By a smart choice of components, the properties can be tuned depending on the application. Here we show for the first time the multifunctional properties of sustainable and biodegradable nanocoatings on textiles. Their promising performances in combination with the fact that the method is based on abundant, economical, and renewable raw materials and simple methods make it interesting for the textile industries.

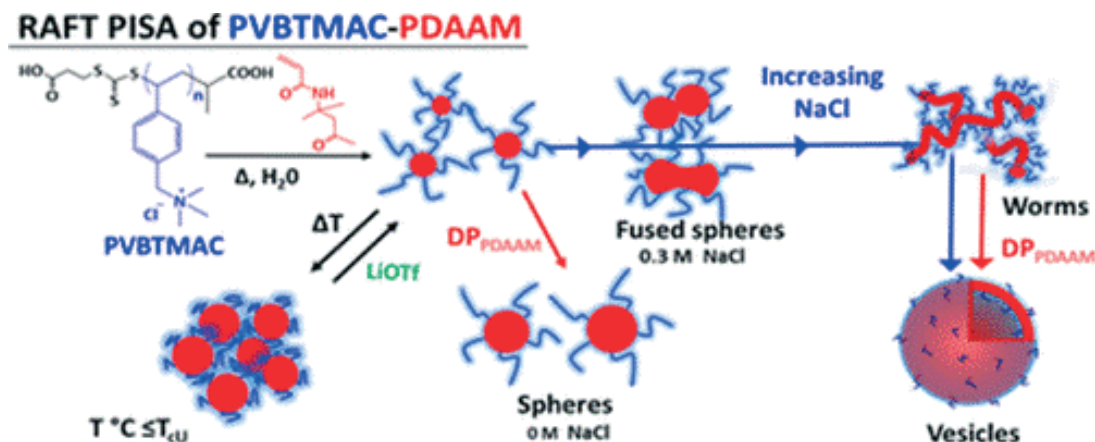
RESPONSIVE POLYCATIONS WITH HYDROPHOBIC COUNTERIONS

Vikram Baddam¹, Erno Karjalainen²,
Heikki Tenhu¹

¹ University of Helsinki, Finland

² VTT Technical Research Center of Finland

Corresponding author: heikki.tenhu@helsinki.fi



The balance of electrostatic and hydrophobic interactions critically affects thermal behaviour of polyelectrolytes in water. Adding hydrophobic substituents or counterions may turn the polymers thermally responsive.^[1] This presentation concentrates on a polycation poly(vinylbenzyl trimethylammonium triflate), PVBTMA, and first, on block copolymers of the polycation and PEG. The counterion in this case was hydropho-

bic triflate, which reduces the solubilities of the polymers, and in aqueous triflate solutions they show UCST behavior. The phase separation process upon cooling aqueous PEG-PVBTMA-OTf is, however, complicated and strongly dependent on the length of the cationic block. When the polymers phase separate, particles are formed. The mechanism of colloidal stability depends on the cationic block length.^[2-3]

A better soluble chloride of the polycation, PVBTMA-Cl has been used as a macroinitiator in PISA polymerization of diacetone acrylamide (DAAM). A whole spectrum of particle morphologies was obtained simply by adjusting the salt (NaCl) concentration. In aqueous triflate solutions the PVBTMA chains on particle surfaces respond to temperature, and interestingly, under certain conditions they show two-step transitions.^[4]

References:

1. E. Karjalainen, N. Survali, H. Tenhu; *Polymer Chemistry* (2020), 11, 5870-5883
2. V. Baddam, V. Aseyev, S. Hietala; E. Karjalainen H. Tenhu; *Macromolecules* (2018), 51, 9681-9691
3. V. Baddam, R. Missonen, S. Hietala, H. Tenhu; *Macromolecules* (2019), 52, 6514-6522
4. V. Baddam, L. Valinen, H. Tenhu; *Macromolecules* (2021), 54, 4288-4299

POLY(IONIC LIQUID) NANOVESICLES VIA POLYMERIZATION INDUCED SELF-ASSEMBLY AND THEIR STABILIZATION OF CU NANOPARTICLES FOR TAILORED CO₂ ELECTROREDUCTION

Yonglei Wang, Jian Chang, **Jiayin Yuan***

Department of Materials and Environmental Chemistry (MMK), Stockholm University, Svante Arrhenius väg 16C, 10691 Stockholm, Sweden

* E-mail address: jiayin.yuan@mmk.su.se

This contribution will discuss a straightforward, scalable synthetic route towards poly(ionic liquid) (PIL) homopolymer nanovesicles (NVs) with a tunable particle size of 50-120 nm and a shell thickness of 15-60 nm via one-step radical polymerization induced self-assembly. Along the increase in monomer concentration for polymerization, the nanoscopic morphology evolves from hollow NVs, dense spheres, finally to one-dimensional worms, where lamellar packing of PIL chains occurred. We investigated the transformation mechanism of NVs' internal morphology by coarse-grained simulations, revealing a corre-

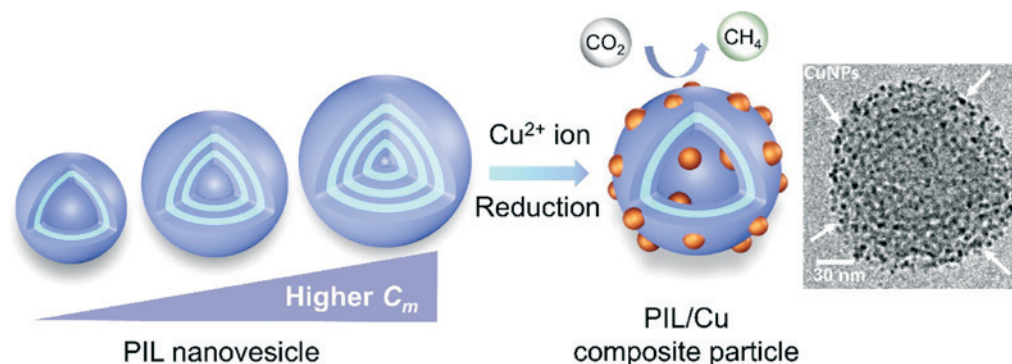


Figure: Morphological evolution of nanostructured poly(ionic liquid) from nanovesicles to dense spheres, and their functionalization by copper nanoparticles.

lation between the PIL chain length and the shell thickness of NVs. In the end, to probe potential applications, PIL NVs with varied shell thickness are in situ functionalized with ultra-small (1 ~ 3 nm in size) copper nanoparticles (CuNPs) and employed as electrocatalysts for CO₂ electroreduction. We found a 2.5-fold enhancement in selectivity towards

C1 products (e.g., CH₄) in the composite electrocatalysts in comparison to the pristine CuNPs. This outcome is attributed to strong electronic interactions between the CuNPs and the surface functionalities of PIL NVs. Our study casts new aspects on using nanostructured PILs as new electrocatalyst supports in CO₂ conversion to C1 products.

References:

1. Pan, X.; Kochovski, Z.; Wang, Y.-L.; Sarhan, R. M.; Haerk, E.; Gupta, S.; Stojkovic, S.; El-Nagar, G. A.; Mayer, M. T.; Schuermann, R.; Deumer, J.; Gollwitzer, C.; Yuan, J.; Lu, Y.; * Poly(ionic liquid) nanovesicles via polymerization induced self-assembly and their stabilization of Cu nanoparticles for tailored CO₂ electroreduction. *J. Colloid Interface Sci.* **2023**, 637, 408-420.

POLYMERSOMES COMPRISING CLEAVABLE BLOCK COPOLYMERS

Karolis Norinkevicius^{1,3*}, Jeppe Madsen¹, Radosław Górecki², Torsten H.B. Regueira³, Anders E. Daugaard¹

1 Danish Polymer Centre, Department of Chemical and Biochemical Engineering, Technical University of Denmark, Søltofts Plads 227, 2800 Kongens Lyngby, Denmark

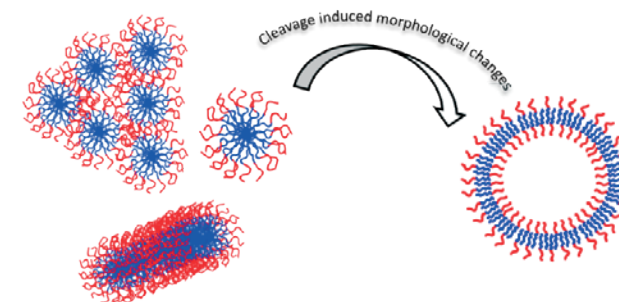
2 Nanostructured Polymeric Membrane Laboratory, King Abdullah University of Science and Technology, Thuwal 23955-6900, 4700, Kingdom of Saudi Arabia

3 Deep Tech Center, Aquaporin A/S, Nymøllevej 78, 2800 Kongens Lyngby, Denmark

* E-mail: karono@kt.dtu.dk, kno@aquaporin.com

Amphiphilic block copolymer materials have gained a lot of attention in the field of nanotechnology within the recent years, due to their unique ability of forming a wide range of self-assemblies both in organic solvents and in aqueous media. The morphology of these nano-structures is dictated by the packing parameter and thus by the ratio of the chain length of the hydrophilic to hydrophobic blocks [1,2]. This work explores poly(ethylene glycol)-block-poly(dimethylsiloxane) (PEG-b-PDMS) based diblock and triblock copolymers, their synthesis and self-assembly. Current techniques for the preparation of PEG-b-PDMS block copolymers rely on ring opening polymerization of cyclic siloxanes with lithium based catalysts and require extensive purification of starting materials and dry reaction conditions [3]. Hereby, we have explored a mild and simple approach of synthesizing PEG-b-PDMS diblock and

triblock copolymers with recently developed chemistry [3]. Hydrolytically unstable silyl ether bond in mPEG-b-PDMS-b-PEG triblock system was exploited in developing a unique method of morphological self-assembly change induced upon cleavage. As a result, a pure polymer vesicle system was produced, yielding a high number of these self-assemblies.



References:

1. Mai Y., Eisenberg A. Self-assembly of block copolymers. *Chem. Soc. Rev.*, **2012**, 41, 5969-5985
2. Discher E. D., Eisenberg A. Polymer Vesicles. *Science.*, **2002**, 5583 (297), 967-973
3. Fuchise K., Igarashi M., Sato K., Shimada S. Organocatalytic controlled/living ring-opening polymerization of cyclotrisiloxanes initiated by water with strong organic catalysts. *Chem. Sci.*, **2018**, 9, 2879-2891

PET-RAFT MEDIATED RROPISA FOR SYNTHESIS OF DEGRADABLE POLYMER NANOPARTICLES

Olivia Wilson¹, Maryam Mousa¹,
Eva Malmström^{1,2*}

¹ KTH Royal Institute of Technology, School of Engineering Sciences in Chemistry, Biotechnology and Health, Department of Fibre and Polymer Technology, Division of Coating Technology, Teknikringen 56-58, SE-100 44 Stockholm, Sweden.

² Wallenberg Wood Science Centre, Department of Fibre and Polymer Technology, KTH Royal Institute of Technology, Teknikringen 56-58, SE-100 44 Stockholm Sweden.

* mavem@kth.se

Engineered polymer nanoparticles have demonstrated significant promise in advanced applications such as biomedicine,

electronics, adhesives, coatings, and agriculture. [1] However, nanoparticle production has inherent consequences including materials loss and environmental damage. In an effort to minimize these consequences, the field of polymer chemistry is increasingly concerned with sustainable polymers and polymer synthesis strategies. As such, novel degradable polymer nanoparticles are increasingly sought after due to their promise in various applications and eco-friendly characteristics. The current strategies to produce degradable polymer nanoparticles are arduous, often requiring multiple steps and exhaustive reaction conditions that result in low solid content and limited morphologies. [2-3] Therefore, there is a desire to synthesize degradable polymer nanoparticles prepared in mild and sustainable reaction conditions with high solid content and tuneable morphologies for utility in versatile applications. Recently, degradable polymer nanoparticles have been synthesized by

copolymerization of cyclic ketene acetal (CKA) monomers that have hydrolysable ester functionalities and traditional vinyl monomers in a technique called radical ring-opening copolymerization induced self-assembly (rROPISA). [3-5] In the current technique, thermally induced reversible addition-fragmentation chain transfer (RAFT) polymerization is utilized to mediate rROPISA, which often requires high temperatures and inert atmosphere. To circumvent these exhaustive reaction conditions, we aimed to implement an oxygen tolerant, ambient, and highly tuneable polymerization technique called photoinduced electron/energy transfer RAFT (PET-RAFT) mediated rROPISA to investigate CKAs as comonomers with traditional vinyl monomers for synthesis of degradable polymer nanoparticles. The milder characteristics and spatiotemporal tunability of PET-RAFT are expected to enable synthesis of enhanced degradable nanoparticles with a broader range of morphologies.

References:

1. Jackson, A.W. Reversible-deactivation radical polymerization of cyclic ketene acetals. *Polymer Chemistry*, 2020, 11, 3525-3545
2. Siebert, J.M.; Baumann, D.; Zeller, A.; Mailänder, V.; Landfester, K. Synthesis of Polyester Nanoparticles in Miniemulsion Obtained by Radical Ring-Opening of BMDO and Their Potential as Biodegradable Drug Carriers. *Macromolecular Bioscience*, 2012, 12, 165-175
3. Guegain, E.; Chen, Z.; Giovanardi, E.; Nicolas, J. Radical Ring-Opening Copolymerization-Induced Self-Assembly (rROPISA). *Macromolecules*, 2019, 52, 3612– 3624
4. Zhu, C.; Nicolas, J. Towards nanoparticles with site-specific degradability by ring-opening copolymerization induced self-assembly in organic medium. *Polym. Chem.*, 2021, 12, 594-607
5. Liu, J.; Wu, W.; Sun, X.; Qian, Q.; Xiao, L. Degradable polymeric nanomaterials with a high solid content and multiple morphologies by polymerization-induced self-assembly. *Chem. Commun.*, 2022, 58, 3182-3185

ANALYTICAL PYROLYSIS, ANOTHER POWERFUL TOOL FOR ANALYZING POLYMERS

Author: **Helena Jönsson**, PYROL AB,
Utmarksv. 23, Lund S-225 92, Sweden

Email: helena.jonsson@pyrolab.com,
Phone: +46 46 139797

Analytical pyrolysis-GC/MS is a powerful method for analyzing polymers to other. Pyrolysis is the thermal degradation of a sample in an inert atmosphere. The chemical bonds break in a specific order when heated and the resulting pyrolysis products are well-defined and if separated by a GC and detected by mass spectrometry or any other type of detector provides a “fingerprint”, specific for the polymer analyzed. By using pyrolysis in combination with another technique the findings of one may be confirmed independently by the other, and in addition provide detailed insight in structures and composition of materials even consisting of a mix of polymers.

One of the advantages of analytical pyrolysis is the simple sample handling. Soluble and non-soluble samples can be analyzed directly without any pretreatment and both volatile and non-volatile fractions can be studied in the same analysis.

Detailed information will be obtained, where even very small differences between samples are detected and complex samples can be analyzed, both qualitatively and quantitatively using different kinds of pyrolysis methods.

In this presentation the background for analytical pyrolysis is described, and the different ways polymers are decomposed by heat.

SYNTHESIS AND PROPERTIES OF ABA-TRIBLOCK COPOLYMERS FROM POLYESTER A-BLOCKS AND EASILY DEGRADABLE POLYACETAL B-BLOCKS

Karolina Cichoń^{1,2*}, Bartłomiej Kost¹,
Malgorzata Basko¹

1 Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Sienkiewicza 112, Lodz 90-363, Poland;

2 The Bio-Med-Chem Doctoral School of the University of Lodz and Lodz Institutes of the Polish Academy of Sciences, Banacha 12/16, Lodz 90-237, Poland.

* karolina.cichon@cbmm.lodz.pl

Currently, scientific research aimed at the design of materials that are easily recyclable or degraded constitutes an important direction in academia and industry.[1] Polyesters such as polylactide (PLA) or polycaprolactone (PCL) due to their nontoxicity and appropriate mechanical properties are broadly exploited materials. The aim of our research was the synthesis of ABA block copolymers capable to accelerated degradation as a result of the combination of hydrophilic polyacetal block with polyester

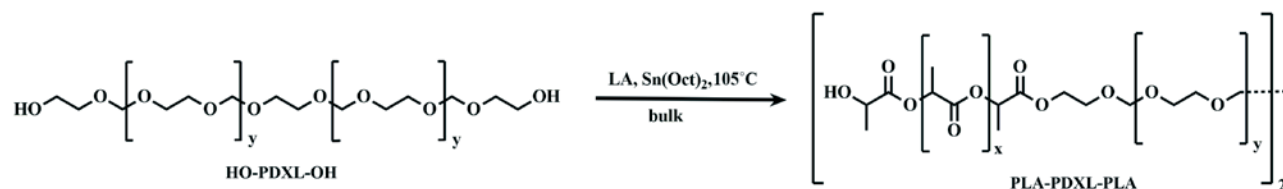


Figure A: Synthesis of “ABA” block copolymers containing polyester external “A” blocks and internal polyacetal “B” blocks.

blocks.[2] Copolymers with a required structure were obtained by the ring-opening polymerization of lactide (LA) or caprolactone (CL) catalysed by commercially available tin(II) octoate, using α,ω -hydroxy-terminated polyacetals as macroinitiators (Figure A).

The results show that the length of polyester blocks could be easily tailored by varying the cyclic ester ratio to hydroxyl groups in the starting polymerization mixture. High con-

versions of cyclic esters (>95%) afforded block copolymers formation with monomodal molar mass distributions and molar masses ranging from 10 000 g mol⁻¹ to 56 000 g mol⁻¹. The obtained copolymers were characterized in terms of their structure, hydrophilicity, and thermal properties. Based on the degradation studies we concluded that the decomposition of these triblock copolymers may be purposefully controlled, making them potentially useful recyclable materials.

References:

1. T. P. Haider, at al. *Angew. Chemie - Int. Ed.*, **2019**, 58 (1), 50-62.
2. K. Cichoń, B. Kost, M. Basko, *Polym. Chem.*, **2022**, 13, 5243-5255.

Financial support from the National Science Centre, Poland, Miniatura 5 Grant No DEC-2021/05/X/ST5/00491 is gratefully acknowledged

CHEMICALLY RECYCLABLE POLYMERS BASED ON DIOLS DERIVED FROM CITRIC ACID

Rauno Sedrik¹, **Olivier Bonjour**^{2*},
Siim Laanesoo¹, Ilme Liblikas¹, Toñis Pehk³,
Patric Jannasch^{1,2} and Lauri Vares¹.

1 Institute of Technology,
Tartu University, Estonia

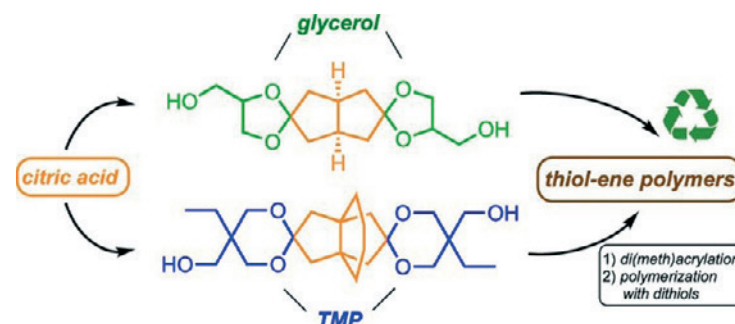
2 Centre for Analysis and Synthesis,
Department of Chemistry,
Lund University, Sweden

3 Laboratory of Chemical Physics,
National Institute of Chemical Physics
and Biophysics, Tallinn, Estonia

* E-mail of corresponding author:
olivier.bonjour@chem.lu.se

Plastics are facing global challenges because of their origin from fossil-based resources, and the environmental threat they pose in terms of plastic pollution and carbon emissions. To address these issues, different strategies are currently developed to produce recyclable

Figure 1: Outline of the synthetic pathway to the spirocyclic diols derived from citric acid, and recyclable poly(β -thioether ester ketal)s



plastics from renewable resources. These polymer materials usually require enhanced properties compared to conventional fossil-based polymers. One efficient approach to obtain high-performance materials is to incorporate rigid cyclic ketal or acetal units in the polymer structure.

In the present work, we have developed monomers derived from citric acid, a widely available platform chemical. Citric acid was efficiently converted to rigid di- and tricyclic diketones, which were subsequently transformed by ketalization reactions with glycerol or trimethy-

lolpropane into rigid spirodiols (Figure 1). [1] The spirodiols were then used to produce di(meth)acrylates that were later employed in thiol-ene polymerizations with different dithiols. The resulting poly(β -thioether ester ketal)s showed thermal stability up to 300 °C and glass transition temperatures ranging from -7 to 40 °C. Next, the possibilities for chemical recycling of the biobased polymers were investigated. The materials were observed to be stable in aqueous acids and bases. However, the spiroketal units were readily hydrolyzed in a mixture of 1 M aqueous HCl and acetone, opening the way for chemical recycling. [2]

References:

- Bonjour, O.; Liblikas, I.; Pehk, T.; Khai-Nghi, T.; Rissanen, K.; Vares, L.; Jannasch, P. Rigid Biobased Polycarbonates with Good Processability Based on a Spirocyclic Diol Derived from Citric Acid. *Green Chem.* **2020**, 22 (12), 3940–3951.
- Sedrik, R.; Bonjour, O.; Laanesoo, S.; Liblikas, I.; Pehk, T.; Jannasch, P.; Vares, L. Chemically Recyclable Poly(β -Thioether Ester)s Based on Rigid Spirocyclic Ketal Diols Derived from Citric Acid. *Biomacromolecules* **2022**, 23 (6), 2685–2696.

LIGNOCELLULOSE-BASED DICARBOXYLATE MONOMERS FOR AROMATIC POLYESTERS: SYNTHESIS, CHARACTERIZATION, AND PROPERTIES

Nitin Valsange¹, Niklas Warlin¹, Smita Mankar¹, Nicola Rehnberg², Baozhong Zhang^{*1}, and Patric Jannasch^{*1}

¹ Centre for Analysis and Synthesis, Department of Chemistry, Lund University, P.O. Box 124, SE-22100 Lund, Sweden.

² Bona Sweden AB, Box 210 74, 200 21 Malmö, Sweden.

* patric.jannasch@chem.lu.se and baozhong.zhang@chem.lu.se

New biobased aromatic monomers has received growing attention as a potential substitute for terephthalic acid in aromatic polyesters.^{1,2} Lignocellulose is an abundant and readily available source of aromatic chemical building blocks.³ The primary objective of the present research is to utilize lignin- and cellulose (sugar)-based building blocks for the development of biobased recyclable aromatic polyesters.

References:

1. A. Llevot, E. Grau, S. Carlotti, S. Grelier and H. Cramail, *Macromol. Rapid Commun.*, 2016, **37**, 9–28.
2. H. T. H. Nguyen, P. Qi, M. Rostagno, A. Feteha and S. A. Miller, *J. Mater. Chem. A*, 2018, **6**, 9298–9331.
3. I. Delidovich, P. J. C. Hausoul, L. Deng, R. Pfützenreuter, M. Rose and R. Palkovits, *Chem. Rev.*, 2016, **116**, 1540–1599.

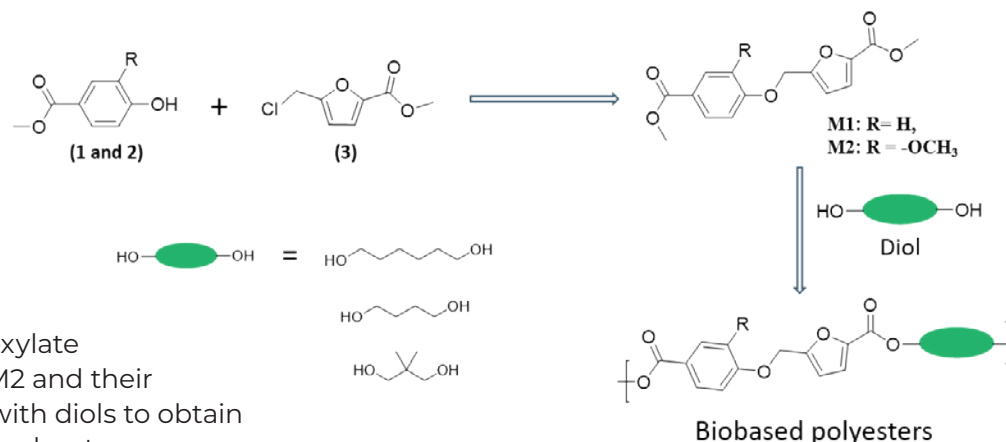


Figure 1: Synthesis of aromatic dicarboxylate monomer M1 and M2 and their polycondensation with diols to obtain biobased aromatic polyesters

Here, we present the facile synthesis of two new dicarboxylate monomers (M1 and M2) by a one-step reaction of lignin-derived methyl paraben (1) or methyl vanillate (2) with sugar-based methyl 5-chloromethyl-2-furoate (3) (Figure 1). The two monomers were polymerized with three biobased diols with different lengths to produce two series of polyesters with reasonably high molecular weights

(13–37 kg mol⁻¹). Subsequently, the polyesters were characterized with regard to thermal and dynamic mechanical properties. The fully amorphous and optically transparent polyesters showed high thermal stability and glass transition temperature tunable in the range ~36–74 °C.

Nordic Polymer Days 2023

BIOPOLYMER PROCESS

HIGHLY DUCTILE CELLULOSE-RICH PAPERS THROUGH INCORPORATION OF LOW MOLECULAR WEIGHT PLASTICIZERS THROUGH ULTRASONICATION 42
Adrian Eliasson, Lars Wågberg, Mikael Hedenqvist, Eva Malmström

EFFECT OF WATER CONTENT ON DIALCOHOL CELLULOSE FIBRES MELT PROCESSABILITY AND ON MATERIALS PROPERTIES 43
Enrica Pellegrino, Katarina Jonasson, Per Larsson, Giada Lo Re

THERMOPROCESSABLE BIO-BASED COMPOSITES FROM DENATURED COLLAGEN 44
Arianna Rech, Nicolas Møller, Angelica Avella, Giada Lo Re, Paul Nicholas, Anders E. Daugaard

UPCYCLING OF INDUSTRIAL BIOMASS AS POROUS BIODEGRADABLE THERMOFORMED PROTEIN-HYBRIDS ABSORBENTS 45
Agnès Jugé, Liliana Hurtado, Jeannine Moreno, Mercedes Jimenez-Rosado, Marco Sabino and **Antonio J. Capezza**

WATERBORNE NANOPARTICLES FOR THE INTERFACE DESIGN OF EXTRUDED CELLULOSE NANOFIBRILS-POLY(BUTYLENE ADIPATE-CO-TEREPHTHALATE) NANOCOMPOSITES 46
Maria Rosella Telaretti Leggieri, **Angelica Avella**, Eva Malmström, Giada Lo Re

REACTIVE POLYHEDRAL OLIGOMERIC SILSESQUOXANE AS A COMPATIBILIZER FOR BIOPOLYMER BLENDS 47
M. Saeed Ullah, R. Yildirim, M. Kodai and **G. Ozkoc**

FUNCTIONAL PROPERTIES OF POLYBUTYLENE ADIPATE-CO-TEREPHTHALATE WITH OLIVE LEAVES EXTRACT 48
Giuseppa Anna De Cristofaro, Marina Paolucci, Daniela Pappalardo, Caterina Pagliarulo, **Giuseppina Forgione**, Giada Lo Re

CELLULOSE BASED CLOTH FOR SOLAR-DRIVEN CLEAN WATER COLLECTION 49
Jian Chang, Miao Zhang, Jiayin Yuan

CONTENT CONTINUES NEXT PAGE >>

Nordic Polymer Days 2023

BIOPOLYMER PROCESS

**BIOBASED AND BIODEGRADABLE BINDERS
FOR PAPER AND NONWOVEN** 50

Maria Wennman, Mårten Hellberg,
Anna J Svagan, Mikael S. Hedenqvist

**EXTRUSION OF PROTEINS WITH DIFFERENT
FUNCTIONAL ADDITIVES AND THEIR IMPACT
IN THEIR VISCOELASTIC PROPERTIES** 51

Mercedes A. Bettelli, Hu Qisong, Antonio J. Capezza,
Eva Johansson, Richard T. Olsson, Mikael Hedenqvist

**ENHANCING RHEOLOGICAL AND MECHANICAL
PROPERTIES OF BIOSOURCED POLY(BUTYLENE
SUCCINATE-CO-BUTYLENE ADIPATE)
THROUGH GREEN REACTIVE EXTRUSION** 52

Michele Gammino, Claudio Gioia,
Roberto Scaffaro, Giada Lo Re

**SYNTHESIS AND THERMAL CHARACTERISTICS
OF RICE HUSKS DERIVED BIOPLASTIC FILMS** 53

Vianney Andrew Yiga, Sathiyaraj Subramaniyan,
Minna Hakkarainen, Michael Lubwama, Karin H. Adolfsson

HIGHLY DUCTILE CELLULOSE-RICH PAPERS THROUGH INCORPORATION OF LOW MOLECULAR WEIGHT PLASTICIZERS THROUGH ULTRASONICATION

Adrian Eliasson^{1,2*}, Lars Wågberg^{1,2},
Mikael Hedenqvist^{1,2}, Eva Malmström^{1,2}

1 Department of Fiber and Polymer Technology, KTH Royal Institute of Technology, Teknikringen 56, SE-100 44, Stockholm, Sweden.

2 FibRe – Centre for Lignocellulose-based Thermoplastics, KTH Royal Institute of Technology, Teknikringen 56, SE-100 44, Stockholm, Sweden

* adrianel@kth.se

Polymeric materials are essential in today's modern society and their production has increased exponentially since their commercialization in the 1940s. One of the largest industrial sectors is packaging, estimated to

be 146 million tons in 2015. A large fraction of the packaging material is single-use and ends up in landfill or is incinerated, as most plastics used are non-degradable and recycling is still challenging in large parts of the world. Material research has focused on decreasing the environmental impact of these kinds of materials by reducing and replacing them with, for example, cellulose-based materials like cardboard, but also more innovative materials like bio-based foams. Cellulose is an abundant biopolymer already widely used, while also being bio-degradable and recyclable. One limiting factor for conventional cellulose-based materials is the limitations when shaping cardboard and paper-based materials. Although cellulose is a polymer it does not show typical polymeric behaviors such as thermo-processability which most synthetic polymers do. Our approach, inspired by the plasticization of gluten, is to incorporate a

small amount of plasticizer into the lignocellulose matrix. Our hypothesis is that the small plasticizing molecules will reduce the strong intermolecular interactions within cellulose and enhance molecular mobility. Successful implementation will increase the lignocellulose's thermo-processability and yield a material that can be processed through conventional thermo-processing such as extrusion or hot-pressing allowing more advanced shaping opportunities than existing methods. Our work has shown that glycerol or urea that is incorporated into fibers through ultrasonication and then formed into sheets can increase their ductility from 0.5% to 30% without losing significant mechanical integrity. As a result, a 100% bio-based material consisting of more than 75 % lignocellulose is under evaluation as a hot pressable material for packaging applications with the potential to be bio-degradable and/or recyclable.

References:

1. Geyer, R., Jambeck, J. R., & Law, K. L. (2017). Production, use, and fate of all plastics ever made. *Science Advances*, 3(7), e1700782.
2. Özeren HD, Wei X-F, Nilsson F, Olsson RT, Hedenqvist MS. Role of hydrogen bonding in wheat gluten protein systems plasticized with glycerol and water. *Polymer* (Guilford). **2021**, 232, 124149.
3. An X, Liu J, Liu L, Zhang H, Nie S, Cao H, et al. Improving the flexibility of bamboo mechanical pulp fibers for production of high soft tissue handsheets. *Industrial Crops and Products*. 2020;150:112410

EFFECT OF WATER CONTENT ON DIALCOHOL CELLULOSE FIBRES MELT PROCESSABILITY AND ON MATERIALS PROPERTIES

Enrica Pellegrino¹, Katarina Jonasson^{1,2},
Per Larsson³, Giada Lo Re^{1*}.

1 IMS, Industrial and Materials Science,
Chalmers University of Technology, Ränn-
vägen 2A, SE-412 96 Gothenburg, Sweden

2 Tetra Pak, Ruben Rausings Gata 2,
SE-223 55, Lund, Sweden

3 Fibre and Polymer Technology,
KTH Royal Institute of Technology,
SE-100 44 Stockholm, Sweden

* giadal@chalmers.se; enricap@chalmers.se

The interest in renewable alternatives has risen due to the awareness of the negative environmental impact of not biodegradable fossil-based plastics. This is especially true for packaging, which accounts for one-third of

their overall use. Cellulose and its derivatives are considered suitable alternatives because they are biodegradable, have strong mechanical properties, exhibit low thermal expansion coefficients, and possess neutral sensory and organoleptic properties¹. Additionally, they have a low density and provide effective oxygen barriers, which are, however, affected by environmental conditions due to their sensitivity to water¹. Increased humidity loosens the strong hydrogen bonds present in the cellulose structure, resulting in a reduction in its ability to act as a barrier against oxygen and moisture. The abundance of hydroxyl groups creates strong hydrogen bonds between the cellulose fibres, which persist to a large extent upon the increase in temperature. This causes the cellulose to degrade before reaching the melt state². This limits the feasibility of producing cellulose through typical melt processing equipment. However, it is possible to lower the glass transition temperature of cellulose

by chemically modifying the cellulose fibres to dialcohol cellulose (DAC) fibers³. The modification of cellulose to form DAC fibers results in a physical alteration that creates a melt processing window between the glass transition and degradation temperatures of DAC fibres, which could be extruded with or with a thermoplastic polymer⁴. Additionally, DAC fibres exhibit strong interactions with water molecules, which can be used as a green plasticizer. The aim of this study is to examine the feasibility of melt processing (compounding and injection moulding) of DAC fibres. We investigated how different processing conditions and water amounts affect the fibre properties, such as fibre length, thermomechanical behaviour, and possible DAC fibres degradation by different characterization techniques, such as morphological (by a fibres analyser and scanning electron microscope, SEM), thermal (using thermogravimetric analysis, TGA) and dynamic thermomechanical (DMTA) analyses.

References:

1. Liu, Y.; Ahmed, S.; Sameen, D. E.; Wang, Y.; Lu, R.; Dai, J.; Qin, W. A review of cellulose and its derivatives in biopolymer-based for food packaging application. *Trends in Food Science & Technology*, **2021**, 112, 532-546
2. Li, C.; Wu, J.; Shi, H.; Xia, Z.; Sahoo, J. K.; Yeo, J.; Kaplan, D. L. Fiber-Based Biopolymer Processing as a Route toward Sustainability. *Advanced Materials*, **2022**, 34(1), 2105196.
3. Larsson, P. A.; Wågberg, L. Towards natural-fibre-based thermoplastic films produced by conventional papermaking. *Green Chemistry*, **2016**, 18(11), 3324-3333
4. Lo Re, G.; Engel, E. R.; Björn, L.; Sicairos, M. G.; Liebi, M.; Wahlberg, J.; Jonasson, K.; Larsson, P. A. Melt processable cellulose fibres engineered for replacing oil-based thermoplastics. *Chemical Engineering Journal*, **2023**, 141372

THERMOPROCESSABLE BIO-BASED COMPOSITES FROM DENATURED COLLAGEN

Arianna Rech^{1*}, Nicolas Møller¹, Angelica Avella², Giada Lo Re², Paul Nicholas³, Anders E. Daugaard¹

- 1 DPC, Danish Polymer Centre, Department of Chemical Engineering, Technical University of Denmark, Søtofts Plads 228A, 2800 Kgs. Lyngby, Denmark
- 2 IMS, Industrial and Materials Science, Chalmers University of Technology, Rännvägen 2A, SE-412 96 Gothenburg, Sweden
- 3 CITA, Centre for Information Technology and Architecture, Institute of Architecture and Technology, Royal Danish Academy - Architecture, Design, Conservation, Philip de Langes Allé 11, 1435 Copenhagen K, Denmark

* arirec@kt.dtu.dk

In the past decades, material depletion and waste production have drastically increased due to global economic development and growth in population. Using waste as a feedstock for the production of new materials would allow for dealing with both problems. [1, 2]

This study investigates the formulation of new thermoprocessable bio-based composites, where plasticized denatured collagen was used as matrix, waste materials from bio-based sources were used as fillers, and various thermoprocessing methods such as compression molding, 3D printing, extrusion and film blowing were explored.

Denatured collagen is a bio-based polymer extracted from the waste of the meatpacking industry, historically utilized as a glue for wood and to preserve artworks over time. [3] The thermoprocessability of this material was investigated through the use of a temporary

plasticizer (water) and a permanent plasticizer (glycerol). The bio-based waste fillers utilized consisted of lignocellulosic fibers coming as waste streams from different industries: bark fibers (BF), wood flour (WF) and lignin (L), which are byproduct from the forestry industry, seagrass (SG), collected from the seaside (or waste from chemicals extraction), and cotton fibers (CT), coming from blue jeans recycling. These lignocellulosic fibers were investigated in compression molding and 3D printing processing. While lignin was specifically investigated as a melt strength enhancer for processing through extrusion and film blowing.

The resultant matrix and various composites investigated showed to be processable with industrially relevant processing methods and to have high stiffness, while the addition of fillers allowed to lower shrinkage and density.

References:

1. OECD, Global Material Resources Outlook to 2060: Economic Drivers and Environmental Consequences, OECD Publishing, 2019.
2. Kaza, S.; Yao, L. C.; Bhada-Tata, P.; Van Woerden, F. What a Waste 2.0: A Global Snapshot of Solid Waste Management to 2050, © World Bank, 2018.
3. Schellmann, N. C. Animal glues: a review of their key properties relevant to conservation. Stud. Conserv., 2013, 52, 55–66

UPCYCLING OF INDUSTRIAL BIOMASS AS POROUS BIODEGRADABLE THERMOFORMED PROTEIN-HYBRIDS ABSORBENTS

Agnès Jugé,¹ Liliana Hurtado,^{1,2}
Jeannine Moreno,² Mercedes Jimenez-Rosado,³
Marco Sabino,² and **Antonio J. Capezza,^{1*}**

1 KTH Royal Institute of technology,
Teknikringen 56, Stockholm, Sweden.

2 USB Simón Bolívar University, Sartenejas,
Caracas, Venezuela,

3 SU Seville University, Seville, Spain.

* ajcv@kth.se

Disposable sanitary articles, hygiene items, and agricultural absorbents still use up to 70% of petroleum-based non-biodegradable plastics to manufacture these items. The current waste handling of the disposed sanitary/hygiene articles is based on incineration or land-filling. However, this is not the case in regions where waste handling policies are unsustainable, leading to incorrect disposal of these items and causing considerable microplastic

and toxic chemicals to the environment once the disposable items start degrading. At the same time, the agro-food industry is generating a high amount of undervalued natural biomass from their production lines, e.g., starch extraction for bioethanol, food, etc. In this work, protein-based porous structures were produced by thermally processing the natural biomass from the agro-food industry and using pilot-scale processing equipment. The structures were assembled into hybrid configurations suitable for single-use biodegradable sanitary items. The formulations are based on a mixture of proteins available as industrial co-products and processed using reactive extrusion, followed by their assembling using conventional thermal methods. The formulations showed versatility in the processing methods and were produced as porous pellets, compressed pads, and/or porous films. The thermal processing versatility of these protein biohybrids is attributed to synergistic effects between the different proteins' aminoacidic profiles. The formulations also included environmental and naturally-extract-

ed crosslinkers, demonstrating the capacity to tune the mechanical and structural properties of the products without affecting their circularity and sustainability. The biodegradability in soil and compost demonstrated the rapid assimilation of the material within less than 30 days. The capillary-driven absorption, the biodegradability of the materials in different environments, and the possibility to assemble the protein-based products as multi-layer components provide excellent performance indicators for their use as micro-plastic-free materials in absorbent items.



Figure: Prototypes based on natural biohybrids as future sustainable single-use sanitary items.

References:

1. Capezza, A. J.; Newson, W. R.; Muneer, F.; Johansson, E.; Cui, Y.; Hedenqvist, M. S.; Olsson, R. T.; Prade, T., Greenhouse gas emissions of biobased diapers containing chemically modified protein superabsorbents. *J. Clean Prod.* **2023**, 387, 135830.

WATERBORNE NANOPARTICLES FOR THE INTERFACE DESIGN OF EXTRUDED CELLULOSE NANOFIBRILS–POLY(BUTYLENE ADIPATE-CO-TEREPHTHALATE) NANOCOMPOSITES

Maria Rosella Telaretti Leggieri¹,
Angelica Avella^{2,3}, Eva Malmström^{1,4},
Giada Lo Re^{2,3*}

1 Department of Fibre and Polymer Technology, KTH Royal Institute of Technology, Teknikringen 56–58, 10044 Stockholm, Sweden

2 Department of Industrial and Materials Science, Chalmers University of Technology, 41258 Gothenburg, Sweden

3 Wallenberg Wood Science Centre, Chalmers University of Technology, Kemigården 4, 41296 Gothenburg, Sweden

4 Wallenberg Wood Science Centre, KTH Royal Institute of Technology, Teknikringen 56–58, 10044 Stockholm, Sweden

* avella@chalmers.se, giadal@chalmers.se

The potential stiffening that nanocelluloses can provide nanocomposites is often hindered by the poor interactions with polymer matrices and by nanocellulose agglomeration, particularly severe during melt processing. In this study, we have developed amphiphilic anchor–tail diblock copolymers with the aim of improving cellulose nanofibrils (CNFs) dispersion and their interaction with biodegradable poly(butylene adipate-co-terephthalate) (PBAT). Two waterborne copolymers were designed with fixed anchor length and different hydrophobic tail length. The copolymers were self-assembled into core-shell nanoparticles and adsorbed on CNFs surfaces in water dispersion. The effect of the addition of nanoparticles with different hydrophobic tail length was studied in extruded nanocomposites, produced via wet-feeding to limit CNFs

agglomeration. The adsorption of nanoparticles increased the mechanical properties of the nanocomposites compared to unmodified CNFs. The copolymer with longer tail better dispersed CNFs, leading to 65 % increase of PBAT Young's modulus, while retaining high deformability (670 %). The short copolymer instead had a greater stiffening effect (90 % increase in Young's modulus) at the expenses of the deformability. The morphological and mechanical analyses indicated that the use of the copolymers at the CNF/PBAT interface was beneficial for the nanocomposites improvement and showed how the design of these third components can be tuned according to the desired properties.

References:

1. Clemons, C.; Sabo, R.; A Review of Wet Compounding of Cellulose Nanocomposites. *Polymers.*, **2021**, 13 (6), 911-937

REACTIVE POLYHEDRAL OLIGOMERIC SILSESQUIOXANE AS A COMPATIBILIZER FOR BIOPOLYMER BLENDS

M. Saeed Ullah¹, R. Yildirim¹, M. Kodal^{1,2} and **G. Ozkoc**^{2,3,4,*}

1 Kocaeli University, Department of Chemical Engineering, Kocaeli, Turkiye

2 Sabanci University, SUNUM, Nanotechnology Res and Appl. Center, Istanbul, Turkiye

3 Istinye University, Department of Chemistry, Istanbul, Turkiye

4 Xplore Instruments BV, Sittard, The Netherlands

* guralp.ozkoc@xplore-together.com, guralp.ozkoc@istinye.edu.tr

Poly(butylene succinate) (PBS) is a worthy biodegradable thermoplastic polyester for blending along with other biopolymers, especially with poly(lactic acid) (PLA), to overcome its inadequacies in mechanical and thermal characteristics. Since binary blends of PLA and PBS showed that they are incompatible, compatibilization is required. In this work, multi-epoxide polyhedral oligomeric silsesquioxane (Glycidyl POSS) was added to PLA and PBS using the melt blending method to make them compatible. The blends were prepared at different weight ratios having different amounts of compatibilizer. SEM analysis showed that the Glycidyl POSS impacted the interfacial adhesion and other properties of PLA and PBS blends. Noticeable improvements in mechanical properties were

revealed by tensile and impact test results. Tensile strength and Young's modulus were improved when epoxy-POSS was added up to 1 and 3wt% into ternary blends, but further increasing POSS concentrations resulted in lower values. FTIR analysis showed a strong interaction between the epoxide group of POSS and the end groups of PBS or PLA. The thermal properties of samples were analyzed using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), respectively. The shifts in glass transition temperatures of the PLA phase towards lower values appeared in DSC, confirming the enhanced compatibility of PLA and PBS. Also, the reinforcing ability of the POSS inorganic core structure impacted the thermal stability of the blends.

FUNCTIONAL PROPERTIES OF POLYBUTYLENE ADIPATE-CO-TEREPHTHALATE WITH OLIVE LEAVES EXTRACT

Giuseppa Anna De Cristofaro¹,
Marina Paolucci¹, Daniela Pappalardo¹,
Caterina Pagliarulo¹, **Giuseppina Forgione**^{1,2},
Giada Lo Re^{2*}

1 Department of Science and Technology,
University of Sannio, Via F. De Sanctis Snc,
82100 Benevento, Italy

2 Department of Industrial and Material
Science, Chalmers University of Technology,
Rännvägen 2, 41296 Goteborg, Sweden

* forgione@chalmers.se, giadal@chalmers.se

The use of biodegradable plastics is increasingly gaining ground in the agri-food industry, especially for the packaging of easily perishable foods. Polybutylene adipate terephthalate (PBAT) promises very well for a wide range of potential applications both for its elastic

properties and for its biodegradable nature that does not release toxic metabolites [1]. The olive leaves represent one of the most abundant waste of the oil supply chain and are a rich source of natural substances with antioxidant and anti-inflammatory properties. The aqueous olive leaves extract (OLE) is rich of polyphenols such as oleuropein, hydroxyglycol and thyrosol [2]. In our study we supplemented PBAT with 20 wt.% of OLE obtained as waste material from pruning in an oil industry. To avoid a rapid release of OLE from PBAT, 10 wt.% of cellulose nanocrystals (CNC) was also added to the composition. After extrusion with a microcompounder we obtained two biocomposites, 20-OLE-PBAT and 20-OLE-CNC-PBAT. Differential scanning calorimetry (DSC) showed that OLE is acting as a plasticizer, while thermogravimetric analysis (TGA) showed that the interaction between OLE and PBAT led to an increase in degradation and onset temperatures. The tensile test

demonstrated that 20 wt.% OLE improved the strength and ductility of PBAT. The thermo-mechanical properties of 20-OLE-PBAT were preserved over time (15 days and 1 month after the extrusion). 20-OLE-CNC-PBAT instead showed variation in the properties due to the release of OLE during the storage time. In fact, the TGA and tensile test reported different picks of degradation and a reduction in elasticity compared to the as processed biocomposite. Considering the possible use of OLE as antioxidant in food packaging, the antioxidant activity of biocomposites was evaluated through 2,2-diphenyl-1-picrylhydrazyl (DPPH) assay. OLE is released gradually in the presence of water and 10% ethanol from the 3 days of storage until 7 days thus confirming the antioxidant hypothesis. So 20-OLE-PBAT has a great antioxidant activity and it could be a promising candidate as an additive in packaging films to improve the preservation of fresh food.

References:

1. Statista, Distribution of the production capacities of bioplastics worldwide in 2021 and 2026, by material type 2021. <https://www.statista.com/statistics/678775/production-capacity-distribution-of-bioplastics-worldwide-by-material/>
2. Di Meo, M. C.; De Cristofaro, G. A.; Imperatore, R.; Rocco, M.; Giaquinto, D.; Palladino, A.; Zotti, T.; Vito, P.; Paolucci, M.; Varricchio, E. Microwave-Assisted Extraction of Olive Leaf from Five Italian Cultivars: Effects of Harvest-Time and Extraction Conditions on Phenolic Compounds and in Vitro Antioxidant Properties. *Food Sci. Technol.*, **2022**, 2 (1), 31-40

CELLULOSE BASED CLOTH FOR SOLAR-DRIVEN CLEAN WATER COLLECTION

Jian Chang¹, Miao Zhang¹, Jiayin Yuan^{1*}

¹ Stockholm University

* jiyin.yuan@mmk.su.se

Given the vast abundance of sunlight, tapping into solar energy to produce clean water seems a viable solution to the current global challenges of water scarcity and energy shortage. Among all solar energy utilization methods, solar-driven water evaporation, which uses photothermal materials to capture sunlight and convert it to heat for the generation of water vapor, is very promising for getting potable water from a variety of water sources like river, lake and seawater. In this work, we prepared a highly stable and flexible photothermal cloth via electrospinning method, which was composed of biodegradable regenerated cellulose nanofibers as the matrix and MXene nanosheets encapsulated inside the matrix as solar absorbent. MXene nanosheets could bond with regenerated cellulose from composite nanofibers through hydrogen bonding. The photothermal cloth with an optimized MXene nanosheets loading shows great photothermal properties, absorbing over 80% of the solar spectrum and giving rise to a great solar energy utilization efficiency of 88% during the pure water evaporation process. Moreover, the cloths are light,

mechanically and chemically stable in various harsh environments and thus offer a solid strategy for practical solar steam generation and distillation processes.

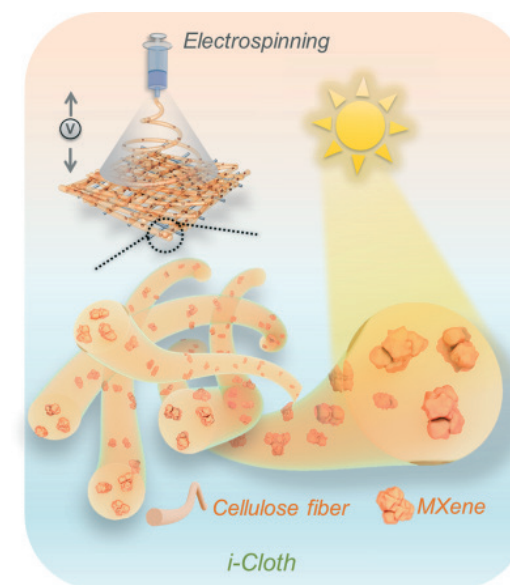


Figure: scheme of cellulose based functional cloth carrying MXene nanosheets.

References:

1. Y. Jin, J. Chang, Y. Shi, L. Shi, S. Hong, P. Wang, A highly flexible and washable nonwoven photothermal cloth for efficient and practical solar steam generation. *J. Mater. Chem. A* 2018, 6, 7942-7949

BIOBASED AND BIODEGRADABLE BINDERS FOR PAPER AND NONWOVEN

Maria Wennman^{1*}, Mårten Hellberg¹,
Anna J Svagan², Mikael S. Hedenqvist^{2*}

- 1 OrganoClick AB, Linjalvägen 9, SE-187 66 Täby, Sweden
- 2 KTH Royal Institute of Technology, School of Engineering Sciences of Chemistry, Biotechnology and Health, Fibre and Polymer Technology, SE-100 44 Stockholm, Sweden

* mwennman@kth.se,
mikaelhe@kth.se

Plastic waste is creating serious impacts on ecosystems, wildlife and the human health. The global production of plastics is +350 M tons and currently ~8 million tons are released into the oceans annually where it is gradually being mechanically degraded to microplastic waste.

The plastic waste is mainly coming from single-use products of plastics of which a consid-

erable amount are nonwoven materials made fully or partly of plastic polymers. Nonwoven, in this particular case, can be considered as a composite material consisting of 80-90% cellulose fibers and 10-20% plastic binders. Typical usage areas are within absorbency such as napkins and wipes. This means, that if such a napkin is released into the ocean, 80-90 % will be degraded but the remaining 10-20 % will be mechanically broken down to microplastics.

OrganoClick has been doing research and development of biobased binders for paper and nonwoven for more than 10 years. Currently, OrganoClick has a portfolio of 20 different, biobased and biodegradable binders that are sold to nonwoven applications within table top, agriculture, fashion and hygiene. The binders are to a large extent made from waste components from the European food and forest industries, which are further modified and combined in formulations to create a homogenous binder formulation used in

nonwoven production. Selection of the binder is dependent on the requirements of the nonwoven application where it will be used, as the requirements regarding e.g. stiffness, softness, printability and wet or dry strength differ between different applications.

Recently, a study on the mechanisms of how the binders react/interact with cellulosic fibers has been carried out during a cooperation between OrganoClick and KTH [1]. The binder itself (consisting of chitosan, carboxymethyl cellulose and citric acid), films made from the binder and cellulosic material impregnated with the binder have been characterised and the improvement in mechanical properties has been linked to covalent bonds established during the curing step. Also, by adding sunflower oil to the composition, an emulsion type of binder with unique and durable hydrophobicity could be created, exhibiting contact angles over 120 ° on impregnated viscose. Additionally, both increased dry and wet strength could be seen [2].

References:

1. Wennman¹, M.; Hellberg¹, M.; Svagan², A.J.; Hedenqvist², M. S. Plastic-free chitosan and cellulose binder providing dry and wet strength to paper and nonwoven. *Carbohydrate Polymer Technologies and Applications*, **2022**, 4, 100240–
2. Wennman¹, M.; Hellberg¹, M.; Svagan², A.J.; Hedenqvist², M. S. A biobased binder of emulsion type that provides unique and durable wet strength and hydrophobicity to paper and nonwoven. *Industrial Crops and Products*, **2023**, 193, 116126–

EXTRUSION OF PROTEINS WITH DIFFERENT FUNCTIONAL ADDITIVES AND THEIR IMPACT IN THEIR VISCOELASTIC PROPERTIES

Mercedes A. Bettelli¹, Hu Qisong¹,
Antonio J. Capezza¹, Eva Johansson²,
Richard T. Olsson¹, Mikael Hedenqvist^{1*}

¹ Fiber and Polymer Technology,
School of Chemical Science and Engineering,
KTH Royal Institute of Technology,
SE-100 44 Stockholm, Sweden

² Departamento de Ingeniería Química,
Escuela Politécnica Superior,
Universidad de Sevilla, 41011 Sevilla, Spain

* Correspondence:
mikaelhe@kth.se, mabdc@kth.se

Polymer foams have an important role in society due to their wide range of densities, and they are extensively used as cushioning, damping, thermal, and sound insulation materials. However, foams are mainly obtained from fossil-based resources and the global warming has to be defeated. Thus, there is a strong motivation to develop foams using from renewable resources used to combat the waste, landfill and green-gases produced. Here we report the production of protein-based foams with biodegradable properties by using proteins from industrial waste, glycerol as a plasticizer, and ammonium bicarbonate (ABC) as a food-grade blowing agent to produce highly porous foams. Diverse natural and low-toxic crosslinkers were also compared to produce the foams

for cushioning applications. CL2 yielded the lowest density and lowest energy loss during repeated compression testing at 10 to 50 % compression. The foams presented recovery in some extend of the foam after compression, and creep relaxation compressed for longer times (1 week). The overall compression set for Protein was lower than that synthetic rubber foams used as training mat, a possible application for the WG foams. This behaviour could be correlated to their microstructure (measured via scanning electron microscopy) and their ability to absorb atmospheric moisture. The results pave the way for an industrially up-scalable foam extrusion process to produce protein-based materials, that can be used in different applications, such as in seals and in training mats.

References:

1. Blomfeldt¹, T. O.J.; Kuktaite², R.; Johansson³, E.; Hedenqvist⁴, M. S. Mechanical properties and network structure of wheat gluten foams. *Biomacromolecules*, **2011**, 12, 1707-1715
2. Capezza¹, A.J.; Robert², E.; Lundman³, M.; Newson⁴, W.R.; Johansson⁵, E.; Hedenqvist⁶, M.S.; Olsson⁷, R.T. Extrusion of porous protein-based polymers and their liquid absorption characteristics. *Polymers*, **2020**, 12, 459

ENHANCING RHEOLOGICAL AND MECHANICAL PROPERTIES OF BIOSOURCED POLY(BUTYLENE SUCCINATE-CO-BUTYLENE ADIPATE) THROUGH GREEN REACTIVE EXTRUSION

Michele Gammino¹, Claudio Gioia²,
Roberto Scaffaro¹, Giada Lo Re^{*3}

¹ Department of Engineering,
University of Palermo,
Viale delle Scienze, ed. 6, 90128, Palermo, Italy

² Department Department of Physics,
University of Trento, via Sommarive 14,
38123 Povo (TN), Italy– CG

³ Department of Industrial and Materials
Science, Chalmers University of Technology,
Rannvagen 2A, SE-412 96 Gothenburg,
Sweden

michele.gammino@unipa.it
*giadal@chalmers.se

Poly(butylene succinate-co-butylene adipate) (PBSA) is a biodegradable and sustainable polymer that is becoming more popular in the market. It has mechanical properties similar to low-density polyethylene but with higher deformability than other biodegradable polymers such as PHAs and PLA. However, the prolonged or repeated melting of PBSA at high temperatures during manufacturing and recycling can cause degradation and a rapid loss of properties. For this reason, the design

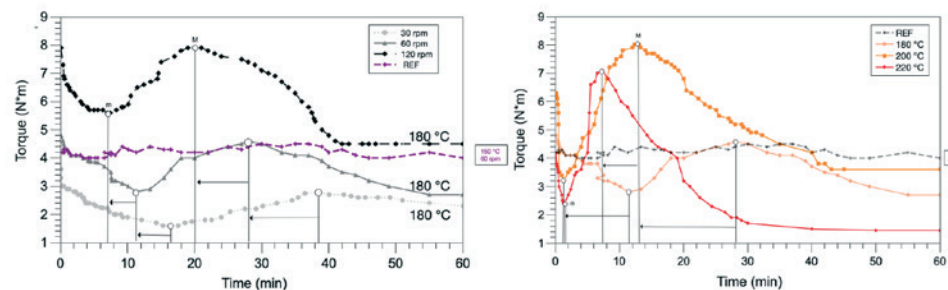


Figure: Time-dependent evolution of the torque recorded during the PBSA melt processing in an internal mixer under different processing conditions. In particular: A) at T=180 °C and different screw speeds, and B) at 60 rpm at different processing temperatures (Ref purple dot line and Ref black dot line is the torque profile recorded at 150 °C and 60 rpm).

of a Reactive extrusion is an open challenge to improve the mechanical and rheological properties of PBSA. This work investigates the possibility of controlling the thermomechanical degradation of poly(butylene succinate-co-butylene adipate) (PBSA) to design a green reactive extrusion approach that would improve PBSA rheological and mechanical properties and not require any additional additives. Different mixing protocols (temperature profile and screw rotation speed) were employed to evaluate the influence on the thermomechanical degradation of the material. The effect on the online PBSA rheological assessment of varying three different mixing

speeds (30, 60, 120 rpm) and four different processing temperatures (150, 180, 200, 220 °C) were studied (Figure). The torque curves recorded during the different PBSA melt mixing for process temperatures above 150 °C and 30 rpm showed consecutive minimum and maximum points, which suggest degradative reactions such as depolymerization followed by branching/recombination. These hypotheses allowed for a reactive extrusion design based on controlling the thermomechanical degradative paths of PBSA by the suitable selection of processing conditions. The reactive extrusion resulted in improved PBSA mechanical, rheological, and viscoelastic properties.

SYNTHESIS AND THERMAL CHARACTERISTICS OF RICE HUSKS DERIVED BIOPLASTIC FILMS

Vianney Andrew Yiga^{1,2,3},

Sathiyaraj Subramaniyan¹, Minna Hakkarainen^{1*},
Michael Lubwama³, Karin H. Adolfsson¹

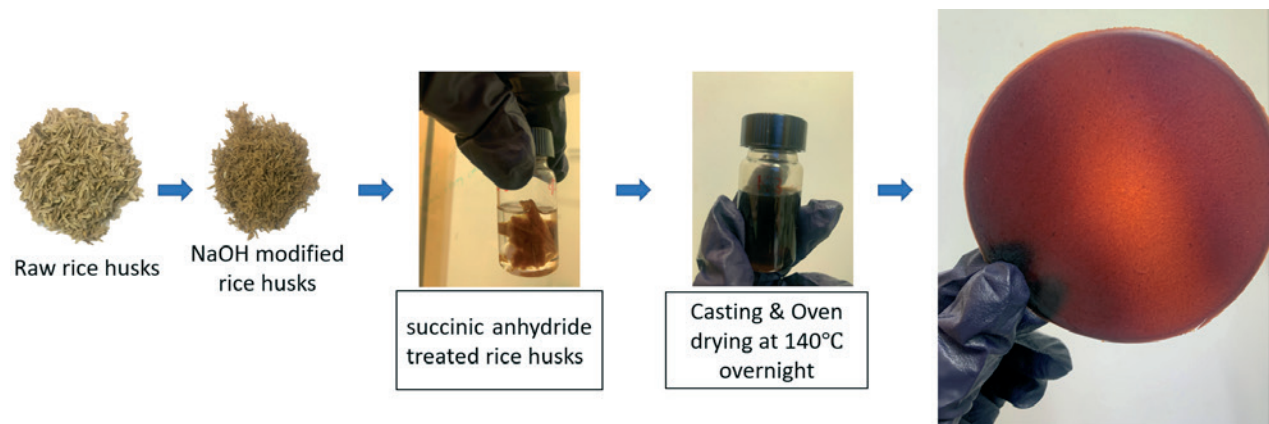
1 Department of Fibre and Polymer Technology, KTH Royal Institute of Technology, Stockholm SE-100 44, Sweden

2 Department of Mechanical Engineering, Kabale University, Kabale, Uganda

3 Department of Mechanical Engineering, Makerere University, Kampala, Uganda

* minna@kth.se

Bioplastics from agricultural residues have received great attention due to the increasing focus on environmental protection, especially in relation to waste management of agricultural residues and petroleum-based plastic materials [1]. In this study, we derived bioplastic films from rice husk. In the first step, rice husks were pre-treated with NaOH alkali, and then the NaOH-modified rice husk



Rice husks derived bioplastic film processing route

was further treated with different amounts of succinic anhydride in the presence of base and solvent. Lastly the obtained product was reacted with different ratios of trimethylolpropane triglycidyl ether at 140 °C for 8 h in the presence of solvent and catalyst to obtain the corresponding bioplastic films. The chemical structure of the developed bioplastic films was characterized by Fourier transform infra-

red spectroscopy. Evaluation of thermal properties of the fabricated bioplastic films was performed by thermogravimetry and differential scanning calorimetry techniques. Peak temperatures ranged between 380.8-397.3 °C and char residues ranged between 11.1-16.2%. The developed rice husk-derived bioplastics are anticipated promising utilization potential in packaging applications.

References:

1. Ortega, F., Versino, F., López, O. V., & García, M. A. (2022). Biobased composites from agro-industrial wastes and by-products. *Emergent Materials*, 5(3), 873-921.

Nordic Polymer Days 2023 **COMPOSITES/NANOCOMPOSITES**

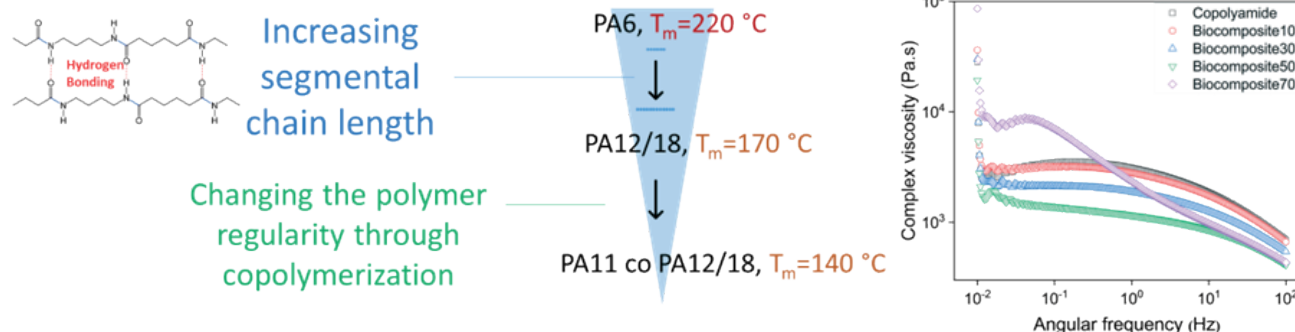
LOW MELTING POINT POLYAMIDE AND ITS BIOCOMPOSITES Hossein Baniasadi, Jukka Seppälä	55
SOFT HYDROXYAPATITE COMPOSITES BASED ON TRIAZINE-TRIONE SYSTEMS AS POTENTIAL BIOMEDICAL ENGINEERING FRAMEWORKS Jinjian Lin, Daniel J. Hutchinson, Michael Malkoch	56
NEXT GENERATION OF BIODEGRADABLE ADHESIVES FOR BONE REPAIR Jorge San Jacinto Garcia, Daniel J. Hutchinson, Natalia Sanz del Olmo, Michael Malkoch	57

LOW MELTING POINT POLYAMIDE AND ITS BIOCOMPOSITES

Hossein Baniasadi^{*}, Jukka Seppälä¹

¹ School of Chemical Engineering,
Aalto University, Espoo, Finland,

* hossein.baniasadi@aalto.fi



Plastic materials derived from renewable resources are gaining a growing interest in scientific research and industry to replace petroleum-based ones. Polyamides (PAs) are among the most frequent engineering polymers with excellent thermal and mechanical properties with various applications in the industries such as automobile parts, packaging, and electrical and electronic devices. Here, synthesis and characterization of a series of low melting point PAs are reported. These new PAs' families are prepared by copolymerizing

caster oil-based and petroleum-based ones through a polycondensation reaction. The samples reveal significant tensile strength, tensile modulus, and toughness compared with the commercial ones. Furthermore, they show significantly lower melting points, i.e., around 140 °C, making them exciting candidates for certain engineering applications, e.g., compounding with thermal sensitivity fillers. Accordingly, some biocomposites with a filler content of up to 70 wt.% are prepared by blending these low melting point polyam-

ides with starch, lignin, and microcrystalline cellulose. Fillers surface modification is done to make fillers compatible with the polyamide matrix. The developed biocomposites show excellent rheology properties even at such a high filler content. Besides, they possess good mechanical properties comparable with petroleum-based polymers like polyethylene and polypropylene. Furthermore, they can have a significant effect on the reduction of CO₂ release, making them exciting candidates for certain engineering applications.

References:

1. Baniasadi H, Lipponen S, Asplund M, Seppälä J. High-concentration lignin biocomposites with low-melting point biopolyamide. *Chem Eng J* **2023**;451:138564. <https://doi.org/10.1016/j.cej.2022.138564>.
2. Baniasadi H, Trifol J, Lipponen S, Seppälä J. Sustainable composites of surface-modified cellulose with low-melting point polyamide. *Mater Today Chem* **2021**;22:100590.

SOFT HYDROXYAPATITE COMPOSITES BASED ON TRIAZINE-TRIONE SYSTEMS AS POTENTIAL BIOMEDICAL ENGINEERING FRAMEWORKS

Jinjian Lin¹, Daniel J. Hutchinson¹,
 Michael Malkoch^{1*}

¹ KTH Royal Institute of Technology,
 Department of Fibre and Polymer
 Technology, Stockholm, Sweden

Presenting author: jinjian@kth.se,
 Corresponding author: * malkoch@kth.se

Recently developed composites based on triazine-trione (TATO) alkene and thiol monomers have positioned themselves as attractive alternatives to conventional methacrylate based dental composites. A high monomer conversion is achieved via high-energy visible light initiated thiol-ene coupling (HEV-TEC) chemistry, resulting in high modulus materials with excellent biocompatibility. Our research group has assessed trifunctional allyl and thiol TATO monomers together with hydroxyapatite

(HA) or glass fillers to develop composites with enhanced stiffness for use in bone fracture fixation^{1,2} and dental applications,³ respectively. However, the stiffness of the HA containing composites engineered for bone fixation is accompanied by brittleness. In order to broaden the scope of the TATO composite platform for biomedical applications, we herein describe new TATO monomers with increased structural flexibility which will widen the possible window of composite mechanical properties.

New alkene TATO monomers have successfully been synthesized containing ester and amide linkages using fluoride-promoted esterification (FPE) chemistry. Upon formulation with

complementary trithiol TATO monomers and HA fillers, the mixtures were cured via HEV-TEC chemistry. The mixtures exhibited similar viscosity to the previously reported formulation; however, the small structural alternation yielded composites with a large increase in flexibility. Taking into account the previously established anti-adhesion properties of our hydroxyapatite TATO-composites^{1,2} makes these new systems potentially suited as soft-tissue adhesion barrier coatings for metal implants. Combining the new ester and amide TATO monomers with the previous TATO should also allow for more fine tuning of the composites' mechanical properties, resulting in new clinical applications for thiol-ene based systems.

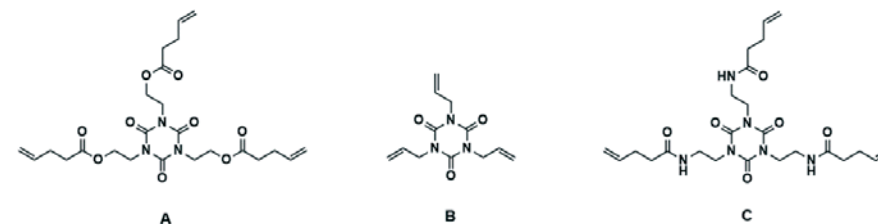


Figure: Morphological evolution of nanostructured poly(ionic liquid) from nano-vesicles to dense spheres, and their functionalization by copper nanoparticles.

References:

1. Hutchinson, D. J.; Granskog, V.; von Kieseritsky, J.; Alfort, H.; Stenlund, P.; Zhang, Y.; Arner, M.; Håkansson, J.; Malkoch, M. Highly Customizable Bone Fracture Fixation Through the Marriage of Composites and Screws. *Adv. Funct. Mater.* **2021**, 2105187.
2. Granskog, V.; García-Gallego, S.; von Kieseritzky, J.; Rosendahl, J.; Stenlund, P.; Zhang, Y.; Petronis, S.; Lyvén, B.; Arner, M.; Håkansson, J.; Malkoch, M. High-Performance Thiol-Ene Composites Unveil a New era of Adhesives Suited for Bone Repair. *Advanced Functional Materials*, **2018**, e1800372.
3. Arseneault, M.; Granskog, V.; Khosravi, S.; Heckler, I. M.; Mesa-Antunez, P.; Hult, D.; Zhang, Y.; Malkoch, M. The Dawn of Thiol-Yne Triazine Triones Thermosets as a New Material Platform Suited for Hard Tissue Repair. *Advanced Materials*, **2018**, e1804966.

NEXT GENERATION OF BIODEGRADABLE ADHESIVES FOR BONE REPAIR

Jorge San Jacinto Garcia, Daniel J. Hutchinson,
Natalia Sanz del Olmo, Michael Malkoch*

Department of Fibre and Polymer Technology,
School of Chemical Science and Engineering,
Fibre and Polymer Technology, KTH Royal
Institute of Technology, Stockholm, Sweden.

E-mail: jorgesjg@kth.se * E-mail: malkoch@kth.se

Open reduction internal fixation (ORIF) metal plates provide exceptional support for unstable bone fractures; however, the implants tend to cause tissue adhesions, which can lead to a reduction in flexibility after healing. In addition, their rigid shape limits the extent to which they can be customized by the surgeon in the operating theatre.

Our strategy for overcoming these issues is to replace the metal plate for a composite patch which is applied by the surgeon directly onto the fractured bone and fixated to the bone with metal screws or by priming the surface. Current composite system is produced from a mixture of allyl- and thiol-containing monomers with a high percentage of hydroxyapatite that is rapidly cured on demand via high-energy visible-light-induced thiol-ene coupling chemistry.^{1,2} The composite patch is a bone-like implantation fixator and in vivo studies in rodents showed no sign of soft-tissue adhesions. The customization, bone-like and soft-tissue repelling properties are highly compelling features that current traditional metal plating fixators lack. Unlike other bone adhesives, which are inserted between the

bone fragments, our composites patches are applied topologically which means that they don't interfere with the bone healing process and do not cause bone necrosis.¹

Thus far, the composites that we have developed do not show degradable behaviour. Isosorbide-based polycarbonates have been synthesized for inclusion in the composite formulation, with the aim of introducing biodegradability while maintaining high mechanical performance and biocompatibility. Polycarbonates exhibit appealing degradation properties, as their degradation does not decrease the pH of the local area which could damage the surrounding tissue.³ Polycarbonates based on isosorbide have also been shown to have high T_g and mechanical properties.^{4,5,6}

References:

1. Hutchinson, D.J; Granskog, V.; Kieseritzky, J.; Alfort, H.; Stenlund, P.; Zhang, Y.; Malkoch, M. Highly Customizable Bone Fracture Fixation through the Marriage of Composites and Screws. *Adv. Funct. Mater.* **2021**, 2105187.
2. Arseneault, M.; Granskog, V.; Khosravi, S.; Heckler I.M.; Mesa-Antunez, P.; Hult, D.; Zhang, Y.; Malkoch, M. The Dawn of Thiol-Yne Triazine Triones Thermosets as a New Material Platform Suited for Hard Tissue Repair. *Adv. Mater.* **2018**, 30, 1804966.
3. Tempelaar, S.; Mespouille, L.; Coulembier, O.; Dubois, P.; Dove, A.P. Synthesis and post-polymerisation modifications of aliphatic poly(carbonate)s prepared by ring-opening polymerisation. *Chem. Soc. Rev.*, **2013**, 42, 1312-1336.
4. Fenouillot, F.; Rousseau, A.; Colomines, G.; Saint-Loup, R.; Pascault, J.P. Polymers from renewable 1,4:3,6-dianhydrohexitols (isosorbide, isomannide and isoidide): A review. *Prog. Polym. Sci.*, **2010**, 35, 578-622.
5. Hult, D.; Garcia-Gallego, S.; Ingverud, T.; Andren, O.; Malkoch, M. Degradable high T_g sugar-derived polycarbonates from isosorbide and dihydroxyacetone. *Polym. Chem.*, **2018**, 9, 2238-2246.
6. Olsson, J.V.; Hult, D.; Garcia-Gallego, S.; Malkoch, M. Fluoride-Promoted carbonylation polymerization: a facile step-growth technique to polycarbonates. *Chem. Sci.*, **2017**, 8, 4853.

Nordic Polymer Days 2023 **ADDITIVE MANUFACTURING**

CRYSTALLIZATION OF POLYAMIDE 11 IN SELECTIVE LASER SINTERING CONDITIONS Anahi Payen, Brendan Huitorel	59
3D PRINTED CONDUCTING POLYMER BLENDS FOR ELECTRONIC DEVICES Ida Östergren , Anna Hofmann, Youngseok Kim, Sven Fauth, Myung-Han Yoon, Anja Lund and Christian Müller	60
3D PRINTABLE BIOPOLYMERS FOR SOFT ROBOTICS Sergejs Gaidukov	61

CRYSTALLIZATION OF POLYAMIDE 11 IN SELECTIVE LASER SINTERING CONDITIONS

Anahi Payen¹, **Brendan Huitorel**^{*}

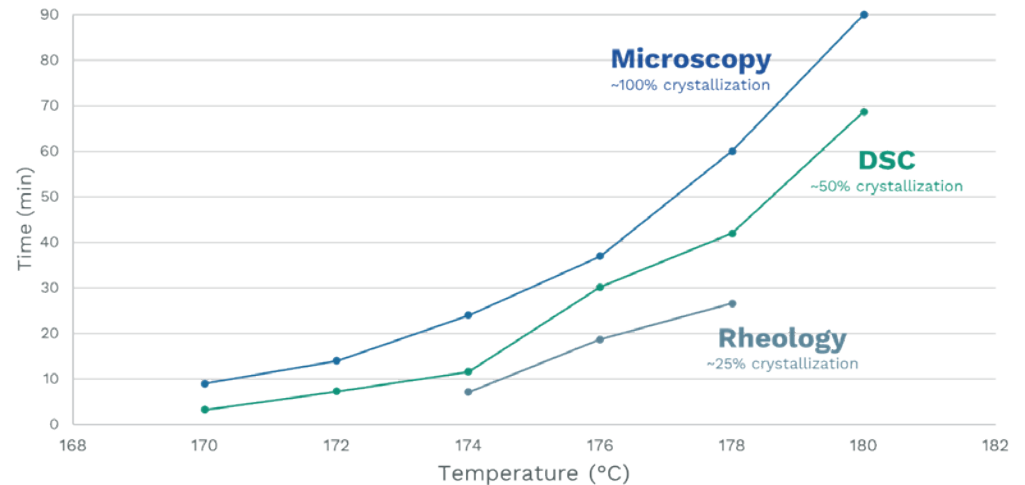
¹ Arkema, CERDATO Research Centre,
Route du Rilsan, 27470 Serquigny, France

^{*} brendan.huitorel@arkema.com

Committed to a sustainable world, Arkema is a global supplier of advanced, biobased, circular, and durable materials. Among them, polyamide 11 (PA11) is one of the most emblematic high-performance polymers offered by Arkema as it is made from castor oil produced in a sustainable way and addresses demanding applications in various markets such as industrial, automotive, sports and 3D printing.

PA11 powders are very suitable for several Powder Bed Fusion technologies such as Selective Laser Sintering (SLS) [1]. SLS is an additive manufacturing technology consisting in spreading a thin layer of powder then exposing the desired areas to a laser radiation to selectively melt the powder and finally iterating

Figure:
Characteristic times of PA11 crystallization derived from POM, DSC and parallel plates rheology.



these two steps [1]. SLS process temperatures lead to quasi-isothermal crystallization conditions of semi-crystalline polymers. As the mechanical properties and dimensional accuracy of the printed parts highly depend on their crystallinity, such conditions have widely been investigated for polyamide 12 [2,3] which is the most used polymer in SLS but much less for PA11.

Crystallization kinetics of PA11 in the range of SLS process temperatures has been investigated by Differential Scanning Calorimetry (DSC) and Polarized Optical Microscopy (POM) as well as its rheological behaviour. These data will help designing new PA11 based materials for SLS and feed numerical models to simulate the behaviour of the materials during the SLS process.

References:

1. Wang, Y.; Xu, Z.; Wu, D.; Bai, J. Current Status and Prospects of Polymer Powder 3D Printing Technologies. *Materials*, **2012**, 13 (10), 2406
2. Balemans, C.; Loojijmans S. F.S.P.; Grosso, G.; Hulsen, M. A.; Anderson P. D. Numerical analysis of the crystallization kinetics in SLS. *Additive Manufacturing*, **2020**, 33, 101126
3. Drummer, D.; Greiner, S.; Zhao M.; Wudy, K. A novel approach for understanding laser sintering of polymers. *Additive Manufacturing*, **2019**, 27, 379-399

3D PRINTED CONDUCTING POLYMER BLENDS FOR ELECTRONIC DEVICES

Ida Östergren,¹ Anna Hofmann,¹
Youngseok Kim,² Sven Fauth,¹
Myung-Han Yoon,² Anja Lund¹
and Christian Müller¹

1 Department of Chemistry and Chemical Engineering, Chalmers University of Technology, 41296 Göteborg, Sweden

2 School of Materials Science and Engineering, Gwangju Institute of Science and Technology, 61005 Gwangju, Republic of Korea

E-mail: idaho@chalmers.se

Plastic electronics is attracting a lot of attention since it promises a cost-efficient large-scale production of light and flexible electronic devices. To date, most conjugated polymers are solution processed and used in the form of sub-micrometer thin films. However, melt processing of conjugated polymers such as the widely used poly(3,4-ethylenedioxythiophene) (PEDOT) is a major challenge. It would be desirable to develop methods that enable the fabrication of different bulk architectures and shapes.

In this work we describe a new strategy, which makes it possible to use Fused Filament Fabrication (FFF) to produce conducting structures

that comprise PEDOT and Nafion.¹ In a first step, the stiffness and adhesion of a melt-processable precursor of Nafion was optimized by blending with the current benchmark polymer for 3D printing, Acrylonitrile Butadiene Styrene (ABS). In a second step, PEDOT was polymerized within a 3D-printed, porous Nafion template, created by chemically activating its precursor and selective dissolution of ABS. A number of melt-processed shapes are realized, such as conducting fibers, as well as various 3D-printed electronic devices, including organic electrochemical transistors (OECTs) and thermoelectric modules, which highlights the versatility of our bulk-processing strategy.

References:

1 Hofmann et. al. Appl. Mater. Interfaces, 12, 7, 8713–8721 (2020).

3D PRINTABLE BIOPOLYMERS FOR SOFT ROBOTICS

Sergejs Gaidukov¹

¹ Institute of Polymer Materials,
Faculty of Materials Science and Applied
Chemistry, Riga Technical University,
P. Valdena 3/7, Riga LV-1048, Latvia

* sergejs.gaidukovs@rtu.lv

Herein we demonstrate the design and fabrication of a novel concept to prepare electromechanical actuators from electronically conductive electrodes and ionic conductive biopolymers. The biobased polymer resins based on vegetable oils in combination with piezoelectric polymer have been applied to prepare the electromechanical device. The developed actuator is suitable for use in electronic devices and soft-robotic applications.

The aim is to adjust the actuating and sensing performance of the vegetable oil-based ionic gel composite materials by resin formulation loaded with ionic liquids and carbon nanotubes. The membrane and electrode materials were developed with minimum use of organ-

ic solvents to preserve eco-friendliness. The developed resin formulations were 3D printed using UV light-assisted printing technologies. The vat and syringe printing methods were developed for the proposed materials processing.

The electroconductivity, mechanical, thermal, structural, and dynamical mechanical properties and electromechanical actuation performance have been investigated. This short report shows the potential of the proposed concept and will serve as a foundation for future studies of vat photopolymerization additive manufacturing processing of bio-based high-conductivity polymers.

Acknowledgment:

ERA.Net project "UV-assisted 3D-printing of Ionic Electroactive Polymer Actuators for Soft Robotics" (UPRINTAROBOT)

Nordic Polymer Days 2023

RECYCLING

ARTIFICIAL TURF - ENVIRONMENTAL CONCERNS AND FUTURE TRENDS Fritjof Nilsson	63
INFLUENCE OF WASHING MEDIA AND TEMPERATURE ON THE PROPERTIES OF RECYCLED POST-CONSUMER FLEXIBLE POLYETHYLENE PACKAGING WASTE Ezgi Ceren Boz Noyan, Antal Boldizar	64
RECYCLING AND REUSE OF GLASS FIBRE (GF)-REINFORCED COMPOSITES FOR HIGH PERFORMANCE ENGINEERING APPLICATIONS Kyriaki Gkaliou, Michael Lei, Allan Hjarbæk Holm, Anders Egede Daugaard	65
STATE-OF-THE-ART THERMOSET RECYCLING Alexander Sandahl, Andreas Sommerfeldt	66

ARTIFICIAL TURF - ENVIRONMENTAL CONCERNS AND FUTURE TRENDS

Fritjof Nilsson (Docent),
Polymeric Materials, KTH.
fritjofn@kth.se



Artificial turf pitches has several advantages compared to traditional grass- and gravel sportsfields for e.g. football. The annual number of available play-hours increases whereas the required maintenance and cost is often reduced. Therefore the number of artificial turf pitches is rapidly increasing. The total number was around 1 150 and 21 000 in Sweden and Europe, respectively (September 2020).

The majority of today's artificial turf pitches consist of artificial grass (mainly LDPE) filled with rubber granulates of e.g. SBR, EPDM, TPE and (to lesser extent) sand and organic infill. In order to reduce the spreading of microplastics, the EU is planning a ban of selling rubber granulates within ca 6 years, which will make today's rubber infill illegal. Unfortunately, also the alternative infills have drawbacks, in particular from player perspective.

Which pros and cons have different alternative infill materials, considering environment, cost, and playability? How can turf fields be constructed in the future to minimize the environmental impact with respect to microplastics, climate change and chemicals? Which are the current trends? Those questions will be addressed in this presentation.

INFLUENCE OF WASHING MEDIA AND TEMPERATURE ON THE PROPERTIES OF RECYCLED POST-CONSUMER FLEXIBLE POLYETHYLENE PACKAGING WASTE

Ezgi Ceren Boz Noyan, Antal Boldizar
Department of Industrial and Materials Science,
Chalmers University of Technology, Sweden

* ezgi.boznoyan@chalmers.se

Plastic packaging products, typically flexible film packaging, has been the largest application area for polymeric materials for many decades, constituting a major source of waste in society. Plastics packaging is also the fastest growing application area but considered to be the most challenging for material recycling. Complexities and challenges in recycling requires better understanding on influence of processing parameters, e.g., compounding and washing, on properties of the recycled materials made of post-consumer flexible plastic packaging waste.

In our previous studies the focus was more on understanding first the properties of untreated post-consumer flexible polyethylene packaging waste and secondly the influence of selected compounding parameters. Two different temperature profiles and screw configurations were used in compounding to assess the influence. The results showed that the studied compounding parameters had no

great influence on the melting temperature, crystallinity, stiffness and strength of the samples. However, thermo-oxidative degradation apparently occurred after washing especially with industrial-scale washing at 70-80°C and deteriorated further when compounded at a high temperature profile. The elongation at break of injection moulded samples made of unwashed waste increased with high temperature compounding but for the washed waste the opposite was observed. Overall results indicated the importance of washing step and its influence on final properties.

The work continued with a focus on the influence of washing media and the temperature on properties of recycled post-consumer flexible polyethylene packaging waste. Laboratory-scale washing was done with three different washing medias: water, water + NaOH and water + detergent. Washings were done both at 25 and 40°C, referred to as hot and cold washing, respectively. The compounding and injection moulding parameters were kept the same for all samples and as in the previous work. The properties of intermediates and the moulded samples were analysed with high temperature gel permeation chromatography, capillary rheometry and both the thermal and mechanical properties were assessed.

The results showed that neither the washing media nor the washing temperature studied in this work had a significant influence on the thermal properties of the samples. The oxidation induction temperatures were on a similar level for all samples, being between 225-232°C, implying that the samples still contained a significant amount of active stabilizers. Similarly, the viscosity curves were in a similar range which was supported with the melt-mass flow rate measurements. However, the pressure losses at capillary flow were differed indicating different elasticity of the melts. Rheotens type of measurements clearly showed differences in the tenacity of melts. Washing with NaOH resulted in the lowest strain at break for the melts whereas the washing with only water and with detergent showed similar levels of strain at break of melts. The melt strengths were in a similar range for all the samples. Concerning the mechanical properties of injection moulded samples, the elongation at break was the most influenced property, the samples washed with NaOH had the lowest values whereas the other washings resulted in mouldings with similar elongation at break. The Young's modulus and the tensile strength values were less changed by the washings. In general the washing temperature had no major impact.

RECYCLING AND REUSE OF GLASS FIBRE (GF)-REINFORCED COMPOSITES FOR HIGH PERFORMANCE ENGINEERING APPLICATIONS

Kyriaki Gkaliou^{1*}, Michael Lei¹,
Allan Hjarbæk Holm¹, Anders Egede Daugaard²

¹ Grundfos A/S,

² Technical University of Denmark, Department
of Chemical and Biochemical Engineering,
The Danish Polymer Centre.

* kyrgk@kt.dtu.dk

Glass fibre-reinforced composite materials are used extensively across the globe due to their highly attractive performance-to-price ratio. They are primarily used in engineering applications such as construction, marine, aerospace, or piping industries [1]. With an increasing demand for such composite

materials, awareness concerning their waste management is rising. Nowadays, the concept of end-of life-cycle behind the design of composite materials is not always considered, which translates into a lack of attention regarding the different recycling possibilities besides landfilling. To add this, incineration or landfills are becoming more restricted due to the environmental pollution as well as the prevention of reuse opportunities [2].

Currently, the most important recycling strategies comprise mechanical, chemical and thermal recycling. Regarding the GF-reinforced composites, thermal recycling, such as pyrolysis, which thermochemically decompose the cross-linked matrix material into valuable liquid and gas products, consumes lower energy, compared to other widely adopted industrial processes (e.g., solvolysis) [3]. In this recycling technique, although the recov-

ered GF can be reused as a reinforcement in thermoplastics [4], a considerable drop in fibre strength often in the 80%–90% range, is observed compared to its original state. On the other hand, mechanical recycling is considered a better recycling option, in terms of material conservation, but still suffers from a shortening of fibres during processing. This pathway enables direct recycling and manufacturing new parts with the ground composites. Typical applications for mechanically recycled composites include their reuse as a reinforcement (fibrous-rich fraction) for less mechanical demanding sectors [5], or their re-incorporation with the pristine material in new composites. This study will focus on the recovery and reuse of GF-based composites regarding to limitations in recycling thermoset and re-manufacturing of thermoplastic composites.

References:

1. Sathishkumar, T. P.; Satheeshkumar, S.; Naveen, J. Glass fiber-reinforced polymer composites—a review. *Journal of reinforced plastics and composites*, **2014**, 33.13: 1258-1275.
2. Rani, M., et al. A review on recycling and reuse methods for carbon fiber/glass fiber composites waste from wind turbine blades. *Composites Part B: Engineering*, **2021**, 215: 108768.
3. Naqvi, S. R., et al. A critical review on recycling of end-of-life carbon fibre/glass fibre reinforced composites waste using pyrolysis towards a circular economy. *Resources, conservation and recycling*, **2018**, 136: 118-129.
4. Gkaliou, K.; Daugaard, A. E. Silane and silazane surface modification of recycled glass fibers for polypropylene composites. *Journal of Applied Polymer Science*, **2023**, 140.5: e53388.
5. Bernatas, R., et al. Recycling of fiber reinforced composites with a focus on thermoplastic composites. *Cleaner Engineering and Technology*, **2021**, 5: 100272.

STATE-OF-THE-ART THERMOSET RECYCLING

Alexander Sandahl¹, **Andreas Sommerfeldt**¹

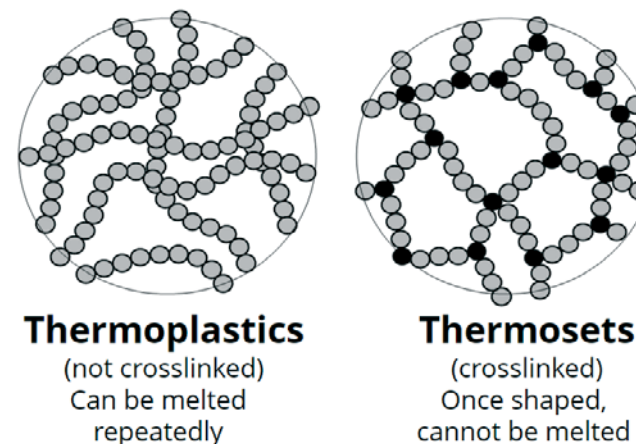
¹ Danish Technological Institute,
Kongsvang Allé 29, Aarhus, Denmark

ales@teknologisk.dk &
asom@teknologisk.dk

Plastic thermoset is applied in products with high durability requirements. Often these materials are used as complex composites, combined with glass or carbon fibers. In total, this represents a major yet unsolved challenge when it comes to recycling. Thermosets represent roughly 15% of our total plastic produced globally. Compared to its melttable thermoplastic counterparts, no clear recycling routes have been identified, beside energy-recycling via incineration. A fair amount of research into new materials such as vitrimers, degradable crosslinks, etc. has

been established academically, and show a future with designed-for-recycling products. This, however, does not counter the legacy burden of end-of-life products discarded today, recently emphasized by the media showing large graveyards of decommissioned wind-turbine blades, destined for landfill. We take a holistic point of view: What are the possibilities within thermoset recycling, showing specific cases for mechanical and chemical thermoset recycling, as well as Danish Technological Institutes newest project regarding enzymatic degradation.

Figure: Comparison of thermoplast and thermoset, main difference being the crosslinkages.



Nordic Polymer Days 2023

POLYMERS FOR ELECTRICAL APPLICATIONS

**DOUBLE DOPING OF A LOW-IONIZATION-ENERGY
POLYTHIOPHENE WITH A MOLYBDENUM
DITHIOLENE COMPLEX**

69

Emmy Järsvall, Till Biskup, Yadong Zhang, Renee Kroon,
Stephen Barlow, Seth R. Marder, Christian Müller

**CATIONIC CELLULOSE NANOFIBRILS-BASED
ELECTRO-ACTUATORS: THE EFFECTS OF
COUNTERANION AND ELECTROLYTE**

70

Frederic Heraly, Bo Pang, Jiayin Yuan

**HELIUM-ION IRRADIATION EFFECTS
IN METALIZED POLYPROPYLENE**

71

Shova Neupane, Serguei Chiriaev,
William Greenbank, Thomas Ebel, Luciana Tavares

**KINETICS AND THERMODYNAMICS OF THE
EFFECTS OF COPPER ON HIGH PERFORMANCE
MATERIAL POLYETHER ETHER KETONE**

72

Sirui Liu, Mikael S. Hedenqvist

**LAYER-BY-LAYER FABRICATION OF
POLYPROPYLENE-BASED NANOCOMPOSITES
FOR CAPACITOR DIELECTRIC APPLICATIONS**

73

William Greenbank, Bartosz Gackowski,
Shova Neupane, Luciana Tavares, Thomas Ebel

**CROSSLINKING METHODOLOGY FOR
IMIDAZOLE-FUNCTIONALIZED SILICONE
YIELDING AN ELASTOMER OPERATED AT LOW
ELECTRICAL FIELDS WITH HIGH STRAINS**

74

Zhaoqing Kang, Liyun Yu, Anne Ladegaard Skov

DOUBLE DOPING OF A LOW-IONIZATION-ENERGY POLYTHIOPHENE WITH A MOLYBDENUM DITHIOLENE COMPLEX

Emmy Järsvall¹, Till Biskup², Yadong Zhang³,
Renee Kroon^{1,4}, Stephen Barlow^{3,5},
Seth R. Marder^{3,5}, Christian Müller^{1*}

1 Chalmers University of Technology,

2 University of Saarland,

3 Georgia Institute of Technology,

4 Linköping University,

5 University of Colorado Boulder,

* Christian.muller@chalmers.se

Doping of organic semiconductors is crucial for tuning the charge-carrier density of conjugated polymers. The exchange of more than one electron between a monomeric dopant and an organic semiconductor allows the polaron density to be increased relative to the number of counterions that are introduced into the host matrix. Here, a molybdenum dithiolene complex with a high electron affinity of 5.5 eV is shown to accept two electrons from a polythiophene that has a low ionization energy of 4.7 eV. Double p-doping is consistent with the ability of the monoanion salt of the molybdenum dithiolene complex to dope the polymer. The transfer of two electrons to the neutral dopant was also confirmed by electron paramagnetic resonance spectroscopy since the monoanion, but not the dianion, of the molybdenum dithiolene complex features an unpaired electron. Double doping allowed an ionization efficiency of 200% to

be reached, which facilitates the design of strongly doped semiconductors while lessening any counterion-induced disruption of the nanostructure

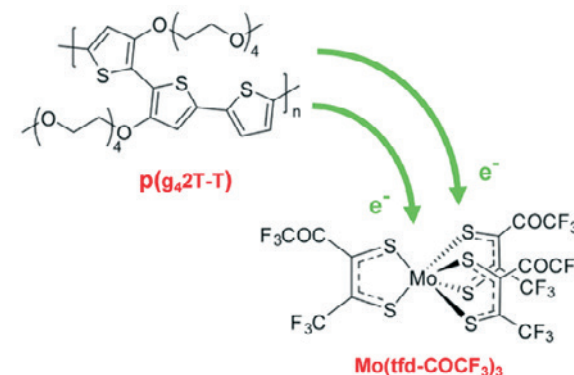


Figure: Schematic figure illustrating double charge transfer from the polymer p(g42T-T) to the dopant F4TCNQ

References:

1. Publication Date: June 13, 2022. Chem. Mater. 2022, 34, 12, 5673–5679. <https://doi.org/10.1021/acs.chemmater.2c01040>

CATIONIC CELLULOSE NANOFIBRILS-BASED ELECTRO-ACTUATORS: THE EFFECTS OF COUNTERANION AND ELECTROLYTE

Frederic Heraly¹, Bo Pang¹, Jiayin Yuan^{1*}

¹ Department of Materials and Environmental Chemistry, Stockholm University, Svante Arrheniusvåg 16C, Stockholm 106 91, Sweden,

* Jiayin.Yuan@mmk.su.se

Cellulose-based electro-actuators have enormous potential in various applications, e.g. artificial muscles, soft grippers, medical devices, just to name a few, owing to their high mechanical strength, lightness and natural abundance. However, significant challenges remain in the fabrication of such electro-actuators featuring low operating voltage and fast response kinetics. We report here a facile fabrication route towards high-performance electro-actuators composed of CNFs films doped with ionic liquids or lithium salts and sandwiched by two thin film gold electrodes. Large bending motion at voltages as low as 3.0 V could be observed. The size effect of both anions and cations on the actuation was comprehensively investigated. CNF-TFSI@LiTFSI and CNF-BF₄@EMIM-BF₄ electro-actuators presented the best bending strain under an AC voltage of 3.0 V. This work pro-

vides new inspiration in the design of natural polymer-based high-performance electro-actuators.

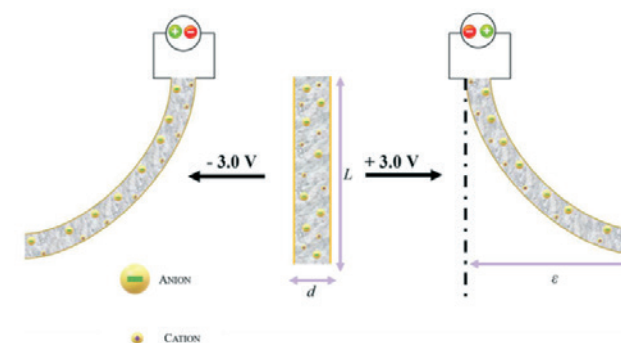


Figure: Scheme of the actuation mechanism of an ionic electroactive polymer actuator. The asymmetric volume expansion leads to a bending motion where here the size of the anion is bigger than the cation size.

HELIUM-ION IRRADIATION EFFECTS IN METALIZED POLYPROPYLENE

Shova Neupane^{1*}, Serguei Chiriaev², William Greenbank¹, Thomas Ebel¹, Luciana Tavares¹

¹ Centre for Industrial Electronics, University of Southern Denmark, Alsion 2, DK-6400 Sønderborg, Denmark

² Mads Clausen Institute, University of Southern Denmark (SDU), Alsion 2, DK-6400 Sønderborg, Denmark.

* neupane@sdu.dk

Polypropylene (PP) films are widely used as dielectric materials for capacitors in high-frequency and high-power applications due to their excellent dielectric strength, reliability, and low dissipation factor. Further improvements in the performance of capacitors requires modified dielectric materials with higher permittivity and breakdown strength, which is crucial to increase the stored energy density. Another approach for increasing de-

vice capacitance is to decrease the dielectric thickness, which can be limited by the fabrication process. In this work, we demonstrate that Helium-ion irradiation (HII) can be used to manipulate the thickness of PP films with nanometer precision. We present the influence of different metallization materials on the dependence of polymer shrinkage on the irradiation dose. Electron-beam deposition was used to metalize two types of PP films: the thinnest commercially available biaxially oriented PP (BOPP) and spin-coating PP films. Three different types of metallization were used: 5 nm of Pd40Pt60, 5 nm of Au, and 15 nm of Al. The irradiation was done with a Helium-ion beam (He-FIB) in a Zeiss Orion NanoFab Microscope at a landing energy of 25 keV with doses in a range of 5.4×10^{-5} nC/ μm^2 to 8.07×10^{-3} nC/ μm^2 . He-FIB was used to construct surface patterns similar to those fabricated in our previous study [1] of other polymer materials irradiated with FIBs. Atomic force microscopy (AFM) and optical microscopy were used to analyze the details of surface modification: the surface height [1] and root

mean square (RMS) roughness. Irradiation-induced reduction in the surface height and negligible sputtering of metallization were observed in all irradiated samples, which is consistent with results of our previous work [1] on other polymer materials. The Al-coated samples demonstrated smaller surface-height losses compared to the losses observed in the Pt40Pd60 and Au-coated samples. Possible factors responsible for this effect include differences in the thickness and the crystalline-grain structure of the metallization films.

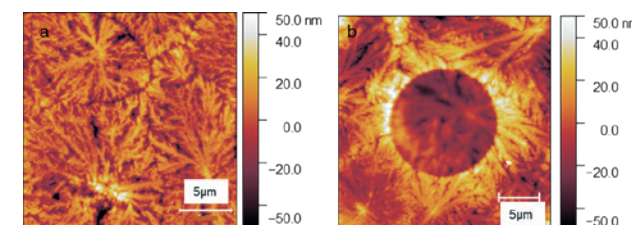


Figure: AFM images of the surface of spin-coated PP film before (a) and after (b) FIB-He irradiation. The irradiated region is the dark circle in b).

References:

- Chiriaev, S.; Tavares, L.; Adashkevich,.; Goszczak, A. J.; Rubahn, H-G. Out-of-plane surface patterning by subsurface processing of polymer substrates with focused ion beams. *Beilstein journals of nanotechnology*, **2020**, (11),1693-1703.

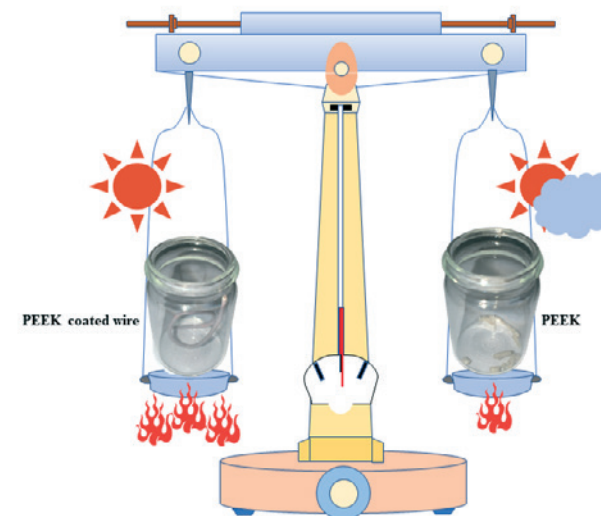
KINETICS AND THERMODYNAMICS OF THE EFFECTS OF COPPER ON HIGH PERFORMANCE MATERIAL POLYETHER ETHER KETONE

Sirui Liu¹, Mikael S. Hedenqvist^{1*}

¹ Department of Fibre and Polymer Technology, Polymeric Materials Division, School of Engineering Sciences in Chemistry, Biotechnology and Health. KTH Royal Institute of Technology, Stockholm 114 28, Sweden.

Presenting author's email:
siruilu@kth.se,
corresponding author's email
*: mikaelhe@kth.se

The environment in electric motors in vehicles is harsh, with the presence of oil, moisture, air/oxygen and elevated temperature. This requires the use of high-performance polymers as electric insulation on the electric wires. Even though the polymers are high performing, it is necessary to understand how these interact with the specific environment to be able to determine the ageing behaviour and ultimately the lifetime of the insulation. We here assess the extent and kinetics of the ageing of polyether ether ketone (PEEK) and polysulphone (PPS) at high temperature alone or in presence of the copper wires. The latter to reveal any copper-induced polymer ageing. The evaluation of the experimental data is based on thermogravimetry (TG) and differential thermal analysis (DTA) with the use of a model-free Ozawa–Flynn–Wall (OFW) method.



References:

1. Wenlong Zhang¹, A. B.; Jia Jia², C. D.; Jiaqing Zhang³, E.; Yanming Ding⁴, F. G. Pyrolysis and combustion characteristics of typical waste thermal insulation materials. *Sci. Total Environ.*, **2022**, 834,155484.
2. Xuanzhe Ling¹, A. B.; Xishuang Jing², C. D.; Chengyang Zhang³, E.; Siyu Chen⁴, F. G. Polyether Ether Ketone (PEEK) Properties and Its Application Status. *IOP Conf Ser Earth Environ Sci.*, Guangzhou, China. Dec 27-29, **2019**.

LAYER-BY-LAYER FABRICATION OF POLYPROPYLENE-BASED NANOCOMPOSITES FOR CAPACITOR DIELECTRIC APPLICATIONS

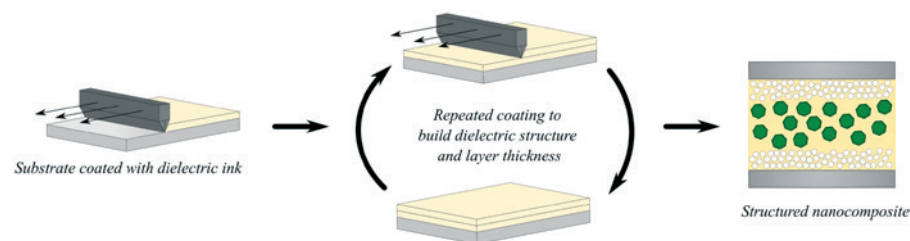
William Greenbank^{1*}, Bartosz Gackowski¹,
Shova Neupane¹, Luciana Tavares¹, Thomas Ebel¹.

¹ Centre for Industrial Electronics,
University of Southern Denmark,
Alsion 2, DK-6400 Sønderborg, Denmark

* greenbank@sdu.dk

Metallised film capacitors are critical devices in many high-voltage power electronics applications, particularly for e-mobility and green energy. They predominantly use polypropylene (PP) as their dielectric, which lends excellent high-voltage breakdown strength and reliability. However, due to a low dielectric constant and a need for cooling, PP-based capacitors must be voluminous and heavy, limiting the potential efficiency of power electronics and range of electric vehicles. Nanocomposite dielectrics in which ceramic nanoparticles are dispersed in a PP (or similar thermoplastic) matrix offer a promising pathway to improving the thermal stability, energy

Figure: A schematic of the layer-by-layer nanocomposite dielectric fabrication process.



density and volumetric capacitance of metallised film capacitors, while maintaining their reliability and high voltage tolerance.

Two of the key barriers to the widespread adoption of nanocomposite capacitors are nanoparticle clustering and scalable fabrication. Polymer melt extrusion (the current industry standard) of homogenous nanocomposite films is challenging due to the difficulty preventing formation of clusters of nanoparticles. The agglomeration sites reduce the contact area between the filler and polymer matrix and lead to an accumulation of space charge, which reduces the mechanical and electrical properties.

For this reason, we have developed a fabrication technique based on polypropylene gel inks,¹ which allows the layer-by-layer fabrication of nanocomposite dielectric layers. We demonstrate that this technique is capable of fabricating structured dielectrics with improved performance compared to polymer-only dielectrics² and discuss the possibilities for this technique to act as a platform for the testing of different nanomaterials in capacitor dielectric applications, and its potential for the large-scale fabrication of commercial nanocomposite capacitors.

References:

- Greenbank, W.; Ebel, T. Layer-by-layer printable nano-scale polypropylene for precise control of nanocomposite capacitor dielectric morphologies in metallised film capacitors. *Power Electronic Devices and Components* **2023**, 4, 100025
- Greenbank, W., Gupta, P., Fiutowski, J. & Ebel, T. Layer-by-layer printed dielectrics: scalable nanocomposite capacitor fabrication for the green transition. in *PCIM Europe 368–374* (VDE Verlag, 2022). doi:10.30420/565822052

CROSSLINKING METHODOLOGY FOR IMIDAZOLE-FUNCTIONALIZED SILICONE YIELDING AN ELASTOMER OPERATED AT LOW ELECTRICAL FIELDS WITH HIGH STRAINS

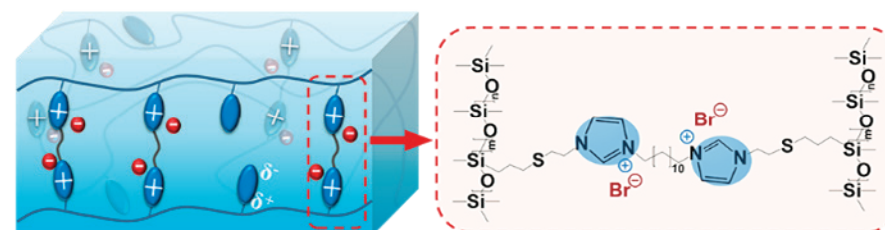
Zhaoqing Kang, Liyun Yu, Anne Ladegaard Skov*

Danish Polymer Center, Department of Chemical and Biochemical Engineering, Technical University of Denmark, Kgs. Lyngby, Denmark

Email: al@kt.dtu.dk zhkang@kt.dtu.dk

Dielectric elastomers (DEs), commonly referred to as “artificial muscles”, can reversibly alter their size or shape in response to an externally applied electrical field, giving them great potential within the area of soft robotics and artificial muscles. A high relative permittivity has been targeted for several years to improve the actuation performance of DEs, but most successful methods then either increase the stiffness of the elastomer and/or introduce notable losses of both mechanical and dielectric nature. For silicone-based elastomers, most high permittivity moieties inhibit the sensitive platinum catalyst used for the addition curing scheme. Different from the

Figure: Preparation of IL-elastomers by the crosslinking reaction between multifunctional imidazole-grafted silicone with difunctional dibromododecane.



traditional ways to prepare silicone elastomers by addition curing reaction, a novel strategy is reported via the crosslinking reaction between multifunctional imidazole-grafted silicone with difunctional bis(1-ethylene-imidazole-3-ium) bromide ionic liquid (bis-IL) in this study. The prepared IL-elastomer entails uniformly dispersed ionic liquid and presents stable mechanical and dielectric properties due to the covalent nature of the crosslinking as opposed to previously reported physical mixing in of ionic liquids. Furthermore, the

IL-elastomer has a relative permittivity of 8 at 10-1 Hz, which is ~3 times as high as that of commercial silicone elastomers (typically ~3). Young's modulus of ~0.04 MPa and strain at break of ~180 % are recognized for the IL-elastomer as well. As a result of the excellent combination of properties, the dielectric actuator developed exhibits an area strain of 20 % at 15 V/ μm . The outstanding actuation performance of this novel elastomer suggests a promising potential for use in artificial muscles, soft robotics, and electroactive devices.

References:

1. Shi, L.; Zhang, C.; Du, Y.; Zhu, H.; Zhang, Q.; Zhu, S. Improving Dielectric Constant of Polymers through Liquid Electrolyte Inclusion. *Adv. Funct. Mater.*, 2021, 31(8): 2007863.
2. Skov, A. L.; Yu, L. Optimization Techniques for Improving the Performance of Silicone-Based Dielectric Elastomers. *Adv. Eng. Mater.*, 2018, 20(5): 1700762.

Poster Presentations



Nordic Polymer Days

Nordic Polymer Days 2023 POSTER PRESENTATIONS

**BENZODIFURANONE-BASED CONJUGATED
POLYMERS MADE SOLUBLE WITH SINGLE
OXYGEN-CONTAINING SIDE CHAINS
FOR THERMOELECTRIC APPLICATIONS**

Diego R. Hinojosa, Nathan Pataki,
Mario Caironi, Michael Sommer

78

**DISPERSIBILITY OF NANOPARTICLES WITH
DIFFERENT SURFACE FUNCTIONALIZATION
AT VARIOUS PROCESSING PARAMETERS
IN THE INTERNAL MIXER**

David Peltner, Siegfried Werner, Dirk W. Schubert

79

**ELECTROSPUN ANTIMICROBIAL MEMBRANES
FROM CATIONIC CHITOSANS FOR
WOUND HEALING DRESSINGS**

Arun Teotia, Isabella Lauren,
Nina Lindfors, Jukka Seppala

80

**SYNTHESIS OF BIO-BASED POLYMERS
WITH USE OF MICROWAVE CHEMISTRY**

Grammatiki Terzi, Jeppe Madsen,
Anders Egede Daugaard

81

**ENHANCED HEAT DISSIPATION PROPERTY FOR
METALLIZED POLYPROPYLENE FILM CAPACITORS**

Odysseas Gkionis-Konstantatos, William Greenbank,
Shova Neupane, Thomas Ebel, Luciana Tavares

82

**IMPACT OF STORAGE AND PROCESSING
ON MORPHOLOGY IN THERMOPLASTIC
POLYETHER-URETHANES**

Michael Redel, Christian Regelman,
Bastian Wölfel, Dirk W. Schubert

83

**GRAFTING ZWITTERIONIC POLYMERS ON
DIALCOHOL CELLULOSE NANOCRYSTALS**

Maryam Madani, Hossein Baniasadi, Jukka Seppälä

84

**THERMOMECHANICAL PROPERTIES
OF ELECTROCONDUCTIVE VEGETABLE
OIL-BASED MEMBRANES FOR SOFT ROBOTICS**

Oskars Platnieks, Maksims Jurinovs, Sergejs Gaidukovs

85

**FABRICATION OF THIN ELECTROACTIVE
POLYDOPAMINE FILMS BY
ELECTROSPRAY DEPOSITION**

Majid Al-waeel, Jukka Lukkari, **Mikko Salomäki**

86

CONTENT CONTINUES NEXT PAGE >>

Nordic Polymer Days 2023 POSTER PRESENTATIONS

CHARACTERIZATION OF “POLYETHYLENE OF RAISED TEMPERATURE RESISTANCE” (PE-RT) MATERIALS – A MINI REVIEW AND NEW INSIGHTS

Nicolai Schneider, Joachim Kaschta,
Ines Heiduk, Dirk W. Schubert

87

NEW ASSESSMENT METHOD FOR THE COMPATIBILITY OF LIGNIN-POLY (LACTIC ACID) POLYMER BLENDS

Oskar Backman, Ellen Sundström, Luyao Wang,
Patrik C. Eklund, Chunlin Xu

88

CONDUCTIVE POLYURETHANE/PEGYLATED GRAPHENE OXIDE COMPOSITE FOR 3D-PRINTED NERVE GUIDANCE CONDUITS

Afsoon Farzan, Sedigheh Borandeh, Jukka Seppälä

89

INVESTIGATING THE SYNTHESIS AND PROPERTIES OF POLYTHIOUREAS AND POLYTHIOCARBAMATES

Rafael N L Menezes, Olga Gordivska, Baozhong Zhang

90

A MODULAR APPROACH TO BUILDING POLYMER-BASED DURABLE PLUGS

Skowyra M.M., **Echarri-Giacchi M.**, Ivanova Y.D.,
Ravnkilde K.M., Frederiksen C.H., Skov A.L.

91

CONVENTIONAL NON-WOVEN VS. NOVEL NANO FFP2 MASKS – A COMPETITIVE STUDY ON THE FILTRATION PERFORMANCE AFTER VARIOUS TYPES OF CONDITIONS

Robin Halamicek, Carolin Wiesmann,
Richard Kröner, Matthias Eber,
Christian Bogdan, Dirk W. Schubert

92

THERMALLY CROSSLINKED HEMP-BASED CELLULOSE BIOPLASTICS WITH TUNABLE PROPERTIES AND REVERSIBLE REACTION

Sergejs Beluns, Sergejs Gaidukovs, Oskars Platnieks

93

KRAFT LIGNIN-GLYOXAL-RESIN ENCAPSULATED PHASE-CHANGE MATERIAL FOR PRODUCING THERMAL-REGULATED WOOD

Chia-feng Lin, Olov Karlsson, Dennis Jones,
Dick Sandberg

94

NOVEL HIGH-SPEED ELONGATION RHEOMETER

Alexander M. Bier, Walter Arne, Dirk W. Schubert

95

CONTENT CONTINUES NEXT PAGE >>

Nordic Polymer Days 2023 POSTER PRESENTATIONS

BIO-BASED HIGHLY CONDUCTIVE IONOGELELECTRODES AS POTENTIAL BIO-ALTERNATIVE FOR ADVANCED APPLICATIONS

Maksims Jurinovs, Anda Barkane,
Oskars Platnieks, Līga Grāse, Sergejs Gaidukovs

96

THERMAL STABILIZATION OF POLYPROPYLENE BY RENEWABLE ANTIOXIDANTS

Richard Kröner, Joachim Kaschta, Ines Heiduk,
Daniel Dorfmueller, Martin Falk, Dirk W Schubert

97

INVESTIGATING THE SYNTHESIS AND PROPERTIES OF POLYTHIOUREAS AND POLYTHIOCARBAMATES

Rafael N L Menezes, **Olga Gordivska**, Baozhong Zhang

98

ANTIBACTERIAL CHITOSAN-BASED HYDROGELS FOR WOUND HEALING APPLICATIONS

Isabella Laurén, Afsoon Farzan, Maryam Madani,
Arun Teotia, Jukka Seppälä

99

MALEIC-BASED POLYMER FORMULATIONS FOR THE MULTIFUNCTIONAL INHIBITION OF GAS HYDRATES, SCALE AND CORROSION IN OILFIELD PRODUCTION OPERATIONS

Janronel Pomicpic, Malcolm Kelland

100

INVESTIGATION ON ACIDIC CHEMICAL RECYCLING OF POLY(ESTER-SPIROACETALS)

Tran Tam Nguyen, Smita Mankar,
Saga Vesterbacka, and Baozhong Zhang

101

BENZODIFURANONE-BASED CONJUGATED POLYMERS MADE SOLUBLE WITH SINGLE OXYGEN-CONTAINING SIDE CHAINS FOR THERMOELECTRIC APPLICATIONS

Diego R. Hinojosa¹, Nathan Pataki²,
 Mario Caironi², Michael Sommer^{1*}

¹ Professur Polymerchemie,
 Chemnitz University of Technology,
 Strasse der Nationen 62,
 09111 Chemnitz, Germany

² Center for Nano Science
 and Technology@ PoliMi,
 via Pascoli 70/3, 20133, Milano, Italy

* michael.sommer@chemie.tu-chemnitz.de

The synthesis of thermoelectric generators utilizing earth-abundant elements necessitates the design of tailored carbon-based conjugated polymers. However, despite impressive results for p-type materials, n-type materials lag behind in terms of performance. To address this issue, BDF (Benzodifuranone) based n-type conjugated polymers have

been developed as a progression of the isoindigo motif.¹ Flanking a benzodifuranone core with two isatins has proven to enhance performance by offering a H-bonded locked backbone structure with a lower LUMO level and high coplanarities. However, such beneficial coplanarity of BDF systems make them challenging to solubilize. Traditionally, long-gang branched alkyl chains are utilized for this purpose, which are tedious to prepare. In this work, a synthetically simple approach to single oxygen-based side chains that can be prepared in one step from commercially available reagents is presented. The procedure is modular as the oxygen-backbone distance can be easily altered, thus accessing highly soluble BDF-based copolymers. The polymers were found to be highly soluble, with solubility values reaching up to 90 mg/mL. The impact of different comonomers and different oxygen-backbone distances on the thermoelectric properties of the polymers was evaluated. Increasing the oxygen-backbone distance enhances thermoelectric performance of the polymers in terms of conductivity and power

factor. We anticipate this synthetic strategy to be applicable to a variety of conjugated polymers for use in organic electronics.

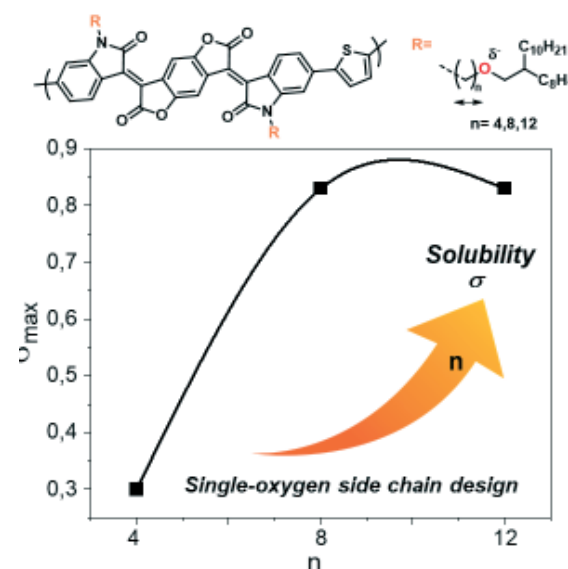


Figure. Solubility and performance enhancement using Single Oxygen side chains

References:

1. Lei, T et al J. Am. Chem. Soc. 2014, 136 (5), 2135–2141.

DISPERSIBILITY OF NANOPARTICLES WITH DIFFERENT SURFACE FUNCTIONALIZATION AT VARIOUS PROCESSING PARAMETERS IN THE INTERNAL MIXER

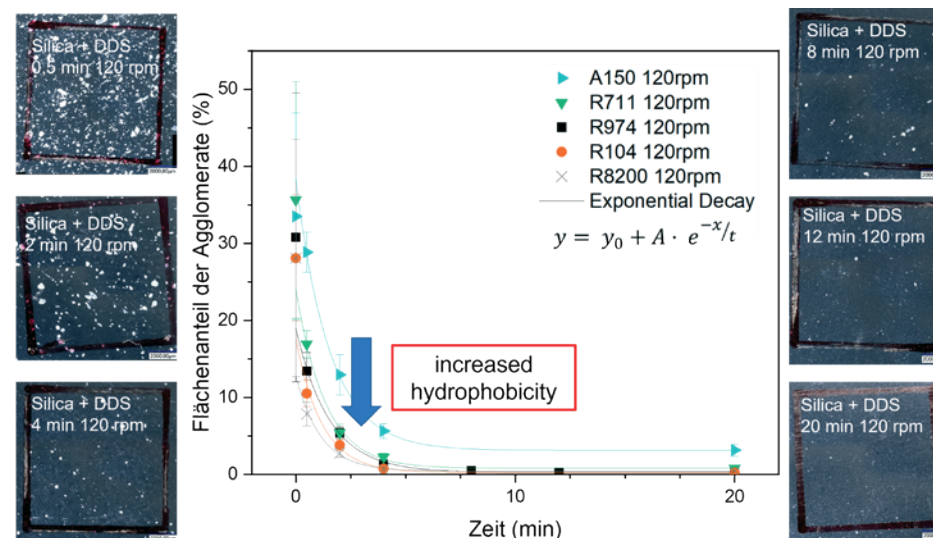
David Peltner, Siegfried Werner,
 Dirk W. Schubert

Institute of Polymer Materials,
 Friedrich-Alexander-Universität
 Erlangen-Nürnberg

david.peltner@fau.de

The present study investigates the dispersibility of silica nanoparticles with different types of hydrophobic surface functionalization in polypropylene. Therefore, the particles and the PP were compounded in an internal mixer at various processing parameters. The obtained compounds were hot pressed into square shaped plugs and biaxially stretched into films. The latter was done to increase the size of the agglomerates, so they could be detected by light microscopy. The agglomerates were analysed using a contrast-based particle detection and a 12-spot pattern over the stretched film. Parameters such as number, size, and area fraction of agglomerates were used to characterize the dispersion and correlated with rotation speed and mixing time.

Figure: Influence of rotation time on area fraction of Silica in PP.



A reduction of number, size and agglomerate area fraction with higher rotation speed and mixing time was found. The latter could be described with an exponential decay function with three adjustable parameters. These parameters correlated with the hydrophobicity of the surface functionalization indicating a faster reduction to lower levels with increasing hydrophobicity. The area fraction of

agglomerates was identified as the most meaningful dispersion parameter as it combines information about size and number of the particles. This study shows a new method of analysing the dispersion of silica nanoparticles in PP and that their dispersibility in dependence of the surface functionalization can be characterized by the mixing kinetics of an internal mixer.

ELECTROSPUN ANTIMICROBIAL MEMBRANES FROM CATIONIC CHITOSANS FOR WOUND HEALING DRESSINGS

Arun Teotia¹, Isabella Lauren¹,
Nina Lindfors², Jukka Seppala^{1*}

1 Aalto University,
School of Chemical Engineering,
Espoo, Finland.

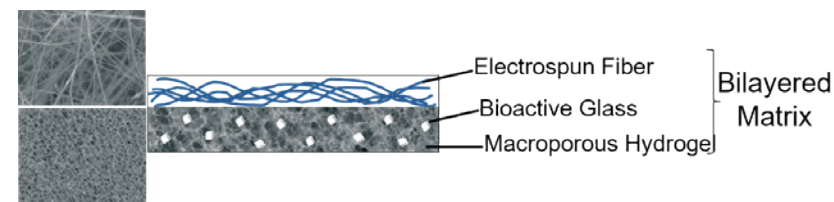
2 HUS-Helsinki University, Helsinki, Finland.

* jukka.seppala@aalto.fi; arun.teotia@aalto.fi

Chronic wounds arising due to bed sores or diabetic condition along with emerging antimicrobial resistance are difficult to treat, often leading to aggressive tissue loss. This has gained interest to development new therapies and dressings to counter infection along with tissue regeneration.

Electrospun polymer fibre provides porous sheets with high surface area which have been employed extensively for skin regeneration. We have developed cationic chitosan

Figure: Schematic representing scanning electron microscope image of electrospun fibres and macroporous hydrogel containing BAG(S53P4) and their integration into a bilayered wound dressing matrix.



derivatives which have demonstrated excellent broad spectrum antimicrobial properties against both Gram-positive and Gram-negative microbes without using any antibiotics¹. This can provide viable solution for antibiotic resistant chronic wounds. Further they were electrospun into high surface area porous membranes and used as upper antimicrobial layer in a bi-layered dressing matrix. The lower macroporous polymeric hydrogel layer further contained bioactive-glass BAG (S53P4) for its pro-healing and antimicrobial properties.

Here we report successful electrospinning of cationic chitosan containing antimicrobial membranes for chronic wound dressings. The membranes were integrated with BAG containing macroporous hydrogen to fabricate bilayered dressing. Such dressings will provide solution for difficult to treat antibiotic non-responsive chronic wounds along with tissue regenerative properties enabling enhanced recovery.

References:

1. Borandeh¹, S.; Lauren², I.; Teotia³, A.; Seppala⁴, J. Dual Functional Antibacterial Chitosan Derivatives: Synthesis, Characterization, and Structure-Activity Relationships. *Adv. Healthc. Mater.* **2023**. (Under revision)

SYNTHESIS OF BIO-BASED POLYMERS WITH USE OF MICROWAVE CHEMISTRY

Grammatiki Terzi*, Jeppe Madsen,
Anders Egede Daugaard

The Danish Polymer Center,
Department of Chemical
and Biochemical Engineering,
Technical University of Denmark

* gramter@kt.dtu.dk

Implementing bio-based polymers into the plastic industry has gained much interest in the past few years. [1] However, their inherent low thermal stability makes them unable to fully replace fossil-based commodity plastics, and there is a need to improve this for a range of applications to extend their use scenarios. For this purpose, aromatic monomers typically enable higher thermal stability and improved mechanical properties compared to correspondingly aliphatic systems. An increasing number of aromatic building blocks are becoming available for synthesizing polymers and copolymers with higher thermal stability. However, classically, this would be done through well-known melt condensation polymerization that requires very long polymerization times, a high amount of energy to produce (co)-polymers and the use of high vacuum techniques to drive polymerizations.

Here we have investigated the possibility of employing microwave chemistry to produce prepolymers from aromatic building blocks and incorporate them into copolymers with

lactic acid. The copolymerization of the different aromatic bio-based monomers with lactic acid using microwave radiation is fast, efficient, and reproducible. Through simple microwave experiments, the bio-based aromatic acids have been incorporated into oligomeric polyesters in 10-30 min, compared to the corresponding days of classical high-temperature reactions. The prepared polymers are non-toxic bio-based materials expected to be biodegradable, and investigations into their mechanical and biological properties are ongoing.

The present work is part of the EU project UPLIFT [2], which will contribute to monomer production for new packaging materials and their end-of-life and recycling options. The target is to convert monomers or oligomer fragments, which are reclaimed from the biological degradation of fossil and bio-based plastics, into new plastics that fulfill the food and drink packaging standardization and are also suitable for recycling.

References:

1. Polylactic Acid (PLA) Market Size, Share & Trends Analysis Report By Application (Packaging, Agriculture, Transport), 2019-2025 [Report]-[s.l.] grandview research, 2019
2. UPLIFT - Upcycling Bio Plastics of Food and Drinks Packaging, <https://upliftproject.eu/>

ENHANCED HEAT DISSIPATION PROPERTY FOR METALLIZED POLYPROPYLENE FILM CAPACITORS

Odysseas Gkionis-Konstantatos¹,
William Greenbank, Shova Neupane,
Thomas Ebel, Luciana Tavares.

¹ Centre for Industrial Electronics,
University of Southern Denmark

* gkionis@sdu.dk,

* tavares@sdu.dk

Metallized film capacitors (MFCs) are widely utilized in high power applications, due to their self-healing capability, high energy density and high reliability [1]. Biaxially-oriented polypropylene (BOPP) is the most commonly used polymer in the capacitor industry [2]. However, the performance and lifetime of these devices are particularly affected in high temperature environments since their maximum operating temperature can be in the range of 80 to 105°C [3]. Therefore, there is significant interest in the enhancement of thermal stability in harsh conditions along with higher volumetric efficiency.

We propose a new multilayer strategy to counteract the issue of efficient heat dissipation in MFCs. In this work, the samples are fabricated with the thinnest commercially

available BOPP (1.9µm thick), with an additional thin ceramic layer deposited on the polymer, the goal of which is to improve the thermal conductivity of the foil. To ameliorate the quality of the polymeric and ceramic sheets used in this multilayer topology, a heat treatment is applied prior to metallization, which was optimised by inspecting different thicknesses. Heat dissipation tests are conducted in both the samples with the ceramic layer and those without it under a thermal camera. The devices performance was then evaluated by investigating the capacitance, equivalent series resistance, electrical breakdown DC testing combined with optical microscopic assessments of the breakdown region. Finally, we obtained reproducible capacitance, breakdown voltage as well as similar ring-shaped breakdown features.

References:

1. Xiao M, Zhang M, Liu H, Du B, Qin Y. Dielectric Property and Breakdown Strength Performance of Long-Chain Branched Polypropylene for Metallized Film Capacitors. *Materials*. 2022 Apr 23;15(9):3071.
2. He, Yushuang, et al. "Effect of Temperature on Dielectric Properties of Metallized Film Capacitor." 2021 International Conference on Electrical Materials and Power Equipment (ICEMPE). IEEE, 2021.
3. Ho J, Schroeder M. Polyimides as high temperature capacitor dielectrics. *Polyimide for Electronic and Electrical Engineering Applications*. 2020 May 25.

IMPACT OF STORAGE AND PROCESSING ON MORPHOLOGY IN THERMOPLASTIC POLYETHER-URETHANES

Michael Redel^{1*}, Christian Regelmann¹,
Bastian Wölfel¹, Dirk W. Schubert^{1*}

¹ Institute of Polymer Materials,
Friedrich-Alexander-University
Erlangen-Nürnberg.

+ michael.redel@fau.de

* dirk.schubert@fau.de

The presented study evaluates the influence of storage conditions as well as the impact of temperature, residence time, throughput and draw down speed in fibre spinning on the phase separation in commercially available thermoplastic polyether-urethanes. Many of the properties inherent to thermoplastic polyurethane (TPU) materials and products are due to the block-copolymer chain of soft and hard segments. The incompatibility of these segments causes demixing into so called “soft” and “hard phases” [1]. The degree of separation as well as the segment content

are, according to literature, detectable via FTIR measurements [2].

Granules of two TPUs with differing composition were stored for up to 900 days to evaluate morphological changes and correlate to material shelf life. Samples consisting of varying ratios of MDI/BD hard and PTMG soft segments (Elastollan®) were subsequently processed by injection moulding. The hard segment ratio and the degree of microphase separation (DPS) were studied for all samples by analysing the peaks of ether and urethane groups as well as the free- and hydrogen-bonded carbonyl (C=O) peaks, respectively. Hard segments feature a significantly higher density compared to soft segments, wherefore the results of the C-O peaks, correlating with the hard segment ratio, were validated. The determined DPS values were further related to the peak ratio of ether and urethane groups showing a linear correlation.

In the second part, one TPU material was processed to nonwovens and characterized

applying the calibrated FTIR method. The goal is to study the impact of the processing conditions during fibre spinning processes and to investigate the analytic capabilities for TPUs.

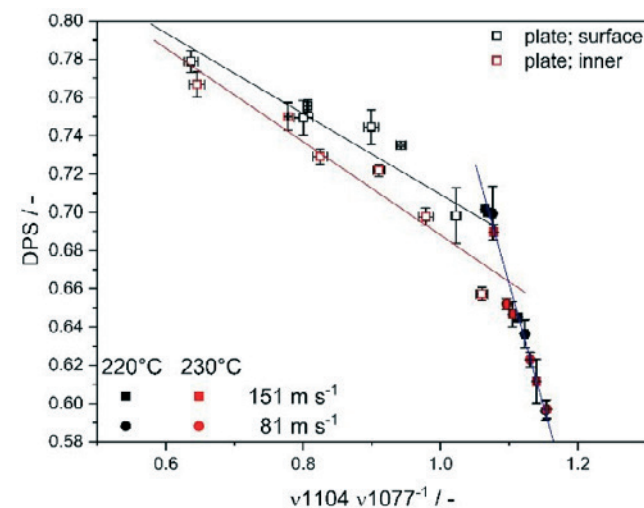


Figure: Relationship between hard segment ratio and DPS for nonwovens and injection moulded plates.

References:

1. Kricheldorf, H.R., Quirk, R.P., and Holden, G., Thermoplastic elastomers, 3rd ed., Hanser Gardner Publications, Cincinnati, 540 p., **2004**.
2. Hiltz, J., Characterization of poly (ether) urethane thermoplastic elastomers, Defence Research Establishment Atlantic/dartmouth (Nova Scotia) **1998**.

GRAFTING ZWITTERIONIC POLYMERS ON DIALCOHOL CELLULOSE NANOCRYSTALS

Maryam Madani*, Hossein Baniasadi,
 Jukka Seppälä

Polymer Technology, School of Chemical
 Engineering, Aalto University, Espoo, Finland

* Maryam.madani@aalto.fi

A number of zwitterionic polymers, including phosphobetaine, carboxybetaine, and sulfobetaine, have been recently investigated as biomedical materials based on their excellent hemocompatibility and biocompatibility [1]. Poly(sulfobetaines) contain anionic (sulfonate) and cationic (quaternary ammonium group) groups with a neutral net charge at a specific pH. Considering that poly(sulfobetaines) is one of the most important classes of smart polymers with unique and specific properties like antifouling and antimicrobial properties, low cytotoxicity [2], we aim to modify dialcohol cellulose nanocrystals (Dia-CNC) with poly(sulfobetaines). Periodate oxidation followed by Sodium borohydride (NaBH_4) reduction converts CNC to dia-CNC. We hypothesize that

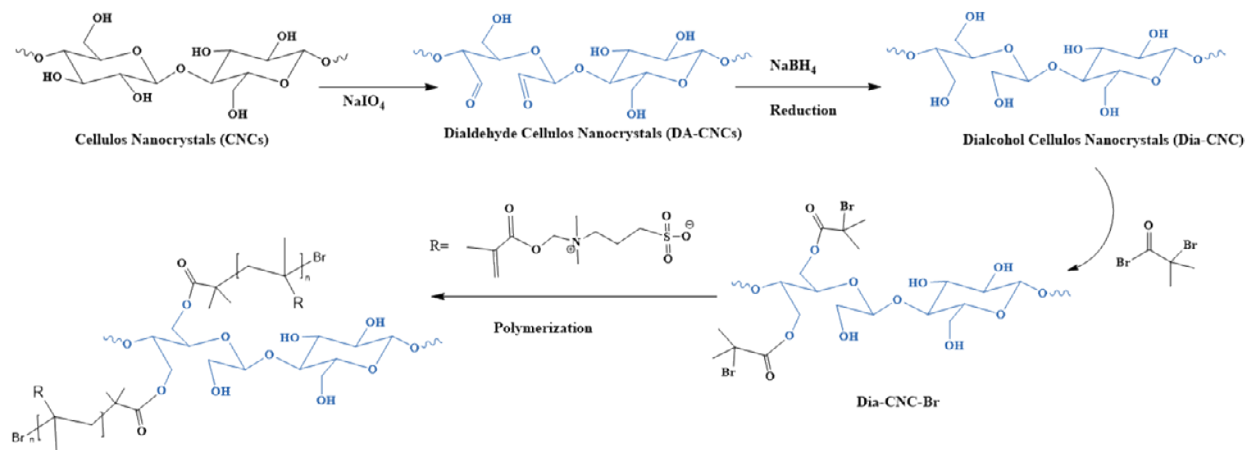


Figure: Schematic pathway of dialcohol CNC-based macroinitiator synthesis and polymer grafting.

Dia-CNC chains are more flexible than CNC chains, allowing more functional groups to be modified with zwitterionic polymers. Here in we demonstrated a new way to prepare high dense of brush zwitterionic polymer chains on CNC surface. The preparation route of Dia-CNC grafted with poly(sulfobetaines) included two steps, substitution of hydroxyl groups by 2-Bromoisobutyryl bromide (BrIb) on Dia-CNC to obtain the macroinitiator (Dia-CNC-Br); and

initiation of polymerization on the surface of nanocrystals. Chemical and morphological characteristics of the materials are thoroughly characterized using various spectroscopic and microscopic measurements. Modified CNCs with poly zwitterionic brushes can be used to design novel hybrid materials that are based on renewable natural resources and sustainable processes for various application such as antifouling and antimicrobial coatings.

References:

1. Stefania Racovita, Marin-Aurel Trofin, Diana Felicia Loghin, Marius-Mihai Zaharia, Florin Bucatariu, Polybetaines in Biomedical Applications. *Int. J. Mol. Sci.* **2021**, 22, 9321.
2. Xia Qiu, Jiamin Zhang, Lilong Cao, Qin Jiao, Junhao Zhou, Lijun Yang, Hong Zhang, Yuping Wei. Antifouling Antioxidant Zwitterionic Dextran Hydrogels as Wound Dressing Materials with Excellent Healing Activities. *ACS Appl. Mater. Interfaces* **2021**, 13, 7060–7069.

THERMOMECHANICAL PROPERTIES OF ELECTROCONDUCTIVE VEGETABLE OIL-BASED MEMBRANES FOR SOFT ROBOTICS

Oskars Platnieks^{1*}, Maksims Jurinovs¹,
Sergejs Gaidukovs^{2*}

¹ Institute of Polymer Materials,
Faculty of Materials Science and
Applied Chemistry, Riga Technical University,
P. Valdena 3/7, Riga LV-1048, Latvia.

* Oskars.Platnieks_1@rtu.lv
Sergejs.Gaidukovs@rtu.lv

The addition of nano-sized fillers in polymer composites has emerged as a highly active research field in polymer science. Carbon nanotubes (CNTs) with high aspect ratios have garnered particular attention due to their exceptional mechanical and electrical properties. However, the challenges associated with their poor dispersion and entanglement have posed significant obstacles in material manufacturing, despite the anticipated substantial improvements in properties. Additive manufacturing resin formulations encompass a wide variety of monomers and oligomers, with the list constantly expanding. Of note are bio-based resins that utilize renewable sources, decreasing reliance on the petrochemical industry. Resins derived from modified vegetable oils have emerged as strong contenders, satisfying the needs of soft polymer matrices while offering a dependable supply of raw

materials due to the established industry. In this study, we undertake challenges related to dispersion of CNTs and bio-based resin formulation for vat photopolymerization. Produced printed samples were tested with dynamic mechanical analysis (DMA) to characterize matrix and filler interactions and understand optimal working temperatures and compositions. The addition of up to 1 wt% CNTs reduced the glass transition temperature by up to 16 °C, thus allowing for the transition to a viscoelastic state to occur at lower temperatures. As a result, the mechanical properties saw a sharper decrease, but CNT reinforcement yielded up to a 1.6-fold enhancement of storage modulus in a viscoelastic state compared to the reference sample without CNTs. All tested compositions retained excellent thermal stability as indicated by thermogravimetric analysis.

Acknowledgments:

Research at RTU was performed under the ERA-NET program funded by VIAA, project UPRINTAROBOT Nr ES RTD/2021/8.

FABRICATION OF THIN ELECTROACTIVE POLYDOPAMINE FILMS BY ELECTROSPRAY DEPOSITION

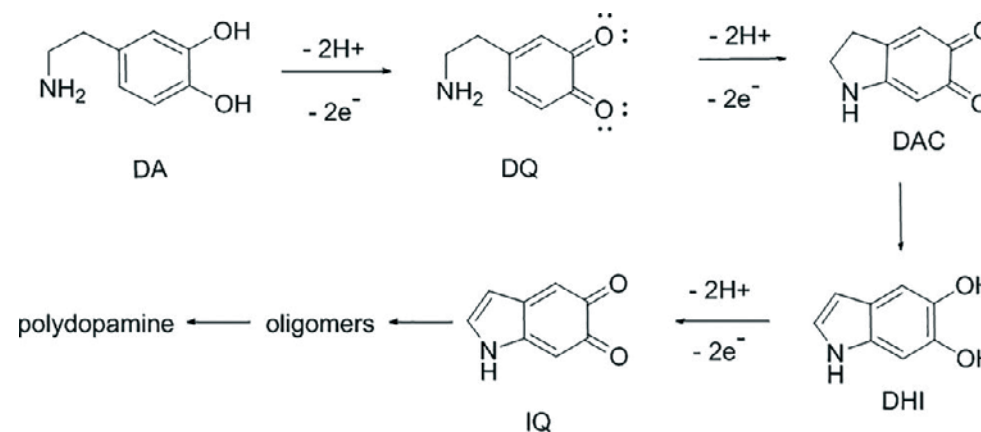
Majid Al-waeel, Jukka Lukkari, **Mikko Salomäki***

University of Turku,
 Department of Chemistry, Turku, Finland.

* mikko.salomaki@utu.fi

Polydopamine (pDA) is a unique and versatile polymer that is obtained when dopamine (DA) undergoes oxidative polymerization. During the polymerization process dopamine passes through multiple oxidized states, such as dopamine-o-quinone (DQ), aminochrome (DAC) and 5,6-dihydroxyindole (DHI) (Scheme 1). The polymerization results in a dark brown or black material that is highly adhesive [1]. The adhesive properties of pDA allow it to be coated onto various substrates, including metals, ceramics, and polymers. pDA is also the subject of interest due to its exceptional properties such as broad band absorption; photoconductivity and electrical conductivity; low radiative quantum yield; and exceptional free radical and redox behavior[2]. There are many proposed applications for pDA films such as:

Scheme1:
 Oxidative
 polymerization
 of dopamine



photovoltaic devices; sensors; optoelectronic and energy storage devices; and photoactive and photoprotective materials. However, these promising properties of pDA are, in most cases, poorly understood and achieved. Many of the aforementioned applications require a functional defect free film that does not include large randomly aggregated structures. These structures of random nature are usually obtained via spontaneous oxidation of pDA precursors, which is the most common preparation method for pDA materials. We are exploring the feasibility

of utilizing electrospray deposition to create thin films of pDA that exhibit favorable electrochemical characteristics. The properties of the films, such as, uniformity and thickness, are tunable by controlling the electrospray parameters and degree of oxidation of precursor materials. The main parameters are the applied voltage, the flow rate and conductivity of the solution, and the distance from the nozzle to the substrate. Our aim is to develop such films for potential applications in biodegradable electronic devices, including supercapacitors.

References:

1. Jaramillo, A. M.; Barrera-Gutiérrez, R.; Cortés, M. T. Synthesis, Follow-Up, and Characterization of Polydopamine-like Coatings Departing from Micromolar Dopamine-o-Quinone Precursor Concentrations. *ACS Omega* **2020**, 5 (25), 15016–15027
2. M. d'Ischia, A. Napolitano, A. Pezzella, P. Meredith, T. Sarna, *Angew. Chem. Int. Ed.* **2009**, 48, 3914–3921

CHARACTERIZATION OF “POLYETHYLENE OF RAISED TEMPERATURE RESISTANCE” (PE-RT) MATERIALS – A MINI REVIEW AND NEW INSIGHTS

Nicolai Schneider¹, Joachim Kaschta¹,
Ines Heiduk², Dirk W. Schubert^{1*}

1 Institute of Polymer Materials,
Friedrich-Alexander-University
Erlangen-Nürnberg, Germany

2 Fränkische Rohrwerke Gebr. Kirchner GmbH
& Co. KG, Königsberg in Bayern, Germany

* dirk.schubert@fau.de

Since the development of the first pipe systems over 5500 years ago, various materials including terracotta, metals and polymers, were used in this field of application. High-density polyethylenes (HDPE) display good processability and chemical resistance at low costs since their first pipe application in 1954 [1, 2].

Polyethylenes in long-term high temperature implementations tend to failure mechanisms such as slowcrack-growth (SCG) and

environmental-stress-cracking (ESC). In both failure mechanisms, long-term stresses lead to the formation of so-called craze-structures, where crystals rotate in stress direction with an alternating pattern of crystalline and amorphous segments (fibrills) between accruing voids, promoted by raised temperatures. The cohesion of crystallites within the craze is mainly assured by tie-molecules, amorphous chains that are incorporated in several crystallites, forming intercrystalline bridges [3]. Therefore, creep resistant materials such as cross-linked polyethylene (PE-X) and polyethylene of raised temperature resistance (PE-RT) were invented to impede the failure in the amorphous regions.

In the case of PE-RTs, the macromolecules in the high molecular mass fractions are short-chain branched by multistep polymerisation with α -olefins. Consequently, their crystallization is hindered. The crystalline matrix is formed by the almost linear low molar mass fractions, whereas the high branched high

molecular mass fractions are incorporated in multiple crystals and so form tie-molecules.

This work reviews several methods to characterize those polyethylenes with respect to their comonomer distribution and tie molecule density. Due to the necessity to locate the comonomer solely on the long chains, polymers will be separated by means of their molar mass by chemical precipitation fractionation or by successive self-nucleation and annealing treatment (SSA). The precipitates molar mass distributions are subsequently analysed by high temperature gel permeation chromatography (HT-GPC) measurements. The comonomer content is determined by Fourier-transform infrared spectroscopy (FTIR), whereas the SSA spectrum provides information about the intra-fractional distribution of the comonomer. The long-term performance of such materials can be estimated by the measurement of their strain hardening modulus (SH-Modulus) at elevated temperature [4].

References:

1. Ronca S.; Polyethylene; Brydson's Plastics Materials 2017; 247-278
2. Gaube E., Diedrich G., Müller W.; Rohre aus thermoplastischen Kunststoffen – Erfahrung aus 20 Jahren Zeitstandsprüfung; Kunststoffe 1976; 66 (1); 2-8
3. Zhang Y., Ben Jar P.-Y., Shifeng X., Li L.; Quantification of strain-induced damage in semicrystalline polymers: a review; J. Mater. Sci.; 2019; 54; 62-82
4. Zhang, C., et al.; Influence of comonomer distribution on crystallization kinetics and performance of polyethylene of raised temperature resistance; Polym. Int.; 2019; 68 (10); 1748-1758

NEW ASSESSMENT METHOD FOR THE COMPATIBILITY OF LIGNIN-POLY (LACTIC ACID) POLYMER BLENDS

Oskar Backman^{1*}, Ellen Sundström,
Luyao Wang¹, Patrik C. Eklund², Chunlin Xu¹

1 Laboratory of Natural Materials Technology,
Åbo Akademi University,
Turku FI-20500, Finland

2 Laboratory of Molecular Science
and Engineering, Åbo Akademi University,
Turku FI-20500, Finland

* oskar.m.backman@abo.fi

Lignin is the most abundant aromatic biopolymer in the world, and millions of tons are obtained annually as a by-product of the pulp and paper industry. The vast majority is burned for energy, but the focus is currently on finding ways to utilize it in higher value products. One such way is as a filler or an additive in poly (lactic acid) (PLA) for replacement. Lignin can bring beneficial properties to the polymer blend, but its amphiphilic nature can cause problems¹. Compatibility is a major issue when trying to introduce lignin into PLA. Depending on the source or fraction of the lignin, compatibility can vary drastically. A straightforward way to quantify the compatibility was developed by using a 3D printed microtomy setup, optical microscope and image analysis software. Thin cross-sectional

slices, produced from filaments of lignin-PLA polymer blends, were imaged using transmitted light microscopy. The images were analyzed using ImageJ with the SurfCharJ plugin². The plugin was originally developed for analysis of topographical images acquired by Atomic Force Microscopy (AFM), but it provided an efficient way of flattening the images and separating the lignin particles from the background. The features of the lignin particles could then be measured and combined into a value describing compatibility. The compatibility value is a useful datapoint when investigating how lignin from various sources or with different modifications may interact with PLA, it can also be used as an input in AI-modeling.

References:

1. Esakkimuthu, E. S.; DeVallance, D.; Pylypchuk, I.; Moreno, A.; Sipponen, M. H. Multifunctional lignin-poly (lactic acid) biocomposites for packaging applications. *Front. Bioeng. Biotechnol.*, **2022**, 10
2. Chinga, G.; Johnssen, P.O.; Dougherty, R.; Lunden-Berli, E.; Walter, J. Quantification of the 3-D micro-structure of SC surfaces. *J. Microscopy*, **2007**, 227(3), 254-265

CONDUCTIVE POLYURETHANE/PEGYLATED GRAPHENE OXIDE COMPOSITE FOR 3D-PRINTED NERVE GUIDANCE CONDUITS

Afsoon Farzan¹, Sedigheh Borandeh², Jukka Seppälä*

Polymer Technology,
School of Chemical Engineering,
Aalto University, Kemistintie 1,
02150 Espoo, Finland

Afsoon.farzan@aalto.fi
*jukka.seppala@aalto.fi

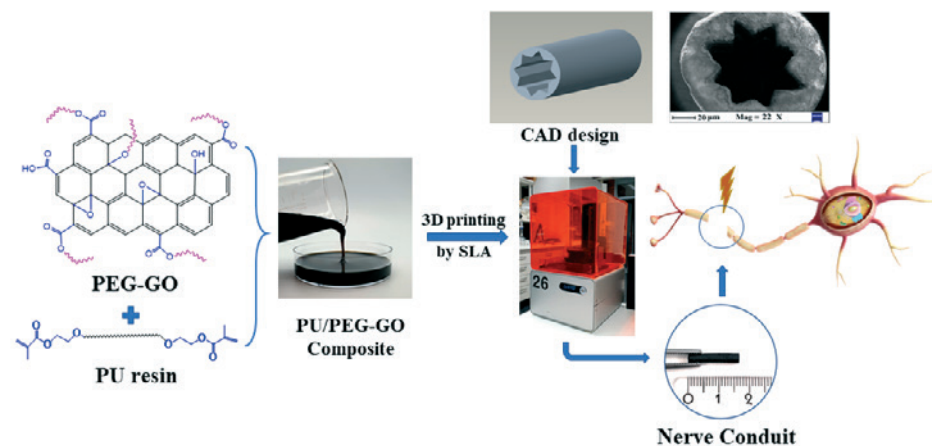


Figure:
graphical abstract

Conductive nerve guidance conduits with precise geometry for nerve regeneration.

Conductive polymeric nanocomposites have made significant contributions in nerve regeneration. To this aim, the best results are obtained by using nerve guidance conduits (NGCs) with conductive, bio-compatible, bio-degradable tubes as well as special topographical features. In this study, biodegradable, conductive, solvent-free polyurethane/PEGylated graphene oxide (PU/PEG-GO) composites were synthesized and successfully

3D printed into flexible nerve conduits with different precise geometries, such as hollow, porous, and grooved tubes, using stereolithography. The composite containing 5% PEG-GO showed the highest tensile stress (3.51 ± 0.54 MPa), tensile strain at break (170%), and conductivity (1.1×10^{-3} S/cm) with the lowest contact angle of 72° attributing to the strong interfacial interactions between PEG-GO nanosheets and the PU matrix. Moreover, the

PU/PEG-GO 5% exhibited higher compression strength compared with pure PU and showed appropriate enzymatic degradation after 6 weeks, which is expected to last sufficiently for an efficient nerve regeneration. Altogether the 3D-printed, conductive, biodegradable, and flexible PU/PEG-GO 5% conduit with precise geometry has potential as NGCs for peripheral nerve regeneration.

References:

1. A. Farzan, S. Borandeh, J. Seppälä, Conductive polyurethane/PEGylated graphene oxide composite for 3D-printed nerve guidance conduits, *Eur. Polym. J.* 167 2022.
2. A. Farzan, S. Borandeh, N. Zanzanizadeh Ezazi, S. Lipponen, H.A. Santos, J. Seppälä, 3D scaffolding of fast photocurable polyurethane for soft tissue engineering by stereolithography: Influence of materials and geometry on growth of fibroblast cells, *Eur. Polym. J.* 139 (2020) 109988.

INVESTIGATING THE SYNTHESIS AND PROPERTIES OF POLYTHIOUREAS AND POLYTHIOCARBAMATES

Rafael N L Menezes¹, Olga Gordivska¹,
 Baozhong Zhang^{1*}

¹ Centre for Analysis and Synthesis,
 Department of Chemistry, Lund University,
 P.O. Box 124, SE-22100 Lund, Sweden

* baozhong.zhang@chem.lu.se

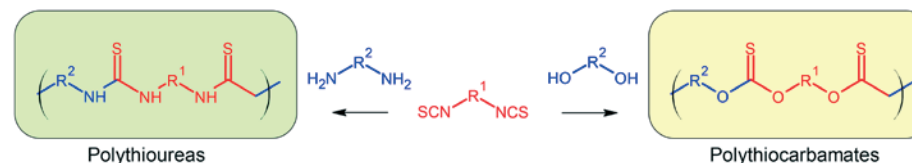
In current study two subclasses of polymers, recently emerging polythioureas, and a new subclass, polythiocarbamates, were targeted [1,2]. In case of polythioureas, the polyaddition of various diisothiocyanates and diamines was achieved under anhydrous conditions without any catalyst in DMF at 50 °C (Figure 1) yielding a series of polythioureas of high molecular weight in decent yield. Polymers were characterized by nuclear magnetic resonance, including DOSY measurements, infrared spectroscopy, and gel permeation chromatography. Subsequently chemical and physical properties of the corresponding polythioureas including solubility, thermal stability, and intrinsic viscosity were studied. The substituents connect-

ed to the thiourea group affect considerably the properties of the resulting polythioureas. Aliphatic polythioureas presented glass transition temperature ranging from 50 to 78 °C and degradation temperature higher than 200 °C, whereas aromatic polythioureas degraded at temperatures below 150 °C and did not exhibit glass transition up to this temperature. Polythioureas synthesized from aromatic diisothiocyanates could be conveniently depolymerized by heating, which may enable recycling process. Newly synthesized polythioureas could find potential application as fibers, screening of the conditions is in progress.

To access polythiocarbamates via polyaddition of diisothiocyanates and diols (Figure 1), screening of the reaction conditions was done: both Lewis acids and bases were tested.

Dibutyltin dilaurate catalysts demonstrated the highest efficiency under anhydrous conditions in DMF at 110 °C yielding oligothiocarbamates, which were further characterized by nuclear magnetic resonance, infrared spectroscopy, and gel permeation chromatography. Later, due to the high toxicity of the tin-based catalyst, it has been replaced with 1,3-dimethylimidazoiun-2-carboxylate, which demonstrated similar results: oligomers consisting of 6-7 carbamate units. Obtained results are in agreement with the thermodynamic calculations, which predict that higher molecular weight polymers cannot be formed [3]. In order to proceed further chain extension concept was applied. Screening of the reaction conditions for polyaddition of oligocarbamates bearing thioisocyanate end groups and diamine is in progress.

Figure 1. Synthetic route for polythioureas and polythiocarbamates.



References:

1. Li, Y. M.; Zhang, Z. P.; Rong, M. Z.; Zhang, M. Q.; Nat. Commun., 2022, 13, 2633.
2. Feng, H; Zheng, N; Peng, W.; Ni, C; Song, H.; Zhao, Q; Xie, T; Nat. Commun., 2022, 13, 397.
3. Powell, C. R.; Foster, J. C.; Swilley, S. N.; Kaur, K.; Scannelli, S. J.; Troya, D.; Matson, J. B.; Polym. Chem., 2019, 10, 2991.

A MODULAR APPROACH TO BUILDING POLYMER-BASED DURABLE PLUGS

Skowyra, M.M.^{1*}, **Echarri-Giacchi, M.**^{1**},
Ivanova, Y.D.², Ravnkilde, K.M.²,
Frederiksen, C.H.², Skov, A.L.¹

1 Danish Polymer Centre, DTU Chemical and Biochemical Engineering, Technical University of Denmark (DTU)

2 Danish Offshore Technology Centre, Technical University of Denmark (DTU)

* magsk@dtu.dk,

** maecgi@dtu.dk

Even though the North Sea is one of the world's largest oil and gas exploitation areas, many of the oil wells present there are reaching the end of their productive life. This means that a large number of them are expected to be plugged and abandoned (P&A) in the coming years to ensure that the remaining fluids are contained safely within the well and that the risk of environmental damage is reduced. Traditionally, cement has been used as the primary material for P&A applications, however, not without limitations such as operational issues, lack of resistance to certain chemicals (H₂S, hydrocarbons, etc.) or tendency to crack. As such, new materials are being developed to address these challenges. Our novel approach is based on the development of a durable temporary polymer plug with a shelf life of up to 18 months. The goal is to reduce the pressure build-up in the oil well's pipeline and B-section and mitigate the risk for the rig entry prior to abandonment, simultaneously lowering the costs. The polymer's working time at room temperature is sufficiently long to allow for the pumping of the liquid solu-

tion down the well. After that, the free-radical cross-linking polymerization process is activated with high temperatures present at those depths, forming a rigid, solid polymer plug with low gas and water permeability. In addition, the material is designed to be environmentally friendly and able to withstand the extreme conditions of oil wells, such as high pressure and aggressive environments.

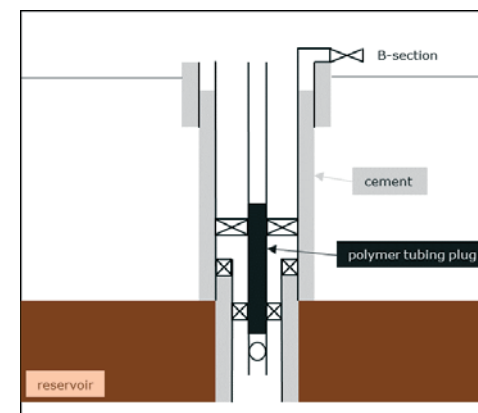


Figure: Schematic of a cross-linked polymer plug inside an oil well.

References:

1. Vrålstad, T.; Saasen, A.; Fjær, E.; Øia, T.; Ytrehus, J. D.; Khalifeh, M. Plug & abandonment of offshore wells: Ensuring long-term well integrity and cost-efficiency. *Journal of Petroleum Science and Engineering*, **2019**, 173, 478-491.

CONVENTIONAL NON-WOVEN VS. NOVEL NANO FFP2 MASKS – A COMPETITIVE STUDY ON THE FILTRATION PERFORMANCE AFTER VARIOUS TYPES OF CONDITIONS

Robin Halamicek^{1*}, Carolin Wiesmann¹,
Richard Kröner¹, Matthias Eber²,
Christian Bogdan³, Dirk W. Schubert¹

1 Institute of Polymer Materials,
Department of Material Science,
Friedrich-Alexander-Universität
Erlangen-Nürnberg, Erlangen, Germany

2 Fiatec-Filter- und Aerosoltechnologie GmbH,
Mainleus, Germany

3 Mikrobiologisches Institut – Klinische
Mikrobiologie, Immunologie und Hygiene,
Universitätsklinikum Erlangen and
Friedrich-Alexander-Universität
Erlangen-Nürnberg, Erlangen, Germany

* robin.halamicek@fau.de

Filtering face piece (FFP) masks, categorized by different filtration efficiency standards, are mandatory to achieve an efficient protection against viruses like the severe acute respiratory syndrome coronavirus type 2 (SARS-CoV-2) [1]. They conventionally comprise an electrostatically treated melt blown non-woven layer as the main filtering medium if the standard is FFP2. However, novel nanofibrous masks with the same standard are arising on the market, promising a higher safety alongside a higher better wearing comfort – but for a higher unit price. This study compared different mask models from both mask types regarding their filtration performance after various types of conditions (change of temperature and air humidity, exposure to isopropyl alcohol (IPA) and an autoclave sterilization) to evaluate the superior FFP2 mask type. Due to the absence of prior electrostatic treatment,

the nanofibrous masks did not show a significant change in filtration efficiency when exposed to IPA, unlike to the melt blown non-woven masks. However, most melt blown type masks maintained a sufficient filtration efficiency after all other treatments and also at the untreated condition – with even better results than the nanofibrous competitors. This applied particularly for the capacity to filter smallest particles/droplets with a size of around 0.1 μm , which is below the range of typical filtering standards but important for the retention of virally contaminated nano-aerosols or unattached viruses [2-4]. Based on their better filtration performance, lower price and potential reusability, it can be concluded that conventional melt blown non-woven masks with an electrostatic treatment are the preferable FFP2 mask type for a protective purpose.

References:

1. Y. Wang, Z. Deng, and D. Shi, Medical devices & sensors, 4, e10163, **2021**
2. A.A. Jazie, A.J. Albaaji, and S.A. Abed, Air quality, atmosphere, & health, 14, 1811, **2021**
3. W.K. Essa, S.A. Yasin, I.A. Saeed, and G.A.M. Ali, Membranes, 11, **2021**
4. M.I. Guzman, The International journal of health planning and management, 36, 257, **2021**

THERMALLY CROSSLINKED HEMP-BASED CELLULOSE BIOPLASTICS WITH TUNABLE PROPERTIES AND REVERSIBLE REACTION

Sergejs Beluns¹, Sergejs Gaidukovs¹,
Oskars Platnieks¹.

¹ Institute of Polymer Materials,
Faculty of Materials Science
and Applied Chemistry,
Riga Technical University,
P.Valdena 3/7, Riga, LV-1048, Latvia,

* sergejs.beluns@rtu.lv

Contemporary bioplastics and biocomposites are typically composed of non-biodegradable or non-sustainable elements despite being partly bio-based. The integration of low-cost, recycled, or waste materials is imperative in creating cost-effective solutions. This research utilized hemp stalk waste, industrial byproducts glycerol and xylan (hemicellulose), and citric acid as primary components. Mechanical processing was employed in the preparation of bioplastics from hemp stalks to form cast papers without any chemical alterations. The cast papers were impregnated with a mixture of glycerol, xylan, citric acid, and polyethylene glycol (PEG), and thermal crosslinking was carried out in a one-step reaction by curing materials at 140 °C. The resulting bioplastics underwent a 48-hour water wash and were extensively tested for water resistance. A sodium hydroxide depolymerization recycling

route was demonstrated as a substitute to biodegradation. The crosslinking reactions were thoroughly analyzed through Fourier-transform infrared spectroscopy (FTIR) and rheology, with supplementary structure analysis via scanning electron microscopy (SEM). The bioplastic's durability was characterized using thermogravimetric analysis and water absorption tests. Water uptake was reduced by a factor of seven compared to cast hemp paper. The obtained bioplastic, after water wash, demonstrated an elastic modulus of up to 2.9 GPa, tensile strength of up to 70 MPa, and elongation of up to 4.3%. The properties of bioplastics were found to be highly tunable from brittle to ductile through component ratio variation. Dielectric analyses demonstrated the potential of bioplastics as electric insulation material.

KRAFT LIGNIN-GLYOXAL-RESIN ENCAPSULATED PHASE-CHANGE MATERIAL FOR PRODUCING THERMAL-REGULATED WOOD

Chia-feng Lin^{1*}, Olov Karlsson¹,
Dennis Jones^{1,2}, Dick Sandberg^{1,2}

¹ Luleå University of Technology,

² Czech University of Life Sciences Prague.

* Chia-feng.lin@ltu.se

The emission of greenhouse gases during energy production is a significant contributor to climate change. The construction of buildings alone accounts for about 40% of the annual total global energy usage, while the heating/cooling necessary for maintaining comfortable conditions constitute 60% of the total consumed energy within constructed buildings.¹ To reduce this energy consumption, the use of organic phase-change materials (PCMs) has been suggested. PCMs typically melt and solidify within temperature ranges close to those of ambient/comfortable building temperatures, realising a potential of absorbing and releasing

up to 15 times more energy than conventional (non-phase change materials) due to their large latent heat capacity.² However, the potential leakage of PCMs during their liquid cycles hinders their wider application. One approach to address this issue has been to encapsulate PCMs with a polymeric shell, such as a phenol-formaldehyde (PF) resin.³ In this study, the use of kraft lignin-glyoxal resin is proposed as a substitute for PF resin for a wood modification process that is potentially more sustainable and less hazardous than its PF analogue.

The optical microscope image in Fig. 1(a) indicates microspheres inside lumina of wood. Furthermore, the microspheres seem to have a shell-core structure of lignin-glyoxal formed around the PCMs, Fig. 1(b). Further studies are under investigation and will be presented for the conference, which will demonstrate the influence of hydrophilic-lipophilic balance (HLB) values on the size distribution of micelles by dynamic light scattering (DLS), the impact

of the mass ratio of paraffin oil/lignin-glyoxal on the thickness of the polymeric shell and diameter of the PCMs core by electron microscope. These results will be supported by the determination of chemical functionalities of paraffin oil with/without encapsulation by Fourier-transform infrared spectroscopy (FTIR), whilst the heat storage capacity of the encapsulated PCMs modified wood by differential scanning calorimetry (DSC) will demonstrate the effectiveness of the PCM system.

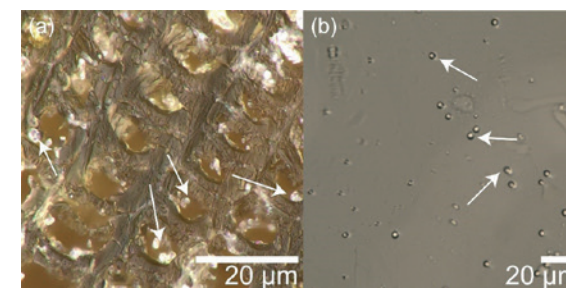


Figure 1: Microscope images of (a) cross-section of modified wood, and (b) paraffin oil micelles.

References:

1. Omrany, H.; GhaffarianHoseini, A.; GhaffarianHoseini, A.; Raahemifar, K.; Tookey, J. Application of Passive Wall Systems for Improving the Energy Efficiency in Buildings: A Comprehensive Review. *Renew. Sustain. Energy Rev.* **2016**, *62*, 1252–1269.
2. Sulaiman, N. S.; Mohamad Amini, M. H. Review on the Phase Change Materials in Wood for Thermal Regulative Wood-Based Products. *Forests* **2022**, *13* (10), 1–19.
3. Liu, C.; Cao, H.; Jin, S.; Bao, Y.; Cheng, Q.; Rao, Z. Synthesis and Characterization of Microencapsulated Phase Change Material with Phenol-Formaldehyde Resin Shell for Thermal Energy Storage. *Sol. Energy Mater. Sol. Cells* **2022**, *243* (May 2021), 111789.

NOVEL HIGH-SPEED ELONGATION RHEOMETER

Alexander M. Bier^{1*}, Walter Arne²,
 Dirk W. Schubert^{1*}

¹ Institute of Polymer Materials,
 Friedrich-Alexander-University
 Erlangen-Nürnberg

+ alexander.bier@fau.de

* dirk.schubert@fau.de

In many processes like film blowing, film casting or fiber spinning elongational strain occurs. For these processes, it is very important to know and understand the occurring elongational viscosities. However, for high elongation rates the elongational viscosity was and still is not accessible with existing methods e.g. the extensional rheometer after Sentmanat (SER), oil bath rheometer after Meissner or tensile rheometer after Münstedt (MTR) [1]. With the limitation of elongation rates to a maximum of 10 s⁻¹, those setups are not suitable in the range up to 100 s⁻¹, which are typical in fiber spinning [2]. With the

“Rheotens”, slightly higher elongation rates of up to 40 s⁻¹ can be achieved, but in comparison to the aerodynamic fiber stretching via an aspirator, it is still by far insufficient for an industrial relevant range.

Therefore, a novel method is developed to calculate the elongational viscosity of polymers during the fiber spinning process. To reduce the complexity of the system two PMMAs (to exclude crystallization effects) with different molar masses are investigated using a capillary rheometer. The diameter of the polymeric strand is determined via a high-speed camera from the die exit to the aspirator. In addition, simulations are carried out to describe the temperature profile of the polymeric strand along the spinline. A two-way calibration method was applied to calculate the force applied by the aspirator on the polymeric strand.

With this information, the temperature and elongation rate dependent elongational viscosity was determined. Furthermore, a Carreau type function was applied to master

all measurements (as shown in Figure 1). With strain rates up to 100 s⁻¹ this work paves the way to learn more about the elongational viscosity in the high deformation range never reached before [3].

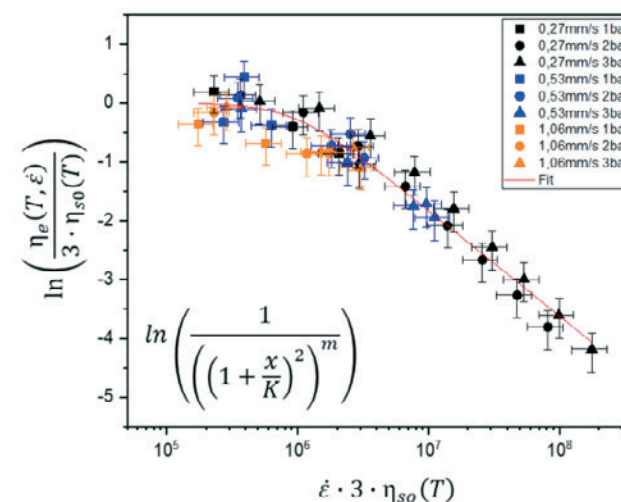


Figure 1: Mastered data points over all spinning parameter sets of PMMA 7N.

References:

1. H. Münstedt, Schwarzl, Deformation and Flow of Polymeric Materials, Springer, New York **2014**.
2. G.-G. Lin, M.-C. Hu, Measurement of elongation viscosity for polymer melts by fiber spinning. Adv. Polym. Technol. **1997**, 16, 199-207
3. A. Bier, W. Arne, D.W. Schubert, Novel High-Speed Elongation Rheometer Macro. Materials & Eng. **2022**, 2100974

BIO-BASED HIGHLY CONDUCTIVE IONOGELELECTRODES AS POTENTIAL BIO-ALTERNATIVE FOR ADVANCED APPLICATIONS

Maksims Jurinovs^{1*}, Anda Barkane¹,
Oskars Platnieks¹, Liga Grase²,
Sergejs Gaidukovs^{1*}.

1 Institute of Polymer Materials,
Faculty of Materials Science and Applied
Chemistry, Riga Technical University,
P. Valdena 3/7, Riga LV-1048, Latvia,

2 Institute of Materials and Surface Engineering,
Faculty of Materials Science and Applied
Chemistry, P.Valdena 3/7, LV-1048, Riga, Latvia.

* Maksims.Jurinovs@rtu.lv,
Sergejs.Gaidukovs@rtu.lv

In recent years, the use of nanotechnology to bio-based polymeric systems has opened new opportunities for increasing characteristics of the materials while preserving cost-effectiveness and environmental friendliness. Vegetable oils are one of the most promising bio-alternatives to fossil-based polymers right now.¹ The combination of vegetable oils and conductive

nanofillers could open up possibilities for novel materials that can be employed in a range of inventive applications, including sensors, shape-memory structures, and soft robots.

In addition, each of the aforementioned sectors might greatly benefit from the use of such materials in conjunction with additive manufacturing (AM). AM allows for the creation of structures with previously unthinkable geometries while requiring surprisingly few resources to operate.² Given this, the soft robotics sector, which aims to provide safe, adaptable, and highly customizable solutions for industry, appears to be the most viable way for fully utilizing every one of the benefits of such a combination. Currently, there is a lack of works applying such a concept, owing to the numerous problems that it entails, which served as the underlying motivation for the proposed research.

In this study, UV-curable resins based on epoxidized acrylated soybean oil with the

addition of ionic liquid and 0.1-1 wt% of single wall carbon nanotubes as filler were used to 3D print highly conductive structures via vat photopolymerization. 3D printing, system optimization, electrical conductivity, and printing resolution of biobased electro-conductive structures were intensively investigated. Electrical conductivity of up to 38.5 S/m was achieved, and developed materials were employed to manufacture the soft robotic actuator as a proof-of-concept. Future research will aim to manufacture entirely bio-based soft robotic actuators as a bio-alternative to typical petroleum polymer analogues.



Figure: 3D printed bio-based highly conductive structure with attached LED at 3V

References:

1. Vazquez-Martel, C.; Becker, L.; Liebig, W. V.; Elsner, P.; Blasco, E., Vegetable Oils as Sustainable Inks for Additive Manufacturing: A Comparative Study. *ACS Sustainable Chem. Eng.* **2021**, 9 (49), 16840-16848
2. Sachyani Keneth, E.; Kamyshny, A.; Totaro, M.; Beccai, L.; Magdassi, S., 3D Printing Materials for Soft Robotics. *Adv. Mater.* **2021**, 33 (19), 2003387.

THERMAL STABILIZATION OF POLYPROPYLENE BY RENEWABLE ANTIOXIDANTS

Richard Kröner^{1*}, Joachim Kaschta¹,
Ines Heiduk², Daniel Dorfmueller²,
Martin Falk², Dirk W Schubert^{1*}

1 Institute of Polymer Materials, Friedrich-Alexander-University Erlangen-Nuremberg (FAU), 91058 Erlangen, Germany,

2 FRÄNKISCHE ROHRWERKE Gebr. Kirchner GmbH & Co KG, 97486 Königsberg i B.

* richard.kroener@fau.de,

* dirk.schubert@fau.de

The thermal stability of recycled polypropylene should be increased by using renewable stabilizers known as antioxidants. These chemical compounds delay the degradation and aging of polymers by offering a hydrogen atom to the radical generated during thermal

decomposition, so that the radical does not react with the polymer chain [1].

In this work the use of Irganox 1010 (industry standard), lignin and α -tocopherol (vitamin E) in polypropylene is investigated [2-4]. To assess the effectiveness of the stabilizers, the oxidation induction time (OIT) is determined according to standard (EN ISO 11357-6) [5]. The oxidation induction time is the time a polymer can resist at 200 °C until degradation occurs after the change from nitrogen to oxygen atmosphere. The objective is to increase that time to more than 10 minutes. By adding different amounts of antioxidant, a critical concentration c^* is calculated at which the objective is achieved.

A linear relationship between concentration and thermal stability is found for all systems, except for the addition of α -tocopherol. The highest thermal stability is achieved by α -to-

copherol and α -tocopherol succinate, whose structures are formed on the basis of BHA (2, 6-di-tert-butyl-4-methoxyphenol) instead of BHT (2, 6-di-tert-butyl-4-methylphenol), as it is the case for the other stabilizers [4]. Compared to the industry standard (Irganox 1010) the efficiency of α -tocopherol is ten times higher in the relevant concentration level, making Vitamin E the most suitable antioxidant found in this research. The wood component lignin also shows good stabilization effects, but requires the tenfold concentration c^* than Irganox 1010.

Furthermore, the stabilized samples are analysed with regard to their rheological properties. At a temperature of 250 °C, that is equal to the processing temperature in the industry, degradation occurs during the measurement, so the unstabilized sample (pure PP) shows a lower viscosity compared to the stabilized samples.

References:

1. R. Maier, M. Schiller, Handbuch Kunststoff-Additive, Hanser Verlag, 4. Auflage, **2016**
2. D. Musajan, M. Mamatjan, R. Beken, M. Yimit; Impact of natural antioxidant systems on the oxidation resistance and mechanical properties of polypropylene; Pol. J. Chem. Tech., **2020**
3. A. S. Kabir, Z. Yuan, T. Kuboki, C. Xu, De-polymerization of industrial lignins to improve the thermo-oxidative stability of polyolefins; Industrial Crops & Products 120, **2018**, 238–249
4. Braithwaite, G.J.C.; Heuer, E.G.; Miller, B.L., Thomas, B.; Spiegelberg, S.H.S.; Ranking Antioxidant Activity by Oxidation Induction Time, 56th Annual Meeting of the Orthopedic Research Society, **2010**
5. Plastics – Differential scanning calorimetry (DSC) – Part 6: Determination of oxidation induction time (isothermal OIT) and oxidation induction temperature (dynamic OIT); EN ISO 11357-6:**2018**

INVESTIGATING THE SYNTHESIS AND PROPERTIES OF POLYTHIOUREAS AND POLYTHIOCARBAMATES

Rafael N L Menezes¹, **Olga Gordivska**¹,
 Baozhong Zhang^{1*}

¹ Centre for Analysis and Synthesis,
 Department of Chemistry, Lund University,
 P.O. Box 124, SE-22100 Lund, Sweden

* baozhong.zhang@chem.lu.se

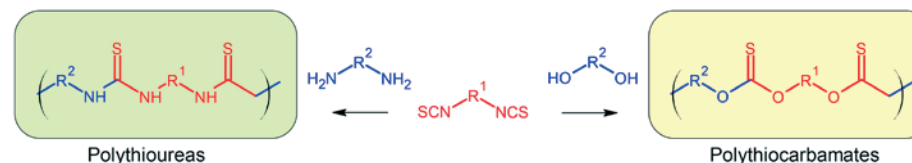
In current study two subclasses of polymers, recently emerging polythioureas, and a new subclass, polythiocarbamates, were targeted [1,2]. In case of polythioureas, the polyaddition of various diisothiocyanates and diamines was achieved under anhydrous conditions without any catalyst in DMF at 50 °C (Figure 1) yielding a series of polythioureas of high molecular weight in decent yield. Polymers were characterized by nuclear magnetic resonance, including DOSY measurements, infrared spectroscopy, and gel permeation chromatography. Subsequently chemical and physical properties of the corresponding polythioureas including solubility, thermal stability, and intrinsic viscosity were studied. The substituents connect-

ed to the thiourea group affect considerably the properties of the resulting polythioureas. Aliphatic polythioureas presented glass transition temperature ranging from 50 to 78 °C and degradation temperature higher than 200 °C, whereas aromatic polythioureas degraded at temperatures below 150 °C and did not exhibit glass transition up to this temperature. Polythioureas synthesized from aromatic diisothiocyanates could be conveniently depolymerized by heating, which may enable recycling process. Newly synthesized polythioureas could find potential application as fibers, screening of the conditions is in progress.

To access polythiocarbamates via polyaddition of diisothiocyanates and diols (Figure 1), screening of the reaction conditions was done: both Lewis acids and bases were tested.

Dibutyltin dilaurate catalysts demonstrated the highest efficiency under anhydrous conditions in DMF at 110 °C yielding oligothiocarbamates, which were further characterized by nuclear magnetic resonance, infrared spectroscopy, and gel permeation chromatography. Later, due to the high toxicity of the tin-based catalyst, it has been replaced with 1,3-dimethylimidazoiun-2-carboxylate, which demonstrated similar results: oligomers consisting of 6-7 carbamate units. Obtained results are in agreement with the thermodynamic calculations, which predict that higher molecular weight polymers cannot be formed [3]. In order to proceed further chain extension concept was applied. Screening of the reaction conditions for polyaddition of oligocarbamates bearing thioisocyanate end groups and diamine is in progress.

Figure 1. Synthetic route for polythioureas and polythiocarbamates.



References:

- Li, Y. M.; Zhang, Z. P.; Rong, M. Z.; Zhang, M. Q.; Nat. Commun., 2022, 13, 2633.
- Feng, H; Zheng, N; Peng, W.; Ni, C; Song, H.; Zhao, Q; Xie, T; Nat. Commun., 2022, 13, 397.
- Powell, C. R.; Foster, J. C.; Swilley, S. N.; Kaur, K.; Scannelli, S. J.; Troya, D.; Matson, J. B.; Polym. Chem., 2019, 10, 2991.

ANTIBACTERIAL CHITOSAN-BASED HYDROGELS FOR WOUND HEALING APPLICATIONS

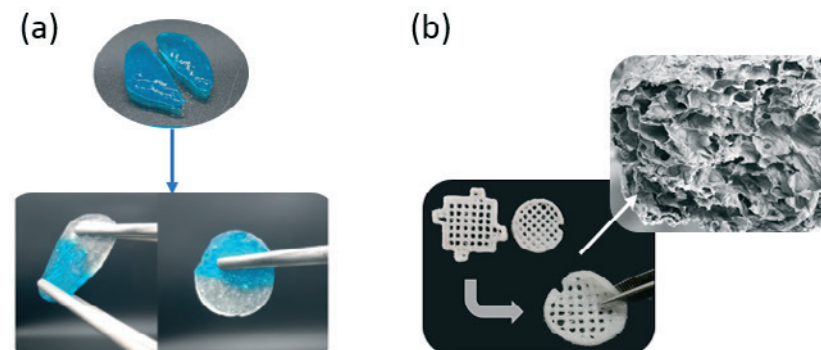
Isabella Laurén*, Afsoon Farzan, Maryam Madani, Arun Teotia, Jukka Seppälä

Polymer Technology, School of Chemical Engineering, Aalto University, Espoo, Finland

* isabella.lauren@aalto.fi

Modified cationic polysaccharides have a huge potential in several applications, thanks to its biocompatibility and antimicrobial properties. Here, a series of quaternized chitosan was prepared, using either [2-(acryloyloxy)ethyl]-trimethyl-ammonium chloride (AETMAC) solely, or a combination of both AETMAC and glycidyl trimethyl-ammonium chloride (GTMAC). These quaternary chitosan derivatives have proven antimicrobial activity against several pathogens at a wide pH range [1]. Quaternary chitosan derivatives, combined with other

Figure: 3D printed hydrogels: (a) self-healing and injectable chitosan/DACNC hydrogel; and (b) porous structures of chitosan/isocyanate-free polyurethane films.



materials, make excellent biobased composites for various biomedical applications, with long-lasting antibacterial properties.

In this research, we have combined modified cationic (quaternary) chitosan with two different materials, creating 3D printable hydrogels with antibacterial properties. In one project, we combined the quaternary chitosan with aldehyde-functionalised cellulose nanocrystals (DACNC), oxidised by NaIO_4 . These 3D-printable and injectable hydrogels

exhibit not only antibacterial activity, but also self-healing properties [2]. Furthermore, in a parallel project, the modified chitosan was combined with isocyanate-free polyurethane, generating non-toxic porous films through direct in writing [3]. The hydrogels, consisting of crosslinked networks, have good gelling and swelling properties, and tailored rheological properties, making them suitable for 3D printing. These biocompatible and nontoxic hydrogels with antibacterial properties have great potential as wound healing dressings.

References:

1. Borandeh, S.; Laurén, I.; Teotia, A.; Seppälä, J. Dual functional Antibacterial Chitosan Derivatives: Synthesis, Characterization, and Structure-Activity Relationships. *Adv. Healthc. Mater.* **2023**. (Under revision).
2. Madani, M.; Laurén, I.; Lindfors, N.C.; Borandeh, S.; Seppälä, J. 3D Printable and Injectable Self-healing Cellulose Nanocrystal Reinforced Chitosan-based Nanocomposite Hydrogels for Wound Healing Applications. (Under progress).
3. Laurén, I.; Farzan, A.; Lindfors, N.C.; Seppälä, J. Direct Ink Writing of Biocompatible Chitosan/Isocyanate-free Polyurethane/Cellulose Nano Fibre Hydrogels for Wound Healing Applications. (Under progress).

MALEIC-BASED POLYMER FORMULATIONS FOR THE MULTIFUNCTIONAL INHIBITION OF GAS HYDRATES, SCALE AND CORROSION IN OILFIELD PRODUCTION OPERATIONS

Janronel Pomicpic^{1*}, Malcolm Kelland^{1†}

¹ Department of Chemistry,
Bioscience and Environmental Engineering,
Faculty of Science and Technology,
University of Stavanger,
Stavanger N-4036, Norway

* janronel.pomicpic@uis.no,

† malcolm.kelland@uis.no

The oil and gas industry faces a long-standing problem of mitigating pipeline blockage due to gas hydrate formation and scale accumulation. Corrosion also makes things worse as this leads to pipeline embrittlement and eventual damage. Oilfield pipelines are usually subjected to extreme environmental conditions which makes the abovementioned problems inevitable. The formation of gas hydrates, scales, and corrosion is considered to be the biggest water-based oilfield production problem, which costs the petroleum industry billions of dollars annually¹. For countries that depend on the petroleum industry for its economic prosperity such as Norway, the inhibition of gas hydrates, scales, and corrosion is imperative in order to minimize the capital expenditures and operating expenses. Although separate inhibitor molecules to combat gas hydrates, scales, and corrosion are already being deployed, no single molecule has ever been developed that can inhibit these three oilfield problems. This is due to the fact that the physicochemical mechanisms underlying the formation of gas hydrates, scales, and corrosion are very different, making the simultaneous inhibition process difficult. The goal

therefore has been to develop a trifunctional inhibitor formulation by harnessing different polymerization and functionalization strategies using cheap and readily available raw materials in facile reaction conditions.

This study highlights the strategies that have been done using maleic-based polymer chemistry in order to reach this goal. Radical polymerization was used in order to synthesize different maleic anhydride homopolymers and copolymers containing pendant functional groups that initially inhibit gas hydrate nucleation and crystal growth. Further enhancement of the performance was done via post-polymerization modification of the anhydride functional groups with several active amines. These polymers could combat gas hydrates, but to inhibit scales and corrosion, they were combined with synergists to produce optimal trifunctional formulations. Interesting synergistic properties were discovered for the first time. Finally, the performance of the best formulations surpassed other commercially available inhibitors making it suitable for upscaling and industrial use.

References:

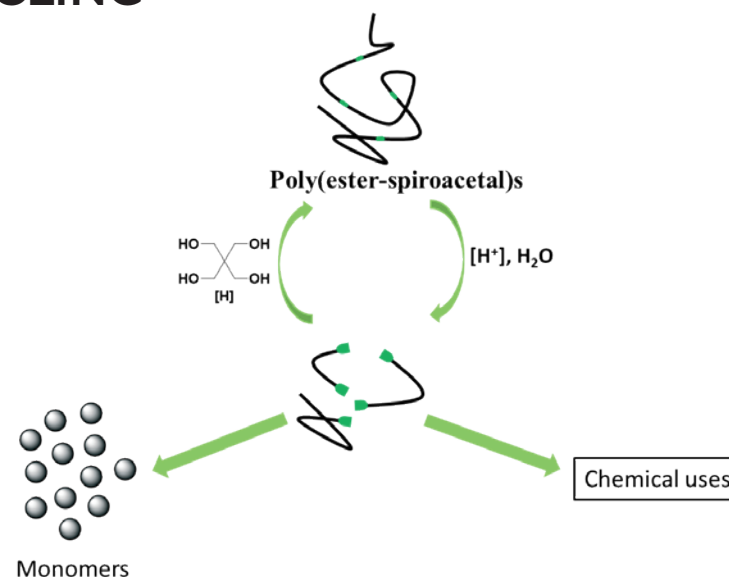
1. Kelland, M. A. Production Chemicals for the Oil and Gas Industry, 2nd ed.; Taylor & Francis Group, LLC: Boca Raton, FL, 2014.

INVESTIGATION ON ACIDIC CHEMICAL RECYCLING OF POLY(ESTER-SPIROACETAL)S

Tran Tam Nguyen, Smita Mankar,
Saga Vesterbacka, and Baozhong Zhang

1 Centre of Analysis and Synthesis,
Department of Chemistry, Lund University,
P.O. Box 124, SE-22100 Lund, Sweden

E-mail address of corresponding authors:
tam.nguyen@chem.lu.se



Poly(ester-spiroacetal)s have received growing attention recently in the development of bio-based polymers due to their enhanced thermal properties and potential recyclability. [1] Among other benefits, poly(ester-spiroacetal)s have acid-sensitive bonds (esters, acetals), which could be used as elements to design recyclable polymers. In the literature, hydroly-

sis of ester or acetal bonds in poly(ester-spiroacetal)s have been investigated, producing various types of building blocks for further uses (e.g., polymerization). [2,3] In this study, the hydrolysis of several poly(ester-spiroacetal)s under acidic conditions was thoroughly investigated. We found that the hydrolysis result in terms of the selectivity between ester

hydrolysis and acetal hydrolysis depended on the molecular structure, which could lead to the formation of telechelic polymers or monomeric molecules. The chemical use of the obtained telechelic oligomers or monomeric molecules was also investigated.

References:

1. Hufendiek, A.; Lingier, S.; Du Prez, F. E. Thermoplastic Polyacetals: Chemistry from the Past for a Sustainable Future? *Polym. Chem.* **2019**, 10 (1), 9–33.
2. Ma, S.; Wei, J.; Jia, Z.; Yu, T.; Yuan, W.; Li, Q.; Wang, S.; You, S.; Liu, R.; Zhu, J. Readily Recyclable, High-Performance Thermosetting Materials Based on a Lignin-Derived Spiro Diacetal Trigger. *J. Mater. Chem. A* **2019**, 7 (3), 1233–1243.
3. Hu, H.; Tian, Y.; Kong, Z.; Ying, W. Bin; Chen, C.; Li, F.; Zhang, R.; Zhu, J. A High-Performance Copolyester with “Locked” Biodegradability: Solid Stability and Controlled Degradation Enabled by Acid-Labile Acetal. *ACS Sustain. Chem. Eng.* **2021**, 9 (5), 2280–2290.

EXHIBITORS AT NORDIC POLYMER DAYS 2023

