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32nd Leoben-Conference on Polymer Engineering and Science

New Materials
New Perspectives

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32nd Leoben-Conference on Polymer Engineering & Science

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32. Leoben-Concerence on Polymer Engineering and Science 2024

For many years now, the Leoben-Conference on Polymer Engineering and Science (LKK) has been a meeting place for graduates, partners and interested groups from the entire polymer community, as well as students and pupils.

The conference is organized jointly by the Department of Polymer Engineering and Science Leoben and the Polymer Competence Center Leoben. Each year, a different institute of the department is in charge of organizing the colloquium. Accordingly, the focus changes every year and thus covers a special range of topics - from the chemistry of polymers to construction and component design to processing and materials testing.

New Materials - New Perspectives

The **32nd Leoben-Conference on Polymer Engineering and Science** took place on November 21st and 22nd, 2024, on the topic **„New Materials - New Perspectives“**.

The Program covered a wide range of interesting topics and aimed equally at participants from industry and academia. In four lecture sessions, topics were dealt with that are trend-setting for many areas of polymer technology:

- Polymers for Sustainability and Circularity
- Materials for Additive Manufacturing
- Polymers for Energy Transformation, Storage and Transportation
- Future Trends in Polymer Technology

An additional highlight was the Plenary Session with invited presentations is a panel discussion on the topic of „Polymers in a World without Oil“, for which participants from business and politics were invited.

This was also the fourth time that the Department of Polymer Engineering and Science Leoben and the Polymer Competence Center Leoben, were presenting the POLYMER SCIENCE SCHOOL AWARD. This Award has been an important part of the conference since 2019 and is intended to recognize forward-looking ideas and innovative projects by students.

The presentation of successful spin-off companies, a poster session and the dinner on the evening of the first day rounded off the program of the 32nd Leoben Conference on Polymer Engineering and Science.

PROGRAM
THURSDAY, NOVEMBER 21ST, 2024

Opening and welcome
09:30 - 10:00

Plenary Session
10:00 - 12:30

Panel discussion on the topic of “Kunststoffe in einer Welt ohne Erdöl” (in German) with the following participants:

Harald Bleier, Ecoplus NÖ

Alexander Kronimus, Plastics Europe

Sabine Nadherny-Borutin, Plastics Europe Austria

Markus Seidel, BMW Group

Martin Wimmer, Bundesministerium für Klimaschutz, Umwelt, Energie, Mobilität, Innovation und Technologie (BMK)

Andreas Leitner, OMV AG

Plenary lectures (given by invited speakers)

Bioplastics - curse or blessing ?
Sabine Nadherny-Borutin, Plastics Europe Austria, and Michaela Plank, Österreichischer Carbon Cycle Circle – Team für nachhaltigen Kohlenstoffkreislauf

Circular Carbon in the Automotive Industry – The BMW Perspective
Markus Seidel, BMW Group

Award ceremony - **POLYMER SCIENCE SCHOOL AWARD**

Presentation of successful spin-off companies

- Circulyzer GmbH, Daniel Schwabl
- SCIOFLEX Hydrogen GmbH, Bernd Schrittesser
- ecolyte GmbH, Georg Rudelstorfer
- Trastic GmbH, Arno Trinkl
- Luxinergy GmbH, Thomas Rockenbauer

Lunch break
12:30 - 14:00

SESSION: A: **Polymers for Sustainability and Circularity** *Erzherzog Johann Auditorium*	**SESSION B:** **Polymers for Energy Transformation, Storage and Transportation** *HS Phys.Chemie*
14:00 **Conventional, Biobased or Biodegradable Microplastic. Which one would you prefer?** Ines Fritz, BOKU University	14:00 **Underground Sun Storage 2030 / EUH2STARS – 100% hydrogen storage in porous reservoirs** Matthias Greiml, RAG Austria AG
14:25 **Bio-based polymers and materials from lignin-derived monomers** Barta Katalin, University of Graz	14:30 **Thermomechanical Characterization and Simulation of Li-Ion Battery Components** Johannes Macher, Polymer Competence Center Leoben
14:50 **Recycling of packaging films: Properties enhancement and application** Katerina Plevova, Montanuniversität Leoben	14:50 **Development of smart coatings for safety applications in battery systems** Daniel Bautista, Polymer Competence Center Leoben
15:10 **Recycling of Wintersport Hardgoods: The Challenges of Circularity** David Zidar, Montanuniversität Leoben	15:10 **Evaluating Encapsulant Materials for c-Si/Perovskite Tandem Modules** Petra Christöfl, Polymer Competence Center Leoben

Poster introduction (2 – 3 min each)
15:30 - 15:45

Coffee break
15:45 - 16:15

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16:45 **Property prediction of polymers using spectroscopy** Márton Bredács, Polymer Competence Center Leoben	16:45 **High cycle fatigue and creep of reinforced PEEK for large size bearings in wind industry** Gabriel Stadler, Montanuniversität Leoben
17:05 **Wet mechanical processing of post-consumer plastics** Daniel Schwabl, Circulyzer	17:05 **Polyethylene pipes for distribution of gaseous hydrogen** Florian Arbeiter, Montanuniversität Leoben
17:25 **Repair solutions for PV modules with damaged polymer backsheets** Sonja Feldbacher, Polymer Competence Center Leoben	17:25 **Enabling glass-free light weight PV modules using honeycomb structures** Nikolina Pervan, Polymer Competence Center Leoben
17:45 **Sustainable polymers in coatings industry** Martin Ocepek, Helios Resins	
Dinner in the Arkadenhof, Leoben 19:30	

PROGRAM

FRIDAY, NOVEMBER 22ND, 2024

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9:30 **Advances in the Detection of Micro- and Nanoplastics: Methods and Technologies** Michael Feuchter, Montanuniversität Leoben	9:30 **Additive Manufacturing Activities at the Polymer Competence Center Leoben** Michael Berer, Polymer Competence Center Leoben
9:50 **Design of covalent adaptable networks for advanced applications** Elisabeth Rossegger, Polymer Competence Center Leoben	9:50 **Wavelength Orthogonal Photochemistry in Additive Manufacturing: Towards 3D Structures with Tailored Properties** Thomas Griesser, Montanuniversität Leoben
10:10 **Bio-based covalent adaptable networks: From monomer synthesis to applications in 3D-printing and nanoimprint lithography** Bernhard Sölle, Polymer Competence Center Leoben	10:10 **Design and Additive Manufacturing of Mechanical Metamaterials for Structural Applications** Mathias Fleisch, Polymer Competence Center Leoben
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11:40 **Polymerization Initiation Systems – How everything will start** Patrick Knaack, TU Wien	11:45 **Analyzing and Predicting Failure Modes in Mono- and Multi-Material Extrusion-based Additive Manufactured Structures** Christoph Waly, Montanuniversität Leoben
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Specialist lectures

PLENARY SESSION

Bioplastics - curse or blessing?

M. Plank[1], S. Nadherny-Borutin[2]

[1] Österreichischer Carbon Cycle Circle – Team für nachhaltigen Kohlenstoffkreislauf, A-1040 Wien
[2] Plastics Europe Austria, A-1040 Wien

Abstract

Bioplastics are materials that are made from renewable raw materials such as vegetable oils, starch or sugar and in some cases are biodegradable. In contrast to traditional plastics, which are made from fossil raw materials, bioplastics promise a reduction in dependence on crude oil and a reduction in the ecological footprint. These properties have led to increased research and development in this area, but the question arises as to whether bioplastics actually represent a sustainable alternative to conventionalplastics or whether they are more likely to create new problems.

One of the main arguments in favor of using bioplastics is the reduction of carbon emissions. On the surface, since bioplastics come from plant sources that absorb CO_2 from the atmosphere as they grow, this can be seen as a contribution to reducing the greenhouse gas effect. However, the entire effort that has to be made to extract these quantities of raw materials and further bioplastics from the plant should also be taken into account. Information on the efficiency of such processes is usually ignored. The question of their actual ecological footprint and the long-term impact on the environment and society remains unanswered. Another critical aspect to consider is the high consumption of resources in the production of bioplastics compared to conventional plastics. This can lead to an increase in greenhouse gas emissions and call into question their ecological benefits. It is therefore crucial that attention is paid to the efficient use of resources in the production of bioplastics to ensure that their ecological potential is actually utilized.

The issue of raw material sourcing and availability also comes to the fore on closer inspection. As the cultivation of the required plants competes with food production for agricultural land and water resources. This can lead to negative social and environmental impacts, especially in regions where resources are scarce. In addition, bioplastics are often more expensive to produce than conventional plastics, which limits their broad market acceptance. In regions where agricultural land is heavily utilized, the production of bioplastics can often contribute to an increase in food prices and cause land use conflicts. Another important aspect is biodiversity. The cultivation of monocultures for the production of bioplastics can lead to a reduction in biodiversity in natural ecosystems and affect the balance of ecosystems. It is therefore necessary to promote sustainable production practices that take both environmental and social aspects into account. Ultimately, the assessment of bioplastics as a curse or a blessing depends on how they are produced, used and disposed of and whether they can actually contribute to improving the environment.

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The question of the sustainability of bioplastics therefore remains topical and complex. The ecological balance of bioplastics is not clearly positive. The production of bio-based plastics often requires intensive agricultural practices that include the use of fertilizers and pesticides, which in turn can have a negative impact on biodiversity and soil. In addition, the full life cycle costs of bioplastics - including cultivation, converting, transport and disposal - must be taken into account. In many cases, the production of bioplastics is energy-intensive and can lead to higher emissions than the production of fossil-based plastics, depending on the source of the raw materials.

In addition to the ecological impact, the social dimension is also of great importance. It is important that social standards are also observed in the production of bioplastics to ensure that no social injustices arise. In addition, the entire bioplastics valuechain should be transparent, from the procurement of raw materials through to disposal. Only by taking a holistic view and handling bioplastics responsibly can their potential as an ecological alternative really be utilized.

Another critical aspect is the disposal of bioplastics. While some bio-based plastics are compostable, many regions require appropriate disposal systems and infrastructure to realise their environmental benefits. In inadequately equipped disposal systems, they can be mixed with conventional plastics and cross-recycled, jeopardizing the entire recycling chain. The complexity and practicability of differentiating between individual plastics and bioplastics by the end user also remains unmentioned. Clear guidelines for the labelling and disposal of bioplastics are necessary to maximise their potential benefits, but the crucial final step always lies with the end user and their intentions.

Another difficulty lies in the misunderstanding of what bioplastics can actually do. Not all bioplastics are biodegradable after use. The social acceptance of bioplastics depends heavily on their perception as a ‘green’ alternative. It is often advertised that biodegradable bioplastics, if disposed of correctly, could reduce landfill waste and plastic pollution and make a significant contribution to solving global plastic pollution, particularly in marine ecosystems. This has led some consumers to believe that they can safely dispose of bioplastics, which contributes to littering. Many bio-based products, such as certain PLA (polylactic acid) and PHA (polyhydroxyalkanoate) plastics, require specific conditions for degradation that are often found in industrial composting facilities. The discussions also neglect the fact that biodegradable plastics do not degrade in aquatic environments, or do so insufficiently. In natural environments, especially in the sea, some bioplastics can persist just as long as conventional plastics. In addition, microplastics can be produced during degradation, which have a harmful impact on the environment.

And finally, the most important question to ask is - in which applications exactly is the biodegradability property actually needed (such as in medicine) and where is it just a desperate attempt to tackle the stupidity and ignorance of people, and is this in proportion to the effort required to manufacture the product?

We must all be aware of one thing: the simplified dissemination of information only encourages the real problem with plastics - the careless use of plastic products. The future of bioplastics depends heavily on technological advances. Research is currently focusing on the development of second-generation bioplastics made from waste or non-food crops to reduce competition for agricultural land. Improving biodegradability under natural conditions is also a key area of research. In addition, the further development of recycling technologies could facilitate the re-utilization of bioplastics and thus further improve their environmental footprint.

Bioplastics undoubtedly offer promising solutions to some of the most pressing environmental problems of our time, but they are not a panacea. Their impact on the environment depends heavily on the type of raw materials, production processes and disposal methods. While they can offer significant benefits in certain applications, there are also significant challenges that need to be addressed to ensure that bioplastics actually contribute to a more sustainable future. Whether bioplastics are a curse or a blessing will therefore largely depend on how we deal with these materials and how we shape their development and application in the coming years.

Specialist lectures

SESSION A
“POLYMERS FOR SUSTAINABILITY AND CIRCULARITY”

Conventional, Biobased or Biodegradable Microplastic Which one do you prefer?

I. Fritz
BOKU University, Environmental Biotechnology, AT-Tulln

Abstract and Summary

Every lifeform on planet Earth has some influence on its surroundings, on the habitat as well as on the other organisms of the biocoenosis. This can be from the level of individual metabolic activity and go up to global habitat shaping by whole communities. Finally, whatever a lifeform has produced by metabolic activity will be degradable by the same or by other lifeforms according to the general principle of closed matter loops. Humans are part of the system.

With one specific difference: ecology is not directed by business plans.
What undoubtedly improves our lives but also what does not, is payed by others. Within significant and acute changes in global climate and environmental pollution with chemicals, one among many impacts is identified as (micro-)plastic pollution.

It all began with the idea of making tools from man-made materials that are more durable as plant and animal based natural materials are. Linseed oil coatings on wood or leather are early examples, later followed by invention of long-chain synthetic polymers, soon known as plastic. In other words: plastic is the response to the desire of having tools made from long-lasting (not biodegradable) materials!

What if a business driven population recognises that such an „immortal“ tool doesn‘t need to be replaced in foreseeable time? Answer: it invents planned obsolescence, fashion and, on top of all, single use products! As a consequence, the ecosystem is spilled with immortal single use products after their single use.

Considering history, should the introduction of biodegradable polymers be seen as innovative solution? Or is it the business version of reverting back towards materials with similar properties as plant and animal based resources are?

Unfortunately, the situation is neither black nor white. We need to dive deep and have a differentiated view on conventional, biobased and biodegradable plastic. Not all conventional plastic is persistent, not all biobased synthetic plastic can be re-integrated into the biological cycles and the introduction of biodegradable plastic is no excuse for failed human behaviour.

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In the lecture we will dive deep into the following:

- A look at the behind-the-scene causes that make a certain material either biodegradable or persistent
- Learning about biodegradability similarly being and not being a substance property
- Knowing the difference between biodegradation and material disintegration
- Finally, answering the question about which type of microplastic to prefer!

During the lecture we will not answer the following questions – making them to your homework:
What does it mean for the longevity of our society if we start to use the best fitting material for a certain application instead of the cheapest?
Who are those that have to pay for our present misunderstanding of welfare? Will it be us in near or will it be our descendants in farther future?

Bio-based polymers and materials from lignin-derived monomers

K. Barta*
Institute of Chemistry, Organic and Bioorganic Chemistry
University of Graz, AT-Graz

Abstract

The quest for high-performance bio-based polymers derived from renewable feedstocks is increasingly recognised as a fundamental step to ensure the transition toward a circular economy. It is therefore crucial to obtain industrially significant polymer precursors from biomass depolymerisation mixtures via highly efficient and selective catalytic methods.

Recently, we demonstrated the synthesis of the commercially relevant aliphatic diamine, namely 4,4‘-methylenebiscyclohexanamine (MBCA), from lignin-based industrial waste streams via an elegant catalytic approach involving the intriguing 4,4-methylenebiscyclohexanol (MBC) as a key intermediate.

This synthetic strategy allowed MBC and MBCA to be delivered as renewable building blocks. The high potential of MBC and MBCA was exploited in the synthesis of fully bio-based thermoplastic and thermosetting polymers exhibiting remarkable thermo-mechanical properties. Additionally, solvent-based recycling methods were optimized for selected cases to enhance the recovery and reuse of the monomers.

Introduction

The utilization of industrial waste as a resource for value-added chemicals presents a compelling approach to sustainable development and circular economy practices. Industrial waste streams, often regarded as pollutants or low-value byproducts, can be transformed into valuable chemicals, fuels, and materials, thereby reducing environmental impact and promoting resource efficiency.

A particularly effective strategy involves leveraging industrial waste streams derived from renewable feedstock to produce valuable building blocks for polymer synthesis. This offers an effective method to establish relevant waste-to-value chains.

Aliphatic diols and diamines, key monomers for thermoplastic and thermosetting polymers, are integral in this context. [1] These versatile compounds are the backbone of a wide array of polymers. [2] They are essential in numerous industrial sectors, ranging from automotive and construction to electronics and textiles. This underscores the appeal of developing sustainable methods to produce diols and diamines from renewable resources like lignocellulosic biomass, making it a highly attractive area of research today. [3]

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The lignin-to-vanillin process is an established industrial process run by the Norwegian company Borregaard. It deals with the alkaline oxidation of softwood lignosulfonate to yield vanillin, the world's most widely produced aroma chemical. [4] During this process, other phenolic aldehydes are produced in smaller amounts along with vanillin, such as syringaldehyde and 4-hydroxybenzaldehyde. The separation and purification of these byproducts is tedious and economically inconvenient, therefore these are either recycled back into the system or used in other applications. However, transitioning towards more sustainable waste management practices by valorizing byproducts obtained from industrial processes aligns better with global environmental goals and the principles of a circular economy. Thus, we aimed to derive aliphatic diols and diamine from such industrial side-streams to enable the efficient conversion of lignocellulose depolymerization mixtures into well-defined building blocks for polymer synthesis.

With the bio-derived polymer precursor in hand, various polymeric materials were synthesized. Specifically, polyesters and polycarbonates were obtained from the MBC diol and its isomers after copolymerization with renewable diesters and diphenyl carbonate respectively.

MBCA diamine was used to prepare benzoxazine monomers that, after curing, allowed to obtain fully bio-based polybenzoxazine thermosets. Additionally, as recently reported, MBCA was employed as hardener to develop epoxy resin thermosets with remarkable properties.

Discussion

The catalytic strategy [5]
The catalytic strategy designed for converting phenolic aldehydes into specific diols and diamines was optimized using commercially available catalysts, widely accessible or potentially bio-derived reagents, and straightforward purification methods.

The synthetic steps reported in Figure 1 involved the (Step 1) hydrogenation using Pd/Al_2O_3

as catalyst; (Step 2) electrophilic aromatic substitution promoted by Amberlyst 15; (Step **3**) selective Raney nickel-catalyzed funneling via demethoxylation/hydrogenation to methylenebiscyclohexanol (MBC); and (Step 4) the direct amination of MBC with ammonia via the hydrogen-borrowing strategy, in near-perfect MBCA selectivity.

The two most challenging steps in the proposed strategy depicted in Figure 1 are the catalytic funneling of the mixture of bisphenol derivatives into the single aliphatic diol MBC (Step 4) and its subsequent amination to MBCA (Step 5).

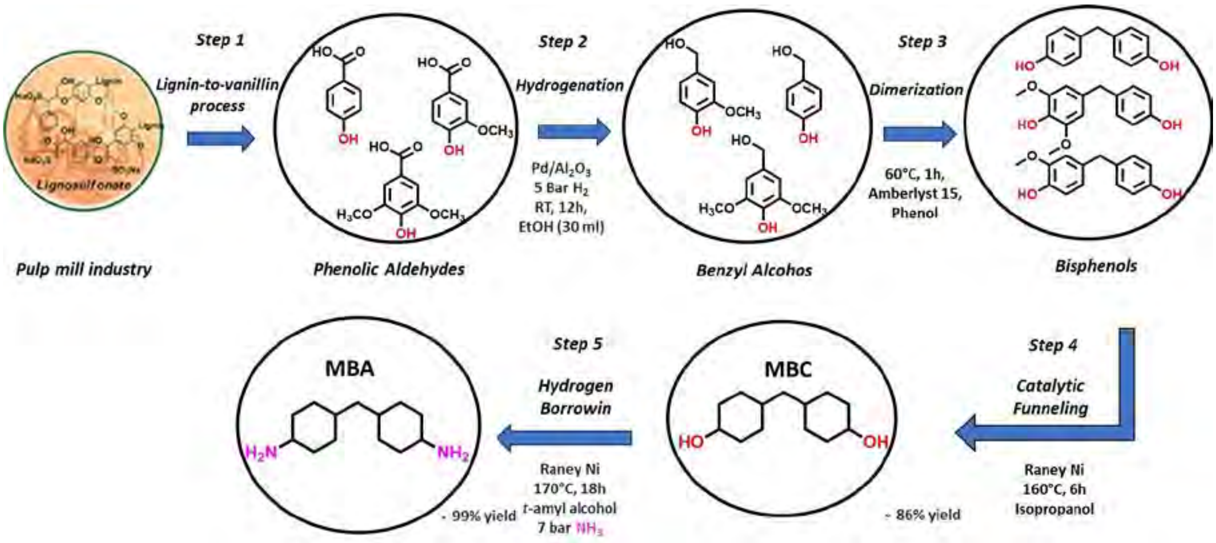

Fig.1: Catalytic strategy to convert phenolic aldehydes from the pulp industry to MBC and MBCA

Optimized reaction conditions for the catalytic funnelling of bisphenol mixtures allowed to obtain MBC with 86% yield using Raney nickel as catalyst, at 160°C for 6h. In addition to this, magnetic Raney nickel was easily separated by means of a magnet showing good reusability.

Next, the possibility to get MBC from aldehyde mixtures was explored, mimicking those originating from alkali lignin oxidation, based on the reaction sequence shown in Figure 1. Specifically, a mixture comprising 1 mmol vanillin, 0.5 mmol syringaldehyde, and 0.5 mmol 4-hydroxybenzaldehyde was hydrogenated in the presence of Pd/Al_2O_3 (5 bar H_2, 30 mL ethanol, RT, overnight) to get corresponding benzyl alcohols in an excellent 94.8% yield. Subsequently, the benzyl alcohol mixture was subjected to reaction in neat phenol over Amberlyst 15 (60°C, 1h) to get a mixture of bisphenols in a high, 78.9% yield. Catalytic funnelling of this mixture over Raney nickel (isopropanol,160°C, 6h)resulted in an overall MBC yield of 62.3% based on the aldehydes mixture.

Finally, the catalytic deamination of MBC directly to MBCA via the waste-free hydrogen borrowing methodology was investigated. Using Raney nickel as a catalyst, MBCA was obtained in near-perfect (99%) GC selectivity and 96%isolated yield at 170°C, 18h with 7 bar NH_3 pressure. In addition, no obvious nickel leaching was observed after four cycles, resulting in high reusability.

The obtained MBC diol and MBCA diamine represent bio-derived building blocks holding great potential for the synthesis of bio-based polymers.

Thermoplastic polymers from MBC

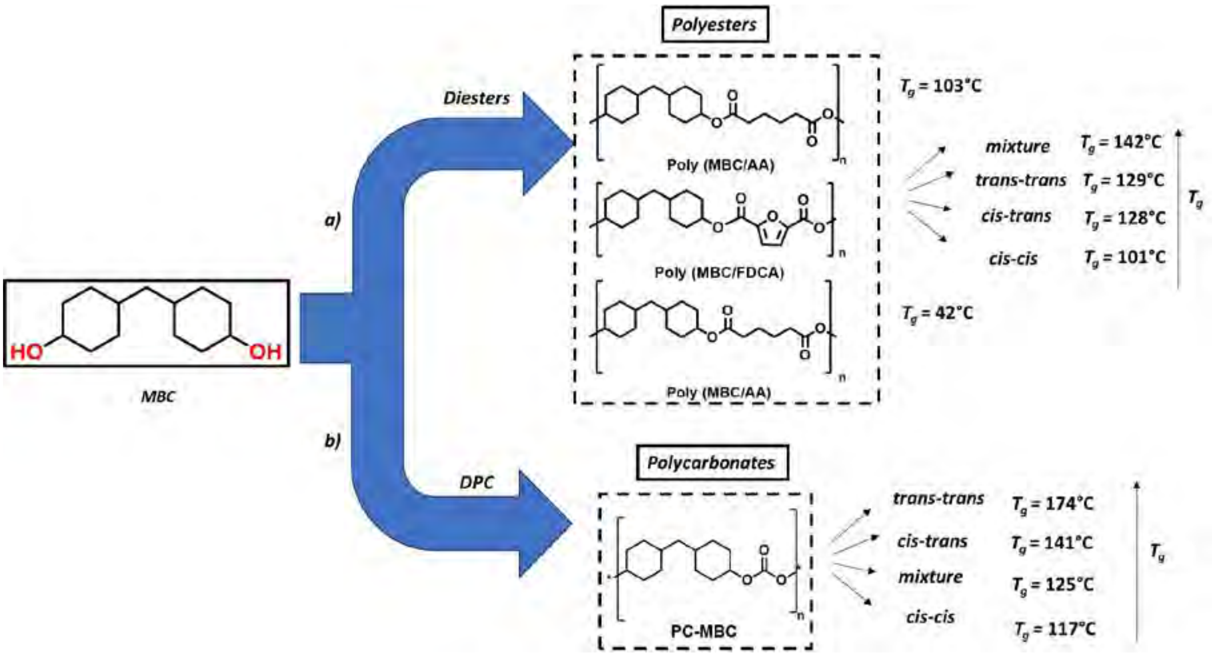

Fig. 2: Polyester and polycarbonate polymers from MBC

High-Performance Thermoplastics from MBCA [6]

MBC is an aliphatic, bicyclic rigid diol. Polyesters derived from similar structures have been shown to display rigid molecular chains and hence high T_g values (> 100 °C).[7] Meeting this requirement is relevant for advancing research on high-performance renewable bio-polymers, since most of the bio-derived polymers generally don't exceed T_g values of 90 °C.[8] This in mind, MBC was investigated for the preparation of versatile, property-tunable, and recyclable fully bio-based polyesters displaying excellent thermal properties. Polyesters were prepared by solvent-free titanium-catalyzed transesterification and polycondensation of MBC (as a mixture of isomers) with three different cellulose-derived diesters, namely dimethyl terephthalate (DMTA), dimethyl furan-2,5-dicarboxylate (DMFD), and dimethyl adipate (DA), resulting in poly(MBC/TPA), poly(MBC/FDCA), and polyTPA)(MBC/AA) respectively (see Fig. 2a). All polymers were obtained in good-to-excellent numerical yields (65−94%) and characterized by means of NMR, GPC, DSC, TGA, and FTIR spectroscopy. The DSC analysis of poly(MBC/TPA) and poly(MBC/FDCA) revealed respective T_g values of 103 and 142°C. In addition, the TGA/DSC analysis of the latter two polymers showed respective melting temperatures (T_m) of 261 and 275°C, and respective decomposition temperatures (T_d) of 272 and 284°C, further underscoring their potential industrial relevance. MBC exists as a mixture of three geometrical isomers, notably cis−cis, cis−trans, and trans−trans MBC. The influence of the MBC pure isomers on the thermochemical properties was investigated for the poly- (MBC/FDCA) case. It was found that polymers made with a pure MBC isomer showed a lower glass transition temperature (T_g) compared to the original poly(MBC/FDCA). Poly(MBC/AA) displayed a low Tg of 42°C, which is attributed to the more flexible AA chain, while displaying a high decomposition temperature (T_d) of 365°C.

As regards recyclability, It was found that all here-presented polymers could be fully and easily degraded into their respective monomers by methanolysis, without the deliberate addition of additives. That way, MBC could be recovered in 90% yield independent of the type of polymer.

Summing up, it was showed the development of a versatile set of bio-based semicrystalline polyesters high T_g and T_m/T_d values that could offer sustainable alternatives to atactic/syndiotactic polyacrylonitrile (PAN), polyether ether ketone (PEEK), polyethyleneterephthalate (PET), poly(tert-butyl vinyl ether) (PTBVE),and certain classes of polyamides (high-heat-resistant ones and nylon).

Novel stereoisomeric lignin-derived polycarbonates [9]

Polycarbonates (PC) are an important class of polymers, which over recent years have found broad applications towards a wide range of fields due to their excellent thermal and mechanical properties, impact resistance and optical features.[10] The main polycarbonate material is Bisphenol A (BPA) polycarbonate (PC) due to its excellent properties, such as high T_g (147 °C), excellent miscibility, transparency, processability, and durability – all characteristics which largely relate to its stable amorphous structure.[11] However, given the significant environmental and health concerns associated with BPA, [12] there is a need for sustainable alternatives.

To this end, a set of novel bio-based, polycyclic, non-aromatic PC-MBC polycarbonates were prepared by copolymerization of MBC stereoisomers (or mixture) with diphenyl carbonate (DPC) via one-pot, two-step melt polymerization processes (see Fig. 2b).

Structural analysis performed by FT-IR and NMR spectroscopy confirmed the successful polymerisation. The polymeric properties of the PC-MBC polycarbonates were investigated by GPC analysis and DSC/TGA. GPC revealed M_w values between ~23 000 g mol^{-1} for PC-$MBC_{mixture}$ (stereoisomer ratio 11 : 42 : 47) and ~28 000 g mol^{-1} for PC-$MBC_{cis-trans}$, and PC-$MBC_{cis-cis}$. PC-$MBC_{trans-trans}$ exhibits a somewhat lower value of 19 200 g mol^{-1} due to the presence of oligomers.

DSC analysis revealed a profound effect of the MBC stereoisomerism on the thermal properties, with PC-$MBC_{trans-trans}$ displaying the highest T_g (174 °C), in line with literature which tends to link higher T_g values to higher trans contents. In contrast, the lowest T_g (117 °C) value was obtained for PC-$MBC_{cis-cis}$. Notably, the T_g value of PC-$MBC_{cis-trans}$ (141 °C) is very close to the one of PC-BPA (147 °C for a Mw of 126kDa and134 °C for a Mw of 16 kDa). For all here evaluated PC-MBC polymers, the decomposition temperature (T_d) is well above 300 °C, the highest recorded value being 331 °C for PC-$MBC_{trans-trans}$.

Thermosets from MBCA

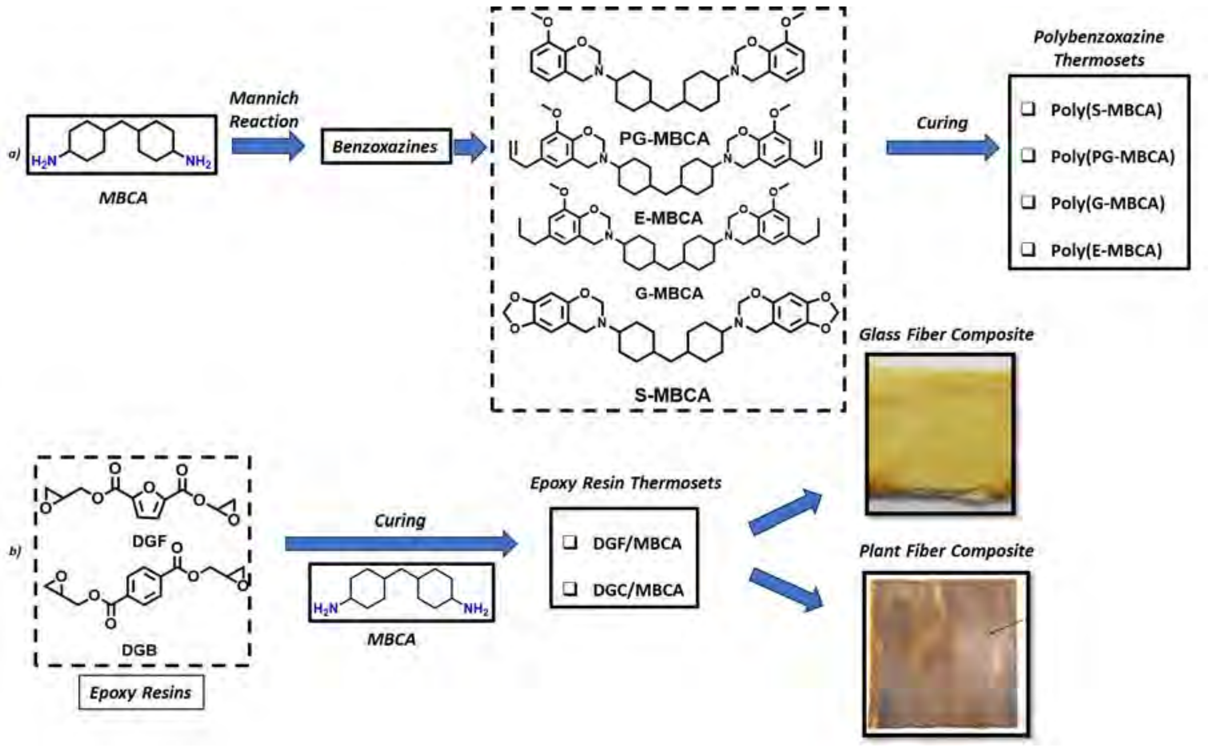

Fig.3: Polybenzoxazine and Epoxy Resin thermosets from MBCA

Bio-based polybenzoxazines with comparable properties to commercial materials [5]
Polybenzoxazines are a class of thermosetting polymers known for their unique properties and wide range of applications. They are notable for their exceptional thermal stability, mechanical strength, and flame retardancy. Additionally, they exhibit low water absorption and excellent resistance to chemicals and solvents. These attributes make polybenzoxazines particularly useful in high-performance materials such as composites, coatings, and adhesives in the aerospace, automotive, and electronics industries. [13] However, polybenzoxazines are generally synthesized starting from fossil-based and, in some cases, make use of BPA. Hence, sustainable and renewable alternatives are highly desired materials with industrial relevance.

MBCA was utilized as an aliphatic diamine building block to design fully bio-based polybenzoxazine resins. The novel benzoxazine monomers S-MBCA, PG-MBCA, G-MBCA, and E-MBCA were prepared through Mannich condensation of MBCA with formaldehyde and four different lignin-derived monophenols: sesamol (S), propylguaiacol (PG), guaiacol (G), and eugenol (E) (see Fig. 3a). Benzoxazines PG-MBCA, G-MBCA, and E-MBCA were obtained by solventless microwave irradiation (output power of 200 W) at 80°C–100°C for total 15 min lead, followed by column chromatography, in 51.4%, 62.1%, and 59.7% isolated yield, respectively. S-MBCA could be obtained after a simple filtration in an excellent isolated yield (98%) upon performing the synthesis in ethanol. The successful synthesis of benzoxazine monomers was confirmed by structural analysis, performed by ^{1}H NMR, ^{13}C NMR, 2D HSQC, 2D COSY and FTIR spectroscopy.

Next, benzoxazine monomers were subjected to ring-opening polymerization by stepwise curing at 170°C–280°C to give poly (S-MBCA), poly (PG-MBCA), poly (G-MBCA), and poly (E-MBCA), as confirmed by FT-IR analysis due to the disappearance of the characteristic signal at 930 cm^{-1}. The thermal properties of these polybenzoxazines were determined by DSC and TGA techniques.

Poly (S-MBCA) showed the best thermal stability, with a T_g up to 315°C. The mechanical properties of poly (S-MBCA) were found to be excellent E' =3.8 GPa at 25°C, E' =2.7 GPa at 200°C. These values are comparable with the commercially available polybenzoxazine resins, such as those produced by Huntsman.

Closed-loop recyclability of a biomass-derived epoxy-amine thermoset [14]

Epoxy resin thermosets (ERTs) constitute a crucial category of polymeric materials, renowned for their exceptional durability and thermal stability, making them essential in various industrial applications, including packaging, composite manufacturing, transportation, construction, and aviation.[15] Despite these advantages, the strong covalent bonds within the cured ERT backbone render these materials generally non-recyclable, leading to unsustainable disposal practices such as incineration or landfilling.[16] Additionally, the production of ERTs typically relies on bisphenol A (BPA), a fossil-derived compound identified as an endocrine disruptor.[17] Consequently, there is an urgent need for readily recyclable ERT alternatives derived from renewable resources to promote sustainability in the thermoset industry.

With this in mind, MBCA was tested as a curing agent in the design of an epoxy-amine ERT. To move away from the traditional bisphenol-based diglycidyl ether structures, diglycidyl esters of 2,5-furandicarboxylic acid and terephthalic acid (DGF and DGB, respectively), in combination with MBCA were used (see Fig. 3b).

The results showed that applying MBCA as a curing agent together with DGF in a 1:2 ratio led to the fully biomass-derived material DGF/MBCA, which displays both a markedly high glass transition temperature (T_g = 170°C) and storage modulus (E 25°C = 1.2 GPa). This ERT, showing such favourable properties, outperforms various previously described bio-based ERTs and is competitive with commercial fossil-based ERT materials that are synthesized from BPA.

We investigated the recyclability of DGF/MBCA, as well as other analogs featuring distinct ester functionalities, by methanolysis under mild reaction conditions. The fully cured DGF/MBCA readily dissolved in methanol at 70°C, in the absence of any additives, whereby the furan monomer dimethyl ester of 2,5-furandicarboxylic acid (DMFD) could be recovered in 90% yield.

Depolymerization of DGF/MBCA was investigated in a range of primary alcohols, among which methanol showed superior performance.

This is attributed to the small nature and appropriate hydrophilic-hydrophobic balance of methanol vis-à-vis the overall polarity of the polymer. Interestingly, DGF/MBCA was found perfectly stable in a wide range of organic solvents, and the material demonstrated excellent hydrolysis resistance, strengthening its potential for industrial applications.

Full solubilization of DGF/MBCA by the established methanolysis protocol enabled the development of a distinct closed-loop recycling strategy. Upon DGF/MBCA dissolution in methanol, the furanicmonomerDMFDwas recovered by an efficient purification protocol, together with a polyol fraction, whichwas subsequently converted to the original building blocks, MBCA and glycidol. The developed methanolysis methodology was adaptable to the depolymerization of a small library of ERTs, consisting of six different analogs. Finally, glass fiber–reinforced composites were synthesized and efficiently reused by applying the mild methanolysis procedure, which smoothly removed the polymer matrix without detectable changes to the recovered glass fibers. Fully bio-based plant fiber composites, with good mechanical properties, were also fabricated.

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Transforming multilayer packaging waste into shrink films

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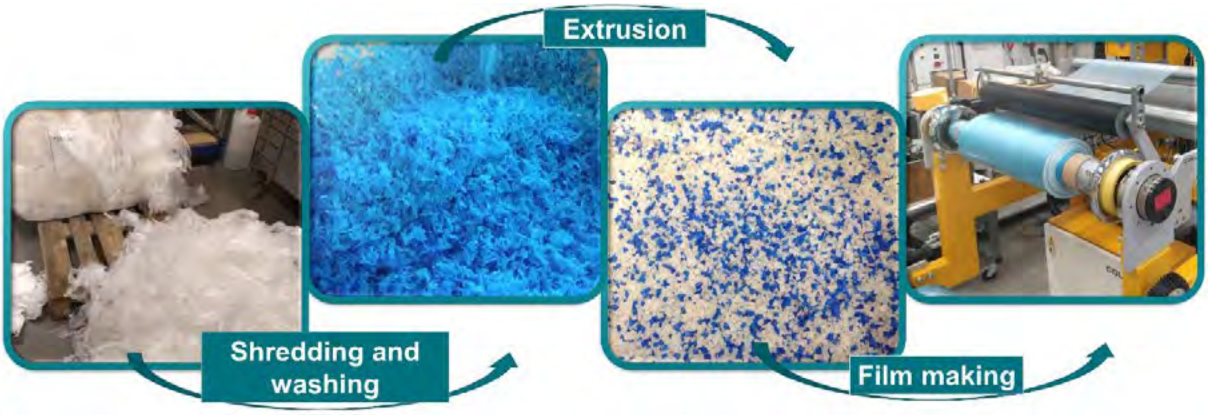

Fig. 1: Graphical illustration of recycling plastic waste into a shrink film

Introduction

Packaging materials constitute a substantial portion of the packaging industry. These materials help to extend the shelf-life of products, transport them safely, and make the products attractive to consumers. Multilayer films represent a category of packaging materials that can be engineered to exhibit specific properties through the combination of different polymers [1]. Common combinations in plastic multilayer films include polyethylene terephthalate (PET) and polyethylene or polypropylene, as well as polyethylene, ethylene vinyl alcohol copolymer, and polyamide. Such multilayer films have excellent gas barrier properties, combined with toughness and strength, thermal sealability, and printability, and are safe to use in contact with food while using fewer materials than single-material packaging.

Despite the numerous advantages of multilayer films in food packaging, their end-of-life management presents significant challenges. Combining different materials leads to problems with recycling and separation from other waste streams. Even if the multilayer films are separated from the rest of the waste, their composition is usually unknown and not easy to determine [2, 3].

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In this work, we will explore the possibility of recycling industrial plastic waste containing multilayer films and the application of recycled material as a shrink film in the packaging process. Four different packaging films were used: a single-layer film made from low-density polyethylene (LDPE), a single-layer film made from linear low-density polyethylene (LLDPE), and two multilayer films made from LDPE, polyamide 6 (PA 6), and ethylene vinyl alcohol copolymer (EVOH).

Materials and Waste Analysis

Plastic waste was collected at PrimAs Tiefkühlprodukte GmbH (Obernhofen, Austria). The annual production of approximately 88 tons of plastic waste was recorded at the Primas company. The plastic fraction was first separated based on color, as there were transparent films and blue films. The blue fraction was mostly in direct contact with food, whereas the transparent films were used as secondary or tertiary packaging and hence not in direct contact with food. Upon further analysis, two multilayer films from the blue fraction were chosen for recycling, along with two transparent single-layer films.

Combining the four films allowed us to test different ratios of polymers: LDPE, LLDPE, PA6, and EVOH. The main focus, however, was to keep the composition of the recycled material as close as possible to the actual waste make-up in the company.

In addition to waste, three compatibilizers were tested: acrylic acid grafted polyethylene (TPPE), 1,3-phenylene-bis-oxazoline, and 1,4-phenylene-bis-oxazoline, as well as their combinations.

Methods

The composition of the films was determined through the analysis of cross-sections using light microscopy and Raman spectroscopy. These two methods revealed the number of layers and the composition of each layer. Differential scanning calorimetry was used to confirm the results from Raman spectroscopy.

After film analysis, preparation for mechanical recycling was done in the following steps: shredding, washing, and drying. The films were cut into long strips, approximately 5 cm in width. The cut films were washed in a standard household washing machine using dishwasher detergent. After washing, all films were dried for at least 24 hours at 60 °C.

The initial mechanical recycling was done using a Brabender mixer (Type 350 E). Different ratios of films were mixed together with or without compatibilizers. Mixing was done at 230 °C with 80 rpm for 5 minutes. The mixed materials were pressed into films with thicknesses between 200 and 400 µm in a vacuum press.

The pressed materials were tested for their tensile strength, strain at break, and shrinkage. Based on these tests, two blends were chosen for upscaled recycling. This was done using an extruder ZSE 18HP 480 from Leistritz Extrusionstechnik GmbH. In the extruder, 50 kg of granules were prepared and used for film processing at Collin Lab & Pilot Solutions.

The outcome was two films with thicknesses of 14 and 20 µm, which were later tested in the industrial packaging line as shrink film.

Shrinkage was tested in an oven at 180 °C for 10, 15, 20, 30, and 40 seconds and compared with conventional shrink film used in the company. This test was designed to imitate the conditions of the packaging line.

Results

Three different approaches were followed during recycling: i) changing polymer ratio between PE-PA6-EVOH, ii) adding compatibilizers and iii) replacing part of LDPE by LLDPE. By combining the waste films, different polymer ratios in the blend were created. The EVOH content was kept at 5%, while the PE content was 80%, 70%, 60%, and 50%, with PA6 making up the rest (15%, 25%, 35%, and 45% respectively). Additionally, one blend with a composition based strictly on the waste make-up in the company was made. This blend contained 87% PE, 2% EVOH, and 11% PA6, which equals 45% of single-layer transparent films and 55% of multilayer blue films in the blend.

The blend based on the waste composition exhibited the highest strain at break, likely attributable to its higher PE content and lower EVOH content. The tensile strength of all blends was very similar, ranging between 13.9 and 15.8 MPa.

In the next step, different compatibilizers were evaluated. The compatibilization of polymers wasn't examined in this study, only the effects of different compatibilizers on mechanical properties (tensile strength and strain at break). The tensile strength wasn't significantly affected by compatibilizers and varied between 13.9 and 14.7 MPa. However, a significant influence on strain at break was observed. Using TPPE or 1,4-phenylene-bis-oxazoline individually led to a drop in strain at break. On the other hand, the addition of 3% 1,3-phenylene-bis-oxazoline increased the strain at break of the blend. Combinations of TPPE with both oxazolines were also tested. The combination of TPPE and 1,4-phenylene-bis-oxazoline showed a slight improvement in strain at break. The combination of TPPE with 1,3-phenylene-bis-oxazoline led to a decrease in strain at break.

The influence of different PE types on mechanical properties was examined in the last step. This was done by changing the ratio of the two transparent single-layer films. As the multilayer films had a high content of LDPE already (60% and 89%), there was always LDPE in the blend. However, one of the single-layer films was made of LLDPE, which enabled us to increase the amount of LLDPE. Three blends were tested: one with only LDPE single-layer film, one with only LLDPE single-layer film, and one blend where LDPE and LLDPE films were used in equal amounts. Partial replacement of LDPE single-layer film by LLDPE film led to a significant increase in strain at break. When the LDPE single-layer film was completely replaced by LLDPE, there was no significant additional increase. The blends containing LLDPE were chosen for upscaled recycling and further shrinkage tests.

Recycled films with thicknesses of 14 and 20 µm were tested for shrinkage alongside conventional shrink film. At 180 °C, the recycled film showed similar shrinkage to conventional film in a short period of time (10 and 15 seconds). All tested films had shrinkage up to 30%. The maximum shrinkage for the conventional shrink film was around 80%, whereas for the recycled films it was below 40%. However, the shrink film spends less than 10 seconds in the oven during packaging, and therefore the results were acceptable for the pilot test in the industry.

Conclusion

A complete recycling process was tested for multilayer films with the aim of producing shrink film. Three different approaches were investigated to develop a blend with properties suitable for shrink film: modifying the PE and PA6 ratio, incorporating compatibilizers, and partially substituting LDPE with LLDPE. The incorporation of LLDPE into the blend proved to be the best option. It improved the strain at break more than twice compared to the blend with only LDPE and didn't require any compatibilizers. This material was used to produce shrink film, which was later successfully tested in the industrial packaging line. This study demonstrates the feasibility of recycling multilayer films in-house, thereby reducing the demand for virgin materials in packaging applications. The recycled film was used as tertiary packaging and did not come into contact with food.

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Recycling of Wintersport Hardgoods: The Challenges of Circularity

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Abstract

The increasing popularity of skiing has led to a rise in discarded sports equipment, presenting significant environmental challenges due to the current practice of incinerating such items as bulky waste. In response, this study explores the potential for recycling winter sports hardgoods, such as skis, ski boots, ski poles, and helmets, as part of a circular economy initiative. The WINTRUST project, seeks to establish a comprehensive collection system in collaboration with local retailers and municipalities in the Pinzgau and Pongau regions of Salzburg, Austria. Initial efforts focus on separating valuable materials from discarded equipment, identifying both logistical and technological challenges. The separation process involves manual disassembly and innovative techniques, such as chemical de-binding and specialized shredding methods, to recover polymers and metals. However, the complex material composition, especially varying polymer types combined with steel and aluminum, poses significant hurdles for the recycling efforts. Preliminary trials in material processing indicate the feasibility of repurposing recycled materials for injection molding, though further refinement is required to enhance quality and efficiency. This project highlights the need for improved collection, separation, and processing strategies to reduce waste and support sustainable practices in the sports equipment industry.

Keywords: Winter sports equipment recycling, Circular economy, Mixed material separation, polymer processing of mixed material recyclates

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As the popularity of skiing continues to rise, so does the accumulation of used sports equipment, posing significant environmental challenges. According to the VSSÖ (Austrian Association of Sporting Goods Manufacturers and Retailers), around 1.8 million pairs of skis and ski boots, 2.3 million pairs of ski poles, and 1.4 million helmets have been sold in Austria between 2017 and 2022 [1]. Currently, used sports equipment is treated as bulky waste at the end of its life, meaning it is incinerated rather than recycled [2]. To improve this situation, there is a need to develop systems for the separation and processing of these materials, create markets for recycled products, and advanced processing technologies. In response to this issue, and in line with the EU Green Deal, France has introduced a levy on every product sold, and it is anticipated that other European countries will follow suit. Implementing these measures is essential for reducing waste and promoting a circular economy within the sporting goods industry.

1. Challenge: Collection

Every recycling process, starts at the end of life (EoL) of a product. To have a chance of recovering the valuable materials that wintersport hardgoods such as skies and bindings, ski boots, ski poles and helmets are made of, they have to be collected separately so that they do not end up in the bulky waste container. As a consequence, a new collection system has to be created. In the WINTRUST project the model region of Pinzgau and Pongau in the district of Salzburg, Austria, was chosen to try to establish this. For that reason, the retailers of sporting goods, Bründl Sports, Giga Sport and Intersport as well as a number of towns and villages in the model region form collection points, where it is possible for a private citizen to discard these wintersport hard goods. This collected waste will then be taken by the waste collection company ZEMKA and transported to the first separation step, that is conducted at the GW St. Pölten Integrative Betriebe GmbH.

This sounds straight forward, but in fact it is a very complicated and delicate matter when going into the details, as shown in Figure 1.

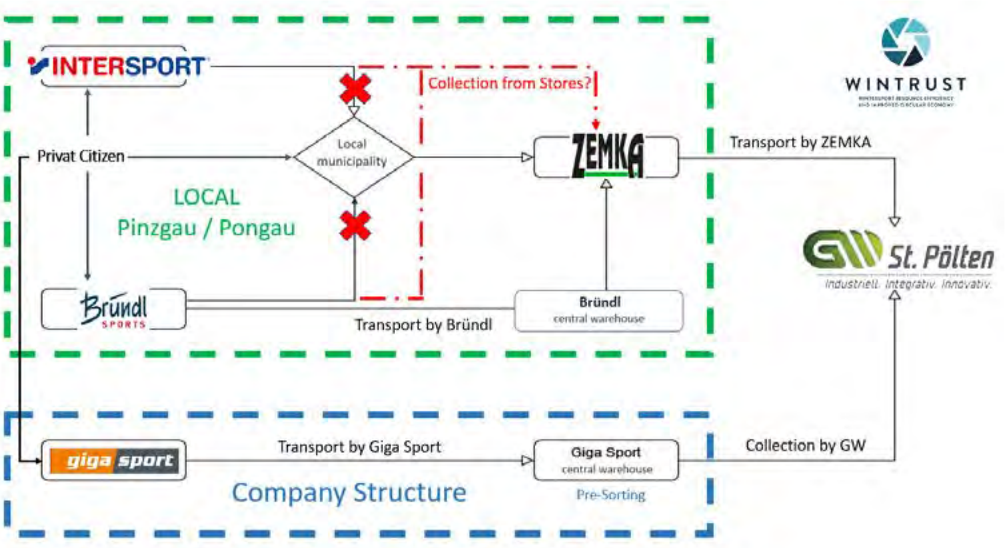

Fig. 1: Collection system of WINTRUST project, August 2024

For a company such as Giga Sport, it is easier to pick up the collected wintersport hardgoods, when delivering new merchandise to their stores and take it back to their central warehouse, as Giga Sport runs its own logistics department and delivery fleet. In contrast, a company like Intersport, that supplies their store via a contractor, this is not possible. The stores themselves also do not have transport vehicles to bring the collected sporting goods to ZEMKA. In addition to that, for many stores ZEMKA is not the closest option for discarding their bulky waste. Therefore, the effort for the stores and the ecological impact for longer transportation routes have to be taken into account. Bründl Sports partially has the option for picking up the EoL products but not for all stores. Therefore, currently the option for a separate collection transport from the stores three times a year, in the high season for the returning of EoL wintersport hardgoods by private citizens is explored under economic and ecologic aspects.

2. Challenge: Separation

To get an overview of the materials used currently and in the past to produce wintersport hardgoods, interviews were carried out with seven project partners, including five manufacturers of winter sports equipment—Atomic Austria GmbH, Blizzard Sport GmbH, Fischer Sports GmbH, HEAD Sport AG, and LEKI Lenhart GmbH—and two suppliers for these manufacturers, Hexcel Corporation and Isosport Verbundbauteile GmbH. The results summarized in Table 1 showing the diversity of involved materials is the first part of the challenge in separation. [3]

Table 1: Number of parts and materials used in the wintersport hardgoods selected as Use-Cases in the WINTRUST Project [3]

Use Case	Ski	Binding	Ski boots	Helmets	Ski poles
Parts	15	14	14	Up to 10	Up to 17
Polymer Type	16	9	9	6	6
Non-Polymer-Material	12	2	2	1	6
Main Polymer Types	ABS, Epoxy, PE, PU	ABS, PA, POM, TPU	TPU, PP/SEBS, PA11, PA12	ABS, EPS, PE, PU	EVA, PA, PP, TPU

Before taking on the challenge of separating the main polymer types from each other the non-polymer-materials especially the metal fraction must be separated from the polymer fraction. First separation trials at GW St. Pölten Integrative Betriebe GmbH revealed that it is possible and economically feasible to separate some parts by hand. That includes separating the binding from the ski, taking out the inner liner from ski boot and taking apart the ski poles and helmets almost entirely.

To separate the skies, a chemical procedure is investigated to debond the multilayer structure of this Use Case. In first tries this was successfully tested as shown in Figure 2, but needs optimization and upscaling trials.

FFig. 2: Ski layers after chemical de-bonding, 1: Lining, 2: Wood Core, 3: Epoxy, 4: Aluminum, 5a+b: Cover layers

In the seemingly clean separated helmets, where the GW St. Pölten Integrative Betriebe GmbH took out all rivets and buckles by hand, a large portion of metal content was found when shredding the helmet shells as shown in Figure 3. Currently an investigation about the origin of these metal parts is ongoing.

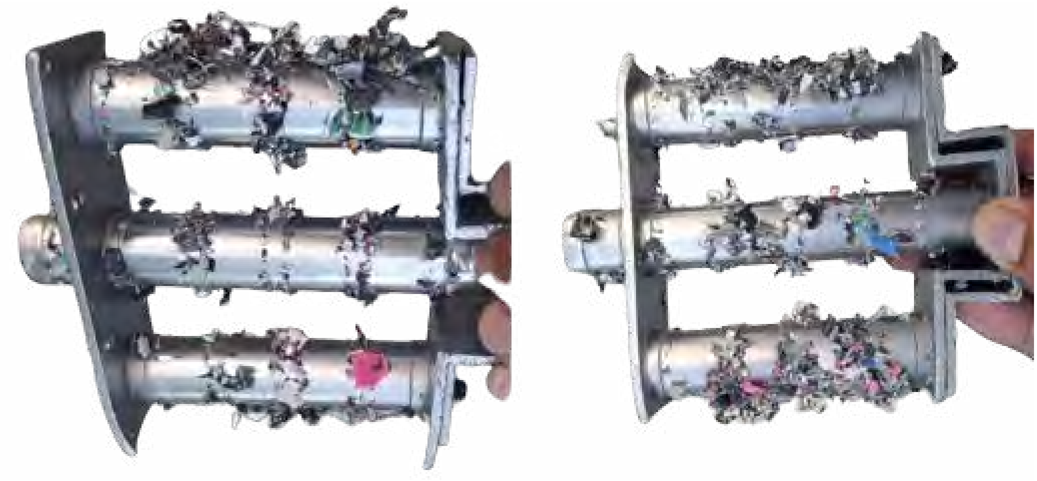

Fig. 3: Metal separator after shredding the shells of ski helmets, picture provided by Gabriel-Chemie GmbH

Ski bindings and boots pose the challenge of a high variety of materials including joined metal and polymer parts. In ski boots the number of used joining technologies is almost as high as the number of different materials. In random sampling checks joining techniques found were: riveting, screwing, adhesive bonding, polymer welding and snap-fitting not including any other joining technology which was used to keep the metal parts of the boots together. For future products, design for recycling will to be taken into account, reducing the number of materials and joining technologies.

Two routes of separation are currently explored. The first route is the route of best separation, whereby the ski boot shells should be separated as good as possible. In laboratory scale trials all metal parts can be taken out and the metal free shells can then be analyzed for their material, shredded and processed. First trials show that it is possible to recover 1.5 – 2 kg of shredded material from one pair of ski boots. The remaining, metal free polymer parts can be shredded so well that it is possible to directly use it for injection molding as shown in Figure 4. Nevertheless, a process like this is impossible to upscale economically as the effort of separation is extraordinarily high and needs to be done by hand.

Fig. 4: Ski boot shells made of TPU (1, 2, 4, 5) and PP/SEBS (3) and the recycled material of them after separating out all metal parts by hand

The second route is to crush the ski boot shells as received and separate the material as far as necessary, finally using a compatibilizer manufactured by the company partner Gabriel-Chemie GmbH to process the moderately well sorted fraction (at least swim/sink separation) into a usable material that then can be used again in the wintersport industry. Because of the high metal content, the shells cannot be shredded with a standard shredder typically used in polymer recycling. Currently options like cross-flow or wave shredders with following separation of ferrous (magnets) and non-ferrous (eddy currents separator) metals are explored. The main issue is, that the machinery used in these processes is scaled for very large quantities that cannot be provided by the project. Therefore, it is hard to find facilities willing to take on minor amounts for trials, which poses the current challenge in the project.

3. Challenge: Processing

Currently, the knowledge base of the extent of degradation of the polymers in the Use-Case wintersport hard goods is built up.

The first material available for injection molding was the material separated by hand as shown in Figure 4. Material analyses with ATR and DSC showed a large fraction of TPU (ski boots 1, 2, 4 and 5) and a smaller fraction of PP/SEBS (ski boot 3). The DSC results already showed different melting points for the TPU fractions covering a range of 215 °C – 230°C. First processing trials with the PP/SEBS fraction were made. It was possible to produce around 50 tensile test specimens as shown in figure 5 out of around 1.5 kg of shredded material.

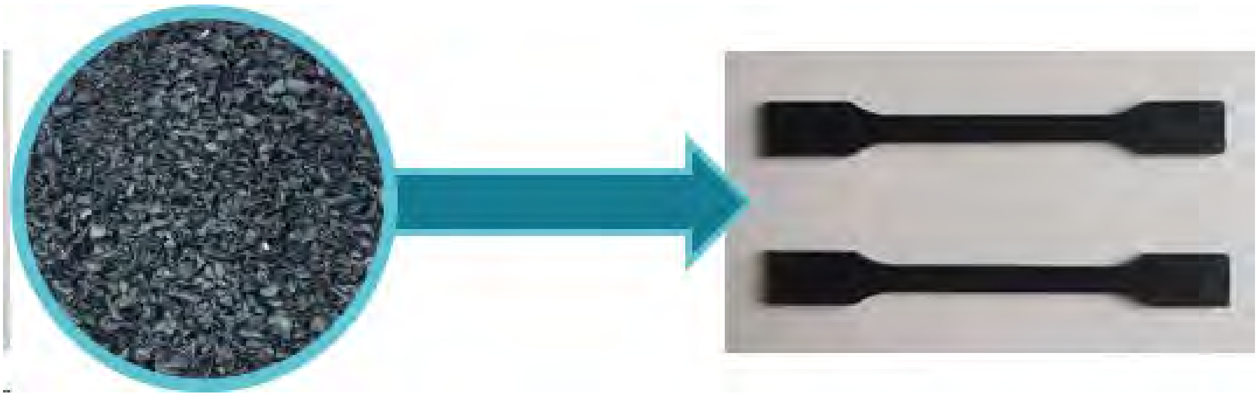

Fig. 5: Shredded PP/SEBS material (left) and the tensile test specimens (right) produced from it

The red TPU fraction, with a measured DSC melting point of 227 °C was not processable in first trials. The viscosity at a processing temperature of 230°C was more like molten wax than molten plastic. In addition to that, the melt was carrying a large amount of air as shown in Figure 6.

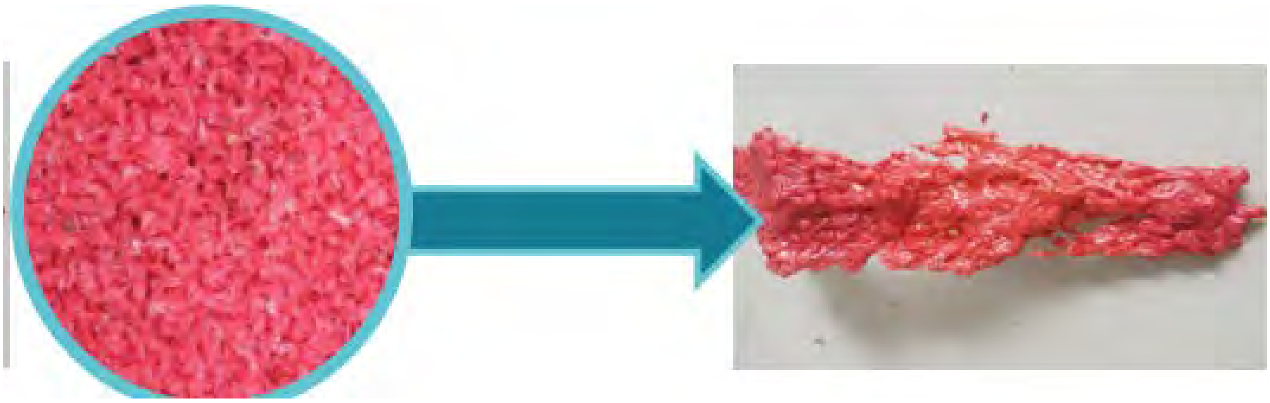

Fig. 6: Shredded TPU material (left) and the material running out from the nozzle of the injection molding machine after cooling down (right)

As the melting points of the different TPU fractions vary, the optimization of the processing condition is the key to be able to process this recycling material. The first step taken is a rudimentary incoming material test, to determine the range of melting temperatures without the need of expensive DSC or rheological testing. The setup consists of a heating plate, a temperature sensor and a camera system. The results of the first trial are shown in Figure 7. The first test was conducted with the material from the single material from manual separation shown in Figure 4 and a mixed TPU fraction provided by the project partner TCKT.

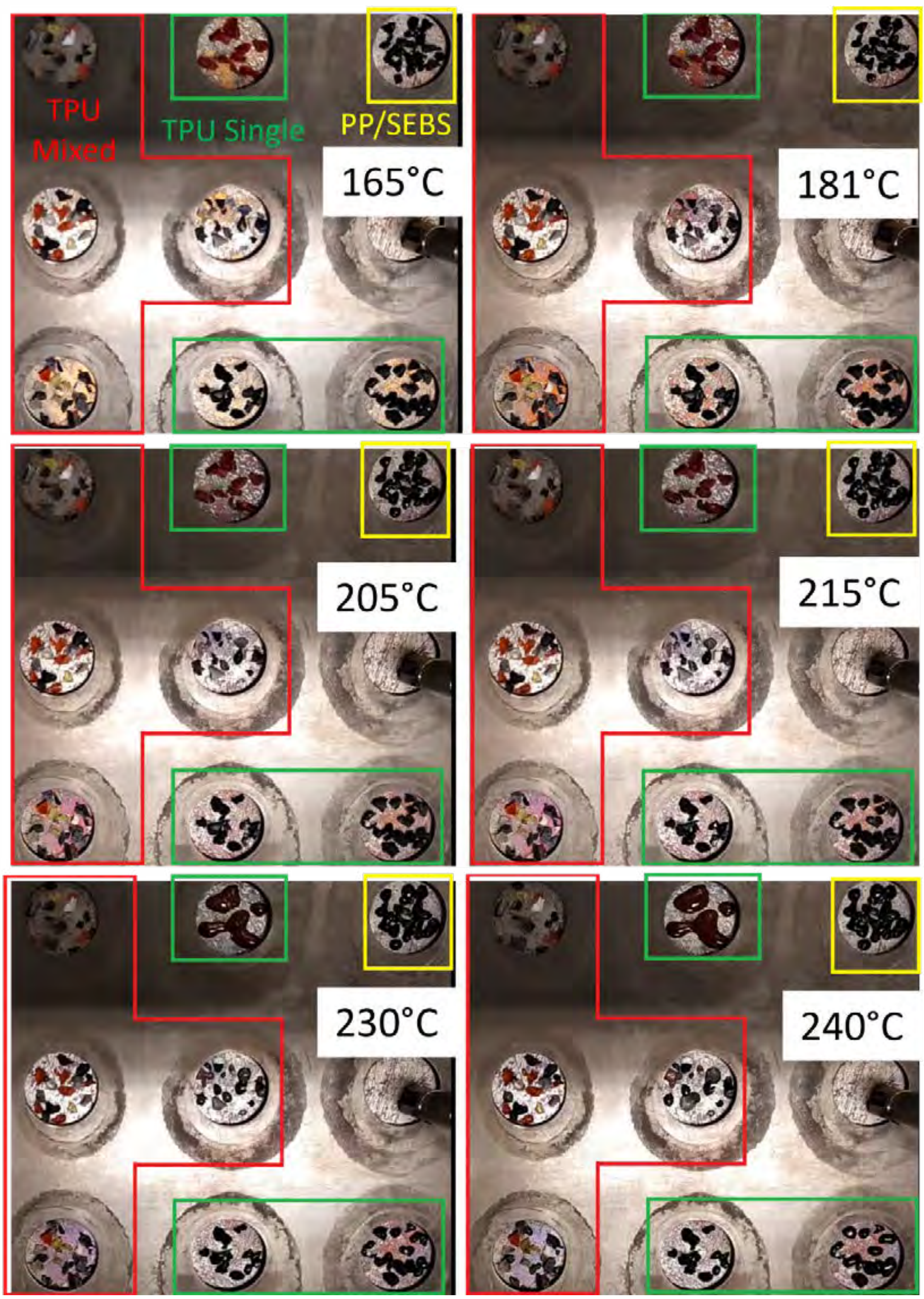

Fig. 7: Pictures taken from the video made for incoming material control at different temperatures. The red box includes samples of the mixed TPU fraction provided by TCKT. The single material fractions from the manual separation trials are in the green boxes (TPU) and the yellow box (PP/SEBS)

It is clearly visible that the form of the black particles in the yellow box containing the PP/ SEBS fraction changes shape at 181°C. With a sped-up video, the change is easier to detect then on a photo. At 205°C the first form changes in the upper green box, containing the red TPU fraction, that was also used in the injection molding trials is showing a change of form. In addition to that, also some particles in the mixed TPU fraction show a slight change in form. At 215°C the form changes become more pronounced and especially visible in the mixed TPU fraction. At 230°C all TPU fractions start to change their shape. However, not even at 240°C all particles were molten while others have already started to degrade. The pictures and video taken with the incoming material control are a prove of concept, but it needs optimization with regard to lighting and the camera system to improve the video and therefore the picture quality. For automated analyses the possibility of a motion detection AI program is explored for faster analysis of the melting ranges for a mixed material-particle fraction.

Summary and Conclusion

Effective recycling starts with collecting separately from regular bulky waste. The WINTRUST project aims to establish collection points for ski equipment in the model region Pinzgau/Pongau. Retailers such as Bründl Sports, Giga Sport and Intersport together with local municipalities are involved, but logistical challenges complicate the process.

Ski equipment contains multiple materials, including various polymers and metals, making recycling complex. Initial separation trials have shown that manually separating components is possible but labor-intensive and limited. Therefore, shredding technologies untypical for polymer recycling are taken into account as an option for the first separation step. Additionally, first experiments for chemical debonding of ski layers have been carried out successfully.

The final challenge is processing the separated materials into new products. The level of degradation in polymers varies significantly, affecting their recyclability. Initial trials have produced recycled materials that can be used for injection molding, but further refinement of processing conditions is required to optimize the quality and usability of recycled products. First incoming material control shows that the melting temperature of the TPU fraction from ski boots varies highly. Therefore, processing this a highly temperature sensitive material will pose one of the biggest upcoming challenges within the WINTRUST project.

Acknowledgement

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Enhanced mechanical recycling of PP

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Abstract

Currently, the use of recycled plastics is still limited due to quality issues. As a result, recyclates are typically used for less demanding applications or are only mixed in small quantities with virgin materials. Challenges in producing high-quality recyclates via mechanical recycling include degradation and contaminations. In addition, mixing different grades of the same polymer type also reduces recyclate quality [1–4].

Polypropylene (PP) is a versatile material and the preferred choice for a wide range of applications ranging from packaging to pipes [5]. PP is available in different types and grades to serve these diverse applications. The types, including homopolymers and copolymers, vary in their chemical structure. The grades further differ in molecular weight, molecular weight distribution, morphology and additives. During recycling, the mixing of different PP types and grades results in the loss of the tailor-made properties of the former grades. In particular, the low viscosity, i.e., high melt flow rate (MFR), and poorer mechanical properties of the resulting recyclate pose a challenge for its use in various applications [1,6].

The aim of this work is to investigate the feasibility of separating different PP types and grades using near-infrared (NIR) spectroscopy to improve the quality of PP recyclates. By using a laboratory NIR spectrometer and an industrial NIR hyperspectral camera, the feasibility of sorting PP samples by type (homopolymer, block and random copolymers) and by processing method (injection molding, extrusion blow molding, thermoforming) was investigated. Multivariate data analysis and machine learning algorithms were used to evaluate the separation capability. Both the separation of PP types and the separation into low and high MFR grades showed promising results. These advancements would help to expand the application range of PP recyclates, thereby contributing to a more sustainable plastic economy by reducing the reliance on virgin materials and increasing the use of recycled materials in high-quality applications.

Acknowledgement

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Wet mechanical processing of post- consumer plastics

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Abstract

This article describes the development of a wet mechanical separation process for post-consumer plastics. It starts with discussing the global polymer production as well as the change in post-consumer plastics recycling over the last 20 years and the challenges lying ahead. It then presents the combination of chemical recycling and wet mechanical processing as a viable way of overcoming these challenges. The article concludes with test results from a wet mechanical lab-scale plant using a centrifugal force separator to recover products from post-consumer plastics suitable for chemical or mechanical recycling.

Introduction

The report “Plastics Europe 2022” [1] states that 4–6% of the global petroleum production was processed into a wide range of polymer products, which amounted to 352 Mt in 2021. Additionally, about 32 Mt were produced using post-consumer plastics and 6 Mt using bio-based plastics as raw material. So, in 2021 about 90% of the global polymer production was still fossil-based. The global demand for polymer products can be classified according to their chemical polymer structure or usage, as can be seen in Table 1 and Table 2.

Table 1: Global polymer production in 2021 by type [1]

Polymer type	**Fraction**	**Exemplary application**
Polyethylene (PE)	26.9%	Bags, containers, toys, houseware
Others	23.9%	-
Polypropylene (PP)	19.3%	Food packaging, automotive, pipes
Polyvinylchloride (PVC)	12.9%	Cable insulation, pipes, coverings
Polyethylene terephthalate (PET)	6.2%	Bottles for drinks and other liquids
Polyurethanes (PUR)	5.5%	Insulation foams, pillows, mattresses
Polystyrene (PS)	5.3%	Packaging, insulations, electronics

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Table 2: Global polymer production in 2021 by application [1]

Application	Fraction	Expected period of Application
Packaging	44%	Days to weeks
Others (furniture, medical, etc.)	12%	Months to years
Building and construction	18%	Years to decades
Automotive	8%	Years
Electrical and electronics	7%	Years
Household, leisure and sport, and	7%	Months to years
Agriculture, farming and gardening	4%	Weeks to months

As can be seen Polyethylene, Polypropylene and Polystyrene (the so-called Polyolefins) amount to approximately 50% of the global polymer production. Since their main application is packaging (foils, containers, bottles etc.) they also have a brief period of application and therefore make up a significant share of post-consumer plastics.

Recycling of post-consumer plastics in Europe

Of the global of polymer production of 390 Mt, 15% or 58.5 Mt were related to Europe (In [1] Europe is defined as the 27 member states of the European Union as well as Norway, Great Britain, and Switzerland). About 29,5 Mt of post-consumer plastics were collected in Europe in 2020 with nearly equal shares via mixed (51%) and separated (49%) waste collection.
For the treatment of post-consumer plastics 3 options are in use:

- Landfilling; disposal of post-consumer plastics in a landfill
- Energy recovery; usage of post-consumer plastics as solid recovered fuels
- Mechanical recycling; usage of post-consumer plastics as feedstock for new polymer products

As shown in Table 3 the share of landfilling of post-consumer plastics has been declining in Europe significantly. Only in countries with waste management systems that are still in development or with challenging geography (e.g. many small islands, remote areas), substantial shares of post-consumer plastics are still landfilled. The share of energy recovery and mechanical recycling has been increasing significantly because of better treatment, collection and raised public awareness. For Austria a similar conclusion can be drawn as shown in Table 4, although here the low share of landfilling (<1%) is compensated rather with a high share of energy recovery (69%) than by mechanical recycling (31%) in 2020.

Table 3: Treatment options of plastic waste fractions in Europe from 2008 to 2020 [1]

Treatment Option	Share of post-consumer plastics in …			
	2008	2012	2016	2020
Mechanical Recycling	21%	26%	31%	35%
Energy Recovery	30%	36%	42%	42%
Landfilling	49%	38%	27%	23%

Table 4: Treatment options of plastic waste fractions in Austria from 2008 to 2020 [1]

Treatment Option	**Share of post-consumer plastics in …**			
	2008	**2012**	**2016**	**2020**
Mechanical Recycling	28%	24%	27%	31%
Energy Recovery	65%	75%	72%	69%
Landfilling	7%	1%	1%	<1%

The tables above indicate that there seems to be a limit, especially regarding mechanical recycling. Several reasons for this have been discussed in publications like “Mechanical and chemical recycling of solid waste” by K. Ragaert et al. [2]. According to it significant properties like homogeneity, contamination, and composition are limiting the usage in mechanical recycling. As figure 1 shows, small shares of contamination with other polymers can significantly decrease the properties of resulting polymer products and cause problems in processing because of their different temperature characteristics (see Figure 2).

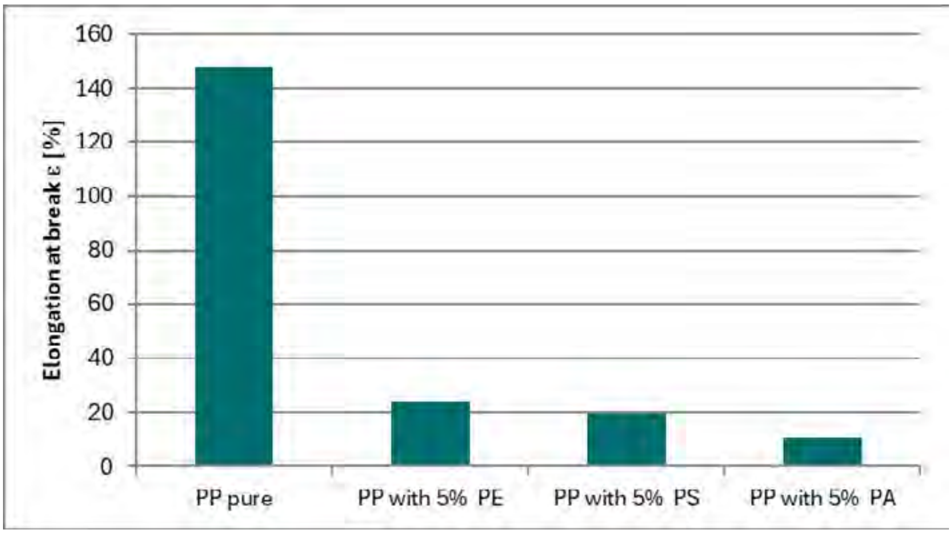

Fig. 1: Change of elongation at break of polypropylene with impurities [3]

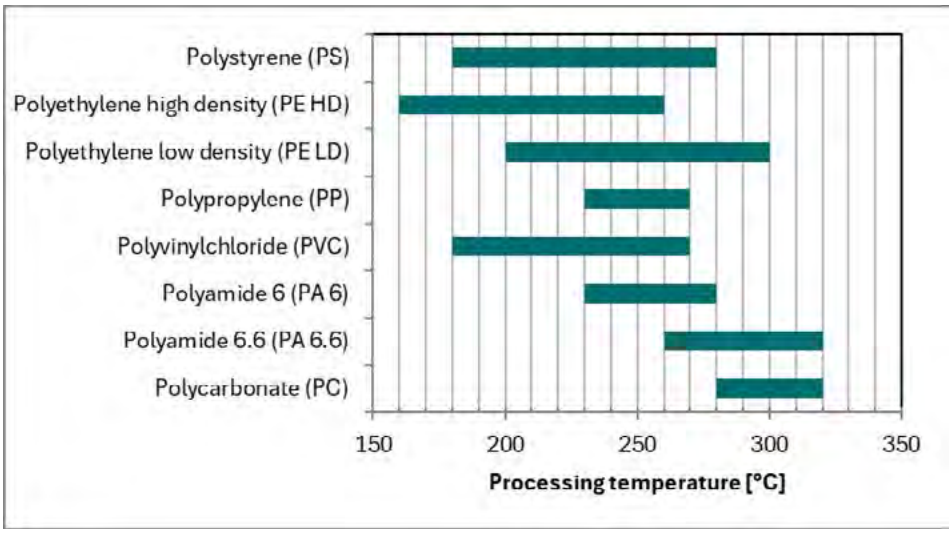

Fig. 2: Processing temperature of different polymer types [3]

Since further treatment can be expensive and some polymer types having a calorific value like commonly used fuels (as can be seen in Table 5), energy recovery is used as an economically viable alternative.

Table 5: Calorific value of different fuels at 25°C [4]

Fuel	Calorific Value	Fuel	Calorific Value
Polyethylene terephthalate (PET)	4,2 MJ/kg	Polystyrene (PS)	40,2 MJ/kg
Wood	18,0 MJ/kg	Petroleum	42,8 MJ/kg
Polyvinylchloride (PVC)	18,0 MJ/kg	Polypropylene (PP)	44,0 MJ/kg
Coal	25,0 – 35,0 MJ/kg	Polyethylene (PE)	46,1 MJ/kg
Polyamide (PA)	31,0 MJ/kg	Propane	46,3 MJ/kg
Natural gas	32,0 – 45,0 MJ/kg	Methan	50,0 MJ/kg

Chemical recycling

To stimulate mechanical recycling of post-consumer plastics the European Union proposed a directive for a circular economy. According to this directive, the proportion of post-consumer plastics recycling shall be increased to 55% by 2025 [5]. To achieve this goal, another technical approach, namely chemical recycling, could be a part of the solution. Therefore, chemical recycling, also called feedstock recycling, has been a topic of research for decades.

In chemical recycling polymer chains are broken into a mixture of shorter chains or other chemical building blocks via thermal cracking or pyrolysis. These molecules can then be purified from additives or contaminants and synthesized into new polymers. Chemically recycled polymers would then be identical in quality to virgin polymers. Consequently, a plastic material cycle could be established which could meet the challenges like material aging and accumulation of aggregates.

Decades of research and a multiplicity of failures indicate that chemical recycling of post-consumer plastics is not a technological but an economic challenge. As Tukker, A. points out in „Plastics Waste: Feedstock Recycling, Chemical Recycling and Incineration“ [6] the main reason for the failure of chemical recycling process was a lack of sufficient amount of feedstock at affordable prices. Since feedstock for mechanical recycling, which would be ideal for chemical recycling, is too expensive, chemical recycling must focus on post-consumer plastics currently used in energy recovery.

A promising option to recycle more mixed post-consumer plastics chemically is the thermo-chemical conversion process developed by OMV. The hydrocarbon intermediates obtained by this process can easily be treated by a state-of-the-art refinery according to their chemical and physical properties and then be used in various parts of the refinery. For this process OMV has comparatively low requirements as can be seen in Table 6.

Table 6: Feedstock requirements for thermo-chemical conversion [7]

Parameter	Requirement
Particle size	<30–40 mm
Bulk density	50–100 kg/m^3
Calorific vale	>30 MJ/kg
Polyolefin share	>90 wt%
Impurity share	<10 wt%
Moisture	<20 wt%
Halogen share	<2 wt%

Processing of post-consumer plastics

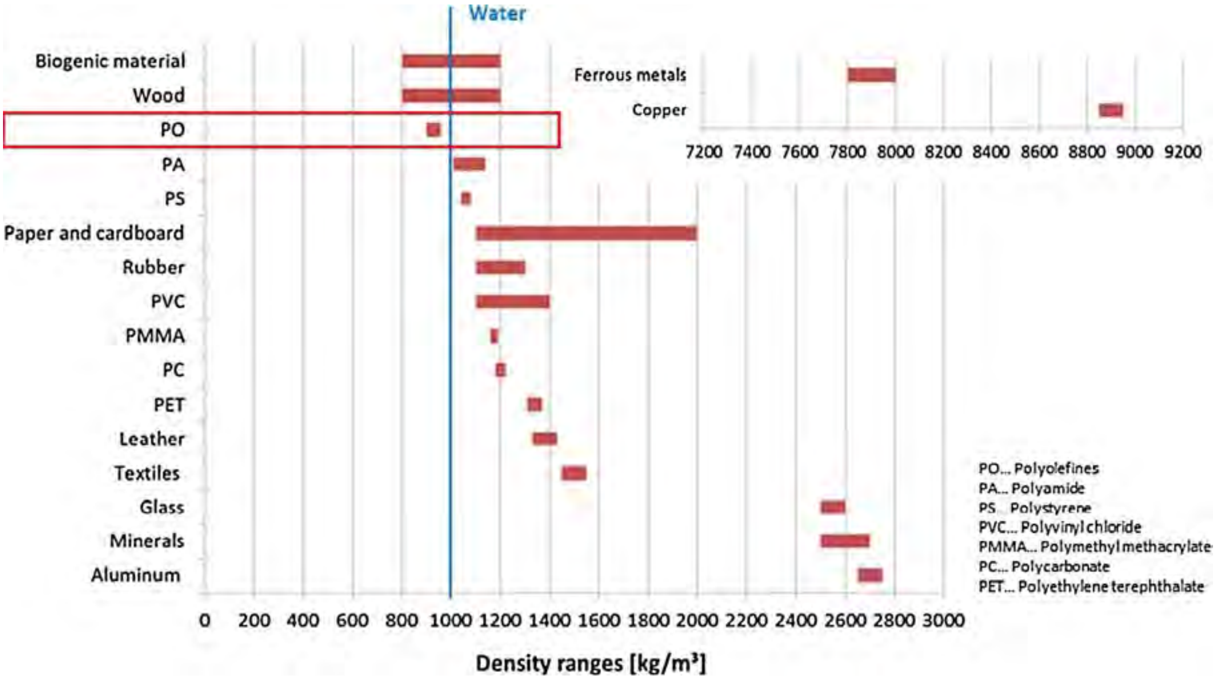

Fig. 3: Density ranges of common components of mixed waste fractions and their respective product of the separation process [8]

To meet the feedstock requirements for thermo-chemical conversion the post-consumer plastics need to be treated. Since polyolefins have a density below 1 g/cm^3 in contrast to most of the other polymers and common impurities – as can be seen in Figure 3 – and the ability of the thermo-chemical conversion of handling a moisture of up to 20%, density separation using water could be a promising as treatment option.

Four types of density separators can be taken into consideration for this treatment step:

- Sink-float separators (SFS)
- Heavy media cyclones (HMC)
- Centrifugal force separator (CFS)
- Centrifuges (CEN)

These four separators were compared by M. Bauer [9] in Table 7 regarding acceleration, throughput, space requirement, adaptability for varying feedstock, investment costs and maintenance.

Table 7: Comparison of sink-float separator (SFS), centrifuge (Cent.), heavy media cyclone (HMC) and centrifugal force separator (CFS) [9]

	SFS*	**HMC***	**CFS***	**CEN***
Acceleration	1 G	100 G	15 G	1000 G
Throughput	Low	High	Mid	High
Space requirement	High	Low	Low	Low
Adaptability	Good	Poor	Good	Poor
Investment costs	Low	Mid	Low	High
Maintenance	Low	Mid	Low	High

M. Bauer concluded that a centrifugal force separator according to the LarCoDeMS model (see Figure 4) was the most suitable apparatus due to its decent throughput via induced centrifugal forces as well as low costs and good adaptability.

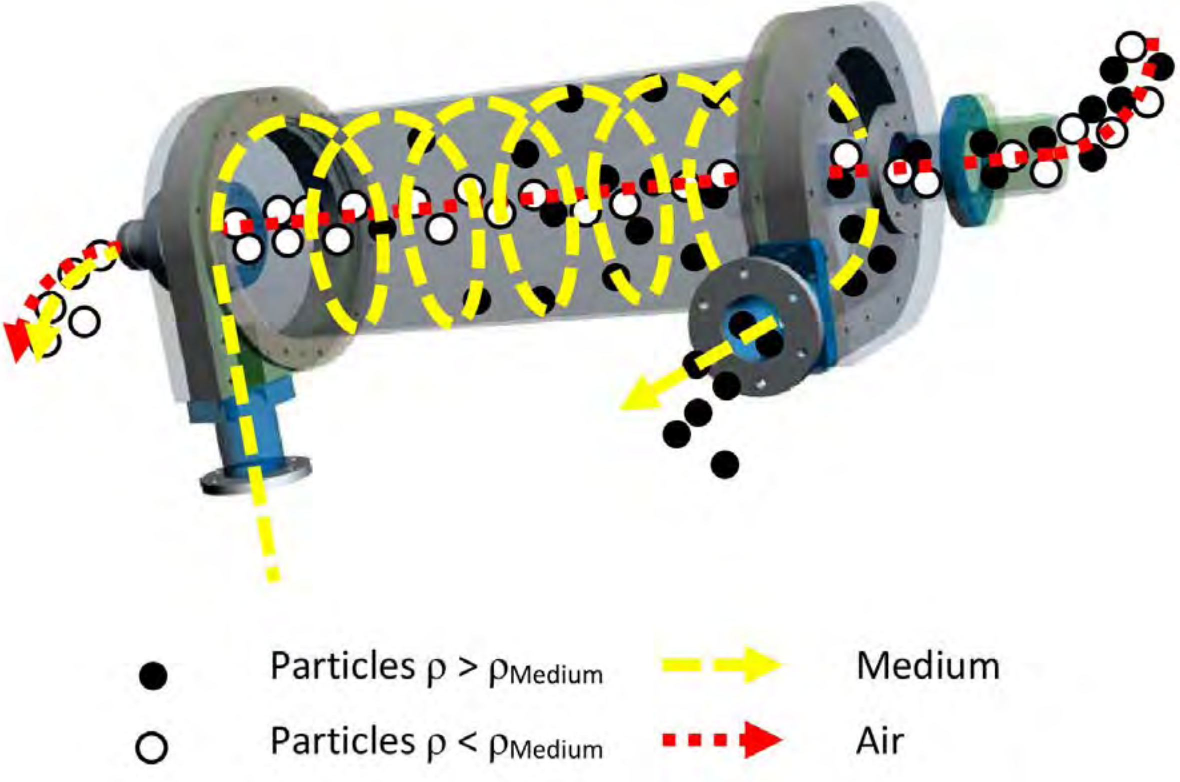

Fig. 4: Function principle of the centrifugal force separator [10]

The centrifugal force separator consists of an inclined cylinder with 4 tube-guided streams in and out of the separator. The feed material is separated by sink-/float-separation in a centrifugal field thus having a higher throughput than a sink-/float tank only using gravity. These centrifugal forces are induced by the separation medium, which is pumped into the separator tangentially at the lower end and thus builds up a medium vortex with an air core. The feed material enters the separator axial from the upper central tube directly into the air core and is dispersed within the separation medium. Particles with a higher density than the separation medium are dragged outwards to the cylinder and exit the apparatus as heavy fraction at the upper tangential outlet together with about two thirds of the separation medium. Particles with a lower density than the separation medium float to the air core and leave the apparatus as light fraction at the lower central outlet together with one third of the separation medium due to the inclination of the apparatus.

Test results

For testing purposes, a lab-scale plant with a centrifugal force separator was built and operated. The centrifugal force separator has a length of 1.250 mm, a diameter of 250 mm and is operated at an inclination of 30°. It can process up to 1 m³/h of feed material using about 25 m³/h of separation medium which is circulated within the plant.

From the multitude of tests conducted over the last years three feed materials of industrial origin with different shares of polyolefin shall be discussed here. The three feed materials are depicted in Figure 5. Their polyolefin share and particle size can be seen in Table 8.

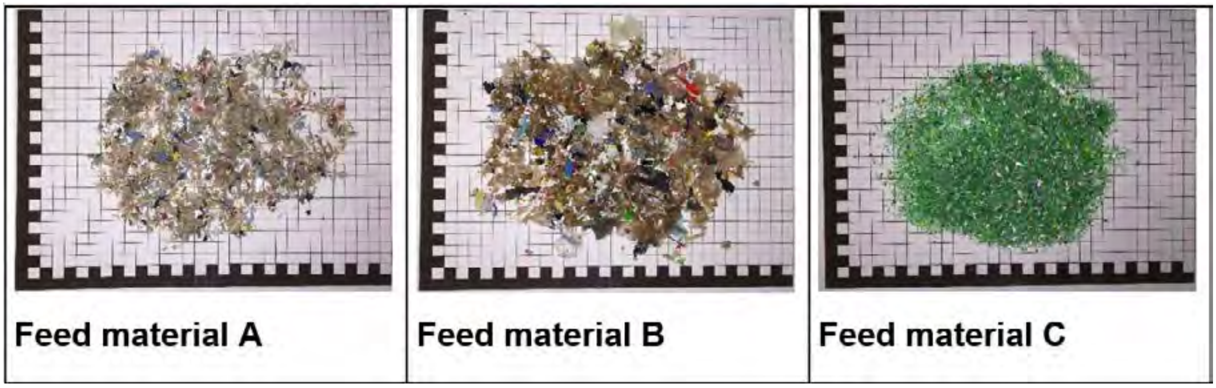

Fig. 5: Used feed materials [11]

Table 8: Particle size and polyolefin share of the used feed materials [11]

	Particle size	**Polyolefin share**
Feed material A	< 10 mm	91,1 wt%
Feed material B	< 20 mm	51,5 wt%
Feed material C	< 2 mm	3,8 wt%

As can be seen in Table 9 feed material A could be further concentrated from a polyolefin share of 91,1 to 96,3% in the light fraction. This further purification of feed material A would perhaps not be necessary in an industrial setting, since the input could already be sufficient for chemical recycling. But it can act as a safeguard for potential variations in the quality of the feed material.

Table 9: Test results of feed material A with one separation stage [11]

Feed material A	**Input**	**Light fraction**	**Heavy fraction**
Polyolefin share (wt%)	91,1	96,3	0,4
Mass share (wt%)	100,0	94,6	5,4
Polyolefin recovery (%)	100,0	> 99,9	< 0,1

Regarding feed material B two separation stages were needed to reach the required share of polyolefins in the light fraction as can be seen in Table 10. Since it is common to use multiple separation stages in post-consumer plastics recycling, this should not pose a problem. The loss of about 9% of polyolefins into the heavy fraction could be reduced by better adjusting the operation parameters of the separator or with additional pretreatment of the feed material.

Table 10: Test results of feed material B with two separation stage

Feed material A	**Input**	**Light fraction**	**Heavy fraction**
Polyolefin share (wt%)	51,5	94,6	8,9
Mass share (wt%)	100,0	49,7	50,3
Polyolefin recovery (%)	100,0	91,3	8,7

Feed material C is not suitable for chemical recycling since the polyolefin share is too low. However, since – as Table 11 shows - the share of non-polyolefins (in this case polyethylene terephthalate) in the heavy fraction is above 99%, this product could be used in mechanical recycling.

Table 11: Test results of feed material C with one separation stage [11]

Feed material C	**Input**	**Light fraction**	**Heavy fraction**
Non-Polyolefin share (wt%)	96,2	51,0	>99,9
Mass share (wt%)	100,0	7,7	92,3
Non-Polyolefin recovery (%)	100,0	4,1	95,9

Conclusions

Chemical recycling of polyolefin-rich materials can open a new path for recycling post-consumer plastics and thus be a part of the solution to achieving a material cycle for polymer products.

Wet mechanical processing via a centrifugal force separator can be used to recover polyolefin-rich fraction of over 90 wt% from post-consumer plastics using water as separation medium.

Another promising usage of this separation process is the recovery of heavy fraction with a share of over 99% of heavy plastics like polyethylene terephthalate, which could be suitable for mechanical recycling.

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Repair solutions for PV modules with damaged polymer backsheets

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Abstract

Although the cost of PV modules has reached a low level, the replacement of not functioning photovoltaic (PV) modules is often challenging due to different designs [1] and sizes and also the questions of recycling. Alternatively, the repair of modules offers the possibility of extending the service life of the PV modules and maintaining a PV system for longer.

However, the repair of early damage in particular, but also of faults after a long period of operation, can be economically and ecological advantageous. Damage to the backsheet, which is one of the most common causes of module failure alongside glass breakage and cell degradation [2], can be reason for further issues like corrosion of the metal parts. The polyamid-based backsheets already showed a high repair potential [3-4] in a previous project.

Here, the project „ReNewPV“ will the introduced. The main objective of the project is to develop an environmentally friendly coating solution for the repair of backsheets to extend the service life of PV modules. The focus is on the repairing of various backsheets within different material classes including current used fluorine-containing ones.

The procedure for achieving the objectives is to survey the repair requirements of the PV installations and identify the production and transportation damage (modules with damaged backsheets of real aged modules and scrap modules), as well as the analytical methodology for determining the material type and composition of the backsheets. Based on this, a raw material screening is carried out in a further step for the development of the repair solutions, based on the requirements of the application and the performance criteria of the coating.
In the material-side development of the repair coatings, the focus is on material compatibility, environmental compatibility (solvent-reduced and halogen-free), adhesion and functionality. This involves characterizing the thermal, mechanical and surface properties of the coatings on the one hand and the weathered backsheet surfaces on the other. After determining the appropriate application method for the newly developed coating solutions, accelerated ageing tests are carried out.

First results will be shown and challenges in development and characterization discussed.

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Sustainable polymers in coatings industry

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Abstract

In recent years, industrial resins and coatings development trends have been significantly influenced by the escalating awareness of sustainability, evolving legislation, and customer expectations.

Our current (industrial) research [1-4] is focused on exploring potential substitutes for fossil-based building blocks for polymer (resin) synthesis to re-shift back to sustainable coatings and other applications. Still, these novel systems must not only have lower environmental impact but also need to meet all visual, protective, and other functional properties.

Bio-based carbon validation can be achieved through [1-4] C or bio-mass-balance (BMB) certification. Simultaneously, diverse alternative bio-substances are under investigation within various coating systems, with considerations for both, performance and cost-effectiveness.
The principal objective of increasing bio-based carbon is the first and most important step. However, accurate Life Cycle Assessment (LCA) is needed to objectively claim sustainable resins and coatings.

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Specialist lectures

SESSION B:

“POLYMERS FOR ENERGY TRANSFORMATION, STORAGE AND TRANSPORTATION”

Underground Sun Storage 2030 / EUH2STARS – 100% hydrogen storage in porous reservoirs

M. Greiml

RAG Austria AG, A-Wien

Abstract

In the lighthouse projects „Underground Sun Storage 2030“ (USS 2030), as well as the EU funded project EUH2STARS, the safe, seasonal and large-scale storage of renewable energy in the form of hydrogen in underground gas reservoirs is demonstrated. In this research project, the only one of its kind in the world, renewable electricity is converted into green hydrogen by means of electrolysis and stored in a in a depleted natural gas reservoir. Starting from the achieved technology readiness level six in USS 2030, EUH2STARS, as a follow-up project, aims to demonstrate competitive, complete and qualified underground hydrogen storage in depleted porous natural gas reservoirs at technology readiness level eight, thus towards market readiness, by the end of the decade.

Introduction – USS 2030

In order to be able to achieve the climate targets and a significant reduction in CO2, actions are needed in the entire energy sector. In addition, affordability and security of supply must be maintained. Without gaseous energy carriers and the associated storage capacities, the energy transition is not possible. Modelling of the future overall energy system shows that in Central Europe there will be a large surplus of renewable energy in the summer months due to the expansion of renewable electricity generation. On the other hand, there will be a massive power shortfall during the winter months due to the lower solar radiation and the low water flow on the one hand and the significantly higher energy demand on the other hand. In Austria, we therefore see an increased divergence between electricity supply and demand, both selectively and seasonally. The transmission system operator APG assumes a seasonal shift requirement of 10 TWh/a (terawatt hours per year) for 2030.

It can be assumed that this power shortfall cannot always be easily covered by imports, as Austria‘s neighbouring countries are facing similar challenges. Energy must therefore be stored in large quantities (on the scale of several TWh) in summer so that sufficient green energy is available for electricity, heat and mobility in winter. Storable gaseous energy carriers, such as hydrogen, are an outstandingly suitable technology for covering this annual storage demand. For a rapid and realistic conversion to a climate-neutral energy supply, it is necessary to convert surplus solar and wind power into gaseous energy carriers such as hydrogen that can be stored in large volumes and seasonally, as shown in Fig. 1.

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Information taken from USS 2030 and EUH2STARS Folder

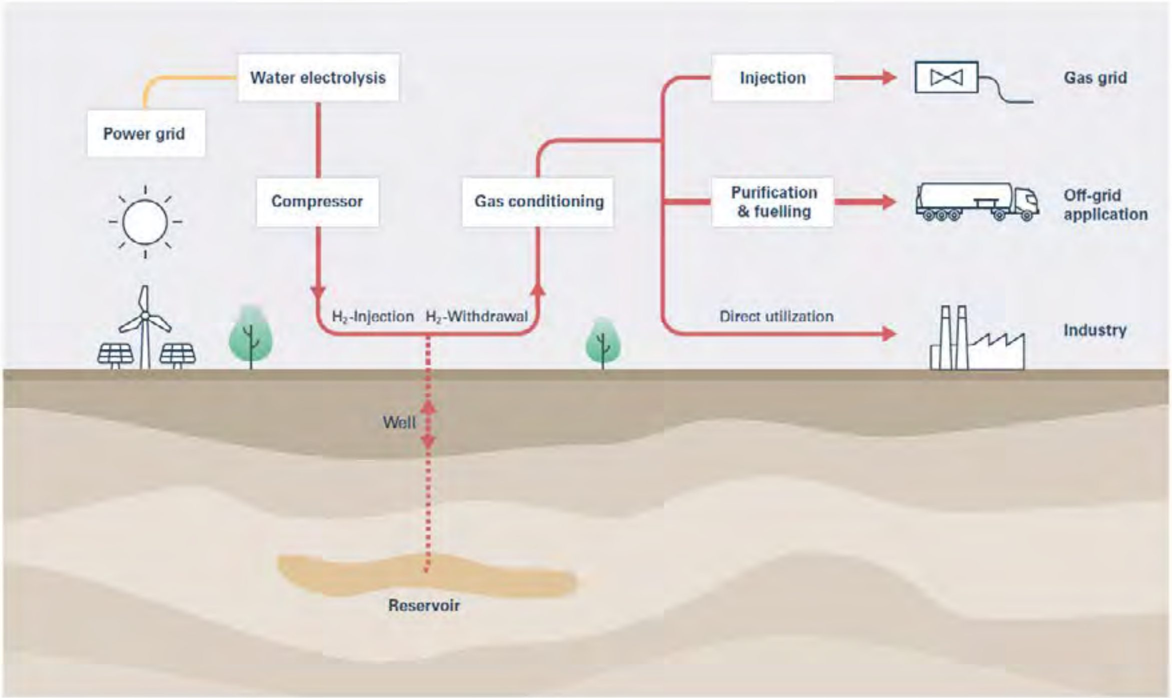

Fig. 1: Schematic representation of the projects USS 2030 and EUH2Stars

Sun and Wind – using surplus energy for gas

Intermittent renewable electricity output is not the only problem. Something will also have to be done with all the surplus electrical power generated by giant wind and solar parks at times when demand is low. This surplus, mainly accruing in summer, needs to be stored so that it can be made available during peak periods, mainly accruing in winter (compare Fig. 2). If 100% of the electricity generated in Austria should come from renewable sources, storage facilities with a total capacity of more than 100 times greater than the potential offered by pumped storage is required [1]. The combined capacity of pumped storage plants and battery storage used to date is far from sufficient. Besides power generation, hydrogen can also be used for heating, in vehicles and as a raw material. The gas transportation and storage infrastructure in place already meets all the requirements, to be used in the future as a storage system for green energy.

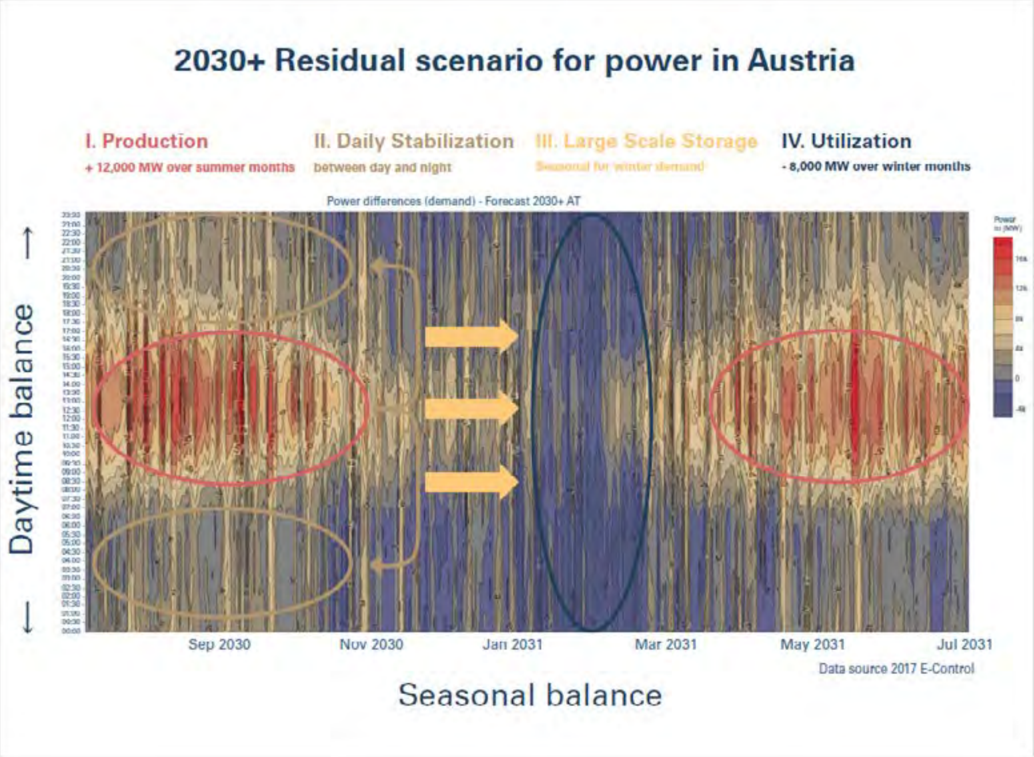

Fig. 2: Comparison of production and utilization of energy over the seasons of a year

Challenges regarding purity and diverse utilization paths

An essential part of the utilization paths consists of the processing or purification of the gas mixture that is withdrawn from the reservoir. The project's goal is to find out to what degree purification is necessary, throughout several seasonal cycles, to meet different quality criteria (e.g. grade A or grade D).

Hydrogen can be used in different ways depending on its purity (see Fig. 3). In the use of hydrogen in fuel cells or in the production of semiconductors, a particularly high purity is required. In industrial processes for heat or other applications, however, the degree of purity required is relatively low. In the chemical industry hydrogen is used, for example for the production of ammonia and methanol. Both chemicals are the starting basis for fertilizers, acetic acid and a variety of other substances. The steel industry is dominated by coal and coke as reducing agents in the production of iron. In direct reduction plants natural gas is used to produce sponge iron, which is melted into steel in electric arc furnaces. In the long term, green hydrogen can replace fossil reducing agents and contribute quantitatively to decarbonization.

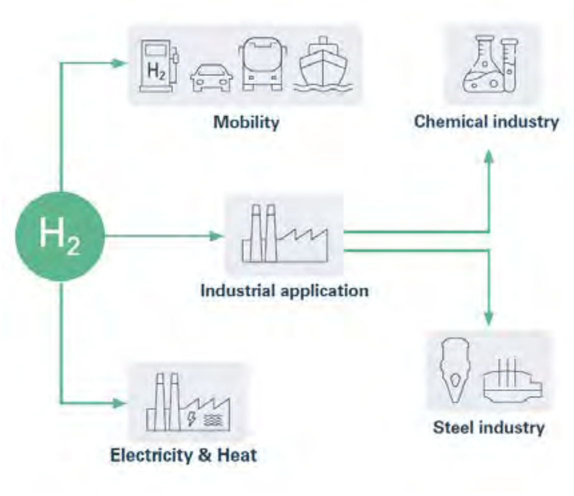

Fig. 3: Various utilization paths of stored hydrogen

EUH2STARS

EUH2STARS is an ambitious, industry-driven flagship project to demonstrate competitive, complete and qualified underground hydrogen storage (UHS) in depleted porous natural gas reservoirs at technology readiness level (TRL) 8 by the end of the decade.

The already operational UHS pilot facility, the Underground Sun Storage 2030, is being contributed by RAG Austria AG to the EUH2STARS project. Complemented with vast project experiences on UHS from consortium partner's research activities, EUH2STARS aims to deliver following key-results throughout the project:

- Demonstration of the storage of pure hydrogen in depleted, porous natural gas reservoirs by operating four seasonal storage cycles at RAG's demonstrator and two storage cycles at HGS's replicator site.
- Development of a beyond state-of-art hydrogen purification system to separate hydrogen from impurities (mainly natural gas) in order to achieve standardized hydrogen purification levels (e.g. hydrogen grade A or better).
- Achievement of a relevant green hydrogen certification for the demonstrator's power to hydrogen electrolysis and engage actively in green hydrogen certificate trading.
- Provision of guidelines to successfully manage all environmental, safety, legal and (future) regulatory, societal and market-related aspects to ensure a successful implementation of UHS facilities in Europe.
- Execution of an active stakeholder engagement strategy including an external expert advisory board to consider third parties‘ opinions and maximize public acceptance, transparency, visibility and exploitation of the project results.
- Set-up of a generic framework on the topic of HSEQ (health, safety, environment and quality) to ensure UHS at an ALARP (as low as reasonably practicable) risk level.
- Presentation of transformation pathways to replicate demonstrator findings in full-scale commercial settings at existing underground natural gas storage facilities and new to be developed UHS sites in depleted natural gas reservoirs in Europe.
- Provision of best practice examples on how to integrate UHS facilities into regional, national and European energy infrastructure and markets.

Acknowledgement

The lighthouse project “Underground Sun Storage 2030“ (USS 2030) is funded within the framework of the FTI initiative “Vorzeigeregion Energie“ of the Climate and Energy Fund, endowed with funds from the Ministry of Climate Protection (BMK) under the leadership of RAG Austria AG together with the project partners – Axiom Angewandte Prozesstechnik GmbH, Energie AG, Energy Institute at JKU Linz, EVN AG, HyCentA Research GmbH, K1-MET GmbH, Vienna University of Technology, University of Natural Resources and Life Sciences, Verbund AG, WIVA P&G and voestalpine Stahl GmbH.

The project EUH2STARS is supported by the Clean Hydrogen Partnership after successfully applying for the HORIZON-JTI-CLEANH2-2023-02-1 – Large-Scale Demonstration of Underground Hydrogen Storage funding program. The partners are RAG Austria AG / Austria, Shell Global Solutions International B.V. / The Netherlands, Energie Beheer Nederland BV / The Netherlands, Hungarian Gas Storage / Hungary, Trinity Energy Storage / Spain, Axiom angewandte Prozesstechnik GmbH / Austria, Axiom Polska Sp.z o.o / Poland, AGGM - Austrian Gas Grid Management AG / Austria, LINZ AG / Austria, Montanuniversitaet Leoben / Austria, The Netherlands Organization for Applied Scientific Research (TNO) / The Netherlands and Energy Institute at JKU Linz / Austria.

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Thermomechanical Characterization and Simulation of Li-Ion Battery Components

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Abstract

Lithium-ion batteries have become increasingly important due to their high energy density and long service life and have driven the development of electric vehicles. However, their increasing energy density and widespread use, particularly in the mobility sector, have raised significant safety concerns. A major risk is thermal runaway, which occurs when internal components fail, leading to short circuits, heat build-up and potentially catastrophic fires or explosions. This not only endangers users and emergency services, but also affects the public acceptance of battery technologies. To mitigate these risks, researchers are focusing on predicting the crash safety of battery systems through experimental and modeling approaches.

This study contributes to these efforts by characterizing the thermomechanical properties of battery cell components. Tensile and compression tests were carried out on electrodes and separators of lithium-ion batteries. The tests showed that, in addition to the tensile properties of the foils and films of the jelly roll, the compressive properties of the active material in particular contribute to the mechanical properties of the battery cells. A new pressure test setup was introduced that enables precise measurement of force-displacement behavior of singular foils.

The results of these mechanical tests will be used to develop detailed finite element models of battery cells. These detailed models will form the basis for the further development of surrogate models for individual battery cells, which in turn will facilitate the simulation of entire battery systems.

Introduction

In recent years, lithium-ion batteries (LIBs) have become one of the most important energy storage solution because of their high power, energy density and long cycle life. As a consequence, LIBs are currently the driving factor for decarbonized private transport by facilitating electrically driven vehicles (EVs), such as fully electric vehicles (BEVs), hybrid electric vehicles (HEVs) and plug-in hybrid electric vehicles (PHEVs) [1–4]. The electric car market is developing rapidly: In 2023, every fifth newly registered car worldwide was an electric car [5].

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Due to their widespread use in our technology and especially in the mobility sector and their increase in energy density, the safety of batteries has become a major concern. Especially in the event of an accident, there is the risk of a so-called thermal runaway in battery cells. In such a case, internal components such as electrodes or separator materials fail, leading to an irreversible internal short circuit, which in turn causes considerable heat generation. As a result, chemical decomposition reactions of the electrode materials and the electrolyte occur, producing large amounts of flammable gases, which leads to an increase in pressure inside the battery cell. Finally, the casing breaks and a fire and explosion occur, which can also affect neighboring battery cells, which in turn leads to the thermal runaway of the whole battery. [1, 6–9]

Therefore, thermal runaways can be dangerous for consumers, emergency services and the environment. Since burning EVs and LIBs generally attract more media attention than fires in well-established technologies, such events reduce consumer acceptance of battery technology [10]. Researchers and engineers are investing in experimental and modeling studies to predict the crash safety of battery systems in order to prevent or mitigate damage to battery cells [3, 6].

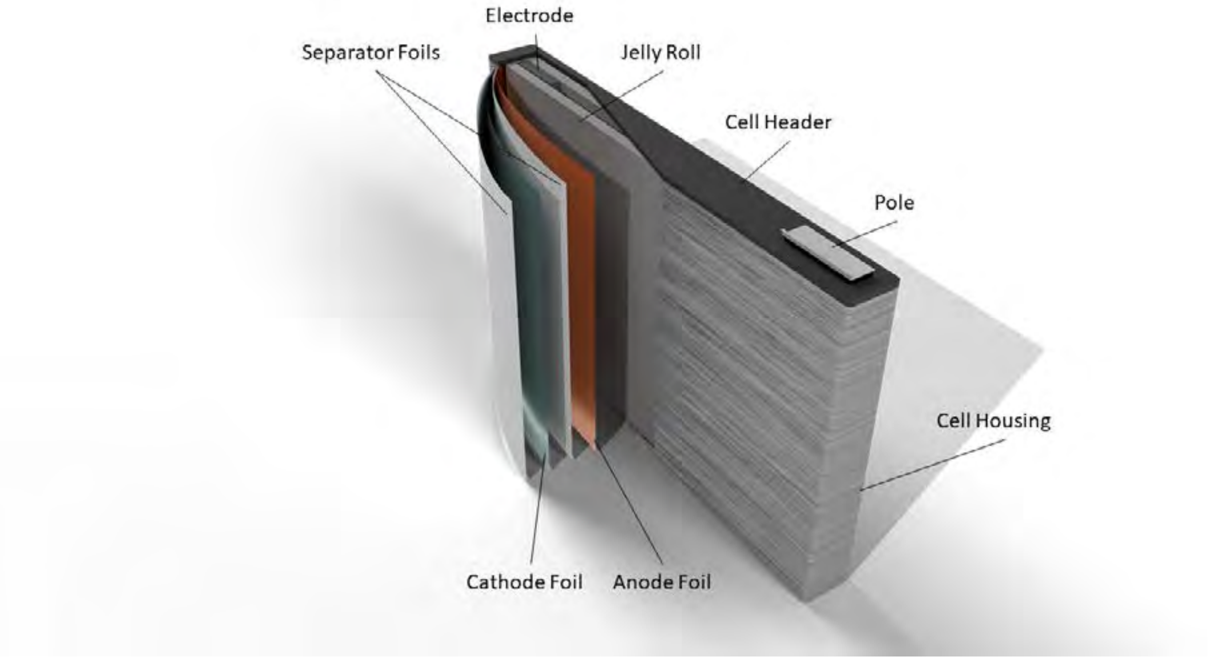


Fig. 1: Sketch of a prismatic battery as an example. The jelly roll in the casing consists of cathode, anode and separator, which are layered as shown and rolled together.

In particular, FEM simulation of crash events can help to understand the effects of mechanical deformation of battery cells, predict the failure of internal components and improve the design of battery systems [11]. The models used vary from fully homogenized to discrete layer models. Fully homogenized models do not resolve the layers within a battery cell, but treat the entire electrodes-separator stack or jelly roll of electrodes and separator as a homogenized medium. Homogenized models can predict the load-displacement behavior of battery cells quite well [12–14], but are usually not suitable to represent all loading cases and do not provide insight into the cell-internal deformation and fracture patterns to predict, for example, an internal short circuit [15].

As detailed models resolve all layers inside the battery (see also Figure 1), they could provide such information. However, the complete discretization of all layers in a stack or jelly roll inside a battery cell requires the complete thermomechanical characterization of the materials inside the battery cell and an additional tuning of the model, for example based on the force-displacement curve of the battery cell. In addition, the calculation effort for detailed models is considerably greater compared to homogenized models. However, only such models can predict the failure of individual layers, which can lead to an internal short circuit. [16–19]

In addition to mechanical load tests on entire battery cells [20–23], the thermomechanical characterization of individual battery cell components is crucial to ensure a good representation of the battery cells in different load cases with a detailed model [6]. Due to the heterogeneous structure of the cell interior, the material properties of the electrodes and the separator have to be investigated separately [24–29]. In addition, separators and electrodes showed significantly different behavior under compression and tension [30, 31]. In compression tests, there was a gradual increase in stiffness due to the porosity of the active material of the electrodes, while tensile tests showed that the tensile behavior of the electrodes is highly influenced by their metallic current collector foils. This behavior adds to the complexity of battery cell characterization and simulation, which is what makes battery cell characterization and simulation such a difficult task.

This study therefore makes the following contributions:

1. The measurement of the tensile properties of separators and electrodes is presented in this paper. In particular, the challenges of testing electrodes consisting of very thin metal foils and a heterogeneous granular material are discussed.

2. The measurement of the compressibility of separators and electrodes with a new compression test setup which extends the Zwick-Roell zwickiLine is presented which was installed at the PCCL in Summer 2024. Since the resolution of the compressive strain with this test setup is in the sub-micrometer range, singular films can be measured under loads of up to 2.5 kN with a comparatively macroscopic indenter. This setup is therefore a suitable addition to nanoindentation tests.

3. The characterization of material parameters of battery cell components with optimized FEM simulation based on the test geometry of the mechanical tests. This enables the flexible selection of suitable material models.

Experiment

Preparation of Samples

The aim of the work is the thermomechanical characterization of batteries whose electrochemistry and material composition are not known, as is often the case with finished battery cells. All tests presented in this paper are carried out on two battery types: A prismatic battery (148 x 91 x 26.5 mm³) and a cylindrical battery of type 21 700. The casing of the batteries was opened in a glove box under a nitrogen atmosphere and the jelly rolls were removed. After separating the layers of the jelly roll into individual electrodes and separator sheets, the layers were removed from the glovebox and washed to remove the electrolyte residues. The layers were then cut into samples for tensile and compression tests (see also Figure 2), and stored in air tight and inert storage boxes.

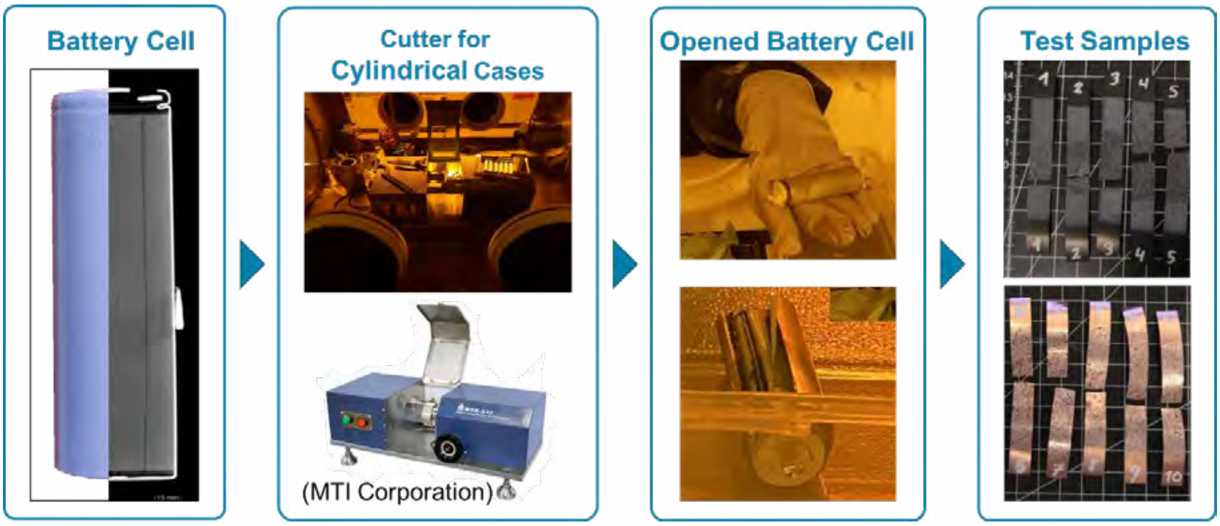


Fig. 2: Sketch of disassembly process of the cylindrical 21 700 battery

Due to the batteries' shape, not all standard test shapes could be cut from the foils. Instead, using 10 mm wide strips yielded comparably good results. This method allowed samples to be cut in different orientations relative to the uncut battery. Samples from electrodes were prepared both with and without the active material to examine its effect on tensile properties and also because strain measurements were complicated by the coating delaminating from the metal foil during tests. All samples were tested under dry conditions so that the influence of the electrolyte on the materials was not evaluated.

Tensile Tests

The tensile tests were carried out on a Zwick-Roell 2.5 kN Zwicki universal testing machine at strain rates between 0.01 mm/s and 1 mm/s (see Figure 3). This made it possible to characterize the tensile properties of the electrode and separator materials at low strain rates, which are far below those of crash situations. Nevertheless, some behavior of the materials can be derived from these tests.

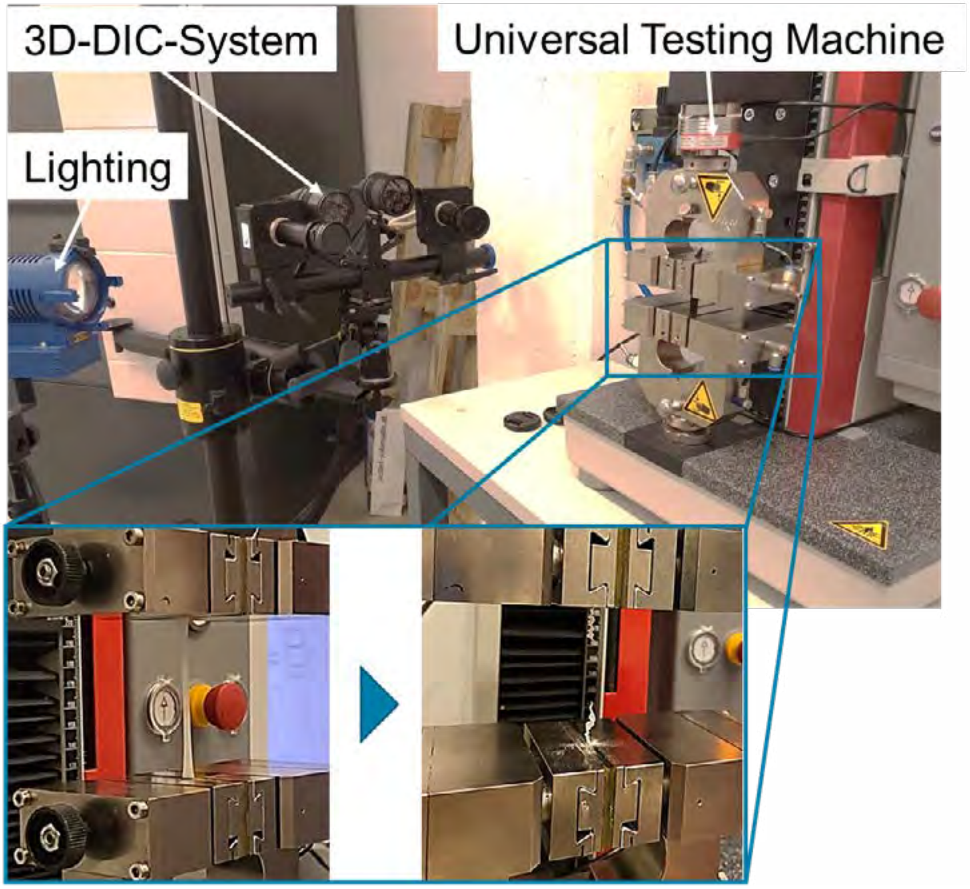


Fig. 3: Example of measuring a release film on the universal testing machine

In particular, delamination was observed between the metal foils and the active material, which prevented accurate strain measurements on the coated electrodes as the speckle pattern was sprayed onto the surface of the active material, which moved relative to the metal foil. In Figure 4, examples for the fractured electrodes, a) a blank anode and b) a covered cathode, can be seen. Because of the high adhesion between the current collector foil and the active material of the cathode, it was not possible to remove the active material without damaging the metal foil.

The metal foils broke very brittle without any necking being observed which led to a very random failure behavior of the foils, as even small defects could be the cause of crack propagation. Weiss et al [32] explained that this behavior is due to the small thickness of such metal foils, as hardly any plastic deformation can take place when the foils are deformed due to the small number of atomic layers along the foil thickness. For these reasons, the results for the strains at break in Figure 4 vary greatly. It is possible that statistical failure models such as the Weibull model will be required in the future to evaluate the failure strain.

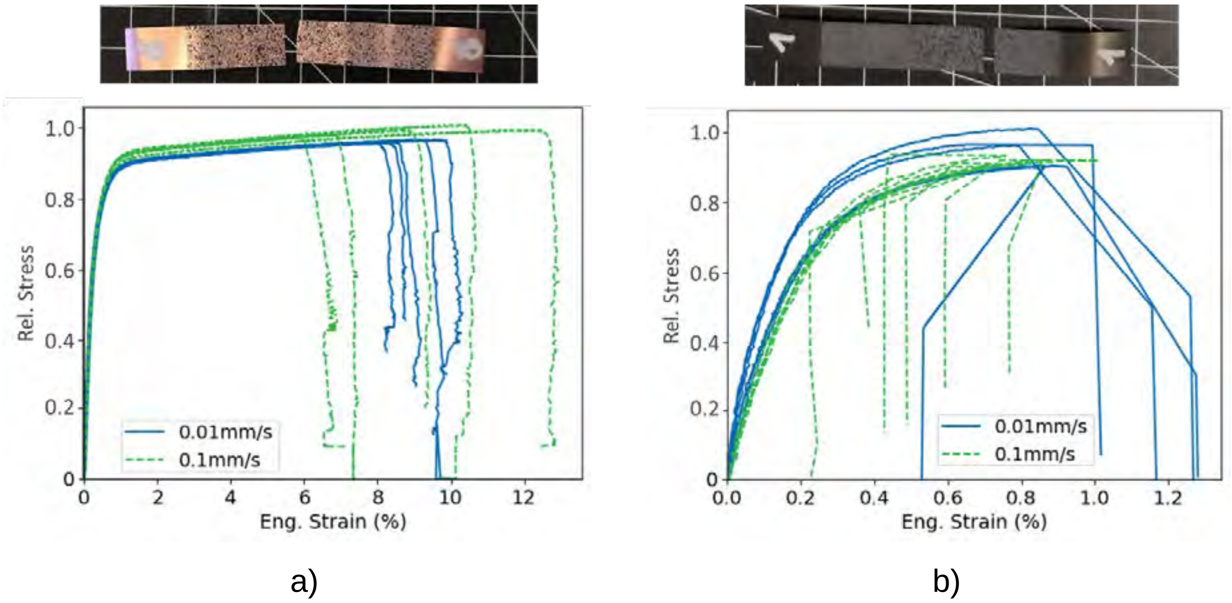


Fig. 4: Tensile tests on a) the blank anode and b) the covered cathode. The strain at break is comparatively low and varied which can

Compression Tests

The compressive properties of the active material on electrodes has a significant influence on the mechanical behavior of batteries in crush load tests, which makes sense since more than 80% of a jelly roll is made of active material [33]. For this reason, it is important to evaluate the compressive properties of the active materials and to investigate how shear is transferred from the compressed granular material to the metallic collector foils. For this reason, nanoindentation tests were carried out in a grid with a sphero-conical tip with a radius of 100 µm to investigate the hardness and the compression modulus of the active material.

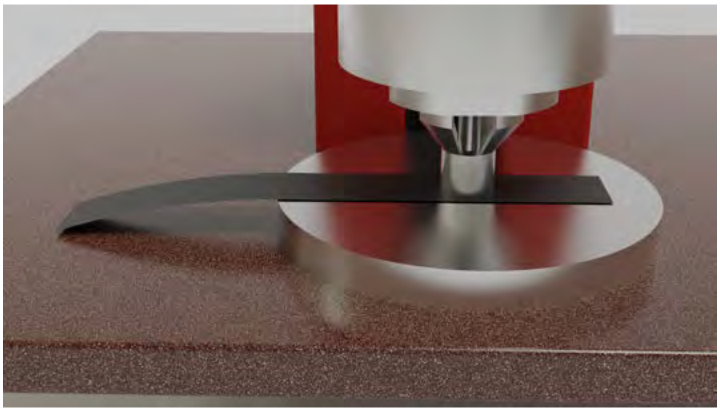
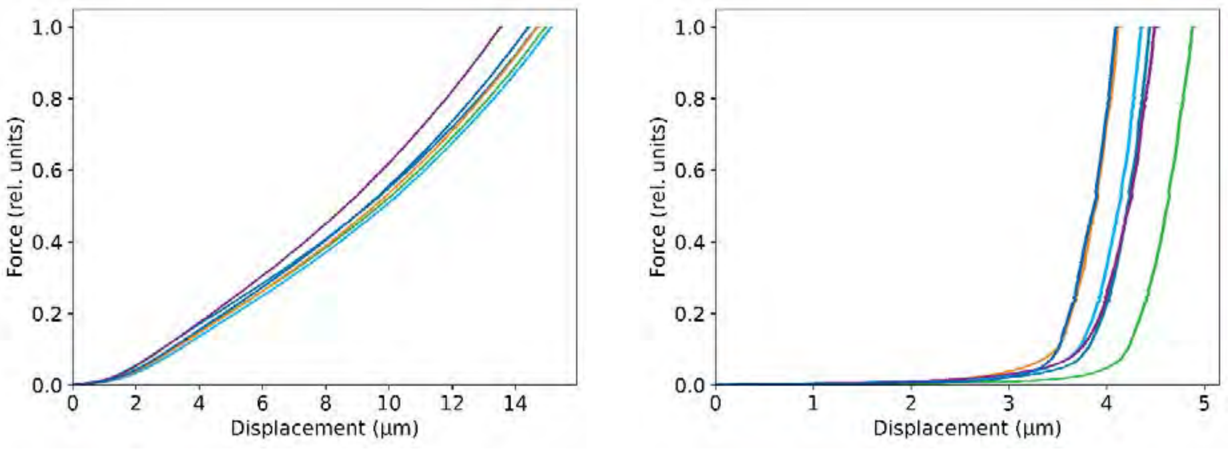


Fig. 5: Rendering of compression testing site

In addition, a new compression test device for battery foils was installed at the PCCL as an extension of the Zwick-Roell zwickiLine 2.5kN (see Figure 5). The device will deliver comprehensive results about the compressive properties of the active materials. This test is based on a flat top cylindrical indenter with an indentation area of 5 mm², force measurement up to 2.5 kN, and a highly accurate position measurement device with a repeatability in the sub-micron range.



a) b)

Fig. 6: Examples of compression test results of the a) anode and b) cathode foils

In Figure 6, first results of the compression test with the new setup are displayed with relative units for the force where the maximum is the same for the measurement of cathode and anode material. While hardening behavior due to compression of the porous material can be seen in both set of curves, whereas the cathode material hardening seems to start at slightly higher displacements, comparison between the measurement results of anode and cathode material shows that the anode material seems to feature a lower compression modulus than the cathode material, because the slope of the force-displacement curves of the cathode is significantly steeper at the higher forces. Nevertheless, characterization of the parameters should be conducted based on the simulation of the compression test by calibrating the material parameters of the involved materials.

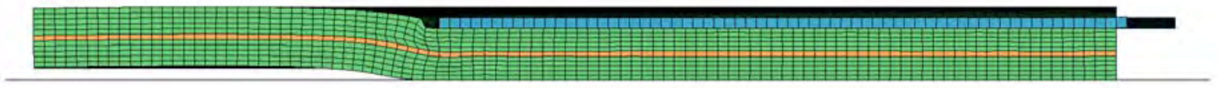
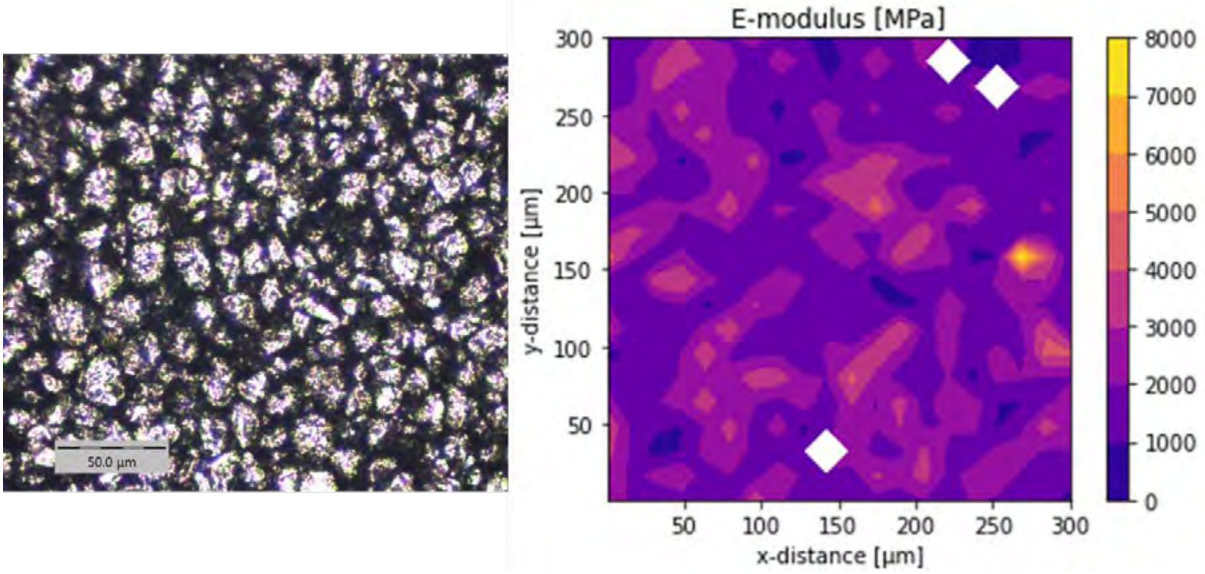


Fig. 7: Example of a simulation of the compression test setup. Blue…cylindrical indenter, green…active material, orange…current collector foil

As can be seen, the repeatability of the measurements is quite good which will facilitate the calculation of a master curve for the optimization process of the simulations of the compression test. Figure 7 shows a first simulation of the test in which the displacement caused by the indenter is exaggerated. Based on this simulation setup, an optimization process is started in which the material parameters are varied until the result of the simulation matches the master curve of the experimental compression results. Several material models will be tested and evaluated based on how well the simulation can be fit to the experimental master curves.

In a verification step, a second experimental setup is required to determine wheter the optimized material parameters are suitable for further simulations. For this reason, nanoindentation tests are conducted on the active material using a sphero-conical tip with a radius of 100 µm. The measurements are conducted in a 20x20 grid with a distance of 15 µm between the measurement locations (see Figure 8). This allows averaging over the heterogeneous, granular material (see Figure 8 a). The resulting curves are in turn calculated into a master curve which is then used in the verification step. Simulations will be created on this experimental setup with the material parameters from the optimization step. If the simulation results agree reasonably well, the determined material parameters will then be used the simulations for entire battery cells.



a) b)

Fig. 8: a) microscopic image of anode material, b) nanoindentation results of a 20x20 grid with 15 µm distance between the measurement points

Summary and Outlook

Thermal runaway due to mechanical abuse is still one of the biggest problems with lithium-ion batteries. For this reason, it is important to find ways to predict the mechanical behavior of battery cells in critical situations, such as accidents, so that possible risk factors can be assessed and risk mitigation measures can be taken in advance.

In particular, the characterization of battery components with regard to their thermomechanical parameters is an important step in simulating the mechanical behavior of battery cells with the best possible accuracy. In addition to tensile tests on electrodes and separators, the PCCL is focusing on investigating the compressive properties of the active material of the electrodes in particular, as it is assumed that these make a significant contribution to the mechanical behavior of battery cells during crushing load tests, since the active materials are the most important components of the jelly rolls inside the battery cells.

The complete characterization will allow the creation of detailed models of battery cells, which in turn will be compared with the results of crush load experiments. The detailed simulation model developed will form the basis for the subsequent development of replacement models of the battery cells and the creation of simulations of larger battery systems.

Acknowledgement

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Development of smart coatings for safety applications in battery systems

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In recent years, the development of electric vehicles (EVs) has significantly been accelerated with the clear goal of reducing the carbon dioxide (CO_2) emissions generated primarily by conventional internal combustion engine vehicles. The transition to EVs is essential to address environmental concerns and promote sustainable and clean transportation. As consequence, it is of crucial importance to ensure the proper functioning of their components in order to safeguard passenger safety. Particular attention must be direct toward the monitoring and detection of possible overheating events of electronic components, especially battery systems, during their lifetime to avoid any irreversible personal damage.

One promising and economical strategy to achieve this monitoring capacity consists in the use of temperature-sensitive polymers coupled with low-cost metal oxide (MOx) gas sensors. At specific critical temperatures, the functional polymer must be able to release traceable gases which can be easily detectable by MOx sensors connected to an interface capable to trigger an alarm. By using polymer coatings, a more complete and accurate assessment of temperature across the entire coated surface is possible.

To achieve the release of the tracer gases at critical temperatures, several approaches were studied. Firstly, thermally activated additives were added to a polymeric matrix which acts as a holder. On the other hand, polymer coatings containing thermally cleavable functional groups were synthesized.

In the first approach, two azo compounds, namely 1,1’-azobis(cyclohexanecarbonitrile) (ABCN) and azobisisisobutyronitrile (AIBN), were individually incorporated into a polyurethane matrix coating. These compounds were selected due to the fact that their decomposition temperatures are in similar ranges than the predefined critical temperatures. The decomposition temperatures and the gases released from both azocompounds were analyzed by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), evolving gas analysis coupled to a mass spectrometer (EGA-MS) among others.

In a second approach, short-chain thiols with low boiling points were used as tracer gases. Blocked model compounds were synthesized via a click reaction between short-chain thiols and 4,4′-Methylenebis(phenyl isocyanate) (MDI). Their unblocking temperatures were calculated using the aforementioned analytical methods. This unblocking reaction, at higher temperatures than the boiling point of the short-chain thiols, leads to the release of the thiols in a gas phase. The most promising thiol, 1-propanethiol, was chemically bonded to a polyurethane matrix based on a polymeric MDI and a polyol. [2]

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In the final approach, we focused our research on the covalent attachment of thiophene molecules to a thiol-ene network. This work exploited a novel strategy to develop functional coatings by taking advantage of the reversibility of the Diels-Alder (DA) reaction between a commercial bismaleimide (BMI-689) and thiophene. The retro Diels-Alder (rDA) reaction facilitates the recovery of reactants at specific temperatures. Our results indicated that this rDA temperature exceeds the boiling point of thiophene, allowing the release of thiophene moieties as tracer gas, which can be clearly detected by various sensors. Similar analytical techniques were employed to evaluate the rDA reaction temperature and identify the released species. [3]

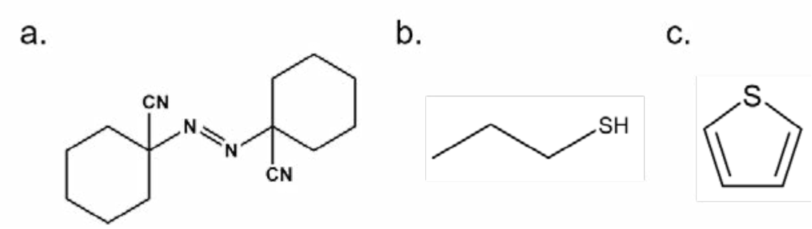

Fig. 1: Chemical structures of ABCN (a), 1-propanethiol (b) and thiophene (c) used for the generation of tracer gases

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Evaluating Encapsulant Materials for c-Si/Perovskite Tandem Modules

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SUMMARY OF THE ABSTRACT

The rapid progress in perovskite solar cell technology has brought about the need for effective encapsulation strategies to ensure their long-term stability and commercial viability. Here, a benchmark study aimed at evaluating and comparing various encapsulation materials for c-SI/perovskite tandem solar modules is presented.

Encapsulation of c-Si/perovskite solar modules is very important in terms of safeguarding from environmental factors, including moisture, oxygen, and light exposure. The encapsulation materials must therefore be as reliable and durable as possible, with the lamination process being crucial for further reliability and durability. Therefore chemical, thermal and mechanical properties of the material facing thermomechanical stresses during lamination process must fulfill several criteria. In this work a comprehensive comparative study of c-Si/perovskite encapsulation materials is shown considering key parameters from the encapsulation material itself as well as threshold values given by the c-Si/perovskite solar cell configuration.

In conclusion the critical role of benchmarking in the ongoing development of encapsulation strategies for c-Si/perovskite solar cells will be highlighted here. It emphasizes the need for comprehensive assessments to guide the selection of encapsulation materials that can support the widespread adoption of perovskite solar technology as a clean and efficient energy solution.

AIM AND APPROACH

For PV (photovoltaic) modules that use c-Si/perovskite tandem solar cells, encapsulation must be reconsidered due to the changed requirements resulting from the module composition. Perovskite modules are temperature-sensitive, which requires the lowest possible lamination temperature. To avoid thermomechanical stresses, the lowest possible shear

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viscosity at laminating temperature and low shrinkage are crucial. The encapsulation concepts and test procedures presented in this work aim to evaluate and classify encapsulation materials in the form of a benchmark.

Recently, perovskite PV configurations have become increasingly popular as they can deliver higher performance compared to conventional crystalline silicon solar cell configurations, particularly thanks to their appealing optoelectronic properties.

However, there are also disadvantages to using perovskite cells, such as temperature sensitivity, instability of the absorber to water vapor from the environment, and oxygen vapor in combination with light is also harmful to some perovskite types. In this study, common, non-crosslinking and crosslinking encapsulation materials were chosen as benchmark materials. Encapsulant ethylene vinyl acetate (EVA) was omitted from the benchmark to avoid the typical degradation modes that occur during EVA operation which are particularly related to acetic acid production during degradation. Acidic acid is linked to PV module failure mechanisms like corrosion of the interconnection, cell metallization or potential induced degradation [1].

Sixteen commercially available encapsulants were tested regarding their chemical, thermal and mechanical behavior (see Table 1). The letter in the encapsulant name displays the manufacturer, the first number displays the type of material and the second number, if any, displays the version of a material. The samples B.1.1 and B.1.2 for example are from the same manufacturer and the same type of material but it is present as two versions. The encapsulants were characterized non-destructively by means of Fourier Transform Infrared spectroscopy in Attenuated Total Reflectance mode (FTIR-ATR) to assess the chemical structure at the surface of the material. Thermal behavior was investigated via Differential Scanning Calorimetry (DSC) to evaluate important transition temperatures (see Figure 1a). Here the melting temperature as well as the onset of the crosslinking temperature should be as low as possible for c-SI/perovskite encapsulation, as the perovskite is temperature sensitive. The shear viscosity is one of the key properties for perovskite modules because of the danger of delamination due to thermomechanical stresses and was therefore investigated with Dynamic Mechanical Analysis (DMA) in shear mode (see Figure 1b). The main characteristics of the benchmarked encapsulants can be seen in Fehler! Verweisquelle konnte nicht gefunden werden.. Shrink characteristics will be examined by determination of the coefficient of thermal expansion (CTE) with the aim to find the lowest possible shrinkage. Higher shrinkage will lead to unwanted mechanical stresses.

Fig. 1: measurement setup DSC (a) and DMA in shear mode (b)

SCIENTIFIC INNOVATION AND RELEVANCE

It is not easy to draw conclusions on perovskite encapsulations on the basis of current literature [2,3,4], because next to the variation of encapsulants also the perovskite formulation and cell configuration differs [2]. In this work a comprehensive benchmark including relevant encapsulants from the market is performed using c-Si/perovskite tandem modules. The systematic investigation gives rise to rank encapsulants from more promising to less promising encapsulants according to the use case and the most suitable encapsulant can be chosen.

RESULTS (OR PRELIMINARY RESULTS) AND CONCLUSIONS

The main characteristics so far of the chosen encapsulants are shown in Table 1.

Table 1: Main properties of the investigated encapsulants: the letter in the encapsulant name displays the manufacturer, the first number displays the type of material and the second number stands for the version.

Encapsulant	Crosslinking during lamination (crosslinking peak temperature[°C])	Melting temperature [°C]	Softening point [°C]
A.1	Yes (161)	59	
A.2	Yes(157)	55	
A.3	Yes(151)	55	55
B.1.1	Yes(151)	64	55
B.1.2	Yes(161)	64	48
B.2.1	Yes(154)	69	67
B.2.2	Yes(158)	68	63
C.1	Yes(164)	62	62
B.3	Yes (153)	65	64
D.1	Yes(162)	72	71
D.2.1	No	71	67
D.2.2	No	73	79
D.2.3	No	63	60
E.1	No	(58)103	67
F.1	No	(61)121	51
B.4	No	103	62

In Table 1 it is obvious, that the non-crosslinking encapsulants show a trend towards too high melting temperatures. The softening point is gained from DMA measurements and shows the temperature, where the materials starts to soften. The softening point is usually slightly smaller than the melting temperature except for the materials E.1, F.1 and B.4 where the softening point lies in between the two melting points, which may origin from a material blend. For the crosslinking materials it is possible to investigate the onset of the crosslinking peak from first heating of DSC measurements (see Figure 2), where the crosslinking procedure starts. The lamination process has to be performed at least at this onset temperatures to get a fully crosslinked encapsulant. Some encapsulants (A.1, A.2 and B.2.2) seem to exhibit an onset temperature of crosslinking above 140°C. Perovskite structures are temperature sensitive and lamination above 140°C will probably damage the perovskite. Moreover, the onset temperature for B.1.1 and B.1.2 as well as for B.2.1 and B.2.2, which are designated as the same materials in two versions, are significantly different.

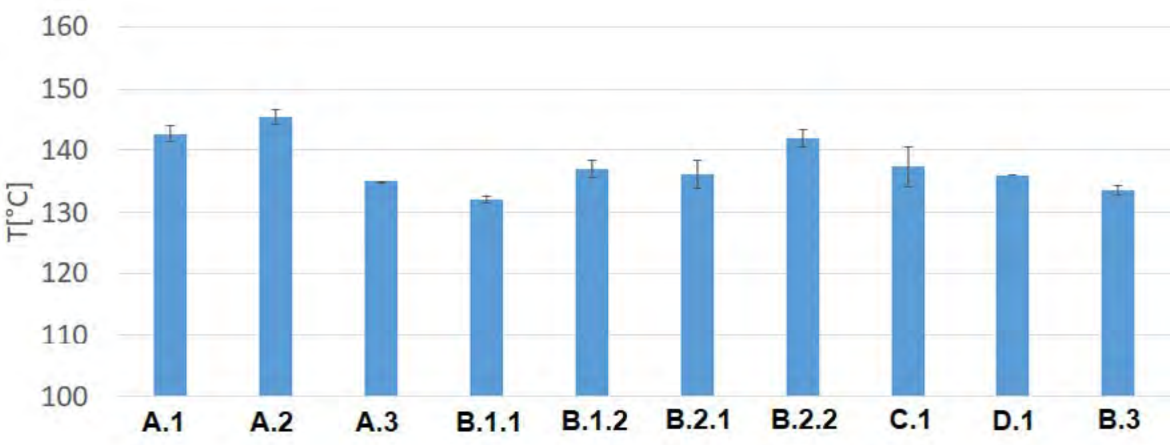

Fig. 2: Onset of the DSC crosslinking peak (first heating) for crosslinking encapsulants: the letter in the encapsulant name displays the manufacturer

The shear viscosity in the lamination temperature range (~ 120°C) should be as low as possible to prevent delamination of Perovskite cell layers due to thermomechanical load. In Figure 3 the DMA shear viscosity is visible for crosslinking encapsulants (up) as well as for non-crosslinking encapsulants (down). Here the materials B.3, D.1, D.2.2 and E.1 seem to have a way too high shear viscosity at 120°C. Interestingly, the samples B.1.1 and B.1.2 as well as D.2.1 and D.2.2, which are the same type of material in different versions exhibit different shear viscosities.

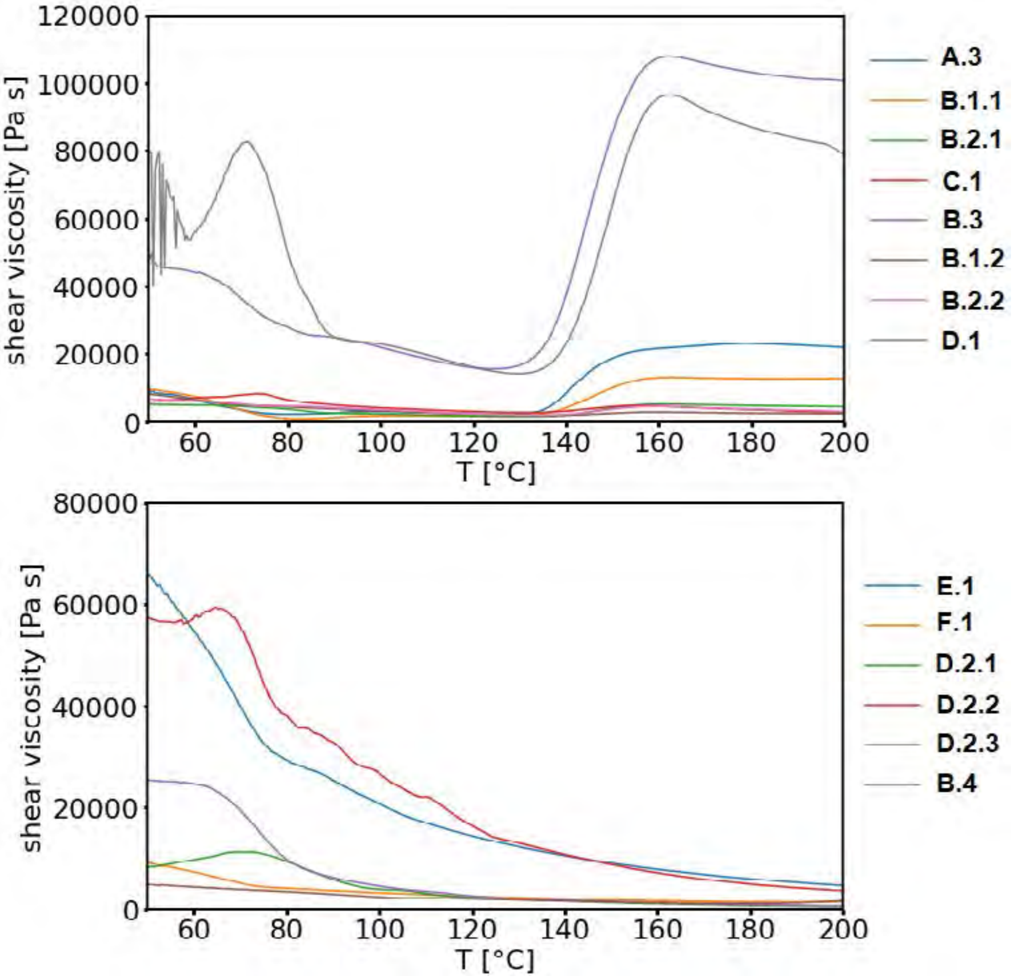

Fig. 3: Shear viscosity gained by DMA measurements for crosslinking encapsulants (up) and non-crosslinking encapsulants (down).

Further investigations of the CTE will complement the results to narrow down the benchmarked materials to five to seven materials which will then are subjected to the lamination process. Main result will be the most suitable encapsulation material for the c-Si/Perovskite tandem modules perovskite solar cell structure.

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Importance of Cryogenic Testing Data for Composites – Matrix dominated properties and permeability

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Abstract

Within this paper critical aspects of composite coupon testing under cryogenic conditions are discussed. The investigations focus on matrix dominant properties such as tensile properties perpendicular to the fibre direction of uni-directional composites and the in-plane shear behaviour. The following parameters were analysed: shape and material of the tab material used for load transfer between the coupon and the fixation, shape of the coupons and different top and bottom layer cross ply architectures in 90° tensile samples.

Multi-scale finite element analyses of the behaviour of the tabbed coupons were performed to assess the thermo-mechanical behaviour of the coupons when loaded under cryogenic conditions. Out of these analyses stress concentration regions will be identified and evaluated with respect to potential early failure that arise from the design of the coupon samples. Special care was laid on the usage of top and bottom cross-ply layers of different angles to avoid early failure around the tab region of the coupons. The results of the FE analyses were verified by experimental results performed on the different coupon designs at cryogenic conditions at -196°C in liquid nitrogen.

Furthermore, a test set-up for the measurement of the permeability of gaseous helium under different temperatures down to 77K is presented. Typical results of the permeability of pure resin and composite materials at room temperature and at 77K are shown.

Introduction

Due to its high specific stiffness and specific strength composite materials are widely used in industries where weight optimization plays a crucial role such as the space industry where the launch costs of 1 kg may reach 10.000s of euro [1]. One key component of launchers are cryogenic propellant tanks containing liquid oxygen and liquid hydrogen. Composite tanks show the potential to further decrease the weight of composite propellant tanks compared to conventional metal tanks. On the other hand, microcracks in the polymer matrix might lead to leakage of the propellant, pressure loss and in worst case explosion under working condition. Such microcracks can appear by combined stresses in the composite structure arising from e.g. internal pressure, general launcher loads (torsion & bending moments, section loads) [2]. Therefore, reliable material data under cryogenic conditions are required

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for fail safe composite cryogenic propellant tanks. The authors of the paper perform cryogenic mechanical testing down to temperatures of liquid helium on different type of materials ranging from metals, over plastics and composites to honeycomb panels since more than 20 years [3]. During that time most of the uni-directional tensile samples tested perpendicular to the fibre direction failed at the tab region leading to a potential underestimation of the transverse tensile strength important for the design of composite structures against matrix cracking. In the following chapter critical aspects of composite coupon testing under cryogenic conditions are discussed where the focus is laid on matrix dominant properties such as tensile properties perpendicular to the fibre direction of uni-directional composites and the in-plane shear behaviour. Furthermore, aspects for the assessment of the tightness of the used composite materials against propellant gases were discussed. A test set-up for the measurement of the He permeability at room temperature and 77K together with typical results on composite materials is presented.

Typical mechanical test results at cryogenic conditions

Mechanical properties of composite materials depend on several different factors such as the used constituents (fibre, matrix), fibre architecture, lay-up, production process and operating conditions (temperature, humidity). On the other hand, general trends in the temperature dependent mechanical behaviour of a specific uni-directional composite material are observed. Figure 1 show the RT normalized stress-strain behaviour of a uni-directional CFRP material in tension, compression, and shear in and normal to the fibre direction at 77K and 4K.

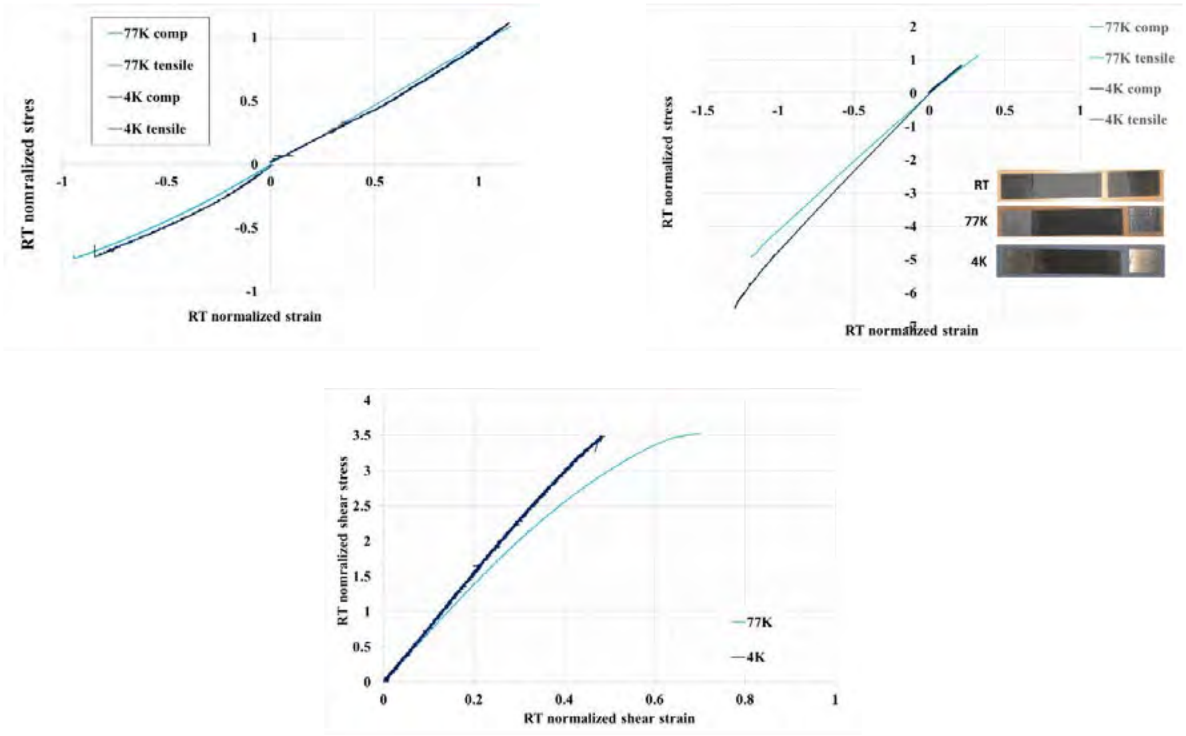


Fig. 1: Normalized stress-strain behaviour of a UD CFRP material in tension and compression in fibre direction (top left), normal to the fibre direction (top right) and in plane shear (bottom) at RT, 77K and 4K together with usual observed failure modes.

The stress strain behaviour in tensile and compression in fibre direction shows only a small influence on the temperature down to 4K. Especially the stiffness and strength in tension does not change significantly, whereas the compression strength values increase when the temperature decreases. Such behaviour shows that the mechanical properties of the carbon fibre in direction of the fibre axis, which is dominant for the behaviour of UD materials loaded in fibre direction, are only very limited influenced by the temperature. The observed failure mode in tension and compression usually indicates valid results. The influence of the temperature on the matrix dominant properties is much higher. The shear modulus and shear strength determined by in plane shear testing of [-45/45] laminates increase significantly at cryogenic conditions. The observed failure mode for the in-plane shear test at all temperatures led to valid results. The Young´s Modulus perpendicular to the fibre direction also increase significantly at cryogenic conditions. For 90° tensile tests only the test specimen tested at RT lead to a failure away from the tab ends. For 90° tensile tests performed at 77K and 4K nearly all samples failed directly at the tab end (top left of figure 2). Therefore, an influence of the bonded tab on the strength results can be expected, which was the motivation to analyse the reason for such behaviour.

Typical mechanical test results at cryogenic conditions

To assess the structural behaviour of 90° coupons tested in tensile under cryogenic conditions Finite Element simulation of different coupon and tab geometries and tab materials were performed in ANSYS. As not all relevant material properties, especially the out of plane components of the stiffness tensor can be reliably measured representative unit cells (RVE) for the coupon and the [-45/45] GFRP tabs were used to calculate the full stiffens tensor of both materials at RT and 77K.

REV for determination of stiffness tensor and material properties for simulation

Two different RVE´s were used. One RVE for the determination of the transverse isotropic stiffness constants for the uni-directional CFRP material and rovings of the GFRP material and a plain weave type for the GFRP material. The material property of the carbon fibre was taken from a predefined material with 290 GPa stiffness out of the ANSYS database. It was assumed that all properties are constant over the temperature. The material properties of the glass fibre at RT were also taken from ANSYS data base and values at cryogenic conditions were taken from literature [4]. The resin properties were adjusted in such a way, that typical measured properties as function of temperature (Young`s Modulus in 0° and 90°, in plane shear modulus) are similar to the values out of the analyses of the RVE´s. The properties of the pure Al tabs were taken from literature [5, 6]. The tensile properties of the used adhesive were measured during earlier projects by the authors of the paper and CTE values were taken from literature [6]. Figure 2 show the used RVE´s.

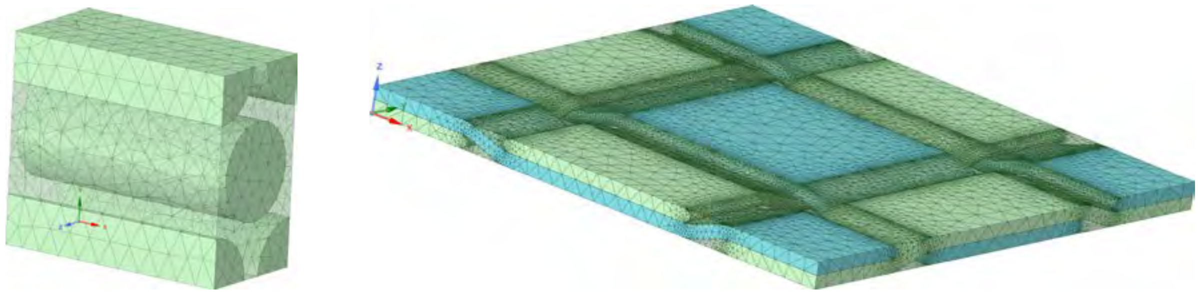


Fig. 2: RVE´s: Left side RVE used for the calculation of the transvers isotropic properties of the unidirectional CFRP material and roving properties of the GFRP tab, Right side plain weave type RVE for the calculation of the orthotropic properties of [-45/45] GFRP tab.

Table 1 till Table 4 show the materials properties used as input for the RVE´s, the resulting calculated values of the CFRP and GFRP material and the material data of the adhesive and the Al tabs.

Table 1: Material properties of C-Fiber

temperature	E_1	$E_2= E_3$	$\mu_{12}=\mu_{13}$	μ_{23}	$G_{12}=G_{13}$	G_{23}	CTE_1	CTE_3
K	*GPa*	*GPa*			*GPa*	*GPa*	*µm/m*	*µm/m*
293, 77	*290*	*23*	*0.2*	*0.4*	*9*	*8.2*	*-1*	*15*

Table 2: Material properties of G-Fiber and resin

temperature	G-Fiber	E	µ	CTE	Resin	E	µ	CTE
K		*GPa*		*µm/m*		*GPa*		*µm/m*
293		*73*	*0.22*	*5*		*2.3*	*0.35*	*69*
77		*80*	*0.22*	*1*		*4.5*	*0.35*	*10*

Table 3: Material properties of adhesive (elasto-plastic at RT, linear elastic at 77K)

temperature	*E*	*µ*	$R_{p0.2}$	*Rm*	$\varepsilon_{plastic}$	*CTE*
K	*GPa*		*MPa*	*MPa*	*%*	*µm/m*
293	*3.6*	*0.35*	*35*	*55*	*3.5*	*55*
77	*9*	*0.35*	*-*			*38*

Table 4: Material properties of Al (elasto-plastic)

temperature	*E*	*µ*	$R_{p0.2}$	*Tangent modulus*	*CTE*
K	*GPa*		*MPa*	*GPa*	*µm/m*
293	*68*	*0.33*	*35*	*0.5*	*23*
77	*75*	*0.33*	*43*	*0.9*	*18*

Model and simulation results.

The different coupon and tabs geometries were modelled in ANSYS. Figure 3 shows the FE Model of a typical coupon with a bonded tab.

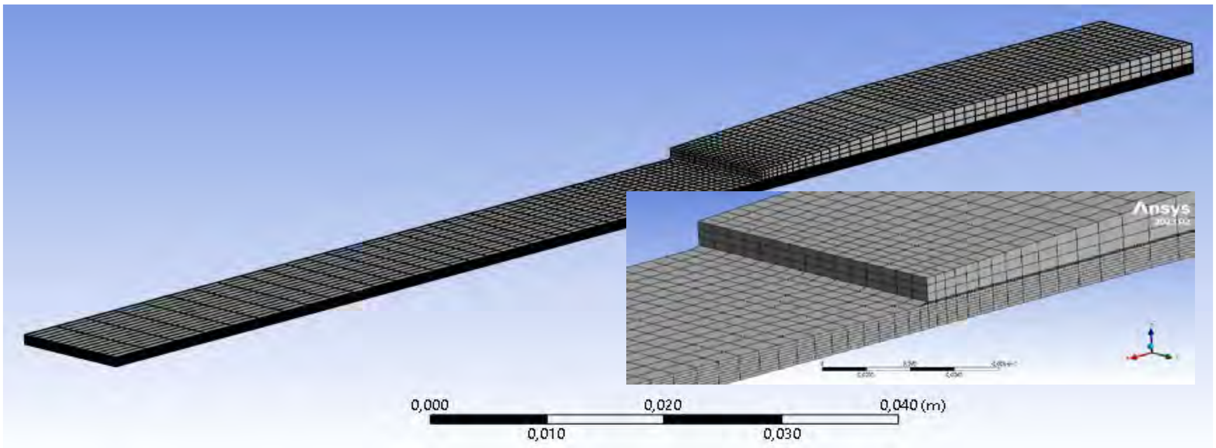
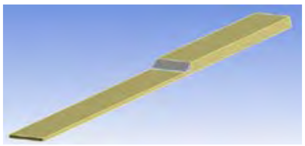
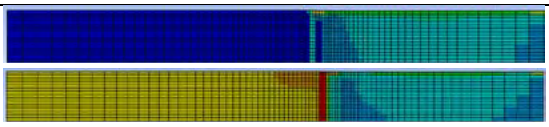
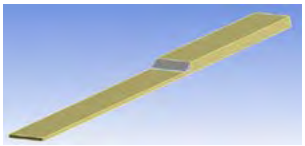
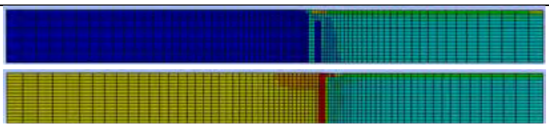
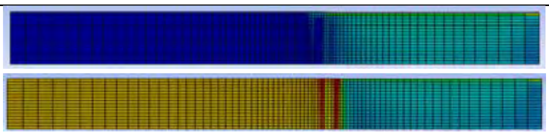
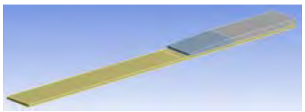
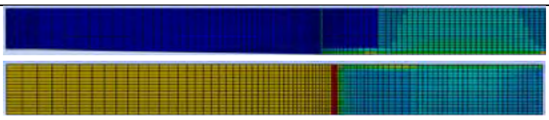
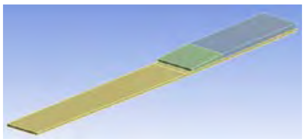
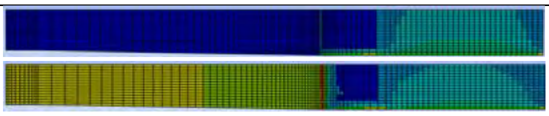
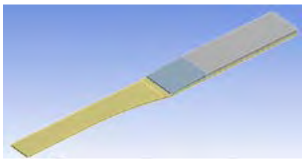
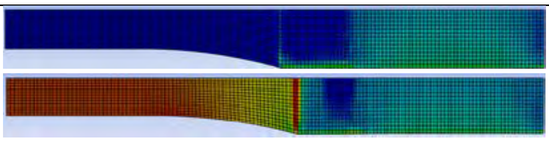
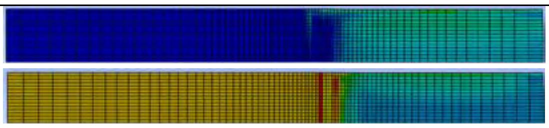
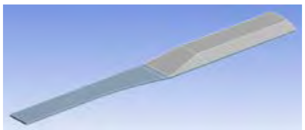
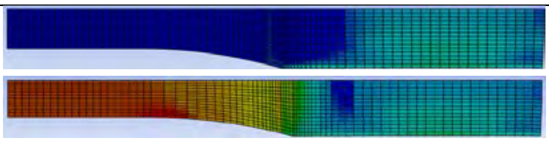


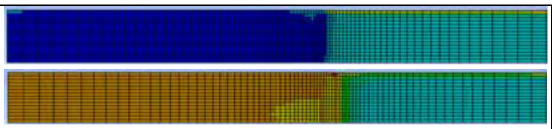
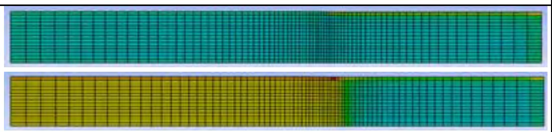
Fig. 3: Typical FE Model of coupon with bonded tab.

Due to symmetry only 1/8th of the whole coupon was modelled, and symmetric boundary conditions were applied to cutting faces. All models are built from eight layers of CFRP material representing 1 mm thickness (half of the nominal coupon thickness of 2mm), a 0.1 mm thick adhesive layer using three elements over the thickness and the tab. All simulations were done in three steps. In a first step the top face of the tab was loaded via a rigid bonded 10mm thick steel clamp (not shown in figure 3) by the clamping force (2000 N) normal to the tab and the pre-load (25N) parallel to the tab applied after placement in the testing machine. In a second step the whole coupon was cooled to 77K under constant clamping load and preload. In a third step a tensile load of 1000N at 77K was applied. At this step also the clamping load was increased to 6000N to account for the used bevelled clamping fixture. These three steps represent a typical cryogenic tensile test.

For the evaluation of the simulation results the distribution of the inverse reverse factor (IRF) in the most critical layer (top layer) of the CFRP material was used. In case of top/bottom cross players the most critical 90° layer was used. For the calculation of the IRF Puck´s 3D failure criterion was used. The required strength values beside the tensile strength in 90° direction, are taken from typical measurement results. For the strength in 90° direction an artificial value of 100 MPa was selected. As the aim of the simulation is to identify critical regions and the relative severity of the critical region only the ratio of the IRF in the critical region relative to the region for envisaged failure away from the tab is important. The region of the tab edge represents a stress singularity region, which is usually difficult to quantify especially in case of orthotropic material bonds and presence of elastoplastic materials (adhesive). Therefore, the mesh size in the singularity region was the same for all models to allow a relative comparison of the results. Table 5 summarizes the simulation results.

Table 5: Analysed designs, IRF distribution after cooling and at cold loading and IRF ratio (in case of two values: top: at tab edge, bottom: at adhesive edge).

Sample / Tab Design	*IRF distribution (top: cooling to 77K, bottom load at 77K*	*IRF ratio*
Al Tab - adhesive fillet 		1.76
GFRP Tab -resin fillet 		1.75
Al Tab – extended adhesive film 		1.48 1.23
Al tab bevelled 		1.64
Al tab bevelled – dogbone 1 		1.47
Al tab bevelled – dogbone 2 		1.37
Al tab double bevelled extended adhesive film 		1.22 1.16
Al tab double bevelled extended adhesive film – dogbone 2 		0.71 0.92

Al Tab [-20/20] top layer		1.18
Al Tab [-45/45] top layer		1.12

It can be shown, that for all tab designs a stress concentration at the edge of the tab/CFRP interface exists. The usage of GFRP tabs lead to similar IRF values at the tab edges and a more uniform, but in average higher IRF below the tabs compared to the pure Al tab after cooling to 77K. The IRF ratio after loading at 77K is similar for both tab materials. The IRF ratio is highest for standard unbevelled tabs for parallel samples. Extension of the adhesive film over the tab edge led to slight improvements. Bevelling of the tabs is only effective if it forms a sharp edge. The lowest IRF ratio for standard parallel CFRP samples was found for sharp double bevelled tabs. Most promising results were found for dog-bone 2 samples with sharp double bevelled tab.

In case of the top/bottom [-20/20] and [-45/45] cross play layers the stress concentration in the outermost 90° layer was much less pronounced compared to the standard parallel samples. However, when looking at the IRF especially for the [-45/45], which is primarily coming from stresses normal to the fibres, after cooling to 77K already a value of 0.3 was observed in the 90° layers. This is caused by the CTE and stiffness mismatch between the -45°/45° and 90° layers. Figure 4 show the effect of the top/bottom cross ply lay up on the thermal induced stresses due to cooling to 77K and the stresses at nominal load of 1000 N at 77K in 90° and cross-ply layers as well as the Young´s Modulus.

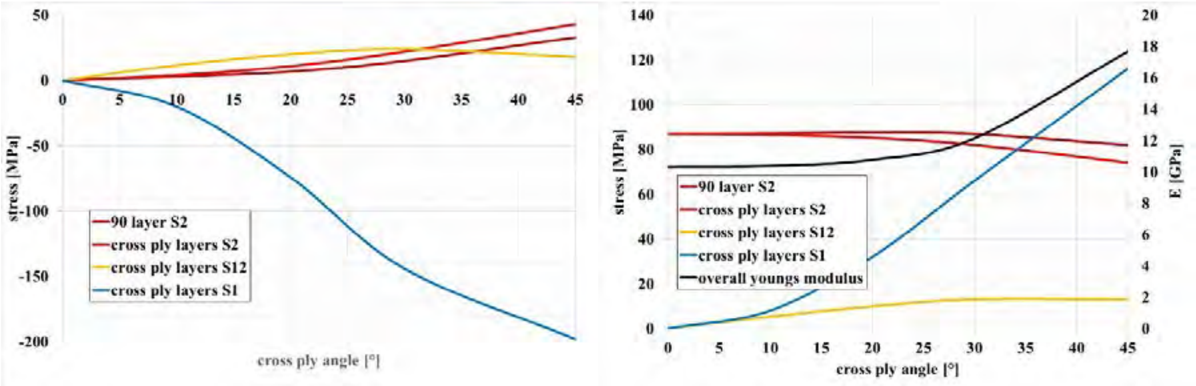


Fig. 4: Effect of the top/bottom cross ply lay up on the thermal induced stresses due to cooling to 77K (left) and the stresses at nominal load of 1000 N at 77K (right) in 90° and cross-ply layers and average Modulus in loading direction.

The higher the cross ply angle the higher are the introduced stress after cooling to 77K in both the 90° and cross ply layers. When loading at 77K with 1000 N the relevant stresses in the 90° layers decrease with increasing cross ply angle. This is caused by the increasing stiffening of the laminate by the cross-ply layers with increasing cross ply angle clearly shown in the strong rise of stresses in fibre direction of the cross-ply layers. The lower stresses in the 90° layers compared to the nominal applied stress in the whole laminate must be considered when evaluating experimental results.

Testing Results

Tests on 90° samples with different sample and tab geometries

Tensile tests of 90° samples were performed on different coupon and tab geometries. Figure 4 shows the relative strength values of the different configurations.

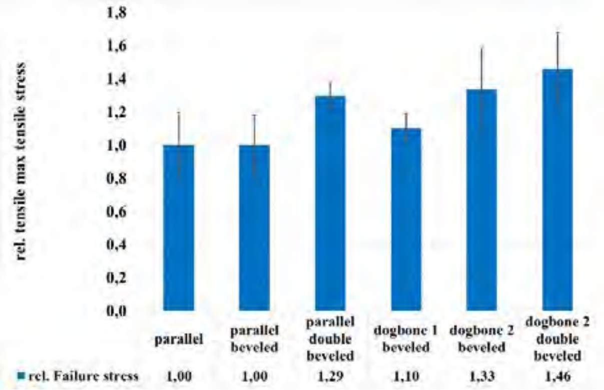


Fig. 5: Relative max tensile stress in dependence on coupon / tab design

Whereas a continuous improvement of the measured maximum stresses in the coupons was achieved even in the most promising dogbone 2 sample with double bevelled tabs the failure appeared at the tab edge or close to the tab edge, indicating that still the effect of the stress singularity could not be eliminated.

Tests on 90° samples with -45/45 top layers with online AE monitoring

To prove the suitability of top/bottom cross ply layers to trigger failure outside the stress singularity tensile tests with online AE measurement of coupons with [-45/45/90/90/90/90/90]s layup were performed at RT and 77K on a typical IM fibre-based laminates with non-toughened epoxy. AE measurements were performed with standard PCI-DISP-4 AE system using two standard broadband PW AE sensors from Mistras. The sensors were clamped in distance of 100 mm between the tabs of the coupons. Prior to testing the wave velocity along the coupon was measured to allow linear event localization. Figure 6 show a typical stress-strain curve and evaluation of the located AE events at RT and at 77K.

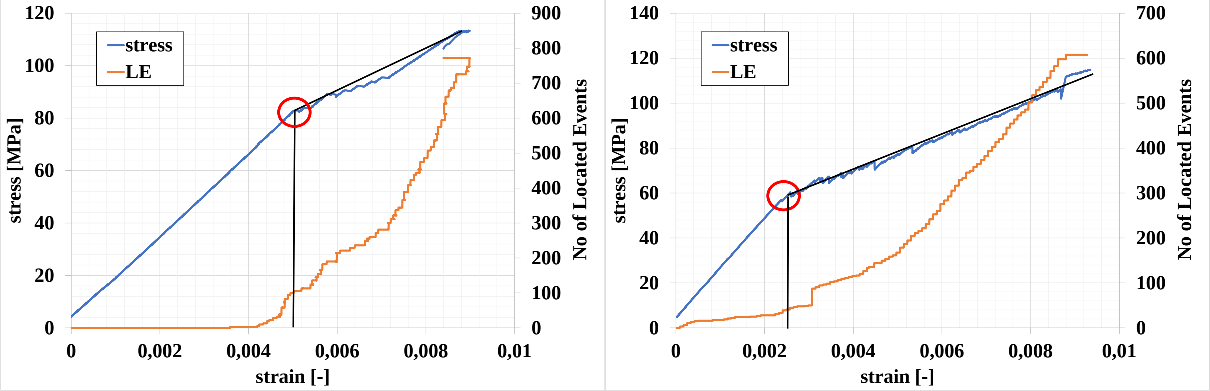


Fig. 6: Typical stress-strain curve and evaluation of the located AE events at RT and at 77K

All samples failed away from the tab edges. The stress strain curves start with an expected linear elastic behaviour up to certain strain/stress level, where first failures in the 90° layers appear. Till that load, the 90° layers impede the -45/45 layers to shear. As soon as failure in the 90° layers appear local shearing of the -45/45 is possible leading to lower average slope of the stress-strain curve. The failure onset can also be seen in the strong increase of located acoustic emission events. As the stress distribution is in the cross-ply layers differs from that in 90° layers and cannot be easily calculated by load and cross section, the strain at the change of the slope of the stress-strain curves is proposed to assess the failure of the 90° layers. Repeated measurements lead to average failure strains of the 90° layers of around 0.5% at RT and 0.25% at 77K, where the results at RT correspond to typical failure strains measured in standard reference materials.

Permeability of Composites

The permeability of composite materials depends on different factors. First of all, even perfect composite materials show diffusion of small gas molecules like hydrogen at room temperature. As diffusion follows an Arrhenius behaviour the diffusion strongly depends on temperature and decrease with decreasing temperature. As such the permeability of perfect composite materials can be described by diffusion laws. The situation changes, when imperfections such as pores or micro-cracks are present. As long as especially the network of micro-cracks is not connected the permeability still can be approximated by a diffusion like behaviour. In case a fully connected microcrack network through the thickness of the component the permeability behaviour changes and can be approximated by flow through porous media through Darcy´s law. The following two chapters describe a He permeability test set-up and typical measurement results on composite materials.

Set-up for Permeability Measurement

To measure the He permeation through the test samples, one test sample will be clamped between two flanges and tightened by two Indium seals. One side of the flange is connected to the pressure side and the other to the vacuum side of the permeation measurement equipment. The vacuum side is connected to Helium leak detector. The vacuum on the vacuum side is controlled by a vacuum gauge. In addition, a calibration leak can be connected to vacuum side. The pressure side can be connected to a pressurized Helium supply and / or a vacuum pumping unit. The vacuum pump is used to get rid of Helium in the supply tubing. The pressure in the pressure side will be controlled by pressure sensor operating in the range between 0 bar to 6 bars. To control and measure the temperature of the sample a Si diode was used. The diode is mounted on the top side of the top flange – above the sample to guaranty a proper temperature control during immersion in liquid nitrogen.

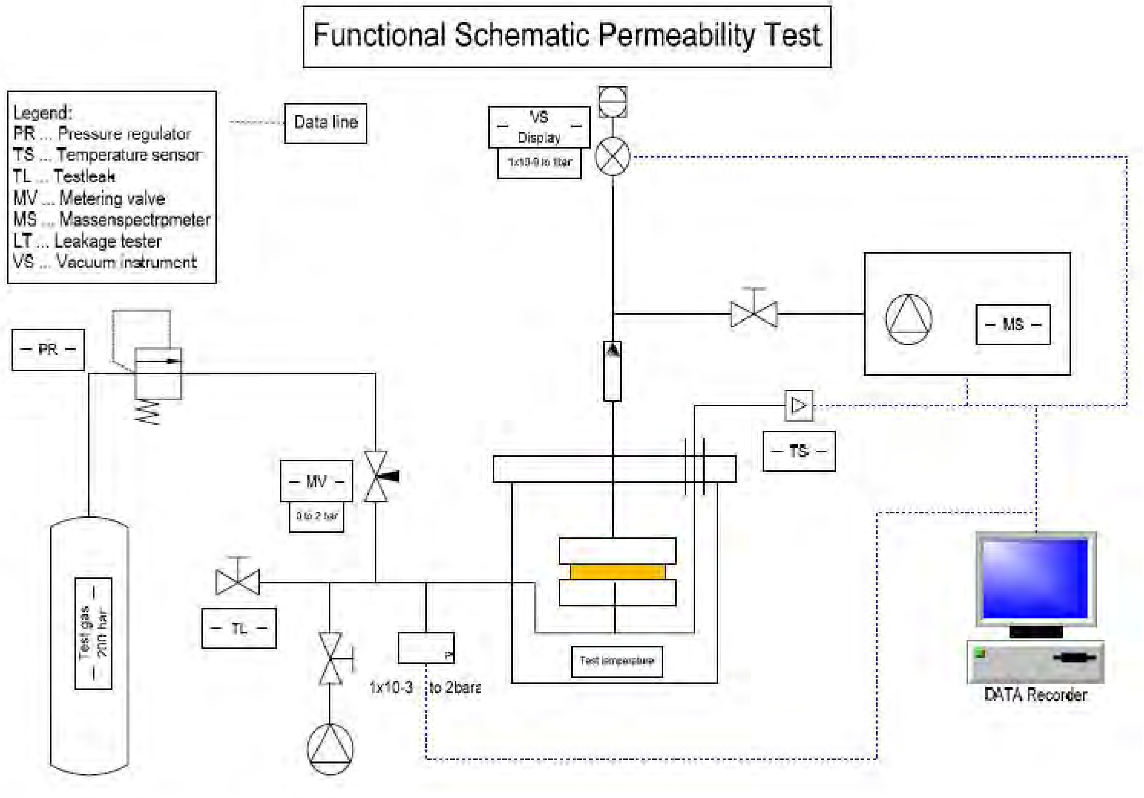


Fig. 7: Test-setup for the measurement of He permeability at different temperatures

Permeability of Composites

The following figure show the evaluation of the He permeability through different materials – pure plastics and composites – at different temperatures – room temperature and 77K.

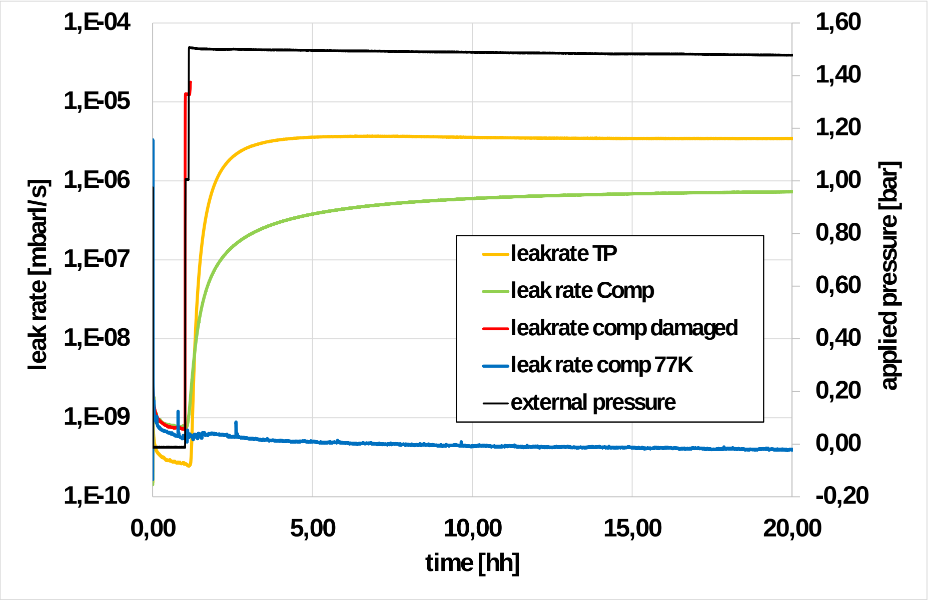


Fig. 8: evaluation of the He permeability through different materials – pure plastics and composites – at different temperatures – room temperature and 77K.

As already described in chapter “Permeability of Composites” undamaged plastics and composites show a diffusion like behaviour characterized by a continuous increase in the He permeability with time till a saturation value was reached. The saturation leak rate of pure plastics is approximately one order of magnitude higher compared to composites with typical fibre contents of around 60%. As such the carbon fibres act as diffusion barriers. At 77K the diffusion is strongly reduced leading to no measurable increase in the leak rate over time. The situation differs in case of through thickness damages, where the leak rate abruptly changes when the He pressure is increased, and the leak rate strongly depend on the applied pressure.

Conclusion

Within this paper the authors presented the analyses and verification results of cryogenic tensile tests of 90° and top/bottom cross ply supported 90° uni-directional coupons of different coupon and tab geometries to mitigate failure at the tab edges that might lead to early failure. Whereas the different coupon and tab geometries were not sufficient to avoid failure of the coupons in the tab edges improved failure stresses could be achieved with double bevelled tabs on parallel and dogbone specimen. Most promising results were found on top/bottom cross-ply supported 90° coupons leading to appropriate failure away from the tab edges. Due to the non-homogeneous stress distribution in such samples, strain--based failure assessment is proposed.

The measured permeabilities confirm the expended temperature dependent behaviour of nearly defect free (no interconnected matrix crack network) and damaged (interconnected matrix crack network) composites. Nearly defect free composites show a diffusion like behaviour at RT that strongly decreases when the temperature decreases. On the other hand, composites with connected matrix crack networks show a pressure dependent rapid increase of the permeability.

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High cycle fatigue and creep of reinforced PEEK for large size bearings in wind industry

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Abstract

Government-mandated energy and greenhouse gas emission goals, along with ethical shifts toward sustainable energy, are driving companies to adopt alternative energy production methods, such as wind power. At the heart of a wind power plant is the driveshaft, which connects the rotor blades to the generator, along with the necessary bearing system. This system includes rings, rolling elements, and a cage—such as a segmented cage designed by SKF. This component experiences creep and fatigue loads, which must be accounted for in lifetime estimation. To achieve this, a method incorporating both creep and fatigue loads in a single sequence was used.

The investigations were conducted using reinforced PEEK material, and the results revealed that static loads significantly impact the material's lifespan. To quickly gather reference data and extend the fatigue testing beyond 10^7 cycles, an innovative ultrasonic testing method for reinforced polymers was employed. This method operates at a frequency of 19 kHz and applies pulsed sequences to the specimens, with additional cooling to prevent hysteretic heating. The resulting S/N curves demonstrated a strong correlation with traditional servo-hydraulic testing methods.

Introduction

New regulations aimed at reducing greenhouse gas emissions (such as Austria's goal of becoming climate neutral by 2040) and a shift toward sustainable practices have driven changes in energy production systems. This shift includes renewable mobility solutions like electric vehicles and trains, as well as alternative energy sources such as photovoltaic, geothermal, hydroelectric, and wind power, reducing reliance on fossil fuel-powered plants. These developments create new opportunities for materials and technologies.

In the wind power industry, efficiency, power output, and sustainability are essential for future applications. Over the past decades, wind turbines have increased in both size and power to meet growing energy demands. As a result, larger components like the driveshaft,

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generator, and bearing systems in the engine nacelle are now required.

Due to the size of the bearing cage, transporting and installing it as a single unit is challenging, which has led to the use of a segmented design (Fig. 1). In this design, every second rolling element is fitted with its own cage, supported by the neighbouring rolling elements. A lightweight and sustainable, reinforced material is used for these segmented cages.

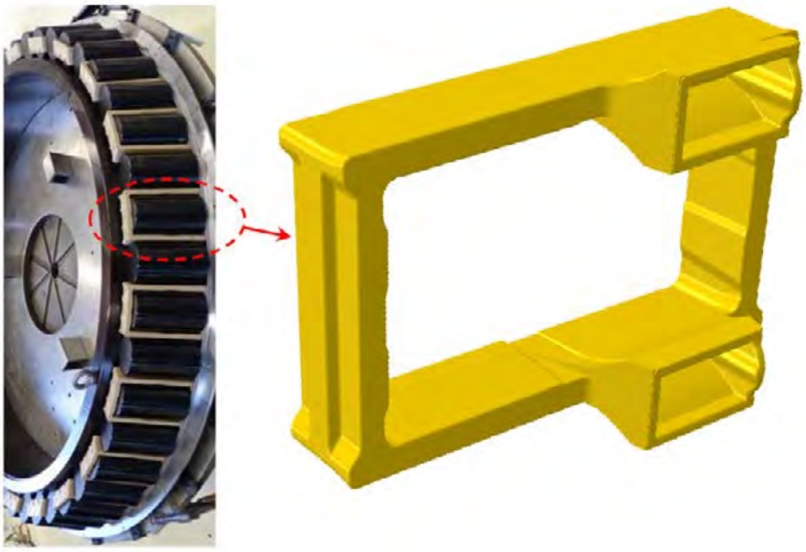

Fig. 1: Segmented bearing cage according to [1]

To assess the lifespan of such reinforced polymers, an approach has been developed and refined over the past 20 years, taking into account various factors such as temperature, fibre orientation, and notches (references [3–5, 7–11], [14, 15]). Given the complex loading conditions, both creep and cyclic loading must be considered in lifetime estimation. A method to account for static loads between cyclic loads was developed and published in 2020 [2], allowing for more accurate testing and evaluation of material performance under combined loading conditions.

Experimental

Creep-fatigue tests

For the experiments, dog boned specimens were taken to perform the creep-fatigue interaction tests. As material, reinforced PEEK was selected and tested fort wo fibre orientations. The tests were performed at stress ratio of R=0.1 and a frequency of 5Hz. The relation between cyclic and static loads was set to 50% to 50% in time with a static load level at the mean load of the cyclic (see Fig. 2).

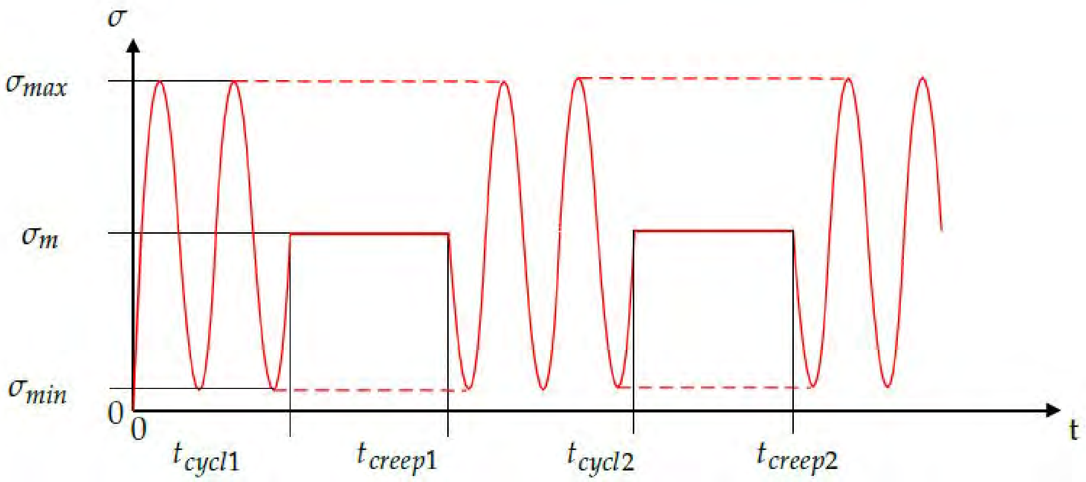

Fig. 2: Testing sequence for creep-fatigue interaction [2]

Pure fatigue tests at the same frequency and stress ratio serves as a reference. To get high cycle fatigue data in a shorter period of time as well as capturing the very high cycle fatigue (VHCF) area (N>10^7 cycles), a method using ultrasonic waves was chosen.

Ultrasonic tests

VHCF tests were performed using self-developed test rig (by University BOKU) using a ultrasonic head directly connected to the specimen [3]. A mass on the non-loaded end of the specimen leads to cyclic forces by acceleration due to resonance caused by the ultrasonic waves. The specimen shape was optimized to reduce the highest loaded volume and results in a test frequency of f = 19 kHz.

Results

The test results show an influence of static loads on the fatigue behavior of reinforced polymers (Fig. 3).

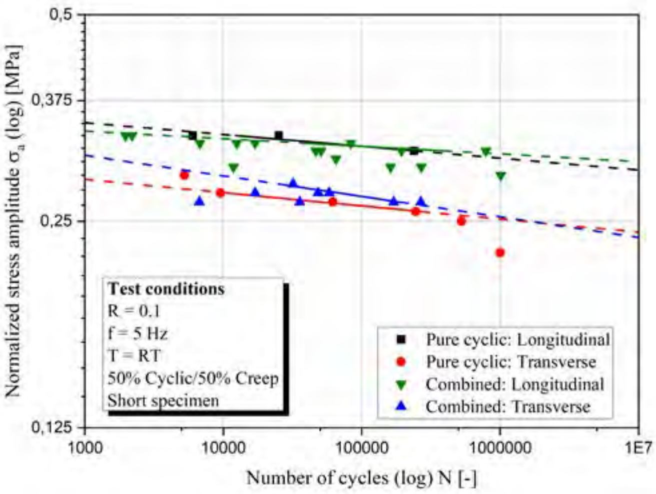

Fig. 3: Resulting S/N-curves for creep-fatigue tests

Especially for transverse oriented specimens, which are more matrix dominated, the effect of relaxation between the cyclic loads acts reinforced. As a result, there is a mor pronounced elongation in lifetime.

The ultrasonic tests show a good match with the servohydraulic and electrodynamic tests (see Fig. 4).

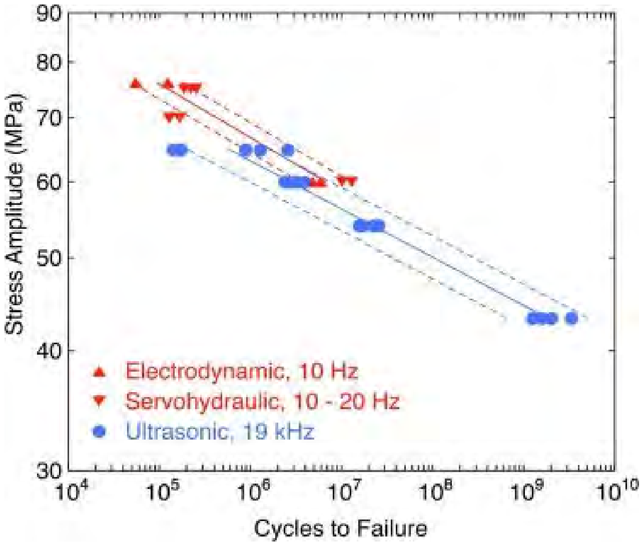

Fig. 4: Resulting S/N-curves for servo hydraulic and ultra-sonic tests [4]

So, the loading frequency doesn't have a big effect in the investigated loading range. Also, the scattering is acceptable for the reinforced PEEK.

Conclusion

Fatigue and creep-fatigue tests were conducted on reinforced PEEK. The results demonstrate the impact of creep on the fatigue behaviour of short fibre-reinforced PEEK, with this effect being more pronounced in transversely oriented specimens. Additionally, cyclic testing using ultrasonic waves was carried out, yielding results that closely align with conventional servo-hydraulic tests. The results also show good reproducibility, as indicated by minimal scatter.

Acknowledgement

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DPI, P.O. Box 902, 5600 AX Eindhoven, the Netherlands
Special thanks to SKF Research & Technology Development, Houten, The Netherlands for data and support.

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Polyethylene pipes for distribution of gaseous hydrogen

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Abstract

The transition to renewable energy systems requires effective methods for storing excess energy, such as converting it into hydrogen (H_2) via electrolysis. A potential method for storing and transporting hydrogen involves injecting it into existing polyethylene (PE) gas networks. However, the effect of hydrogen exposure on the mechanical properties and lifetime of PE pipes remains unclear, especially regarding slow crack growth (SCG). While some studies report minimal impact on polymeric pipes, recent research suggests high-pressure hydrogen could influence SCG performance. This study investigates the effects of long-term exposure to gaseous H_2 at operational pressures (~10 bar) on PE pipes using fracture mechanics methods, specifically cyclic Cracked Round Bar (CRB) tests. Two sets of PE100-RC pipes were tested: one exposed to gaseous H_2 for two years and another subjected to water pressurization for over 1000 hours. The results revealed similar SCG behavior between pipes exposed to both hydrogen and water, indicating that the applied pressure, rather than hydrogen itself, may be the primary factor influencing SCG performance. Future research will focus on chain orientation changes induced by pressure and further long-term testing of PE pipes exposed to both hydrogen and water.

Introduction

A central challenge for future and sustainable energy supply based on renewable systems lies in making the required amounts of energy available at the right place and at the right time. One way to utilize excess energy from renewable sources, which cannot be consumed immediately at the time of generation, is to convert it into hydrogen (H_2) via electrolysis. The disadvantage of using H_2 is the difficulty of storing or transporting it without losses. One option for storing or transporting gaseous H_2 is to inject it into existing gas networks, which largely consist of polyethylene (PE) pipes.

However, doing so in large quantities necessitates knowledge whether the transportation of gaseous hydrogen could influence the properties or lifetime of the pipes. While there is a rather large amount of research addressing this issue for metallic materials [1–5], or short term properties in polymers [6–8], there is hardly any literature available dealing with the

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issue of lifetime estimation [9]. While some studies have found no impact on the expected lifetime of polymeric pipes used for the transportation of gaseous hydrogen based on classical quality safety tests, such as oxidation induction time [10], a more recent study by Byrnes et. al. [11], has shown an impact on the slow crack growth (SCG) performance of PE after the exposure to gaseous H_2 at high pressures of 80 bar. Since the SCG performance is vital to the overall lifetime of PE pipes, these findings necessitate further close examination. Especially the high applied pressure of 80 bar could have introduced artificial orientations in the material, that change the resistance against SCG, but do not necessarily stem from the exposure to gaseous H_2 per se.

To evaluate a potential impact on the expected service life, material taken from pipes used at actual maximum operation pressure (MOP) of around 10 bar with 100% gaseous H_2 are tested within this study using fracture mechanics methods—specifically, the “Cracked Round Bar” (CRB) test. The test is performed both before and after exposure to gaseous H_2.

Materials

The current study entails two sets of tested materials. The first set of material stems from pipes, which have been part of a prior project of the partner DBI†. In the project H_2-Netz and H_2-Infra‡, several types of polyethylene pipes, as well as trenching technologies were tested with regard to possible impacts on hydrogen transportation. From this project, two pipes with a nominal diameter (DN) of 110 mm, made from a high-density polyethylene grade of excellent resistance against crack growth (PE100-RC) were obtained for this study. One of the pipes was unused (retain sample), while the other pipe was used for the transportation of gaseous H_2, at a pressure close to MOP of 8.9 bar for a duration of two years.

The operation at 8.9 bar for two years could have introduced orientation effects in the pressurized pipes, compared to an unused pipe – similar to possible effects of the study in [11]. Therefore, to check for potential influence of the applied pressure itself, a second set of pipes made from a PE100-RC material was used for reference. In this case, two pipes with a DN of 160 mm and a standard dimension ratio (ratio of diameter to wall thickness) of 11 were used. While one of the pipes was again kept as a retain sample, the second pipe was internally pressurized with water at 10 bar and 23°C for a duration of 1376 h.

Experimental

To determine the resistance against slow crack growth, cyclic CRB tests were performed. The samples were manufactured out of the pipe walls of the pipes described in the section materials above. The testing procedure followed ISO 18489:2015 as closely as possible with a frequency of 10 Hz and a load ratio of R=0.1. However, in the case of the pipes pressurized with hydrogen, the minimum specimen diameter of 10 mm (acc. to ISO 18489:2015) could not be achieved due to the thin pipe wall thickness. For these tests, specimens with a diameter of 9.6 mm were used. For the pipes manufactured from

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‡ https://www.dbi-gruppe.de/leistungen-projekte/leuchtturmprojekte/h2infra

the DN 160 pipes, specimens of 14 mm, as proposed by ISO 18489:2015 were manufactured and tested. To compare the results of different sizes, the evaluation via the stress intensity factor (KI) as described in Annex A of the standard was applied.

Results

The results of the first set of cyclic CRB tests is shown in Fig. 1. The results shown are for samples taken from the pipes from the previous project of H_2-Netz. It can be seen, that similar to the results of Byrne et. al. [11] there is a shift in the slope of the fracture curves when comparing samples from the exposed and unexposed pipes. After exposure to gaseous hydrogen at 8.9 bar the slope is shifted in a way, that at high applied stresses the expected lifetime is shorter, while at lower applied stresses the lifetime is shifted towards a higher cycle number, indicating an overall longer lifetime under static pressure as well.

In Fig. 2, the results of the cyclic CRB tests are shown for samples taken from pipe walls after exposure to water with a pressure of 10 bar for more than 1000h and no exposure at all. Interestingly, the curves show the same behavior after pressurization with water, as they did for gaseous H_2. This might be an indication, that the change of slope is not primary due to an impact of the exposure to H_2, but rather an effect of the applied pressure itself.

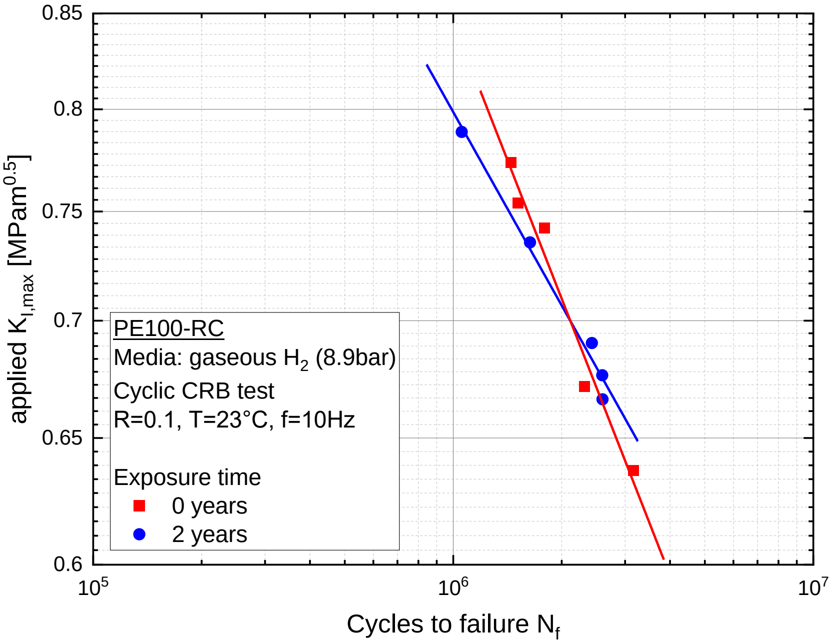

Fig. 1: Results of the cyclic CRB tests of PE100-RC material exposed to gaseous H_2 for 2 years and without exposure

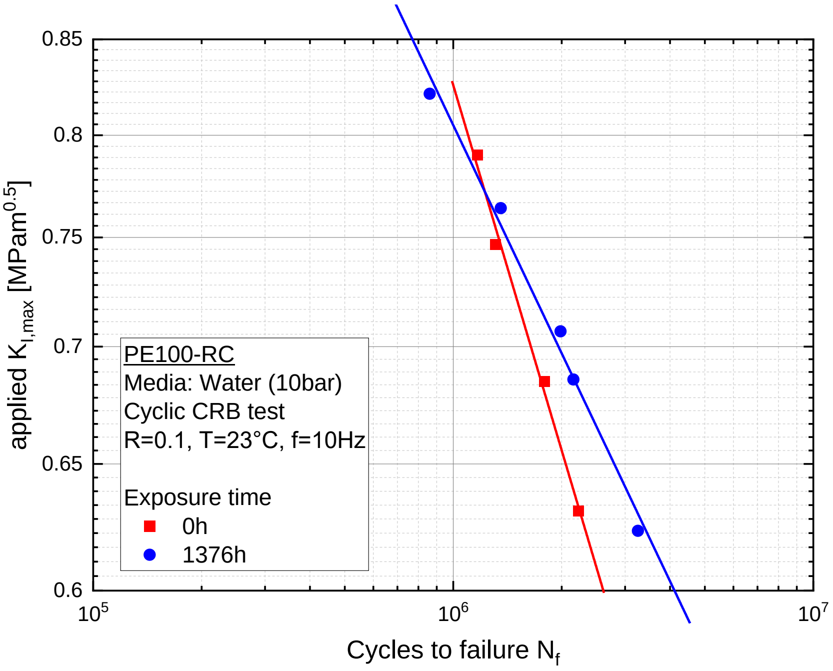

Fig. 2: Results of the cyclic CRB tests of PE100-RC material exposed to water for 1376 hours and without exposure

Discussion and outlook

Based on the preliminary results presented in this work, changes in the resistance against SCG after exposure to gaseous H_2 that were found in literature could stem from the applied pressure itself, instead of ageing due to, or interaction with gaseous H_2. To confirm this hypothesis, further analysis of the tested samples with regard to changes in the chain orientation after exposure to pressure is planned. Additionally, more samples from pipes that were exposed to both gaseous H_2, as well as water, over longer periods of time (5 years for H_2, as well as >5000h for water) will be tested in the coming months.

Acknowledgement

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Enabling glass-free light weight PV modules via honeycomb structures

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BIPV systems need to combine primary building envelope functionalities, (stiffness, wind and water tightness, roof and facade cladding) with the generation of solar electricity [1]. One major challenge for integration of PV into buildings is the weight of standard PV modules, that can reach up to 20 kg/m², with racking even 40 kg/m² [2,3]. Lighter PV modules would enable installation and allow easier integration into areas where standard modules could never be placed.

One approach for glass-free, lightweight PV modules is based on honeycomb sandwich materials used as the back of the PV modules. First iterations of this technology relied primarily on aluminum or Nomex honeycombs. In this work, the properties and suitability of mainly polymeric honeycomb structures is investigated. Suitability for use in PV modules is assessed on the basis of (i) characterization of thermal properties (melting behavior, thermal conductivity), (ii) dimensional stability (CTE), (iii) material compatibility and stability as well as water vapor permeability.

Particular attention is paid to the suitability of honeycomb structures with regard to their behavior during PV module lamination. In addition, the possibility of water condensation in the honeycomb structure and its possible adverse effect on the electrical insulation properties is evaluated.

Key words: glass-free, light weight PV, BIPV, reliability, polymers

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Specialist lectures

SESSION C:
”MATERIALS FOR ADDITIVE MANUFACTURING“

Wavelength Orthogonal Photochemistry in Additive Manufacturing: Towards 3D Structures with Tailored Properties

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Abstract

Photopolymerization driven additive manufacturing (AM) is an established technology for creating polymer 3D structures with high resolution and complex geometries. Recent advancements have focused on AM techniques that support multi-property designs through wavelength-orthogonal photochemistry. In this study, a dual-cure, single-vat resin was developed, utilizing the radical photopolymerization of a thiol-methacrylate monomer system featuring covalently attached chalcone moieties as dimerizable crosslinkers. The additional crosslinking allowed precise control of the glass transition temperature and modulus over a broad range by adjusting the illumination dose with 405 nm light. This spatial modulation of the glass transition temperature in thiol-methacrylate networks facilitated the creation of complex architectures with multiple shape memory transitions, demonstrated on 3D structures produced via DLP-based stereolithography.

Introduction

Orthogonal photoreactions have gained significant attention in polymer chemistry and additive manufacturing due to their ability to provide spatial and temporal control of material properties. These processes leverage the distinct UV-Vis absorption of chromophores to activate separate reactions. However, systems with full wavelength orthogonality remain rare due to overlapping absorption bands at lower wavelengths. Notable advancements include Bochet et al.’s surface-modifying λ-orthogonal deprotecting groups[2], Feringa et al.’s photoswitches combining azobenzene and donor-acceptor Stenhouse adducts[3], and Barner-Kowollik et al.’s two-color flow reaction inducing polymer folding via [2+2] cycloaddition.[4] Despite some systems requiring sequential illumination, they still offer multi-step control over material properties.[5]

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While photoinitiators are standard in light-controlled additive manufacturing, integrating reactive chromophores into 3D structures remains underexplored. These chromophores, such as conjugated π-systems undergoing [2+2] cycloaddition reactions, enable selective control of crosslinking density and material properties.[6-21] Molecules like cinnamic acid, coumarin, and chalcone, known for their photoreactivity for decades [22,23], have been applied in photoresists, nanocarriers, and shape memory polymers (SMPs) over the past 20 years.[21,24,25] Coumarin and cinnamate pendants, for instance, have been used to create temporary crosslinks in SMPs for reversible shape fixation [12,13,15,18,26] or induce shape transitions and swelling behavior in hydrogels via light-modulated crosslinking density.[19] Recent innovations include Rossegger et al.'s work integrating coumarin into a 3D-printable acrylate resin.[11]

Despite progress, cycloaddition reactions remain underutilized in additive manufacturing. Developing photocurable resins containing polymerizable chromophores with orthogonal [2+2] reactivity could enable spatial control of network density, paving the way for multi-property 3D architectures.

Results and Discussion

1.) Spatial Control of Crosslink Density in Photopolymer Networks

The integration of chalcone groups into photopolymer networks enables spatial control of crosslink density through orthogonal photoreactivity to the photoinitiator used as revealed in Figure 1A. Specifically, 4'-hydroxy chalcone was functionalized with methacrylate groups and incorporated as a co-monomer into a thiol-methacrylate system. This system included triethylene glycol dimethacrylate, hexanedithiol, pyrogallol (stabilizer), and bis-(4-methoxybenzoyl)diethyl germane (BMBDG) as the photoinitiator (Figure 1B). BMBDG absorbs visible light up to 470 nm, while the chalconyl chromophore absorbs primarily in the UV region (Figure 1C).

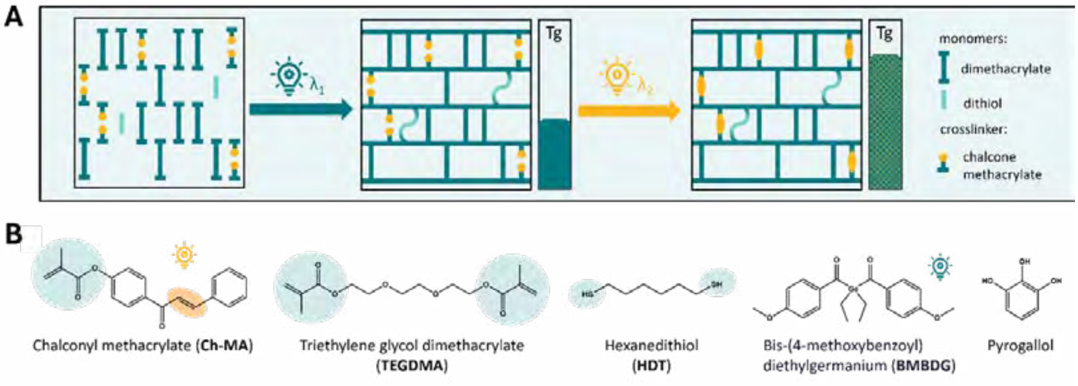

Fig. 1: (A) Schematic representation of the spatial control of the network density using the orthogonal dimerization reaction of pendant chalcone groups. (B) Molecular structure of the resin components.

The orthogonal reactivity of the photoinitiator and chalconyl groups was confirmed via FT-IR and UV-Vis spectroscopy. Under 450 nm light (10.8 J/cm²), the thiol-methacrylate monomers polymerized through radical reactions, incorporating chalconyl methacrylate into the polymer network. FT-IR data revealed rapid conversion of thiol (75%) and methacrylate (98%) groups, while UV-Vis showed no reactivity of chalcone groups at this wavelength. Subsequent exposure to 405 nm light (204 J/cm²) resulted in 95% conversion of chalcone groups without further reaction of methacrylate groups, demonstrating system orthogonality.

Dynamic mechanical analysis (DMA) showed that additional crosslinking through chalcone dimerization increased the glass transition temperature (Tg). Networks without post-exposure exhibited a Tg of 18 °C, while irradiation at 405 nm increased Tg to 41 °C. Increasing chalconyl methacrylate concentration from 20 to 40 mol% further enhanced Tg modulation, with post-exposure raising Tg from 19 to 48 °C.

2.) Local Control of Network Density Enables Stimuli-responsive 3D Macrostructures

The homogeneous thiol-methacrylate networks provide narrow glass transitions, facilitating sharp shape-memory effects. Spatial control of the Tg in 3D-printed parts enables complex architectures with multiple shape-memory transitions.

To demonstrate this, a butterfly structure was molded under 450 nm illumination, and the lower wings were further exposed to 405 nm light (408 J/cm²) in a post-processing step (Figure 2). During shape memory experiments, the structure was heated above both Tg values (60 °C), deformed, and cooled to 4 °C to fix the deformation. Stepwise heating above Tg1 (25 °C) and Tg2 (60 °C) caused sequential relaxation of the wings, following the illumination pattern.

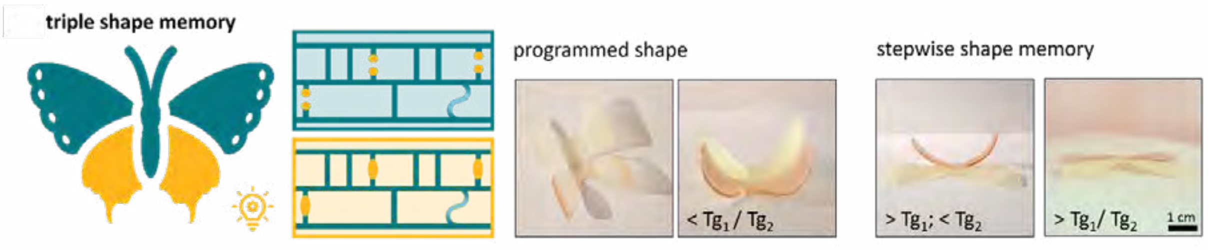

Fig. 2: Schematic representation of the change in the polymeric network upon partial illumination with light of 405 nm (λ2) and photographs monitoring the shape memory sequence.

Conclusions

This study explores a dual-cure, single-vat resin system based on the radical polymerization of a thiol-methacrylate monomer formulation incorporating covalently attached chalcone moieties as dimerizable crosslinkers. This method provides spatial and temporal control over the thermo-mechanical properties of thiol-methacrylate networks through λ-orthogonal [2+2] cycloaddition of pendent chalcone groups, either during printing or in a subsequent post-processing step.

Reaction kinetics were analyzed using infrared (IR) and ultraviolet-visible (UV-Vis) spectroscopy to confirm the λ-orthogonality of the polymerization and crosslinking processes. The additional crosslinking facilitated precise adjustment of the glass transition temperature and modulus across a broad range by modulating the illumination dose with 405 nm light. Spatial control of the glass transition temperature enabled the creation of complex architectures with multiple shape memory transitions, as demonstrated in a 3D structure fabricated via DLP-based stereolithography.

Acknowledgement

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Design and Additive Manufacturing of Mechanical Metamaterials for Structural Applications

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Abstract

Mechanical metamaterials are a class of engineered materials with unusual mechanical properties, such as negative Poisson's ratio, negative or tunable stiffness, high strength-to-weight ratio or folding structures, among others. Their uncommon properties can be tuned by geometric parameters and realized with a wide variety of manufacturing technologies and materials. This variety opens new prospects for engineering and functional designs for structural applications. Herein we present the design, additive manufacturing and mechanical testing of newly developed mechanical metamaterials. First, a new kind of bending dominated structure with independently tunable stiffness in the three spatial directions was developed. This enables precise engineering of structural responses, where mechanical properties can be tailored to exhibit varying degrees of directionality - from completely uniform (isotropic) behavior to highly directional (anisotropic) responses. By introducing an asymmetry into well-established chiral-based metamaterials, we were also able to increase the tunability of the Poisson's Ratio, Young's modulus and porosity of such structures. Similar designs also allow for tunable normal-strain shear coupling effects in compliant structures. Different additive manufacturing techniques were used to manufacture polymer-based specimens, namely Fused Filament Fabrication, Digital Light Processing and Selective Laser Sintering. The properties of the structures were determined by means of mechanical tests. Additionally, numerical models were developed to verify the applicability of simulations to represent the mechanical tests and to investigate the influence of the geometric parameters onto the mechanical properties.

Introduction

Figure 1 (left) depicts a mechanical metamaterial with tunable stiffness [1]. Advancing from well-established mechanical metamaterials concepts, the proposed geometry allows to vary the stiffness in the three spatial directions independently. This is achieved with a grid of cubes, connected by alternating struts. The stiffness of the structure can then be tuned by increasing or decreasing the thickness of the struts. In addition to the independent tunability, local and gradual stiffness variations can also be incorporated in the design. The proposed

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metamaterial design permits to create a customizable stiffness distribution across several orders of magnitude, based on simple geometric parameters. This opens the possibility to create components for complex load and/or boundary conditions with a single material, reducing the need for multimaterial and composite designs. Single material structures simplify the design process and improve the recyclability of a component. Since the structures can be produced with various additive manufacturing techniques and their respective materials, the possible applications range from soft, dampening to stiff, load bearing structures.

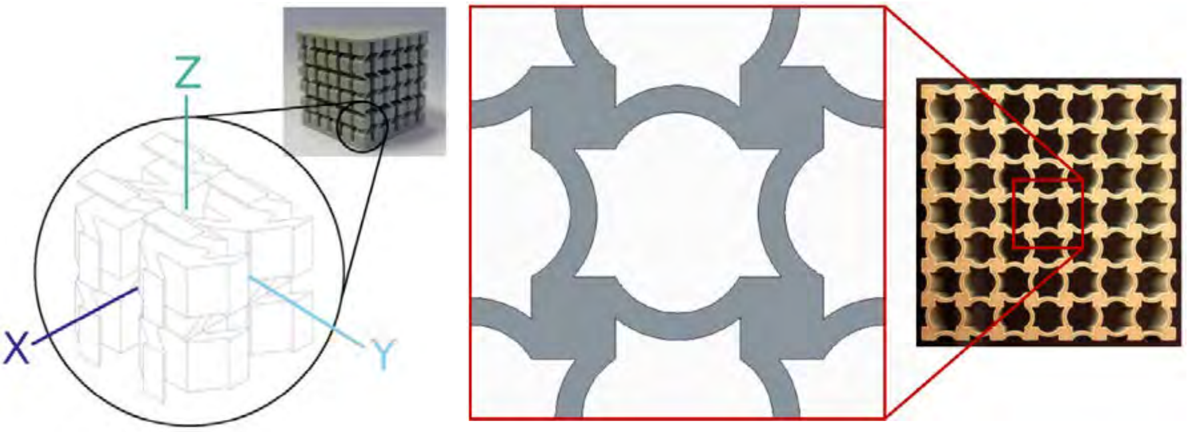

Fig. 1: Mechanical metamaterials with variable stiffness (left, [1]) and variable Poisson‘s ratio (right, [2]).

Additionally, we studied the behavior of so-called (anti-)chiral structures, which basically consist of specifically aligned nodes and their rod connectors (see Figure 1, right, [2]). From an engineering point of view, this topology represents a sequence of very small solid-state joints. Depending on the number of the connecting rods, the symmetrical alignment of the node-rod pairs and the geometrical features of nodes and rods, the mechanical behavior of such structures can be widely varied. One of the most important characteristics of these structures is their auxetic behavior, that is, they show a negative Poisson’s Ratio, which is additionally tunable (common materials in engineering and nature - polymers, metals, ceramics, etc. - have a positive Poisson’s ratio typically in the range of 0.2 – 0.5). Using the tunability of the Poisson’s ratio and the compression-shear coupling (see Figure 2, [3]) of some of these structures we created metamaterial designs, which reversibly changed their shape upon loading. This shape morphing capability is highly tailorable. The development was conducted numerically (using simulations, genetic algorithms and optimization tools) and experimentally verified using 3D-printed samples. The presented structures allow for a 2-dimensional or even 3-dimensional deformation upon loading in one single direction. Moreover, their mechanical compliance is tunable over a wide range and, if designed correctly, completely reversible. Hence, there are numerous potential applications, for example for transversal positioning and / or setting elements, (reversible) joining elements, drive coupling (clutch), seals, adjustable damping elements or adaptable molds.

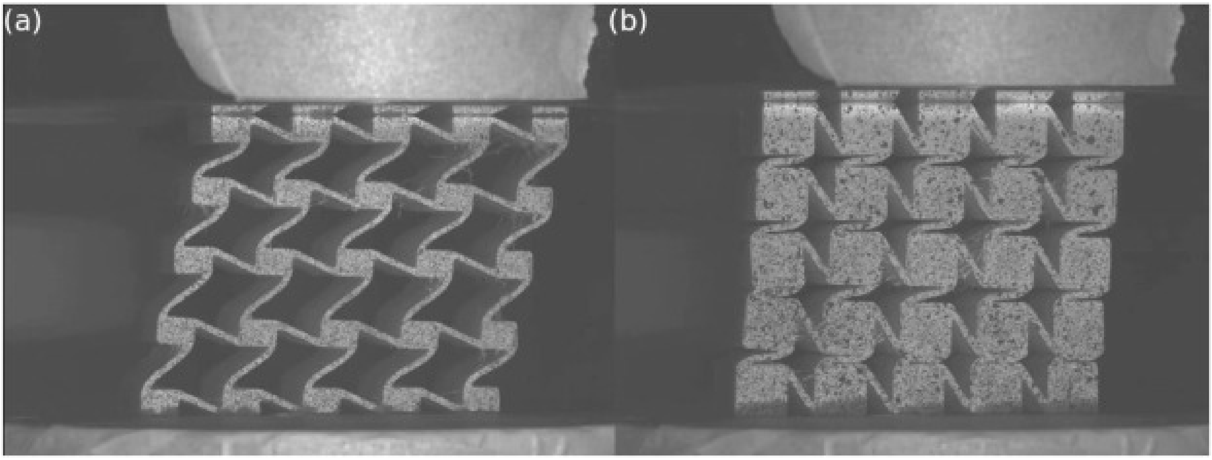

Fig. 2: Compression tests of mechanical metamaterials with tunable normal-strain shear coupling effect for compliant structures. (a) Structure with strong shear effect and (b) structure with small shear effect [3].

The design, additive manufacturing and experimental investigation of the structures is accompanied by the development of software tools [4,5]. On one hand, these tools allow for an automated development of new metamaterial designs based on porous structures. On the other hand, they enable an automated distribution of metamaterial unit cells to create a predefined deformation behavior under load. These software tools speed up the design of new metamaterials in general, as well as the development of metamaterials for specific applications.

Acknowledgement

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Strategies for robot based large-scale polymer additive manufacturing

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Abstract

Robot based large scale additive manufacturing is a cost-efficient production strategy for complex designs and low to medium production rates, due to the flexibility of the multi-axis machine configuration. The stability of this production process mainly relies on the development of appropriate materials and the validation of material and process parameters that enable the exploitation of the full potential of this approach. State-of-the-art planar and non-planar slicing strategies in combination with dynamic material control increase the number of designs that can be manufactured with robot based additive manufacturing systems.

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Setup of a large-scale additive manufacturing robot cell

The basis setting for research or industrial applications of a robot cell for additive manufacturing mainly consists of the 6-axis robot, that is guided by a controlling unit. This unit ensures that the robot follows the path that is defined by the operator or by the slicing software directly. Depending on the kind of additive manufacturing approach that is considered the design of the printing head that is attached to the robot flange differs. When it comes to polymer-based products, the heads cand be split into two groups with regard to the process. To begin with there are heads that are designed for filaments as the basic material, whereas the second group only considers granulates. Both groups fulfill the needs of industries with different requirements, like costs, part size and production rates [1]. The head and especially the local output rate is managed by the head control unit that is guided by the controller unit of the robot. As a consequence of the temperature dependent material behavior and the pressure dependent nonlinear material output function [2], a calibrated control unit is essential to ensure a constant material quality throughout the complete print.

Static planar printing tables or existing nonplanar parts act in a 6-axis setting as the substrate to print on. More complex designs, that for instance consider overhangs or regions that are horizontal, require more sophisticated robot cells that take one or two axis positioners into account. Those additional axes position the part in a way during the whole production process so that the cone limitation requirement of the print head, which ensures a stable material flow is achieved.

Beyond that, there is also the trend towards printing larger parts, especially in the boat industry. Each robot offers a certain work envelope that can be covered, depending on the robot size. When it comes to significant large parts that exceed this envelope the robot can be mounted on rails that are controlled as an additional external axis by the robot controller.

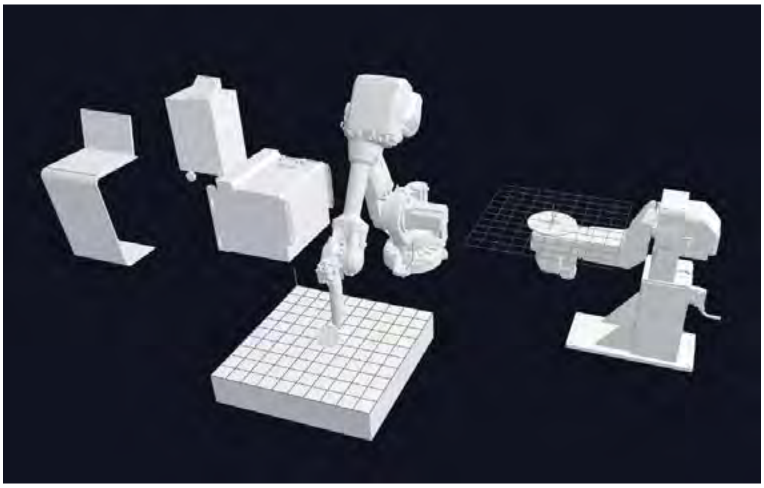

Fig. 1: Example of a robot cell for additive manufacturing

In a robot cell all the axis and the extrusion rates of the print head require and overall orchestration to apply planar or non-planar slicing strategies, which is achieved by state-of-the-art slicing and robot software applications, like the software AdaOne, where a certain workflow and different slicing strategies are applied to ensure the correct robot behavior based on the part design.

Engineering workflow for robotic additive manufacturing

As a consequence of the complexity of handling robot cells, a creation of a digital twin in a slicing and robot software is essential. The robot cell is rebuilt as a 3D scene in the software and the relative positions and orientations of the cell components, like a positioner or static components, to the robot. A calibration of the print head ensures the print quality, taking standard procedure like the multiple approach paths technique to ensure triangulation into account.

Next to the creation of the digital twin the validation and development of process parameters are essential to ensure stable production processes. The parameters (perimeter width, perimeter overlap, print speed, etc.) depend on the sort of material, if it is reinforced, the extruder setting and extruder design and the kind of part that is supposed to be printed (for instance: wall, solid block, number of layers). Based on these definitions and calibrated data, the engineering process for the path creation for any kind of part design is performed.

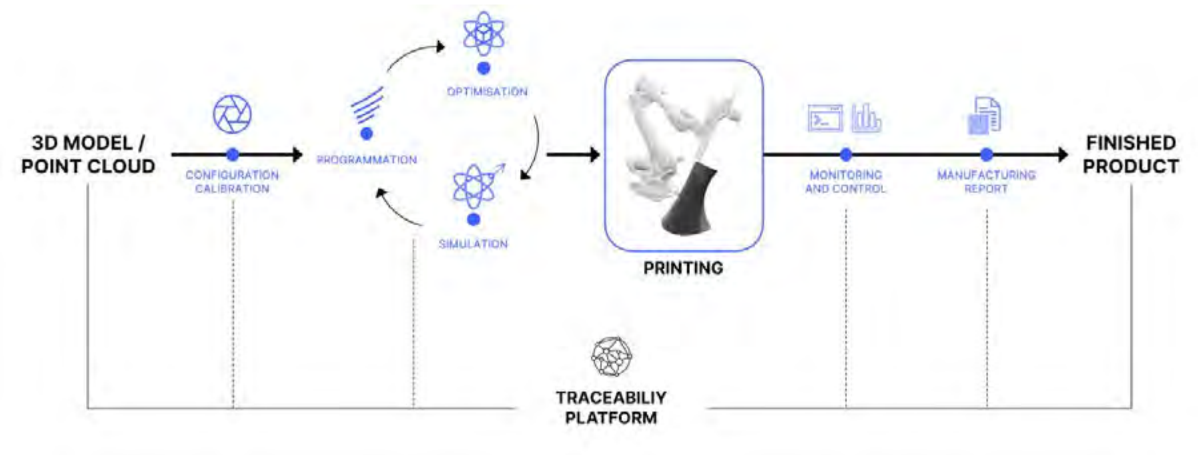

Fig. 2: Engineering process for additive manufacturing

When it comes to slicing it needs to be distinguished between planar and nonplanar slicing strategies. Planar slicing strategies require at least three axes to make the print work. In case of overhangs at least one additional axis is mandatory to align the head towards the curvature. Additive manufacturing technology is applied on different use cases and a few of them are listed below.

Slicing strategy for radial symmetric designs

Radial symmetric parts, like vases, offer the possibility to be printed by a planar horizontal slicing approach. However, this approach could lead to staircase effects [3] or curvature dependent changes of the thickness. Beyond that, if a certain overhang limit is reached, whose limit is also related to the ratio between bead width to bead height, the design cannot be printed with this approach. As consequence a strategy is required that aligns the head towards the local orientation of the curvature, to cover those issues.

Fi. 3: Slicing strategy for radial symmetric designs

Slicing strategy for bent designs

In different applications the design features a certain curvature that needs to be taken into consideration when the path is created. One example is a bent pipe. The print head requires a defined orientation for each point that is stated by the path data so that it is tangent to the curvature. What is more, because of the curvature, the distance between the layers on the inner radius is smaller than on the outer radius. That requires dynamic control either of the velocity or the material extrusion of the print head, so that less material is applied on the inner region and more material is applied on the outer radius. Figure 4 shows the distribution of the material deposition of a bent pipe with a hexagonal cross-section.

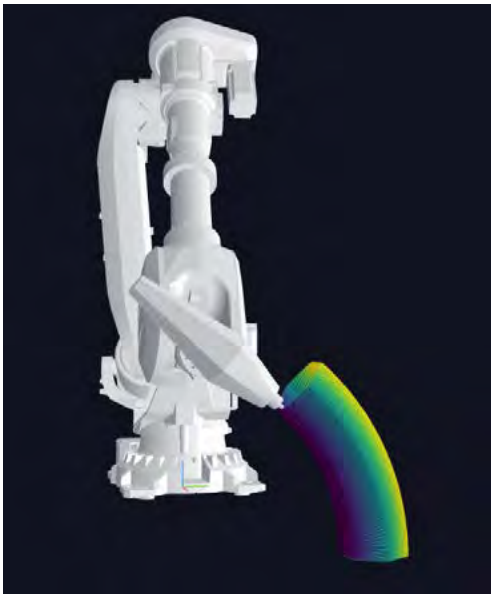

Fig. 4: Slicing strategy for bent designs: The different colors show the local change of the deposition

Slicing strategy for large nonplanar designs

Designs with a closed top surface that contains overhangs, a support or infill structure is required, that increases the material consumption and the weight of the part.

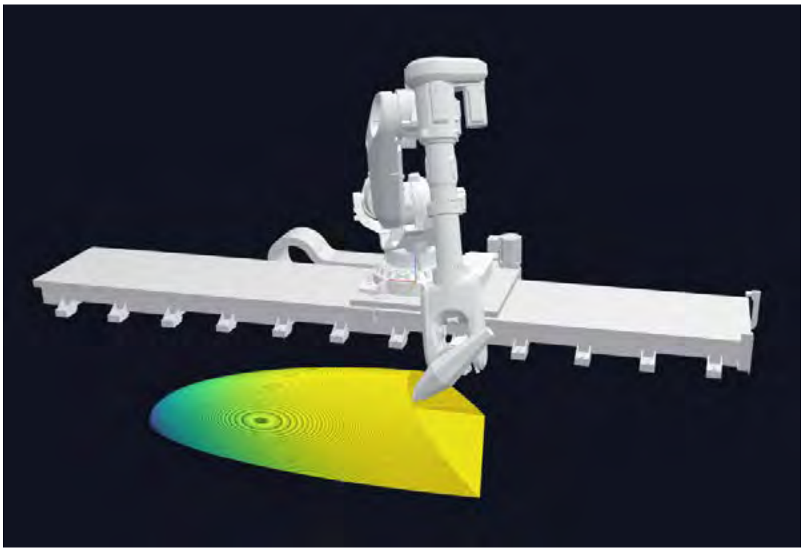

Fig. 5: Slicing strategy for large nonplanar designs: Printing of a boat

Therefore, the orientation of the print plane is turned until an orientation is reached, where the angle of the initial overhang area to the reoriented print plane is below the overhang limits. This is a common approach to print boats, as it is shown in Figure 5 and molds. In those cases, a reduced density for infill structures or just perimeters are necessary to withstand the loads during the lifetime.

Slicing strategy to print on existing nonplanar designs

The flexibility of the robot based additive manufacturing systems allows the printing on various existing parts to increase the functionality or stability of the existing product or for maintenance purposes. Certain cladding strategies are applicable that create robot paths to thicken the non-planar surface that are considered or print stiffener structures onto it. The head is aligned towards to local orientation of the surface to ensure a constant quality throughout the whole print.

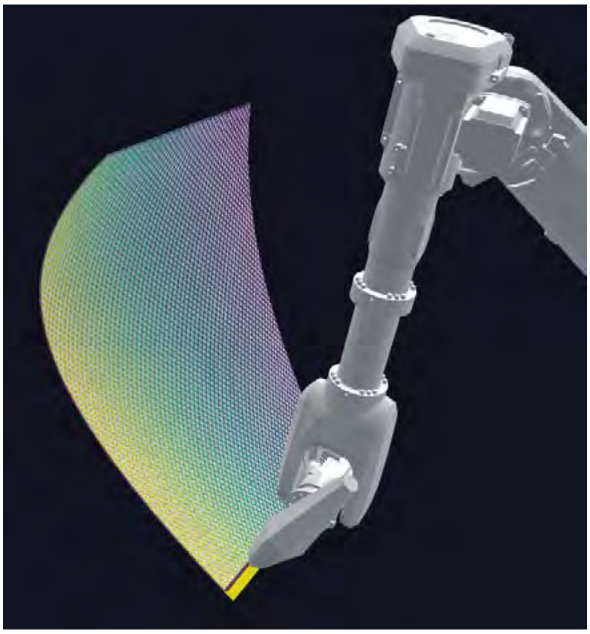

Fig. 6: Slicing strategy to print on existing nonplanar designs: Printing of a hexagrid stiffener structure and a flange at the bottom

In the case where a defined design should be added onto the existing nonplanar design the curvature needs to be considered as the substrate and the path is aligned towards the surface. The head needs to be tilted according to the substrate orientation and the path is required to be designed in a way to level out the uneven design and make a print of the additional design possible.

In addition to these approaches there are other slicing techniques that enable the creation of even more complex designs, like sculptures, and the combination of different slicing approaches heightens the level of possibilities even more.

The down streaming process is the surface finishing step that is performed by the robot as well to ensure an increased surface quality. Therefore, additional thickness for the machining and adapted surface finishing paths are required to ensure drilling, surface finishing and cutout operations on a nonplanar part.

Acknowledgement

These developments would not have been possible without dedicated researchers in the field of robotic engineering and additive manufacturing that shift the limits of this technology further and further.

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Analyzing and Predicting Failure Modes in Mono- and Multi-Material Extrusion-based Additive Manufactured Structures

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Abstract

Since the inception of fused filament fabrication (FFF), its applications have rapidly expanded into fields like medical technology, where reliability is crucial. The layer-by-layer nature of FFF results in interfaces between deposited strands and layers, whose strength varies based on process parameters and material combinations. By manipulating these interfaces, the mechanical performance and especially the crack propagation path in the material can be controlled. The study draws on the pioneering models of Cook & Gordan and He & Hutchinson criteria, which predict crack behavior based on interface strength and fracture toughness ratios, respectively. To evaluate the applicability of failure prediction models, various materials and printing parameters were selected for both mono-material and multi-material FFF structures. Mono-material tests involved four polymers, including PETG, PLA, and two PMMA variants, while the multi-material tests combined PETG with a thermoplastic elastomer (TPC) as an interlayer. The results indicate that the C&G criterion is capable of accurately predicting the failure mode in mono-materials, provided that the assumptions of LEFM are not significantly violated. However, at lower strain rates and with the inclusion of soft interlayer materials (multi-material systems), the predictions no longer hold, highlighting the need for more innovative or expanded criteria in the future. The H&H criterion, on the other hand, fails to accurately predict the crack path in mono-materials.

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Introduction

Since the development of fused deposition modeling (FDM), also known as fused filament fabrication (FFF), in the late 1980s [1], the range of potential applications has continuously expanded, penetrating fields such as medical technology [2], where high reliability in component functionality is essential. Due to the layer-by-layer construction of components in the FFF process, interfaces form between the deposited strands and layers, which may vary in mechanical properties. This variation largely depends on process parameters (e.g., nozzle temperature, print speed, print orientation, infill, etc.) and material selection (mono-material or multi-material). By intentionally manipulating the interface properties, it is possible to adjust the mechanical performance and control crack propagation direction, influencing failure behavior and specifically the fracture toughness. As schematically illustrated in Figure 1, the control of interface properties can be achieved through process control in mono-materials or material control in multi-materials. When a crack approaches a weak interface, it tends to deflect into the interface (crack deflection). Conversely, if the interface is strong, the crack is more likely to penetrate subsequent layers (crack penetration).

Based on this knowledge, the following questions arise from an engineering and scientific point of view: What conditions (e.g., strength, fracture toughness) must be met at the interface to direct crack growth in a desired direction, and are there methods to predict the crack propagation path?

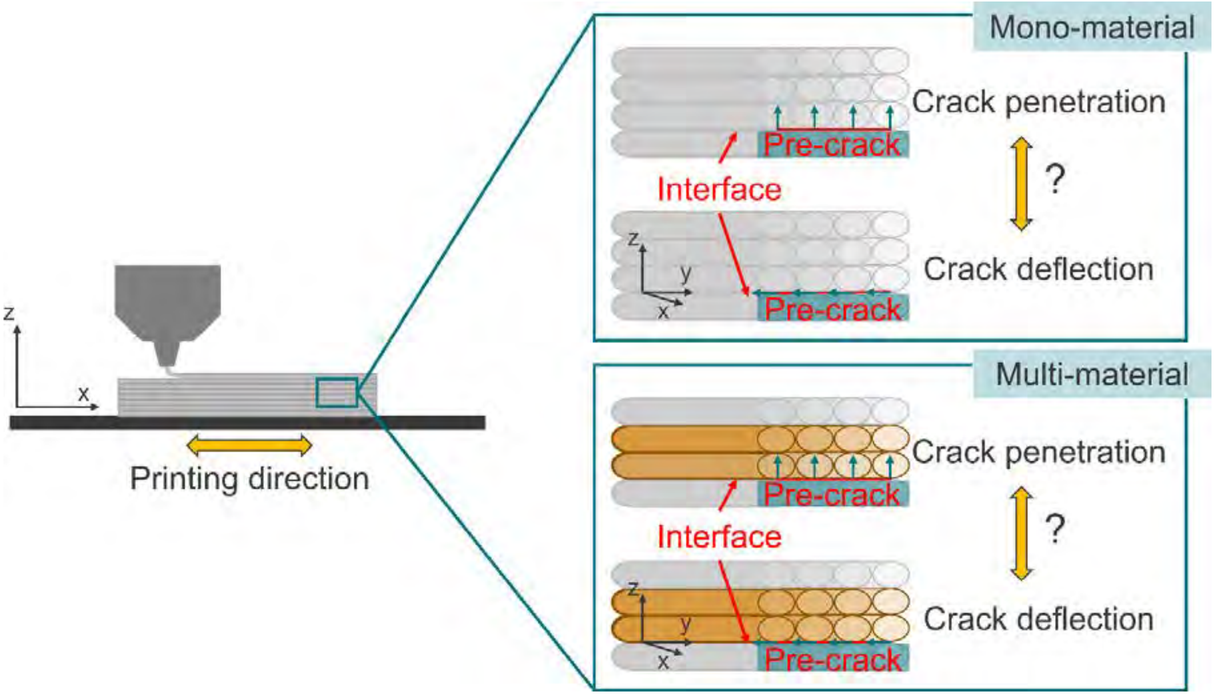

Fig. 1: Schematic representation of possible crack propagation paths in mono-material and multi-material FFF structures.

These questions were first addressed by Cook & Gordan in 1964 [3] in a brittle fiber-reinforced material system. Using stress field analyses at the crack tip, they observed that cracks preferentially deflected when the theoretical tensile strength of the interface was less than 1/5 of the tensile strength of the matrix material (the material adjacent to the interface). Beyond this threshold, crack penetration was more commonly observed. He & Hutchinson (1989) [4] took a different approach, describing the problem using linear elastic fracture mechanics (LEFM). They identified a critical value of 0.25 (ratio of interface fracture toughness to matrix fracture toughness) at which the transition between crack deflection and penetration occurs. Below this value, cracks tend to deflect; above it, they tend to penetrate.

To date, these models and approaches have been refined and expanded [5], including combined criteria. However, experimental work remains limited, with a few studies in ceramics [6-9] and even fewer in polymer materials [10-12]. On this account, this study aims to evaluate the applicability of these models from C&G and H&H for predicting failure mode (crack deflection vs. penetration) in various FFF-printed polymers, both in mono-material and multi-material configurations.

Experimental

To assess the applicability of the proposed approaches for predicting failure modes, a range of materials and printing parameters were selected for both mono-material and multi-material structures, as shown in Figure 2. Each approach was investigated in detail using distinct experimental methods.

For the mono-material investigations, four different materials were examined: glycol-modified poly(ethylene terephthalate) (PETG) and polylactic acid (PLA), both sourced from Prusa Polymers (Prusament PETG Jet Black and PLA Jet Black, Czech Republic); poly(methyl methacrylate) (PMMA) from Mitsubishi Chemical Europe GmbH (3Diakon™, Germany); and a PMMA variant from Herz Austria GmbH (Austria), referred to as PMMA-s.

In the multi-material investigations, PETG was employed as the stiff matrix material, while a thermoplastic elastomer (TPC) based on copolyester from Formfutura BV (FlexiFil™ White, Nijmegen, Netherlands) served as the compliant interlayer material.

Tensile specimens were printed under the conditions outlined in Figure 2 to evaluate the C&G approach. To assess the validity of the H&H criterion, single-edge notched bending (SENB) specimens were printed. In both cases, the specimens were manufactured to allow the determination of interface strength (σi) and fracture toughness (Πi) (printed vertically in the z-direction) as well as matrix strength (σm) and fracture toughness (Πm) (printed horizontally in the x-direction). Detailed information regarding specimen preparation can be found in e.g Ref. [13].

Tensile strength testing was conducted in accordance with DIN EN ISO 527-2 [14], with a constant crosshead speed of 10 mm/min, irrespective of whether the samples were mono- or multi-material. Fracture toughness measurements for the mono-material specimens, corresponding to the H&H criterion, were carried out following ASTM D 5045 [15], using the same crosshead speed of 10 mm/min.

In addition, the effect of strain rate (0.1, 10, 1000 mm/min) on failure behavior was investigated, along with the ability of the C&G criterion to predict the correct failure mode under varying conditions.

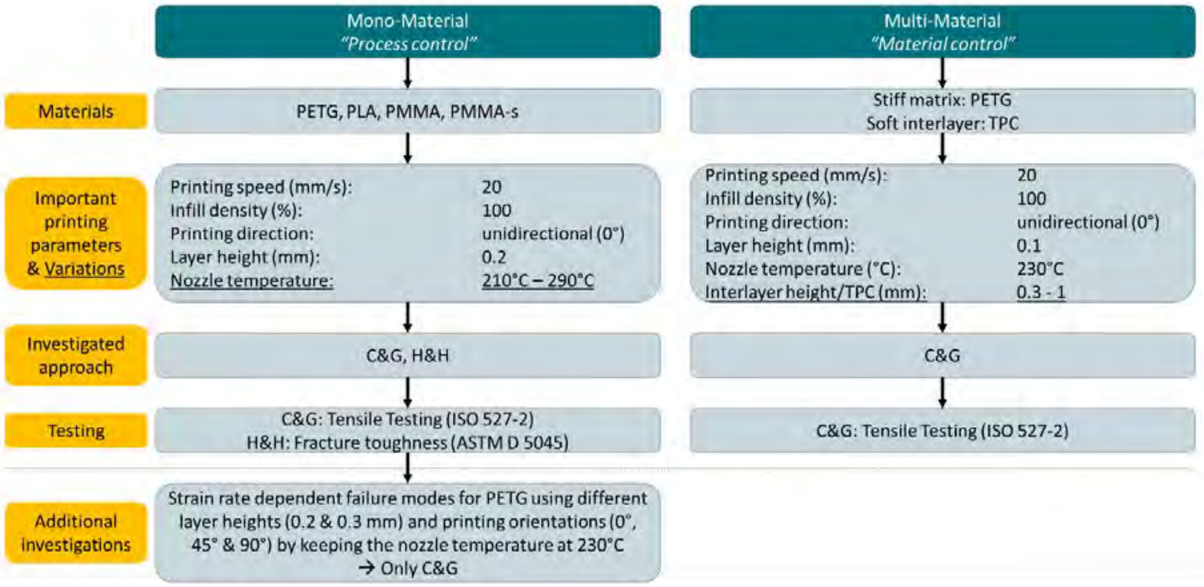

Fig. 2: Representation of the materials used, printing parameters, investigated approaches, testing methods, and additional investigations for mono -and multi-material.

Results

The results of the mono-material investigations demonstrate that the crack path can be controlled through variations in nozzle temperature. Lower nozzle temperatures lead to a weaker interface, generally allowing cracks to deflect. This failure behavior was correctly predicted by the C&G criterion for all tested materials, whereas the H&H criterion did not show accurate matches. Possible reasons for this include the partial failure to meet the assumptions of the LEFM, as well as the difficulty of precisely introducing a crack at the interface (H&H assumes the crack is already at the interface, while C&G does not). Additional studies on PETG at different strain rates revealed that the C&G criterion is capable of accurately predicting the crack path as long as the conditions remain close to those required by LEFM (i.e., small plastic zone size and minimal nonlinearity), regardless of print orientation and layer height. These conditions appear to be met at moderate to high loading rates (> 10 mm/min). However, at lower loading rates, the criterion is unable to accurately predict the failure mode.

In the multi-material investigations, it became clear that the C&G criterion is not capable of correctly predicting the crack path. Similar to the behavior observed in PETG at low loading rates (0.1 mm/min), the inclusion of a soft interlayer deviates further from the LEFM requirements, rendering the criterion unreliable for failure mode prediction. The threshold for the transition between crack deflection and penetration seems to shift to higher values (~0.5, instead of 0.2).

Overall, the H&H criterion appears unsuitable for accurately predicting crack propagation in FFF-printed structures. In contrast, the C&G criterion remains reliable as long as conditions stay near the LEFM requirements. To address the challenges posed by increased nonlinearity, innovative approaches such as the Equivalent Material Concept [16] or the Fictitious Material Concept [17] could be integrated with the C&G model in future work, potentially mitigating issues associated with nonlinearity.

Acknowledgement

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Feedstock Development for Material Extrusion of Aluminium: Printability and Debinding

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Abstract

Metal material extrusion (MMEX) is a fabrication method that involves the progressive deposition of metallic materials in distinct layers. This process is followed by debinding and sintering, ultimately resulting in the formation of fully dense metallic structures. The sintering temperature of aluminium (Al) alloys is relatively low, which approaches the degradation temperature of the polymers employed and needs special sintering regimes. Additionally, the binder systems utilized in this process must fulfil several criteria, including filament flexibility, appropriate rheological properties, and satisfactory performance during the debinding process. Consequently, the development of an effective binder system that satisfies all these requirements presents significant challenges. In this study, polypropylene (PP) and polyethylene (PE) as the backbones along with thermoplastic elastomer (TPE) as the soluble part of the binder system were used in the feedstock. Filaments with a powder loading of 55 vol.% were successfully produced from the feedstocks, and their printability was assessed. Rheological analysis was performed to evaluate the flow characteristics of the feedstocks, ensuring their suitability for the printing process. Additionally, the thermal properties, including thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), were conducted to compare the degradation behaviour of the various binder systems.

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Manufacturing of Soft Dielectric Actuator Assemblies by Material Extrusion (MEX)

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Abstract

Dielectric soft actuators use the Coulomb forces to generate motion. Their commercial availability, and hence, their technological relevance are still rather limited for different reasons. In-depth material know-how in terms of electrical and mechanical behavior is required, materials have to be available in thin sheets, and the complicated fabrication is prone to errors. In order to change this, the paper presents a novel soft dielectric assembly produced by Material Extrusion (MEX). The soft dielectric actuator was 3D printed completely in using and is fully functional without any further manufacturing steps. By incorporating a third material into an FFF 3D printer, a soft dielectric actuator assembly in the form of a 3-finger gripper was successfully 3D printed. Since the FFF machines are already quite widespread nowadays, our manufacturing approach offers the potential for user customized actuators, which are easily accessible and comparably affordable. Only requirement is an FFF printer with at least two independent printing nozzles.

Introduction

“Soft actuator” is the term that describes a highly adaptable and multi-functional actuator, with the added advantage of safe interaction with humans [1,2]. This paper is dealing with a soft actuator sub-type known as “Dielectric Elastomer Actuator” (DEA). They are activated by a high electric field and do not need any additional fluids (like compressed air) or high magnetic fields. Therefore, these actuators are highly energy-efficient, do not need mechanical components for their actuation (valves, compressors, pumps etc.) and are maintenance-friendly. Their typical applications are, for example, in the fields of animatronic actuators, Micro Electro Mechanical Systems (MEMS) and soft robotics [3–4]. Such actuators can be integrated into a larger structure, referred to as a soft dielectric assembly.

Various additive manufacturing (AM) technologies have advanced over the past decade,

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prompting researchers to explore their potential in fields where traditional manufacturing technologies may fall short of meeting specific requirements. In this work, Filament Fused Fabrication (FFF), a subtype of Material Extrusion (MEX), is used to manufacture the Dielectric Elastomer Actuator (DEA). Our research group has already demonstrated the usability of FFF in the DEA field with the first fully 3D-printed DEA [5]. The main goal of this work was to extend and upgrade simple DEAs into more complex structures, enabling the fabrication of soft dielectric assemblies through FFF.

At Montanuniversität Leoben and PCCL GmbH, extensive experience has already been gained with MEX 3D printing. Numerous projects involving various polymers and applications have been conducted. In this work, this expertise has been further expanded into the field of soft actuators.

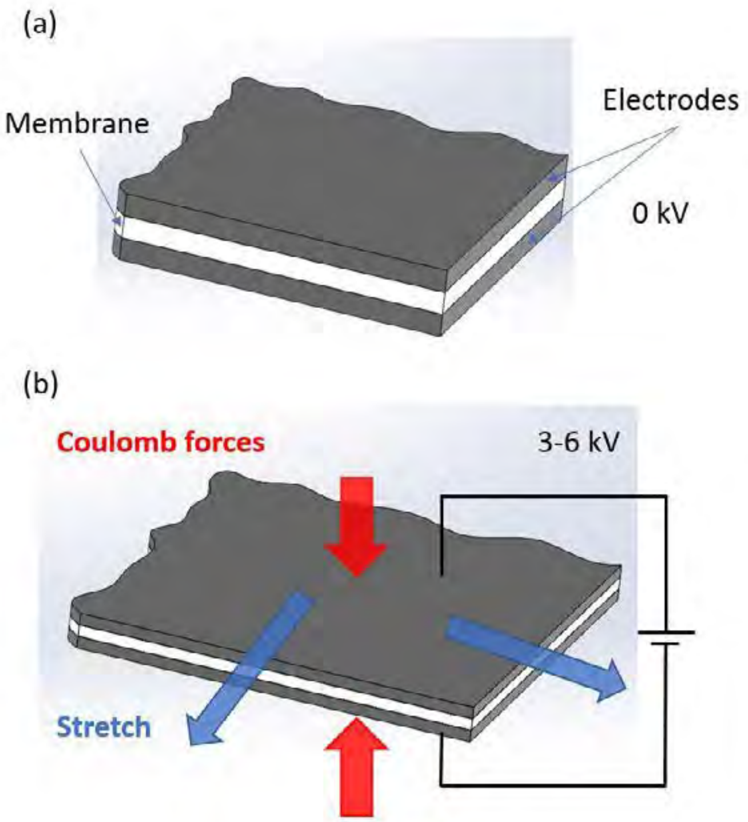

Fig. 1: Graphical representation of the actuation principle of a Dielectric Elastomer Actuator (DEA): (a) **Non-actuated** – no voltage (0 kV) is applied to the electrodes, and therefore no Coulomb forces are present to compress the membrane. (b) **Actuated** – a high voltage (3-6 kV) is applied to the electrodes, generating Coulomb forces that compress the membrane, resulting in a stretch in the orthogonal direction. [5]

The actuation principle of Dielectric Elastomer Actuators is shown in Figure 1 and described in [6,7]. It is based on Coulomb forces that occur between two electrodes with different electrical potentials. Thus, DEAs consist of two main parts: an electrode and a membrane. Combining this actuation principle with soft and flexible materials results in soft actuators that are only driven by (high) electrical voltage.

The actuation pressure, acting on the membrane, caused by Coulomb forces is calculated according to the mathematical expression shown in Equation 1.

$$p = \varepsilon\varepsilon_0 E^2 = \varepsilon\varepsilon_0 \left(\frac{V}{z}\right)^2 \qquad (1)$$

The equation result p is the pressure caused by Coulomb forces, ε is the dielectric constant of the membrane material, is the permittivity of free space and E represents the electric field. The electric field between the DEA's flat parallel electrodes is actually the voltage V applied on the electrodes divided by the membrane thickness z. Hence, to maximize the Coulomb forces and thus the actuation force of a DEA, the following three points have to be considered [5]:

- a maximum dielectric constant of the membrane material is required,
- the membrane thickness has to be minimized and
- a maximum actuation voltage has to be used.

The membrane thickness and the actuation voltage are parameters that are easy to adapt. On the other hand, as an intrinsic property, the dielectric constant is a material-specific parameter.

Additive Manufacturing in context of DEAs

Different researchers were trying to produce DEAs using different AM technologies. Since the DEA consists of two different materials with contradictory material properties, it is not an easy task. For example, the electrode material must ensure electrical conductivity, while simultaneously being flexible, and thus „soft".

3D printing of DEAs by Fused Filament Fabrication (FFF)

Fused Filament Fabrication (FFF) is widely used AM Technology. Due to its simplicity, many hobbyists use it for various projects, but it is also employed to produce functional technical parts. The main advantages of FFF are the affordability of 3D printers, the simplicity of the process, and the wide range of available materials. Over the past 10 years, many different 3D printing filaments have been developed and are now commercially available. For 3D printing of DEAs, two important filament properties are flexibility and electrical conductivity.

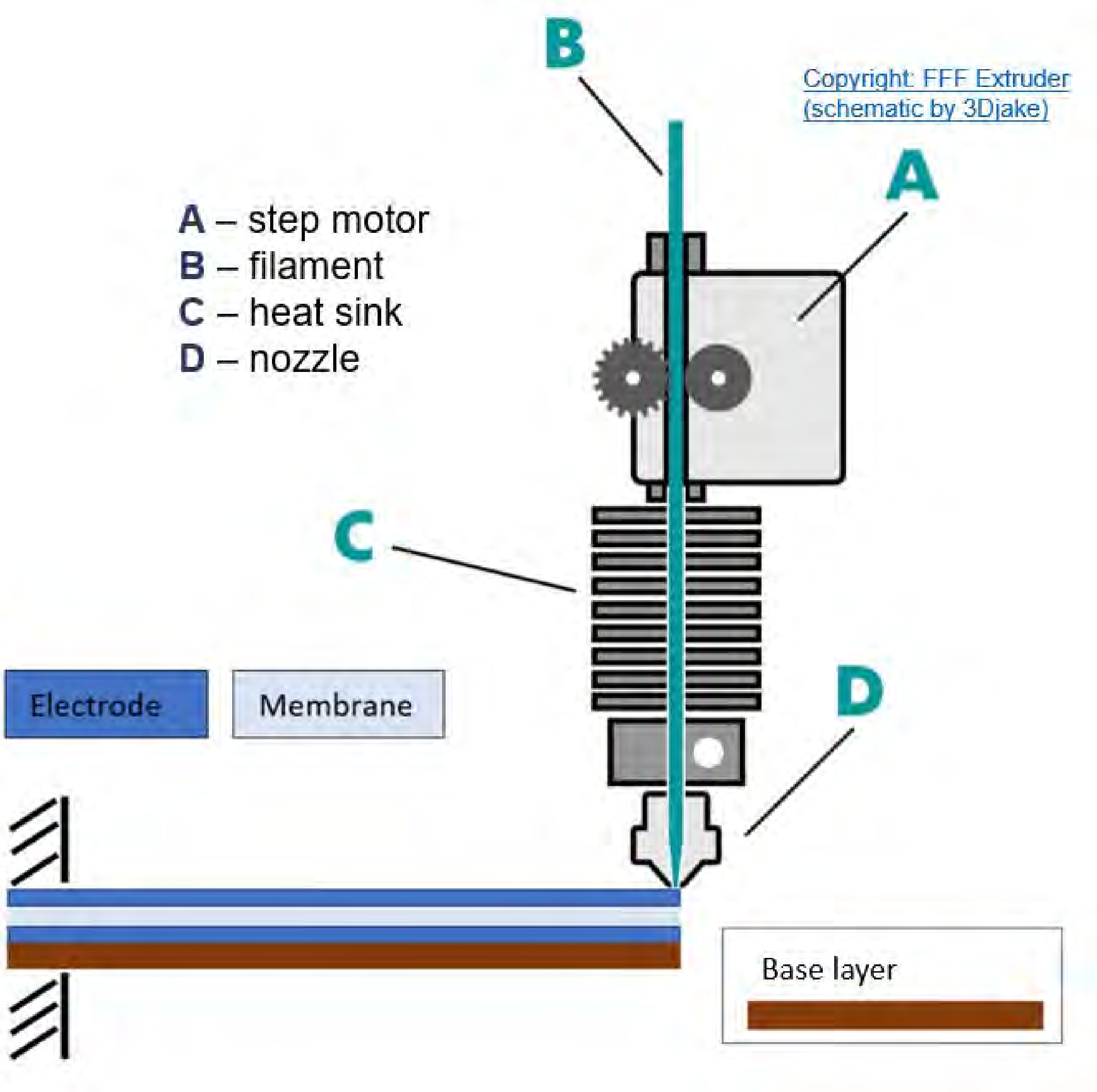

Fig. 2: Principle of 3D printing of the DEA as a one printing job by a standard FFF 3D printer.

Figure 2 shows a typical FFF 3D printing head and a DEA printed using it. Since FFF is mostly used for layer by layer printing, DEA printing jobs are optimized for this sequential printing process. The main components of DEAs are usually designed in layers, making the FFF printing process theoretically straightforward. However, because DEAs consist of two different materials -a dielectric material and an electrode - a multi-material FFF 3D printer is required. Finding the correct printing settings can be challenging, and improper settings may lead to electrical breakdown, ultimately resulting in the failure of the printed DEA.

State of the art

After explaining the basics of DEAs and FFF 3D printing, the current advancements in this field will be discussed. Numerous papers have already reported research on soft dielectric actuators [8–10]. The first DEA, which was partially additively manufactured but not fully produced using 3D printing, was reported by Rossiter et al. [11] in 2009. Gonzalez et al. reported the first 3D printed membrane using FFF in 2019 [12]. However, the first fully 3D printed DEA using FFF was reported by Raguž et al. [5] in 2023.

First FFF 3D printed membrane

The first real implementation step of FFF in the production of DEAs was reported by Gonzalez et al. [12]. They used the FFF process to print the membrane, an essential part of the DEA. Second essential part of the DEA, the electrode they painted manually with a carbon grease. The carbon grease is a material that has good electrical conductivity and is viscous, allowing the movements and strains of the whole DEA.

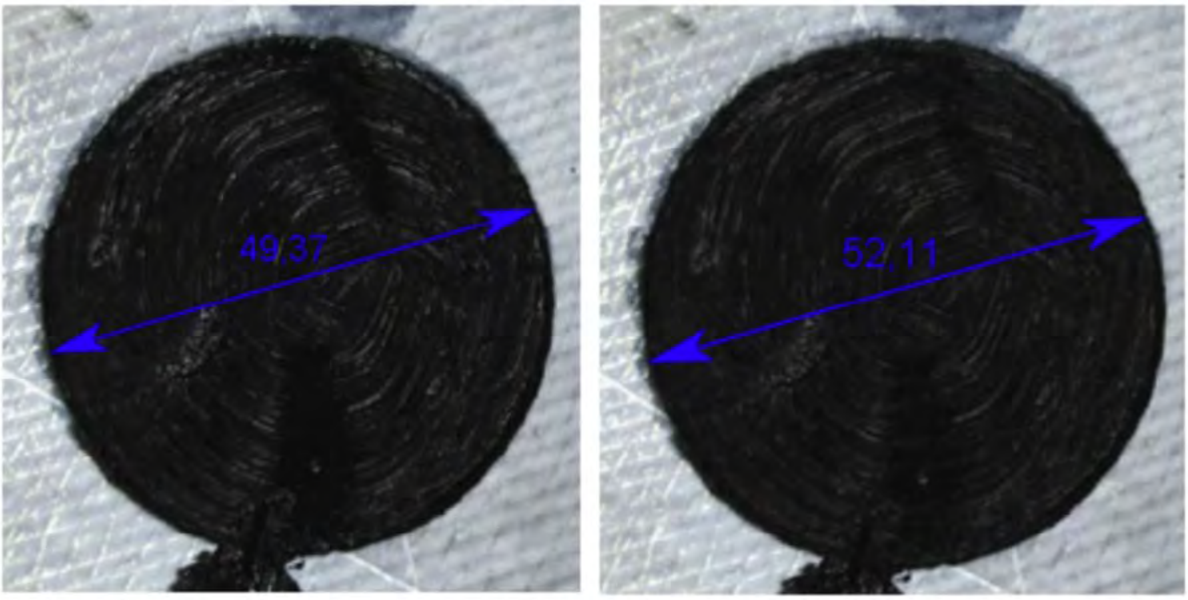

Fig. 3: DEA made out of FFF 3D printed electrode and a carbon grease done by Gonzalez et al. The image on the left shows the unactuated state, while the image on the right shows the actuated state. [12] (© Gonzalez et al.).

After applying a high direct current voltage (DC) the membrane was squashed by Coulomb forces. This resulted with a planar deformation. This proved a possibility of a use of FFF 3D printed membrane. After that, 3D printing of the electrode and the whole actuator remains an unsolved problem.

DEA development

Our preliminary research focused on evaluating commercially available materials to identify a suitable one for the production of the DEA’s electrode.

Commercially available materials

The 3D printing market is abundant in filaments with various mechanical properties, making it relatively easy to find a suitable filament for the membrane. A soft thermoplastic polyurethane (TPU) with a Shore A hardness under 90 is already suitable for these purposes. However, finding an electrically conductive filament that is also sufficiently flexible proved to be more challenging. Due to the actuator‘s mechanism, the electrode will stretch along with the membrane. Therefore, the electrodes must also be flexible, to avoid significantly affecting the overall mechanical properties of the actuator. Two electrically conductive filaments suitable for DEAs are „Proto-Pasta – Composite PLA filament“ and „Eel™ TPU 3D (Fenner Inc., USA)“.

First fully 3D printed soft dielectric actuator

Additive manufacturing is not only an alternative to traditional manufacturing processes but also to assembly processes. The idea is that by using multi-material FFF 3D printing, the DEA can be assembled during the printing process itself. To enable this, 3D printing parameters must be optimized.

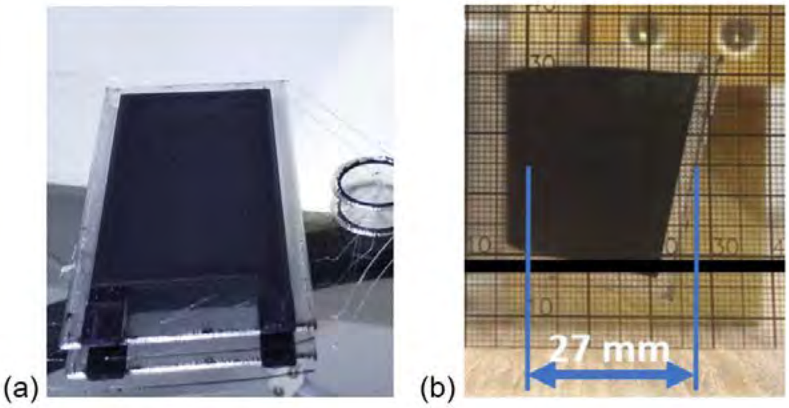

Fig. 4: (a) One of the first successfully 3D printed DEAs (dimensions 90 x 45 mm). (b) The maximum displacement of 27 mm achieved by the Fully 3D printed DEA.

To achieve a functional DEA, the tool-change between filaments/nozzles during the print should be as clean as possible (Figure 4a). Even small amounts of conductive material trapped in the dielectric membrane can cause electrical breakdown, leading to actuator failure.

To demonstrate the functionality of the fully 3D printed DEA, the maximum displacement was measured. The actuation voltage of 4.5 kV was used. The maximum displacement achieved was 27 mm, as shown in Figure 4b. The total free length of the actuator was 65 mm, so the displacement corresponds to approximately 42% of its total free length. When the actuation voltage is turned off, the actuator returns to its initial straight shape, as 3D printed.

Fabrication of Fully 3D printed soft dielectric assembly

Achieving a fully 3D printed DEA made from two materials marked a crucial milestone in the development of fully 3D-printed soft dielectric assemblies. Adding an additional material to the multi-material FFF process introduces an additional set of mechanical properties, enabling the creation of true assemblies. This additional material will enhance the stiffness of the upper part (red color) of the soft dielectric assembly, which is demonstrated in the showcase example that follows.

Figure 5 depicts a fully 3D-printed soft dielectric assembly comprising three separate DEAs. All three DEAs are connected to the same actuation wires, which are also 3D-printed. The assembly was designed so that no additional processing beyond FFF 3D printing is necessary.

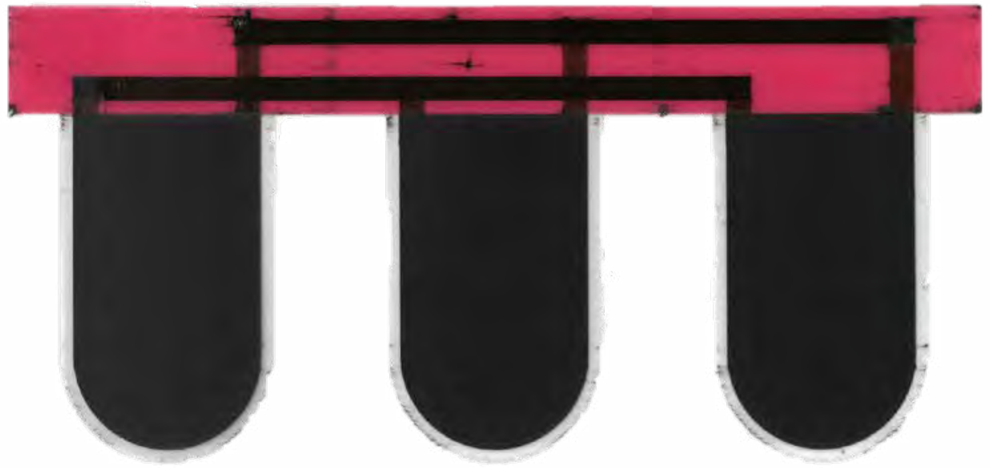

Fig. 5: The fully 3D printed soft dielectric assembly consists of three DEAs, connecting wires, and supporting material, all produced in a single printing job.

Conclusions

This work demonstrates the successful implementation of the MEX 3D printing process for fabricating dielectric elastomer actuators. It shows that commercially available FFF-based printers can manufacture fully 3D-printed soft dielectric assemblies without modifications. Initially, the FFF printing of the DEAs and soft dielectric assemblies was not straightforward. However, it has been shown that commercially available filaments meeting the requirements for 3D-printed DEAs already exist.

The 3D printed DEAs achieved comparatively high actuation displacements when driven by an actuation voltage in the range from 3 to 6 kV. Afterwards, as a showcase example the soft dielectric assembly, which consists of: three DEAs, connecting wires and supporting material was fully 3D printed in a single printing job.

The fully 3D-printed soft dielectric assembly developed in this study represents a significant step toward fully 3D-printed robotic systems. In principle, only additional printing heads are needed for manufacturing such systems. As in this study, two printing heads were used for membrane and electrode materials and the latter printing head/material was used for the stiffer support. FFF machines with more than two printing heads are already on the market.

Acknowledgement

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Specialist lectures

SESSION D:
“FUTURE TRENDS IM POLYMER TECHNOLOGY”

Materials and methods for the enzymatic cross-linking of hydrogels

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Abstract

Plant based alginic acids ([D-ManA(β1→4)]$_m$-[L-GulA(α1→4)]$_n$) and their salts are very often investigated to create hydrogels for tissue culture and regeneration. [1] [2] To solidify the aqueous polymer solutions, these materials are commonly gelled by multivalent ions or covalently e.g. by (radical) polymerization of previously attached reactive functional groups. While effective, these methods of gelation often face limitations in terms of stability and biocompatibility, causing a need for new cross-linking strategies compensating those drawbacks. This work therefore investigates new gelation methods for alginates, based on small molecular crosslinkers and enyzme catalysis. Monitoring the gelation process via time-dependent oscillatory rheology measurements gives insights into the curing kinetics and the mechanical properties of the gels. The formed three-dimensional network provides stability at physiological conditions compared to ionically cross-linked hydrogels, which are prone to cation exchange. The methods and material properties obtained are elaborated in this paper.

Introduction

The polysaccharide alginate is commonly gelled by the addition of bivalent calcium ions and several methods exist to control the kinetics and intensity of solidification. [1] Gelling of alginate has also been shown to be useful in extrusion 3D printing of fibrillar biomedical materials for which the curing can be executed post printing. [3] It is known however that the ionic crosslinking is reversible, that ions tend to leach, and that the stability of the ionic bonds strongly depends on the ionic strength, pH value, or the presence of complexing agents. [3] Alternative methods for gelling therefore include covalent crosslinking of (meth) acrylated, allylated or norbornylated polysaccharides via radical processes, also allowing for stereolithographic printing. [4] Whilst being efficient, fast and precise, these methods require radical (photo-) initiators, light or heat, and often problematic solvents or monomers for derivatization. Other methods for crosslinking of polysaccharides therefore use enyzmes as catalysts with the advantage of substrate specific and biocompatible reaction conditions. [5] Surprisingly, there are relatively few different enyzme classes described for that purpose in literature. These include transglutaminases imitating the enyzme catalyzed blood clot formation, phenoloxidases, peroxidases, lysyloxidases imitating the crosslinks f collagen, phosphatases and a few others. [5] The reasons for this might be the limited

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availability of the enzyme and therfore its high price, and the need to chemically attach enzyme-specific substrates to the polysaccharide backbone. Such substrates could also be polysaccharide-petide conjugates which were shown to be useful as biomaterials e.g. for cell culture but which have not been enyzmatically derivatized until now. [6] We herein report the development of an alternative method to synthesize gels containing polysaccharide chains joint together via well-defined peptide bridges using enzyme catalysis. The materials investigated are likely biocompatible, and the bonds formed a susceptible to specific biodegradation. This could lead to interesting properties for potential applications in tissue culture or as injectable hydrogels.

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Advances in the Detection of Micro- and Nanoplastics: Methods and Technologies

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Abridged version

The growing concern over the environmental and health impacts of micro- and nanoplastics has catalyzed significant advancements in detection technologies. These polymer-based particles, originating from the degradation of larger plastic debris or from direct industrial production, are now recognized as pervasive pollutants across various ecosystems. Their small size, diverse polymer composition, and potential to interact with living organisms have driven the development of increasingly sophisticated methods for their detection, characterization, and quantification. This work focuses on the latest advances in the detection of polymer-based micro- and nanoplastics, emphasizing the analytical methods and technologies that have been refined or newly developed to meet the challenges posed by these contaminants. The detection of microplastics, typically defined as particles smaller than 5 millimeters, has benefited from improvements in visual, spectroscopic, and microscopy-based techniques. For nanoplastics, generally considered to be particles smaller than 1 micrometer, emerging technologies are being developed to overcome the difficulties associated with their detection, given their even smaller size and greater potential for environmental mobility [1,2].

Sample Preparation and Filtering Techniques

The refinement of sample preparation techniques has been crucial in enhancing the accuracy and reliability of micro- and nanoplastic detection. Among these techniques, filtering has emerged as a pivotal method for isolating micro- and nanoplastics from complex environmental samples. Filtering is a straightforward and powerful method that relies on passing environmental samples through filters of specific pore sizes to capture micro- and nanoplastic particles. The choice of filter material and pore size is critical to the success of this technique. Common filter materials include glass fiber, cellulose, polycarbonate, polytetrafluoroethylene, and stainless steel meshes, each selected based on the specific requirements of the sample matrix and the target particle size range.

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Fig. 1: Filtration setup using filters with decreasing pore size and vacuum pump assistance.

For microplastics, filters with pore sizes ranging from 0.45 to 5 micrometers are typically used. These sizes are effective in capturing most microplastic particles while allowing the flow of water and smaller non-plastic particles. However, filtering nanoplastics, which are smaller than 1 micrometer, requires even finer filters with pore sizes less than 0.2 micrometers. While smaller pore sizes increase the likelihood of capturing nanoplastics, they also heighten the risk of filter clogging, especially in samples with high organic or particulate content. One of the main challenges in filtering is the potential for clogging, which can occur when filtering samples rich in organic matter or suspended solids. This issue is particularly pronounced when using ultra-fine filters necessary for isolating nanoplastics. To prohibit clogging, pre-filtration steps using larger pore sizes are often employed to remove bulkier particles and organic debris. Additionally, optimizing the filtration process, such as adjusting the sample flow rate and applying vacuum or pressure filtration, can enhance the efficiency and effectiveness of micro- and nanoplastic recovery.

Visual and Microscopy-Based Techniques

Visual inspection, often using microscopy, remains a foundational method for identifying microplastics. Light microscopy, combined with staining techniques, allows for the identification of larger microplastic particles, although it is limited by resolution and operator bias. Scanning electron microscopy (SEM) has provided higher resolution imaging, allowing for more detailed morphological characterization of smaller microplastics. However, SEM’s limited ability to provide compositional information necessitates the use of complementary techniques [2].

Spectroscopic Techniques

Spectroscopic methods, particularly Fourier-transform infrared (FTIR) and Raman spectroscopy, have become the cornerstone of microplastic detection due to their ability to identify polymer types based on their unique vibrational signatures [2]. FTIR spectroscopy, especially in its attenuated total reflectance (ATR) mode, is widely used for identifying polymers in microplastic particles. The improvement of micro-FTIR and micro-Raman techniques has further enhanced the detection capabilities for smaller particles by coupling spectroscopy with microscopy, enabling both morphological and chemical characterization at the microscale. These methods, however, require extensive sample preparation and are time-consuming, making them less suitable for high-throughput analysis.

Raman spectroscopy, in particular, has proven to be highly effective for detecting micro- and nanoplastics due to its ability to provide detailed information about the molecular structure of polymers [2]. The development of surface-enhanced Raman spectroscopy (SERS) has further improved the sensitivity of Raman techniques, allowing for the detection of even smaller particles and lower concentrations of nanoplastics in complex environmental samples. The ability of Raman spectroscopy to distinguish between different polymer types and additives, even in highly heterogeneous samples, makes it a powerful tool in the field of microplastic research [3].

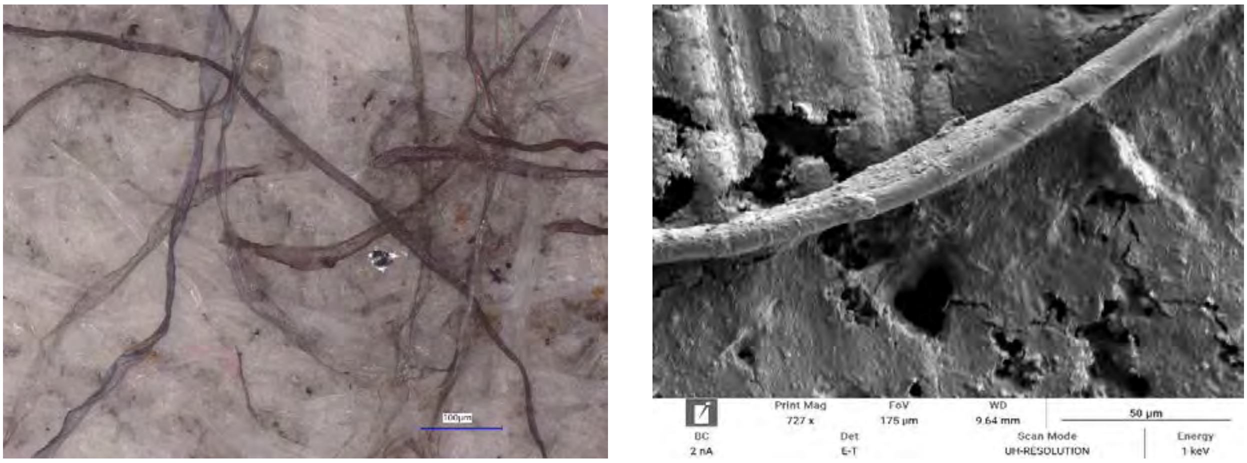
Photo-Induced Force Microscopy (PiFM)

Photo-induced force microscopy (PiFM) represents a significant advancement in the detection and analysis of nanoplastics. PiFM combines the high spatial resolution of atomic force microscopy (AFM) with the chemical specificity of infrared (IR) spectroscopy. This technique allows for the simultaneous imaging of nanoplastic particles at the nanoscale and the identification of their chemical composition. PiFM works by detecting the mechanical forces induced by the interaction of light with the sample, providing both topographical and chemical information with nanoscale resolution [4]. This dual capability makes PiFM particularly useful for studying nanoplastics, as it can accurately characterize particles that are difficult to detect with other methods.

PiFM’s ability to provide high-resolution chemical mapping of nanoplastics in complex matrices, such as sediments and biological tissues, offers significant advantages over traditional AFM and IR techniques. As this technology continues to develop, it is expected to play a crucial role in advancing our understanding of the environmental distribution and impact of nanoplastics.

Use Case: Washing Machine

To investigate the release of micro- and nanoplastics during clothes washing, the wastewater from a washing machine was carefully analyzed. In this study, garments made of 100% cotton, 100% polyester, and a blend of both were washed. The resulting wastewater was collected, and 300 ml of it was filtered through a filtration tower equipped with filters of varying pore sizes: a 4 µm cellulose filter, followed by 1 µm, 0.45 µm, and 0.05 µm polytetrafluoroethylene (PTFE) filters. The filtered particles were then examined using an FTIR microscope, Raman spectroscopy, and light microscopy to identify and characterize the residuals, focusing particularly on areas with smaller particles as well as fibers. Further analysis using PiFM is planned but has not yet been conducted.



a) b)

Fig. 2: In (a), a microscopic image showing the residual fibers remaining after the machine washing process and subsequent filtration, while (b) provides a more detailed view using electron microscopy.

Conclusion and Future Directions

The detection and analysis of micro- and nanoplastics have become critical in understanding their environmental and health impacts. This review has highlighted the significant advancements in detection technologies, focusing on the refinement of visual, spectroscopic, and microscopy-based techniques, as well as the development of emerging methods like Raman spectroscopy and Photo-Induced Force Microscopy. These advancements have enhanced our ability to identify and characterize these pervasive pollutants with greater accuracy.

Filtering, a key component of sample preparation, has proven essential in isolating micro- and nanoplastics from complex environmental matrices. The continuous improvement in filter materials, pore sizes, and filtration techniques has been crucial in addressing the challenges associated with the detection of these tiny particles, particularly nanoplastics.

Despite the progress made, challenges remain in standardizing methods and improving the detection of nanoplastics. Future research should focus on further optimizing these techniques and developing new methodologies to ensure accurate, reliable, and comparable results across studies. As our understanding of micro- and nanoplastics deepens, these advancements will be vital in guiding environmental monitoring and mitigation strategies to address the growing concern over these pollutants

Acknowledgement

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Design of covalent adaptable networks for advanced applications

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Abstract

Dynamic covalent bonds endow polymer networks with advanced properties such as self-healability, recyclability, malleability and reshape-ability. Currently, the most studied dynamic networks are vitrimers, which rely on thermo-activated exchange reactions such as transesterification of hydroxyl ester moieties. Due to various commercially available monomers, featuring ester- as well as free hydroxyl-groups, and catalysts they are already extensively investigated. Herein, we demonstrate the design of covalent adaptable networks relying on transesterification reactions for various applications, such as light induced 3D-printing of functional devices, multi-material 3D printing of soft robotic grippers, self-healing applications and frontal polymerization of recyclable thermosets. In addition, we will explain how local control of this exchange reactions can be achieved. By incorporation of appropriate catalysts, these dynamic network rearrangements can be activated on-demand and successfully controlled even on the microscale level.

Introduction

Covalent adaptable networks (CANs) are a distinctive type of functional polymers that are capable of altering their network structure through dynamic covalent bond exchange reactions in response to specific stimuli. [1–3] These bond exchanges can occur via either dissociative or associative pathways, which affect the viscoelastic properties of the related networks. In dissociative CANs, exchange reactions go through bond cleavage with subsequent bond formation leading to a reduction in crosslink density and a distinctive drop in viscosity. Conversely, associative CANs maintain their average degree of crosslinking during topological rearrangements, as the bond exchange is initiated with the formation of a new bond. [4] The viscosity follows an Arrhenius-type relationship and decreases with increasing temperature. At a sufficiently high bond exchange rate, dynamic polymeric networks become malleable, weldable and recyclable. [5,6]

Leibler and co-authors introduced the term „vitrimer “by their work on dynamic epoxy-acid and epoxy-anhydride networks, which undergo thermo-activated transesterification reactions. [7] Over the past years, transesterification-based vitrimers became one of the most reported class of CANs due to the commercial availability of monomers which contain ester and hydroxyl groups and/or form them during the polymerization/curing process. [1,6] To accelerate the transesterification reactions and to facilitate healing, welding or recycling

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of the materials at lower temperatures, external or internal catalysts are required, such as Brønsted acids/bases, Lewis acids or phosphate esters (see Fig. 1). [8]

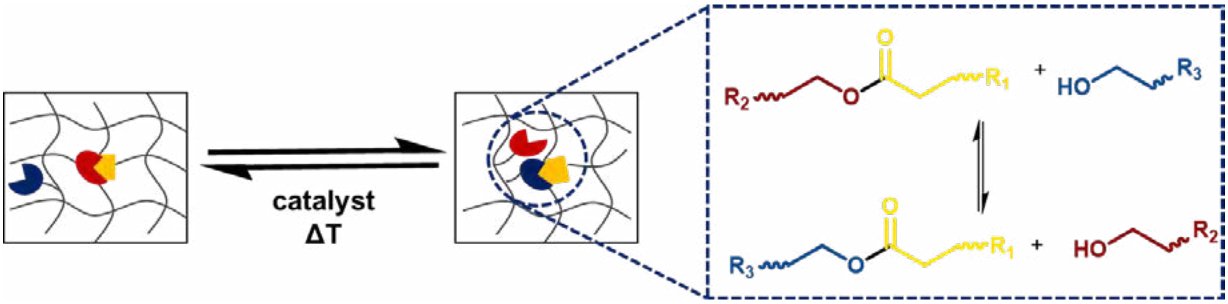

Fig. 1: Transesterification reaction scheme

In the present work, we show the design of covalent adaptable networks based on transesterification reactions for different advanced applications, such as digital light processing (DLP) 3D printing, multi-material 3D printing of soft robotic grippers, frontal polymerization, thermally induced healing and recycling. In addition, on-demand activation of these dynamic properties on the microscale level will be discussed, to underline the versatility of the developed systems.

Discussion

Design of covalent adaptable networks

To develop dynamic networks based on transesterification reactions, monomers with a sufficient high number of ester moieties and free hydroxyl groups have to be used. Additionally, catalysts, such as acids, bases, Lewis acids or phosphate esters, have to be introduced to lower the activation energy of the exchange reactions. Figure 2 provides an overview of the monomers and catalysts most frequently used in our studies.

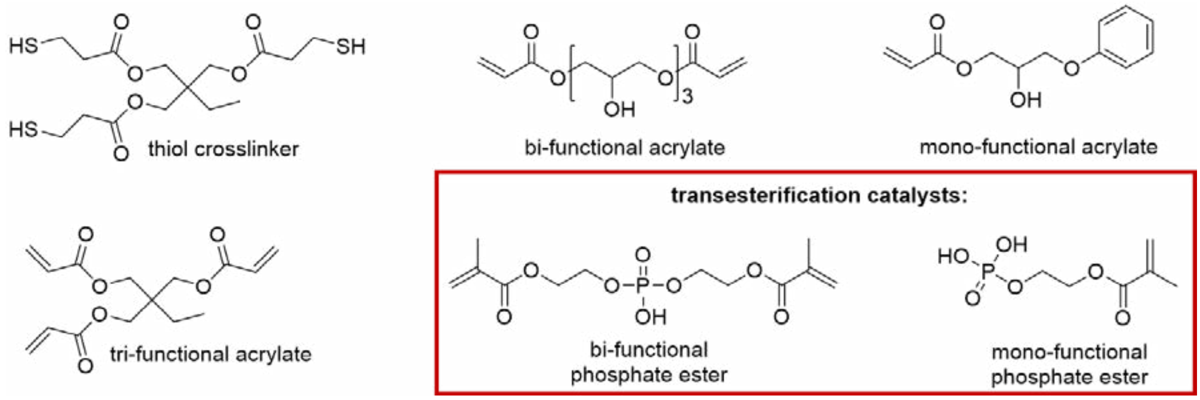

Fig. 2: Molecular structure of monomers and catalysts most frequently used

DLP 3D printing of covalent adaptable networks

Additive manufacturing technologies (AMTs) have gained significant attention in recent years, as they facilitate the creation of complex and uniquely shaped structures from a variety of materials. Unlike traditional methods such as injection molding or extrusion, AMT allows for the design and production of intricate structures with enhanced functionalities and/or improved performance. An appealing approach to create 3D objects with additional capabilities is the additive manufacturing of CANs to impart unique characteristics to the polymer networks, such as reshaping (Fig. 3a) or self-healing (Fig. 3b and 3c). [9-13]

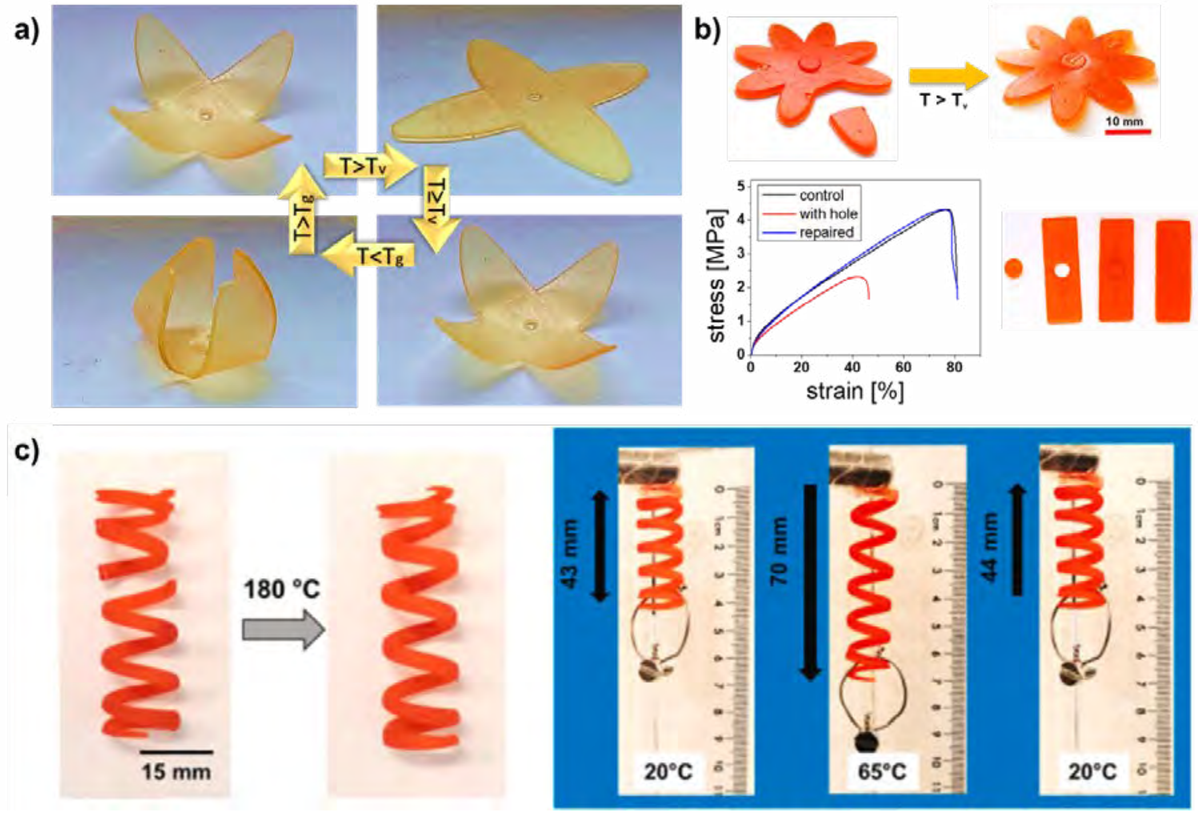

Fig. 3: DLP 3D-printing of thiol-acrylate vitrimers to demonstrate a) reshaping, [10] b) self-healing of a flower that can be characterized by tensile tests [10] and c) self-healing of a shape-memory spring. [11]

Multi-material DLP 3D-printing

Whilst DLP 3D printing of single materials is already well studied for vitrimers, the multi-material printing of covalent adaptable networks is still a quite new topic. Multi-material 3D printing enables the integration of materials with different chemical, mechanical, electrical or optical properties in one object. We use a dual-vat DLP printer based on an automatic vat exchange for the multi-material 3D printing of vitrimers (Fig. 4a). By combining dynamic network chemistry with dual-vat printing, thermally induced bond exchange reactions across the interfaces increase the interlayer adhesion between soft and stiff domains (Fig 4b and c). The printing and temperature triggered healing of functional devices with locally controlled heterogeneity and shape memory properties along the three axis is demonstrated, giving rise to the versatility of the multi-material 3D printed vitrimers. [14-16]

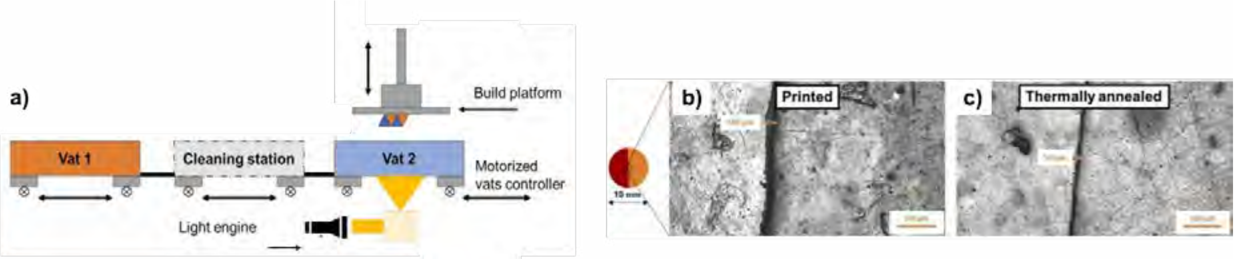

Fig. 4: a) Schematic representation of the multi-material DLP 3D printer prototype and optical micrographs of the interface between soft (right) and stiff (left) domains b) directly after printing and c) after thermally induced transesterification reactions. [15]

Local control of dynamic properties

The use of photolatent transesterification catalysts offers a novel method for controlling dynamic bond exchange reactions in vitrimers at a local level. In their unilluminated state, the polymer network acts like a permanently crosslinked thermoset. When exposed to light, these catalysts generate an active species on-demand, enabling network rearrangements above the so-called topological freezing temperature (Tv). In the case of photopolymers, photoacid generators serve as effective latent catalysts, providing advantages such as excellent solubility, high temperature stability, and the ability to release strong Brønsted acids as active species, which efficiently catalyse thermo-activated transesterifications. Furthermore, they are generally transparent to visible light, allowing for radical-induced curing of photopolymers with 405 nm light without premature acid release. We used photoacid generators to design photocurable vitrimers suitable for dual-wavelength 3D printing and subsequent local reshaping (Fig. 5a) and photopatterning by local depolymerization (Fig. 5b). [17-21]

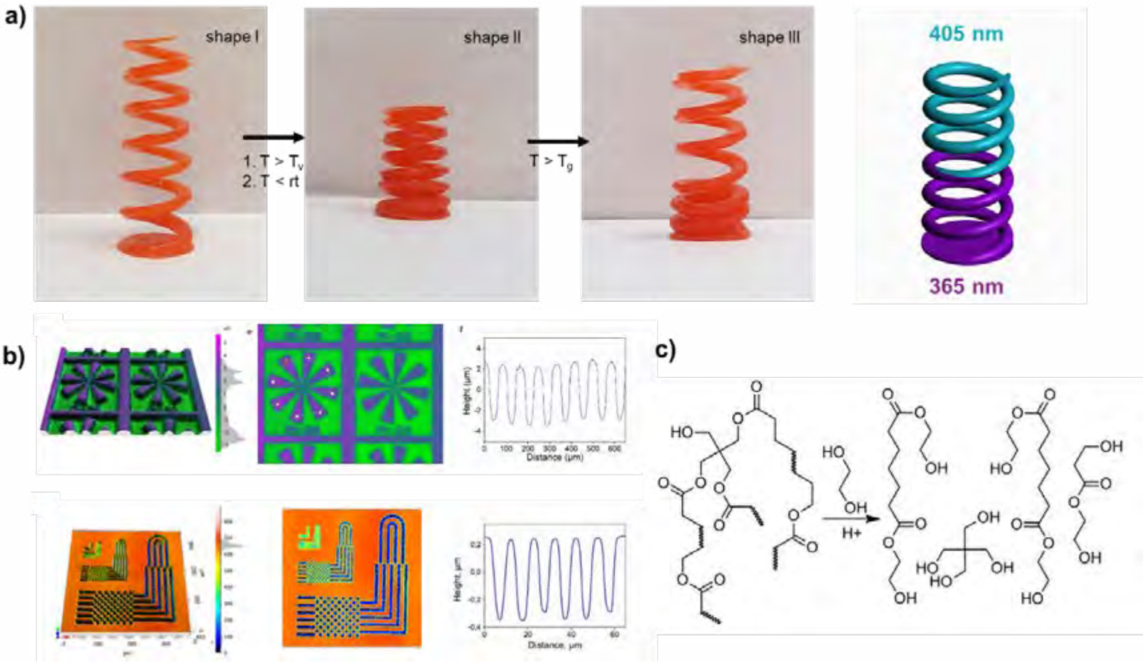

Fig. 5: Demonstration of local control of dynamic exchange reactions on a) the macroscale by dual-wavelength 3D printing and subsequent local reshaping [17] and b) the microscale by local depolymerization. c) Underlying depolymerization mechanism. [19]

Frontal polymerization of covalent adaptable networks

Frontal polymerization describes autocatalyzed reactions which lead to high conversions, short reaction times and low energy consumption. Autocatalysis occurs due to the exothermicity of the polymerization reaction and spreads through the monomers by thermal diffusion. To induce the chain reaction, an external trigger, such as heat or light, has to be applied (Fig. 6a). Once started, the chain reaction is only terminated when either the entire monomers are consumed or due to heat loss. [1] However, the resulting materials are typical thermosets that cannot be reprocessed, reshaped or recycled. We combined the energy efficiency of frontal polymerization with the unique post-processability of covalent adaptable networks to further increase sustainability in thermoset production. Due to transesterification reactions at elevated temperatures, vacuum compression molding of cryo milled frontal polymerized networks was performed to demonstrate the feasibility of reprocessing (Fig. 6b). Additionally, glass fibers of a frontally polymerized composite could be successfully recovered owing to the dynamic exchange reactions (Fig. 6c). [22]

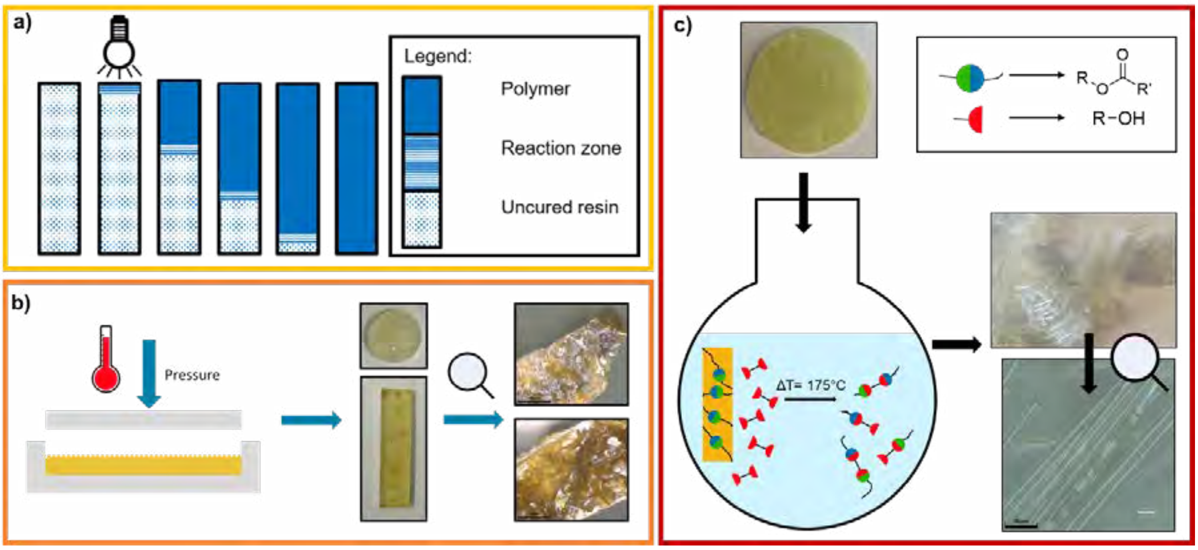

Fig. 6: a) Frontal polymerization reaction scheme, b) reprocessing of frontally polymerized networks [22] and c) glass fiber recovery from a frontally polymerized composite. [22]

Conclusion

Covalent adaptable networks (CANs) offer significant advantages in materials science, particularly through their unique ability to undergo reversible bond exchange reactions, such as transesterification reactions. This dynamic behavior enables improved processing flexibility and enhanced mechanical properties, allowing materials to self-heal and adapt to changing conditions. By designing the resin in a precise way, the temperature at which the exchange reactions predominate can be exactly defined and the materials can be reconfigured or recycled, contributing to sustainability efforts. Their tunable properties make them suitable for various applications, including advanced coatings, adhesives and smart materials, ultimately paving the way for innovative solutions in numerous industries.

Acknowledgement

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Bio-based covalent adaptable networks: From monomer synthesis to applications in 3D-printing and nanoimprint lithography

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Abstract

In order to drive the development of high-performance polymers with improved sustainability, conventional thermosets need to be replaced by materials that are recyclable, repairable or reusable and at the same time have excellent mechanical properties. Dynamic covalent polymers are a promising way to achieve this goal.

One approach to make polymers more sustainable is to use functional, bio-based monomers that can be derived from renewable sources such as vegetable and plant oils, carbohydrate feedstocks and platform chemicals derived from lignin.[1,2] A key advantage of vegetable and plant oils is the presence of carbon double bonds, which enable a wide range of functionalization options. In addition, these oils are biodegradable, readily available and environmentally friendly.3 A commonly used reaction pathway is the oxidation of the carbon double bonds to form epoxide groups, which can then undergo a nucleophilic ring-opening reaction with different functional acids, e.g. acrylic or allylic acid resulting in the formation of acrylates or allyl double bonds.[4]

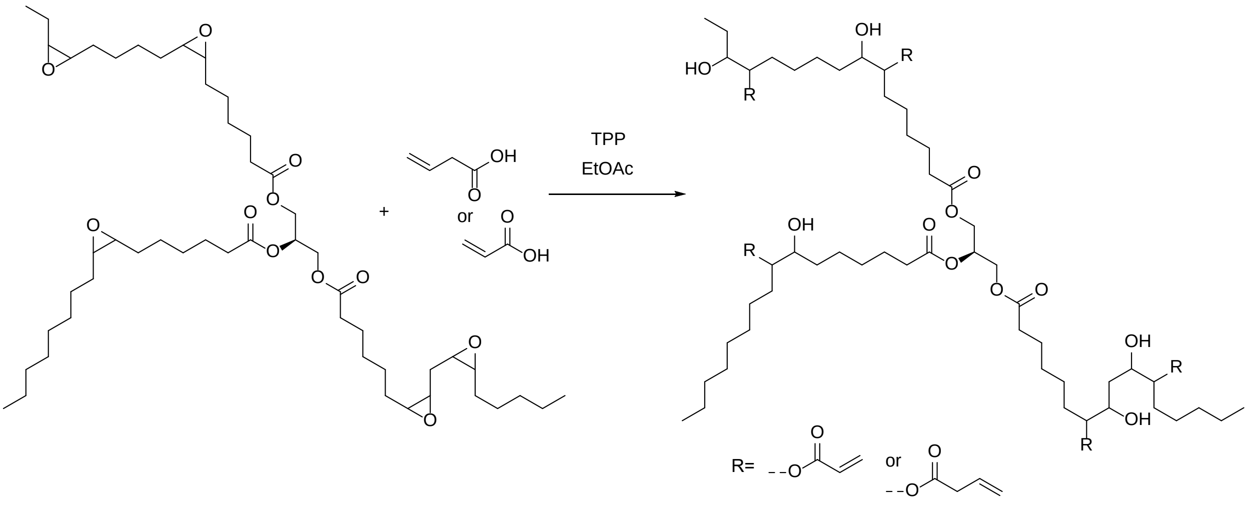

Fig. 1: Reaction pathway for either an acrylated or allylated linseed oil [5,6]

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In this study, we synthesized organic phosphates starting from eugenol and citronellol that effectively catalyze bond exchange reactions between hydroxyl ester bonds at high temperatures. The new catalysts were produced in high yields and showed good solubility in various photoreactive resins. With the aim of producing fully bio-based dynamic photopolymers, the catalyst was incorporated into two different systems. For the first one an acrylated linseed oil (AELO) based resin was used. To improve the printability and reduce the viscosity of the AELO resin, acrylated eugenol (AEUG) was synthesized and used as a bio-based reactive diluent. The resulting resin benefited from high cure rates and low viscosity, which enabled the production of complex 3D structures by vat photopolymerization 3D printing.

After photocuring, the polymer exhibited abundant -OH and ester groups that thermally transesterified in the presence of the newly developed catalyst. To test the catalytic activity of the biobased phosphates, stress relaxation measurements were performed. Therefore, three resin mixtures were prepared. One catalyzed with eugenolphosphate (EUGP) one with citronellolphosphate (CitrP) and one uncatalyzed reference system. The characteristic relaxation times were determined as the time needed for the sample to relax 63% (1/e) of its initial stress according to the Maxwell model.

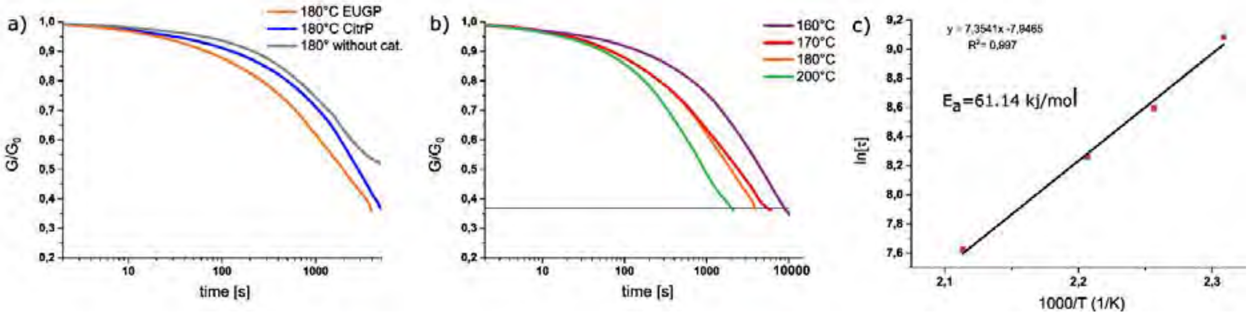

Fig. 2: (a) Normalized stress relaxation results of CitrP, EUGP and uncatalyzed reference system (b) Normalized stress relaxation plot of EUGP_A50:E50 samples as a function of temperature. (c) Arrhenius plot of the EUGP_A50:E50 system, confirming the linear temperature dependent behavior. Reproduced from Polym. Chem., 2023,14, 4994-5003 with permission from the Royal Society of Chemistry

As it can be seen in Figure 3a, the uncatalyzed reference system shows some relaxation but was not able to relax 63% of its initial stress, even after a longer measurement period. It is known that light-curing acrylate-based networks exhibit thermal relaxation at higher temperatures even without a transesterification catalyst. This is due to the release of volumetric shrinkage stresses generated during network formation. When either EUGP or CitrP was used as a catalyst, significant relaxation of the storage modulus occurred, albeit at different rates. EUGP showed higher catalytic activity than CitrP, with the initial stress decreasing within 65 min at 180 °C. In contrast, CitrP networks took 81 min to reach a relaxation of 63 %. This difference in catalytic efficiency can be explained by the well-documented fact that carboxylic acids with aromatic groups have a higher acidity than those with aliphatic structures. In the case of EUGP, the presence of an aromatic ring in eugenol causes a shift in electron density away from the phosphate group, which facilitates the dissociation of the hydrogen of the hydroxyl group and thus increases the catalytic activity.

The resulting macroscopic material reflow was then used to thermally heal and reshape 3D printed objects. As it can be seen in Figure 3a when the originally printed structure was heated above topological freezing temperature (Tv) and compressed along the x-axis and cooled to room temperature (RT) again a new shape 1 could be fixed. This is possible due to the exchange reactions in the material. This shape is now the new fixed shape since it is stable even at high temperatures. When heating shape 1 above the glass transition temperature (Tg) of the material and compressing it along the y-axis, shape 2 could be programmed. When shape 2 was again heated above Tg, shape 1 could be fully recovered, proofing the shape memory of the material.

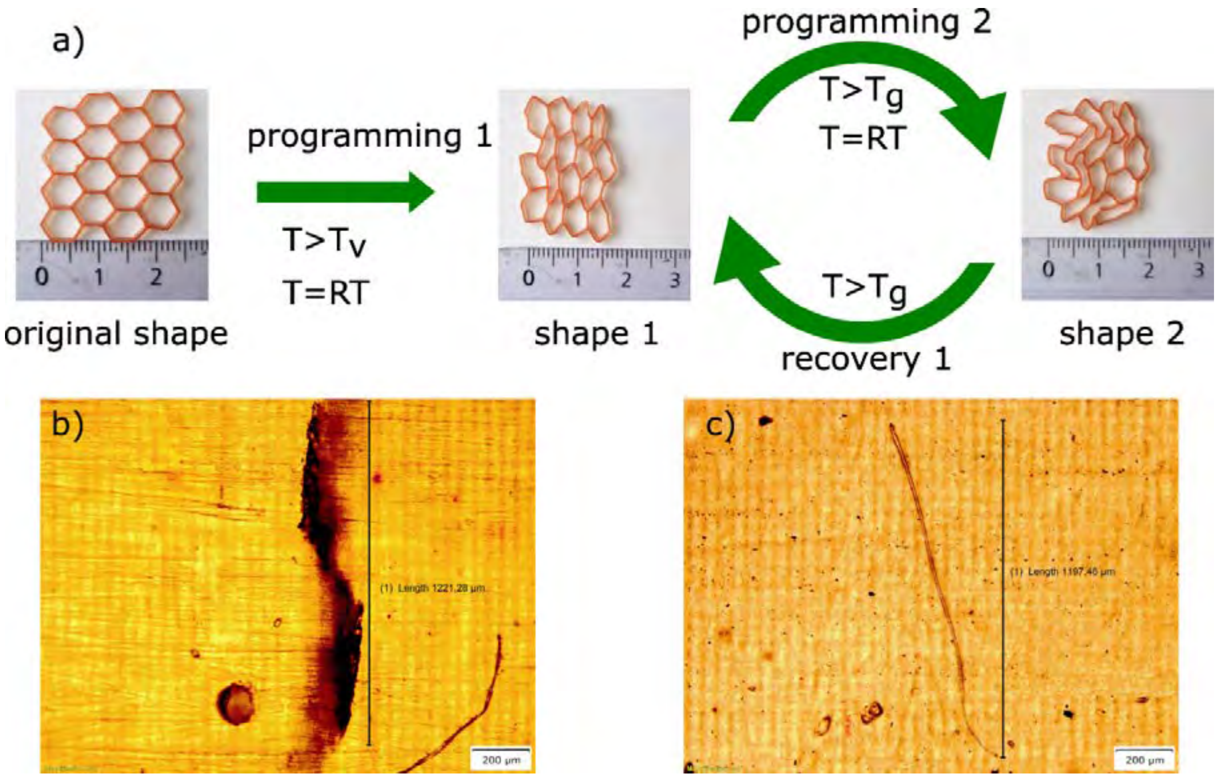

Fig. 3: a) Shape memory experiment of a 3D-printed honey comb structure b) Microscopic image of the top surface of the 3D-printed rectangular sample marked with a scratch at the center. c) Microscopic image of the scratched specimen after thermal treatment at 180 °C for 4 hours. Reproduced from Polym. Chem., 2023,14, 4994-5003 with permission from the Royal Society of Chemistry

For the second system, in order to reduce shrinkage during polymerization a fully biobased thiol ene network was developed. Therefore, a multifunctional thiol based on eugenol was synthesized and cured along with an allylated linseed oil. The biobased eugenol phosphate was again used as transesterification catalyst. It has been seen, that the cured polymer network was stable up to 250 °C. Stress relaxation tests were performed and have shown a relaxation within 62 min at 160 °C. Due to the underlying thiol-ene step growth mechanism and the therefore reduced polymerization stresses it was possible to use the resin in nanoimprint lithography applications. Films with micropillars, featuring an aspect ratio of 1:2.5 were fabricated. The dynamic network's macroscopic reflow capability allowed for reorientation of the imprinted structures during a thermal reshaping process. The resulting imprints were analyzed using 2D/3D optical microscopy and µCT imaging.

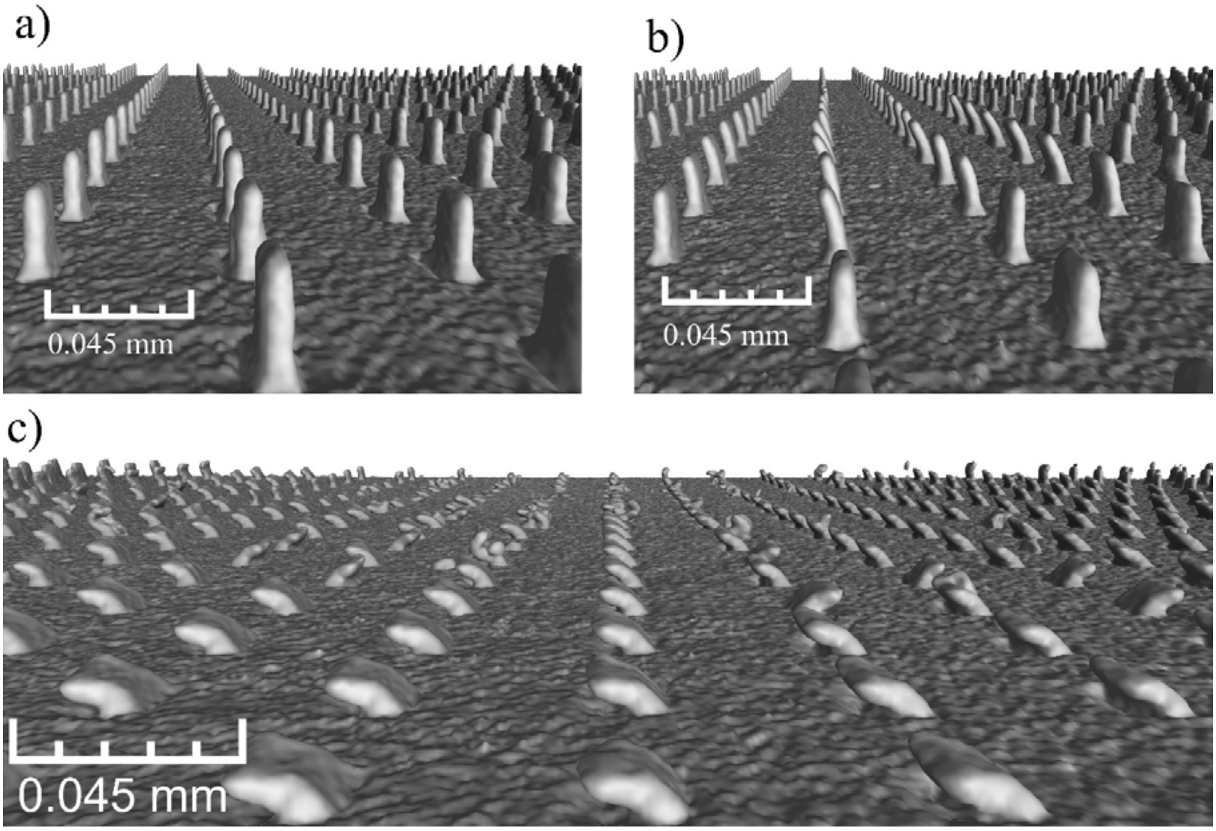

Fig. 4: µCT images of imprints (a) prior to heat treatment, (b) of the reference after heat treatment and (c) of the catalyzed sample after heat treatment.

Figure 4a shows the imprint immediately after demolding, with the micropillars aligned vertically and allowing precise positive replication of the mold. Figures 4b and 4c show the reference sample without EUGP and the catalyzed sample after heat treatment and tilting of the columns, respectively. In Figure 4b, the columns of the reference sample are straight again, indicating that no macroscopic reflow took place. Since the Tg of the material is well below room temperature, the reference sample only showed shape memory behavior, with the columns returning to their original shape as they relieved the stress built up during tilting. In contrast, in Figure 4c, the columns of the catalyzed sample remain tilted as the accumulated stresses were relieved by transesterification reactions, fixing the new shape and demonstrating the successful adaptability of the surface.

Further investigation of the surface was performed by static water contact angle measurements. It could be shown, that depending on the orientation of the micropillars, the water contact angle varied between 118° and 95°, suggesting potential applications in microfluidic devices.

Acknowledgement

The research work was performed within the COMET-Module project”Repairtecture” (project-no.: 904927) at the Polymer Competence Center Leoben GmbH (PCCL, Austria) within the framework of the COMET-program of the Federal Ministry for Climate Action, Environment, Energy, Mobility, Innovation and Technology and the Federal Ministry for Labour and Economy with contributions by Technical University of Graz. The PCCL is funded by the Austrian Government and the State Governments of Styria, Upper and Lower Austria.

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Beyond carbon: novel inorganic polymers for applications in biomedicine and sustainable material development

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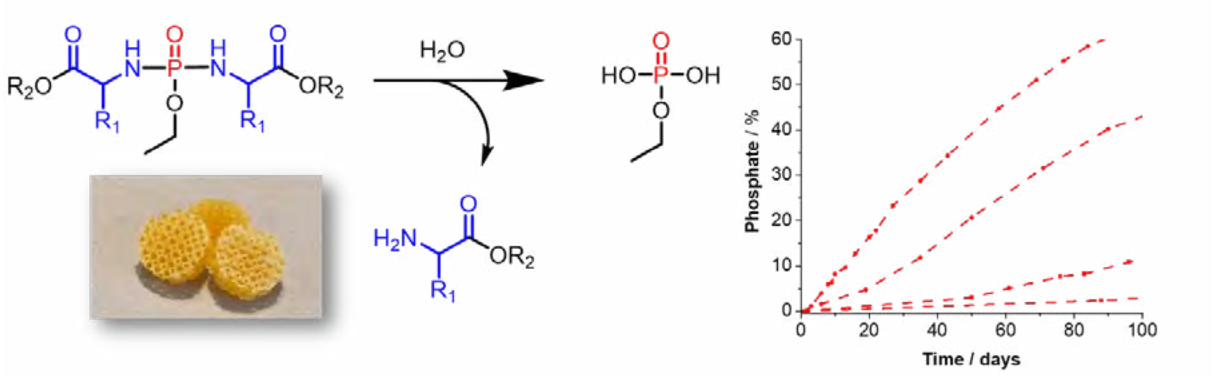
Abstract

Traditional polymer chemistry has historically focused on producing exceptionally thermodynamically stable carbon-based macromolecules. In stark contrast, nature employs heterogeneous building blocks, such as phosphates, to create molecules in a state of constant flux. In this work, we harness the potential of dynamic inorganic bonds, namely phosphorus and boron-based molecules to incorporate, cleavable or dynamic reversible bonds into cured polymers. We describe the design and synthesis of various materials, including biodegradable photopolymers for 3D printing, dynamic covalent polymer networks as well as super-soft elastomers.

Amino Acid-phosphoramide photopolymers



.Fig. 1. The hydrolysis mechanism for amino acid phosphoramidate hydrolysis (left) and exemplary hydrolysis profiles which are determined primarily by R_1 (right) allowing for precise design of degradation rates. Image reproduced from ref [1]

Photochemical 3D printing is a rapidly evolving technology for creating complex structures with customizable mechanical properties, and it is gaining significant attention in biomaterial scaffolds and personalized medicine. Currently, most biodegradable polymers used in this field are based on polyesters and polycarbonates, but these materials degrade too slowly for some applications like tissue scaffolds. In this study, we design and develop new amino acid phosphoramide-based vinyl ester and carbonate resins (Figure 1). Model studies show that these materials undergo hydrolysis into endogenous amino acids and phosphates, with degradation rates adjustable by changing the amino acid components [1]. These insights

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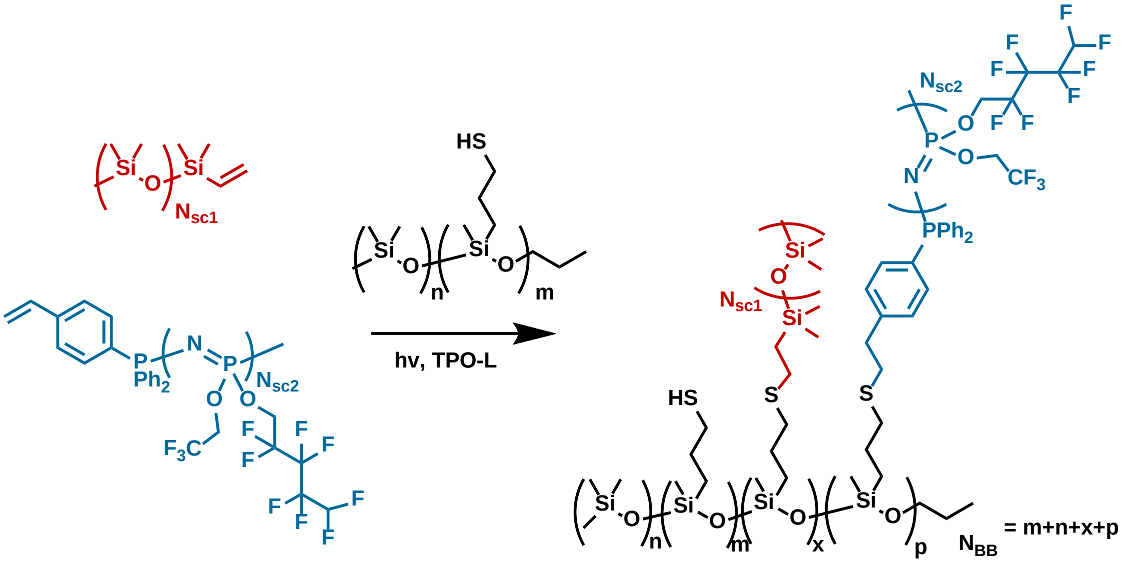
Corresponding author: ian.teasdale@jku.at were applied to create photopolymer resins with controlled degradation rates, ranging from days to several months, under mild, pH-neutral conditions. 3D printing was successfully performed using a desktop digital light processing (DLP) printer and multiphotolithography (MPL) [2]. Due to the amino acid phosphate building blocks, we show that the polymers have excellent cytocompatibility, cell viability, and osteogenic differentiation and thus hold considerable promise as scaffold materials for bone regeneration [1]. This research, therefore, offers a potential solution to overcome the current limitations of biodegradable photopolymer materials used in 3D printing in tissue regeneration scaffolds and beyond.

Supersoft elastomers



$PDMS_{BB}$ - PNF_{SC} - $PDMS_{SC}$

Fig. 2. The chemical structures of selected hybrid bottlebrush polymers [3]

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A further field where inorganic polymers show high promise compared to their carbon-based analogues is supersoft elastomers [4]. In this study, we design and synthesize a new class of inorganic bottlebrush polymers by combining polydimethylsiloxane (PDMS) and polyphosphazene (PPz) chemistries [3]. This non-carbon-based approach enables easy modification of key architectural features—namely, the backbone (N_{BB}), side chain lengths (N_{SC}), and grafting density (N_g^{-1}). Grafting PDMS to PPz, and vice versa, allows us to combine the unique advantages of both polymers, such as their ultra-low chain rigidity, thermal and chemical stability, and biocompatibility, into a single material (Figure 2). These novel hybrid bottlebrush polymers were cured into ultra-soft, solvent-free elastomers. We conducted a thorough investigation into how their architectural features and chemical functionalities influence their rheological behavior (Figure 3). Along with forming ultra-soft elastomers, these materials demonstrate notably enhanced energy dissipation compared to PDMS-based elastomers and, hence, could be useful in applications that require damping materials.

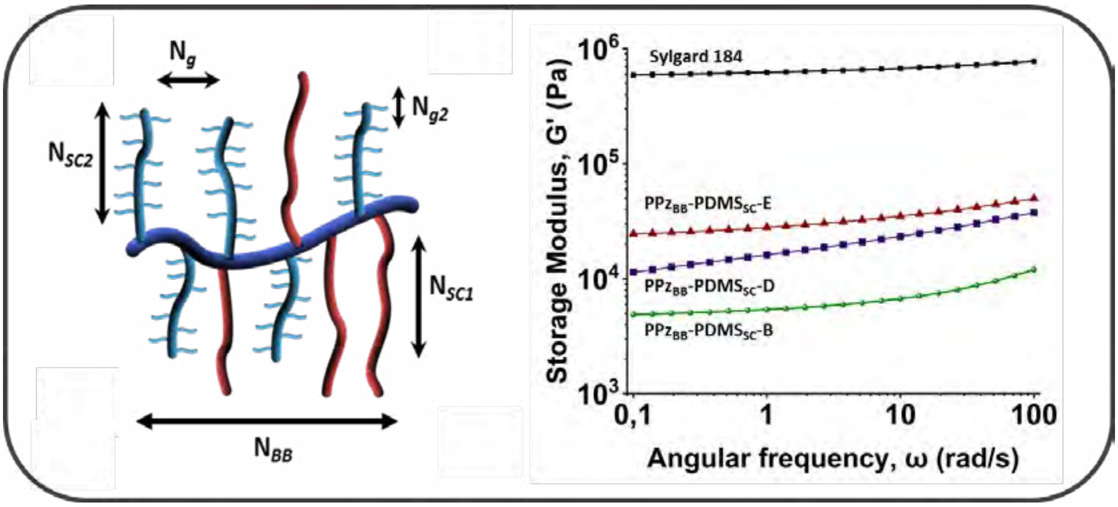

Fig. 3. Dimensional variations of hybrid bottle brush polymers (left) and the supersoft properties of their elastomers as seen in rheological measurements (right). Reproduced from ref [3]

Elastomers from Organoborane Lewis-Pairs

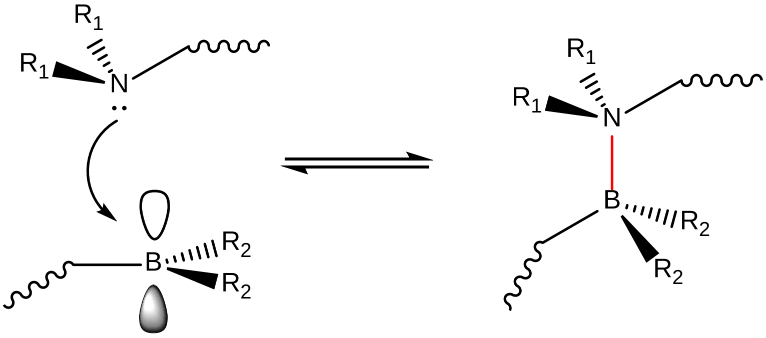

Fig. 4. Lewis pair bonding with organoboranes

A further example of the utilization of inorganic chemistry in polymer chemistry is the development of dynamic covalent polymer networks (DCPNs). DCPNs, also known as covalent adaptable networks (CANs), describe how dynamic reversible chemistry is incorporated into cured polymer networks [5,6]. Traditional network polymers like thermosets and elastomers rely on strong covalent bonds, which contribute to their outstanding performance and industrial significance. However, these strong bonds can also limit their processability and sustainability. To address this, dynamic bonding is introduced into network polymers to improve their processability and recyclability while preserving many of the advantageous properties of thermosets. Examples of such reversible covalent bonds include Diels-Alder reactions, oxime-urethane exchanges, and esters, often referred to as vitrimers [7]. Lewis pairs, known for their reversibility, have been somewhat overlooked as a dynamic bonding system in the recent advancements of DCPNs. In Lewis pairs, a covalent bond is formed between a Lewis base (LB) and a Lewis acid (LA), and the bond's strength and dissociation rates can be adjusted by modifying the chemical groups attached (R_1 and R_2 in Figure 4). LB pairs has considerable potential due to dissociation rate constants that span around seven orders of magnitude. The combination of accessible synthesis and high tunability make organoborane LPs excellent candidates for the preparation of CANs. Compared to other dynamic reactions like Diels-Alder or transesterification, Lewis pairs exhibit fewer side reactions, making them an attractive option for dynamic covalent networks. In this contribution we describe the chemical design, synthesis and characterization of a series of polydimethylsiloxane (PDMS) elastomers cured via Lewis-Pairs.

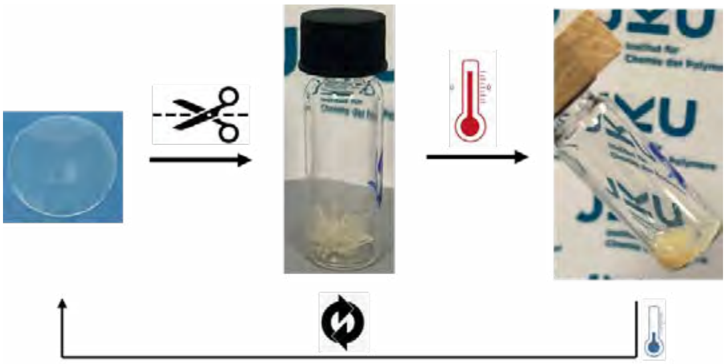

Fig. 5. Example of a PDMS elastomer cured with reversible organoborane LPs

Acknowledgement

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Polymerization Initiation Systems – How everything will start

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Abstract

Polymers are a valuable and important substance class. But to convert monomers into polymers an additional substance class is needed. Initiators are responsible for the transformation of a trigger signal into “chemical energy” that can start the polymer reaction. The expectations for initiators are high since they are expected to be non-hazardous, soluble, cheap, colorless, highly reactive in their activated state but should be very stable before activation. The activation trigger could be temperature, light, mixing with another component or other, more specialized, forms of energy.

In this lecture some developments for

- radical initiators
    a. amine-and peroxide-free 2K system[1]
    b. thermal initiator systems for radical induced cationic frontal polymerization[2]
    c. nonaromatic photoinitiators[3] [4]
    d. MAPO derivates as alternatives for TPO[5]

- ionic initiators
    a. sulfonium borate initiators for cationic photopolymerization[6]
    b. photobase generators[7]

- initiators with a coordinating metal center
    a. Iron centered photoinitiators for poly-trimerization[8]

will be discussed.

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Controlling Monomer Curing with Orthogonal Photochemistry: Towards Continuous Printing of Thiol-Ene Resins

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In this study the use of light as a trigger for controlling thiol-ene photopolymerization kinetics was explored, leveraging wavelength-selective activation to achieve spatial and temporal precision. The integration of different chromophores, responsive to distinct wavelengths, has been extensively explored in photochemistry.[1] In particular, antagonistic photochemistry, where one wavelength activates and another wavelength quenches a reaction, has shown significant potential in applications such as Stimulated Emission Depletion (STED)-lithography and volumetric stereolithography.[2, 3] However, to the best of our knowledge, the concept of antagonistic photoreactions has not been applied to radical-mediated thiol-ene polymerisations.

Thiol-ene networks are known for their biocompatibility and superior toughness to (meth) acrylic systems and are therefore widely researched. Typically, thiol-ene reactions are classified as “click” reactions due to their high yields and efficiency.[4] However, Bowman et al. demonstrated that basic amines are able to retard thiol-ene reactions by converting thiols into thiolate anions. Subsequently, these thiolate anions inhibit the formation of thiyl radicals, severely hindering the polymerization.[5] Taking this concept a step further, the present work presents a light-driven approach to the spatially controlled release of an amine base.

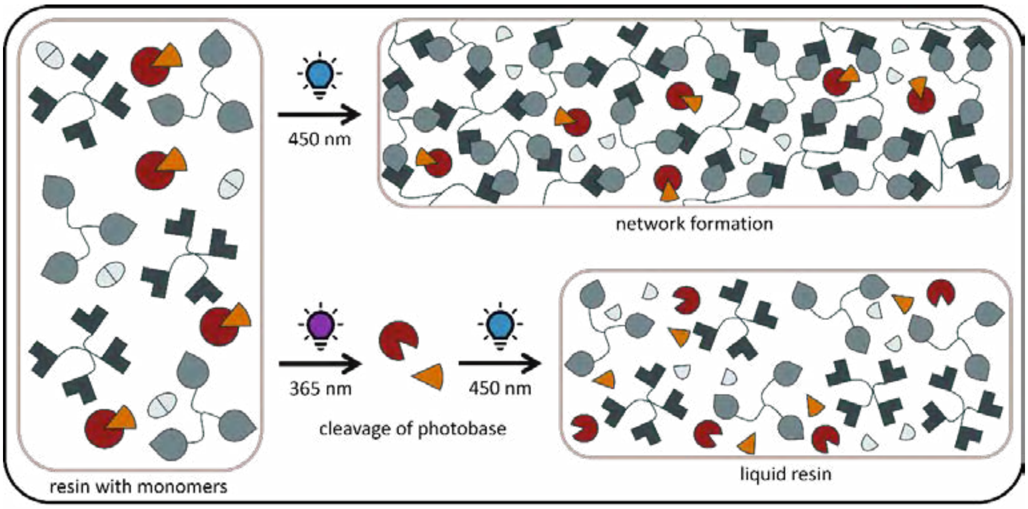

Fig. 1: schematic illustration of the photoinduced reactions within the presented thiol-ene resin

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In the resin system presented here, camphorquinone (CQ) is used as a photoinitiator, which initiates polymerisation when illuminated with 450 nm light, but remains virtually inactive at 365 nm. A photobase generator with a corresponding absorption spectrum – NPPOC-TMG – is chosen to release a strong amine base upon exposure to light of 365 nm. It is demonstrated that the two photoreactions initiated by CQ and NPPOC-TMG respectively take place in an orthogonal and also antagonistic manner, enabling precise control over the thiol-ene polymerization. Under 450 nm light, polymerization proceeds, as observed by FTIR spectroscopy, where the consumption of C=C and thiol groups indicates network formation. Upon subsequent exposure to 365 nm light, the reaction kinetics slowed down significantly, stopping polymerization by releasing the amine base that quenches the reacting radicals. This wavelength-dependent inhibition allows spatial and kinetic control over the polymerization process.

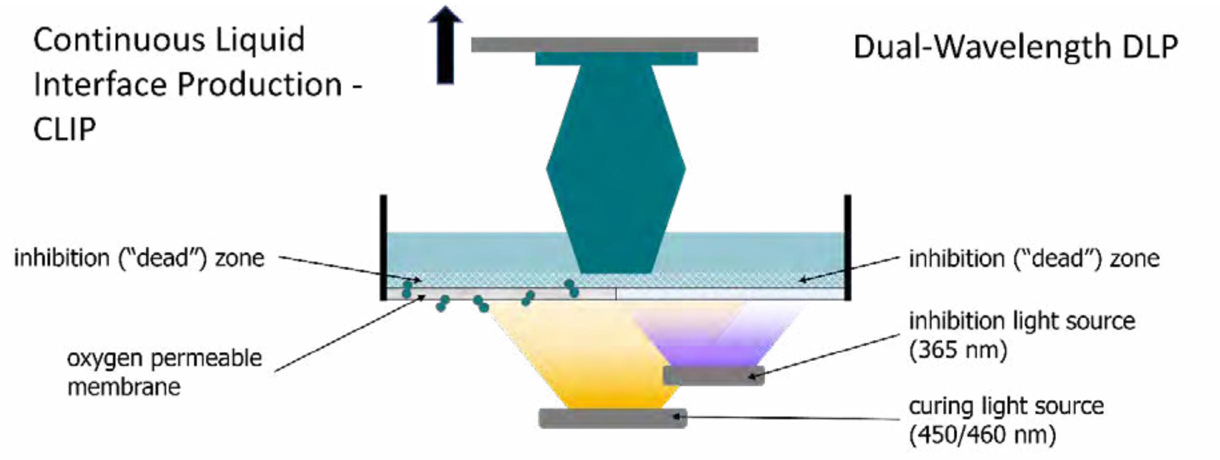

Fig. 2: schematic illustration of two continuous printing processes - CLIP (left side), and the dual wavelength approach introduced in this work (right side)

Further investigations using photorheology show that introducing the photogenerated base prevents the formation of a polymer network, as evidenced by the absence of gelation in samples exposed to 365 nm light before illuminating with light of 450 nm. In the study also the spatial resolution of the inhibition process through mask lithography experiments is explored. Additionally, a dual-laser setup is used to successfully create polymer structures in the micrometer range with 450 nm. Both wavelengths illuminating the resin simultaneously lead to inhibition of the polymerization, further showcasing the antagonistic nature of the system. Additionally, the ability to modulate reaction kinetics through varying illumination doses is investigated in gray-scale experiments, where structures of different heights are produced in dependence on the intensity of inhibition.

In conclusion, this work presents a novel antagonistic photoreactive system for thiol-ene networks, enabling localized and tunable control of polymerization kinetics. The dual-wavelength approach opens up new possibilities for advanced lithographic techniques and especially continuous stereolithography using thiol-ene based resins.

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Surface-Initiated Photopolymerization with Ge-based Initiators - Applications and Perspectives

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Abstract

Applications of photoinitiators (PI) based on the group IV-element Ge will be presented, highlighting their advantages over conventional photoinitiators, and accessible polymerization techniques.

These PI are based on acylgermanes, which undergo Norrish type I cleavage. As a result, highly reactive germanium centered radicals (germyl radicals) are generated, which readily add to monomeric double bonds. Acylgermane-based PI offer several advantages over their organic P-based counterparts (e.g., phosphinoxide-based PI). These include low toxicity, high reactivity towards monomers and an extended absorption up to 480 nm enabling excitation of the PI in the visible range. [1]

In our work we employed (bromotris(2,4,6-trimethylbenzoyl)germane) (GeBr-PI) as an effective PI for surface initiated radical polymerization. In this context, hydrophobic layers of poly(perfluorodecyl acrylate), hydrophilic coatings of poly(acrylamide) as well as fluorescent films of poly(fluorescein-o-acrylate) were immobilized onto inorganic substrates. Patterned polymer layers were prepared to monitor the spatial resolution of the PI (see Fig.1a). [1] Moreover, polymer shells of poly(styrene) and different poly(acrylates) were grown onto silica nanoparticles and investigated with regard to layer thickness and grafting density (see Fig.1b). [2]

Our latest results revealed that acylgermane-based PIs can also be utilized for free radical promoted cationic photopolymerization of monomers such as epoxides and vinylethers. This enabled surface initiated cationic photopolymerization for the very first time. The detailed reaction mechanism is still under investigation.

The low toxicity, the absorption in the visible range, and the radical / cationic reaction mechanisms provided by acylgermane-based PI makes them suitable for the use in high end applications such as dental nanocomposite resins, controlled drug release systems, cancer therapy, dye-doping, silica coated quantum dots and many more.

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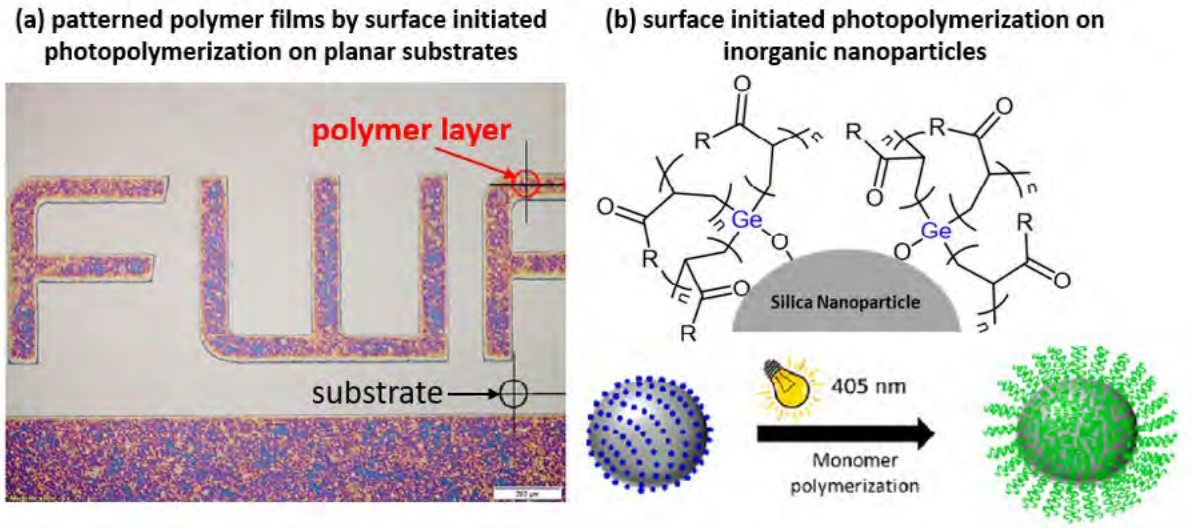

(a) patterned polymer films by surface initiated photopolymerization on planar substrates

(b) surface initiated photopolymerization on inorganic nanoparticles

Fig. 1: Example for surface initiated photopolymerization employing Ge-based PI

Acknowledgement

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Enhancing the Sustainability of PhotopolymERs ANd phoToinduced prOcesses

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Poster contributions

Polydopamine Deposition on Carbon Felt via Self-Polymerization and Hydrothermal Synthesis Methods: A Comparative Study

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Abstract

Polydopamine (PDA) has emerged as a versatile material for surface modification in various field of materials engineering from composites to biomedical applications to energy storage devices. In this study, the synthesis and deposition of PDA on carbon felt was studied using two distinct methods of self-polymerization and hydrothermal synthesis using an autoclave. In the self-polymerization approach, dopamine monomers were spontaneously oxidized in a weak alkaline solution achieved by using Tris(hydroxymethyl)aminomethane (TRIS), leading to uniform PDA coating on the carbon felt. Conversely, the hydrothermal method involved the use of an autoclave to achieve controlled polymerization and deposition at elevated temperatures. The resulting PDA-coated electrodes were characterized using X-ray photoelectron spectroscopy (XPS), Fourier-transform infrared spectroscopy (FTIR), as well as scanning electron microscopy (SEM). These techniques provided insights into the atomic composition, chemical structure, and surface morphology of the modified electrodes. The choice of synthesis method influences the properties of PDA coatings on carbon fiber, which in turn affects their potential applications.

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Activation of Carbon Felt Electrodes via Chemical Method and Plasma Treatment: Application to Redox Flow Batteries

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Abstract

Enhancing the electrochemical activity and efficiency of electrodes is crucial for the large-scale production of high-performance redox flow batteries (RFBs) [1]. Besides the redox active components and the membrane, the carbon felt is a crucial component for enhancing the power density and efficiency of an RFB system [2]. This study investigates the modification of carbon felts using KOH activation and plasma treatments (with oxygen and nitrogen) to improve the hydrophilicity and electrochemical activity of carbon felt electrodes. In this context, changes in surface chemistry were analyzed using X-ray photoelectron spectroscopy (XPS), Furthermore, field emission scanning electron microscope (FESEM) was utilized to study the morphology of pristine and modified electrodes. The performance of the prepared carbon felts was further assessed through polarization experiments with organic (quinone based) and inorganic (vanadium based) RFBs. Achieving an optimal level of surface modification is crucial, as excessive functionalization can deteriorate electrochemical performance by affecting the electrical conductivity and structural integrity of the carbon materials. These findings underscore the importance of precise control over the surface modification parameters to optimize the electrochemical performance of electrodes in redox flow batteries.

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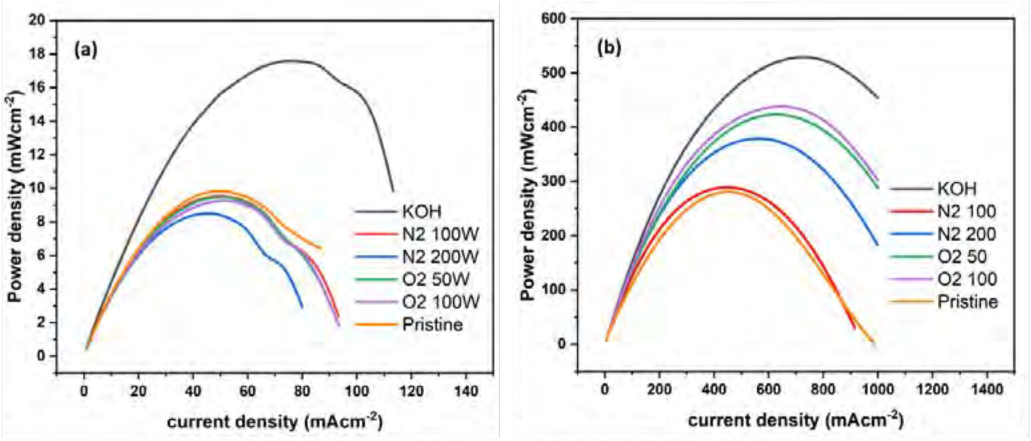

Fig 4. Polarization curves of pristine and modified electrodes in a) ORFB and b) VRFB.

Fig.1. Polarization curves of pristine and modified electrodes in a) organic RFBs and b) inorganic RFBs.

Acknowledgement

This research has received funding from the European Innovation Council program under the grant agreement No 101115293 (VanillaFlow).

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The preparation of a host-guest complex involving a di-thioxanthone disulfide photoinitiator and TPGDA with methylated β-cyclodextrin and its utilization in thiol-ene click polymerization in the presence of L-cysteine

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Abstract

Cyclodextrins are a category of toroidal oligosaccharides constituted by 6, 7 or 8 glucopyranose units linked together by α-1,4 bonds, which are called α-CD, β-CD or γ-CD, respectively [1-3]. This molecular structure has a hydrophilic outside due to the presence of hydroxyl groups onto the surface rims, while it has a hydrophobic inner cavity, which could receive organic guest molecules in order to form water-soluble inclusion complexes [4-5]. Thiol-ene click chemistry, which involves the reaction of thiol groups with various unsaturated functional groups such as acrylates, norbornenes,maleimides and carbon-carbon double bonds, has received significant attention in recent years due to its remarkable efficiency, selectivity, and reliability. Thiol-ene click reactions have been widely used in the polymer and materials industries to produce highly effective networks and films due to its durability under a variety of conditions and exposure to different solvents. Applications of thiol-ene click reactions in water-based formulations can be displayed more attractively with high efficiency, selectivity, and reliability with low toxicity, high biodegradability, and biocompatibility, in order to produce more environmentally friendly polymers and materials [6-7].

In this study, the main approach is to achieve complexation of an oil-soluble dithioxanthone disulfide photoinitiator and a diacrylate with Me-β-CD in water and then the addition of L-cysteine for a thiol-ene click reaction to produce novel polymers is successfully performed.

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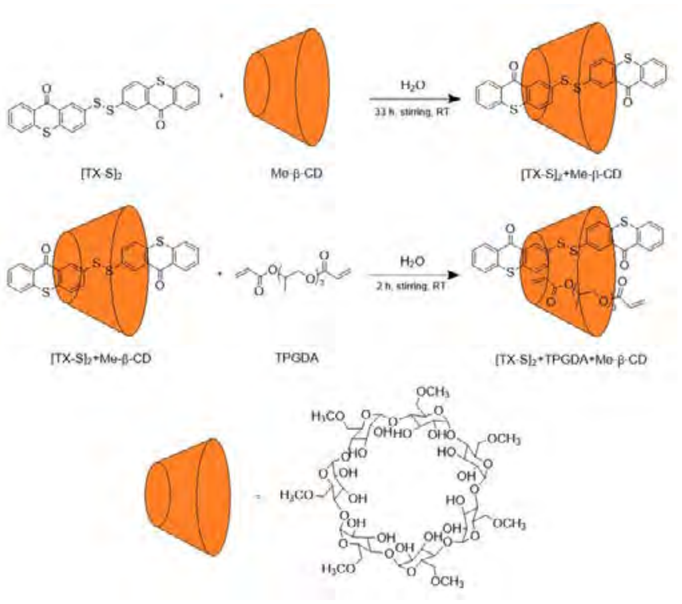

Fig. 1: Complexation of the thioxanthone disulfide photoinitiator $[TX\text{-}S]_2$ and TPGDA as diacrylate with Me-β-Cyclodextrin in water

Acknowledgement

This project received funding from the #horizoneurope20212027 programme under the Marie Skłodowska-Curie Doctoral Networks (MSCA-DN) grant agreement No. 101073432.

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Topographically controlled self-matting hydrophobic coatings by UV-curing

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Nature can impart remarkable properties to surfaces, including superhydrophobicity and anti-reflectivity, through the synergistic interplay of hierarchical structures and appropriate functional groups.[1] Various techniques have been employed to repli-cate the topography of natural substrates, including etching, lithography, and self-assembly processes.[2]

This study focuses on the investigation of self-patterning coatings promoted by the diffusion of the oxygen-inhibited layer during UV curing.[3] The primary objective is to understand the mechanisms underlying patterned thin layer coatings (below 100 µm) with a focus on the impact of crosslinking degree. Additionally, this phenome-non is examined in conjunction with hydrophobic diluents, based on an enthalpy-driven migration to the coating-air interface, and clay nanoparticles to enhance the hydrophobicity and hardness. Special attention is paid to the hydrophobization of the clay particles to improve their dispersion state in the resin and the robustness of the cured composites.

Acknowledgement

This project received funding from the #horizoneurope20212027 programme under the Marie Skłodowska-Curie Doctoral Networks (MSCA-DN) grant agreement No 101073432.

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Mass Customization 2.0 project produces BIPV market outlook analysis and first series of semi-fabricates based on design documents of four BIPV-products

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The Horizon Europe (HE) Mass Customization 2.0 (MC2.0) project will demonstrate how automated manufacturing of Integrated PV (IPV) elements using the mass customization approach can deliver a cost breakthrough in BIPV-products like IPV facades, IPV windows and IPV roofs, considering also sustainability.

This poster describes the production of PV elements called semi-fabricates by utilization of the MC pilot line. First, the design guidelines of the semi-fabricates need to be considered for the various production steps. This is realized in close collaboration with the IPV-product developer by initial identification of the design requirements and guidelines of the full IPV product. Furthermore, the methodologies followed for the cost calculation and the sustainability assessment are presented.

Preliminary results show that the roll-to-roll process has been successfully applied to the mass-customization pilot line, producing initial stable batches of semi-fabricates. The market outlook provides not only an assessment of constraints but also offers prospects for future analyses, extending beyond the steps involved in façade construction.

Importantly, emphasizing sustainability, backed by Life Cycle Assessment (LCA) among other factors, serves as a Unique Selling Point (USP). This makes the mass-customization process attractive for adoption by European industrial partners, contributing to the market's growth on a larger scale within Europe.

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Development of LED-Activated Photobase Generators for 3D Printing

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The shift towards sustainable manufacturing has driven innovation in photopolymerization, with recent efforts focused on developing more environmentally friendly and efficient systems.[1] Among these advancements, photoinitiators are gaining traction for their potential to initiate polymerization reactions with precision and minimal waste.[2] These catalysts show promise for enhancing polymerization processes by triggering key reactions such as thiol-Michael, thiol-isocyanate, epoxy polymerization, and ring-opening without the drawbacks of traditional methods.[3]

This study addresses two key areas: the synthesis and characterization of novel photobase generator (PBG) compounds, and their subsequent performance in photopolymerization under LED irradiation. The first aspect involves synthesizing PBGs, followed by comprehensive characterization using techniques such as UV-Vis spectroscopy, NMR, and mass spectrome-try to confirm their structure and properties. Detailed photophysical and photochemical inves-tigations will further assess their behavior under light exposure. Additionally, the research will establish guidelines for sustainable production by evaluating the life cycle and environmental impact of these materials. The second part explores the practical applications of these PBG compounds in photopolymerization, with a focus on minimizing challenges during the process, such as oxygen inhibition and the formation of unwanted byproducts. By improving their pho-tochemical performance, the study seeks to open new pathways for advanced material fabri-cation, particularly in additive manufacturing techniques like 3D printing. The outcomes are expected to contribute to innovative approaches in polymer science, positioning LED-sensitive PBGs as key enablers of next-generation materials.[4]

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ESPERANTO
Enhancing the Sustainability of PhotopolymERs
ANd phoTolnduced prOcesses

Funded by
the European Union

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Photoinduced Frontal Polymerization of Biobased Acrylatesù in the Presence of Natural Fillers

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Frontal polymerization (FP) is a self-sustaining reaction where an initial trigger (such as thermal or photoinitiation) generates a localized reaction zone known as the “polymerization front.” The exothermic heat released in this zone raises the temperature sufficiently to initiate further polymerization at the interface between the polymer and unreacted monomer, often leading to planar propagation [1].

Compared to conventional polymerization methods, FP offers several advantages: (a) a simple process without the need for stirring; (b) rapid reaction rates that save time; (c) cost-effective and eco-friendly operation without continuous external energy input; (d) reduction of multiple processing steps; (e) high product uniformity and homogeneity of polymer chains, as phase separation and sedimentation are avoided by the propagating front; (f) high conversion rates; and (g) minimal to no solvent usage [2].

This study presents findings on the curing of thick samples and monomers located in dark areas using photoinduced frontal polymerization of biobased acrylic monomers. The effects of incorporating natural fillers (wood powder and cellulose powder) were explored. Characterization techniques included FT-IR, viscometry, thermal imaging, and FESEM. Additionally, process optimization was examined with respect to thermal effects, frontal velocity, monomer conversion, reaction mechanisms, formulation type, and environmental and processing conditions.

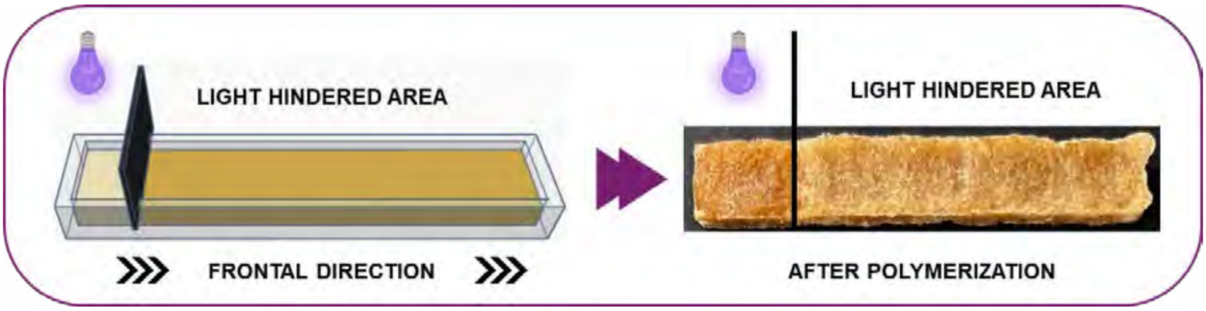

Fig. 1. Irradiation process scheme and a photo of biocomposite after polymerization.

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Spatially resolved photoactivation of dynamic thioester-networks

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Covalent adaptable networks (CANs) are crosslinked polymer structures that undergo dynamic bond exchange reactions when heated, enabling a reorganization of their topology. This unique characteristic allows these polymers to merge the durability and chemical resistance of thermosets with the processing versatility and recyclability of thermoplastics. [1]

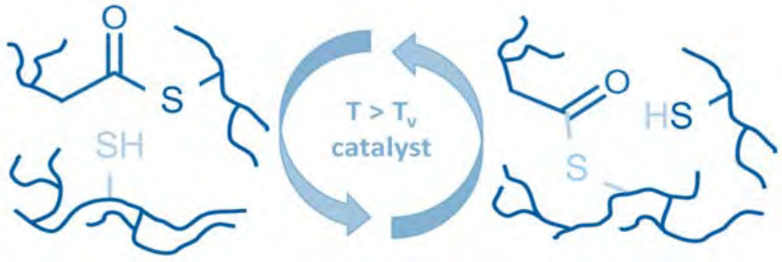

Fig. 1: Thiol-Thioester exchange mechanism

In this study, we concentrated on thiol-thioester exchange reactions (see Figure 1), which can occur rapidly even at low temperatures when appropriate catalysts are used, a property that is particularly relevant for biomedical applications. Initially, we produced vinyl monomers with thioester functionalities to promote network formation through a thiol-ene click reaction under visible light exposure. To achieve a spatial resolution of dynamic exchange reactions, a photobase generator (TMG-PLB) was synthesized. The purity of the monomers and the TMG-PLB was characterized by ^{1}H- and ^{13}C-NMR spectroscopy. By using equimolar amounts of thiol and vinyl monomer, 3mol% TMG-PLB and photoinitiator, the photosensitive resin was prepared. After curing the resin via 450 nm irradiation, spatially resolved activation of the photobase was accomplished through 365 nm UV-light illumination. To explore the resulting dynamic behavior, we conducted stress relaxation measurements at various temperatures. Additionally, a reshaping experiment was carried out to visualize the spatial activation of dynamic exchange reactions in a macroscopic manner.

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Separation of EoL PV modules using liquid-based methods to achieve better recycling quality

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ABSTRACT

In terms of future waste, a large quantity of End-of-Life (EoL) photovoltaic (PV) modules is expected in the next 20 years. This fact makes it reasonable to consider the regaining of other PV module components such as cell and polymeric materials in addition to the main component, glass. Such holistic recycling approach needs adequate separation methods, where a minimum loss of all PV module layers (front sheet, encapsulant, back sheet, cell, connectors…) is guaranteed as well as a certain fraction quality in terms purity is given. At status quo of recycling PV modules, the organic parts are eliminated by incineration and just the glass, copper and aluminum components are recovered. Herein, approx. 20% mass of PV module weight is lost for recycling and therefore a waste of resources [1].

Within this work a combination of mechanical and non-conventional physical and chemical recycling methods was processed to possibly regain all PV components in a good quality. Herein, fraction generated by water jet cutting, milling and shredding were further processed by density/centrifugal separation and dissolve/extraction methods. Fractions like back sheet material, contaminated with encapsulation material respectively cell material covered with encapsulant including connector parts, in different particle sizes, adhering to each other or as free particles resulted from the mechanical pretreatment. The advantage of the density difference in those fractions was used to refine the quality after this first recycling step. Such separation can be carried out in large quantities using the Circulyzer© process. Furthermore, in terms of chemical recycling, preliminary tests shown a weakening of the insoluble encapsulation material, mainly crosslinked ethyl vinyl acetate, by swelling in solvents and after light grinding a mixture of detached cell and encapsulant material was present, which again can be separated by density. For the shredded fraction, a disassembling of the layers could be detected through weakening the interconnection by circulating hot solvent using

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the Soxhlet apparatus, which also provides the possibility to wash out flame retardants and other additives [2] for pure polymer fractions.

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Plastic STRAW - Smart Technology for Recycling of Assorted plastic Waste

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The recycling of plastics is a current research topic around the world - research is being carried out into more effective recycling methods. Current research in the field of recycling is focusing on the processing of material flows. For example, research is being carried out into multi-sensor-based sorting systems with artificial intelligence or so-called tracing systems. These have the disadvantage that material composites (such as multi-layer structures in packaging) cannot be specifically separated. These waste streams usually end up in the downcycling channel, including thermal recovery, and thus disappear from the material cycle.

The two universities involved in the Plastic STRAW project (Montanuniversität Leoben and Graz University of Technology) have developed a new type of separation process to ensure that plastics that cannot be sorted or are difficult to separate do not disappear from the material cycle. This differs from existing recycling processes in one key aspect: the material streams are separated in the molten state of the polymers. The developed continuously operating centrifuge makes it possible to convert these plastic fractions into unmixed material streams. The process also has a side effect: the use of high temperatures also results in the removal of low-molecular substances (e.g. substances that have diffused into the polymer, such as oils and fats). The process can be integrated into a conventional recycling process in order to ensure industrial implementation following the project.

Acknowledgement

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3D printing of dynamic photopolymer composites containing recycled polyester fillers

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Abridged version

Low-viscosity resins utilised in vat photopolymerization 3D printing enable the production of composite materials with fillers. By incorporating recycled polyester fillers, both the unit cost of the resin can be reduced, and waste material can be effectively repurposed. However, the inclusion of fillers often negatively impacts the material's properties, primarily due to the increased interfacial area. To mitigate this, resins containing ester bonds and hydroxyl functional groups that facilitate catalysed covalent bond exchange will be employed. The formation of bonds between the polyester filler and the resin matrix helps overcome the adverse interfacial effects, thus enhancing the overall properties of the material.

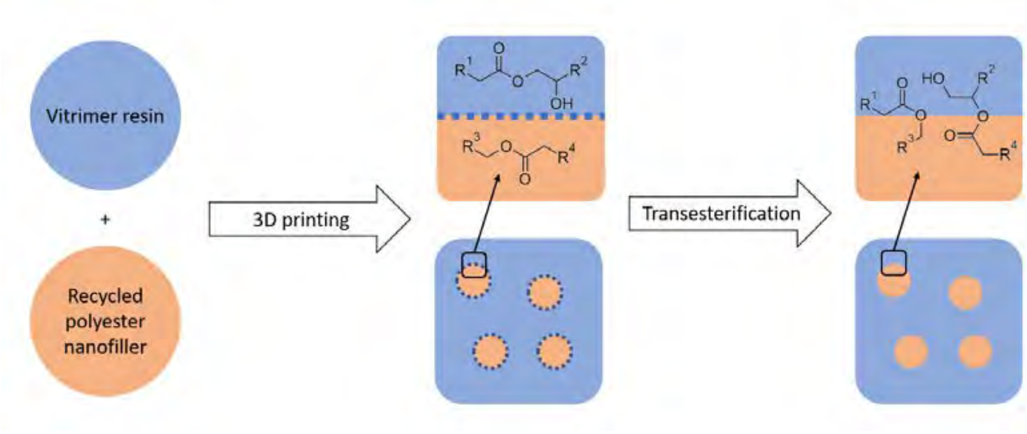

Fig. 1: Visualization of resin/filler compounding and filler/matrix integration in 3D printed objects.

Acknowledgement

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ALGINATE-BASED UV COATING

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The increasing number of research studies devoted to the development of bio-based materials reveals their great ability to substitute petrochemical–based materials. Coatings are one of the main applications concerned by this interest. Developing new synthetic routes combining bio-based building blocks and environmentally–friendly processes such as UV irradiation is a very promising emerging field of research. In this study, we present a new approach for the synthesis of bio-based alginate derivatives for photopolymerization without the use of traditional photoinitiators. Their potential adverse effects on human health and the impact on the environment are avoided thanks to this original approach. Alginate, a biopolymer derived from seaweed, is chosen as the primary material for its biocompatibility and sustainability. They are functionalized by allyl ether or maleimide. Their photocopolymerization will be presented (Figure 1). The photocopolymerization step employs maleimide and allyl ether as a key component to form new potential materials.

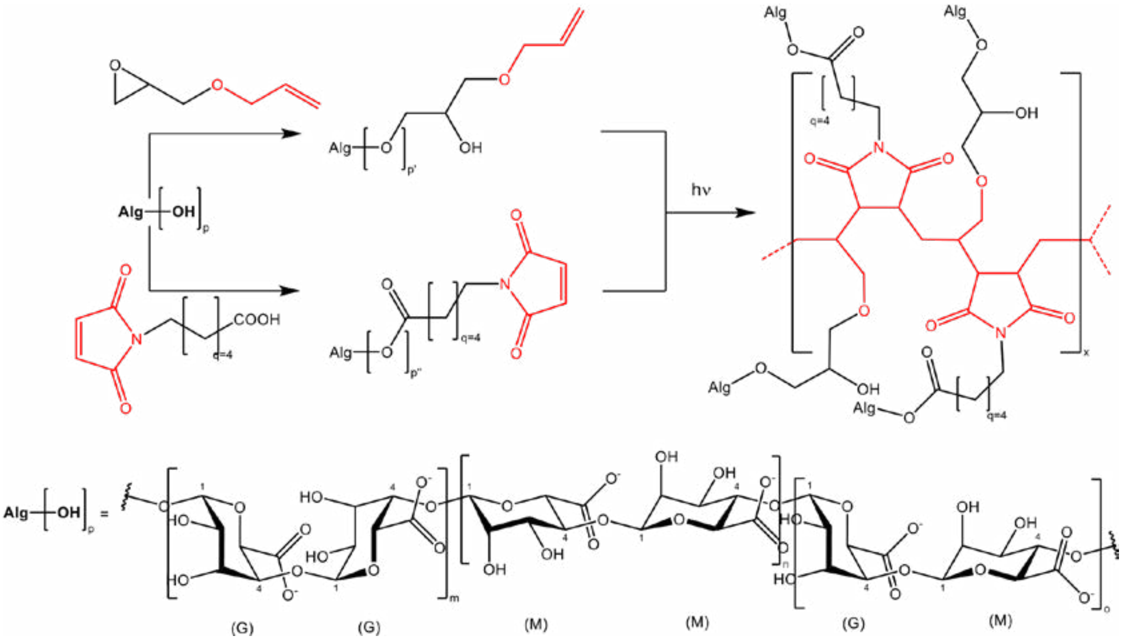

Fig. 1. Alginate derivatization and photocopolymerization with allyl ether and maleimide

This project received funding from the #horizoneurope20212027 programme under the Marie Skłodowska-Curie Doctoral Networks (MSCA-DN) grant agreement No 101073432”.

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Different strategies for the fabrication of micro-patterns to introduce functionality into polymer surfaces

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Surface texturing represents a promising route to engineer material properties, such as a surface's wettability or the tribological properties. Many examples in nature are known where micro- and nano-sized textures with different surface patterns (geometries and topologies) determine the functionality of the surface (e.g., lotus leaf water repellency or gecko adhesion) [1].

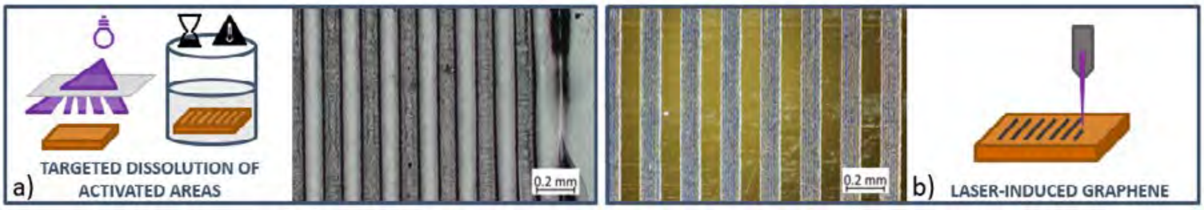

Fig. 1: Micro-sized surface patterns (100 µm line-width and distance) fabricated by a) controlled dissolution and b) laser-induced pyrolysis

Herein, we present two different approaches for the fabrication of surface patterns and assess their characteristics. The first strategy combines photolithography with dynamic covalent bonds to create positive tone surface patterns. The photoreactive resin can be cured with a wavelength of 450 nm. Micro-patterns are then inscribed into the surface by selective exposure to light with a wavelength of 405 nm. This allows for selective dissolution of the micropatterns using a solvent-assisted transesterification mechanism. An alternative approach is using a UV laser to form laser-induced graphene (LIG) in various patterns on the surface of a polymer substrate. The laser writing and the resulting transformation of the precursors into graphene through a fast photochemical and thermal pyrolytic process can be used to synthesize different LIG patterns directly. These LIG-patterned surfaces represent a promising method of surface functionalization as they were previously shown to enable tuning of surface wettability [2].

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Material Characterization by Optimized FEM-Simulations: Evaluation and Modelling of Compressibility Tests

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Abstract

Over the past few decades, the number of battery systems in our daily lives has steadily increased. In addition, the energy density within each battery has increased, allowing for smaller and more powerful batteries. However, this has led to an increase in battery accidents because the increased energy density makes batteries more susceptible to failure. A common type of battery failure is thermal runaway, which is a cascading failure of the entire battery system triggered by the failure of individual battery cells. [1]

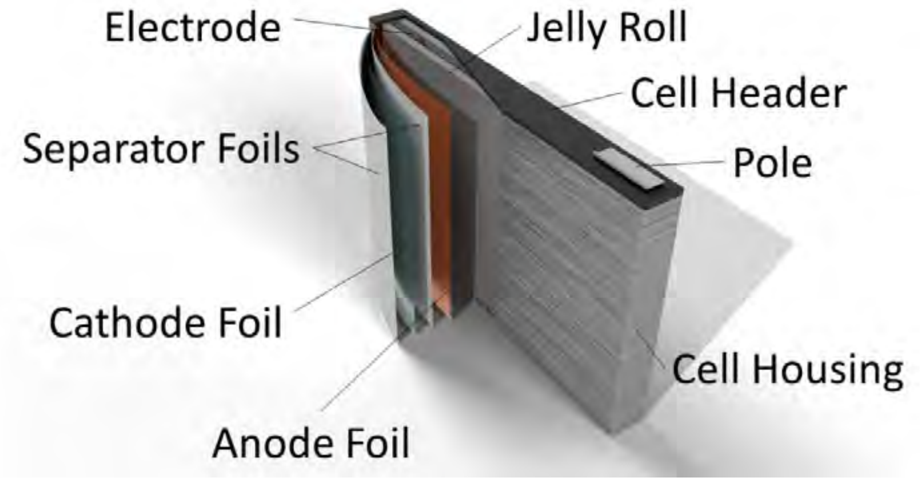

Fig. 1: Schematic structure of a prismatic battery cell

The internal workings of a battery consist of the electrodes and the jelly roll, as shown in Figure 1. The jelly roll consists of rolled up layers. These layers are the anode, cathode, and separators. The anode and cathode are three-layer-systems with a metal collector foil in the middle and active layers on either side of the collector foil.

The goal of this work is to create a virtual model of battery systems that can be used to

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simulate the effects of thermo-mechanical loads on the battery system and the resulting failure behavior. To achieve this, the material parameters of the different jelly roll layers need to be determined. The active layers are of critical importance because the compression and resulting shear behavior of the active materials determine the behavior of the battery cells in crush tests [2].

Acknowledgement

The research work was performed within the COMET-Module Project ”BattLab” (project-no.: 904924) at the Polymer Competence Center Leoben GmbH (PCCL, Austria) with contributions by AIT Austrian Institute of Technology GmbH (Sustainable & Smart Battery Manufacturing), Budapest University of Technology and Economics (Department of Inorganic and Analytical Chemistry), Montanuniversitaet Leoben (Chair of Materials Science and Testing of Polymers), 4a engineering GmbH and AVL List GmbH.

“BattLab” is funded within the COMET – Competence Centers for Excellent Technolgies Programme by the Austrian Federal Ministry for Climate Action, Environment, Energy, Mobility, Innovation and Technology, the Austrian Federal Ministry for Labour and Economy and the province Styria and SFG. The COMET Programme is managed by FFG.

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Design of Thermo-Responsive Coatings for Battery Safety: Evaluation and Pathways to Sustainability

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The improvement of batteries systems used in e-mobility remains a focus of continuos research due to the significant number of unfortunate accidents caused by their malfunctioning. These events can occur for various reasons, including overcharging, mechanical damage, short circuits, external heat, and other factors, eventually leading to overheating and triggering thermal propagation or in the worst case, explosions. While recent studies have focused on preventive safety techniques, such as exploring fire-resistant materials for cells, safety devices for battery packs,1 and managing battery pack operations,2 this work presents a precautionary approach by employing a thermo-responsive polymer coating that releases a detectable gas at a very well-defined temperature. A thiol component, acting as a tracer gas, is incorporated into the polymer matrix through a click reaction. Upon an overheating event, the thiol is cleaved and released as a gas, which can then be detected by metal oxide (MOx) sensors, thereby triggering an alert for the hazardous condition of the batteries. To enhance the sustainability of the coating, it can be recycled after gas release by reintroducing the thiol compound into the polymer matrix. By FT-IR and thermogravimetric analysis, evidence of covalent bond formation between the tracer gas and the system, as well as the restoration of tracer gas content, is demonstrated. Furthermore, to extend the life cycle of the coating, a covalent adaptable network was designed within the polymer matrix, allowing it to be reshaped after the gas is released.

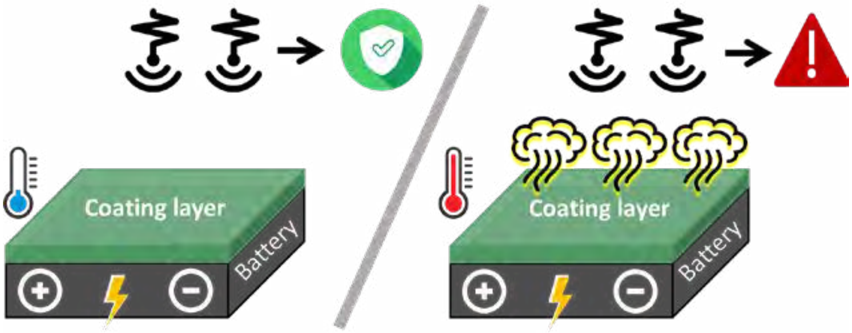

Fig. 1: Gas release and sensor mechanism in thermo-responsive coatings

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Novel recyclable and reshapeable interpenetrating phase composites through photo-induced frontal polymerization

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Efficient strategies for reusing thermoset materials hold significant potential for reducing material waste. Advancing the development of novel thermoset polymers and composites, produced through energy-efficient and environmentally friendly polymerization methods, can play a crucial role in this effort. To achieve this, improvements in the reprocessability, reshapeability, and recyclability of these materials are essential. In view of consumer goods applications, the proposed research aims to develop novel photo-curable composites with controllable compliance and shape, achieved with the utilization of photo and/or heat-reversible precursors [1]. The resin system is based on a reactive thiol-acrylate system that is able to develop a self-sustaining reaction induced by light, called photo frontal polymerization [2]. The controllable compliance of the proposed system is built on the reversible nature of the exchangeable disulfide bonds. Effective incorporation of the reactive precursors into the open-cell foam is reached through the implementation of a vacuum-assisted liquid impregnation process, producing a vitrimer composite [3]. This research focuses particularly on analyzing the degree of reprocessability exhibited by the composite. Ultimately, the final goal is to recover the monomers through chemical degradation of the polymer chains. First results will be presented here on the development and characterization of the reactive thiol-acrylate system. In particular, the influence of the ene-thiol ratio on the equilibrium relaxation stress, and hence on the ability to be reshaped will be presented.

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A Simulation-Based Approach Allowing for the Prediction of Mechanical Properties of Vulcanizates

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Determining the most efficient process parameters for manufacturing injection molded rubber products through the Design of Experiments (DOE) can be highly laborious and resource-intensive. Simulation methods offer a viable approach to optimize rubber processing within a shorter timeframe. To accurately represent the mechanical properties of injection molded parts under various vulcanization temper-atures and degrees of cure, Traintinger et al. [1] further improved Weinhold's ap-proach [2], i.e., the so-called average curing speed model (ACS-Model), for injection molding. This extended method combines second-order polynomials with a logistic growth function, allowing for the first time accurate approximation of the real part performance (FTQ), especially for parts with a low degree of cure. To utilize the model for predicting part properties in an injection molding simulation, access to ki-netic data from the raw rubber compound is essential. The transmitted torque, ac-quired from viscometry measurements, indicates of the temperature-dependent cur-ing reaction and provides information about the function variables: degree of cure c and extent of reaction X.

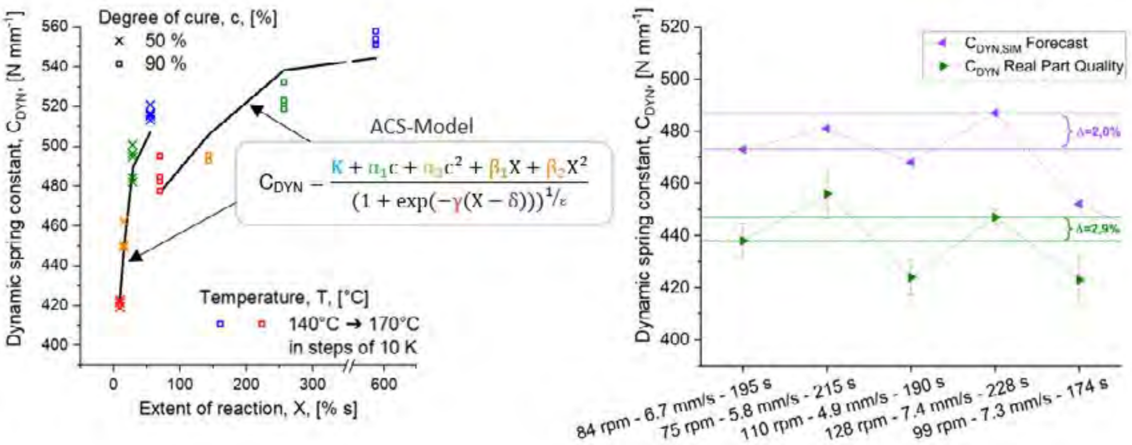

Fig. 1: Enhanced approximation of part quality through the logistic growth function approach, even for low degrees of cure (left). Comparison of dynamic spring constant – $C_{DYN,SIM}$ Forecast vs. C_{DYN} Real Part Quality.

Physical experiments were conducted to validate the outcomes of the simulated results for specific process settings, as shown in Figure 1. For parts produced at T = 160°C, the simulation results accurately captured the relative changes in the dynamic spring constant, demonstrating alignment with the trends observed in physical measurements. Although the-

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Corresponding author: margarete.hufnagl@pccl.at re are some differences in absolute values, the consistency in the direction and magnitude of changes across both simulated and experimental data confirms the model’s accuracy in reflecting real part quality. This indicates that the simulation is not only capable of predicting mechanical properties but also offers a reliable tool for initial process optimization.

Overall, the research highlights the successful application of a simulation-based approach for initial setpoint optimization in rubber injection molding processes. The findings confirm the effectiveness of using simulations to optimize process settings, providing a valuable tool for improving the efficiency and sustainability of these manufacturing processes.

Acknowledgement

The research work was performed within the COMET-project „Virtual Rubber Injection Molding Machine II“ (project-no.: 2.04) at the Polymer Competence Center Leoben GmbH (PCCL, Austria) within the framework of the COMET-program of the Federal Ministry for Climate Action, Environment, Energy, Mobility, Innovation and Technology, and the Federal Ministry for Digital and Economic Affairs with contributions by Montanuniversitaet Leoben (Institut of Polymer Processing) and MAPLAN GmbH, Semperit Technische Produkte Gesellschaft m.b.H, SIGMA Engineering GmbH, and MAGMA Giessereitechnologie GmbH. The PCCL is funded by the Austrian Government and the State Governments of Styria, Lower Austria and Upper Austria

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Roughness and Nanoindentation – mortal enemies.

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Abridged version

Nanoindentation can be used to characterize even the slightest change in local mechanical properties. It can even measure local effects introduced by either welding or aging. However, indentation experiments need careful sample preparation and resulting surface quality because of the surface-sensitive nature of nanoindentation testing. However, this is not always possible. In this work, the effect of the surface finish of a polyethylene sample on evaluated values obtained from nanoindentation is shown. Additionally, the measurements included the impact of variations of the maximum load, as well as the loading, and unloading speed. The obtained modulus, calculated following Oliver & Pharr´s method, is compared with a tensile test. The experiments show that the nanoindentation tests yield a modulus comparable to the tensile tests, as long as the surface quality is good enough. In the case of the examined polyethylene material, even a surface roughness R_a of roughly 20 % of the indentation depth for forces of 1 mN and more were found to produce acceptable results. However, smaller values of R_a drastically decreased scattering of data values.

Acknowledgement

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The help from the Chair of Functional Materials and Materials Systems, in regard to roughness testing on their confocal laser scanning microscope is highly appreciated.

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Efficient surface classification based on tactile properties with a robotic setup

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Abridged version

The tactile feel of surfaces is starting to gain significance across different industries. As a result, advanced inspection systems are required to assess the tactile characteristics of a surface both accurately and efficiently. Such systems could help establish tactile standards, compare the tactile properties of different surfaces, or detect tactile defects during inline quality inspection. In this work, we introduce a robotic system combined with a deep learning-based approach that learns to classify surfaces based on their tactile properties. The system uses a collaborative robot that moves an artificial finger over the surfaces of interest, gathering temporal data on perceived friction and roughness. A neural network then classifies the surfaces based on this collected data. Feedback on misclassifications and the average confidence levels is provided to the robot, which determines if more data is required from certain surfaces to enhance classification accuracy. The neural network is subsequently fine-tuned with the updated data. The objective is to gather the minimum amount of data needed to achieve satisfactory accuracy. In a case study involving four surfaces with subtle tactile differences, the system classified them with over 90% accuracy. The key contribution of this work is the development of a system capable of accurately classifying surfaces with subtle tactile variations and autonomously updating the deep learning model's dataset to ensure balanced performance across all surfaces under study.

Acknowledgements

The authors would like to acknowledge the funding support of this project by Volkswagen AG and Konica Minolta. The research work was partly performed within the COMET-project „Deep on-line learning for highly adaptable polymer surface inspection systems" (project-no.: 879785) at the Polymer Competence Center Leoben GmbH (PCCL, Austria) within the framework of the COMET-program of the Federal Ministry for Climate Action, Environment, Energy, Mobility, Innovation and Technology and the Federal Ministry for Digital and Economic Affairs. The PCCL is funded by the Austrian Government and the State Governments of Styria, Lower Austria and Upper Austria.

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How to control transesterification reactions on the microscale

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Abridged version

Covalent adaptable networks (CANs) are a unique class of polymers that are characterized by reversible covalent bond exchange reactions that enable self-healing, reshaping, reprocessing and/or recycling of crosslinked polymer networks, in response to external stimuli, such as temperature. However, achieving spatial control in these thermo-activated systems remains challenging. Herein, we introduce a covalently attachable non-ionic photoacid generator to locally manipulate bond exchange reactions in thiol-ene photocurable vitrimers at the microscale level. Upon UV-light exposure, a strong immobilized sulfonic acid species is released, efficiently catalyzing dynamic exchange reactions. As proof of concept, we inscribe positive-toned microstructures with a resolution of 5 µm in thin films and demonstrate the possibility to locally reprogram bulk material properties. This advancement highlights the versatility of this novel catalyst in creating light-processable and adaptable functional materials [1].

Acknowledgement

The research work was performed with the “SMART” project. This project has received funding from the European Union’s Horizon 2020 research and innovation programme under the Marie Sklodowska-Curie grant agreement no. 8400088. Part of the research was also carried out within the COMET-Module project ”Repairtecture” (project-no.: 904927) at the Polymer Competence Center Leoben GmbH (PCCL, Austria) within the framework of the COMET-program of the Federal Ministry for Climate Action, Environment, Energy, Mobility, Innovation and Technology and the Federal Ministry of Labour and Economy. The PCCL is funded by the Austrian Government and the State Governments of Styria, Upper and Lower Austria.

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The uprising possibilities of new thermally latent catalysts with tailored activation temperatures for the use in covalent adaptable networks

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The development of new thermally induced healing materials has gained increased attention over the past years, following the environmentally friendly options of waste reduction as well as enhanced lifetime of future polymer-based products. Vitrimers are well studied intrinsically healable covalent adaptable networks, which are capable of undergoing thermo-activated dynamic associative exchange reactions. Succeeding the topology freezing transition temperature (Tv), the exchange reactions are accelerated rapid, and the polymeric material has the ability to flow similar to a viscoelastic liquid. Although, it is still in a crosslinked solid state. [1] Vitrimers, relying on dynamic hydroxyl ester links, require the addition of a transesterification catalyst to facilitate fast bond exchange reactions above Tv. Subsequently, a library of thermally latent bases for catalyzing the transesterification in vitrimers has been studied.[2]

Selected thermo-base generators (TBGs) were synthesized and the thermal decomposition as well as the thermally triggered release (TTBG) of the base were studied in detail employing thermal gravimetric analysis (TGA), evolved gas analysis (EGA), nuclear magnetic resonance spectroscopy (NMR) and gas chromatography mass spectrometry (GCMS). Due to the molecule-structure of the thermally latent catalyst, the decomposition temperature and the inducing period could be adjusted over a wide temperature range. Hence, different decomposition temperatures of the thermally latent catalysts lead to different applications in vitrimers with varying Tv and consequently a broad field of future applications in the polymer industry.

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Welding of incompatible polymers employing vitrimer chemistry

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Abstract

Various welding techniques are well-established and commonly used in joining metal parts. They are being adapted and applied to thermoplastics due to their enormous market share and the continuous tendency for development of increasingly complex products. In the welding of thermoplastics, the molecular entanglement between the materials is the main factor determining bond strength. However, with incompatible materials the entanglement is very limited to none, resulting in welds of very low strength, if any. Without molecular entanglement and mechanical interlocking aside, chemical bonding contributes to the strength of the weld. With the induction of vitrimer chemistry in incompatible materials, materials can form reversible crosslinks through which the materials can be joined.[1, 2]

Acrylonitrile butadiene styrene (ABS) and polypropylene (PP) transesterification vitrimers were prepared in twin-screw extruder. ABS or PP grafted (ABS-MAH, PP-MAH) with maleic anhydride (MAH) was used as a matrix, mixed with diglycidyl ether of bisphenol A (DGEBA) in 1 mol equiv to MAH groups in matrix and triphenyl phosphate (TPP) as transesterification catalyst. Materials were injection moulded and test specimens were welded at elevated temperatures and various times, so that the optimal temperature and welding time were determined. Neat PP and ABS were not weldable, while PP-MAH and ABS-MAH as well as vitrimer PP and vitrimer ABS joined. Longer times at elevated temperatures resulted in improved bond strength, even more so than increasing the temperature of the welding above 160 °C since the transesterification reaction proceeds slowly. Debonding was performed with modified tensile test and forces of the weld up to the maximum of 48 N were achieved for weld of vitrimer samples and maximum of 46 N for weld between grafted polymers. Trigger debonding of heated vitrimer samples at 160 °C was performed to evaluate debonding properties and heated specimen separated with force of maximum 20 N.

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Tuning Surface Properties of Thiol-Ene Polymers for Microfluidic Systems

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In this work thiol-ene based photopolymers are surface-functionalized to create hydrophilic and hydrophobic areas for the development of microfluidic systems via photopolymerization. In this context, thiol moieties on the polymer surface are oxidized with UV-light and patterned with photomasks to yield spatially controlled hydrophilic sulfonate groups. In a further step, the remaining mercapto groups are functionalized with fluorinated acrylates via base catalyzed thiol-michael addition or with gold nanoparticles to create hydrophobic regions. The proper functionalization of the surface is monitored via contact angle measurements and X-ray photoelectron spectroscopy. Using this method microfluidic channels will be created with this method that are able to guide blood samples and detect viruses through rapid diagnostic testing.

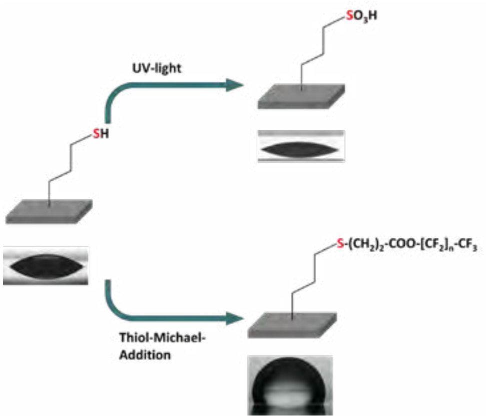

Fig. 1: Scheme of the different surface functionalization strategies used of a thiol surface.

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Christian Doppler Laboratory for Impact of Recycled Materials on the mechanical lifetime estimation of polymers

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Abridged version

Understanding the interactions between pipe design, loading conditions, and materials used is crucial for safe polymer pipe operation. Using recycled materials in polymer pipes presents additional challenges, particularly with polypropylene (PP), as there is only limited knowledge regarding long-term failure mechanisms under realistic loading conditions.

The CD laboratory will focus on the impact of the materials' constitutions on the performance of different types of PP that also contain recycled materials. Mechanical properties, local loading situations, failure mechanisms, morphology, and base constitution are thoroughly analyzed to include them in the structure-property relationships and lifetime estimation.

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Eco-Friendly Polymer Networks from Castor Oil and Di-Thioxantone disulfide as Photoinitiator: A Thiol-Ene Reaction Approach

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Abstract

Thiol-ene reaction has attracted attention in the polymer field due to its unique mechanism, which combines the advantages of classical radical and step-growth polymerizations as a radical stepgrowth procedure [1-3]. It also has a „click chemistry“ feature [3] as it exhibits properties such as being fast, solvent-free, insensitive to oxygen, showing late gel points, with a high yield [4], not forming by-products, forming a uniform polymer structure, and giving products with a narrow glass transition temperature [3]. Thiol-ene polymerization was first used on surface coatings and films by photo-curable polymers and resins .

Harnessing these attributes that thiol-ene reactions provide we investigated thiol-ene reaction between a biobased material such as castor oil and a one-component type II dithioxanthone-disulphide photoinitiator [TX-S-]2 to develop novel polymeric materials with enhanced properties. Castor oil, a renewable resource rich in unsaturated fatty acids, serves as the ‘ene’ component, while the dithioxanthone-disulphide photoinitiator [TX-S-]2 [5] provides the ‘thiol’ functionality by forming thiyl radicals [TX-S.] under UV irradiation. The reaction mechanism, driven by UV-induced radical generation, shall be explored to establish optimal conditions for efficient synthesis of biobased photoinitiators and polymer formation [6]. One-component systems are easier to handle and formulate since they eliminate the need to separately add a co-initiator. Moreover, type II photoinitiators generate radicals through a hydrogen abstraction mechanism when exposed to UV or visible light and are generally less sensitive to oxygen inhibition. One-component system ensures that radical generation is well-controlled, leading to efficient initiation of polymerization. Hence, this research approach shall open pathways for developing sustainable and functional materials with potential applications in coatings, adhesives, and biocompatible polymers.

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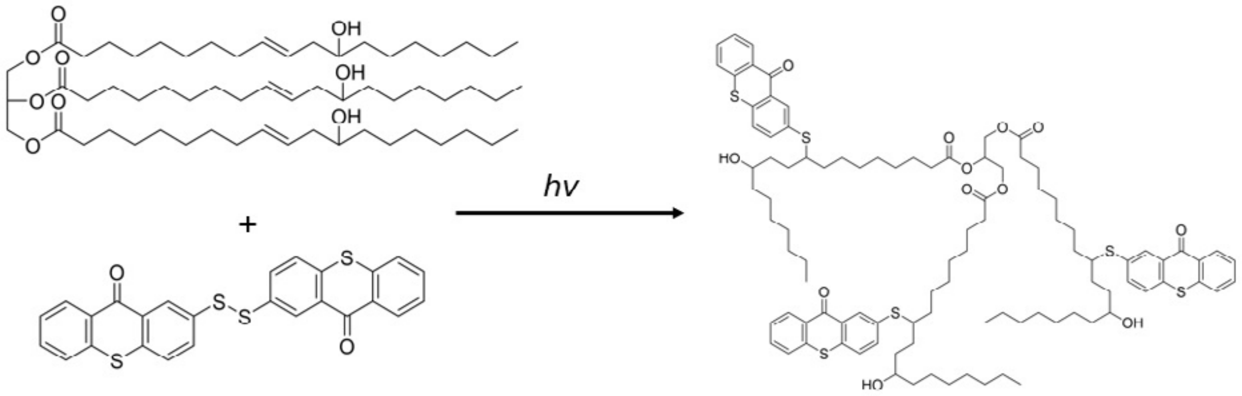

Fig. 1: Thiol-ene reaction between castor oil and dithioxanthone-disulphide photoinitiator [TX-S-]$_2$

Acknowledgement

ESPERANTO
Enhancing the Sustainability of PhotopolymERs ANd phoToinduced prOcesses

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the European Union

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3D Printed Hand Orthoses: Enhancing Design Through Contact Pressure Measurement and Optimization Technique

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This research presents a novel approach to enhancing the design of 3D printed hand orthoses by integrating contact pressure measurement and topology optimization. Utilizing flexible Force Sensing Resistor (FSR) sensors and a Teensy 3.5 circuit board, contact pressure was measured at critical points on hand orthoses. This data serves as input for topology optimization procedure to refine the orthosis design, improving wear comfort by alleviating high pressure areas. The optimized and non-optimized designs were additively manufactured using FDM techniques. Results demonstrate significant improvements in comfort and design efficiency, highlighting the potential of combining advanced measurement, optimization and manufacturing techniques in orthotic design.

This research confirms that integrating contact pressure measurement with topology optimization significantly enhances the design of 3D printed hand orthoses, improving comfort by reducing high-pressure areas. Future research should apply this approach to a broader range of orthotic devices and patient demographics, explore advancements in sensor and optimization technologies, and evaluate long-term durability and user feedback. Expanding these efforts will enable more personalized and effective orthotic solutions, paving the way for advancements in both clinical practice and patient outcomes.

Acknowledgement

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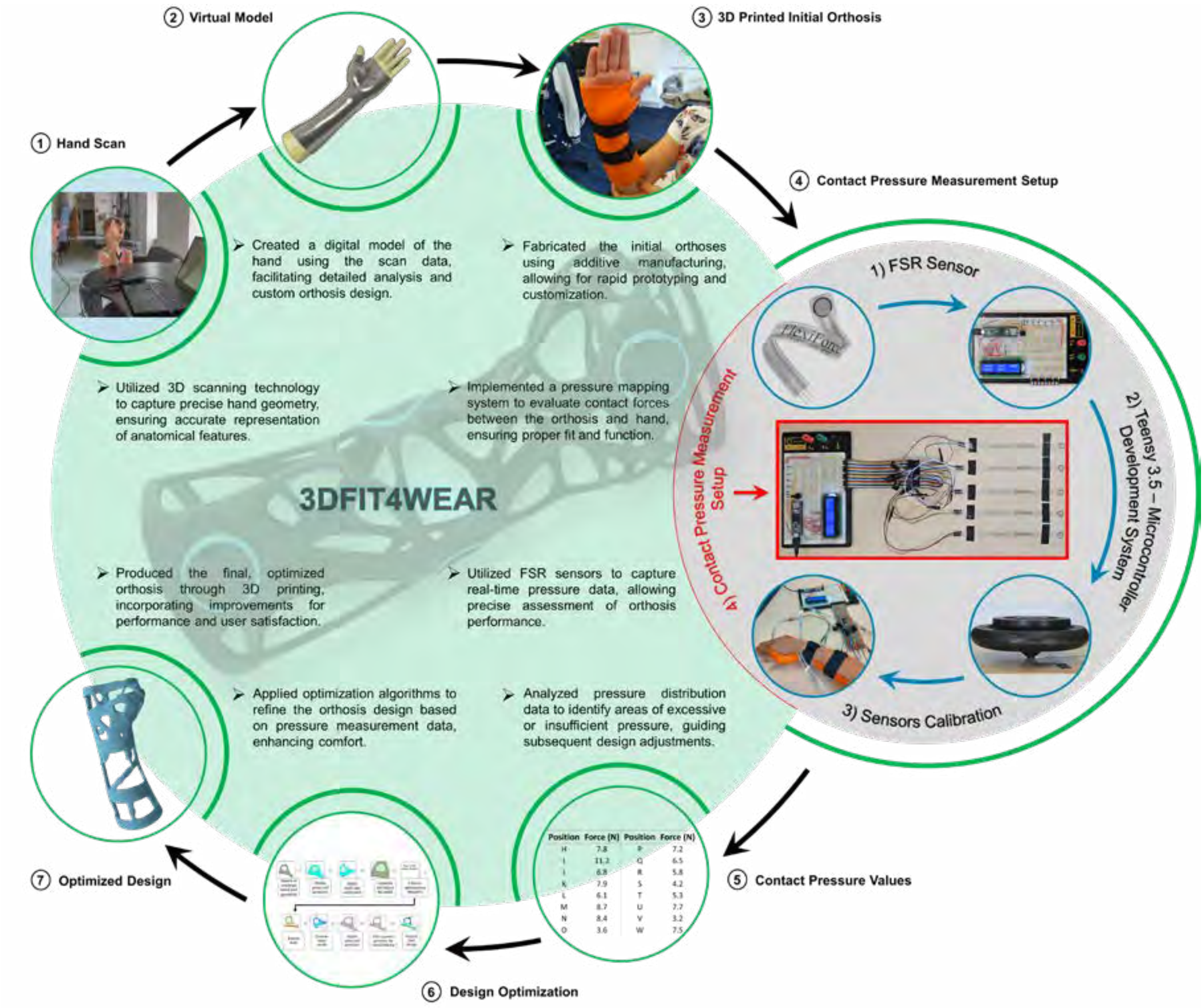
mers), In-Vision Technologies AG, and Luxinergy GmbH. The PCCL is funded by the Austrian Government and the State Governments of Styria, Lower Austria and Upper Austria.



- Created a digital model of the hand using the scan data, facilitating detailed analysis and custom orthosis design.
- Fabricated the initial orthoses using additive manufacturing, allowing for rapid prototyping and customization.
- Utilized 3D scanning technology to capture precise hand geometry, ensuring accurate representation of anatomical features.
- Implemented a pressure mapping system to evaluate contact forces between the orthosis and hand, ensuring proper fit and function.
- Produced the final, optimized orthosis through 3D printing, incorporating improvements for performance and user satisfaction.
- Utilized FSR sensors to capture real-time pressure data, allowing precise assessment of orthosis performance.
- Applied optimization algorithms to refine the orthosis design based on pressure measurement data, enhancing comfort.
- Analyzed pressure distribution data to identify areas of excessive or insufficient pressure, guiding subsequent design adjustments.

Position	Force (N)	Position	Force (N)
H	7.8	P	7.2
I	11.2	Q	6.5
J	6.8	R	5.8
K	7.9	S	4.2
L	6.1	T	5.3
M	8.7	U	7.7
N	8.4	V	3.2
O	3.6	W	7.5

Fig. 1: Optimization procedure.

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Tackling the fire safety in glass free PV modules

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Recent trends in creation of sustainable cities and needs for greener source of electrical energy have made building integrated photovoltaic modules (BIPV) and building attached photovoltaic modules (BAPV) attractive and widely available. Researchers and industry are working together on making photovoltaic (PV) module lighter, safer, reliable, sustainable, etc. Emphasis on 20+ years reliability and light weight of BIPV/BAPV brought plenty of new design solutions to the market [1].

To make PV modules lighter industry moved from glass - glass design, and introduced polymeric backsheet - glass solution, with further research and development of transparent frontsheets thin-film modules saw the light of the day with their polymer - polymer compositions. Incorporating polymers on front and back of the PV modules brought benefits like flexibility, enabled complex shapes and installation of modules into different infrastructure. This composition can have downsides like decreased mechanical stability, dimensional instability (warpage, delamination), higher impact on fire safety, and so on.

Fire safety presents important concern in the development of BIPV modules, various standards are created to classify PV modules regarding their safety. BIPV modules have to pass fire safety requirements for electrical and building-related sectors. BIPV present fire hazard due to their composition which is usually highly combustible. BIPV fire hazards include ignition due to hot spots, arcing and installation error; fire propagation from outer source; and hazards to rescue operations related to electric shock and toxic gas emissions [2].

This poster is intended to provide a technological overview of ways in which glass-free PV modules can be made more fire-resistant using various methods. Technological solutions and their challenges in implementation for PV industry are shown. Implementing these aspects in the future design of PV modules would enable safer and environmental friendlier product.

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Ultra-thin flexible glass as environmental shield for CIGS photovoltaic modules

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As a thin-film PV technology CIGS solar cells can be deposited on flexible substrates which offers the potential for building integrated photovoltaics (BIPV). With the highest conversion efficiency, amongst the thin-film photovoltaic materials, which recently reached 23.25% on the laboratory scale [1] CIGS PV is a promising candidate for BIPV. While the silicon PV modules represent the major part of the PV modules installed in the world, their disadvantages in BIPV applications are low flexibility, simple (2D) design approach and on top of this their weight, that can reach up to 20 kg/m² [2]. CIGS can provide lightweight, flexible solutions and enable installation of PV modules in more complex designs (3D) and systems.

Task of this work is to find a flexible material combination to protect CIGS PV modules from environmental factors, like humidity, which are causing module degradation [3]. To protect CIGS from aging and degradation it needs to be sandwiched between back and front protection that is providing flexibility, extremely low permeability of water, high transparency of front sheet, UV stability and stable design. Combination of ultra-thin flexible glass (as frontsheet) with stainless steel (SS) (as back sheet) in CIGS PV module design could be optimal solution.

The goal here is to select the best encapsulating material, which will connect all parts in reliable and hermetically sealed system, amongst different polyurethane, polyolefin and acrylic based liquid encapsulants. Mini PV modules will be created by connecting stainless steel with deposited CIGS and ultra-thin flexible glass together using encapsulating layer. Determination of reliability of the encapsulating material is based on current-voltage curve (IV-curve) of the PV modules that will be measured:

- immediately before and after application of the encapsulant,
- during storing conditions,
- after exposure to damp heat conditions (85 ˚C and 55 % humidity).
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Finally, the performance results of the different encapsulants will be compared. For a reliable encapsulation the module efficiency should not drop more than 20% (compared to the initial efficiency) over 500h in damp heat conditions.

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Automated surface inspection of plastic components using novel one-class learning methods

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Abridged version

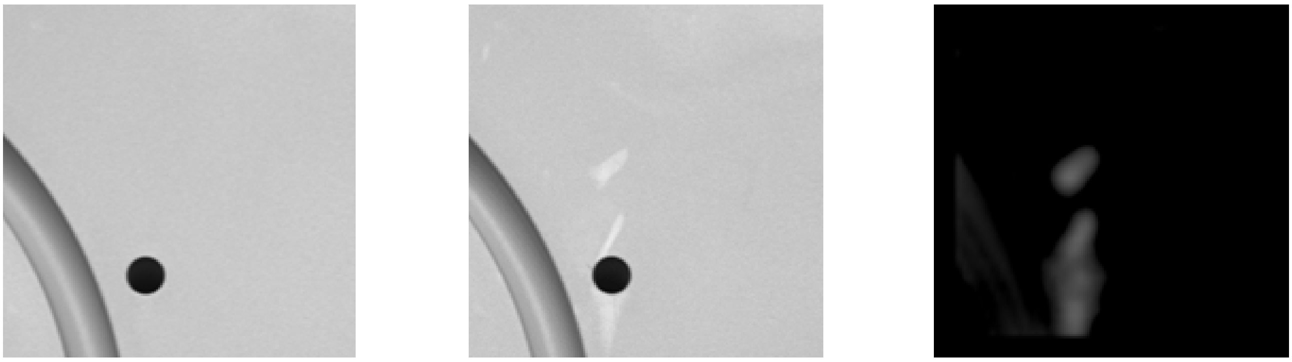

Fig. 1: Automatic Defect Detection and Segmentation of Image Patches using One-Class Classifica-tion. (Left) Example of a defect-free plastic component. (Center) Defects on the surface of an injection-molded plastic component. (Right) Highlighted areas indicate the segmented defects corresponding to the image in the center.

In this work, novel approaches in the field of defect segmentation have been ex-plored using the example of inline inspection of freeform surfaces on mixed con-vex/concave-shaped plastic components. The central focus is on the issue of gen-eralizability, aiming for the inspection algorithm to detect defects within defined product groups without requiring extensive retraining for new components. The pri-mary approach involved the use of one-class classification methods. A key ad-vantage of these methods is that they only require training examples from the nor-mal class—in this case, defect-free components—which are generally available in large quantities. Additionally, there is no need for data annotation. However, unlike supervised learning, the detection performance of one-class methods in this particu-larly challenging environment does not meet the high-quality standards typically demanded by industry without modification. Standard one-class methods assume a fixed viewpoint with minimal variation in object placement and orientation. Conse-quently, additional data augmentation stages [1], modifications and extensions to algorithms [2] were investigated. The captured component images showed variations in orientation (translation, rotation, scaling, and shearing), causing inconsistencies in the feature space representation when the images were divided into smaller patches. To address this, an automated post-processing strategy was developed to correct the image orientation for improved feature representation. Through this ap-proach, it became possible to extend

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an efficient one-class classification method to the given dataset (see Figure 1), achieving excellent detection results for a selected defect type.

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Reliable sample preparation of electrode material from Liion batteries for mechanical characterization

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Abridged version

Component characterization of Li-ion batteries is essential for the development of suitable battery models for risk and performance prediction. When dealing with delicate samples, such as thin electrode foils precise sample preparation is in particular important for precise and repeatable measurement results. This work analyses the challenges of tensile testing of electrode and separator material, which arise from the individual testing standards of the different material types, as well as the sensitive nature of the materials to be characterised. Furthermore, potential solutions to fundamental issues of foil sample preparation are discussed.

Acknowledgement

The research work was performed within the COMET-Module Project “BattLab” (project no. 904924) at the Polymer Competence Center Leoben GmbH (PCCL Austria) with contributions by AIT Austrian Institute of Technology GmbH (Sustainable & Smart Battery Manufacturing), Budapest University of Technology and Economics (Department of Inorganic and Analytical Chemistry), Fundación CIDETEC (Energy Storage), Montanuniversitaet Leoben (Chair of Materials Science and Testing of Polymers), 4a engineering GmbH and AVL List GmbH. “BattLab” is funded within the COMET - Competence Centers for Excellent Technologies Programme by the Austrian Federal Ministry for Climate Action, Environment, Energy, Mobility, Innovation and Technology, the Austrian Federal Ministry for Labour and Economy and the province Styria and SFG The COMET Programme is managed by FFG.

BattLab
High performance battery systems driven by
polymer science and virtual material engineering

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Exploring Crystallinity in Polymers Blends on Nanoscale

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Crystallinity is a key property of polymers that determines their mechanical, thermal, and optical characteristics. Understanding how crystallinity changes in polymer blends is essential in designing and developing polymer-based materials.

This work presents the use of PiFM (Photo-induced Force Microscopy) to study the crystallinity of polymers and polymer blends at the nanoscale. The technique involves using an infrared laser to induce molecular vibrations within the sample, which are then detected and analysed to provide information on the material's structure and composition. The high spatial resolution of PiFM, capable of resolving features below 10 nm, makes it an ideal technique for analysing crystalline behaviour in complex polymer blends, where changes in crystallinity are highly dependent on the local composition and structure. [1] Moreover, PiFM is a non-destructive and non-contact method, allowing for repeated measurements of the same sample without altering its crystalline structure.

Results of two different polymer blends - PE-EVOH-PA and PE-PLA - are shown. The influence of polymer ratio and processing conditions on polymer crystallinity is investigated. Spectra of matrix polymer were measured in precise positions, and changes in spectra - especially in peaks assigned to the crystalline part of the polymer - were observed in dependence on the distance from the minor domains. Also, the size of minor domains was considered. [2]

This work provides insights into the crystallinity of polymer blends and how it can be controlled, which can have significant implications for their performance in various applications.

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Circular Economy Potential of Sustainable Bio-Based Composites: Repair, Recycle and Reuse

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Abridged version

Bio-based materials are increasingly recognized as sustainable alternatives to fossil resource-based materials, aligning with circular economy principles. However, the thermosetting nature of bio-based epoxy systems poses a significant challenge, limiting their suitability for conventional repair and recycling methods commonly applied to thermoplastics [1]. This limitation complicates the management of their end-of-life scenarios, raising concerns about sustainability. To address these challenges, efforts have been directed toward integrating bio-based precursors into transesterification vitrimers, leading to the creation of advanced bio-based vitrimer systems that align with green chemistry principles. The QB3R project (Quality controlled high-performance components consisting of 100% bio-based resins with high potential for repair and recycling) is at the forefront of this approach. The focus of this research project is on the development of a 100% bio-based material system composed of natural fibers and bio-based polymers. The project explores various manufacturing techniques to process this system and demonstrates its applicability in mechanically demanding applications through the production of a sledge demonstrator. Additionally, it aims to analyze the vitrimer functionality of the material, exploring repair options via matrix re-linking and re-infiltration [2]. The project also investigates the mechanical recycling potential and material re-use within the composite processing [3], contributing to the advancement of sustainable composites within a circular economy framework.

Acknowledgement

The financial support through project QB3R (project no. FO999889818) provided by the Austrian Ministry for Climate Action, Environment, Energy, Mobility, Innovation and Technology within the frame of the FTI initiative “Kreislaufwirtschaft 2021”, which is administered by the Austria Research Promotion Agency (FFG) is kindly acknowledged

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Exploring Immobilization Strategies of Nucleic Acids on Thiol-Ene Photopolymer Surfaces

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Abstract

Biomolecule-functionalized photopolymers have become increasingly valuable in bio- sensinganddiagnostics.Traditionalmethodsforfunctionalizingpolymerswithbiomol- eculestypicallyinvolvecovalenttetheringtothepolymericsurface,whichcancompro- mise the reactivity of DNA essential for biological processes [1]. To address this issue, wedevelopedastraightforwardimmobilizationstrategy(seeFigure1)fornucleicacids on thiol-ene photopolymer surfaces via physical interaction. In our approach, the sur- face-bound thiol groups were first activated using a multifunctional acrylate. Subse- quently,polyethylenimine(PEI)wascoupledtotheactivatedregions.Thismodification facilitated the physicalimmobilizationof DNAthrough electrostatic interactions, which are formed between the phosphate groups of DNA and the protonated amine groups inthePEIstructure.Theeffectivenessofthismethodisconfirmedthrough X-raypho- toelectron spectroscopy (XPS) measurements.

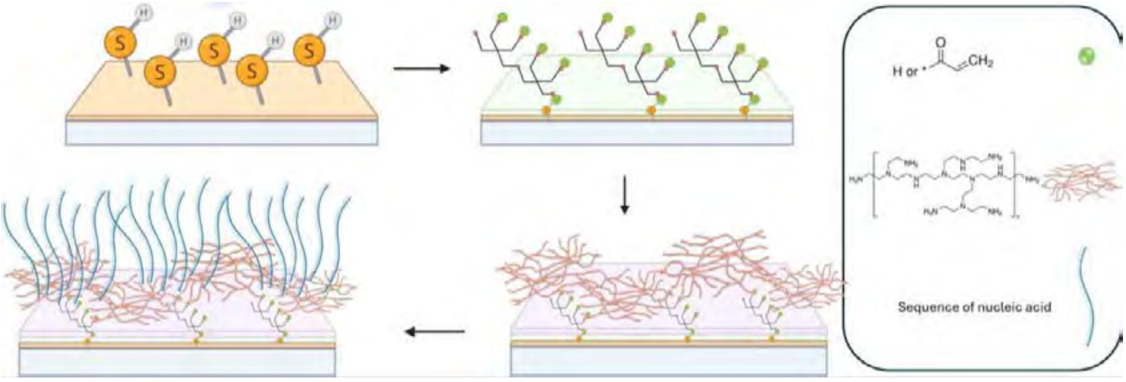

Fig.1: SchemeoftheimmobilizationstrategyofDNAonthiol-enesurfaces

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Synthesis of Covalent Adaptable Networks via Frontal Polymerization

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Frontal polymerization (FP) is defined as the conversion of monomers into polymers in a wave like manner (front).[1] The driving factor during this reaction is the heat generated by the exothermicity of the polymerization. Thus, only a local external energy input is required during the initiation process.[2] The used initial stimuli are usually either UV-light or thermal energy.

Consequently, shorter curing times can be achieved, larger objects can also be cured with light and less energy is required overall. Nowadays, beside energy efficiency also other material properties such as recyclability, reusability and reprocessability gain significance in polymer science. These can be implemented by introducing dynamic bonds into thermoset materials. Commonly, transesterification reactions between free hydroxy- and ester moieties are introduced by using suitable catalysts, such as organic phosphate esters, bases, Zn(II)-salts.[3]

In this work, we have combined the advantages of frontal polymerization and covalent adaptable networks. Radical frontal polymerization of thiol-acrylate resins (bearing ester and hydroxyl groups) lead to dynamic networks which undergo rapid stress relaxation at elevated temperatures and exhibit adjustable material properties depending on the amount of thiol used. This was confirmed by determining frontal properties as well as DMA measurements, demonstrating a decrease in reactivity and glass transition temperature with increasing amount of thiol. Additionally, photo-DSC measurements displayed a reduction in reaction enthalpy for higher amounts of thiol. Moreover, stress-relaxation tests at elevated temperatures were conducted to characterize the dynamic behaviour of the materials. The materials showed Arrhenius-dependent behaviour, which proves the existence of dynamic bond exchange reactions. To demonstrate the reusability of the investigated material, reprocessing tests were carried out which resulted in an 88.9 % restoration of the original Shore D hardness. The recovery of fillers such as glass fibers by decomposing the polymer matrix of a composite in ethylene glycol has also been verified.

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CircularBioMat

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Circular bio-based polymers for the construction industry

In the CircularBioMat project we want to minimize the environmental footprint by substituting petroleum-based polymers with bio-based polymers for building services engineering. We also want to improve the resource efficiency and bring the materials into a circular economy. To do this, we need to develop a catalogue of requirements, taking into account the current standards for the construction industry. First, we evaluate the existing materials and then we can select bio-based or recycled polymers. These are processed using standard technologies such as injection moulding and extrusion, but also using Additive Manufacturing via Material Extrusion (MEX). During these trials, the power supply and the amount of cooling water will be measured to provide better data for the Life Cycle Assessment (LCA). The LCA will then show how the different materials perform in respect to the carbon footprint.

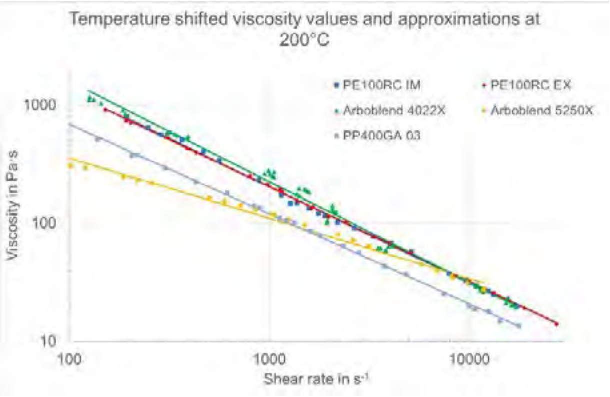

Fig. 1: Temperature shifted viscosity values

As a first step, we have selected bio-based polymers that are expected to perform well compared to the petroleum-based polymers. All materials are characterised at the Institute of Polymer Processing using the High Pressure Capillary Rheometer for viscosity, Differential Scanning Calorimetry for thermal properties and pvT measurements (specific volume as a function of pressure (p) and temperature (T)).

The viscosity (Figure 1) of two standard PEs is almost identical to that of the bio-based Arboblend 4022 X, while the Arboblend 5250 X has a different slope.

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The partners are FH Salzburg, Department Green Engineering and Circular Design, and Montanuniversitaet Leoben, Institute for Polymer Processing, as scientific partners and the industrial partners Miraplast GmbH, Schnabl Stecktechnik, Tecnaro GmbH and agru Kunststofftechnik Gesellschaft m.b.H.

Experimental Evaluation of Particle Filtration During the Vacuum Assisted Resin Infusion Process

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Abridged version

Particle loaded composites are widely used for enhanced/tailor-made properties (mechanical, thermal, electrical, etc.) in the end product. While impregnating fibrous reinforcements with particle loaded resin , the particles may be retained by the fibre array and filtration takes place. As a result, the filler content and the subsequent properties are not homogeneous throughout the composite part [1]. However, very little information is available on the fabrication of particle loaded composites using Vacuum Assisted Resin Infusion (VARI) process, and the characterization of particle filtration. This study focused on the fabrication of composite plates by VARI from glass woven fabric and a suspension of silica particles in vinyl ester resin. The suspensions were prepared with different concentrations of silica particles (0.5%, 1.0%, 1.5%, and 2.0%) in the resin. These suspensions were then infused into the mold cavity (200 mm long, 80 mm wide) following a flow method.

To investigate the silica particle filtration in the cured composite part, the coefficient of thermal expansion (CTE) was used as a macroscale indicator [2]. An increase in silica particle concentration is expected to decrease the CTE of the resulting composite material. The effect of particle filtration on the thermal expansion coefficient (CTE) along the composite length was observed, as shown in Figure 1(a). Three values were recorded for each test and its mean value was reported. For ease of understanding, the position at which CTE was determined from the composite plate was expressed as a non-dimensional position, i.e., the ratio of sampling position (x) to the total length of the mold cavity (L). It was found that the CTE was low at the inlet indicating a high particle concentration. Then a gradual decrease in the particle concentration was observed from the inlet toward the outlet. Near the outlet, the particle concentration was found to slightly increase due to particle deposition, as shown in Figure 1(b). This can be attributed to the release back of some unstable (loose) filtered particles into the flow regime. These particles get deposited near the outlet, as the vent is closed at mold filling, thus causing a localized increase in the particle concentration.

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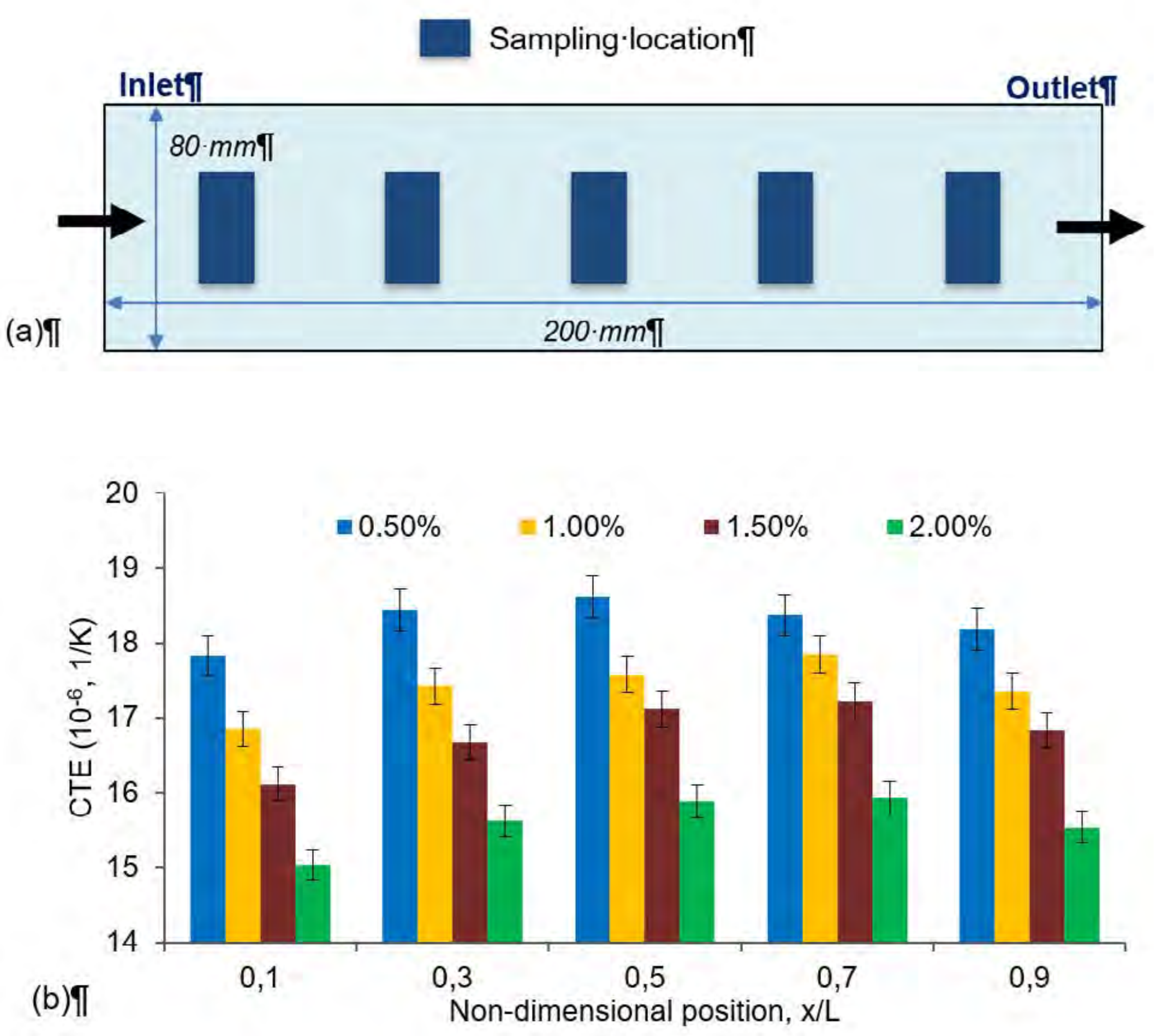

Fig. 1: Sampling plan for CTE specimen to characterize particle filtration (a), CTE results of composite samples at different positions (b).

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Photo-induced crosslinking for green electrospinning processes

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Abridged version

Electrospinning is a fascinating and versatile technique that allows to prepare polymeric micro- and nanofibers and nonwoven fibrous mats through the application of high electrostatic forces. Herein, we show how the photo-induced crosslinking can be coupled with electrospinning (Figure 1) to develop innovative green processes to fabricate polymeric fibrous membranes with enhanced properties and thus improved applicability [1,2]. We demonstrate that by carefully selecting the composition of the electrospinnable system and photo-crosslinking process parameters, it is possible to efficiently and independently control the mat surface area, its porosity, its wettability, and the amount of active functional groups available on the surface of the crosslinked nanofibers. In this way, multifunctional active fibrous nanomaterials and coatings, with antibacterial, superhydrophobic or sensing properties, can be obtained.

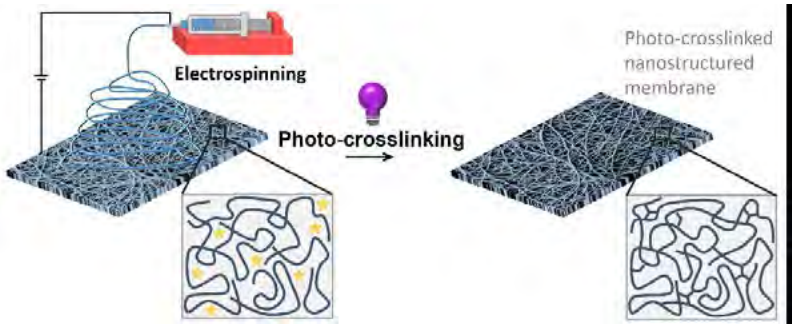

Fig. 1: Coupling electrospinning and photo-induced crosslinking as a green process for the fabrication of polymeric nanofibrous materials.

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Ministry of Foreign Affairs
and International Cooperation

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Different approaches to quantify the interfacial adhesion of hybrid composites produced by additive manufacturing

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Approaches

Additive manufacturing allows more freedom for the manufacturing part during one single production step. Material extrusion (MEX) is especially popular due to the low costs and broad range of available materials. The concept of depositing hot material to a surface allows it to bond new layers even if the surface was not produced in the same process step. Even more, it does not need to be from the same material or produced by the same technique. However, combining materials or processes always raises the question: How well do they bond? The combination of a thermoplastic polyurethane (TPU) on polyamide (PA) was studied using two different approaches – a fracture mechanical one and a quasi-static method. The former was done on a single-leg bending (SLB) specimen (Fig. 1a), for which selective laser-sintered PA was overprinted with TPU utilizing MEX. The second approach requires a T-shaped specimen (Fig. 1b) of which the TPU-rib was printed on injection moulded PA.

SLB specimens depend on their overall bending stiffness; with too flexible overprinted layers the predefined crack does not initiate a delamination. As expected, higher production temperatures enhance generally the bonding strength. The quasi-static approach showed only marginally stronger bonding for rougher surfaces, caused by mechanical interlocking, but higher values for lower printing speeds. Increased interfacial areas can be counterproductive by the resulting internal stresses in the bonding layer.

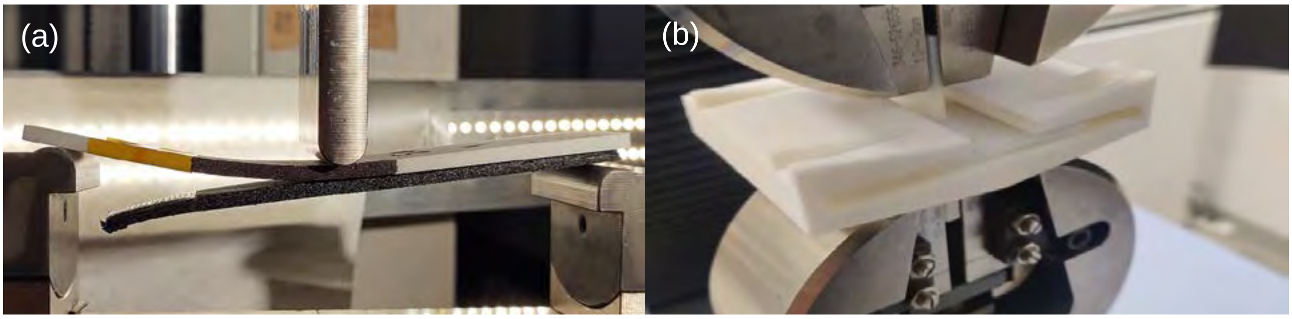

Fig. 1: (a) Single-leg bending test setup and (b) pull-off test setup [1]

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Thiourethane-based photopolymer systems for 3D printing

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Additive manufacturing, particularly 3D printing, is increasingly becoming a key technology in scientific, industrial and commercial sectors, with the potential to significantly influence everyday life [1]. Among the various 3D printing techniques, light-induced polymerisation stands out for its rapid processing speed and high precision in addition to its minimal energy and solvent requirements [2]. The photopolymerisation market is currently dominated by (meth)acrylate and epoxy resins produced via radical and cationic polymerisation [1]. Such resin systems often suffer from oxygen inhibition, yellowing, shrinkage, and moisture sensitivity. These drawbacks highlight the need for novel, light-sensitive materials with enhanced performance characteristics [3].

Anionic photopolymerisation presents a promising alternative, enabling the development of advanced materials that overcome the shortcomings of the above-mentioned traditional resins [4]. Photolatent base generators (PBGs), as initiators of anionic reactions, release reactive bases and nucleophiles when exposed to light, thereby triggering polymerisation. Example reactions are ring-opening polymerisation (ROP) of cyclic ethers or carbonates; polyurethane catalysis and click reactions between thiols and isocyanates or acrylates [2]. These systems have the possibility to facilitate the synthesis of bio-based, biodegradable polymers as well as materials with dynamic covalent bonds (DCBs) capable of being repaired or reprocessed. Such new materials could address environmental concerns regarding the degradability and recyclability of 3D-printed thermosets [5].

The present study aims to develop new photopolymers for 3D printing by photobase-catalysed anionic polymerisation with a specific focus on thiourethane-based systems. Thiourethanes are well-regarded for their exceptional mechanical, physical, and optical properties, as well as their rapid reaction rates and near-complete conversions, owing to their click reaction nature [2], [6]. The incorporation of thiourethanes into other dynamic click-based systems, such as epoxies via ROP or acrylates through Thiol-Michael addition, offers the potential to create hybrid systems with tuneable mechanical and chemical properties [2]. In this work, the stability and reactivity of thiourethane systems were accessed with and without the addition of a second monomer system. The kinetics of dark curing and light induced reaction were investigated in the presence of different stabilisers and solvents in order to achieve printable formulations for 3D printing applications.

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ESPERANTO

Enhancing the Sustainability of PhotopolymERs ANd phoToinduced prOcesses

Funded by the European Union

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Numerical simulation of non-pressure polypropylene pipes in underground operating conditions

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Abridged version

Numerical simulations of buried non-pressure polymer pipes to determine stresses and deformations are necessary for investigating their long-term behavior. Although these calculations might be straightforward, they usually face fundamental challenges in obtaining soil material data. Such data is hard to find, difficult to measure, and, if available, typically very scattered. Models using this data are subsequently hard to verify. This contribution offers a workaround by linking numerical simulations with available standards, such as the ATV German standard for designing buried polymer pipes.

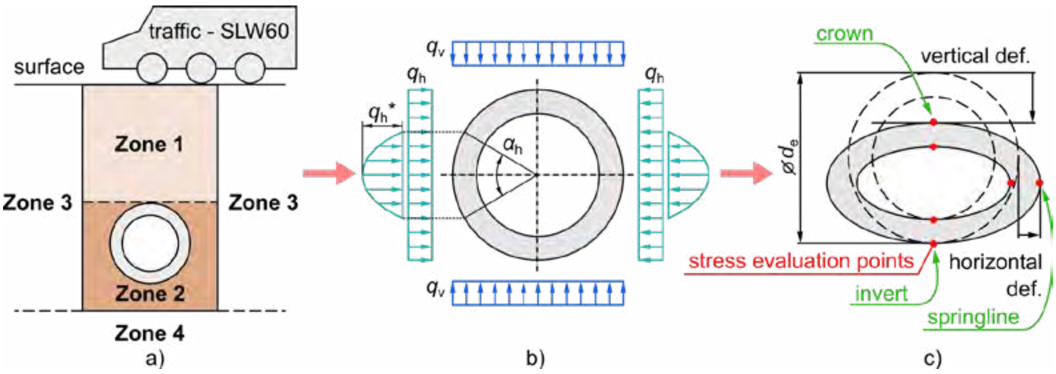

Fig. 1: (a) Definition of the input parameters; (b) Calculation of external forces using ATV standard; (c) Deformation and stress evaluation.

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Insights on the effect of photoinitiator to the thiol-thioester dynamic bond exchange: a kinetic study

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Abridged version

This study investigates the influence of photoinitiators on the manipulation of thiol-thioester exchange reactions, focusing on their often-overlooked role beyond initiating polymerization. By systematically varying photoinitiator type and concentration, a two-factor parametric study reveals significant correlations with the kinetics of thiol-thioester exchange. UV-Vis spectroscopy and rheometry were employed to monitor absorption spectra and stress relaxation behavior, respectively.

Our findings demonstrate that photoinitiators play a complex role in the dynamic covalent chemistry of these systems, influencing exchange rates and material properties. The research also considers other critical factors, including the presence of photoacids[1] and the properties of the catalyst[2], highlighting the need for a holistic approach in understanding and controlling thiol-thioester dynamic bond exchange. This study contributes to the growing field of dynamic covalent polymers and provides guidance for designing responsive materials with potential applications in optimizing new material systems for higher-resolution photolithography.

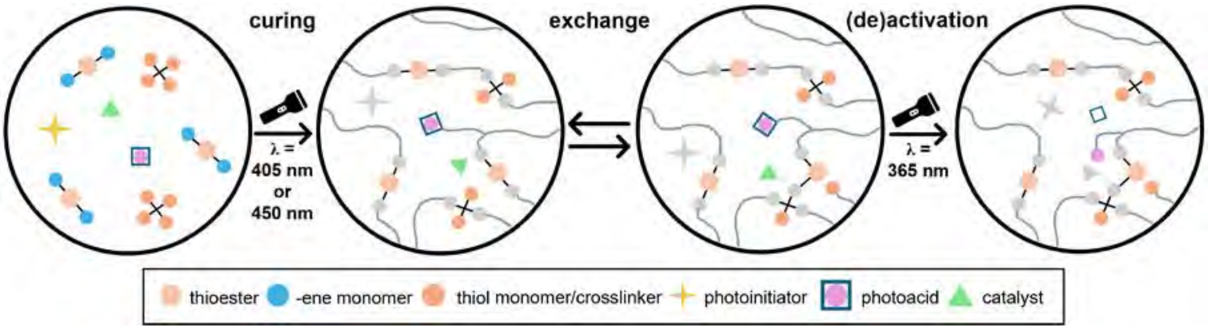

Fig. 1: Schematic of the five-component resin formulation.

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Innovative electrospun nanofibrous membranes by coupling electrospinning and photoinduced process

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Abridged version

Electrospinning is a versatile and prominent technique for generating fibers and nano- fibrous membranes down to the nano-scale, with widespread application across vari- ous areas [1]. Electrospun nanofibrous membranes (ENMs) show exceptional charac- teristics, including high surface area, high porosity, and adjustable pore structure. A photo-crosslinking process could be applied to the membranes to tune their final mor- phology while improving the thermal, mechanical, and solvent resistance [2].

In this study, the electrospinning of styrene-butadiene rubber latexes (thus using only water as an electrospinning medium to mitigate environmental and human concerns) and subsequent thiol-ene photoinduced curing are studied. The influence of variation in the electrospinning suspension, the electrospinning set-up, the photo-crosslinking parameters, and conditions are assessed to tailor the final properties of the ENMs. The innovative ENMs have the potential to be applied in a wide range of applications, in- cluding water treatment for the removal of heavy metal ions.

Acknowledgment

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Towards a Greener Household: Efficient Cooling and Heating Solutions with Suitable Polymer Applications

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Abridged version

In modern households, appliances such as refrigerators, dishwashers, washing machines, dryers, small water heaters, and advanced kitchen taps with hot/cold water functions are integral to daily life, enhancing convenience and comfort. As the demand for more energy-efficient and sustainable cooling and heating solutions in these devices continues to rise, innovative approaches from both scientific research and industrial development are imperative. Among these, materials science - specifically polymer engineering - emerges as a key area with substantial potential to drive advancements in contemporary cooling and heating technologies.

Polymers, with their viscoelastic properties and inherent damping properties, are particularly well-suited for mitigating vibration and noise in these systems. Additionally, their tunable thermal properties provide opportunities to optimize thermal management, thereby significantly improving the energy efficiency of cooling and heating systems.

Nevertheless, polymers used in such applications are often subjected to extreme environmental operational conditions, as exemplified by their use in refrigerant compressors. These conditions include elevated service temperatures, high pressures, and prolonged exposure to oils, coolants, and other media. Consequently, polymers must exhibit exceptional long-term stability, both in terms of thermo-mechanical performance and resistance to aging.

To achieve this, appropriate testing methods are essential for the efficient selection of suitable materials, tailored to the specific operational requirements of each component. These testing protocols typically encompass preliminary material selection through basic characterization techniques following accelerated aging processes, including Melt Flow Rate (MFR) assessments, Infrared (IR) spectroscopy, and mechanical short-term tests. On a service-oriented level, evaluating the long-term thermo-mechanical behavior and fracture mechanics properties is crucial to ensuring the reliable operation of these components over time.

The overall objective is to establish correlations between short-term and long-term performance data and to critically assess the relevance and limitations of basic characterization methods in predicting the long-term operational reliability of polymers in these demanding applications.

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Development of a stress relaxation-based test methodology for unpressurized pipes

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Abridged version

The properties of modern virgin polymer grades for unpressurized pipe systems, such as those used in sewage- or drainage systems, easily exceed the requirements of the applied loadings. The trend towards increasing the use of recycled materials in these polymer pipe systems could change this situation. Since virgin material pipe systems effortlessly fulfill a minimum service lifetime of 50 years or more, the knowledge about the exact long-term performance of unpressurized polymer pipe systems is limited.

Current testing procedures for lifetime estimation of unpressurized polymer pipe systems do not reflect realistic loading conditions. Deformation induced stress resulting from the surrounding soil is the primary load on these pipe materials. A promising method is the already developed Janson stainability test, which, however, has not yet gained broad acceptance due to high material usage and long testing times.

In the context of the CD laboratory “Impact of recycled materials on the mechanical lifetime estimation of polymers”, a stress relaxation-based methodology will be implemented that mimics the real failure behavior of a buried unpressurized pipe and also works on a specimen level.

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Radical-promoted Cationic Photopolymerization with a Tri- sacylgermane Photoinitiator immobilized on the Surface of Silica Nanoparticles

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Nanoparticle's exceptionally high surface area and surface chemistry enable it to reach higher levels than other common drug delivery carriers. Surface modification based on “grafting from” techniques provides a versatile tool for industry and science. In our re- search, a highly efficient and visible light sensitive (up to 450 nm) photoinitiator, which is based on germanium, was immobilised on the surface of spherically shaped silica nanoparticles (30 nm in diameter)1. We demonstrated that this species can be em- ployed for a novel and unique cationic “grafting from” process: surface-initiated radical promoted cationic photopolymerization (SI-RPCP)2. The successful “grafting from” ca- tionic photopolymerization under visible light (450 nm) was proven via FTIR spectroscopy, TGA measurements, XPS, Solid-state NMR, ToF-SIMS and SEM.

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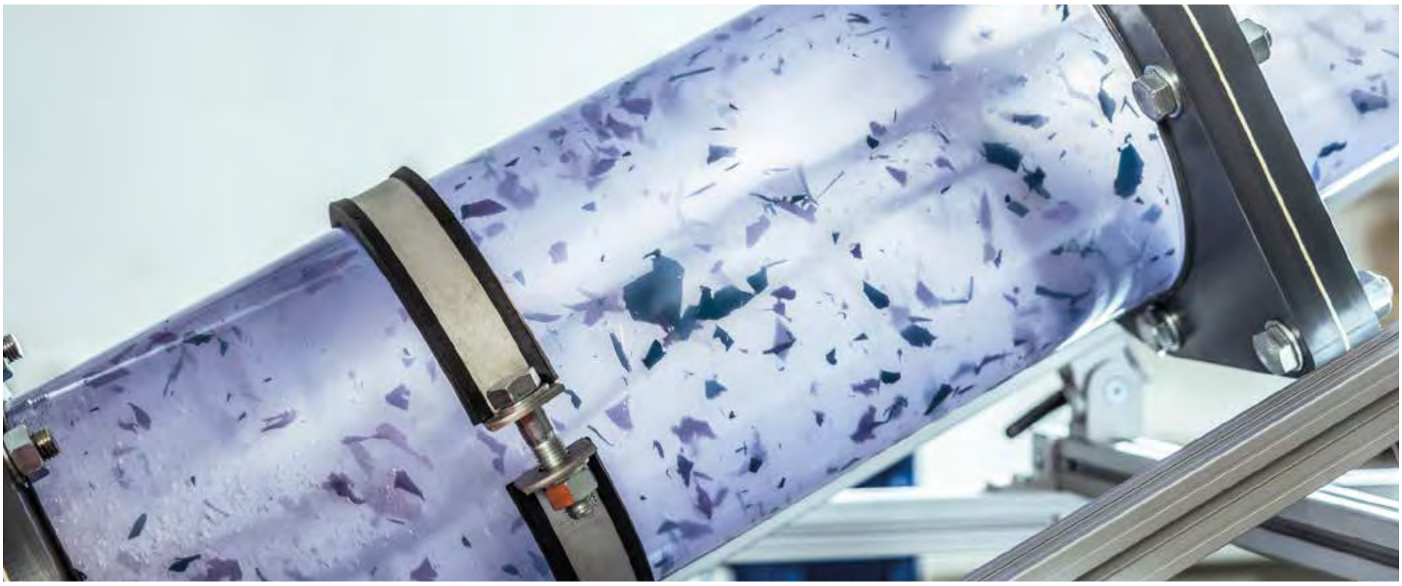


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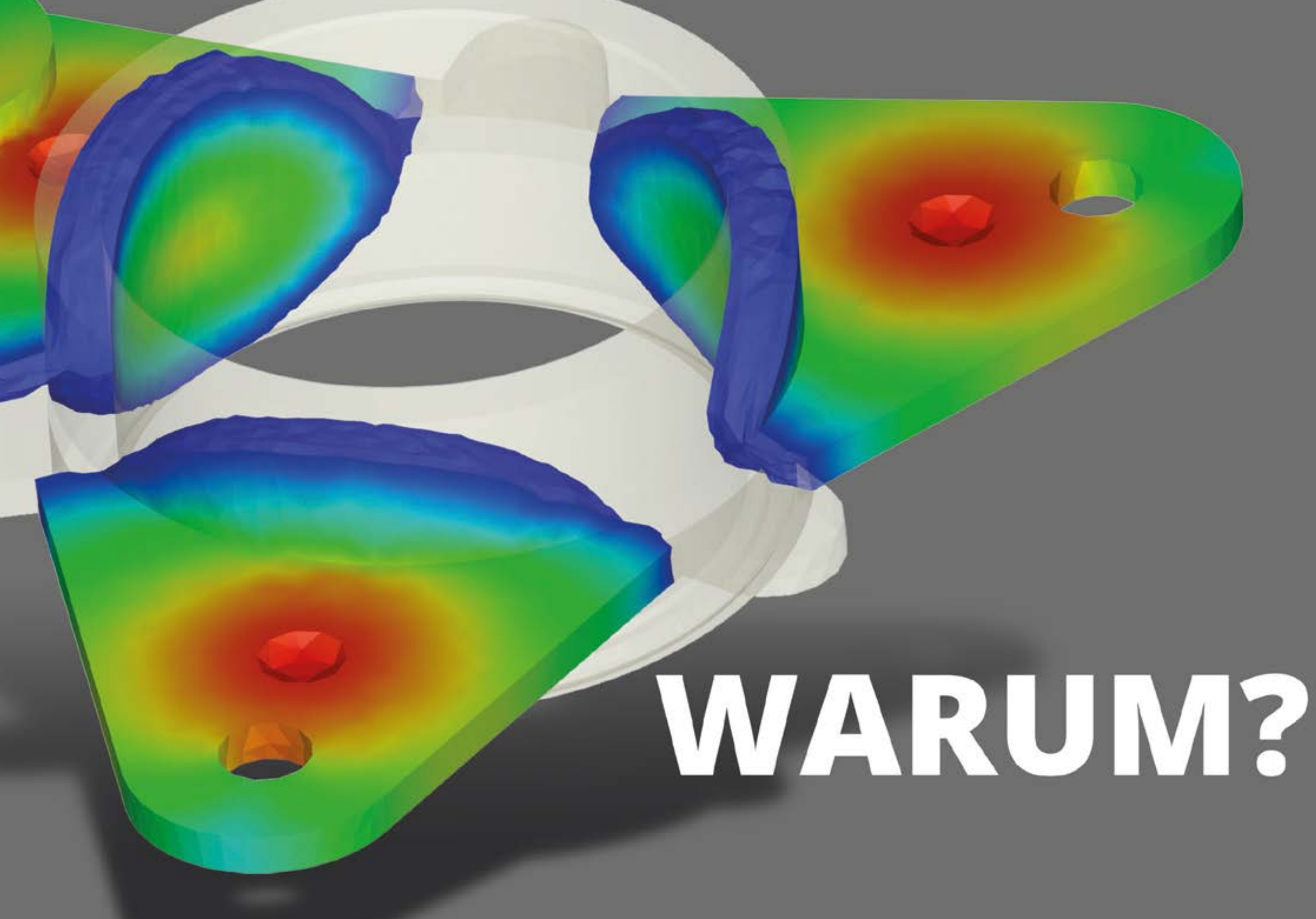
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