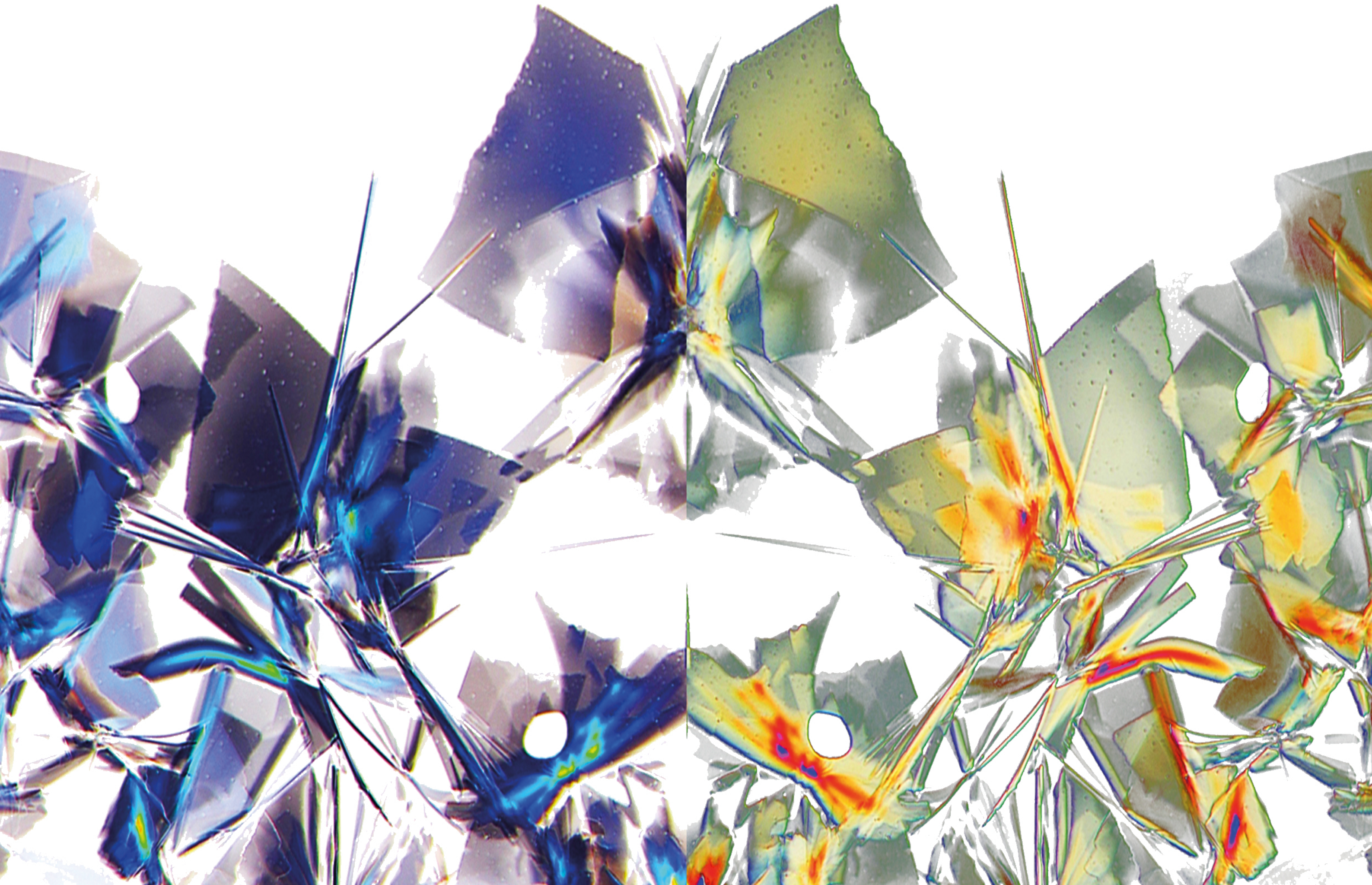
Polymer Meeting 14

Graz University of Technology

Aug. 30-Sept. 2, 2021

BOOK OF ABSTRACTS



Impress

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Foreword

Welcome to the 14th Polmyer meeting PM14!

We cordially welcome you to the Graz University of Technology. It is a great honor and pleasure to us to be the host of the 14th polymer meeting.

The 14th Polymer Meeting in Graz is the continuation of the very successful three river DVSPM-conference series (Danube-Vltava-Sava-Polymer meeting) which became one of the most important meeting in polymer science in Central Europe, as well as on the predecessor conferences “Austrian Slovenian Polymer Meetings” and “Advances in Polymer Science & Technology”. However, the origin can be traced back to the Austrian Polymer Meetings, which started more than 25 years ago in Seggau, very close to Graz
Polymers are everywhere in today´s life and find applications in packaging, storage, buildings, agriculture, transportation, mobility, electronics, medicine, energy and many more.

The 14th Polymer Meeting in Graz will address all major aspects of polymer science spanning from novel synthetic approaches, the creation of new functional polymers, the characterisation of macromolecules and polymers, innovative processing technologies, polymer testing, and polymers@work in many applications, but will also include topics of renewable polymers, recycling and sustainability aspects.

In memoriam of Prof. Klaus Hummel, who passed away on May 15th 2021 the Klaus Hummel prize will be established and awarded for the most outstanding contributed lecture.

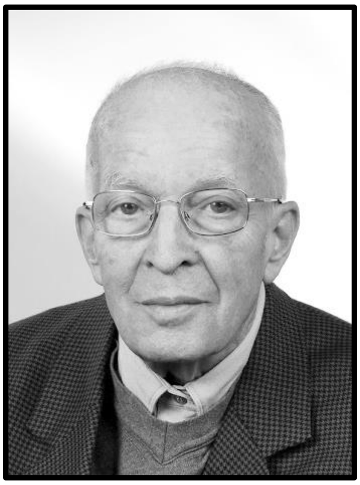
We are very thankful for your support in these difficult times caused by the Covid-19 pandemic. Thus, for us it is important to restart “normal” academic life. We hope that you enjoy this conference and get inspired by the presentations and vivid discussions within the polymer community.

Sincerely,

Gregor Trimmel,

on behalf of the organizing committee

In memory of Em. Univ.-Prof. Klaus Hummel



Klaus Hummel (born: 14 May 1930 in Jena, died: 15 May 2021 in Graz) attended various schools in Stadtroda, Jena, Eisenberg and graduated from high school in Bremen in 1949. He studied first physics and then chemistry at the Free University (FU) Berlin-Dahlem and obtained his Diploma in chemistry at the FU Berlin-Dahlem (with R. Riemschneider) in 1956. Afterwards he wrote his Doctoral thesis at the Rubber Institute of the TH Hannover (with W. Scheele) and became Dr. rer.nat. in 1959. He became scientific assistant at the same institute and later he moved to Munich where he conducted his Habilitation at the Technische Hochschule München, Institute for Technical Chemistry (with F. Patat). He received Habilitation for Technical Chemistry in 1967. After a short period at Chemische Werke Hüls AG, he accepted a substitute position at the Technische Hochschule Munich. In 1971 Klaus Hummel accepted a full professor position at Technische Universität Graz and became co-chairman of the Institute for Organic Chemistry and Organic Chemical Technology. In 1979 he became head of the newly founded Institute for Organic Chemistry and Technology of TU Graz. He held this position until his retirement in 1998. In the years 1991-1993 he was appointed dean of the faculty of natural sciences of TU-Graz. After his retirement he was given Emeritus status and continued research with enthusiasm and creativity for several years and remained an active part of the Austrian polymer community.

The research of Klaus Hummel mainly focused on the field of rubber chemistry and technology. He considerably contributed with over 200 publications to the advancement of vulcanization, crosslinking of polymers, and olefin metathesis. With the application of the well-defined metathesis degradation reaction, he introduced new ways and opened far reaching perspectives to the analysis of crosslinked rubbers.

As an academic teacher he introduced the field of Polymer Chemistry and Technology to the Curriculum of Chemistry at the Graz University of Technology, in addition to general Technical Chemistry and Organic-chemical Technology. With his appointment the foundation for the later Institute for Chemistry and Technology of Organic Materials was laid, now part of the Institute for Chemistry and Technology of Materials after fusion of twin institutes. He supervised far more than 100 PhD-theses and several Habilitations and was also a highly acknowledged reviewer for various journals, academic projects, and audits.

Klaus Hummel received various awards such as the R. Zsigmondy Fellowship of the Colloid Society in 1961, the Medal of the University of Helsinki in 1988, the Grand Golden Decoration of Honor of the Province of Styria in 1991, the Golden Decoration of Honor of the Graz University of Technology on ribbon in 1993, or the H. F. Mark Medal in 2000.

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TIMETABLE

Morning-Sessions

	Mon 30.8.	Tue. 31.8.	Wed. 1.9.	Thu. 2.9.
8:35		IL-9 B. Ivan	IL-20 B. Carbonier ▨	IL-28 Z. Major
9:00		IL-10 A. M. Coclite IL-11 F. Arbeiter	IL-21 D. Pahovnik ▨	IL-29 A. Manian IL-30 P. Krajnc ▨
9:30		IL-12 S. Hild	IL-22 F. Wiesbrock	IL-31 E. Fauster
10:00	Opening IL-1 A. Bismarck	Coffee	Coffee	Coffee
10:30	IL-2 S. Schlögl	IL-13 K. Loos	CL-A13 Fleisch / CL-B13 Woodward ▨ CL-A14 Alabiso / CL-B14 Zojer ▨	CL-A26 ▲ Stocken-huber / CL-B26 Müller
11:00	IL-3 S. Amancio-Filho	IL-14 S. Baudis	CL-A15 Taschner / CL-B15 ▨ Barkan-Öztürk Short Break	CL-A27 ▲ Kruta / CL-B27 Biermaier CL-A28 ▲ Pernusch / CL-B28 Murat-spahic
11:30	IL-4 K. Bretterbauer Shimadzu	IL-15 W. Friesenbichler	CL-A16 Schwaiger / CL-B16 Bandl CL-A17 Mohan / CL-B17 Wallner	Short Break CL-A29 ▲ Akhras / CL-B29 Schwarz CL-A30 ▲ Plevová / CL-B30 Göpperl
12:00	Lunch	IL-16 ▲ J. Fischer	CL-A18 Mautner / CL-B18 Gleißner CL-A19 Verdross / CL-B19 Obereigner Lunch	CL-A31 ▲ Freuden-thaler / CL-B31 Stritzinger Lunch
12:30		Lunch		
13:00				

▲ CHASE — Competence Center CHASE GmbH — Recycling Session

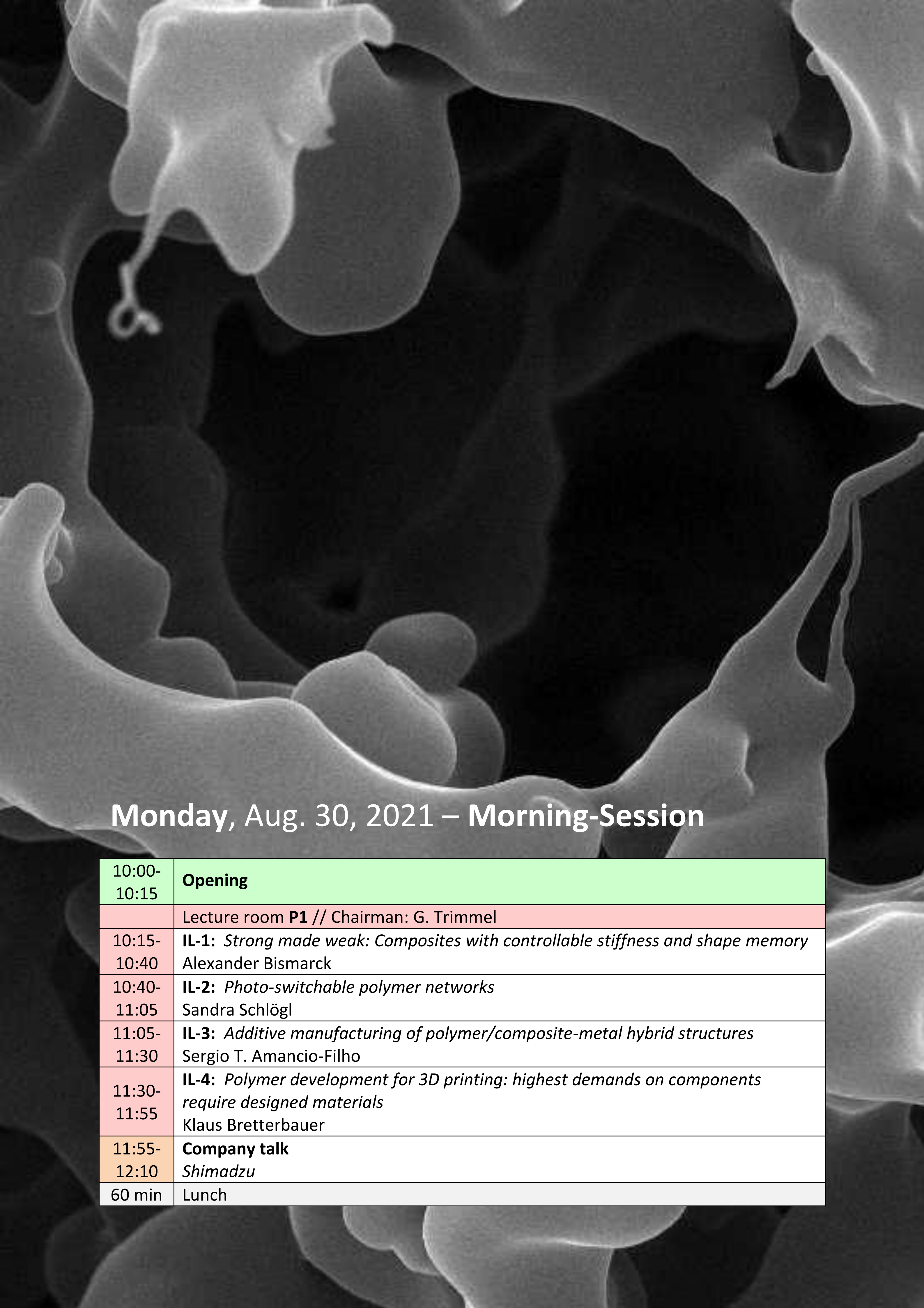
▨ Porous Materials@Work — Porous Polymer Session

Afternoon-Sessions

	Mon 30.8		Tue. 31.8		Wed. 1.9.		Thu. 2.9
13:15	IL-5 J. Kotek						
13:30			CL-A7 Cristurean	CL-B7 Ritten-schober	CL-A20 Kargl	CL-B20 Heinz-mann	IL-32 C. Holzer
	IL-6 P. Knaack						
			CL-A8 Ratzenböck	CL-B8 Roland	CL-A21 Mayer	CL-B21 Zdovc	
							IL-33 T. Grießer
14:00	IL-7 A. Kutnar		CL-A9 Ret	CL-B9 Traxler	CL-A22 Todorovic	CL-B22 Kreuzer	
			Short Break		Short Break		
			CL-A10 Wolff	CL-B10 Koller	CL-A23 Ročnik	CL-B23 Kukrálová	IL-34 J. Stampfl
	IL-8 M. Strlič						
14:30							
			CL-A11 Strasser	CL-B11 Chung	CL-A24 Weiland	CL-B24 Saller	
							Award Ceremony
	Coffee		CL-A12 Pühringer	CL-B12 canceled	CL-A25 Wild	CL-B25 Weingrill	
15:00							Closing
			Coffee		Coffee		
	CL-A1 Sinawehl	CL-B1 Omastová					
15:30							
					IL-23 I. Lacík		
	CL-A2 Cazin	CL-B2 Yousefi	IL-17 M. Sangermano				
	CL-3A Ebner	CL-B3 Wolfsgruber					
16:00					IL-24 G. Oreski		
			IL-18 A. de Sousa				
	Short Break						
	CL-A4 Petersmann	CL-B4 Haiden					
					IL-25 B. Likozar		
16:30	CL-A5 Rossegger	CL-B5 Hubert	IL-19 O. Brüggemann				
	CL-A6 Ruppitsch	CL-B6 Feuchter					
					IL-26 M. Pletz		
			Bus ride & Conference dinner				
17:00	Poster session even numbers						
					IL-27 M. Unterlass		
17:40	Public lecture R. W. Lang						
18:25	Poster session odd numbers						
19:10	Conference party						

🟥 invited lecture (20+5 min)
🟨 contributed lecture (12+3 min)
🟦 poster session
🟩 event
⬜ break

PROGRAM

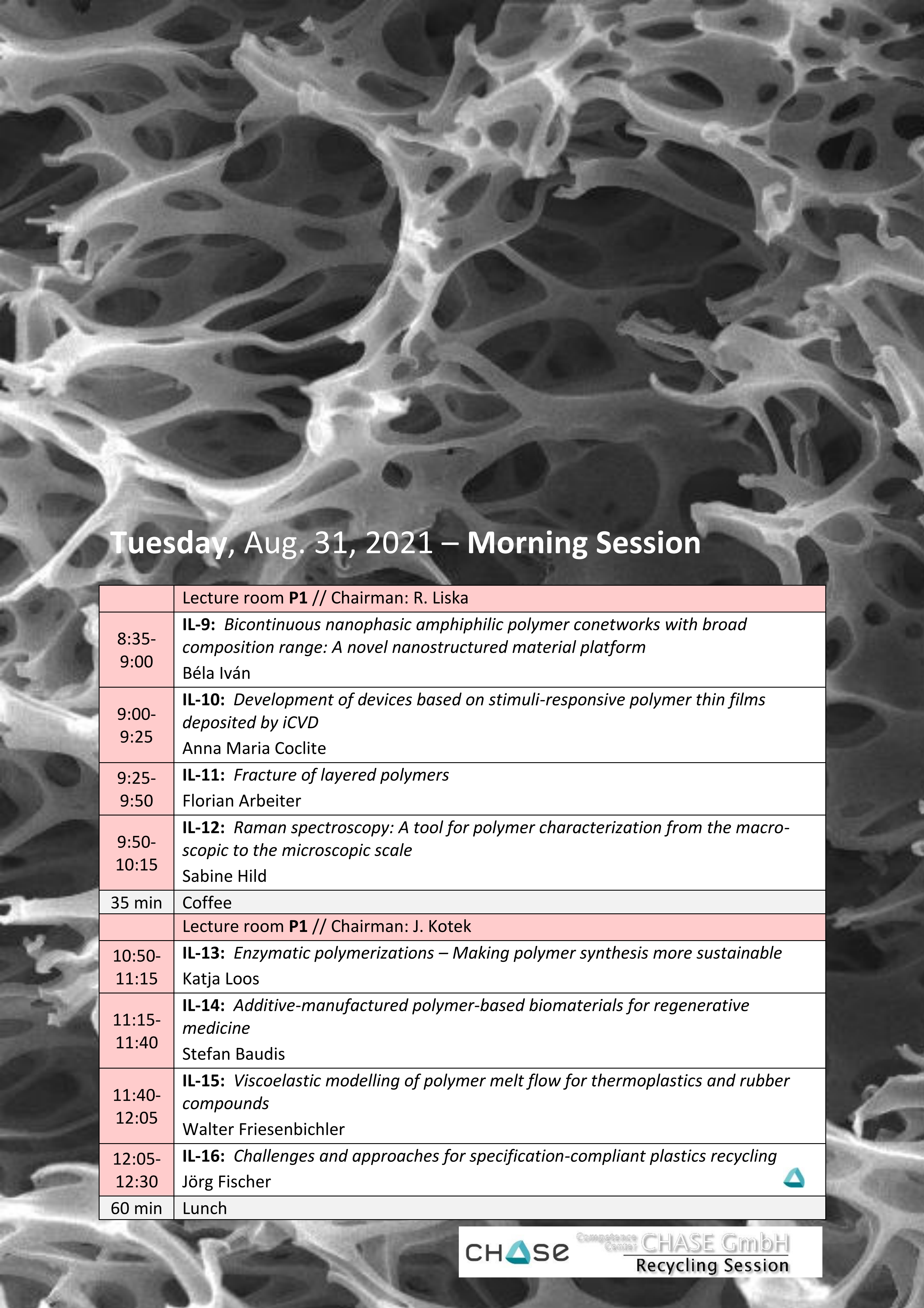


Monday, Aug. 30, 2021 – **Morning-Session**

10:00-10:15	**Opening**
	Lecture room **P1** // Chairman: G. Trimmel
10:15-10:40	**IL-1:** *Strong made weak: Composites with controllable stiffness and shape memory* Alexander Bismarck
10:40-11:05	**IL-2:** *Photo-switchable polymer networks* Sandra Schlögl
11:05-11:30	**IL-3:** *Additive manufacturing of polymer/composite-metal hybrid structures* Sergio T. Amancio-Filho
11:30-11:55	**IL-4:** *Polymer development for 3D printing: highest demands on components require designed materials* Klaus Bretterbauer
11:55-12:10	**Company talk** *Shimadzu*
60 min	Lunch

Monday, Aug. 30, 2021 – **Afternoon-Session**

	Lecture room **P1** // Chairwoman: K. Stana-Kleinschek	
13:10-13:35	**IL-5:** *Degradable all-aliphatic polyurethane films* Jiří Kotek	
13:35-14:00	**IL-6:** *Cationic frontal polymerization* Patrick Knaack	
14:00-14:25	**IL-7:** *Cascade use of wood - from boards to fibers and chemicals* Andreja Kutnar	
14:25-14:50	**IL-8:** *Lifetime modelling of heritage polymers* Matija Strlič	
35 min	Coffee	
	P1 // Chairwoman: S. Schlögl	**P2** // Chairman: S. T. Amancio-Filho
15:25-15:40	**CL-A1:** *High-performance photo-curable adhesives for bone repair* Lisa Sinawehl	**CL-B1:** *Polymeric composites and hybrids with 2D nanofillers* Mária Omastová
15:40-15:55	**CL-A2:** *Multi-material digital light processing 3D printing based on a dual-curing acrylate-epoxy system: Myth or reality?* Ines Cazin	**CL-B2:** *High CNT loading nano and hierarchical composites* Neptun Yousefi
15:55-16:10	**CL-A3:** *Frontal photopoly-merization of photobleachable resins based on long-chain polyetherpolyol dimethacrylates* Catharina Ebner	**CL-B3:** *Influence of filler and matrix on the thermal conductivity and mechanical properties of the composite* Nina Wolfsgruber
5 min	Break	
16:15-16:30	**CL-A4:** *Changing morphological features in a semi-crystalline polymer in material-extrusion based additive manufacturing* Sandra Petersmann	**CL-B4:** *Optical reflectivity of fiber-reinforced epoxy laminates modified by nanoparticle decorated carbon fibers* Lukas Haiden
16:30-16:45	**CL-A5:** *Digital light processing 3D-printing of covalent adaptable networks* Elisabeth Rossegger	**CL-B5:** *Polymer electrolyte as separator for structural super-capacitors* Olivier Hubert
16:45-17:00	**CL-A6:** *Difunctional low shrinkage monomers performing light-induced cyclopolymerization* Larissa Alena Ruppitsch	**CL-B6:** *Functional hierarchical composites for structural applications* Michael Feuchter
17:00-17:40	**Poster session** // even numbers	
17:40-18:25	**Public lecture:** *The Role of Plastics in Navigating the Great Societal Transformation. A story on the future of plastics narrated as "Wag the Dog" puzzle* Reinhold W. Lang	
18:25-19:05	**Poster session** // odd numbers	
19:10-	**Conference party**	



Tuesday, Aug. 31, 2021 – **Morning Session**

	Lecture room **P1** // Chairman: R. Liska
8:35- 9:00	**IL-9:** *Bicontinuous nanophasic amphiphilic polymer conetworks with broad composition range: A novel nanostructured material platform* Béla Iván
9:00- 9:25	**IL-10:** *Development of devices based on stimuli-responsive polymer thin films deposited by iCVD* Anna Maria Coclite
9:25- 9:50	**IL-11:** *Fracture of layered polymers* Florian Arbeiter
9:50- 10:15	**IL-12:** *Raman spectroscopy: A tool for polymer characterization from the macroscopic to the microscopic scale* Sabine Hild
35 min	Coffee
	Lecture room **P1** // Chairman: J. Kotek
10:50- 11:15	**IL-13:** *Enzymatic polymerizations – Making polymer synthesis more sustainable* Katja Loos
11:15- 11:40	**IL-14:** *Additive-manufactured polymer-based biomaterials for regenerative medicine* Stefan Baudis
11:40- 12:05	**IL-15:** *Viscoelastic modelling of polymer melt flow for thermoplastics and rubber compounds* Walter Friesenbichler
12:05- 12:30	**IL-16:** *Challenges and approaches for specification-compliant plastics recycling* Jörg Fischer
60 min	Lunch

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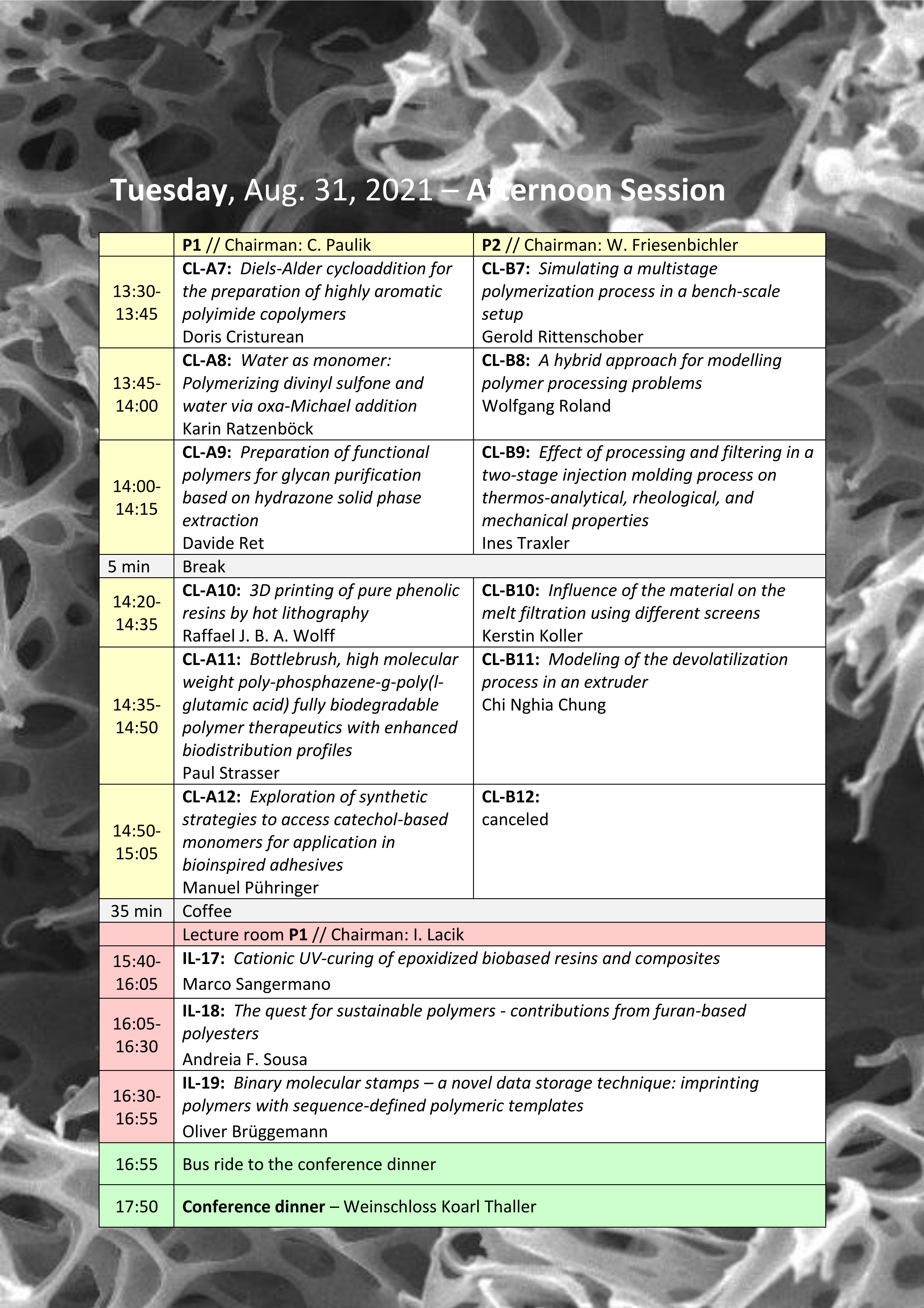
Recycling Session



Tuesday, Aug. 31, 2021 – **Afternoon Session**

	P1 // Chairman: C. Paulik	**P2** // Chairman: W. Friesenbichler
13:30-13:45	**CL-A7:** *Diels-Alder cycloaddition for the preparation of highly aromatic polyimide copolymers* Doris Cristurean	**CL-B7:** *Simulating a multistage polymerization process in a bench-scale setup* Gerold Rittenschober
13:45-14:00	**CL-A8:** *Water as monomer: Polymerizing divinyl sulfone and water via oxa-Michael addition* Karin Ratzenböck	**CL-B8:** *A hybrid approach for modelling polymer processing problems* Wolfgang Roland
14:00-14:15	**CL-A9:** *Preparation of functional polymers for glycan purification based on hydrazone solid phase extraction* Davide Ret	**CL-B9:** *Effect of processing and filtering in a two-stage injection molding process on thermos-analytical, rheological, and mechanical properties* Ines Traxler
5 min	Break	
14:20-14:35	**CL-A10:** *3D printing of pure phenolic resins by hot lithography* Raffael J. B. A. Wolff	**CL-B10:** *Influence of the material on the melt filtration using different screens* Kerstin Koller
14:35-14:50	**CL-A11:** *Bottlebrush, high molecular weight poly-phosphazene-g-poly(l-glutamic acid) fully biodegradable polymer therapeutics with enhanced biodistribution profiles* Paul Strasser	**CL-B11:** *Modeling of the devolatilization process in an extruder* Chi Nghia Chung
14:50-15:05	**CL-A12:** *Exploration of synthetic strategies to access catechol-based monomers for application in bioinspired adhesives* Manuel Pühringer	**CL-B12:** canceled
35 min	Coffee	
	Lecture room **P1** // Chairman: I. Lacik	
15:40-16:05	**IL-17:** *Cationic UV-curing of epoxidized biobased resins and composites* Marco Sangermano	
16:05-16:30	**IL-18:** *The quest for sustainable polymers - contributions from furan-based polyesters* Andreia F. Sousa	
16:30-16:55	**IL-19:** *Binary molecular stamps – a novel data storage technique: imprinting polymers with sequence-defined polymeric templates* Oliver Brüggemann	
16:55	Bus ride to the conference dinner	
17:50	**Conference dinner** – Weinschloss Koarl Thaller	

Wednesday, Sept. 1, 2021 – **Morning Session**

	Lecture room **P1** // Chairman: C. Slugovc	
8:55- 9:20	**IL-20:** *New trends in functional porous and permeable polymer materials for sustainability and life sciences* Benjamin Carbonnier	
9:20- 9:45	**IL-21:** *Porous polymers prepared by ring-opening polymerization* David Pahovnik	
9:45- 10:10	**IL-22:** *Compensation of volumetric shrinkage by expanding monomers* Frank Wiesbrock	
30 min	Coffee	
	P1 // Chairman: R. Kargl	**P2** // Chairman: C. Slugovc
10:40- 10:55	**CL-A13:** *A novel mechanical meta-material with customizable stiffness distribution* Mathias Fleisch	**CL-B13:** *Hypercrosslinked polymers for visible-light-driven CO_2 photoreduction* Robert T. Woodward
10:55- 11:10	**CL-A14**: *Investigation of shape memory-assisted self-healing of thiol-acrylate vitrimers* Walter Alabiso	**CL-B14:** *Understanding intermolecular bonding in organic materials and its impact on electronic properties* Egbert Zojer
11:10- 11:25	**CL-A15:** *Bismuth- and pyrylium-based onium salts as initiators for radical induced cationic frontal poly-merization* Roland Taschner	**CL-B15:** *Hypercrosslinked polyHIPEs as Pd-catalyst supports* Hande Barkan-Öztürk
5 min	Break	
11:30- 11:45	**CL-A16:** *Curing of epoxidized plant oils with solid acid hardener* Markus Schwaiger	**CL-B16:** *Anti-adhesive organosilane coatings functionalized with markers for visibility-on-demand* Christine Bandl
11:45- 12:00	**CL-A17:** *3D printing and stabilization of nanofibrillated cellulose-alginate scaffolds by different crosslinking methods* Tamilselvan Mohan	**CL-B17:** *Water-borne model epoxy varnishes for µm-thin adhesive bonding of electrical steel laminates* Gernot M. Wallner
12:00- 12:15	**CL-A18:** *Plastic or elastic: Fungi-derived composite nanopapers with tunable properties* Andreas Mautner	**CL-B18:** *Activation of polyamide fibers for subsequent metallization* Carolin Gleißner
12:15- 12:30	**CL-A19:** *Catalytic metal bonding of phosphinated cellulose and form-ation of nanocellulose in the process* Philip Verdross	**CL-B19:** *A study on the mechanism of blistering of pigmented organic coatings in warm-humid environments* Barbara Obereigner
60 min	Lunch	

Wednesday, Sept. 1, 2021 – **Afternoon Session**

	P1 // Chairman: D. Pahovnik	**P2** // Chairwoman: S. Hild
13:30-13:45	**CL-A20:** *Biomimetic models of the aortic arch for surgical planning* Rupert Kargl	**CL-B20:** *Software-based simulation and method optimization for polymer- and nanoparticle separa-tions by Field-Flow Fractionation* Gerhard Heinzmann
13:45-14:00	**CL-A21:** *Balancing strength and ductility – Tough and transparent nanopapers through mercerisation* Florian Mayer	**CL-B21:** *Effect of sequence blockiness on the retention behavior of gradient copolymers with various liquid chromatographic techniques* Blaž Zdovc
14:00-14:15	**CL-A22:** *Fully bio-based high-performance composite* Andrea Todorovic	**CL-B22:** *Degradation of monomers during hydroxyl-terminated polyester synthesis and their influence on the polymer structure* Viktoria Kreuzer
5 min	Break	
14:20-14:35	**CL-A23:** *Solvent and operating condition effects on the reaction rates of typical lignin bond cleavage during organosolv pretreatment* Tina Ročnik	**CL-B23:** *Differential Scanning Calorimetry with pressure cell for determining the polymer crystallinity changes in presence of gaseous penetrant* Martina Kukrálová
14:35-14:50	**CL-A24:** *Bio-Pulping: Delignification and hybridisation of lignocellulosic material utilising fungi* Kathrin Weiland	**CL-B24:** *Sulfonation of unsaturated polyester – analytical challenges due to solubility change* Klara M. Saller
14:50-15:05	**CL-A25:** *Bio-based polymers for transport packaging – possibilities & limitations* Nadine Wild	**CL-B25:** *Integrative material characterization of crystalline nanocellulose reinforced filaments for fused filament fabrication* Helena Weingrill
30 min	Coffee	
	Lecture room **P1** // Chairman: W. Kern	
15:35-16:00	**IL-23***:* *Impact of counterions on the propagation rate coefficient in radical polymerization of ionized monomers* Igor Lacík	
16:00-16:25	**IL-24:** *Improving the quality of recycled polymer waste through advanced mechanical sorting* Gernot Oreski	
16:25-16:50	**IL-25:** *Engineering catalytic conversion pathways of lignocellulose to functional alcohol or carboxylic monomers* Blaž Likozar	
16:50-17:15	**IL-26:** *Modeling macro-effects of micro-structures* Martin Pletz	
17:15-17:40	**IL-27:** *Polyheterocyclics by hydrothermal synthesis* Miriam M. Unterlass	

Thursday, Sept. 2, 2021 – **Morning Session**

	Lecture room **P1** // Chairman: B. Ivan	
8:35-9:00	**IL-28:** *Digital materials – Vision or reality? Applicability of micromechanical modeling for material design* Zoltan Major	
9:00-9:25	**IL-29:** *Environmental impact of the textiles sector and the role of bio-based resources* Avinash P. Manian	
9:25-9:50	**IL-30:** *Tricks with polyHIPEs: Combined templating approaches for hierarchical porosity* Peter Krajnc	
9:50-10:15	**IL-31:** *Processing of fibre-reinforced polymer composites based on phenomenological models* Ewald Fauster	
30 min	Coffee	
	P1 // Chairman: J. Fischer	**P2** // Chairman: E. Fauster
10:45-11:00	**CL-A26***: Investigation on the recycling of biobased polymers on the example of PHBV* Sabine Stockenhuber △	**CL-B26:** *Destiny of drag reducing agents in turbulent pipe flows* Hans Werner Müller
11:00-11:15	**CL-A27:** *Effect of different experimental setups on the removal efficiency of surface and matrix contamination in PE-LD* Konstanze Kruta △	**CL-B27:** *Impact of silver seed formation on electroless copper deposition for conductive textiles* Christian Biermaier
11:15-11:30	**CL-A28***: Poison study based on chemically recycled plastic waste impurities and their influence on the performance of Ziegler-Natta catalysts* Daniel Christian Pernusch △	**CL-B28:** *Hydrophobically modified copolymer associations - A promising path to improve drag reduction?* Emina Muratspahic
5 min	Break	
11:35-11:50	**CL-A29:** *The influence of the sample preparation steps on the properties of pre-treated polyolefin waste – Problems & Solutions* M. Hassan Akhras △	**CL-B29:** *Viscosity reduction of magnesium alkyls used for Ziegler-Natta catalysts* Julia Schwarz
11:50-12:05	**CL-A30:** *Recycling of multilayer films from food packaging* Kateřina Plevová △	**CL-B30:** *Effects of different process parameters on improved comonomer incorporation distribution in Ziegler-Natta catalysis* Lukas Göpperl
12:05-12:20	**CL-A31:** *Comparison of chromatographic, spectroscopic, thermal, and mechanical measurement techniques for polyethylene recyclate characterization* Paul J. Freudenthaler △	**CL-B31:** *Application of hybrid modeling in polymer processing* Ursula Stritzinger
70 min	Lunch // in parallel: **Board meeting**	

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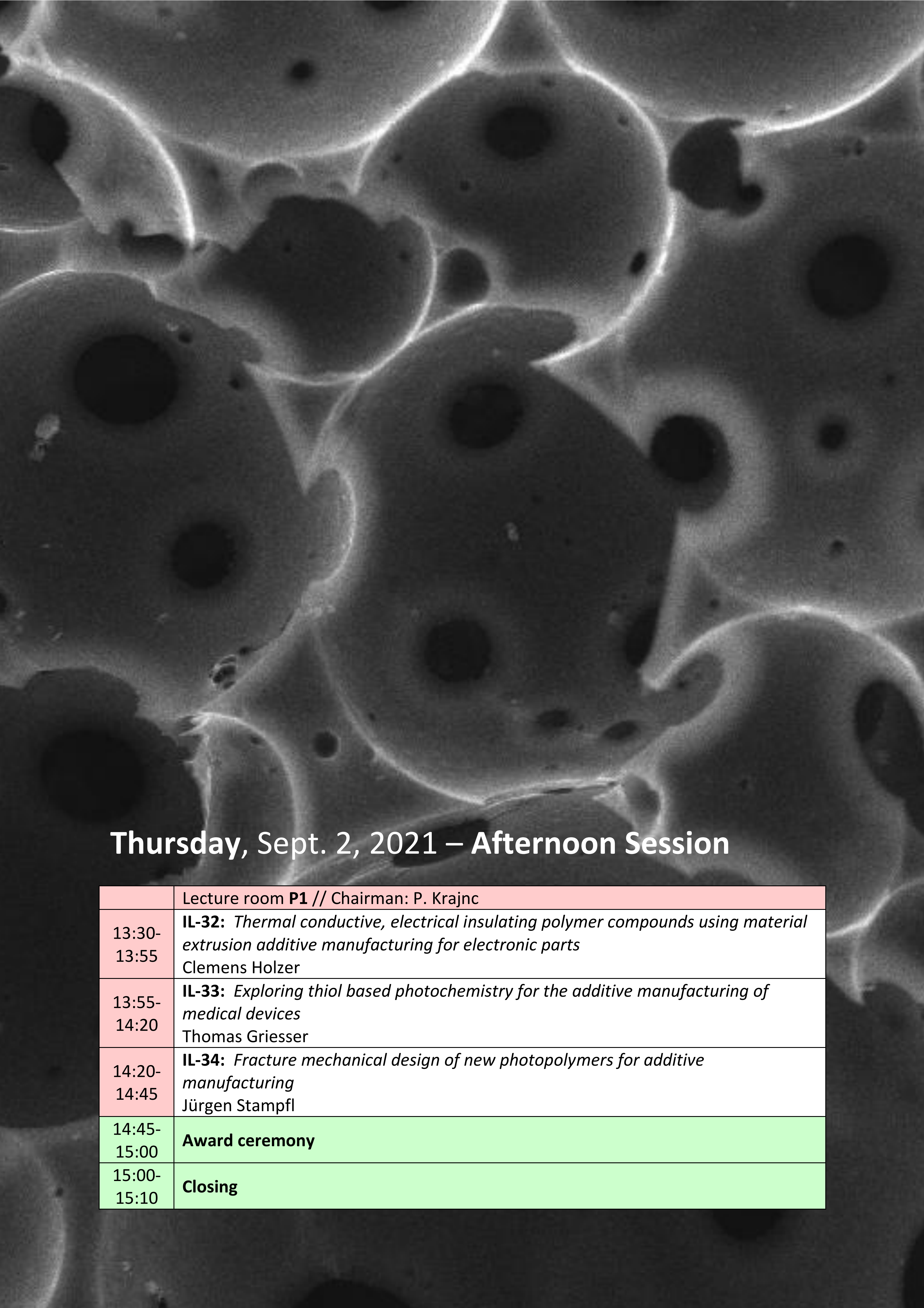
Recycling Session



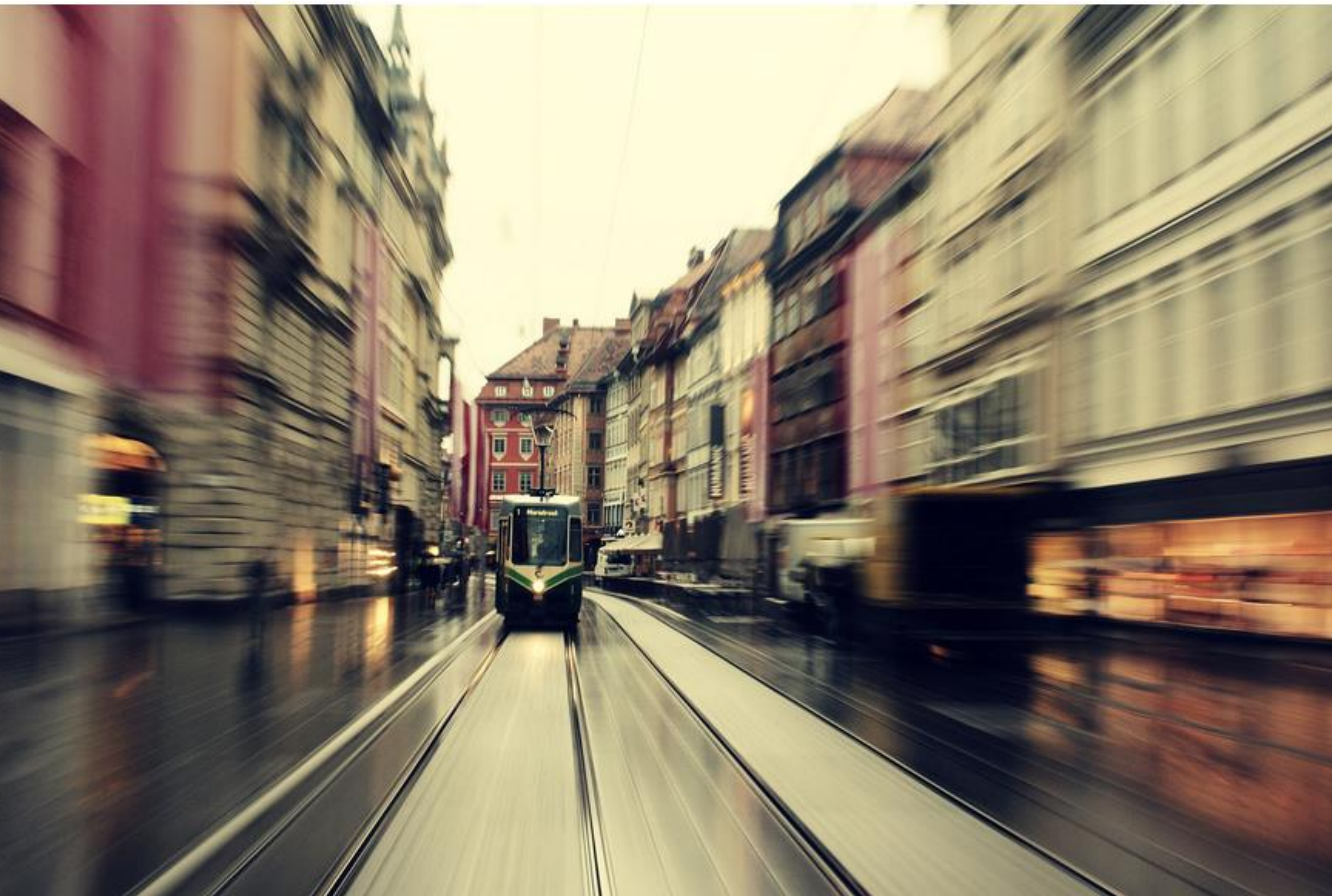
Thursday, Sept. 2, 2021 – **Afternoon Session**

	Lecture room **P1** // Chairman: P. Krajnc
13:30- 13:55	**IL-32:** *Thermal conductive, electrical insulating polymer compounds using material extrusion additive manufacturing for electronic parts* Clemens Holzer
13:55- 14:20	**IL-33:** *Exploring thiol based photochemistry for the additive manufacturing of medical devices* Thomas Griesser
14:20- 14:45	**IL-34:** *Fracture mechanical design of new photopolymers for additive manufacturing* Jürgen Stampfl
14:45- 15:00	**Award ceremony**
15:00- 15:10	**Closing**

PUBLIC LECTURE

Monday, Aug. 30, 2021

17:40



The role of plastics in navigating the *great societal transformation.*
A story on the future of plastics narrated as *"Wag the Dog"* puzzle

Reinhold W. Lang

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The call for and the urgency of a *Great Societal Transformation* has gained increasing support by academics, the scientific community and a steadily growing number of societal groups ever since the concept of *Sustainble Development*[1] first emerged in 1987 as a new intra- and inter-generational equity paradigm that requires comprehensive, deep and radical societal changes, pervading essentially all aspects of human life. In recent years, huge additional momentum has been gained through worldwide civil society endeavors such as the *Fridays for Future* school strike movement and *Extinction Rebellion*, with the necessity for a *Great Societal Transformation* within the next decades now being progressively more accepted by mainstream politics, in some recent policies perhaps even as a "categorical imperative" on which the persistence of an organized and just civilization may depend.

Representing such policies on a global scale are (1) the *UN Sustainable Development Agenda 2030*[2] with its 17 *Sustainable Development Goals (SDGs)*, designed to *"achieve a better and more sustainable future for all"*, and (2) the *Paris Agreement*,[3] aiming at reducing and limiting the risks and impacts of climate change, both adopted in 2015 by UN bodies. Specifically topic relevant on a European level is the *European Green Deal*, a set of policy iniatives by the European Comission, unveiled by its president von der Leyen in Dec. 2019 as *"man on the moon moment"*. On a national level worth citing is the *Green Deal for Industry and Commerce* in the *Austrian Governmental Program 2020-2024*.

Meeting the desire of a growing world population for prosperity in a *sustainable* manner, clearly also necessitates radical changes in production (and consumption) patterns, which in turn require adequate technologies along with proper choices of materials and handling of matter/material streams. On a meta-level, two essential pillars of an innovation-driven, *sustainable* technological transformation have emerged: (1) the transition of the energy system from a fossile fuel based energy system to an all-renewable enegy system, and (2) the transition of the matter/material resource system from a currently linear resources-to-waste system to a future circular material/matter system (i.e., circular economy).

In the lecture, the potential role of plastics and the plastics industry in these technology transitions will be explored, addressing the following questions: can plastics assume a key role in the *Great Societal Transformation* and will the plastics industry become a key driver of *sustainable* transformative change? Considering that roughly only 5% of the worldwide crude oil production are used for producing plastics, the transformation storyline will refer to and evolve around the "Wag the Dog" puzzle as a suitable methaphor.

References:

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INVITED LECTURES

Strong made weak: Composites with controllable stiffness and shape memory

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Common to all fibre reinforced composites is that fibres carry the load and the matrix holds them in place and protects them while load is transferred through composite interfaces. Engineering composite interfaces provides a means to adjust strength, stiffness and toughness of composites. However, by clever design much more is possible; by tuning composite interphases multifunctional composites can be designed, which besides being structural materials can simultaneously provide alternative functions, such as energy storage, shape memory capabilities and morph, or can be easily repaired. For multifunctional composites design of the interfaces and/or interphases between the composite constituents is of outmost importance. We will highlight approaches that enable "smart" composites with active stiffness control by using otherwise "stupid" polymers, which enable potential morphing applications for deployable structures and easy repair of composites.

The common design principle for our multifunctional composites, which besides load baring capabilities have shape memory, is based on the fact that polymers are glassy and stiff below their glass transition temperature (T_g) and undergo a significant stiffness reduction when passing T_g. Considering typical high-performance thermosetting composites with polymer matrices with T_g of around 150 – 180 °C, strong composite interphases which can undergo a stiffness change can be created by 1) coating either all reinforcing fibres or 2) composite plies with a (amorphous or semicrystalline) thermoplastic thin film, whose T_g is significantly lower than that of the composite matrix but higher than the service temperature of the composite material. When heating the composite to temperatures above T_g of the thermoplastic interphase but below that of the matrix T_g the interphase softens, which decouples the mechanical response of the composite matrix from the fibres or subsections of composite plies (in the case of the interleaved composite), which significantly reduces the overall bending stiffness of the composites.

We will introduce our design concept and methods to manufacture such composites. We will demonstrate that clever engineering of composite interfaces enables the production of composites with active stiffness control and shape memory capabilities without the need to incorporate any shape memory materials. Furthermore, these composites can also easily be repaired.

Photo-switchable polymer networks

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Advancing from polymers with structural or passive functions, the present work highlights the design of stimuli-responsive polymers by introducing molecular switches into polymer networks. In particular, photo-cleavable chromophores such as *o*-nitrobenzyl ester (*o*-NBE) groups are applied to design polymer networks, which change specific material properties after exposure to UV-light.[1] Along with a spatially controlled network degradation, *o*-NBE chemistry is applied to tailor the surface properties of photopolymer networks. The photo-triggered change in surface polarity and wettability is used to conveniently prepare polymers with multi-gradient surfaces allowing a directed motion of liquids across photopolymer surfaces.[2]

Whilst the introduction of *o*-NBE links in polymers enables a “one-time” switch of the material properties, synthesis routes towards photo-responsive polymer networks further involve the preparation of photo-activated dynamic polymer networks.[3] For a repeated change of material properties in response to light at different wavelengths, the reversible cycloaddition reaction of anthracene and coumarin chromophores is applied. The transfer of these concepts towards additive manufacturing techniques enables the fabrication of 3D objects with locally controllable mechanical properties and soft active devices with additional functions such as shape memory and self-healing properties.

Moreover, photo-switches are introduced in dynamic polymer networks (vitrimers), which undergo catalyzed bond exchange reactions at elevated temperature.[4] By applying photocleavable chromophores, microstructures can be repeatedly written at the same area of thin vitrimer films by photolithography and erased by a thermal annealing step. In addition, by using selected photolatent catalysts, topological rearrangements are activated in vitrimers on-demand by light exposure. This is a versatile strategy to fabricate soft active devices, which are able to undergo locally programmable shape change.

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Additive manufacturing of polymer/composite-metal hybrid structures

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Transportation engineers and designers are required to reduce structural weight of conventional vehicles and airplanes to mitigate the emmission of CO_2 and other greenhouse gases. Future electric-powered and hydrogen-powered transportation concepts will require heavy battery blocks, fuel tanks or cells. Therefore high-performance lighter structures will play an important role to improve the autonomy of vehicles and airplanes. Polymer/Composite-Metal Hybrid Structures (PM-HS) have been identified as potential candidates to fulfill this demand.[1] These hybrid structures are characterized by the presence of solid interface(s), normally with a sharp gradient in properties. The intrinsic dissimilarity between metals and polymer/composites imposes huge engineering challenges, requiring creative and material-friendly manufacturing approaches. AddJoining is a novel additive manufacturing method for PM-HS.[2] The technology uses fused filament fabrication (FFF) to hybridize metals – i.e. to form the polymeric/composite part around the metal parts. Hence, the parts can be produced with complex 3D-geometries by depositing extruded material layer by layer on a metallic substrate. The new process has been demonstrated for different combinations of materials, such as ABS with aluminum 2024,[3] unreinforced, continuous-carbon-fiber reinforced PA6 with aluminum 2024 [2] and titanium Ti64,[4] as well as short-fiber-reinforced PA 6 with laser-powder bed fusion additively manufactured titanium Ti64.[5] This invited lecture will review recent developments of AddJoining. Emphasis will be set on the correlations between process parameters, microstructure and mechanical performance.

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Polymer development for 3D printing: highest demands on components require designed materials

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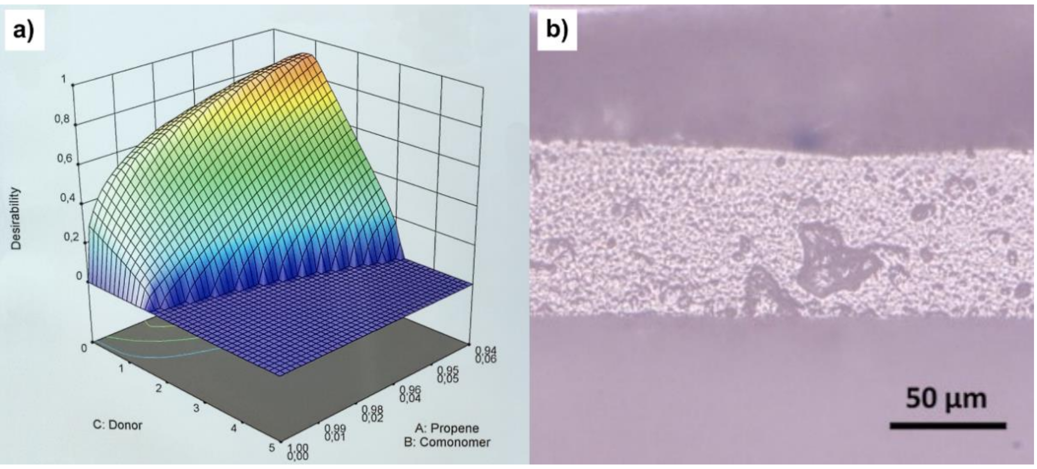
3D printing technologies have developed to the point of industrial use in recent decades and enable function-oriented component design. More than 10 main additive manufacturing techneques and a variety of sub-processes allow the 3D printing of metals, ceramics and polymers but also silicones, wax and construction materials can be processed. In the early days, only a few printable materials were available and material development started with the development of printing technologies. The market for 3D printing materials is still growing rapidly and offers a variety of different materials. Considering the polymer sector, a wide range of commodity polymers (PP, ABS, PET), engineering polymers (PA, PC) and high performance polymers (PEEK, PEKK), resines, composites and hybrid materials are available. Nevertheless, functinalized materials leading to taylored component properties, e.g. light weight materials, are still of interest.



Desirability plot for a fused filament fabrication optimized polypropylene copolymer (a) and a cross-section of 10 layers printed, NIR foamed and UV cured ink for PolyJetTM 3D printing (b).

The development of new polymeric materials, their monomers and necessary additives is presented with two examples, a tailormade polypropylene (PP)[1] and a UV curable resin that foams during printing[2]. A design oriented approach was used to synthesize a PP copolymer applicabel in fused filament fabrication (FFF). The material influencing properties viscosity, molecular weight, and crystallinity were optimized for the FFF printing process. PolyJet^{TM} 3D printing, an inkjet-based process, makes printing of several materials in one print-step possible. Thus, light-weight materials can be achived by combination of standard- and foamable inks. The development of a foamable and UV curable ink including the synthesis of a modified blowing agent, to fulfill the demands of the 3D printing ink, is presented.

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Degradable all-aliphatic polyurethane films

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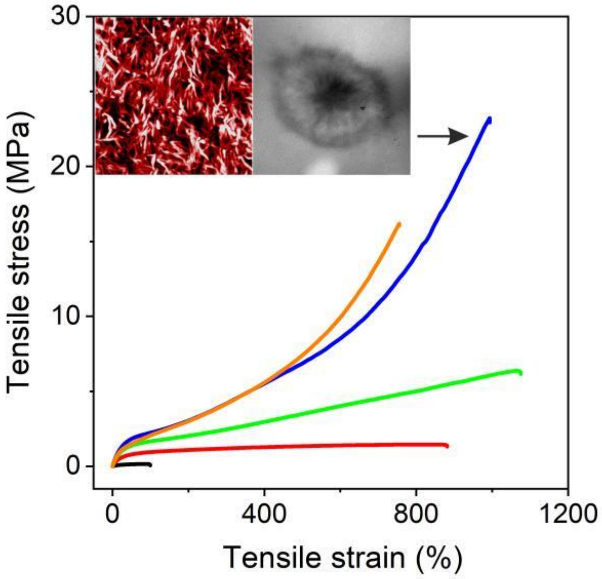
The contribution is aimed at the synthesis and multiscale characterization of complex all-aliphatic polycarbonate-based thermoplastic polyurethane (PU) and films derived thereof. The products with targeted properties are intended for usage as advanced materials in (bio)medical applications, e.g. as covering material for covered self-expandable gastrointestinal biodegradable stents. PU films were prepared either in bulk or from waterborne PU dispersions. Both preparation techniques enabled also the preparation of PU nanocomposites with filler nanoparticles differing in origin (organic, inorganic), shape, size and nanoparticle content.

PU materials made from 1,6-hexamethylene diisocyanate, polycarbonate-based macrodiol and butane-1,4-diol (at different ratios of hydroxyl groups of both diols) in bulk lead to hydrolytically stable films with favourable end-use mechanical properties. The degradation was tailored by building-in the D,L-lactide-based oligomeric diol (DLL) into the PU backbone. In this way, the hydrolytically degradable materials were prepared. It has been shown that the extent of degradation can be controlled not only by the content of the DLL but also by DLL chain length.

The syntheses of waterborne PU dispersions (WPUD) by two innovated procedures: (i) without any chain extender or (ii) in the presence DLL improved the application potential for the production of either stable films (see Figure) or degradable films. Targeted functional properties and degradability extent can be further set by the WPUD-to-nanofiller ratio. Film preparation is simple, environmentally friendly and energetically undemanding, consisting in water evaporation from WPUD or WPUD/nanofiller mixture.



Stress-strain characteristics of a PU film made from WPUD without any chain extender at different isocyanate/hydroxyl excess (5 mol % black, 20 mol% red, 30 mol% green, 40 mol% blue, 50 mol% orange). Left top insert: AFM image of film surface, right top insert: TEM image of spherulite detection.

Cationic frontal polymerization

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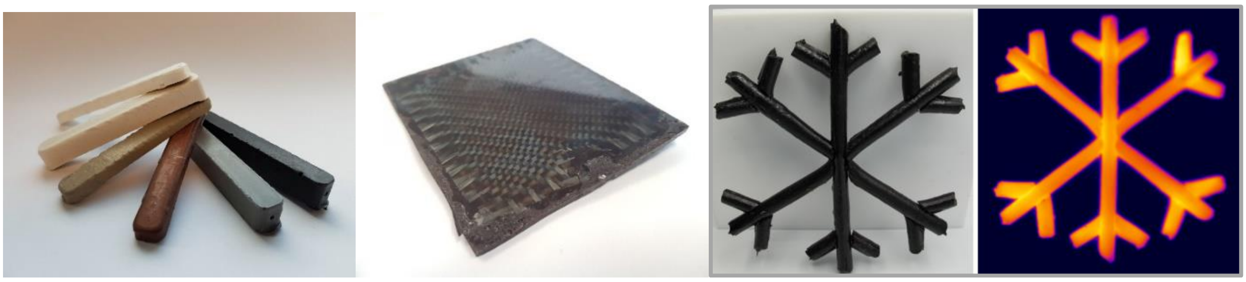
Frontal polymerization is a phenomenon that was characterised by Pojman in 2012[1] as polymerization process in which polymerization occurs directionally in a localized reaction zone. A lot of development was put into that topic since that time to bring frontal polymerization from an academic curiosity to industrial demanded applications.
Cationic Frontalpolymerization utilizes cationic polymerizatin (e.g. ringopening of epoxy resins) to liberate the necessary heat energy to keep the polymerization front running. For this kind of monomers the usage in fiber and/or particel filled composites is very common. Therefore the implementation of composite preperation techniques into the filed of frontal poymerizaton was investigated.



Composites prepared by frontal polymerizaton

Latest result of partice filled composites, preperation procedures of fiber reinforced polymer composites[2] shall be presented. Also the preperation of frontaly polymerizable carbon fiber prepregs[3] and their possible applicaations will be introduced.

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Cascade use of wood - from boards to fibers and chemicals

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Wood products can contribute to climate change mitigation as they (1) act as a carbon pool during their service lives, (2) withdraw CO_2 from its natural cycle, and (3) can substitute for more energy-intense products after their service life.

In this presentation the potential to improve the re-usability and recyclability of wood composites and construction material as well as utilization of industrial sidestreams will be presented.

Efficient resource use is the core concept of cascading, which is a sequential use of a certain resource for different purposes. This means that the same unit of a resource is used for multiple high-grade material applications (and therefore sequestering carbon for a greater duration), followed by a final use for energy generation and returning the stored carbon to the atmosphere. Intelligent concepts for reuse and recycling of valuable materials at the end of single product life will reduce the amount of waste to be landfilled.

Industrial stream residues contain bioactive compounds with a wide range of potential high-value applications. Of these compounds, polyphenols are present in large amounts and are of commercial interest because they can act as alternatives to oil-based chemicals. Many polyphenols are shown to have a high antioxidative activity and free-radical scavenging capacity and have therefore a high potential to be used in the pharmaceutical, cosmetic or functional food sector. They can be also applied in research programs for coronary heart disease prevention, anticancer activity, and anti–HIV functions. These biochemicals are also a potential source of numerous product innovations. Finding methods to remove large amounts of these extractives is of great environmental importance and presents an economic opportunity.

The activities of the project Selective extraction of high value molecules from forest products processing residues in the speciality chemicals sector will be discussed and challenges in industrial applications outlined.

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Lifetime modelling of heritage polymers

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In the context of technical applications, it may often be possible to define material *lifetime* on the basis of retention of a physical property critical for its function. In the context of heritage, the function becomes less of a technical issue and more the question of value retention, where *value* could be any combination of reasons why a heritage object is culturally significant. The fact that the issue is cultural, also requires an open discussion about the desired period of time over which a heritage material is meant to retain desirable properties, and manage its conservation accordingly. To address these research questions, intensely interdisciplinary research is needed, based on materials, environmental and social science.

Cellulose is a ubiquitous heritage polymer and paper is a well-studied heritage material with lots of existing knowledge about its chemical and mechanical degradation, and thus represents an interesting case study. There is surprisingly little research on how material degradation is perceived by users of heritage, i.e. library and archival readers and visitors, who may have important views on what degradation is aceptable and over what period of time.

To resolve this, a wide-ranging study of attitudes to degradation was conducted among users, with almost a thousand involved in two types of experiments.[1] In the first experiment, the values attached to archival and library heritage were explored and how these might affect the views held on degradation and damage. This experiment involved a value questionnaire followed by factor analysis, a typical social science experimental technique. Nine types of values were determined, of which one was specifically related to material properties of the documents. In addition, quantiative views related to lifetime expectations were revealed. Secondly, a composite central design of experiments was used to explore what element of degradation (chemical and mechanical) should be prioritised in terms of end of fitness-for-use.

In combination with known and quantiative effects of environmental stressors on the rate of degradation of historic paper (dominated by temperature, humidity and material acidity), it s thus possible to model the environmental conditions under which the desired lifetime is achievable. This puts quantitative science in the context of heritage management and enables decisions to be made by specialists who do not necessarily have a deep knowledge of material science. Heritage science is the rapidly developing field where exact physical sciences work in close collaboration with social sciences and humanities.[2]

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Bicontinuous nanophasic amphiphilic polymer conetworks with broad composition range: A novel nanostructured material platform

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Gergely Kali,[a] Péter Mezey,[a] Szabolcs Pásztor,[a] Ákos Szabó,[a] Attila Domján,[a]
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Unprecedented high value-added opportunities exists with amphiphilic conetworks (APCNs), consisting of covalently bonded, otherwise immiscible hydrophilic and hydrophobic polymer chains, which belong to a new class of rapidly emerging nanostructured materials (see e.g. Refs. 1-8). Due to the immiscibility of the components, the synthesis of such macromolecular assemblies is quite challenging. Several successful synthetic routes have recently been developed by us, including various protection-deprotection schemes. Unique bicontinuous (cocontinuous) nanophase separated morphology exists in APCNs with domain sizes in the range of 2-30 nm in a broad composition window. This provides challenging possibilities to obtain various new specialty intelligent (smart, responsive) and selective organic solvent superabsorbent poly(ionic liquid) conetwork gels, and organic-inorganic nanohybrids by applying one of the nanophases as nanoreactor. The resulting novel materials have a variety of high value-added potential for applications from intelligent drug delivery to antibacterial biomaterials, nanocatalysis, photonics, energy and environment protection related materials, sensors, actuators and specialty superabsorbents etc.

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Development of devices based on stimuli-responsive polymer thin films deposited by iCVD

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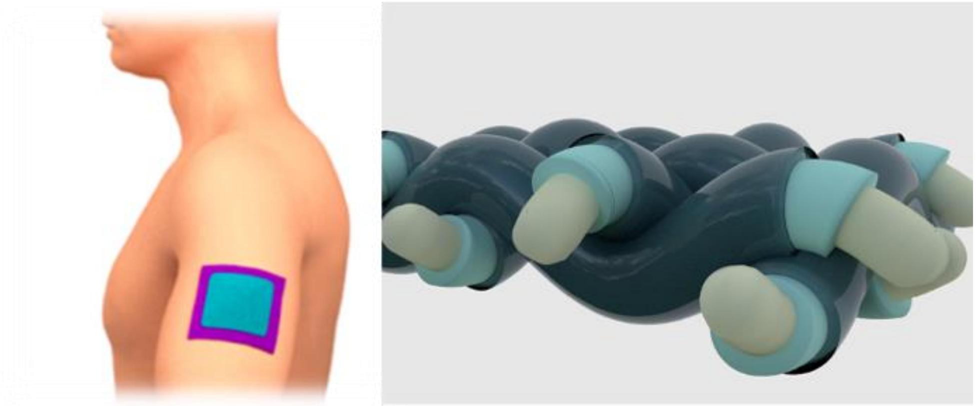
Stimuli-responsive materials are characterized by dynamic switching of their properties depending on external stimuli (e.g. light, pH, temperature, humidity). Functional and responsive polymer thin films have been successfully deposited by initiated Chemical Vapor Deposition (iCVD) on a variety of substrates. iCVD allows to obtain stimuli-responsive polymer thin films without the use of solvents and with high chemical specificity and this is important to obtain a large responsiveness amplitude. In addition, the thin film form allows obtaining fast response.

Fast response and large signal amplitude are fundamental requirements for good sensors. Fast and ultra-fast humidity sensors based on the optical detection of the change in thickness of the iCVD hydrogels will be shown. The setup was designed without electric components in the vicinity of the active sensor layer and is therefore applicable in harsh environments such as explosive or corrosive ones.[1] The implemented sensor prototype delivered reproducible relative humidity values and the achieved response time for an abrupt change of the humidity was about three times faster compared to one of the fastest commercially available sensors on the market.

Another case of study will be presented in the field of multi-stimuli-responsive materials.[2] A chemical functionalization of the hydrogel surface was performed to add multiple stimuli-responsive functionalities and obtain a smart material that responds to two stimuli at the same time. Such polymers were used as drug encapsulants to achieve controlled drug release upon stimuli, with possible application as wound dressings.[3]



Polymer thin films (represented in dark blue in the right figure) deposited on cotton for drug delivery devices on skin.

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Fracture of layered polymers

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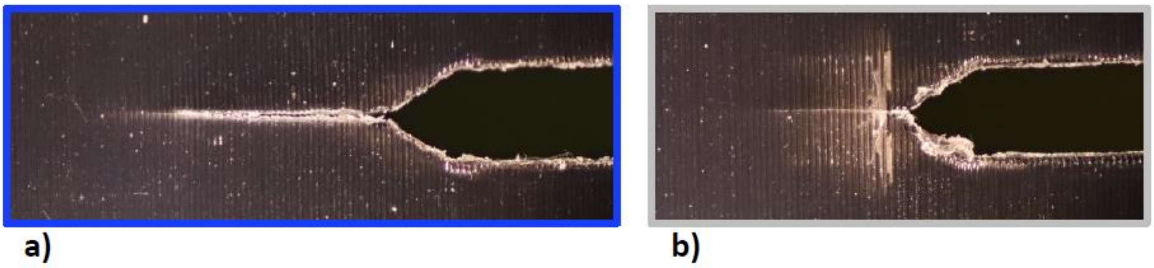
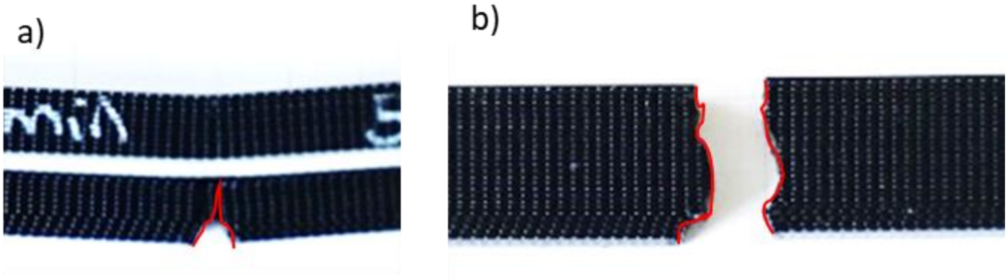
The rise of modern processing techniques, such as additive manufacturing, or complex multi-layer co-extrusion, has led to an increased interest in the fracture behavior of layered polymers. Depending on the used materials, processing technique, orientation and exact thermal history, complex fracture mechanisms can occur. As shown in the figure[1] below, for a compact tension specimen with fatigue crack growth perpendicular to the layer orientation, even the exact applied load level can change the behavior drastically – switching from layer penetration, which is usually connected to rather strong interfaces, to crack deflection, which is usually a sign of weak interfaces[2].



Crack growth perpendicular to the print orientation in a Compact tension specimen with strong (a) and weak (b) strand to strand interfaces[1]

The additional use of different materials within a layered structure further complicates the behavior and subsequent description of the fracture properties. However, the application of aforementioned multi-material combinations can be utilized for extrinsic toughening of layered, otherwise rather brittle, polymers, similar to effects observed in biological materials.



Effect of a soft interlayer (a) on the fracture behavior of a brittle polymer (b), produced via additive manufacturing

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Raman spectroscopy: A tool for polymer characterization from the macroscopic to the microscopic scale

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A high-throughput Raman spectrometer can be combined very easily with a wide variety of external devices. This greatly expands the possibilities for non-destructive online characterization of polymeric materials with high chemical sensitivity.

In polymerization reactions, Raman spectroscopy can be used to determine the reaction conversion or the degree of crosslinking. Combining this method with rheological data, e.g. gel point and vitrification point, gives a better insight into the overall processes taking place and allows to estimate the influence of different preparation parameters on the obtained rheological/mechanical data. For the simultaneous monitoring of chemical changes and their influence on rheological properties during in-situ investigations of polymerization or crosslinking reactions, the combination of an oscillating shear rheometer (Anton Paar 502) with a Raman spectroscope (ThermoFischer Labram) has proven to be a powerful tool. A homemade Rheo-Raman setup was used to study crosslinking processes of various chemically and physically crosslinked polymer systems at different temperatures (20 - 200 °C) or with the application of UV radiation.

Combining a Raman spectrometer with a confocal microscope provides the capability for non-destructive testing of a wide range of polymer-based materials where a combination of high chemical sensitivity and high spectral and spatial resolution is required. One example of high practical importance is the study of phenomena occurring at the interface between two polymers. For example, the mechanical strength of functional laminate structures fabricated either by bonding different polymer layers or directly in a co-extrusion process is determined by the formation of a so-called interdiffusion layer. Therefore, in the second example, the interfacial formation of different multilayer polymer composites is investigated by confocal Raman microscopy (CRM). The resolution of confocal Raman spectroscopy is not high enough to directly investigate the first few nm of a surface, but from optically transparent polymers and polymer matrices, effects of interpenetration and molecular interactions in interfacial layers can be visualized on a submicron scale by depth profiling, as shown in Figure 1. To investigate interfaces in non-transparent samples, e.g. co-extruded colored multilayers with fillers, cross-sections are prepared by ultramicrotomy and the interfaces are thus imaged. For two co-extruded polyolefin-based materials, the first CRM results are discussed, showing the influence of the process parameters on the formation of the interdiffusion layers.

Enzymatic polymerizations – Making polymer synthesis more sustainable

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The in vitro enzymatic synthesis of polymers via non-metabolic pathways is a relatively old area of precision polymer synthesis. The enzymatic polymerization of polysaccharides was for instance already reported more than 50 years ago. But soon other polymerization methods using cheap petroleum-based monomers replaced research on biocatalytic polymerization techniques. However, these days fast depletion of the petroleum stock and increase in the cost of petroleum based monomers puts limit to their use in the future and enzymatic polymerizations are currently facing a Renaissance. At present, petrol-based monomers are still predominately used in enzymatic polymerizations. By combining biobased monomers and enzymatic polymerizations in polymer synthesis, not only the research field of enzymatic polymerization could be greatly accelerated but also the utilization of renewable resources will be promoted. This will provide an essential contribution for achieving sustainability for the polymer and coatings industry, which will eventually play an important role for realizing and maintaining a sustainable society.

Here we will discuss various enzymatic syntheses of biobased monomers and polymers. Saturated and unsaturated aliphatic polyesters can for instance be easily synthesized via enzymatic polymerization of biobased monomers derived from renewable resources. Itaconate-based aliphatic polyesters are appealing for many applications, as they are renewable functional polymers that can be biodegradable, biocompatible, and photo-curable, and might be bioresorbable. We successfully produced various biobased saturated aliphatic polyesters and itaconate-based unsaturated aliphatic polyesters via Candida antarctica Lipase B (CALB)-catalyzed polycondensation of biobased dimethyl itaconate, 1,4-butanediol and various diacid ethyl esters, using a two-stage method in diphenyl ether. Another example is the enzymatic polymerization of 2,5-furandicarboxylic acid (FDCA), one of the key building blocks for the preparation of furan polymers. The traditional synthesis is often accompanied with side reactions (e.g. decarboxylation) and ue to the mild reaction conditions, enzymatic polymerizations became an excellent candidate to address this issue. Here, we present a green and effective method to prepare different furanic polyester, polyamides and poly(ester amide)s.

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Additive-manufactured polymer-based biomaterials for regenerative medicine

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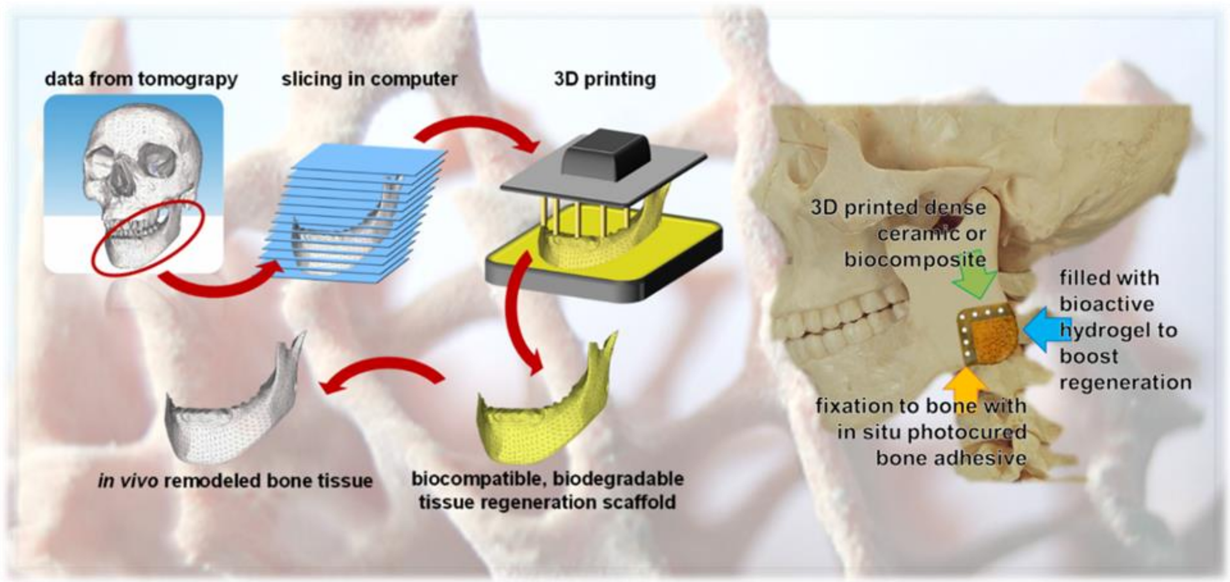
Photopolymers are an ideal material platform for biomedical applications. They can be cured in seconds, opening up manifold application scenarios, incl. *in situ* curing of, e.g., adhesives and 3D printed individual medical devices, e.g., implants.[1] Their characteristics, e.g., their mechanical properties, can be adjusted over several orders of magnitudes to perfectly fit to the according application.[2] For example, photocured hydrogels are an excellent mimicry for soft tissue while highly filled photopolymer composites perfectly resemble bone.



3D printed individualized bone implants

Hence, our main interest is to continuously extend the toolbox of biocompatible photopolymer precursors. An important example for such materials are vinyl esters[3] and a range of use cases in the field of biomedicine were presented previously.[4-7]

In this contribution, an overview of the precursor design principles is presented, including synthesis and adjustment of material composition to satisfy required material properties. Finally, successful application scenarios for biocompatible photopolymers in the field of biomedicine are demonstrated.

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Viscoelastic modelling of polymer melt flow for thermoplastics and rubber compounds

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Thermoplastic melts and rubber compounds are viscoelastic fluids. They exhibit a complex flow behavior, which is influenced by various factors like polymer type, molar mass distribution, additives, filler content, and in some cases wall slip. Neglecting the viscoelastic nature of polymers most state-of-the-art simulation software packages use purely viscous material models for the calculation of the flow, pressure, and temperature fields. Consequently, flow phenomena influenced by viscoelasticity (inlet vortices, extrudate swell) are not predicted correctly and pressure drops are underestimated. In case of rubber compounds the Payne effect caused by the filler-filler network additionally impacts the flow behavior at low shear rates while for a variety of thermoplastic melts e.g. PS, PP, ABS, PMMA, PC etc. the pressure dependency of the viscosity is of crucial importance.

This contribution focuses on how to determine, and best fit rheological data (shear and extensional viscosity, storage and loss moduli) with the K-BKZ model for thermoplastics, and rubber compounds taking into account the pressure dependency of the viscosity, and the influence of viscous dissipation in capillary rheometry at higher shear rates.

Comparing CFD simulation results to experimental data only viscoelastic modelling provides a correct prediction of the pressure demand as well as the streamline pattern in contraction flow dominated geometries. Examples will be given for PP-PNCs, SBR and NBR.

Challenges and approaches for specification-compliant plastics recycling

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The versatility of plastics is leading to a steady increase in annual production, which amounted to around 58 million tons across Europe in 2019.[1] However, the downside of this rapid growth is vast amounts of waste generated by the large number of short-lived plastic products, such as packaging plastics. In addition to the logistical problem resulting from the high waste volume of about 29 million tons, non-compliant handling of plastic waste also leads to significant environmental pollution. This has prompted the European Parliament and the European Council to publish two important directives, the “Packaging and Packaging Waste Directive”[2] and the “Single-Use Plastics Directive”.[3]

The requirement of doubling the recycling rate for plastic packaging in Austria from currently approximately 25 % to the EU recycling target of 50 % in 2025 will only be achieved through more intense cooperation and networking within the value chain in plastics recycling.[4] The regional and seasonal variability in quality of plastics waste streams as well as the complexity of the production and supply chain in plastics recycling leads to problems in continuous quality assurance to allow for high-quality plastic recyclates. Thus, much more intensive cooperation and networking within the value creation cycles is necessary.

In order to allow for specification-compliant plastics recycling focus should be given on quality assurance along the process chain. Consequently, specific adaptations of the recycling processes for plastics according to the existing qualities of the input stream are required. For the realization of a sustainable circular economy for plastics, the overall objective should be the optimization of the value-added cycles in plastics recycling with regard to (a) high quality, (b) high output volume, and (c) low reject. An adequate adaptation of the recycling processes to the respective waste streams should allow for expanding the portfolio of input streams. Accordingly, the outcome is an increase in the recycling rate by expanding the capabilities of value-added cycles in plastics recycling.

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Cationic UV-curing of epoxidized biobased resins and composites

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Epoxy resins are among the most important building blocks for fabrication of thermosets for many different applications thanks to their superior thermo-mechanical properties and chemical resistance. The recent concerns on the environmental problems and the progressive depletion of petroleum feedstocks have drawn the research interest in finding biobased alternatives. Many curing techniques can be used to obtain the final crosslinked thermoset networks. The UV-curing technology can be considered the most environmentally friendly because of the absence of volatile organic compound (VOC) emissions and mild curing conditions.[1]

Studying the reactivity of epoxidized cardanol derivatives, we have demonstrates the high reactivity and potentiality of bio-renewably obtained cardanol-based epoxy monomers as well as the possibility of tuning the final thermomechanical properties by changing either the epoxy content or the chemical structure of the starting photocurable resin.[2]

We continued our investigation focusing on the valorization of vegetable oils (VOs) into thermoset materials by using epoxidation of the VOs through the “double bonds to epoxy” synthetic route and the synthesis of crosslinked homopolymers by UV-curing processes achieving the synthesis of 100% biobased EVO thermoset materials whose thermomechanical performances were proved to linearly increase with the EVOs' epoxy content.[3]

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The quest for sustainable polymers - contributions from furan-based polyesters

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Due to its unique set of properties, polymers has quickly become an irreplaceable material and valuable resource to our society. In particular their malleabilility, durability and lightness together with competitive production costs has allowed them to be (almost) irreplaceble materials for a variety of uses! However, in more recent years, polymers' status has been deeply questioned due to their fossil-based origin and non-circular fate after use. In this context, our group has turned to the exploitation of biomass derived key building-block chemicals such as, for example, the 2,5-furandicarboxylic acid (FDCA), in polymer synthesis.[1] The initial focus was on the synthesis and characterisation of poly(ethylene 2,5-furandicarboxylate) (PEF), the so-called renewable counterpart of poly(ethylene terephthalate) (PET). Afterward, motivated by the quest for adequate polymers' fate we introduce a new leitmotif in the furan polymers development – the (bio)degradable furanic-aliphatic copolyesters, for instance the copolyesters based on PEF and PLA.[2] Then, we extended the concept to homopolymers with poly(1,20-eicosanediyl 2,5-furandicarboxylate) which has interest among food packaging applications (equilibrium moisture uptake very near 0% due to its hydrophobic character but biodegraded).[2] More recently, our focus turned also to use tailor degradation in recycling though mild eco-friendly catalysis of, *e.g*, PEF. The whole-value chain of furans have attracted EU funding through the COST Action FUR4Sustain (CA18220) (Fig.1).

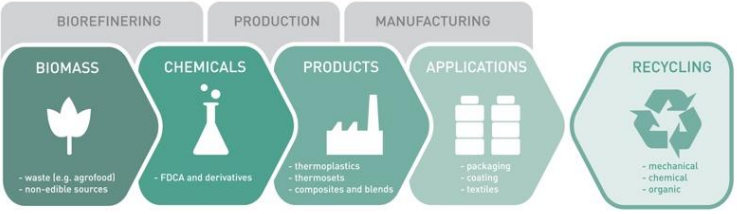

Fig. 1 Overview on furans' whole value chain.

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Binary molecular stamps – a novel data storage technique: imprinting polymers with sequence-defined polymeric templates

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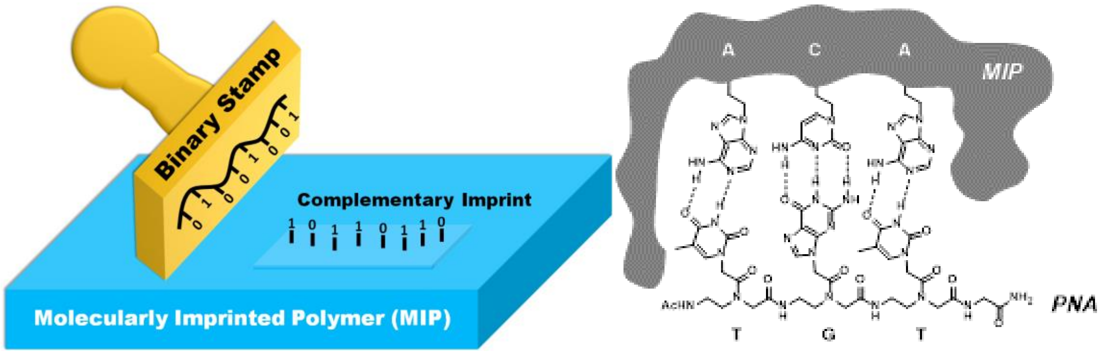
Long before our time, nature has developed the archetype of a data storage medium: DNA. Beside its original purpose of storing genetic information, DNA nowadays can be artificially synthesized and used for storing digital data, such as text files, audio and video recordings in their binary versions.[1,2]

This paper presents recent developments of our novel concept aiming on the design of molecularly imprinted polymers (MIPs) for storing binary codes using, e.g., peptide nucleic acids (PNAs) as templates.[3] In terms of depiction of binary codes in the templates, two types of monomers are necessary to represent “1” and “0”. For this purpose, we first have to synthesize PNA-monomers bearing two different nucleobases (thymine = 1 and guanine = 0). With these PNA-monomers, macromolecular PNA-templates, the “binary stamps”, with defined sequences, i.e. defined binary codes, can be generated efficiently via liquid phase synthesis. After the addition of MIP-monomers with template-complementary nucleobases (adenine and cytosine) as functional side arms, followed by self-assembly of the PNA-template with these MIP-monomers, polymerization takes place. By this means, the nucleobase sequences of the PNA-templates, i.e. the binary codes, are in a complementary form transferred to the molecular imprints of the MIPs. Using for instance a trimeric template (TGT, representing, e.g., the binary code 101), the resulting MIP contains its complementary sequence (ACA) as stored information.



Concept of storing binary codes in molecularly imprinted polymers (MIPs). Left: Principle of using a binary molecular stamp for leaving complementary imprints in a polymer (MIP). Right: exemplary approach: the TGT sequence (representing, e.g., the binary code 101) of a peptide nucleic acid (PNA) template is stored as its complementary sequence (ACA) in a MIP by applying nucleobase-functionalized MIP-monomers

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New trends in functional porous and permeable polymer materials for sustainability and life sciences

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Over the last decade, the generation of organic porous (nano)materials with tunable pore sizes and desired functionalities has been the subject of increasing attention in materials science. Interest in such porous frameworks originates from the large variety of applications in which they are involved, encompassing advanced separation techniques, tissue engineering, drug delivery, heterogeneous catalysis and flow chemistry. This class of materials exhibit undeniable advantages over their inorganic counterparts, namely their synthesis is cost-effective, and their mechanical properties as well as the chemical nature of the pore interface can be finely tuned.

In this context, we have developed a series of polymer-based materials with well-defined porosity, pore size, permeability and surface interaction ability holding high potential as mimics for natural materials, catalytic flow microrectors, sorbents for biomarkers analysis, on-command drug delivery *via* stimulus-cleavable chemistry and eco-friendly insulating materials.

This contribution will particularly focus on recent progress in designing polymer monoliths designed as bulk or in-microchannel materials. Correlation between the surface chemistry and the surface interaction ability of the monolithic sorbents will be clearly evidenced through applications in analytical chemistry and heterogeneous catalysis. Indeed, the robust and site-specific immobilization of nanometals acting as supported catalysts for organic dye reduction, hydride-mediated reduction of nitroaromatic compounds, and C-C homocoupling of benezeneboronic acid derivatives will be presented together with exemples of separation of biologically relevant molecules under reversed-phase, hydrophilic interaction, and chiral chromotography.[1] The possibility to provide dual functionality to the monolith, acting as an electro-osmotic flow pump beyond separation and catalysis will also be discussed. Emphasis will also be given to applications of monolithic materials for the preconcentration and analysis of phosphorylated proteins/peptides in microfluidic devices.[2]

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Porous polymers prepared by ring-opening polymerization

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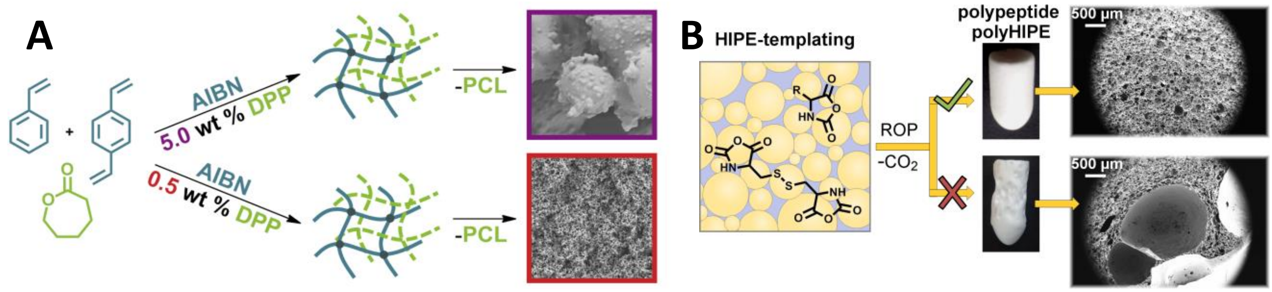
Porous polymers are useful materials in a wide range of applications. While porous materials used for separation and catalytic purposes need to be non-degradable, materials for biomedical applications, on the other hand, require degradable materials in many cases, often prepared by ring-opening polymerization (ROP) of heterocyclic monomers, such as lactones for polyesters and *N*-carboxyanhydrides (NCA) of α-amino acids for polypeptides. In this lecture, various methods employing ROP to prepare different types of porous materials will be presented. For example, semi-interpenetrating networks (semi-IPN) were prepared by in situ simultaneous orthogonal polymerizations, where poly(ε-caprolactone) (PCL) was synthesized by ROP of ε-caprolactone (CL), while polystyrene (PS) network was formed by free-radical polymerization of styrene and DVB.[1] PCL domains were then selectively removed to obtain the non-degradable porous PS monoliths. By varying the relative polymerization rate, the time order of gelation versus phase separation was modulated, which had a fundamental impact on the final morphology of the obtained PS porous networks. To synthesize fully degradable porous polyesters or polypeptides the ROP of suitable monomers was performed directly in the continuous phase of the anhydrous high internal phase emulsions (HIPEs) serving as a soft template. In this way, polyHIPEs based on cross-linked PCL have been prepared by organocatalyzed ROP of CL, which are distinguished by shape memory behavior with excellent shape fixity and shape recovery.[2] The synthetic method has been extended to the ROP of various types of NCAs in HIPEs to prepare synthetic polypeptide polyHIPEs.[3] The polymerization rate has been shown to be an extremely important parameter for the successful preparation of polypeptides with typical polyHIPE morphology, as it determines the rate of carbon dioxide release from HIPE during ROP.



*ROP was utilized to prepare various porous polymers; (**A**) PS monoliths from semi-IPNs and (**B**) fully degradable monoliths by ROP of suitable monomers in continuous phase of HIPEs.*

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Compensation of volumetric shrinkage by expanding monomers

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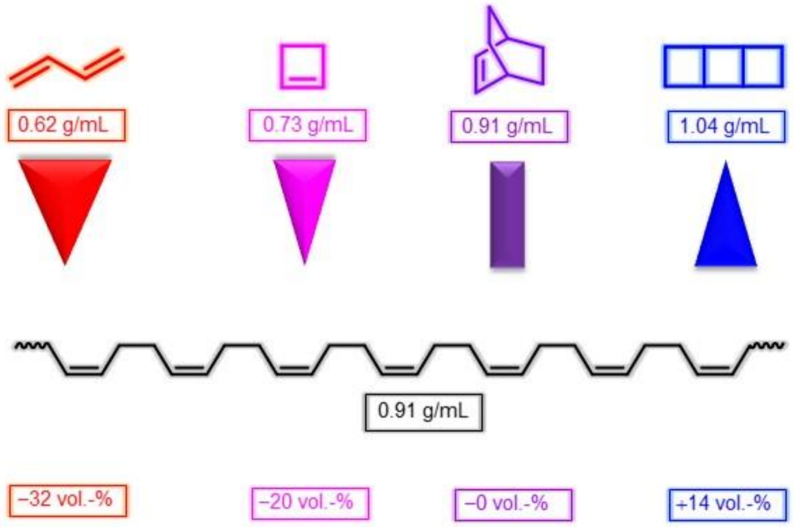
Volumetric shrinkage occurs in the course of chemical reactions due to the shortening of the equilibrium van-der-Waals distance of two molecules to the length of a significantly shorter covalent bond. In order to overcome this volumetric shrinkage, the so-called expanding monomers can be used, which show volumetric expansion during polymerization reactions. Such monomers exhibit cyclic or even oligocyclic structural motifs with a correspondingly dense atomic packing.[1]



(Hypothetical) polymerizations of monomers of the composition $C_{4n}H_{6n}$ (n = 1, 2) and the volumetric shrinkage/expansion, calculated from density changes.

In this presentation, the synthesis and application of spiroorthoesters (SOEs) will be focused on. SOEs can be used as additives/ring-opening monomers in thiol-ene resins,[2] enabling the control of the shrinkage/volumetric expansion during the curing reaction as well as the preparation of 3D-printable high-κ materials. In combination with polyamides and *pseudo*-polyamides such as poly(2-oxazoline)s,[3] the SOEs could be used to fine-tune the volumetric changes during the copolymerisation reactions; the dielectric properties of the poly(2-oxazoline)-based materials, which were derived from natural resources, were found to be competitive with those of the fossil-derived polamide-based materials.

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Impact of counterions on the propagation rate coefficient in radical polymerization of ionized monomers

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The kinetics and mechanisms for the radical polymerization of ionized monomers has been a matter of interest for decades. This knowledge has been, however, limited due to the unavailability of rate coefficients for the individual kinetic steps, which is the key condition to describe the main features that control the polymerization of ionized monomers.

This contribution is devoted to the quantitative understanding of the role of counterions on the propagation step in radical polymerization of ionized monomers, exemplified for two cationic monomers [2-(methacryloyloxyethyl)]trimethylammonium chloride (TMAEMC) and [3-(methacryloylaminopropyl)]trimethylammonium chloride (MAPTAC) polymerized in aqueous solution. The propagation rate coefficient, k_p, was determined by pulsed-laser initiated polymerization combined with size-exclusion chromatography over a broad range of monomer concentration, temperature, pH, and salts.[1]

A number of novel features were identified. The concentration of counterions introduced to the polymerization system either by monomer only or by both monomer and salt determines the level of screening of repulsive electrostatic interactions in the propagation step. At very low counterion content, these interactions dominate and the propagation rate is similar for both monomers. Upon screening of these interactions by counterions, the k_p values follow the trends seen for the family of non-ionized monomers, i.e., the k_p value for the methacrylester-type monomer TMAEMC was about a factor of two higher than that of the methacrylamide-type monomer MAPTAC. Remarkably, in this range of high counterion concentration, a linear correlation between k_p values and the molar concentration of counterions was observed. This resulted in a simple expression representing the variation in k_p on counterion concentration and temperature. Arrhenius parameters indicate that the difference between k_p values for TMAEMC and MAPTAC is given by a lower pre-exponential factor for MAPTAC compared to TMAEMC, whereas the activation energies of around 14.5 $\text{kJ}\cdot\text{mol}^{-1}$ are similar for both monomers.

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Improving the quality of recycled polymer waste through advanced mechanical sorting

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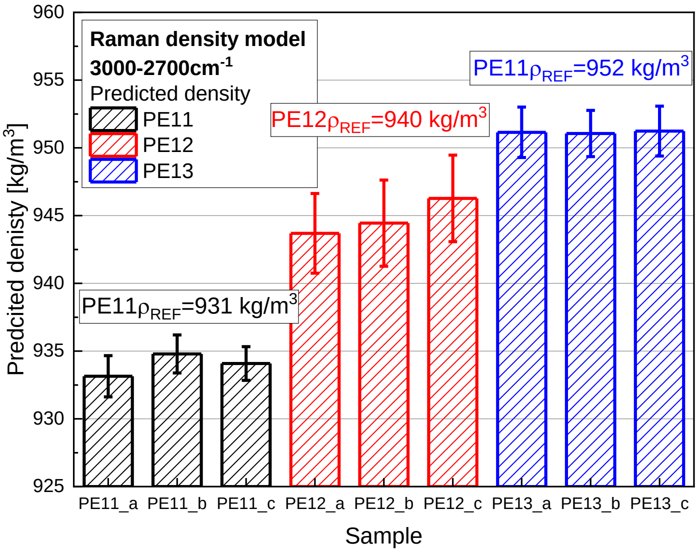
A key target of the Circular Plastic Alliance Declaration is to include 10 million tons of recycled plastic per year into new plastic products in Europe by 2025. To meet this objective mechanical recycling has to overcome two main obstacles. First, new reliable, and cost-efficient technologies with high material separation accuracy are required. Secondly, the quality and performance of recyclates must be improved significantly. Polyethylene (PE) is a globally dominant polymer as a result of its wide range of variations in molecular structure and morphology. State-of-the-art near infrared (NIR) sorting systems easily identify base materials, but they can hardly account for specific characteristics in the molecular structure of PE. The processability and applicability of such recycled materials for high quality applications is limited due to the wide range of variation in the chemical structure of PE grades, e.g. molar mass and molar mass distribution or short and long chain branching. The main aim of this paper is to separate the post-consumer PE into various classes based on specific molecular characteristics, like density or melt flow rate. In a first step different PE types have been investigated using Infrared and Raman spectroscopy and the resulting spectra have been evaluated using multivariate data analysis (MVDA). Applying multivariate data analysis (MVDA) on spectroscopy data allowed the prediction of density. The results showed a good agreement with the measured values, where the calculated densities showed a less than 0.5% deviation from the measured values, indicating that processing relevant information can be extracted from FTIR and Raman data. In a second step the PE samples were measured on a state of the art NIR based sorting line. In a first analysis the PE samples could be classified with respect to its processing methods. However, this work is still ongoing and the model still needs to be improved. The results indicate that existing NIR sorting lines can be used for further differentiation of post consumer plastics based on specific molecular features, which would results in an improved quality of the recycled material.



Prediction of PE density based on Raman spectroscopy

Engineering catalytic conversion pathways of lignocellulose to functional alcohol or carboxylic monomers

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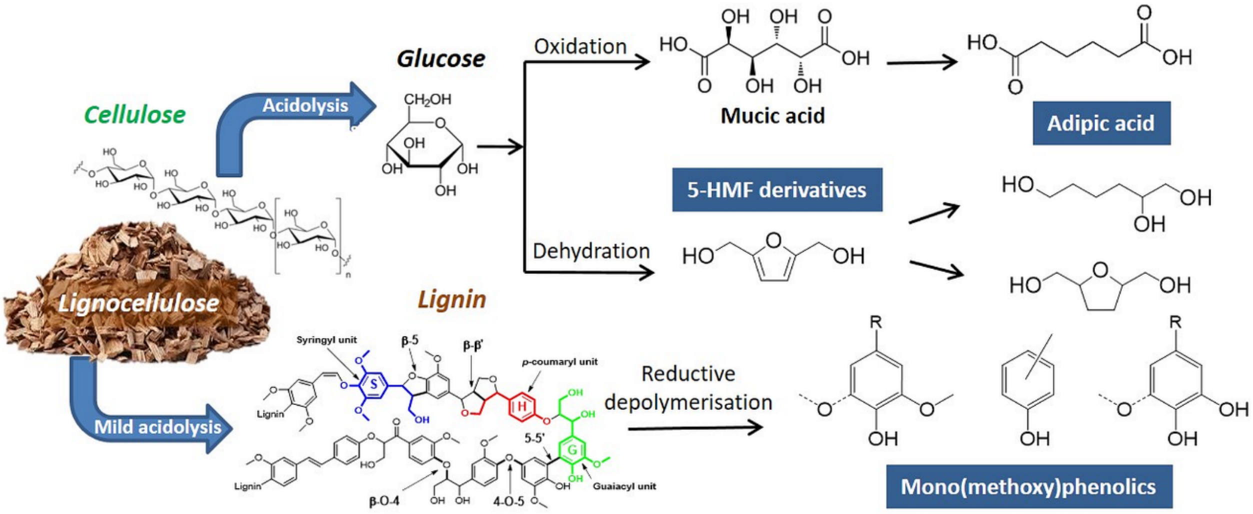
Efficient biomass fractionation provides qualitative streams which could be coverted into various value-added chemicals. Cellulose is a polysaccharide that can be hydrolzed into its monomers, i.e., glucose molecules. A very promising upgrading pathway targets the important polymer precursor adipic acid. Glucose is first oxidatively converted into aldaric acids, e.g. mucic acid, and subsequently fully dehydroxylated over supported Re catalysts. Combining dehydroxylation and Pt-catalyzed hydrogenation in a one-pot process, bio-based adipic acid is directly accessible.[1] Alternatively, glucose can also be dehydrated to 5-hydroxymethylfurfural (5-HMF), a highly versatile bio-based platform chemical for bio-polymer and biofuel production. The diols 2,5-bishydroxymethalfuran (BHMF), and 2,5-bishydroxymethyltetrahydrofuran (BHMTF), and the triol, 12,6-hexanetriol (1,2,6-HT) are of particular interest. Catalytic hydrotreatment of 5-HMF has then been recognized as an effective conversion route to obtain these value-added chemicals from 5-HMF using nickel-based catalysts and high hydrogen pressures.[2] Lignin is a natural polymer composed of aromatic monomeric units representing a renewable source for chemical production considering its aromatic, highly-functionalized structure and abundancy. Reductive depolymerisation is a promising method to convert lignin to aromatic monomers and oligomers. Thus, by mimicking the functional properties of the conventional toxic reactants (phenol, BPA) depolymerized products are successfully applied as green functional substitutes in polymers formulations.[3]



Catalytic conversion pathways of lignocellulose to functional monomers.

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Modeling macro-effects of micro-structures

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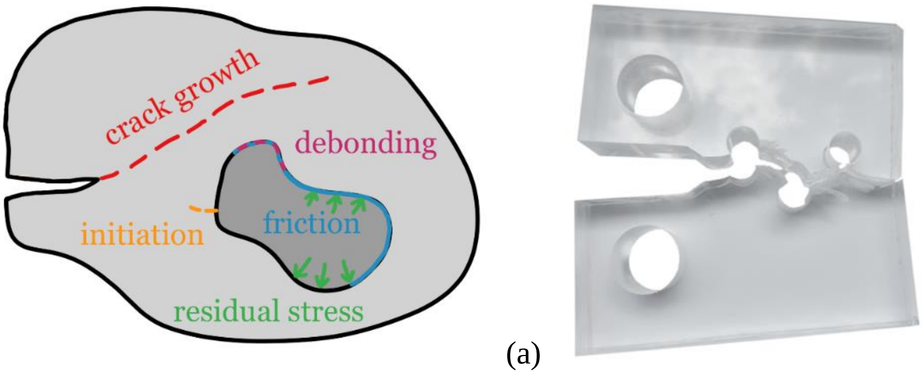
In heterogeneous material, effects on the local scale determine the macroscopic properties such as the fracture toughness. If the local constituents are considerably smaller than macro-components, the fracture toughness can be homogenized. On the microstructure level, cracks can deflect, arrest, initiate, and debonding between constituents can occur, see Figure 1a. Friction between debonded interfaces and existing cracks can also play a role in the fracture toughness on the macro scale.

The finite element method and fracture mechanics concepts can be used to capture most of those effects. For predicting crack initiation, the combined criterion[1] can be used, which states that for the initiation of a crack, both a stress- and an energy criterion must be fulfilled. In common heterogeneous materials such as fiber-reinforced composites, it is hard to monitor the local damage and validate developed damage mechanisms.



(a) (b)

a) part of a component containing a crack and an inclusion with mechanisms that affect the local damage and influencing factors and b) fractured specimen containing holes

The author's idea is to use artificial microstructures that are easy to manufacture and test and first implementing the damage models for them. This is done by scaling the micro-structures to the macro scale and by developing specific specimens to study the mechanisms that affect local fracture separately. Projects by the authors focus on different aspects of this local damage. To model crack deflection, arrest, and initiation, a modified compact tension specimen containing holes is used, see Figure 1b, where models show similar crack paths as the tests. In an additional work, the incremental crack propagation method is extended towards the configurational force concept[2] for crack growth and debonding of interfaces. In another project, a layered specimen with materials that reach high plastic strains prior to failure is modeled and computes the energy release rate from the whole strain energy in the model. Furthermore, an efficient method for predicting crack initiation from arbitrary-shaped pores or notches is presented.

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Polyheterocyclics by hydrothermal synthesis

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Organic materials that are mainly built up of heterocyclic and aromatic moieties often feature outstanding materials properties with respect to, e.g., thermal stability, resistance to harsh environments, and optoelectronic properties. Their molecular structure lies at the basis of these properties (through mainly strong bonds plus delocalization plus additional intermolecular interactions). Examples of such materials span from small molecules (e.g., high-performance pigments, such as rylene bisimides) to liner polymers (so-called polyheterocyclics, such as polybenzimidazole) and networks and frameworks (e.g., heterocycle-linked covalent-organic frameworks (COFs)). Unfortunately, their syntheses are – again across all molecular sizes – harmful, tedious, and expensive. I will present our attempts to overcome these harmful preparation routes through hydrothermal synthesis (HTS), i.e., the use of high-temperature liquid water as reaction medium. HTS bears additional advantages compared to conventional procedures, including (i) high-to-quantitative yields, (ii) high product purity, and (iii) high product crystallinity. The latter is intriguing at a fundamental level and also generates several changes in the materials properties.

Digital materials – Vision or reality? Applicability of micromechanical modeling for material design

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The methodology Integrated Computational Materials Enginnering (ICME) was introduced a decade ago and recently is intensively used for scientific and practical engineering problems. The typical ICME methodology involves different activities, e.g. virtual material development, virtual testing, effect of processing and life cycle analysis. In addition to the conventional physical model based material development the novel data science based development is increasingly moving into the spotlight.

Artificial structures for model digital materials can be constructed at various scales in computer. We are distinguishing two different material classes, heterophase and cellular structures:

- The heterophase structures are two or multiple phase systems, typically consist of a polymer matrix and polymer or other filler particles. The two (or more) phases may be arranged in various spatial configurations and connected by various interactions which results in different mechanical behavior of the heterophase compound.
- Based on the microstructure cellular materials are divided into foams, which reveal an irregular microstructure and lattice structures, which show a regular microstructure. The properties of cellular materials are highly dependent on three design variables: bulk material properties, cell topology and shape as well as relative density. Hence, a systematic variation of these variables may result in a wide range of conventional and unconventional (e.g., auxetics or bistable) deformation behavior.

A material across several true scales can be described by micromechanics approach. The material behavior can directly be modeled as a function of the underlying microstructure. Micromechanics material engineering requires two complementary concepts and simulation methods; (i) Mean-field homogenization and (ii) Full-scale finite element homogenization. The specific microstructure can be virtually constructed, predicted in a processing simulation or experimentally determined using various techniques (i.e., CT).

Several examples of heterogenous polymer, composite and cellular structures will be presented in our talk and the application of above techniques will be represented. The realization of the entire ICME methodology in scientic and industrial environment will be discussed. In addition to the virtual modelling novel additive manufacturing techniques makes the physical relaization of several grades of digital material possible. Using these models a proper verification of the model simulations is possible.

Environmental impact of the textiles sector and the role of bio-based resources

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Textile manufacturing and processing is identified as a major industrial contributor to environmental damage. The primary areas of concern are water use, energy consumption, greenhouse gas emissions, and air and water pollution. In addition, solid waste pollution has come to the forefront as a significant problem in recent times. One strategy pursued to help remedy the problem is by replacing petroleum-based materials and process chemicals with bio-based alternatives and many reports can be found in the literature on such investigations. However, many peculiarities of the international textile trade, e.g. highly fragmented supply chain, price pressures, and the significant influence of consumer behavior, pose significant challenges in the adoption of laboratory results into industrial practice. In the lecture, we will discuss the realities of international textile trade as it pertains to the implementation of cleaner production strategies, and the scope for use of biobased remedies.

Tricks with polyHIPEs: Combined templating approaches for hierarchical porosity

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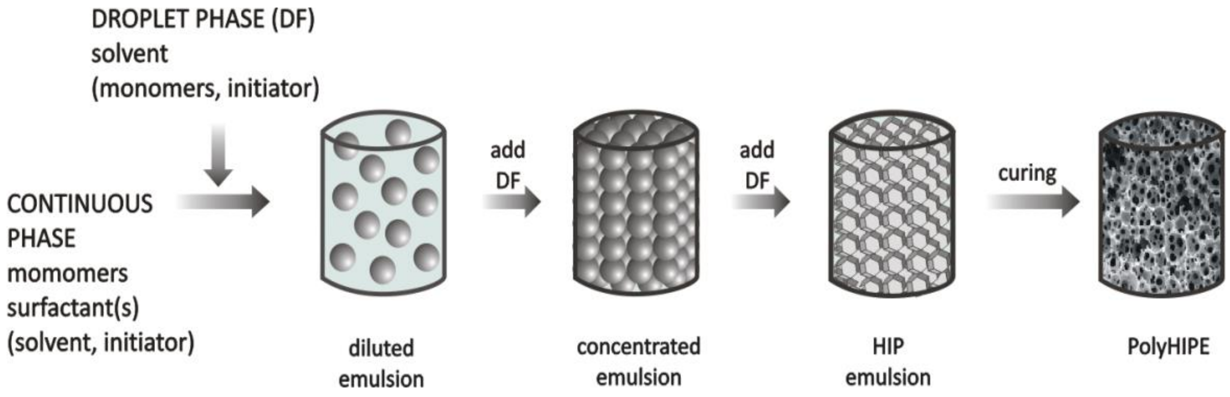
Preparation of emulsions with a high degree of internal droplet phase presents a templating tool for macroporous polymer fabrication.[1] In this manner, polymer materials (polyHIPEs) with a unique cellular, porous, interconnected topology is produced and can have a very high pore volume, low density while the pore size distribution on multiple levels can be tailored.[2] This make polyHIPEs atractive materials for a number applications, especially in the biomedical field.[3] Emulsion templating can, however, be combined with other techniques, such as additive manufacturing technologies, electrospinning, sintered solid bead templating, etc., in order to obtain more levels of porosity and structural hierarchy. Such combined approaches will be shown and discussed.



Schematic representation of polyHIPE preparation

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Processing of fibre-reinforced polymer composites based on phenomenological models

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Model-based manufacturing of fiber-reinforced polymer composites is based on transferring process-related knowledge from the level of process modelling to the level of active process management. This requires fundamental understanding of the most significant process mechanisms in terms of phenomenological models. Although the approach is applicable to a wide range of composite manufacturing technologies, this contribution addresses the resin transfer moulding (RTM) process. There, three major steps can be identified from the point of view of process mechanisms:

1. Preform compaction: When closing the RTM mould, the dry preform is compacted in transverse direction and effects such as yarn compression, yarn flattening, gap condensation and inter-layer nesting[1] occur.
2. Preform impregnation: By injecting the resin system into the RTM mould, the preform is impregnated, which can be understood as a superposition of macroscopic (inter-yarn, inter-layer) and microscopic (intra-yarn) flow processes[2]. In addition, preform saturation results in a significant change in transverse preform compaction pressure due to lubrication effects[3].
3. Resin curing: In RTM, the system of thermoset resin and hardener is chemically cured at elevated temperature resulting in phase transitions from viscous over gel to solid prior to demoulding the final composite part.

The contribution at hand gives insight in recent research work of the authors on various aspects of RTM processing. Particular focus is put on: (i) a novel testrig developed for characterizing transverse preform compaction allowing for in-situ impregnation and/or testing at elevated temperature, (ii) active process management such that an optimal level of flow front velocity is guaranteed during preform impregnation, which is beneficial with respect to the final porosity in the composite part[4], as well as (iii) sensing and online control techniques in order to minimize curing time while ensuring a desired degree of cure.

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Thermal conductive, electrical insulating polymer compounds using material extrusion additive manufacturing for electronic parts

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Global energy consumption and the shift to more environmentally friendly power sources and uses demand an increasing number of power electronic components.[1] Efficiency and reliability of power electronic components strongly rely on a maximum temperature. As they generate a certain amount of heat this thermal energy has to be deduced from the source into the environment. The mostly used passive coolers are manufactured by extrusion and are made of highly thermal conductive metals. By using extrusion technology, the shapes are limited to, in one direction, uniform shapes. These mostly finned heat exchangers are easy and cheap to produce. One of the biggest disadvantages is the limited design and that the heat exchanger needs a coupling to the source surface. This is mostly done by a thermal conductive paste which also can act as a glue. These pastes need a second step for applying and the life span is limited. The heat transfer from the source goes into the paste and from the paste into the heat exchanger and limits therefore the possible amount of transferred heat. Using polymer processing technologies, the shapes can vary much more and additional freedom comes into design, by using additive manufacturing. The biggest draw back is the limited heat conductivity,[2] were metals like aluminium has values of up to 230, Copper 390 and unfilled polymers as Polyamides have lower than 0.3 $W \cdot (m \cdot K)^{-1}$. With different shapes and fillers, compounds were produced and the heat conductivity was measured. One of the challenges with highly filled systems is the stiffness of these compounds, which hinders the use of a filament for extrusion based additive manufacturing. Therefore, we added a thermoplastic elastomer into the compound to soften the material so that we can process it into filaments.

Different polymer compounds were pressed into plates and the most promising candidates were extruded into filament and used on a Material Extrusion Printer. The heat exchanger was directly printed on a power resistor, which is used for testing the heat transfer into a measuring device.

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Exploring thiol based photochemistry for the additive manufacturing of medical devices

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The last years have seen an increasing interest in the development of photo-polymerizable resins that provide high biocompatibility[1] and toughness[2] in their cured state. This fact can mainly be explained by the rapid progress in UV based additive manufacturing technologies such as stereolithography, digital light processing or 3D ink-jet printing, which enables the fast and accurate fabrication of tailor-made medical devices. Besides residual monomers, also commercially used photoinitiators (PIs) and their cleavage products provide a significant toxicological potential and thus have to be considered in photopolymers with direct tissue contact.

In this contribution, the versatility of thiol-based photo-click reactions[3] for the realization of tough and biocompatible 3D structures is demonstrated. Besides the utilization of thiols as functional monomers, derivatives of them have been tested successfully as low toxicity photoinitiators. These PIs hardly show any negative effect on the shelf-life of thiol-(meth)acrylate-based resins and, most importantly, the formed cleavage products do not contain reactive aldehyde groups, which are held responsible for skin sensitization reactions, making them interesting for an application in biocompatible resin systems.

Moreover, inspired by the challenges of the actual corona crisis, remaining mercapto moieties at the surface of thiol-based photopolymers have been evaluated for the immobilization of antiviral surface coatings. In this context, the successful immobilization of Cu nanoparticles has been demonstrated providing a remarkable biocide effect and thus the potential to inactivate SARS-CoV-2 at the surface of 3D printed objects.

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Fracture mechanical design of new photopolymers for additive manufacturing

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Lithography-based methods for additive manufacturing of polymers, ceramics and metals enable the fabrication of precise, complex-shaped parts with excellent surface quality in applications like biomedical engineering, electronics and consumer products. Photopolymers contributed 33% to the worldwide materials sales in 2020, thus making lithography-based AM (L-AM) the most widely used AM technology. Although polymers are the dominating material class for L-AM, it is also possible to manufacture composite, ceramic and metallic materials using L-AM.

The goal in the development of innovative photopolymers for AM is to achieve similar thermomechanical properties like engineering thermoplastics, e.g. ABS or polyamide. In this work, a fracture mechanical approach is used to understand the influence of processing conditions and chemical structure of the utilized monomers on the finally observed mechanical properties.

Traditional photopolymers for L-AM provide high strength and stiffness, but typically lack sufficiently high fracture toughness[1] due to the high cross-link density which prevents plastic deformation. Several approaches are available for increasing toughness,[2] e.g. the introduction of cross-linkers with spacers which increase the physical interaction within the final polymer chains (e.g. hydrogen bonds). Dedicated chain transfer agents[3] are also beneficial for improving ductility of the polymer without sacrificing the reactivity of the resin.

In addition to presenting new concepts for improving thermomechanical properties of photopolymers, an overview of recently developed 3D-printable materials will be given, allowing to tackle challenges associated with innovative applications in biomedicine, electronics and engineering.

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CONTRIBUTED LECTURES

High-performance photocurable adhesives for bone repair

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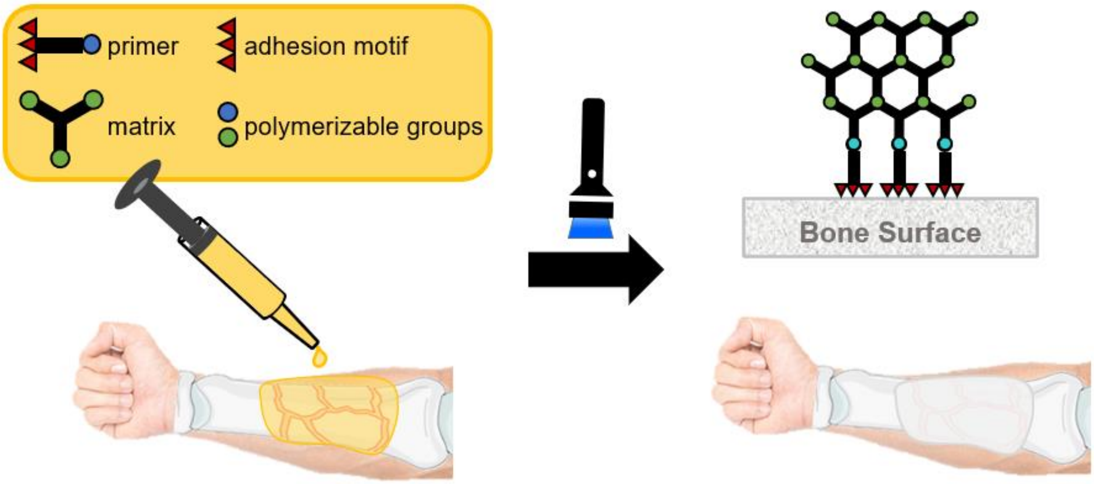
Due to increasing life expectancy and increasing numbers of patients suffering from osteoporosis, the number of fracture incidents is rising steadily. For the treatment of complicated bone traumata such as comminuted fractures or for the fixation of small bone fragments, conventional means such as metal plates and screws cannot be used or result in severe bone loss. Hence, usage of biocompatible and biodegradable bone adhesives could revolutionize fracture fixation with shorter operation times, homogeneous force distribution and no need for revision surgeries.[1] Despite three decades of research, no practically applicable bone glue system has been identified yet, due to high requirements such as biocompatibility, sufficient bonding strength and ease of usage.[2]



Schematic principle of the 1-step bone adhesive system

In this work, we present the first-known adhesive system, based on thiol-ene "click" chemistry, which is curable by UV-light in a fast, surgically realizable one-step process. The system contains adhesive molecules, so called primers, with high binding affinity to bone and implants, which were inspired by nature and self-etching dental adhesives. Their high nanoscopic adhesion force was recently confirmed.[3] Selected primers, containing ene moieties exhibit different reactivity towards the thiol component resulting in improved primer incorporation into the polymer network and realization of the 1-step process. Results show, that this easily applicable system exhibits exceptional shear bond strengths on bone and implant surfaces, which are significantly higher than commercial bone glues currently reviewed by the FDA. Hence this adhesive system paves the way towards future fracture treatment.

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Multi-material digital light processing 3D printing based on a dual-curing acrylate-epoxy system: Myth or reality?

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3D printing of materials with anisotropic mechanical properties is still a challenging and unexplored area of digital light processing (DLP) additive manufacturing methods.[1] Our goal is to print polymer parts with heterogeneous material properties without the need for a physical change of the vats. Stiffness and flexibility during the printing process can be controlled by two orthogonal photoreactions working at two different wavelengths.

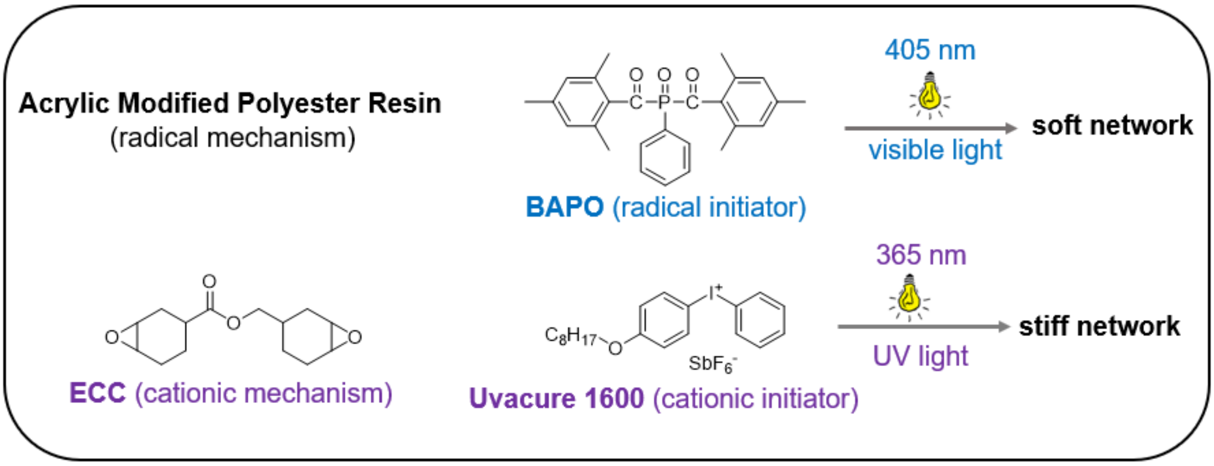

Figure 1 *Representation of the developed dual curable acrylate-epoxy system.*

Herein, we present a dual photocuring system where radical induced curing (405 nm) of multi-functional acrylates and cationic curing (365 nm) of bi-functional epoxy monomers are combined (Figure 1). Dynamic mechanical analysis has shown that by increasing the ratio of the epoxy resin in the system also stiffness increases. By selectively switching on the cationic curing of the epoxy resins, the mechanical properties of printed objects can be locally tuned and tailored layer-by-layer.

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Frontal photopolymerization of photobleachable resins based on long-chain polyetherpolyol dimethacrylates

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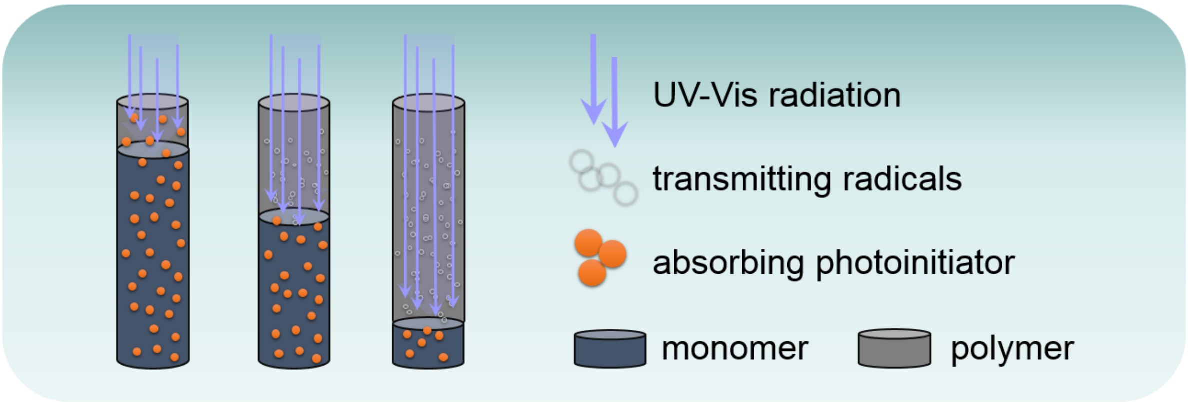
Photopolymerization offers significant advantages in terms of time, temperature, energy consumption, and spatial control of the initiation. The application, however, is strongly limited due to the constrained penetration of light into thick films. Strategies to overcome the problem of limited curing depth involve dual curing, frontal polymerization and up-conversion of particles. Unlike thermal frontal polymerization, frontal photopolymerization (FPP) requires only photoinitiator and light to cure centimeter-thick films, thereby maintaining a high degree of control over polymerization. Although excellent results have been accomplished applying frontal photopolymerization on a theoretical level, few studies report on practical applications achieving high curing depths within short time.



Schematic representation of frontal photopolymerization involving bleaching of the initiator

The potential of FPP is evaluated, using resins based on long-chain polytetrahydrofuran dimethacrylates, which tolerate high-intensity irradiation, in combination with TPO-L as an efficient photobleachable initiator. Resins of varying monomer content and photoinitiator concentration are cured under uniform conditions and characterized with regard to homogenous polymerization. Height-resolved UV-Vis spectroscopy tracks PI-decay precisely and indicates the decisive role of the applied intensity for in-depth radical formation. Compared to resins containing 0.5 wt.-% initiator, formulations with 1.0 wt.-% TPO-L exhibit excellent curing down to 52 mm in depth, regardless of the monomer ratio.[1] Mechanical characterization of FPP-cured polymers shows elastic moduli ranging from 5.3 to 1000 MPa, with elongation at break not exceeding 200% and a maximum tensile strength of 32 MPa.[2] Based on the presented data, both high through-cure as well as targeted optimization towards special mechanical properties seem possible with FPP suitable resins.

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Changing morphological features in a semi-crystalline polymer in material-extrusion based additive manufacturing

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Despite the high proportion of research activities in the field of material-extrusion based additive manufacturing, this technology still faces major challenges. In particular, when 3D printing with semi-crystalline polymers, a variety of process-related morphological and crystallographic changes can occur apart from general problems such as shrink-age and warpage. The complex relationships between the material, its processing and the final properties are still not fully understood. Hence, the influence of process-related orientations on the morphology and material properties of 3D-printed polypropylene (PP) was analysed by polarisation microscopy, wide-angle X-ray scattering, dynamic differential calorimetry, thermomechanical analysis, thermal conductivity measurements and "trouser tear" tests. By vary-ing two standard process parameters, four sample types with a completely different property portfolio with regard to morphology were generated. Low (200 °C and 2.25 mm/s) and high (250 °C and 22.5 mm/s) parameter settings for nozzle temperature and printing speed were investigated. Through in-depth analyses of four parameter sets, new in-sights into the formation of complex crystalline structures in 3D-printed semi-crystalline polymers are offered. It shows that minor changes of the printing parameters can have a great influence on the resulting material properties in different length scales. For example, for a high nozzle temperature in combination with a high printing speed layers with changing spherulite size were found. This finding could be correlated with the printing sequence of the slicer software, which confirms that the printing sequence proposed by the slicer software should not be chosen arbitrarily, but can be used to control the morphology and thus the mechanical properties of 3D-printed semi-crystalline poly-mers. Therefore, when handling semi-crystalline polymers such as PP, the characterisation of process-related morphological changes is particularly important and should never be neglected for future product developments.

Digital light processing 3D-printing of covalent adaptable networks

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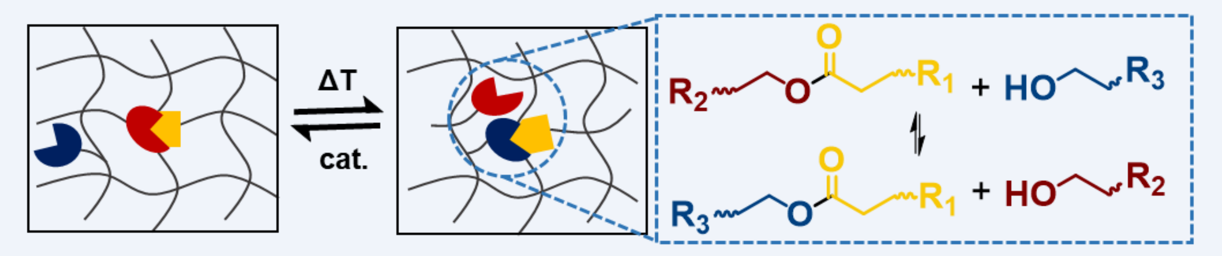
Traditional photosensitive resins for DLP (=digital light processing) 3D-printing techniques are characterized by fast curing rates, low viscosity, high resolution and tunable mechanical properties. Once processed, they behave like classic thermosets and neither reprocessing, re-cycling or malleability is feasible. By introducing dynamic covalent bonds into photopolymers, topology rearrangements upon an external stimulus are enabled, even after manufacturing. These so-called covalent adaptable networks (=CANs) are based on bond exchange reactions above the topological freezing temperature (T_v) of the network. One prominent example are thermo-activated and catalyzed transesterification reactions between carboxylic ester linkages and free hydroxyl groups.



Schematic representation of dynamic transesterification reactions

Commonly used transesterification catalysts suffer from poor solubility and compromise on the curing rate and pot life of photopolymers. Thus, a mono-functional methacrylate phosphate was introduced as new transesterification catalyst to overcome these limitations. Thiol-acrylate- and acrylate-based vitrimeric systems were developed for prototyping of soft-robotic 3D objects. After photocuring, the dynamic networks were able to rapidly undergo thermal induced rearrangement reactions. Triple shape memory and thermal mendability of the 3D printed objects were successfully demonstrated, even of highly crosslinked networks.[1] Advancing from classic initiators for thermally triggered bond exchange reactions, photolatent transesterification catalysts can be applied to spatially control topology rearrangements. The usage of photoacid generators as latent transesterification catalysts leads to the local formation of Brønsted acids upon UV exposure, which can efficiently catalyze thermo-activated transesterification reactions. By utilizing a dual-wavelength 3D printer (operating at 405 and 365 nm) the fabrication of soft active devices, which undergo locally controlled topology rearrangements at elevated temperatures is feasible.[2]

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Difunctional low shrinkage monomers performing light-induced cyclopolymerization

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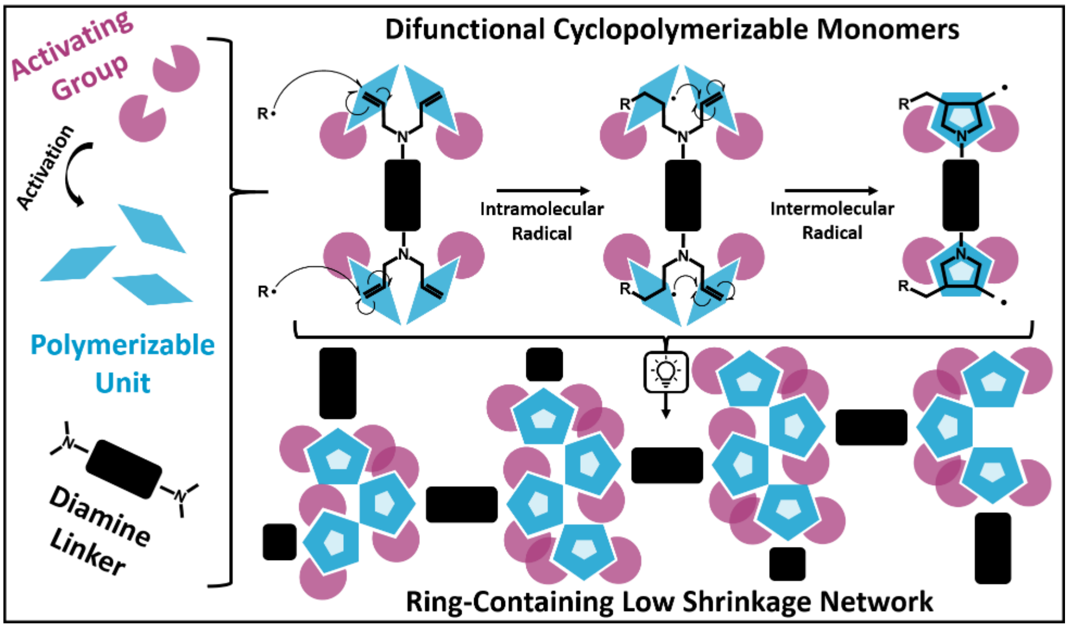
Light-induced cyclopolymerization of non-conjugated dienes as polymerizable units leads to polymer networks upon forming cyclic structures in the polymer backbone. These cyclic units may counteract the shrinkage, which occurs during radical photopolymerization. Therefore, cyclopolymerizable monomers (CPM) can be seen as a promising strategy for shrinkage reduction. The cyclization mechanism is described as an intra-inter-molecular polymerization, whereby the cyclization tendency results from the poor homo-polymerization behavior of the corresponding monoene monomers.[1]



Light-induced cyclopolymerization obtaining low-shrinkage networks

CPMs based on allyl-moieties are nowadays used as state-of-the-art coating applications, and for this reason, they were chosen as basic motive in this study. Herein, the synthesis of novel diamine-linked difunctional 1,6-diene CPMs with varying double bond activation (allyl-, methacryloyl-, and ester-activated allyl-moieties) is presented. Their characterization regarding reactivity, shrinkage behavior, and mechanical properties was performed using photo-DSC, photorheology, DMTA, and tensile testing. The activated CPMs demonstrated improved reactivity (up to 60%), reduced shrinkage behavior (up to 40%), and enhanced mechanical properties compared to the corresponding monoene compounds, highlighting the influence of double bond activation and ring formation in the polymer backbone upon light-induced cyclopolymerization.

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Polymeric composites and hybrids with 2D nanofillers

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The isolation of graphene and its special properties has stimulated interest in other free-standing two-dimensional (2D) nanoparticles. The current intense interest about 2D materials is due to their unique properties resulting from their structure. In the last decade the fast-growing family of 2D nanomaterials are MXenes. MXenes are inorganic materials, transitional metal carbides, nitrides or carbonitrides. Different MXenes are prepared from different MAX phases of the formula $M_{n+1}AX_n$, where M is the most common transition metal, A is an element of the 13 or 14 group of the periodic table of elements, X is usually C and/or N[1]. By etching of the A layers from MAX phase, MXene are formed. General formula of MXenes is $M_{n+1} X_n$.

Carbon nanotubes (CNT), which are tubular structures rolled as cylinders and have nanoscale diameter, possess excellent physical and mechanical properties CNT have been widely used as filler for different kinds of polymers nanocomposite preparation. Hybrids can be created by combination of 2D nanosheets with zero-dimensional nanoparticles as quantum dots, or 1D nanoparticles as CNT. This combination used in polymeric composites provides interesting 3D structures and properties. We studied the incorporation of MXene and perovskite quantum dots (PQDs) monolayer at the charge transfer layer/perovskite active layer interface in planar direct and inverted perovskite solar cells (PSC) as direct application of new prepared hybrids.

Next part of our work was aimed to preparation and characterization of composites where poly(methyl methacrylate) was used as matrix and MXenes and CNT as a conducting fillers. In PMMA/CNT, PMMA/MXenes, and PMMA/MXenes/CNT composites the range of fillers varied from 0.5 to 10 wt. %. Composites were prepared by solvent casting method. The higher the MXene amount, the higher the final conductivity of polymeric composites, but highest value of conductivity was about 10^{-7} S/cm. Much higher conductivity was achieved for composites with hybrid 2D and 1D nanofillers. PMMA/1% MXene/1% CNT, about 10^{-3} S/cm. 1D-2D synergized nanostructures are reason for better electrical properties, when compared with composites containing only 2D or 1D fillers.

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High CNT loading nano and hierarchical composites

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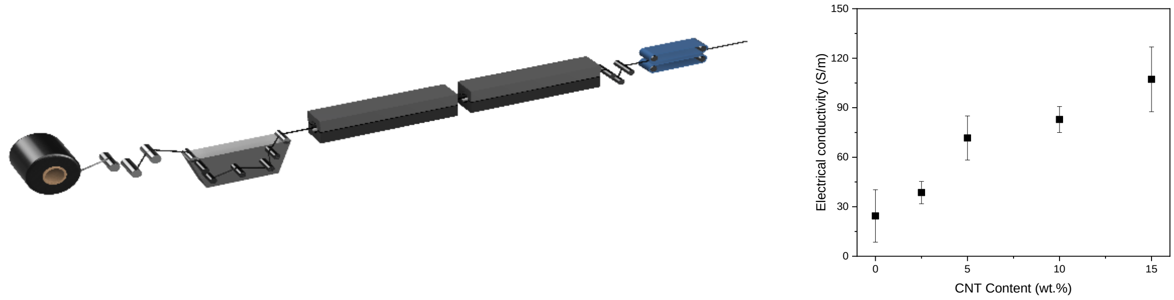
Resins reinforced with carbon nanotubes (CNTs) possess improved moduli and strengths.[1] Such nanocomposites can be used as matrix systems for conventional carbon fibre composites to try to improve compression strength and through-thickness electrical conductivity in these hierarchical composites (HC). Although solid epoxy resins are mainly used for protective coatings, they are typically much cheaper than liquid epoxy resins, which are commonly used in composite production. The development of a novel manufacturing method allowing high CNT loading in solid epoxies has the potential to improve the matrix-dominated properties of composites.[2]

Using a wet powder impregnation process, we prepared solid epoxy resin prepregs with resins containing high carbon nanotube loadings of up to 20 wt.%. Through a simple melt-blending process, the CNTs were introduced in the solid epoxy resin. A homogenous dispersion of CNTs within the solid epoxy resins was confirmed by microscopic imaging. The prepregs were consolidated into laminates with volume fraction of 60%. The alignment of the HCs was determined by microscopic imaging and the interlaminar shear strength of hierarchical composites improved by almost 20%. The addition of CNTs led to significant improvements in both electrical conductivity and compression strength of HCs.



High carbon nanotube reinforced composites

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Influence of filler and matrix on the thermal conductivity and mechanical properties of the composite

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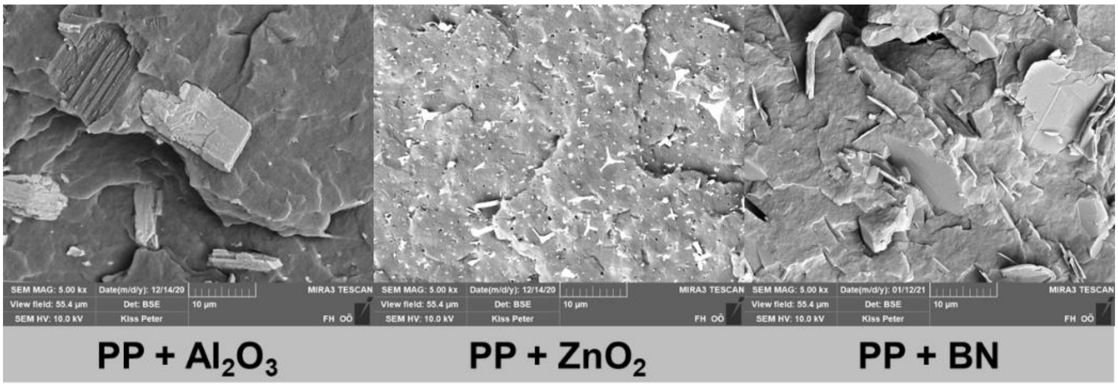
A continuing trend in plastics technology is the integration of functions with simultaneous miniaturization of components, especially in electrical components such as headlights or charging columns. This miniaturization increases power density, and heat must be dissipated to avoid damaging the components[1]. One promising option here is electrically insulating, thermally conductive plastics, as these can be brought into direct contact with the electronic components. However, the properties of such polymer matrix composites of fillers and plastics are currently not satisfactory, since above all the achievable thermal conductivities are very limited despite the use of highly thermally conductive fillers. Not only the material itself, but also the quantity, size and shape of the filler strongly influence the thermal conductivity. For example, a mixture of elongated particles or platelets with a spherical filler can achieve a significant improvement in thermal conductivity, since the different particle shape creates thermal conduction paths that improve thermal conductivity[2 3].



SEM images of PP with different fillers

The aim of this work is to understand the interaction of filler and matrix at the interface. We prepared compounds from four different matrices and four different fillers to investigate the mechanical properties and the thermal conductivity and to get a better understanding of the interaction between the filler and the matrix. An attempt was also made to describe the measured values by means of a mathematical model in order to obtain information about the interaction between matrix and filler at the interface. We found that the largest influence on the thermal conductivity is the particle shape of the filler. This correlation is also found for the mechanical properties.

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Optical reflectivity of fiber-reinforced epoxy laminates modified by nanoparticle decorated carbon fibers

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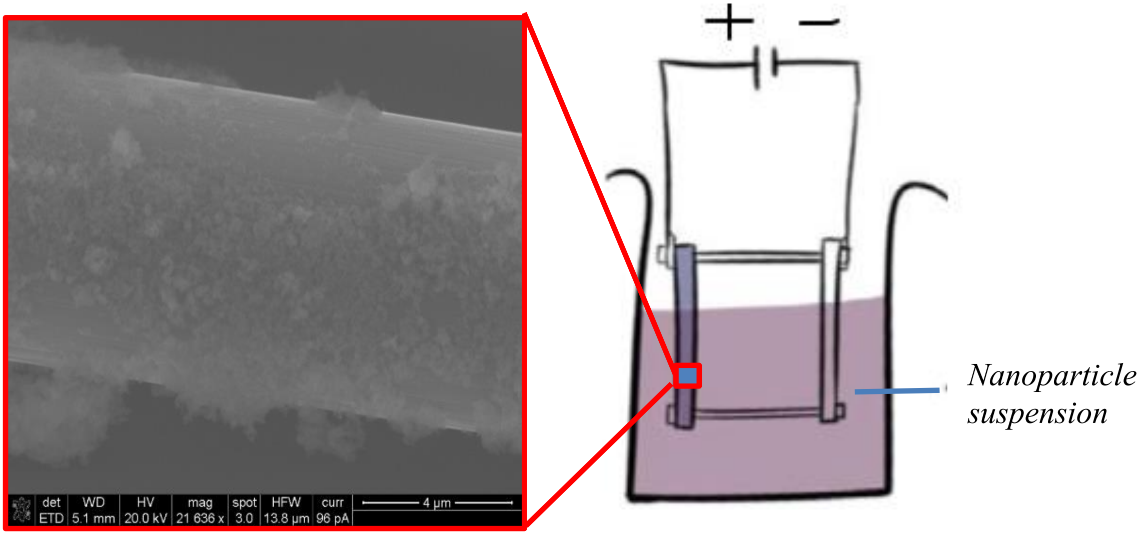
Carbon fiber reinforced epoxy composites are widely used in several industrial fields, e.g., aerospace, automotive and sport applications, but also in civil engineering. The laminate morphology with the carbon fibers and thermoset matrix provides excellent mechanical properties as well as long-term durability for structural applications. Carbon nanotubes have been shown to yield a highly light absorbing polymer composite.[1] Snow, on the other hand, yields an almost perfectly reflecting surface by a combination of material and micron- or nano-sized porosity.[2] Hence, the question is whether suitable combinations of nanoparticles embedded in a polymer composite yield surfaces with adaptable reflectivity.



SEM picture of SiO_2 coated fiber (left), schematic picture of quasistatic EPD process (right).

In this work, continuous carbon fibers were decorated with nanoparticles (multi-walled carbon nanotubes, silica, silver) with an electrophoretic deposition (EPD) process before manufacturing laminates. The optical behavior is compared with UV/Vis spectroscopy. First results show a change in reflectance depending on the type of particle and on deposition time/voltage, and, hence, on the particle distribution on the fiber.

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Polymer electrolyte as separator for structural supercapacitors

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Structural composite supercapacitors are multifunctional devices able to both carry load and store electrical energy. Truly multifunctional composites could reduce the total weight of electric vehicles by permitting the embedding of parts of a vehicle's energy storage system into its structure. In such devices, carbon fibres are used simultaneously as mechanical reinforcement and electrodes, while glass fibres are typically used as separator.[1] However, the volume taken by the glass fibres does not contribute actively to the device, adding additional, potentially unnecessary, weight. For the material to bear load, it is necessary to use a solid electrolyte to transfer load between the fibres. Previous studies have shown that poly(ethylene glycol) diglycidyl ether combined with ionic liquid can be used as a solid electrolyte for structural supercapacitors.[2]

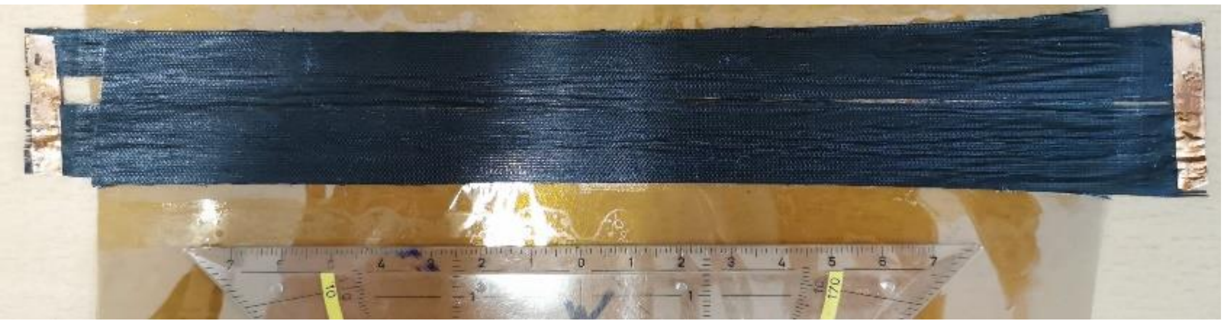

Fig. 1: Picture of a separator-free structural composite supercapacitor demonstrator

In this study, we show that such an electrolyte can also act as a separator. First, graphene was coated on the carbon fibres via electrophoretic deposition to prepare tape electrodes. Then, these electrodes were impregnated with a poly(ethylene glycol) diglycidyl ether, crosslinker and ionic liquid mixture and subsequently cured in a hot press. The resulting devices are separator-free structural supercapacitors (Fig. 1). The composites prepared through this process were able to carry load and store up to 16.9 mWh/kg, exceeding values reported before for structural supercapacitors containing a dedicated separator.[2,3]

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Functional hierarchical composites for structural applications

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Polymer nanocomposites emerged as important structural materials, competing with neat polymers and classical composites. These materials exhibit a combination of exceptional properties that usually cannot be achieved in standard composites. Some of the most studied systems are nanocomposite thermosets, which are filled with various forms of carbon nanotubes, graphene, silica nanopowders, and other nanofillers. This work presents the development, characterization and technological implementation of a new class of composite materials: functional, hierarchical composites for structural applications.

These materials have microstructure engineered on multiple scales and will provide enhanced modulus, strength and toughness compared to the equivalent materials in use today. In addition, they could be engineered such that the state of damage will be monitored while in service (structural health monitoring). This feature classifies them as functional materials.

For this purpose, epoxy resins reinforced with glass fibres are used as base material. The epoxy resin is modified with nano- and micro-scaled additives for composite preparation. The additives are functionalized silica nanoparticles, production waste (as a kind of micro-scaled filler), and nano-carbon (carbon nanotubes, graphene). The carbon filler generates electrically conductive paths through the material, which could be used for health monitoring. The influence of the fillers (and the content) on the mechanical properties will be presented briefly in this work. Therefore, the influence of different formulations was carried out through tensile and flexural tests as to demonstrate the improvement of the mechanical properties. The toughness under monotonic load (Kc) and impact strength were determined as well.

Diels-Alder cycloaddition for the preparation of highly aromatic polyimide copolymers

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Herein, we describe a novel synthesis route to highly aromatic polyimides and their copolymers using a Diels-Alder reaction for the chain extension and the formation of multiblock copolymers.[1] Synthesizing block polyimides is experienced to be rather challenging due to chain scrambling reactions that take place during the polymer synthesis.[2] We describe a novel route to obtain distinct block copolymers, where polyimide oligomers end-capped with phenylethynyl groups act as a dienophile. A biscyclopentadienone monomer provided the diene moiety. The resulting Diels-Alder reaction is accompanied by irreversible chelotropic CO release yielding 1,4-bis(pentaphenylphenyl)benzene containing polymers (Figure 1). Various polyimides can be combined with this method, resulting in polymers with ultra-high T_g's, soluble in common organic solvents, and showing good film-forming ability. This Diels-Alder chain extension method provides access to novel multiblock or segmented structured polyimides with tailorable properties that are not accessible by standard polyimide synthesis.

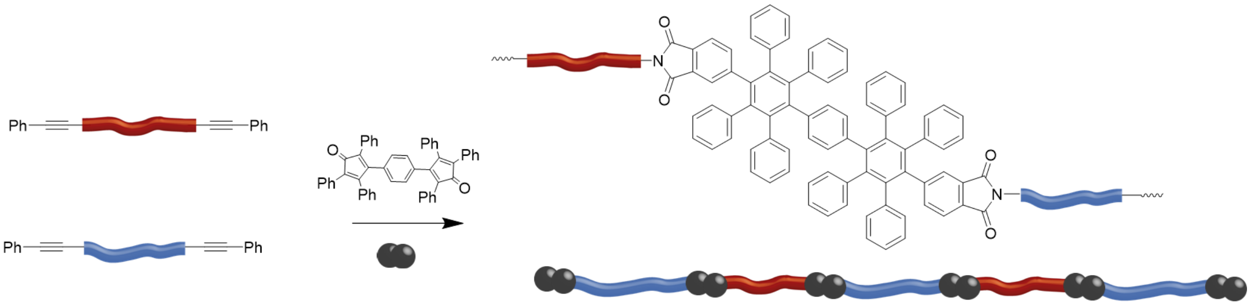

***Figure 1**: Diels-Alder reaction used for the synthesis of chain extended telechelic polyimide oligomers. [taken from [1]]*

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Water as monomer: Polymerizing divinyl sulfone and water via oxa-Michael addition

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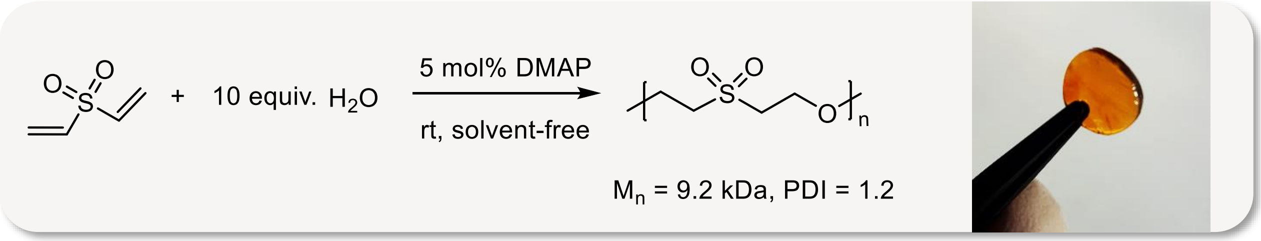
Using water as monomer in polymerization reactions presents a unique and exquisite strategy towards more sustainable chemistry. While the upcycling and polymerization of other natural resources such as CO_2 has been of high interest in polymer synthesis over the last decades,[1] water itself as a polymerizable substance has not been studied yet.
Herein, we show an oxa-Michael polyaddition of water and divinyl sulfone by exploiting the function of water as a Michael donor and in a further step, as an alcohol. We obtained polyethersulfones with high molecular mass (M_n = 9.2 kDa, PDI = 1.2) via nucleophilic initiation with 4-dimethylaminopyridine (DMAP). The polymerization proceeds at room temperature under solvent-free conditions within an hour reaction time.



Reaction scheme for the polymerization of water and divinyl sulfone; free-standing membrane of polymer and LiTFSI as solid polymer electrolyte.

Further, the material was tested as solid polymer electrolyte. By adding 15 wt.-% LiTFSI salt, a conductivity of 1.45×10^{-8} S cm^{-1} was obtained at room temperature. This is close to values of the state-of-the-art material PEO (unoptimized and without any additives).[2] Moreover, the polymer offers nice processability as well as self-healing characteristics. The contribution will discuss these aspects and will focus on a mechanistic understanding of the polymerization reaction.

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Preparation of functional polymers for glycan purification based on hydrazone solid phase extraction

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Simone Knaus [a]

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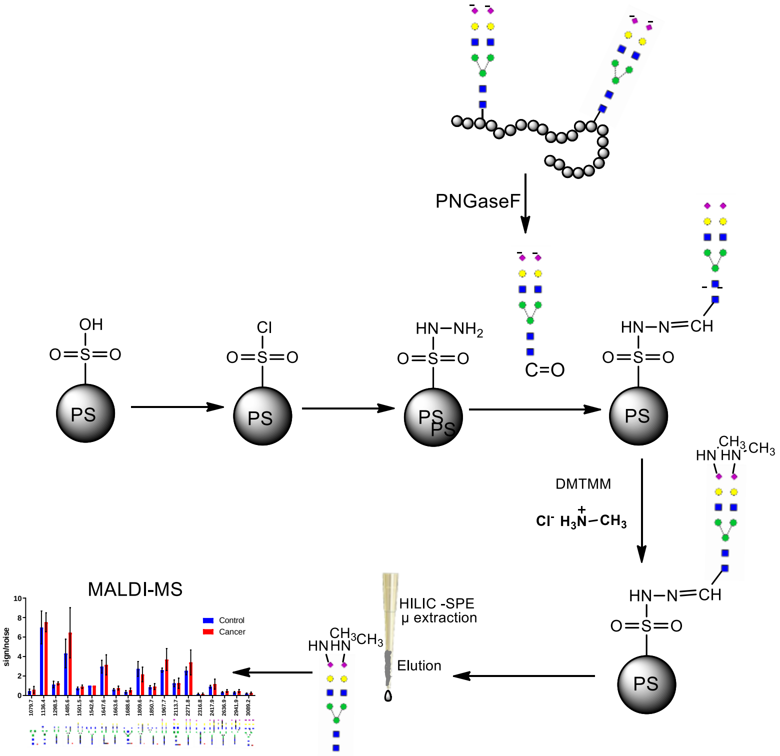
Glycans are key components in most biological and pathological processes including: recognition, inflammation, cytotoxicity, cancer, autoimmune diseases, viral infections, bacterial infections are some examples. Characterization of body fluids glycans with matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS) in positive-ion mode needs a derivatization step to stabilize and neutralize the negative charge on sialic acids, a class of acid sugars attached to the end of glycoproteins, glycolipids or gangliosides. Hydrazide beads to capture reducing end free glycans are a powerful and efficient method for purify glycans from complex matrix. The capture-release method simplifies the glycan preparation, producing pure samples.



Schematic preparation of functional resin synthesis and glycan purification

Hydrazide functionalized beads are synthetized starting from sulfonated polystyrene (PS) ion exchanger beads. PS beads are chlorosulfonated with chlorosulfonic acid and then converted into PS sulfonyl hydrazide by reaction with an excess of hydrazine. Hydrazide activated PS beads can be produced in large amount, high yield and allow an easy and fast purification of free reducing end glycans from complex samples mixture for spectrometry analysis.

References:

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3D printing of pure phenolic resins by hot lithography

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This study describes the direct 3D printing of phenolic resins. Also known as Bakelite, the cured products, phenoplasts, are considered the first synthetic plastic. These resins, produced by polycondensation, have always been known for their chemical resistance, excellent flame properties and thermal stability. Therefore, they are still used today in space and aviation as well as in the automotive industry. Originally, pressure and temperature are required for processing and limited the production of phenoplasts to compression and injection molding. However, with the invention of lithography and 3D printing, new processing possibilities emerged. Previous work in this area has focused on thin-layer photoresists or parts that can only be printed using other polymers as matrix. Here we report a direct 3D printing method, without binders or matrix polymers, using hot lithography, a stereolithography-based 3D printing technology at elevated temperatures. Formulations could be presented that are stable under the selected conditions and yet reactive enough for the printing process. In addition to the onium-salt based photo acid generators (PAG), novolaks and curing agents (CA) are required to obtain a solid thermoset. Novolaks are temperature-stable, non-self-condensing phenolic resins that can only form a network with the help of a CA, usually based on formaldehyde. The most satisfactory results were achieved with a self-prepared CA. In simultaneous thermal analysis (STA) and photo-DSC we investigated the UV-induced polycondensation of the phenolic resins in a temperature range of 80-120 °C. Furthermore, the formulation shown could be 3D printed directly using hot lithography at below 100 °C and cured to a bubble-free component in a post curing step. Compared to the conventional production of novolaks by injection molding at high temperatures and pressure, a simple production of complicated components could be achieved without the complex application of injection molds.

Bottlebrush, high-molecular-weight polyphosphazene-*g*-poly(l-glutamic acid) fully biodegradable polymer therapeutics with enhanced biodistribution profiles

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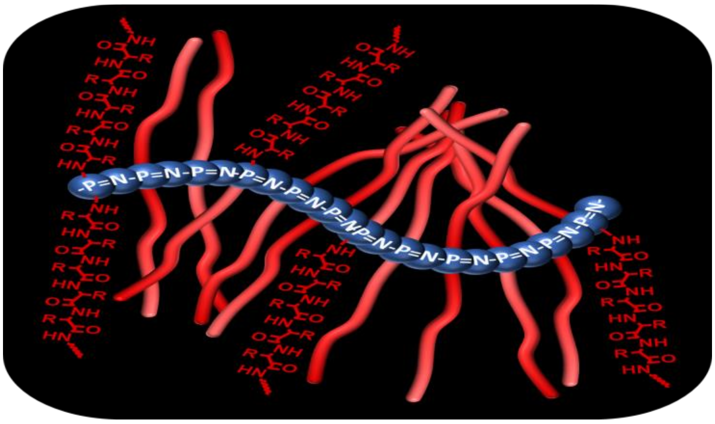

Polymer therapeutics, macromolecular systems serving as pro-drugs or drug carriers, offer distinct advantages over their small molecular analogues, as for example, improved solubility or enhanced blood circulation half-life. The improved pharmacokinetics are determined not only by their higher molecular weights but also by the macromolecular architectures. Bottlebrush polymers have drawn considerable attention in this field, providing an increase in functional sites, decreased viscosity or improved pharmacokinetics.[1] Polyphosphazenes (PPz) are a class of organic-inorganic hybrid polymers with manifold applicability in biomedicine and as polymer therapeutics.[2] Poly(l-glutamic acid) (PGA) is a leading polymer in biomedicine constituted of the endogenous amino acid glutamate and therefore inherently biocompatible and degradable, evenmore, its already in clinical trials as Opaxio®/Polyglumex.[3] Herein, we demonstrate a synthesis method for novel bottlebrush, high-molecular weight polymers based on a PPz-backbone and PGA-grafts, see figure. Furthermore, the synthesis of a series of polymers of different molecular weights and their labeling with a fluorophore at the N-terminus of the PGA-grafts is shown. Finally, *in vitro* and *in vivo* studies of the biodistribution profiles of the bottlebrush polymers are presented and compared to a linear PGA analogue. These materials have considerable potential applications as nanocarriers for various drugs providing water solubility and improved pharmacokinetics while being fully degradable and biocompatible.

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Exploration of synthetic strategies to access catechol-based monomers for application in bioinspired adhesives

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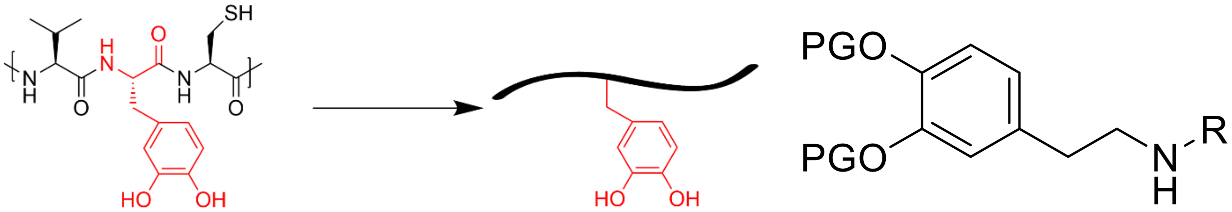
Observation of natural processes along with subsequent artificial replication has irrefutably contributed to the development of modern civilisation and understanding the mechanisms underlying these phenomena greatly facilitates this process. For example, marine mussels can adhere under water not only to rough stones but also very smooth ship surfaces.[1] These mussels can teach about strong adhesives in aquatic environments. In recent years, the research on these mussels grew rapidly making it possible to connect adhesion to two main mussel foot proteins (mfp), mfp3 and mfp5 to be precise.[2] Looking at their amino acid sequence gives insight, that the high amount of L-DOPA (up to 30%) plays a significant role in the adhesion mechanism. Based on these findings, a range of catechol-based polymers with adhesive properties have been developed in recent time.[3]



Schematic presentation of reducing a DOPA-containing peptide to a simple catechol-containing polymer (right) and dopamin based monomer with protection groups on the phenolic alcohols (left).

In this work Dopamin was chosen as a simple, cheap and easily modifyable monomer which contains this catechol group. Due to the fact, that catechol acts not only as a radical scavenger but also as a proton donor, radical and anionic polymerisation techniques are rendered challenging to realise. Tackling this problem, various different protecting groups are introduced to the phenolic alcohols aswell as functionalisation of the amine to receive a monomer for polymer production. Therefore, different protecting groups are implemented and compared. The monomers are fully characterised with various characterisation methods (i.e. NMR, DSC, IR, etc.). Finally, various polymerisation conditions as well as a range of co-monomers are examined.

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Simulating a multistage polymerization process in a bench-scale setup

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Using two or more polymerization reactors in multistage polyolefin processes enables distinct reaction conditions in each reactor. The properties of the resulting polymers can therefore be varied over a wide range, allowing adaption to specific needs. The individual reactors do not have to be of the same type and nowadays combinations of slurry/gas phase polymerizations are used in industry.

5 L reactor setup for simulating a multistage polymerization process

In the presented work, such a continuous industrial process was simulated in a bench-scale reactor setup by carrying out the polymerization steps sequentially. The first step, a slurry polymerization in liquid propane, was extensively studied by varying process conditions like reaction temperature and monomer concentration. A multistage process was realized by releasing propane from the reactor and continuing the reaction in gas phase. The polymer properties were influenced by varying the amount of the comonomer 1-butene and of the chain transfer agent hydrogen added during this process step. The recorded activity profiles of the Ziegler-Natta catalyst provided a basis for theoretical calculations to gain insight into kinetic parameters.

Analysing the obtained polymers with size exclusion chromatography gave information on the bimodal molecular weight distribution and the concentration of incorporated comonomer. In addition to differential scanning calorimetry (DSC), samples were further characterized by mechanical tests.

A hybrid approach for modelling polymer processing problems

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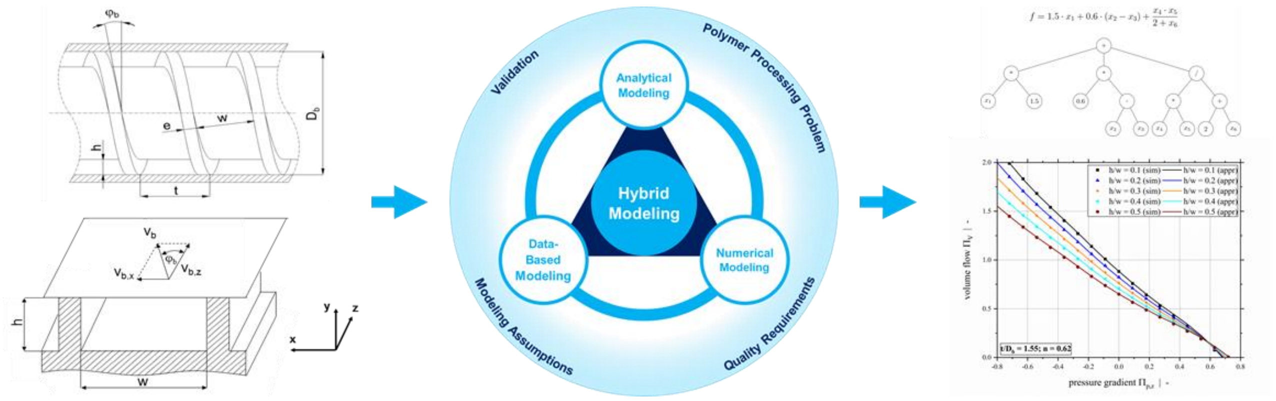
Modelling and simulation are essential for predicting and understanding polymer processes. Models are used for troubleshooting, as well as for process improvement and optimization.[1] Traditionally, modelling polymer processing includes analytical and numerical methods. Both require various assumptions to create a simplified representation of the reality. Analytical methods provide closed-form mathematical expressions of the problem, but are limited to a few idealized problems. Numerical methods can be applied to much more complex problems yielding approximate solutions. Thus, reducing the assumptions, the reality is represented more accurate. With the explosive growth of available data, the importance of data-based modelling has grown enourmously over the last few years, and it offers completely new potentials in polymer processing.

We present a new hybrid approach, that incorporates analytical, numerical, and data-based techinques into one integrated method. Hence the advantages are combined and limitations of the single methods omitted. Our proposed strategy covers following steps: first, a fundamental analysis of the governing equations and a dimensional analysis are performed; second, based on these findings, a parametric design study is set up, which design points are solved numerically; third, an analytical model is developed by applying symbolic regression based on genetic programming; and, finally, the model is validated. We originally applied this hybrid approach to model the flow of polymer melts in single-screw extruders.[2,3] Currently, we are investigating twin-screw extrusion and co-extrusion processes. This approach, however, is not limited to polymer melt flows. In fact, it can be used in any engineering discipline (e.g., solid-mechanics, and electro-dynamics).



Schematic of the hybrid modelling approach

References:

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Effect of processing and filtering in a two-stage injection molding process on thermoanalytical, rheological, and mechanical properties

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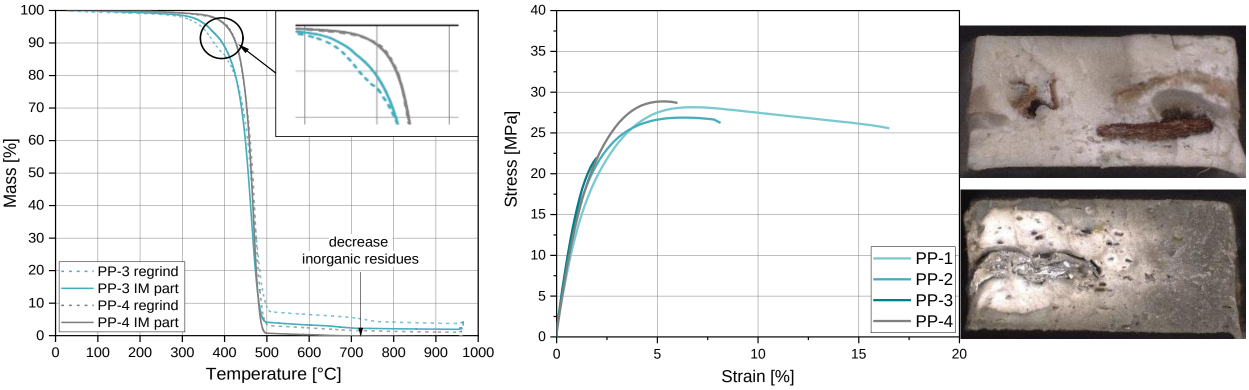
Thermal and mechanical loads during application and subsequent mechanical recycling, which consists of shredding, sorting, washing and multiple melting, lead to poor properties of the plastic products after recycling. To prevent the material from further damage, a novel two-stage injection molding process could be applied for pre-treated and clean post-consumer as well as post-industrial waste to decrease the number of processing and thus melting steps.[1]

This work shows some characterization methods to determine the influence of the two-stage injection molding process on specific thermoanalytical, rheological, and mechanical properties. Therefore, various polyolefinic post-consumer and post-industrial regrinds were converted by the mentioned process and tested with selected methods to evaluate the performance of the machine. Thermoanalytical and rheological methods were used to determine the material degradation and the effect of filtering and converting on the materials.[2] Furthermore, defects from remaining contaminants were determined using different mechanical methods introducing brittle fracture mechanism and allowing for the detection of critical contaminants. The obtained fracture surfaces were observed using optical microscopy in order to analyze the size and shape of the contaminants.[3]



Decrease of inorganic material after processing and filtering (left) stress-strain-curves of specimens (middle) and fracture surfaces with contaminations (right)

References:

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Influence of the material on the melt filtration using different screens

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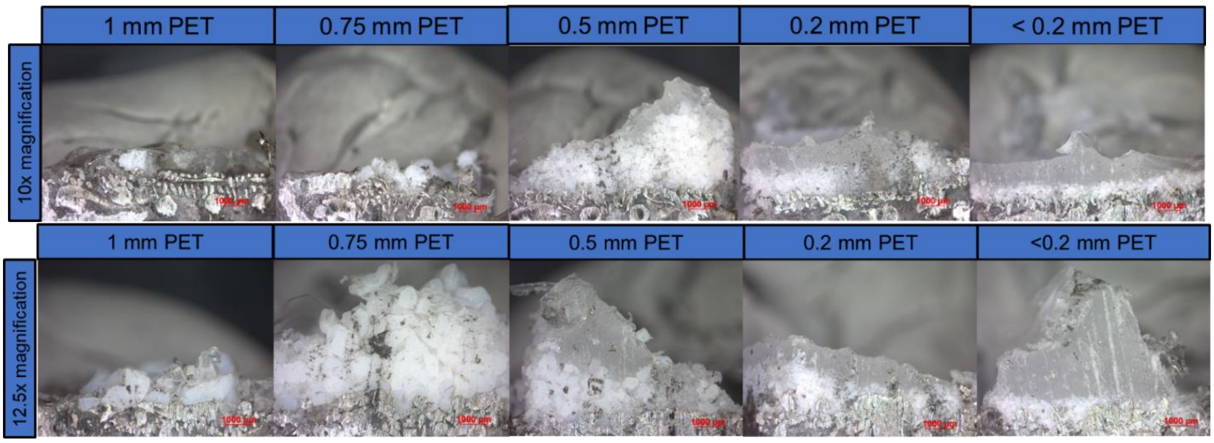
Various types of polymers are nowadays produced due to the broad field of applications such as packaging, automotive, electrical & electronics, household and building & construction. For these applications materials should be clean and free from contaminants, such as gels, unconverted polymers, agglomerated additives, dirt or dust. The production of PP, PE, PVC, PET and PA correlates very strong with further utilization. It is even more important to bring the material back into the cycle. Therefore, recycling is an important topic. The benefit which comes up when polymers can be recycled is the market price and the economic and social issues will change positively. The aim of this work is to understand the underlying mechanisms of filtering a melt in an extruder, to see how effective the process can be, which influence the used screen has and also the limitations of particles which should be filtered.[1,2]



Microsopic investigation of assembled (top) and fused (bottom) screens after melt filtration of PET particles (scale 1000 µm).

Investigations were done concerning assembled and fused screens to see the difference in their filtering behaviour due to their structure.[3] Time vs. pressure curves were recorded to see the pressure increase. Different particles sizes (PET particles) and amount of contaminants (glass beads) were used to see the behaviour in hard and soft materials and also the filter efficiency, which was investigated by ash content and optical microscopy. We found, that it is possible to filter even soft materials like PET, and that the filtering performance depends on the filter type used.

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Modeling of the devolatilization process in an extruder

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Sophie Pachner,[c] Georg Steinbichler [d]

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The devolatilization of the polymer melt during polymer extrusion plays a crucial role in ensuring the quality of the recyclates. In order to remove the undesired volatile constituents (so-called VOCs) from the polymer melt, vented screw extruders are often used. Single- or multi-shaft screw machines are used, with devolatilization taking place under atmosphere or vacuum. To increase the devolatilization efficiency and to prevent the melt from flowing out of the degassing openings, devolatilization zones are operated partially filled. Figure 1 shows a schematic representation of a vented extruder together with the degree of filling and the prevailing pressure profile.

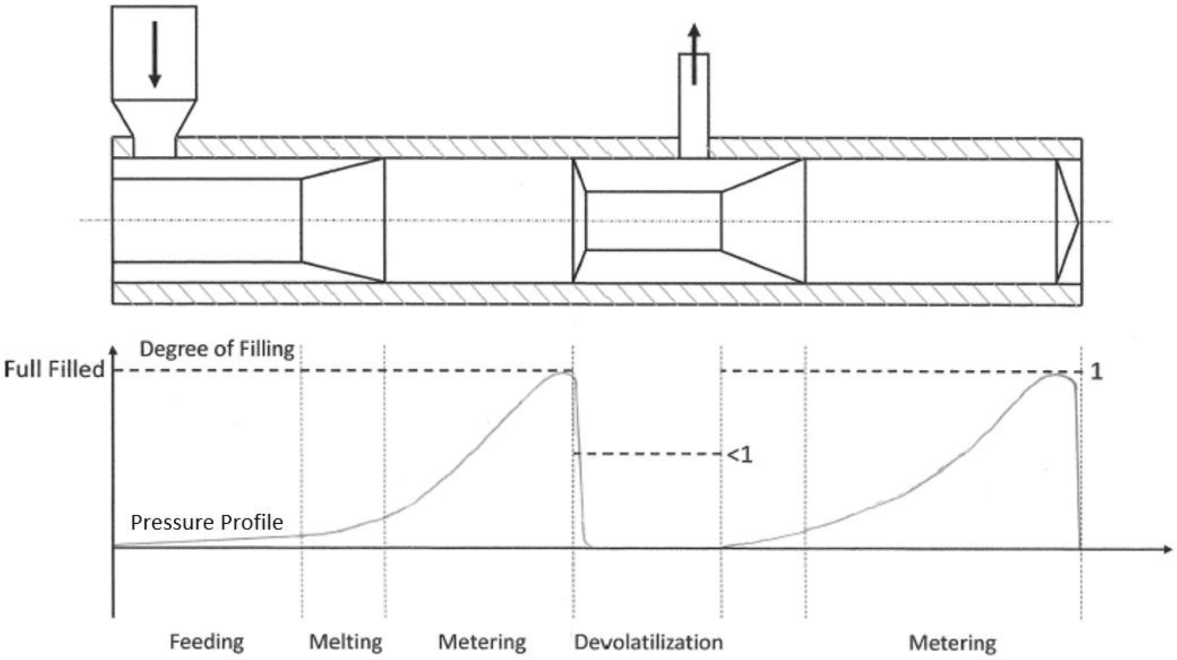

Figure 1: Schematic representation of a degassing screw

When designing extruder screws for polymer extrusion, the prediction of the devolatilization performance is extremely important. The literature provides only few theroretical modeling approaches to estimating mass transport processes in the degassing zone of extruders. Most of these models describe this process via bubble-free diffusion on the free surfaces. We present a comparative study of three models from literature based on different theories. The models are validated with experimental extrusion data to allow an assessment of the predictions accuracies of the models. The aim is to be able to make a statement as to which model reflects the experimental extrusion data qualitatively well.

A Novel Mechanical Metamaterial with Customizable Stiffness Distribution

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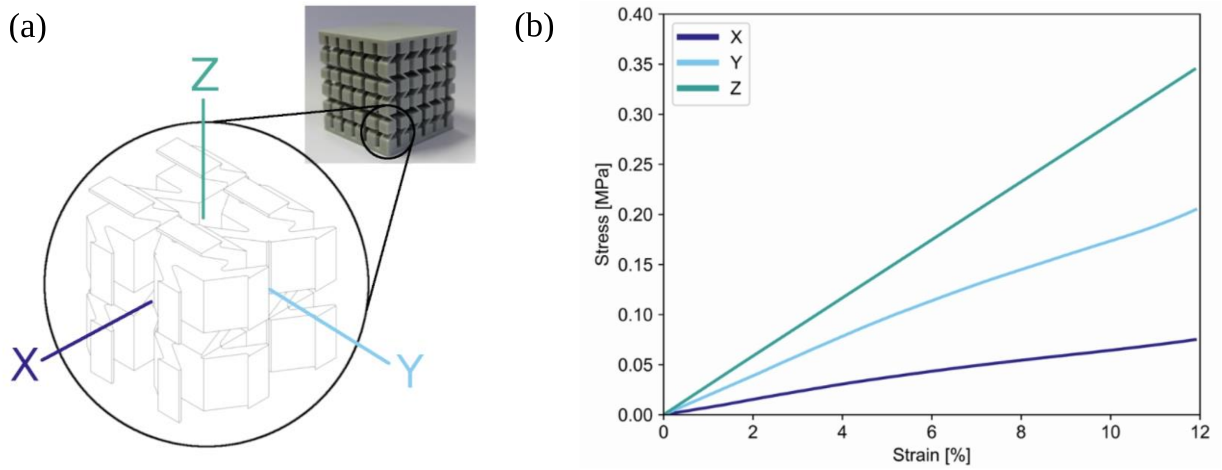
Mechanical metamaterials allow for structures with variable mechanical properties based on geometric parameters. They offer unique properties, such as negative Poisson's Ratio or tunable stiffness. This adaptability opens new possibilities for engineering and functional applications.[1]



(a): Sketch of the metamaterial, (b): Compression test result for an anisotropic structure.

Herein, we present the design, additive manufacturing and mechanical testing of a new kind of bending-dominated metamaterial.[2] Advancing from well-established mechanical metamaterial concepts, the proposed geometry allows to vary the stiffness in the three spatial directions independently. Therefore, structures with different orientational properties can be designed, ranging from isotropic to anisotropic structures, including orthotropic structures. Gradual transitions from one unit cell to the next can be realized, enabling smooth transitions from soft to hard regions. Different additive manufacturing techniques have been employed to manufacture polymer-based specimens, namely Fused Filament Fabrication, Digital Light Processing and Selective Laser Sintering. The properties of the structures were determined by compression tests. Additionally, simulation models were developed to verify the applicability of simulations to represent the mechanical tests. The test results were in good agreement with the simulations and showed a wide range of achievable mechanical properties. The possibility to create a customizable stiffness distribution offers a wide design-flexability with a single material.

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Investigation of shape memory-assisted self-healing of thiol-acrylate vitrimers

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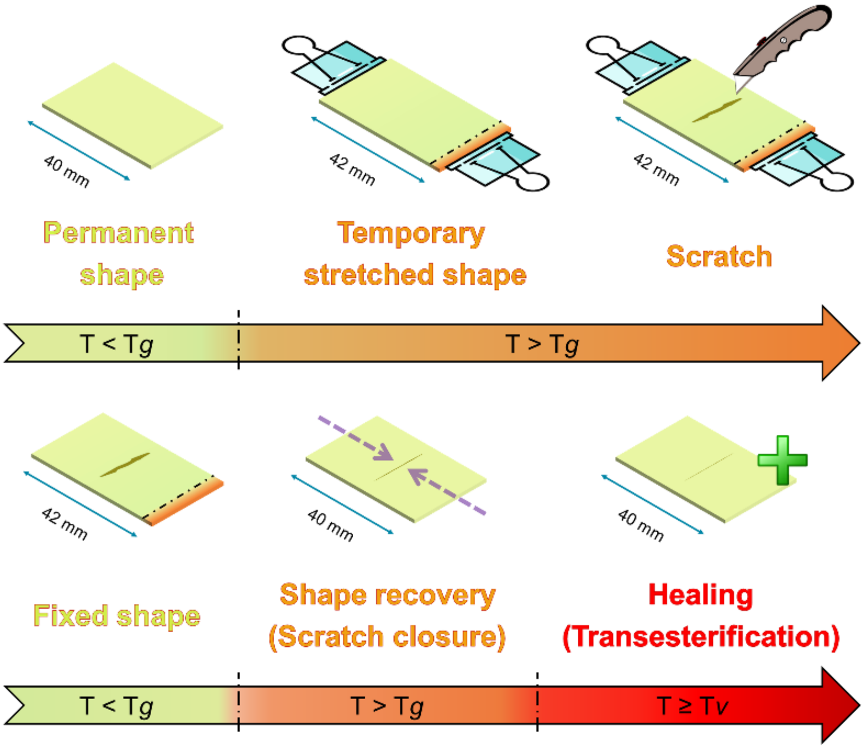
Self-healing polymers are tremendously attractive due to their ability of repairing macroscopic damage and defects, thus opening doors to sustainable and reliable smart functional polymers. In this scope, vitrimers are in the spotlight as a special class of thermosets exhibiting properties such as self-healability, recyclability and malleability.[1] The possibility of healing macroscopic damages on the molecular scale repeatedly is undoubtedly appealing, although it would strongly benefit from an additional driving force bringing the surfaces of the defect together. We present here a study on the synergistic combination of physical and chemical healing of a thiol-acrylate vitrimeric network based on transesterification. This close-then-heal approach, already known as SMASH in literature, was investigated as a function of increasing molar content of the thiol cross-linker present in our systems. We selected four networks and characterised their mechanical, chemical, shape memory properties and healing efficiency via optical microscopy, FTIR, DMA, rheometer measurements, TGA and tensile testing. Thanks to this methodological approach, we provide a comprehensive picture of the role of physical recoil, bond exchanges and network mobility on self-healing efficiency. As a conclusion of our study, we narrowed the selection down to one network, which exhibited 90% healing efficiency, thus demonstrating the potential of SMASH for vitrimers.



Schematic illustrating the concept of shape memory-assisted self-healing

References:
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Bismuth- and pyrylium-based onium salts as initiators for radical induced cationic frontal polymerization

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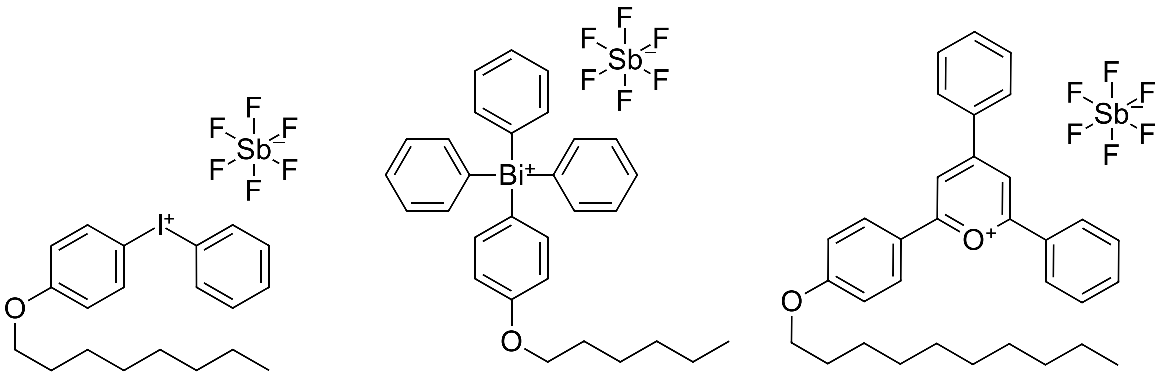
Cationic polymerization is a powerful tool when it comes to adhesive, coating, composite and bulk material production. Suitable monomers for cationic polymerization range from unsaturated molecules like vinyl ethers, to heterolytic compounds such as epoxides. However epoxy-based systems are used in many applications, due to their high reactivity and versatility. With the introduction of radical induced cationic frontal polymerization (RICFP), an even more efficient pathway to cure epoxides and with it, a variety of new applications were obtained.[1] The prevailing initiator class for RICFP applications are iodonium salts, which can be cleaved by light as well as suitable radicals.[2] Fine-tuning of the formulations and a lot of research lead to a highly effective and versatile initiator system. With the introduction of bismuthonium- and pyylium-based salts for frontal polymerization, the well-known iodonium salt is challenged. Bismuthonium hexafluoroantimonates show fast frontal velocities of 6.2 cm min^{-1}, a high polymerization rate and conversions of 84% in an epoxy system.



I-Sb **Bi-Sb** **O-Sb**

Commercially used iodonium salt ***I-Sb*** *and the new initiators based on the bismuthonium salt* ***Bi-Sb*** *and the pyrylium salt* ***O-Sb***

Bismuthonium-based systems show excellent pot life of the formulations, which can be cured at the press of a button. In this study, iodonium salts last around three days in epoxy-based formulations before a significant viscosity increase is measured, while the bismuthonium initiator lasts over 10 times as long with no significant drop in reactivity or frontal velocity.

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Curing of epoxidized plant oils with solid acid hardener

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The usage of bio-based thermosets for the manufacturing of composites has got more attention in recent years. As resin component, typically functionalized plant oils are used, whereas the most common functionalization is the epoxidation of the unsaturated double-bonds.

The present research work addresses the development of bio-based thermosets, which are soft/mechanically flexible, by curing different epoxidized plant oils with a dicarboxylic acid. The focus was on a catalyst and solvent-free curing process. The resin/hardener composition and the curing parameters were systematically optimized by Differential Scanning Calorimetry and Infrared-Spectroscopy. The thermo-mechanical properties of the optimized materials (example visualized in Fig. 1) were investigated by Dynamical Mechanical Analysis. The glass transition temperature (T_g) decreased with increasing epoxy weight equivalent of the applied oil (linseed: 2.5 °C; hempseed: -8.8 °C; soybean: -27.2 °C). The strain at break (ε_b) in tensile tests at room temperature was 27 % for linseed, 21 % for hempseed, and 32 % for soybean oil and was found to be highly dependent on the temperature. With decreasing temperature ε_b increased to a maximum around T_g. A further decrease in temperature resulted in a decrease of ε_b. The next step is the manufacturing of flexible composites with these mechanically flexible thermosets to receive technical textiles.

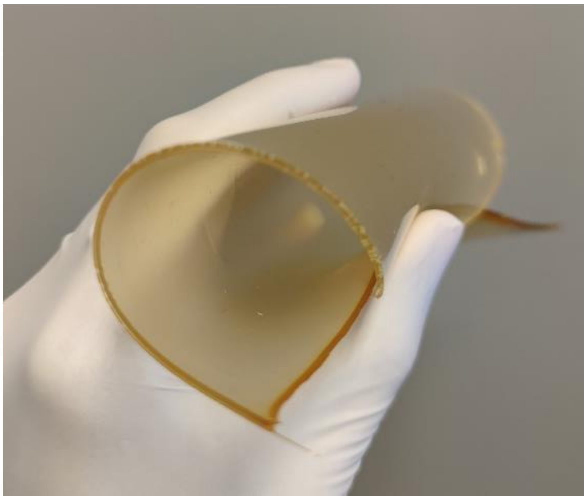

Fig. 1: Demonstration of the flexibility of an acid cured epoxidized plant oil.

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3D printing and stabilization of nanofibrillated cellulose-alginate scaffolds by different crosslinking methods

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Three-dimensional (3D) structures produced from the combination of nanofibrillated cellulose (NFC) and alginate (Alg) are suitable materials for various applications, including cell culturing.[1,2] The mechanical properties and dimensional stability of such structures were improved by cross-linking with salts ($CaCl_2$, $Cu(NO_3)_2$, $FeCl_3$).[3] In this study, we prepared two types of inks for 3D printing: NFC/Alg/$CaCO_3$ (Ink 1) or NFC/Alg/$CaCO_3$/photoacid generator (Ink 2). The 3D printed structures of Ink 1 and Ink 2 were ionically cross-linked with gluconolactone and UV-light. Besides the rheological properties (viscose and elastic moduli) of the inks, the mechanical properties and dimensional stability of the printed structures were investigated as a function of concentration of the gluconolactone and UV irradiation intensity and exposure time. It is suggested that the acidic proton generated by gluconolactone or PAG, when dissolved in water or exposed to UV irradiation, allows for the dissociation of $CaCO_3$, and consequently the release of Ca^{2+}. These ions form complexes with carboxyl functional groups of Alg and NFC. Scaffold materials with different microstructures and tuneable properties obtained by this water-based cross-linking approach could be suitable for cell growth and bio catalysis.

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Plastic or elastic: Fungi-derived composite nanopapers with tunable properties

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Fungi always played a vital role in many aspects of life, from antibiotics and medicines to food products, such as beer, wine, or bread. Recent academic and commercial interest in fungi is increasingly focused towards the potential of fungal structural polymers, i.e. chitin, to produce composite and nanomaterials.[1,2] Fungal chitin is a cheap, renewable, easily isolated and abundant alternative to crustacean chitin. Being covalently decorated with β-glucan, fungal chitin exhibits a native nanocomposite architecture that varies in fibre diameter and chitin:glucan ratio from species to species, resulting in mechanical properties ranging from brittle, high tensile strength, plastic-like properties to very tough and elastomeric rubber-like properties.[3]

This study utilized a mild alkaline process to extract chitin-β-glucan (CG) complexes from tree bracket fungi (*D. confragosa*) and white button mushrooms (*A. bisporus*), which were then bybridised in varying ratios and hot pressed to form engineered composite nanopapers with tunable tensile properties. Papers prepared from common mushrooms, with almost proportional contents of chitin and β-glucan, exhibited a nano-fibrous architecture resulting in high tensile strengths (> 200 MPa) outperforming crustacean-derived chitin. CG nanopapers could furthermore be plasticized in a controlled fashion through hybridising with CG from tree bracket fungi, which contains large quantities of β-glucan, to produce composite papers of high flexibility, while maintaining high strength. The fungal chitin extracts were significantly more hydrophobic than crustacean chitin, suggesting potential as a coating agent for hydrophilic materials, such as cellulose. These remarkable and controllable characteristics make fungi-derived materials versatile for a wide range of applications, including coatings, membranes, packaging and paper.

Composite nanopapers from tree bracket fungi and common white button mushrooms[3]

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Catalytic metal bonding of phosphinated cellulose and formation of nanocellulose in the process

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The possibility to produce nanoparticles from biopolymers capable to bind transition metals has attracted considerable attention in recent years.[1] Medical applications of cellulose nanoparticles binding metals are of particular interest in this context.[2] Other relevant applications of this substance class could be as a biologically decomposable color pigment or as a heterogeneous catalyst[3] in chemical industry. As cellulose is renewable and biodegradable it can be inferred that such cellulose-metal compounds have a lower impact on the environment after use than nanoparticles with comparable properties derived from petrochemical sources.[4] However, to ensure biodegradability and a low impact on the environment, the native natural material must be modified as little as possible, while still facilitating binding the targeted metal in high quantities. Only a catalytical process, during which metal is bound to the cellulose backbone can assure this behaviour. To the best of the authors knowledge, no such system has been reported to date.

Herein, HCl-gas hydrolyzed and subsequently phosphinated cellulose is reported to form stable copper complexes in various oxidation states. Cellulose I_α derived from birch wood pulp treated with chlorodiphenylphosphine binds up to 20% (by weigth) of copper(II) at room temperature. The resulting products are stable in air, water and various organic solvents at elevated temperature. Furthermore, during metal binding nanoparticles are formed from the bulk fibers that were deployed for the synthesis. Monitoring the pH-value during the reaction and the sulfur content of the product assured a genuine binding of cellulose and copper. The structures, oxidation states and mechanism of formation of the complexes obtained are discussed on the base of comparing theoretical/literature results with recorded X-ray photoelectron spectra (XPS), attenuated total reflection infrared spectra (ATR-IR) and nuclear magnetic resonance (NMR) spectra. The formation of nanoparticles is discussed on the base of recorded X-Ray powder diffractograms and scanning electron microscope (SEM) images.

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Hypercrosslinked polymers for visible-light-driven CO_2 photoreduction

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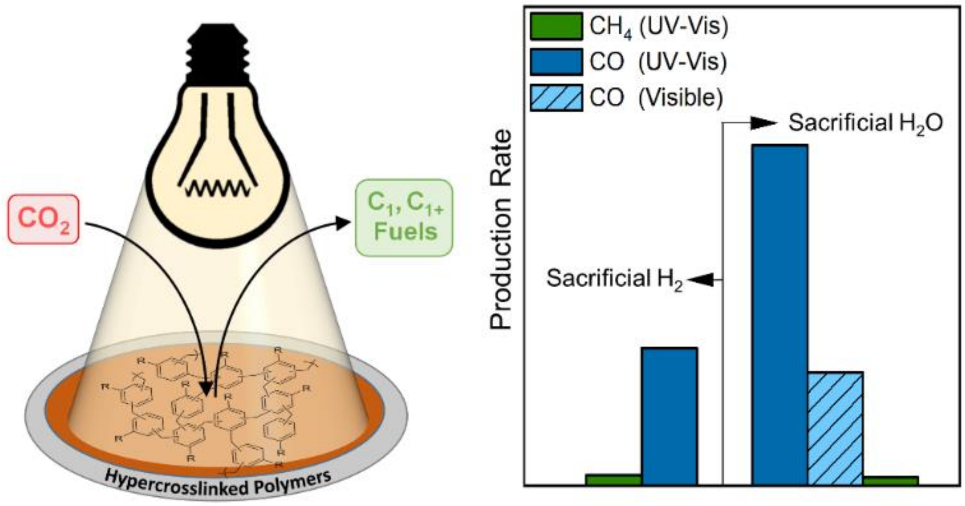
Porous organic polymers are at the forefront of many research efforts owing to broad chemistries and excellent textural properties. One promising family of such materials is hypercrosslinked polymers (HCPs), a set of low-cost nanoporous networks.[1] These polymers are prepared by the crosslinking of aromatic compounds using simple Friedel–Crafts chemistry, allowing broad 'bottom-up' design for a fraction of the cost of many leading porous materials. Unlike many leading porous organic polymers, HCPs do not contain or require rare-earth metals, presenting significant sustainability benefits.

We recently reported the first examples of HCPs as the sole active material in the selective photocatalytic reduction of CO_2 to CO, requiring only sacrificial H_2O for visible-light-driven photocatalysis.[2] HCPs significantly outperform the benchmark material TiO_2 P25 and achieve gaseous product selectivities of >95 %. We hypothesise that superior H_2O adsorption capacities of these HCPs facilitate access to photoactive sites, improving photocatalytic conversion rates when compared to sacrificial H_2. These networks are an intriguing set of organic photocatalysts, displaying no long-range order or extended pi-conjugation. They require no added co-catalyst doping or photosensitiser, representing a highly versatile platform for solar-energy conversion. Given the versatility of HCP synthesis, an unfathomable number of design iterations are possible, presenting a huge opportunity for organic photocatalyst design.



Hypercrosslinked polymers for CO_2 photoconversion.

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Understanding intermolecular bonding in organic materials and its impact on electronic properties

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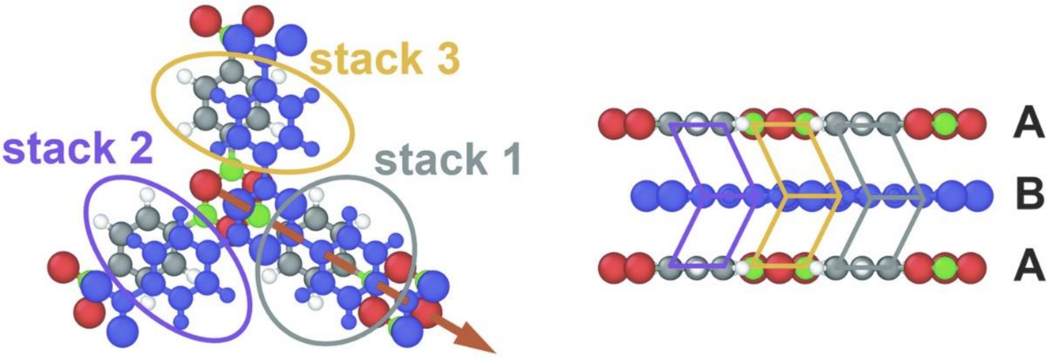
Inter-molecular interactions crucially dtermine the structure of organic materials, which, in turn, has a profound impact on their electronic properties. In the present contribution, we use state-of-the art dispersion-corrected density-functional theory simulations to partition interaction energies into contributions from van der Waals interactions, Coulomb interactions, Pauli repulsion, and the impact of orbital rehybridisation. Specifically, we will highlight the crucial role of Paulis repulsion, whose dominant impact for preventing cofacial interactions is often overlooked.

The focus of the discussion will be, on the one hand, on organic semiconductor crystals (α-quinacridon and pentacene), where we will show that there exists a natural driving force due to Pauli repulsion that distinctly favors inter-molecular arrangements with minimized inter-molecular electronic couplings. This results in crystal structures with only comparably small charge-carrier mobilities.[1]



Serrated packing motif in planar, 2D covalent organic framewoks (from Ref. 2)

On the other hand, we will show that Pauli repulsion is also the main reason for the occurrence of the common serrated packing motif in planar, 2D covalent organic framewoks (COFs), again with a distinct impact on COF properties.[2] This is, in fact, at variance with the widespread notion that shifted structures are typically triggered by Coulomb repulsion between polar entities in the COF backbones. We show that such effects occur, but overall, Coulomb interactions would be attractive in all considered structures due to charge-penetration effects. Thus, they would trigger a cofacial arrangements of the COF sheets, which is not what is typically observed.

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Hypercrosslinked polyHIPEs as Pd-catalyst supports

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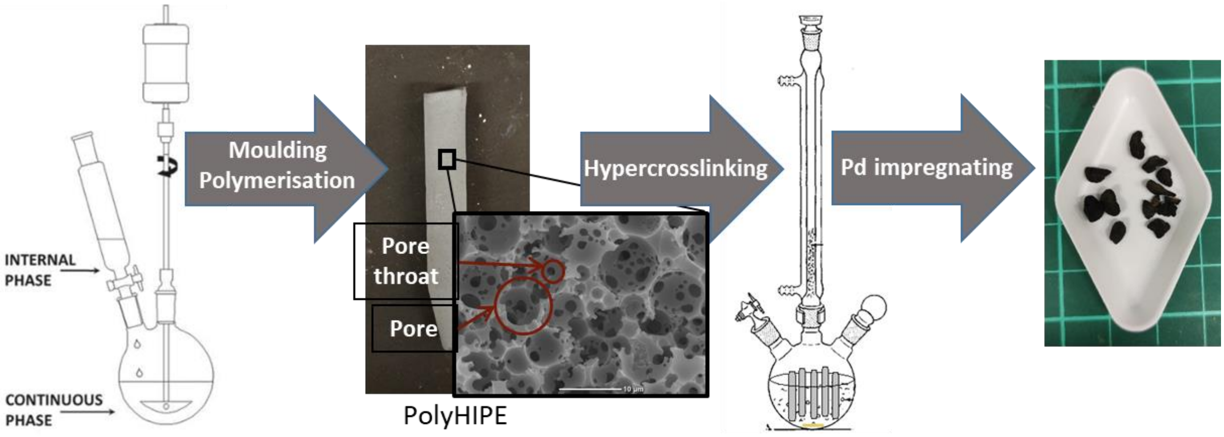
Emulsion templated macroporous polymers, so-called poly(-merised) High Internal Phase Emulsions (polyHIPEs), have found a wide variety of applications ranging from filters to bone replacements, owing to their lightweight, chemical stability and tailorable morphological properties. HIPE templates are used to generate macroporous polymers with well-known morphologies by polymerization of a monomeric continuous phase, and subsequent removal of the dispersed phase. Although highly porous, the low surface areas of polyHIPEs hinder them from some applications in separation and/or catalysis. Hypercrosslinked polymers (HXLs) have been prepared by variety of bottom-up strategies such as the 'knitting method',[1] the Scholl coupling reaction[2] and solvent stitching techniques.[3] Such approaches can be used to introduce significant nanoporosity in polyHIPEs without detriment to their emulsion-templated macropores, producing hierarchically porous structures with excellent permeability.



Schematic preparation of the Pd-impregnated HXL polyHIPEs

Using a variety of hypercrosslinking approaches, we produced polyHIPEs with surface areas of up to 900 $m^2 \cdot g^{-1}$. The introduction of nanoporosity allowed for significantly increased loadings of Pd nanoparticles at polyHIPE surfaces. A combination of high surface areas and the interconnected pore-structures of HXL polyHIPEs, allows reactants to be in contact with Pd across the entirety of their inner surface. Macropores allow for excellent mass flow, while nanopores provide a high concentration of catalyst sites. We demonstrate the use of these Pd-impregnated polyHIPEs as heterogeneous catalyst supports in the hydrogenation reaction of 4-nitroacetophenone. Due to the monolithic nature of polyHIPEs, they were easily collected and reused several times, post-reaction.

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Anti-adhesive organosilane coatings functionalized with markers for visibility-on-demand

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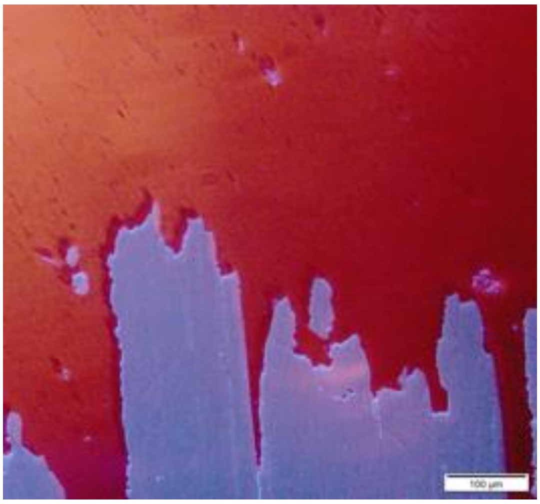
Organosilanes are well known for their application as coupling agents and surface modifiers as used in anti-adhesive coatings, self-cleaning surfaces and separation layers. The wide range of available organosilanes enables a precise adjustment of the properties of the coating to meet individual requirements. Our previous studies demonstrated that perfluorinated organosilanes (based on mono- and dipodal components processed from the liquid phase) are applicable as anti-adhesive layers for metallic molds and dies in the field of polymer processing.[1,2] The control of film thickness as well as monitoring of wear still remain challenging topics, especially during technical applications.

In the present study, the dependence of the thickness of anti-adhesive organosilane layers on various processing parameters was studied systematically using spectroscopic ellipsometry. Moreover, the kinetics of the different silanes used for the coating are considered.

To facilitate detection and control of deposition, the anti-adhesive organosilane layers were functionalized with marker molecules bearing a trialkoxysilyl anchoring group. These markers were synthesized and deposited together with fluoroalkylsilanes of an anti-adhesive formulation in a sol-gel process, which is based on hydrolysis and condensation reactions. The incorporation of the marker introduces a visibility-on-demand property, and consequently constitutes a rapid and reliable method to prove the deposition and homogeneity of the coating as well as its abrasion during long-term use. Coated surfaces were investigated with regard to their surface energy by contact angle measurements, while different spectroscopic techniques such as XPS, FTIR, UV-Vis etc. were used to study their surface composition and optical properties. Potential applications of these functional surface coatings are highlighted.

Acknowledgment; the participation of F. Doubek (Chemie-Akademie Graz) in the experimental investigations is gratefully acknowledged.



Example for the visibility-on-demand property of the anti-adhesive organo-silane layer

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Water-borne model epoxy varnishes for µm-thin adhesive bonding of electrical steel laminates

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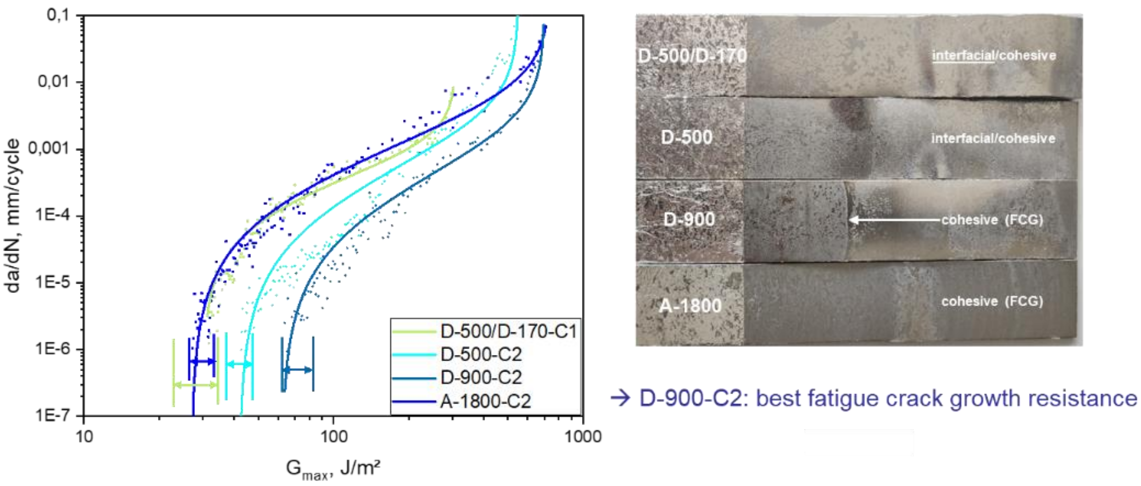
Epoxy varnishes for stacked electrical steel are of high relevance for renewable energy and electric mobility technologies. The main objective of this paper was to develop, implement and evaluate well-defined water water-borne model epoxy varnishes and to evaluate their effect on performance properties of electrical steel laminates. Therefore, epoxy resins with systematically varied equivalent epoxy weight (EEW) based on DEGBA were blended and modified with the latent crosslinking agent DICY. Emulsifiers with melting peak temperatures of 52 °C (C1) and 57 °C (C2) based on fatty alcohol ethoxylates were used. After shear emulsification, distilled water droplets were added. The model varnishes were applied onto M800 electrical steel. The coatings were pre-cured at a peak metal temperature of 210 °C. Coated steel sheets were stacked and laminated at 180 °C for 2h.

By X-ray photoelectron spectroscopy of partly cured coatings a non-linear correlation between EEW and C-O-C to C-C ratio was ascertained. Hence, the amount of reactive terminal oxirane groups was significantly lower for high EEW formulations. As confirmed by infrared spectroscopy, the hydroxyl functionality was increasing and levelling off with EEW of the epoxy resin. Performing dynamic mechanical analysis in torsional mode, the fully cured laminates exhibited glass transition temperatures (T_G) in the range from 81 to 102 °C. Within the investigated EEW range a negative linear correlation of EEW and T_G was obtained. Presumably, higher EEW of the varnish is associated with a less densely cross-linked network. Roll peel testing and fatigue fracture mechanics testing at ambient and elevated temperatures up to 140 °C clearly showed an effect of EEW, blending and emulsifier on peel strength and crack growth kinetics (s. Figure). Best performance on laminate level was obtained for an EEW of 900 g/mol allowing for a compromise of cross-link density and OH-functionality.



→ D-900-C2: best fatigue crack growth resistance

Fatigue crack growth kinetics and failure mode of electrical steel laminates at ambient based on different water-borne model epoxy varnishes (numbers indicate EEW).

Activation of polyamide fibers for subsequent metallization

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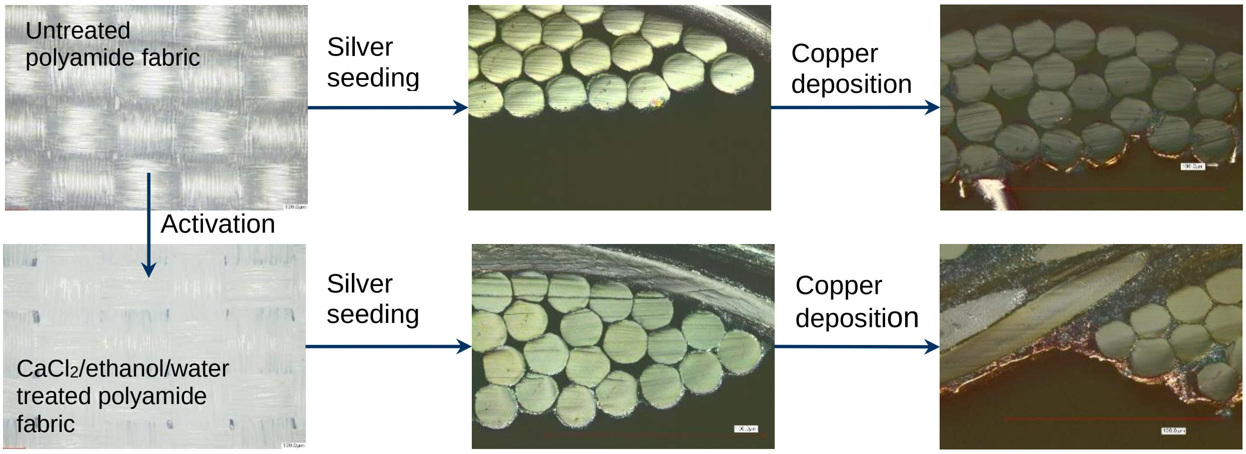
High-performance polymer fibers, such as aliphatic and aromatic polyamides are of high importance in the smart textile, personal protection equipment, automotive or medical sector due to their excellent tensile strength, operating temperature, or chemical resistance. They are often equipped with functional coatings to expand their functionalities or in composites to provide these. Activation and functionalization of the polymer surface are essential to introduce functional groups and to change the topography of the surface in order to strengthen the interface stability and create a durable composite.



Scheme for the preparation of an untreated and an activated, metallized polyamide fabric.

The effect of different activation techniques on polyamide surfaces and their impact on subsequent metallization is investigated. The modification techniques include atmospheric pressure plasma treatment with air and wet chemical treatments like acidic oxidation and complexation mediated solubilization with $CaCl_2$/ethanol/water.[1] These techniques can change the amount of functional groups, the surface roughness and the wettability. The activated polyamide substrates are metallized via a two step method including silver seeding and electroless copper deposition.[2] The copper uptake between 7 and 10 % does not show a treatment dependency. In contrast, abrasion tests reveal a higher abrasion stability for $CaCl_2$/ethanol/water and plasma treated samples with 1.5 Ω and 130 Ω, respectively, after 10 000 abrasion cycles. The untreated samples show higher values in the kΩ range. It can clearly be demonstrated that the preactivation of polyamide substrates is essential for subsequent conductive coatings in order to enhance the adhesion and therefore the lifetime of the polyamide-metal composite.

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A study on the mechanism of blistering of pigmented organic coatings in warm-humid environments

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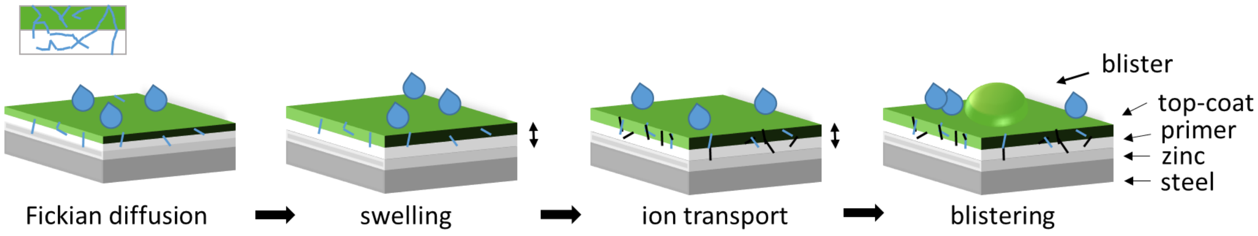
Blistering of organic coatings on steel substrates is of high practical relevance. In particular in warm-humid environments a two-stage water sorption process is observed. This diffusion controlled process may result in a thermodynamical favoured local accumulation of condensed water at the metal-coating interface (binding energy[1] of 25 kJ/mol between paint and metal vs. 40-65 kJ/mol between water and metal). The sources of blistering can be diverse due to the heterogenous composition of paints and the complexity of physicochemical properties, such as temperature gradients, internal stresses, crosslinking densities, dissolved ions, pH-values, impurities and corrosion reactions on the paint-metal interface.



Schematic of the blistering mechanism.

In the present study the pigmentation of two different thermoset polyurethane primers is varied to investigate the effect of coating composition on blistering. Primer and top-coat are applied with a total dry-film thickness of 50 µm on Hot-dip galvanized (HDG) steel. Accelerated laboratory tests at 70 °C and outdoor exposure exhibit a major influence of the primer formulation on blistering. Coating barrier properties are also assessed with EIS as a complementary technique. Leaching experiments show that the extent of leached ions correlates with the extent of blistering. Partial dissolution[2,3] of anticorrosive pigments of organic coatings is an important feature for corrosion protection, as a protective layer is formed at defects. However, excessive leaching of anticorrosive pigments increases the osmotic pressure at the interface between paint and metal, consequently osmotic blistering is favored.

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Biomimetic models of the aortic arch for surgical planning

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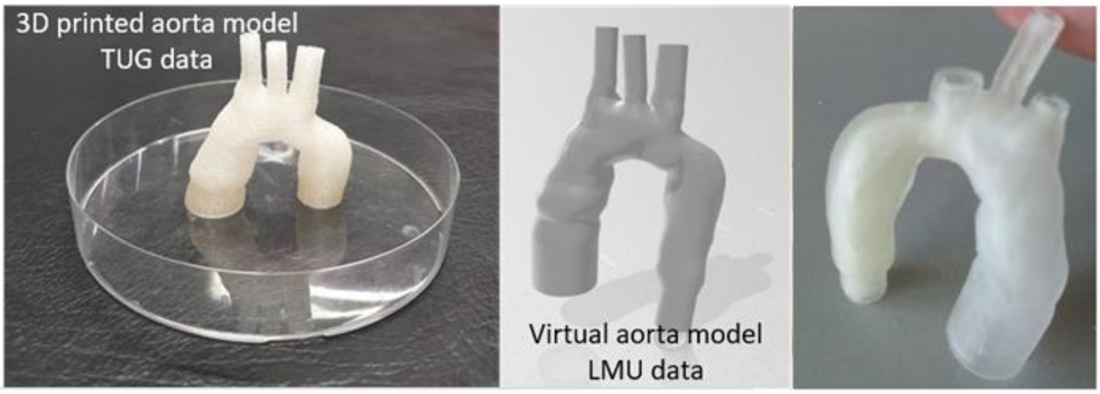
Cardiovascular diseases (CVD) are one of the main and multifactorial health burdens of our ageing and growing global society. An often-encountered disease (1,7-12,7%) are aortic aneurisms that can lead to life-threatening ruptures. A widely used treatment method is endovascular aneurism repair (EVAR) based on implanting metal stents combined with woven Teflon® or polyethylene terephthalate tubes to exclude blood flow through the diseased vessel.[1] For diagnosis and surgical planning, angiographic imaging techniques (ultrasound, computer tomography, MRI) are used and implant sizes and form are adopted to the patients' needs. It is therefore of interest to develop and manufacture patient specific aorta models that allow pre-surgical planning and testing of implant properties and performance. For patient specific anatomies such models have been prepared previously using a combination of imaging data, computer aided design (CAD) and additive manufacturing techniques (3D printing).[2-4]



Polymeric aorta models obtained via additive manufacturing techniques.

Biological tissue has very peculiar biophysical and mechanical properties due to being extremely complex and hierarchically organized and being composed of protein nanofibers embedded in a polymer matrix.[5] Aortic models that imitate these biomechanical properties have up to now not been manufactured. This presentation gives an overview of recently obtained results in the design and production of patient specific three dimensionally printed aortic models that mimic the biophysical and anatomical properties of healthy and diseased tissue.

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Balancing strength and ductility – Tough and transparent nanopapers through mercerisation

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Cellulose nanopapers have a wide variety of possible applications such as reinforcements in composites,[1] as substrates for printable electronics, and for use in water filtration and treatment.[2] One major shortcoming of these materials currently is their brittle nature and low ductility.[1] To overcome this, an alkaline treatment process, commonly known as mercerisation was investigated. Mercerisation of cellulose fibres is a traditional process to alter mechanical and optical properties by changing the crystal structure from the strong and brittle cellulose I allomorph to the more ductile cellulose II allomorph. This process was investigated as an option to prepare dense and strong cellulose nanopapers.

Cellulose nanopapers were treated with NaOH to (partially) transform the native cellulose I allomorph into the cellulose II allomorph. Swelling and interdigitation of the individual fibrils accompanied this transformation, which in turn increased the optical transparency of the nanopapers, another desirable quality for products such as electronics, surface coatings or flexible displays. Furthermore, this partial conversion into cellulose II significantly increased the strain to break (up to 340% compared to an untreated reference sample) while still reaching tensile strengths of over 100 MPa. The relation between maximum stress and maximum strain followed an inverse linear trend depending on the treatment conditions, which allows the easy control and tailoring of the properties of nanopapers for a multitude of applications in which flexibility and ductility as well as high tensile strength are required. Simultaneously, the work of fracture, i.e. the toughness of all samples, could be greatly increased (up to 220% of the reference value) as a result of balancing the ductility of cellulose II with the strength of cellulose I nanofibers.

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Fully bio-based high-performance composite

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The interest in high-performance composites based on renewable resources is growing vigorously. Recently, the authors presented a fully bio-based epoxy resin produced from epoxidized linseed oil (ELSO) and pure crystalline citric acid (CA) [1]. The main objective of the present study is now to produce a fully bio-based composite based on the novel ELSO/CA resin matrix and flax fibers, which exhibits a high stiffness and strength.

In order to receive a homogeneous mixture and simultaneously fine CA particles, the grinding process was done in two steps. At first 100 g of crystalline CA together with 1 g of Epinal HDK (anti-caking agent) was milled into a fine grain powder by applying a self-constructed laboratory ball mill set-up. To transform the ELSO into a curable resin, 100 wt.% ELSO and 25 wt.% CA were mixed and grinded in a bead mill, applying a grinding time of 6 hours.

Composite plates were manufactured by Resin Transfer Molding (RTM). Prior to processing, the reinforcing flax fabric Biotex 400g/m² 2x2 Twill (5 layers; Composites Evolution, Chesterfield, UK) was dried at 120 °C for 1 h. Composite plates with a thickness of 4 mm were produced by curing for 24 h at 80 °C followed by 24 h at 120 °C. Composite specimens were cut out and analyzed by 3-point bending tests at room temperature.

The produced composite exhibits a flexural modulus of 5500 MPa and a flexural strengthof 80 MPa, Thus, regarding the mechanical properties, the composite represents an interesting alternative to conventional composites.

By RTM a novel, high-performance composite with a bio-based carbon fraction of 100 % was produced, which is uncritical in terms of environmental and safety issues. However, since the applied hardener is solid, a homogeneous fiber impregnation and the manufacturing of large components is somewhat challenging. Thus, we currently work on optimizing the resin system, i.e. preparing a liquid hardener based on CA.

The research project is funded by the Austrian Ministry for Transport, Innovation and Technology in frame of the program "Produktion der Zukunft" under contract no. 858688, within the context of the project "Reliable and Sustainable composite production for Biobased Components". Epoxidized linseed oil was supplied by Kompetenzzentrum Holz GmbH. Epinal HDK was supplied by bto epoxy GmbH.

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Solvent and operating condition effects on the reaction rates of typical lignin bond cleavage during organosolv pretreatment

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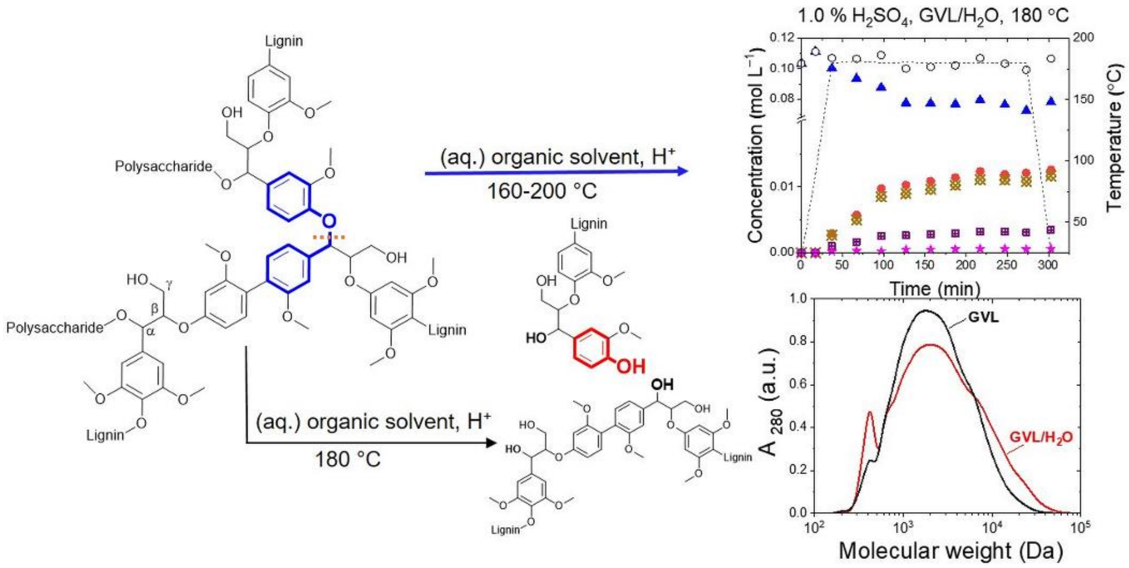
The selective conversion of lignin, a promising renewable feedstock, into bio-based organic mono-aromatics is a major challenge due to complex structure itself/additional macromolecule modifications, caused by the cleavage of the ether bonds during the lignocellulosic biomass organosolv pulping in acidified (aqueous) solvents. Therefore lignin model compound, being a representative model compound with α-O-4 linkage, have been undergone to organosolv treatment in order to investigate influence of solvent (methanol, ethanol (EtOH), EtOH/water, γ-valerolactone (GVL) and GVL/water), lignin functionalities and operating conditions on the course and rate of typical lignin bonds cleavage. Once the ether bond was cleaved, the reaction proceeded in two different ways, depending on the solvent reactivity. This resulted in the addition of new functional groups to the molecule. EtOH and MeOH was found to be reactive, acting as a capping agent and terminating the possible coupling/condensation reactions, which were found to be characteristic in the case of GVL (non-reactive reaction media). In addition, the rate of the α-O-4 bond cleavage in tested solvents decreased in the following order MeOH > GVL > EtOH > EtOH(aq) > GVL(aq). Differences between the organosolv lignins, isolated under moderate reaction conditions, supported the findings with the model compound. A beneficial effect of the added water is reflected in the higher aliphatic OH group content and less intact lignin structure. This type of analysis of the reaction mechanisms represents an initial step toward structure–activity correlations for biorefining and resources.[1,2]



Elucidation of typical lignin bond cleavage during the organosolv pretreatment using lignin model compound – lignocellulosic biomass approach.

Acknowledgments: This research was funded by the Slovenian Research Agency (J2-2492 and P2–0152).

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Bio-Pulping: Delignification and hybridisation of lignocellulosic material utilising fungi

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Over the recent years fungi are being recognised as a new biological manufacturing platform for the production of low cost and sustainable materials.[1] While processing lignocellulosic material into paper products traditionally is chemical and energy intensive,[2] bio-pulping utilising white rot fungi poses a sustainable pathway for the separation of lignin from cellulose and hemicellulose.[3] Flying in the face of traditional stigma and limited short-term bio-pulping processes, we demonstrate that the benefits of utilizing *P*. ostreatus and *T*. versicolor fungal growth stretch well beyond merely delignification to the hybridisation of animal waste derived lignocellulosic material, ultimately yielding paper with improved mechanical and surface properties. Considerably more hydrophobic paper surface characteristics were achieved. Longer growth periods, spanning several weeks resulted in interfacing of cellulose microfibrils by nanoscale fungal chitin-β-glucan networks, through which considerable improvements in tensile strength and elastic modulus were achieved. This highlights the missed opportunities in traditional delignification-based bioprocessing and demonstrates the considerable potential of the fungal biorefinery as a so far underexploited technology.

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Bio-based polymers for transport packaging – possibilities & limitations

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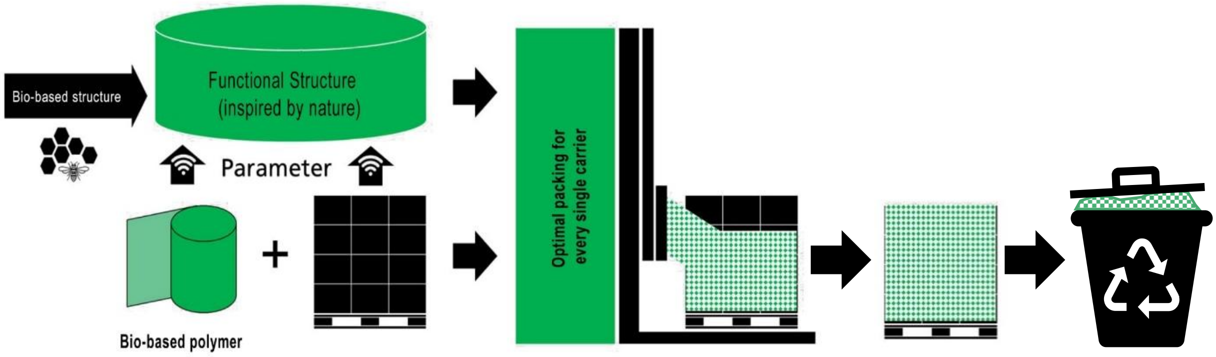
Within the FTI initiative "Production of the future" the FFG project "EFFIE – efficient, bio-based and recyclable stretch wrap" works on an eco-design-study for stretch wrap. The whole product-life-cycle will be displayed, beginning from the material selection followed by a biomimetic design, the usage and completed by the end of life options for the stretch film.



Eco-Design study for a material-efficient, bio-based and recyclable stretch wrap

Within the material-selection process a material profile was created based on a systematic literature research and interviews with the project and LOI partners. This profile includes: besides mechanical, optical and thermal properties also sustainable aspects (bio-based content, biodegradability and recyclability). In the first step the mechanical properties (e.g. tensile strength, strain at break, stress retention) of 25 biopolymers were analysed and compared with the properties of a conventional stretch wrap. Due to the results 3 biopolymers were selected for further characterization. Which include optical, thermal and sustainable aspects and a large-scale test on an automatic palette wrapping machine. The large scale-test should serve to evaluate: the behaviour of the bio-based stretch wrap during the winding process, the stress retention after the winding process, and the containment force of the bio-based stretch wrap. These results serve as a basis for the following biomimetic design process and the optimization of the bio-based material.

Software-based simulation and method optimization for polymer- and nanoparticle separations by Field-Flow Fractionation

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Field-Flow Fractionation (FFF) was invented in 1966 by Prof. Calvin Giddings, a scientist at the University of Utah in Salt Lake City, USA.[1] FFF nowadays is a reliable analytical tool for the separation and comprehensive characterization of synthetic polymers, biopolymers and nanoparticles.[2] Basic principle of the FFF technique is a separation field that is applied perpendicular to the laminar eluent flow inside a flat flow channel (Figure 1). The separation field can be a cross flow,[3] an electrical field,[4] a centrifugal force,[5] a temperature gradient[6] or a gravitational field.[7]

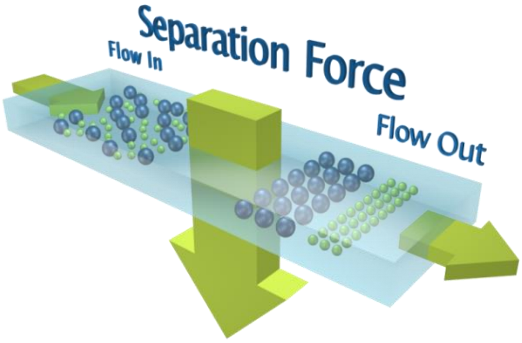

Figure 1: Principle of FFF Separation Technology

Historically, method development in FFF has been an extensive and potentially time consuming and demanding procedure. However, compared to classical chromatographic techniques, this has been also an significant advantage, as more than normal parameters can be modified for optimized separation conditions. In order to address this and help scientists to work more efficient and achive better output, Postnova has developed a complete new software module. So-called NovaAnalysis can be used for fast and easy simulation of FFF experiments and method development based from zero or from existing data, and for systematic optimization of existing methods in a timely manner.

The possibilities of this new piece of software will be demonstrated with applications from the area of polymers, proteins and nanoparticles.

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Effect of sequence blockiness on the retention behavior of gradient copolymers with various liquid chromatographic techniques

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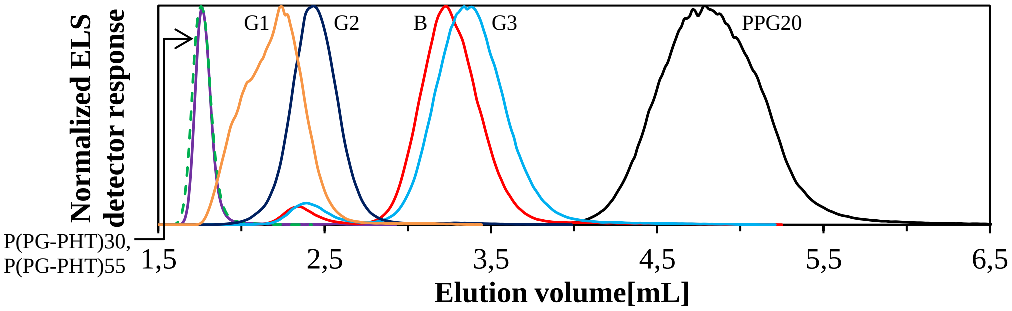
The microstructure of copolymers describes, among others, the distribution of two different comonomer units along the copolymer chains. The transition from A to B repeating units is defined by a gradient steepness that affects the physical, chemical and mechanical properties of copolymers. The main focus of this contribution is to demonstrate the effect of gradient steepness on the chromatographic behavior of copolymers consisting of propylene glycol (PG) and propylene glycol phthalate (PG-PHT) repeating units, which otherwise have comparable molecular weights and chemical compositions.



LCCC chromatograms obtained on a PS-DVB reversed stationary phase for the P(PG-PHT) and PPG homopolymers, their block copolymer as well as gradient copolymers with different gradient steepness.

The copolymers were separated by gLAC on a C18 reversed stationary phase and at critical conditions for P(PG-PHT) on a PS-DVB reversed stationary phase. On both stationary phases, gradient copolymers eluted from the column according to the gradient steepness between both types of homopolymers as predicted by theory. Interestingly, the gradient copolymer with the highest steepness eluted from both columns somewhat after the block copolymer, which is attributed to the ~5 mol % higher fraction of PPG comonomer segments. Separation at critical conditions on the PS-DVB reversed stationary phase shows improved resolution between copolymer peaks. In additions, the chromatograms reveal the presence of a small amount of low molecular weight species, causing additional low intensity peaks in the chromatograms of the block copolymer and the gradient copolymer with the highest steepness or peak broadening in the case of the gradient copolymers of medium and lowest steepness as demonstrated by 2D (LCCC×SEC) experiments and further fractionation of the chromatographic peaks and their characterization.

Degradation of monomers during hydroxyl-terminated polyester synthesis and their influence on the polymer structure

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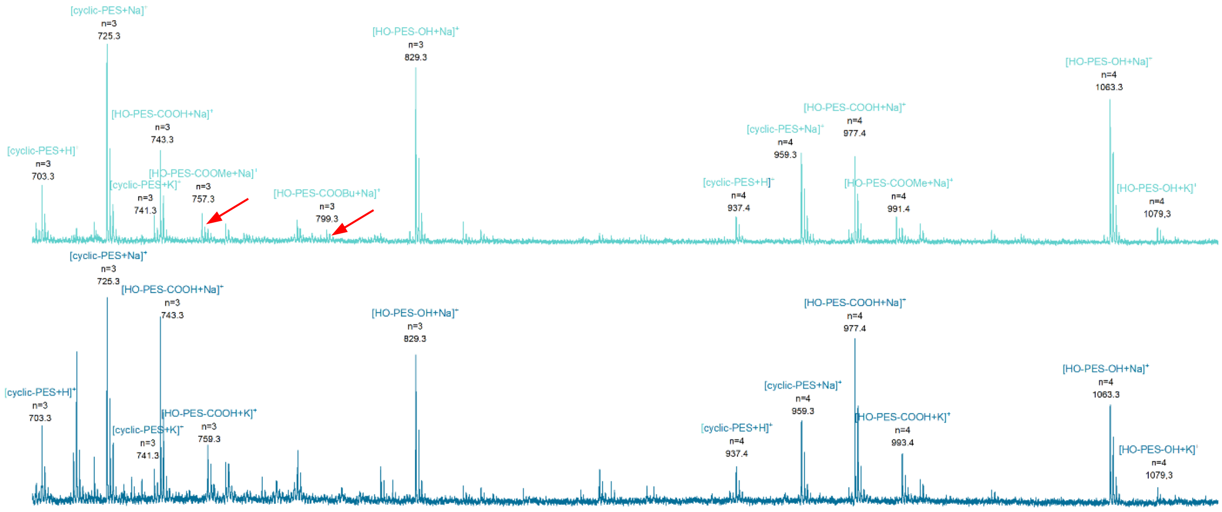
Polyesters are strongly represented in the plastics industry hence new systems are constantly being developed to meet various requirements. Isophthalic acid and neopentyl glycol are widely used in polyester synthesis and due to an excess of neopentyl glycol hydroxyl-terminated polyesters can be generated.[1] Neopentyl glycol can be easily oxidised and is converted to its precursors formaldehyde and isobutyraldehyde as well as other decomposition products.[2] To prevent this degradation, stabilisers such as sterically hindered phenols, phospites and phosponites are used.[3]



MALDI-ToF mass spectra of two hydroxyl terminated polyesters with different heating rates.

Matrix-assisted laser desorption ionisation time-of-flight mass spectrometry (MALDI-ToF MS), Size Exclusion Chromatography (SEC), ^{1}H-NMR and determination of acid and hydroxyl values by titration are the typical methods for characterisation of the polymer. The degradation products of neopentyl glycol are characterised via GC-MS. Heating rates during polyester synthesis have great influence on the structure of the polymer chains. A faster heating rate causes degradation of neopentyl glycol and the formation of reactive species. Thus, not only the desired excess of diol for the formation of hydroxyl terminated chains is lost but also chain termination by esterification with the breakdown products occurs.

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Differential Scanning Calorimetry with pressure cell for determining the polymer crystallinity changes in presence of gaseous penetrant

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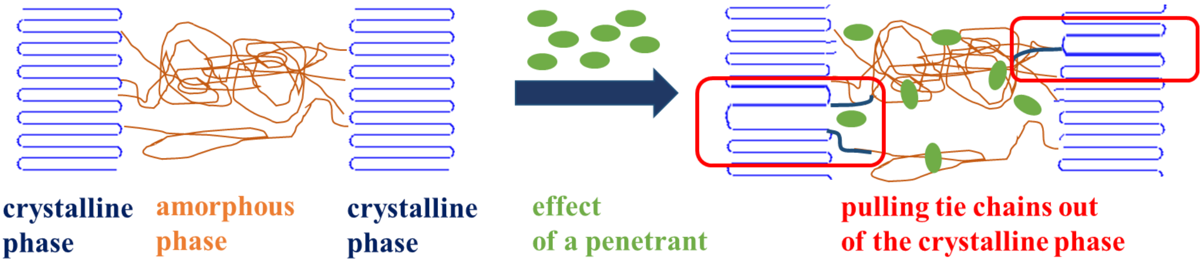
Differential scanning calorimetry (DSC) has become an established method for determining the crystallinity of pure and dry polymers. However, the industrial manufacturing of polymers mainly takes place in presence of an organic solvent that partially sorbs into the polymer and changes its semicrystalline morphology. Therefore, we developed a new DSC method for sorption experiments in the organic phase.



Schema of polymer crystallinity changes when penetrant is applied.

Semicrystalline polyethylene (PE) morphological changes were investigated for various samples from LLDPE to HDPE. Their heat of fusion and melting temperature were studied. The experiments with PE were conducted in a pressure cell possibly up to 150 bar. We applied ethylene atmosphere at various pressure and sorption time. The obtained data have shown crystallinity decrease when the penetrant was applied. The higher pressure, sorption time and longer penetrant molecule caused bigger morphological changes, i.e., changes in crystallinity. Our results are validated by TD-NMR measurements. Thus, sorption experiments carried out in DSC pressure cell could be an effective tool for determining polymer crystallinity in an organic solvent. For future we plan to modify the experimental apparatus to carry out experiments with a vaporised liquid organic solvent directly in our DSC pressure cell.

Sulfonation of unsaturated polyester – analytical challenges due to solubility change

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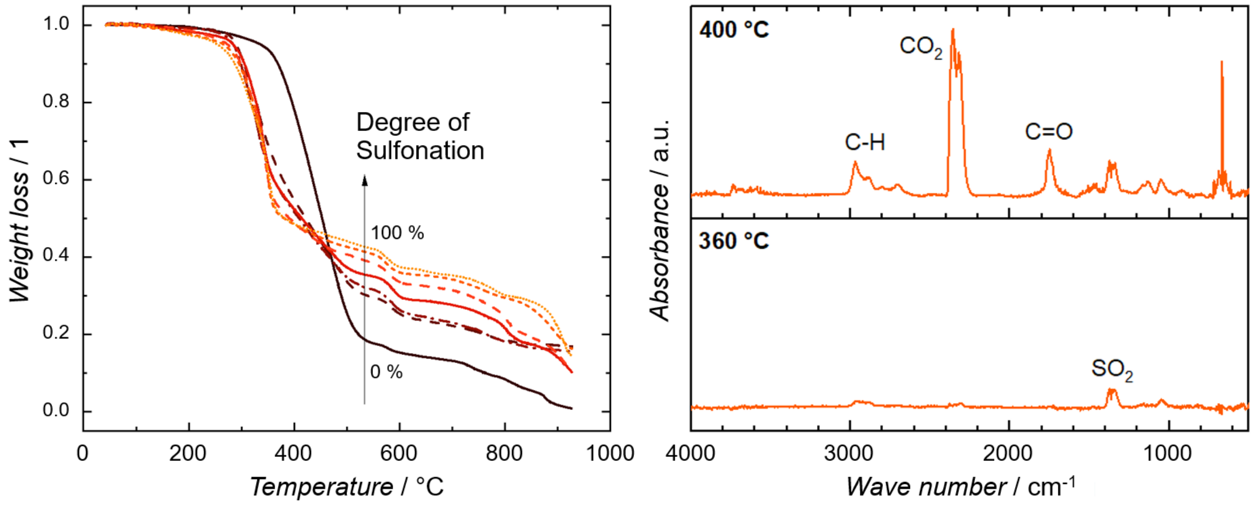
Polyesters are conventionally characterized by acid/base titrations of terminating groups, size exclusion chromatography (SEC), differential scanning calorimetry (DSC), and viscosimetry. Those analyses only generate limited knowledge on polyester composition and, hence, development of new products is often based on experience. Recently, a combination of nuclear magnetic resonance (NMR) and matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-ToF MS) was implemented which gives qualitative and quantitative information on monomer ratios and terminating groups of unsaturated polyesters containing maleic and fumaric acid.[1]

Although the double bonds of fumaric acid units in unsaturated polyesters are commonly used for crosslinking via a radical mechanism, they additionally provide an active site for further functionalization e.g. via Michael additions. Sulfonated products can be simply obtained by adding sodium sulfite to an aqueous suspension of the polyester at elevated temperatures.[2] The change to clear solutions or opaque dispersions indicates a successful reaction but the change of solubility compared to the original polyester poses a significant challenge for the established analytical methods.



Thermograms of sulfopolyesters including structural information gained by TGA-IR coupling

Combining MALDI-ToF MS, SEC and NMR gave partly contradictory results concerning molar mass distribution, terminating groups and degree of sulfonation. Problems presumably arose due to co-solubility effects in all methods and interactions to the column in SEC measurements. Hence, solvent-free thermoanalytical methods such as pyrolysis-GC-MS, thermogravimetric analysis (TGA) coupled with infrared spectroscopy (IR) and elemental analysis were combined to give a conclusive structure elucidation and to finally allow quantification of sulfonated species.

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Integrative material characterization of crystalline nanocellulose reinforced filaments for fused filament fabrication

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Crystalline nanocellulose (CNC) has recently been in the scientific community's focus as natural reinforcement material for polymers following the ubiquitous strive for green engineering and increased sustainability. Due to the combination of its high stiffness and low density, CNC displays a high specific modulus of approximately 90 MPa/(kg.m^3).[1] However, during fused filament fabrication (FFF), the material is subjected to a combination of thermal and mechanical loads. Thus, these loads need to be considered when characterizing and predicting the composite's properties in the final additively manufactured specimen.

Herein, the CNC was introduced into a recycled 3D-printable polypropylene at filler contents up to 15 vol%. As interactions between the cellulose and the polymer matrix are decisive for maximizing the CNC's reinforcement effect,[2] a maleic-acid-anhydride-based compatibilizer was used for the coating of the CNC. Shear rheological investigations, dynamic-mechanical analysis (DMA) and measurements regarding the shrinkage behaviour were applied to characterize the novel composite. An unexpected decrease in viscosity with increasing filler content accompanied by a distinctive colour change was attributed to degradation, further confirmed by differential scanning calorimetry (DSC). Thus, a tailored ageing procedure to imitate the FFF procedure was integrated into the DMA measurements of the filaments. This methodology enables a reliable material characterisation to establish the baseline for predicting the properties of the final printed part.

The research was partially carried out within the FFG-funded project "Natural3D" under Project No. 860384.

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Investigation on the recycling of biobased polymers on the example of PHBV

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Polyhydroxyalkanoates (PHA) only make up a small percentage of the bioplastic market but are getting more and more important. PHA's show much better mechanical and barrier properties than PLA, but bad elongation at break properties, what makes compounding and adding additives necessary. Their degradation temperature is below their melting temperature, so they are difficult to process.[1,2]

Till now, PHA's are not recycled since they are biodegradable and not easy to process. Regardless we tried some common recycling routes, due to the fact, that the production of PHA's itself is very costly and time consuming.

The polymer *ENMAT™ Thermoplastics Resin Y1000P*, which is a PHBV resin, is taken for this investigation.

For the mechanical recycling seven recycling cycles are carried out with the pure polymer, to show the thermal and mechanical degradation while processing. Following the same process is carried out with addition of additives, to improve the processability and the thermal stability of the polymer.[3]

After every recycling cycle the materials are analysed via mechanical, thermal- and chemical techniques, to check the progress of decomposition.[3]

Another recycling route we take, is the solvent-based recycling. For this recycling route, the polymer is dissolved and separated from additives and impurities and precipitated again.[4]

We also carry out a biolysis step, where we try to feed bacteria with PHA's to produce fresh PHA's and a solvolysis recycling route [5].

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Effect of different experimental setups on the removal efficiency of surface and matrix contamination in PE-LD

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The worldwide production of plastics reached a level of 368 million t/a in 2019 and therefore, a major challenge of today`s society is plastic waste recycling.[1] Although there are many studies about plastic recycling, publications dealing with the washing step are scarce.[2] However, contamination of plastic packaging material can easily occur during usage, transportation, storage, and/or disposal.[3] The importance of a clean feed for mechanical recycling is considerable, because contaminants may lead to fouling of the equipment, deteriorate the material and reduce the value of recycling products.[2,3,4]

Principally, impurities are transferred from the plastic into the washing medium and consequently removed via washing.[3] There are various cleaning options since wet as well as dry cleaning can be applied.[4] From an economical point of view, the price of recycled plastics is highly dependent on the operating costs of polymer recycling plants. Therefore, an optimum between economic efficiency and good recyclate quality due to sufficient washing is targeted.[3]

Regarding poly(ethylene terephthalate), an appropriate washing procedure is already implemented,[5] but due to chemical composition, the cleaning of polyolefins is more complicated.[6] To achieve the aim of the European Union to reach a 50 % recycling rate by 2030, research and new technologies are needed.[5] In order to acquire a profound understanding of the washing step, the influencing parameters of the washing step have to be evaluated.

Since plastics are used for numerous applications, contaminations and residues can be various. For the generation of representative and comparable results, the definition of marker compounds is crucial. In this study, various model compounds are chosen to investigate the washing behaviour of surface as well as bulk contaminants.

Moreover, the experimental setup has to be defined to generate representative results and to be capable of observing the effects of individual processing parameters. Different alignments of the samples are tested and compared to present optimal experimental setups. Both, vertical and horizontal alignments, are evaluated using different model compounds. Furthermore, the effect of additional movement via a countercurrent stirrer is discussed.

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Poison study based on chemically recycled plastic waste impurities and their influence on the performance of Ziegler-Natta catalysts.

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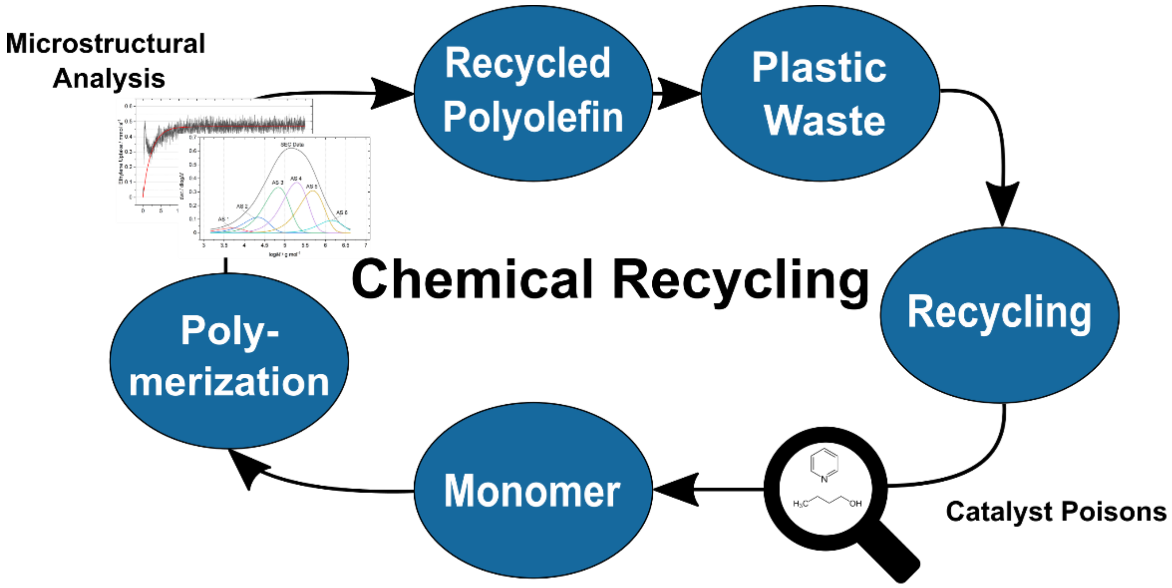
Chemically recycled monomer feed streams from post-consumer plastic packaging waste are expected to contain impurities that act as catalyst poisons.[1] This work investigated the impact of such impurities on a commercial fourth-generation Ziegler-Natta catalyst system. We simulated a recycled monomer feed stream in two different procedures by adding representative catalyst poisons (pyridine and *n*-butanol) in various quantities to the reactor setup. Measuring catalyst activity and molecular weight distribution (MWD) and performing kinetic and MWD deconvolution modeling, we evaluated the impact of the catalyst poisons on polymer product properties at the microstructural level.[2] Our results demonstrate that, beyond a certain concentration (120 ppm), catalyst poisons have a substantial impact on the activity levels of the catalyst system tested. MWD deconvolution modeling showed an influence of the poisons on the composition of the resulting polymer product in the form of a shift towards lower or higher molecular weights (depending on the procedure). This microstructural analysis highlights the importance of purifying chemically recycled monomer feed streams.



Schematic recycling process with microstructural analysis of plastic packaging waste

Our results indicate that the polymerization process can yield products with different properties depending on whether the input material does or does not contain chemically recycled monomers. This represents a potential limiting factor in the processability and applicability of chemically recycled plastics and addressing these limitations will require a stronger focus on purification of chemically recycled monomers.

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The influence of the sample preparation steps on the properties of pre-treated polyolefin waste – Problems & Solutions

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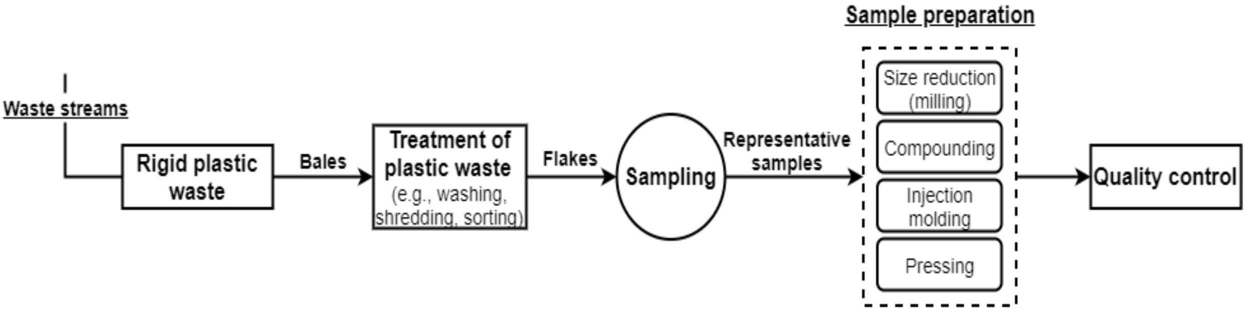
For the conversion of plastic waste into high quality recyclates, the characterization and quality control of incoming materials is essential. Therefore, a proper sample preparation is required to generate datasets with a high precision. Based on the acquired data, it is possible to optimize process steps and processing parameters while meeting target quality characterisitcs of specific products.

Milling and compounding of the incoming materials can, potentially, be used to improve the homogenization of plastic waste. Hence, the representativeness of the generated data will be increased. This study, comprehensively, investigates the influence of sample preparation by comparing the impact of milling and compounding on the properties of different polyolefin (PO) waste streams.



Simplified schematic illustration of the sample preparation steps for the characterization of plastic waste

Samples of five different pre-treated PO feedstocks, two polypropylene (PP) dominated and three color-sorted high-density polyethylene (PE-HD) dominated mixtures, were milled and compounded. Additionally, further processing technologies (e.g., milling technologies, injection molding, pressing) were conducted on one PP and one PE-HD grades to find the best practice sample preparation. Melt flow rate (MFR), plate-plate rheology test, differential thermal analysis (DTA), and mechanical tests were performed to determine the impact of processing on melt properties, material resistance to oxidation, and mechanical performance. For both POs, the detected properties were affected by the various sample preparation steps. However, the impact of milling was less evident in the rheology of the materials than that of compounding. Nevertheless, both processes can be used to map out the property profile of a waste stream. While milling can help determine the actual material property profile of the flakes, compounding can provide an approximate prediction of the property profile of granules after processing with a recycling machine.

* The datasets have already been generated.

Recycling of multilayer films from food packaging

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Multilayer films are widely used in food packaging for the possibility of tailor-made properties. The layering of different materials can provide the film with desired medium barrier properties within excellent mechanical strength. At the end of their service life the problem arises how to re-use or recycle material, which composes from different immiscible materials.[1]

Mechanical recycling of multilayer films leads to material with worse properties than the original film. To return the waste material to the packaging process it is necessary to reach the requested properties. Two approaches are available to improve the properties of recycled materials. One way is to find the best ratio of different polymers, and the other way is using a compatibilizer. Adequate compatibilizer should provide "bonding" between two immiscible polymers and thus improve the mechanical properties of the blend.[2] This approach is becoming more challenging with more than two materials in the blend.

This work demonstrates the influence of different compatibilizers and different composition of the blends on their properties. Two multilayer films made of polyamide (PA), polyethylene (PE) and ethylene vinyl alcohol (EVOH) and two different PE films were used as input for the recycling process. The standard recycling process (washing, drying, shredding and mixing and kneading) was adjusted for the lab-scale. At the end of the recycling process, films from the blends were pressed in a vacuum press. Elongation at break and tensile strength of different films were compared. Moreover, observation of the film transparency was conducted as it is one of the important parameters for application in the packaging process.

Results show that desired properties can be obtained not only by adding suitable compatibilizer but also more conveniently by changing the ratio of different films.

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Comparison of chromatographic, spectroscopic, thermal, and mechanical measurement techniques for polyethylene recyclate characterization

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The new regulation of the European commission sets high goals on the recycling of plastic packaging waste.[1] Plastic pipe products might take up high amounts of the resulting recyclates, especially in lower performance/non-pressure applications. While packaging products usually are short-term applications and are therefore sparingly stabilized, pipe products should withstand environmental influences for several decades. Furthermore, PE-HD packaging products are mostly injection- or blow-molded and therefore require different flow properties than pipe materials.

In this study, three commercially available polyethylene post-consumer recyclates (rPE-1, rPE-2, and rPE-3) produced from packaging waste streams are characterized in terms of stabilization and flow properties and compared to a virgin pipe grade PE-HD of the PE100-RC class.

Two methods were used for stabilization characterization, high pressure liquid chromatography with ultraviolet detection (HPLC-UV) and oxidation induction temperature (T_{OX}) measurement. For characterization of flow properties melt flow rate measurements (MFR) were performed. Furthermore, tensile tests of injection-molded specimens and molar mass measurement via gel permeation chromatography with infrared detection (GPC-IR) were conducted and correlated with the flow properties.

The three recyclates show significant differences in stabilization to the virgin PE100-RC. While the stabilizer contents (active and unconsumed Irganox 1010 and Irgafos 168) of the recyclates range from 0.01 ppm to 0.08 ppm, PE100-RC contains in total 0.20 ppm of these stabilizers. T_{OX} measurements show a similar trend with the recyclates ranging from 228 °C to 242 °C, while PE100-RC delivers values of up to 261 °C.

The characterization of flow properties showed a wide range of properties for the recyclates and substantiate the differences between packaging and pipe PE-HD. The MFRs of the recyclates range between 0.8 g/10 min and 2.5 g/10 min, while the PE100-RC showed a much lower MFR of 0.23 g/10 min. The strain-at-break values of the recyclates range between 35 % and 120 %, while PE100-RC already broke at 21 % strain. Finally, the mass average molar masses (M_w) of the recylates range between 142,000 and 168,000 g/mol, while PE100-RC shows a higher M_w of 188,000 g/mol.

Both methods for stabilization characterization succeed in differentiating between the tested materials and correlate to each other. While the MFR correlates to the strain-at-break for all recyclates and the virgin polymer, the GPC results of the recyclates follow no trend. Despite its higher MFR, rPE-1 shows a higher M_w than the other recyclates.

References:

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Destiny of drag reducing agents in turbulent pipe flows

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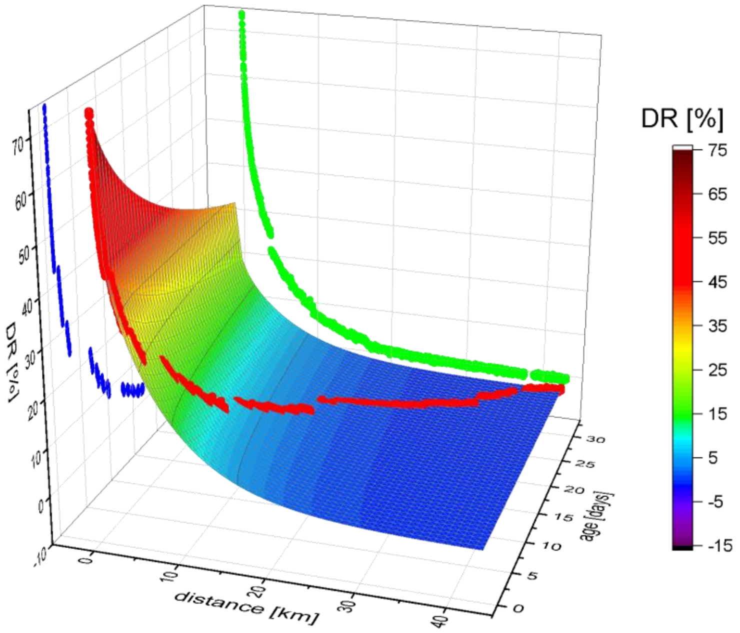
Already 100 wppm of flexible long chain polymers added to liquids allow for a significant drag reduction in turbulent pipe flows of up to 80%.[1] Such drag reducing agents have a wide range of applications in fracking, irrigation and fire fighting to enhance flow rates or outlet pressure or to reduce energy costs. Drag reduction is generated by the interplay of polymer and flow field. The detailed mechanism is still unrevealed.[2] Bending and stretching of the polymer chains in the sheared flow at the pipe wall or in turbulence vortices causes irreversible breaking of the polymer backbone preferably in the centre region of the chain.[3] A widely used empirical description of the associated loss in drag reduction capability was provided by Brostow which utilises a finite number of breaking points.[4] If the mechanical polymer degradation comes to an end before the critical lower threshold in molecular weight for effective drag reduction is reached was still an unsettled question.

This was examined in turbulent pipe flow of the pilot-scale flow facility ViEDRA (**Vi**enna **E**xperiment for **D**rag **R**educing **A**gents) at a Reynolds number of 10^5. In cyclic operation an aqueous 100 wppm Polyethylen Oxide (PEO) solution was monitored over a distance of up to 40 km. A complete loss of the drag reduction capability was found.



Complete loss of drag reduction capability due to mechanical degradation and ageing.

The data quality allowed to identify two relevant processes causing polymer fragmentation: shear induced degradation and ageing of the polymer solution. The polymer fragmentation was monitored by triple detection gel permeation chromatography.

References:

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Impact of silver seed formation on electroless copper deposition for conductive textiles

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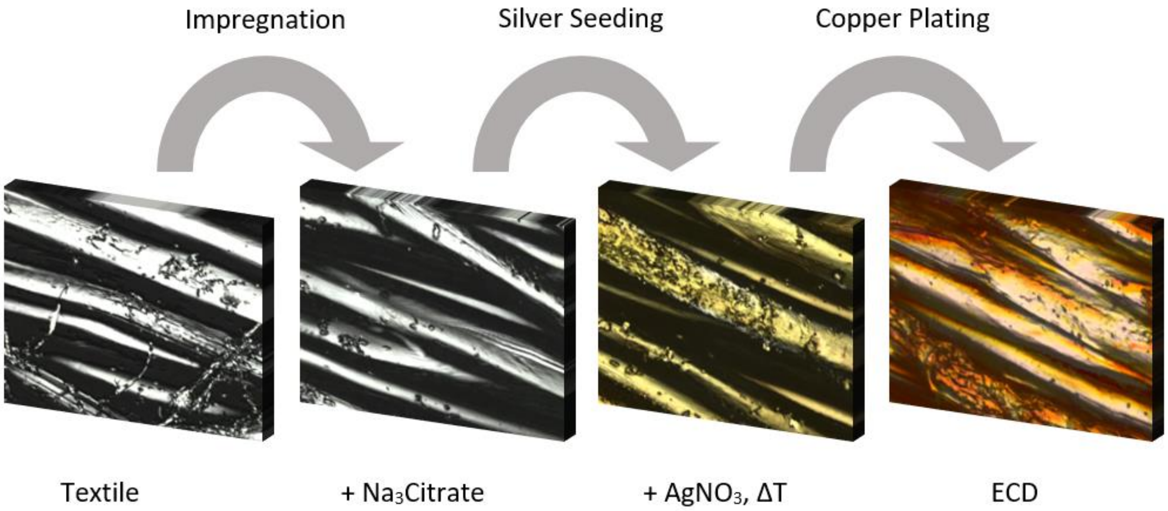
Conductive textiles and their applications have been getting more and more attention over the last years. There is a wide variety of material possibilities for the combination of conductors and flexible substrates. An approach for generating conductive fabrics utilises electroless copper deposition (ECD). Due to the very high resistance of polymeric textile substrates, conductive preactivation of the textile is required. This role is often taken by silver particles because of their simple synthesis.[1] The latest trend of silver deposition is based on the thermal decompositon of metal precursors e.g. silver carboxylates.[2]



Conductive preparation of a cellulose textile using silver citrate decomposition, laser microscope, magnification ×100.

Herein, a new simple but efficient approach is presented that combines the advantages of carboxylate based silver reduction with electroless copper deposition. Silver particles for metal preactivation seeding are synthesised additive freely and directly on the polymer surface. The polymer promotes the silver citrate decompostion with possible reaction temperatures below 100 °C. On cellulose textile substrates, the formation of silver nanoparticles results in a low percolation threshold and a smooth copper coating. In contrast, the formation of microparticles with a rougher copper surface after ECD was observed on polyamide 66 textile substrates. This method can be applied for printing of conductive lines, with an electrical resistance below 10 Ωm^{-1}. An excess of trisodium citrate on the textile surface enhances the aesthetics of its edges.

References:

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Hydrophobically modified copolymer associations - A promising path to improve drag reduction?

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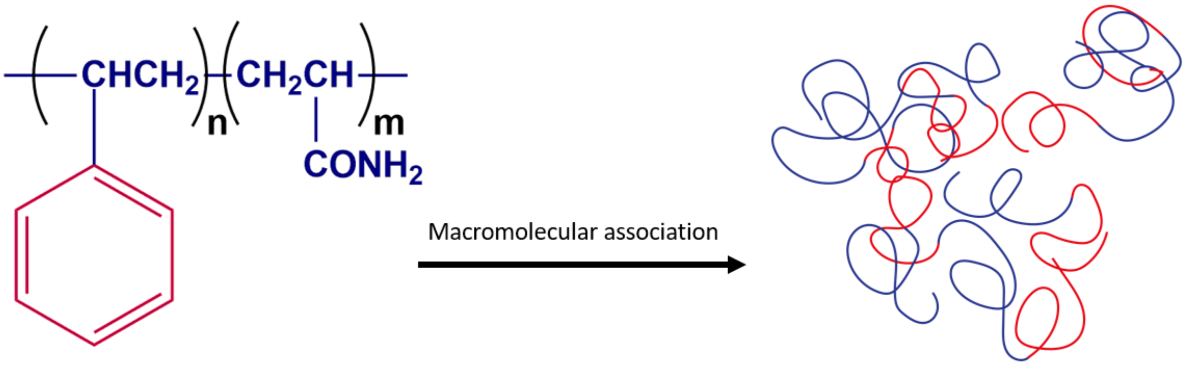
Fluid flow in pipes faces turbulence thus causing drag and leading to a significant dissipation of the input energy driving the flow. To reduce drag, polymeric agents in 100 wppm concentrations are commonly added to the fluid.[1] The drag reduction in turbulent flows offers large economic benefits for fluid transportation systems in industry, agriculture and infrastructure. Nevertheless, there are still severe limitations in the use of polymeric drag reducing agents as the mechanical stress in the fluid's velocity shear breaks them up.[2] Upon the degradation polymers lose their potential as drag reducing agents. To overcome this issue we produced hydrophobically modified polymers of acrylamide (poly(acrylamide-co-styrene)) forming ultra-high molecular weight associations. These associations provide weak links and are reversible meaning that they protect the polymer backbone and allow for "self-healing" through the recovery of hydrophobic interactions.



Hydrophobically driven macromolecular associations

To obtain water soluble poly(acrylamide-co-styrene) with high hydrophobe content, micellar polymerisation has been employed. Herein, the amount of styrene moities in the polymer reached 4 mol%. Furthermore, the copolymer microstructure was modified by varying the hydrophobic blocks' length. The molecular weight of the synthesised materials has been determined by triple detection gel permeation chromatography to be in the range of 1.3 to 1.8 $*10^6$ g/mol. In dilute aqueous salt solutions the association capability of the synthesised polymers has been verified by multi angle static light scattering. In the future studies, we will examine the polymer aggregation impact on the rheological properties. A focus will be on the recovery potential after shear stress. Moreover, we will chracterise the colloidal properties (surface and interfacial tension, foam stability) of synthesised materials and their drag reducing capabilities in a pilot-scale flow facility.

References:

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Viscosity reduction of magnesium alkyls used for Ziegler-Natta catalysts

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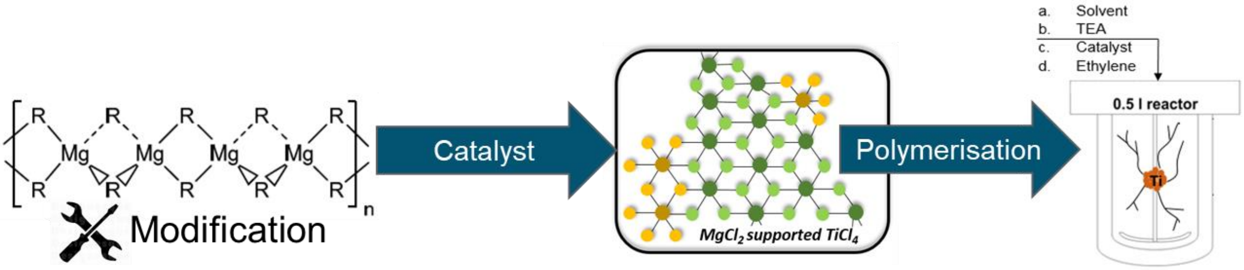
Magnesium alkyls are used as precursors for water-free magnesium chloride support material for highly active Ziegler-Natta catalyst systems.[1] The structure and morphology of $MgCl_2$ are key parameters for the efficiency and activity of the catalyst and therefore also affect the polymer characteristics.[2] Unfortunately, magnesium alkyls have the unfavorable property of being highly viscous or even solid. This is attributed to the polymer-type chain structure formed by magnesium alkyls.[1]



Experimental setup for testing modified magnesium alkyls

In this work theoretical structures of magnesium alkyls were studied by applying density functional theory (DFT) calculations. Furthermore, additives were tested for their ability to reduce the viscosity of butyl-octyl-magnesium (BOMAG) and butyl-ethyl-magnesium (BEM). The investigations showed that heterocumulenes such as isothiocyanate and carbodiimide have the ability to reduce the viscosity. In further experiments, it was evaluated, if the modified magnesium alkyls are suitable as a precursor for the Ziegler-Natta catalyst synthesis according to a standard preparation procedure. In this case, the catalyst synthesis is based on the precipitation method.[3] In the last step the additive effect on the homopolymerisation of ethylene was studied.

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Effects of different process parameters on improved comonomer incorporation distribution in Ziegler-Natta catalysis

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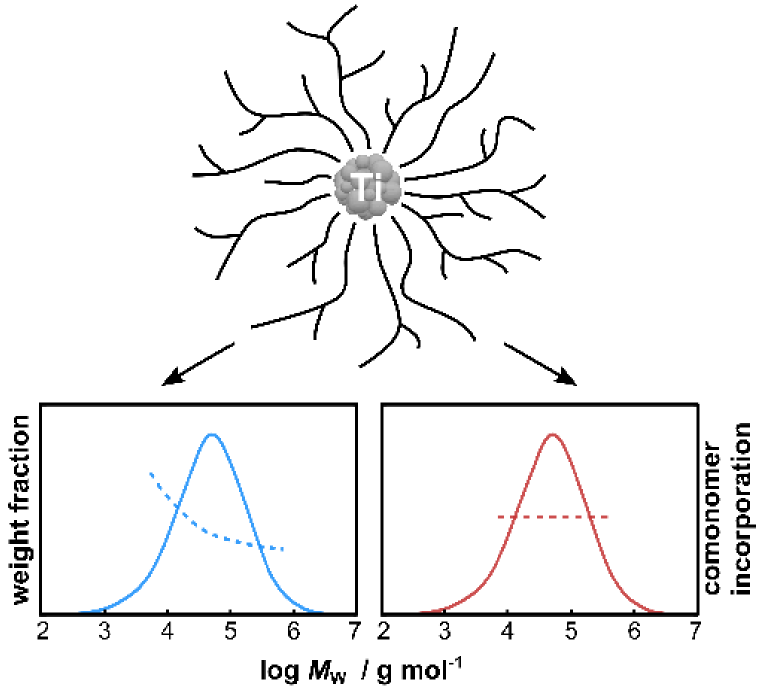
Linear Low Density Polyethylene (LLDPE), produced by Ziegler-Natta (ZN) based catalyst systems usually creates a less uniform comonomer distribution compared to metallocene-based systems. The comonomer is incorporated predominantly in lower molecular weight fractions, while the incorporation of the comonomers decreases towards higher molecular weight fractions.[1]



Comonomer incorporation behavior of ZN catalyst systems[1]

The advantages of ZN-based catalyst systems are the wide range of possibilities for modifying the product properties. Our group is working on catalyst synthesis procedures based on a precipitation process. The temperature variation during titanation gives an interesting opportunity to influence the incorporation behavior of comonomers. This change in the catalyst synthesis procedure leads to a significantly more uniform comonomer distribution (see figure), a characteristic which is highly beneficial and commonly more likely known from metallocene catalysts.

This work focuses on the influence of the polymerization parameters comonomer type, comonomer concentration, and temperature in the polymerization process of LLDPE. The relationships between the influencing factors temperature and comonomer concentration as well as the limits of the uniformity of the comonomer distribution for *n*-butene, *n*-hexene, and *n*-octene have been studied.

References:

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Application of hybrid modeling in polymer processing

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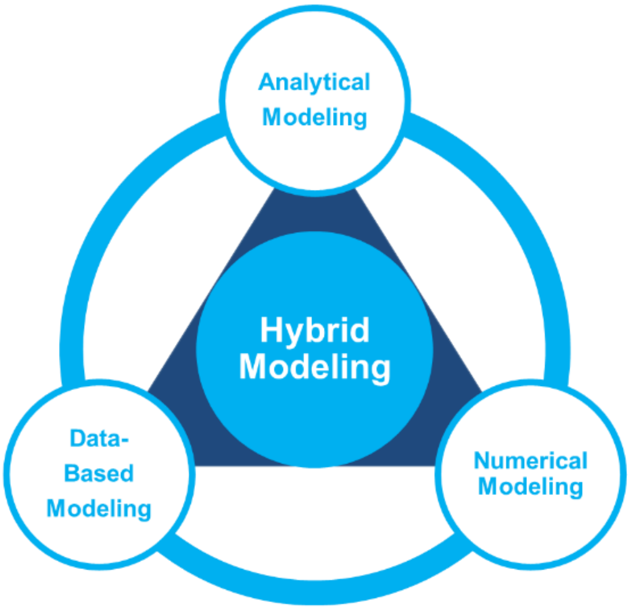
For many decades, the setup and solution of polymer processing models involved use of analytical or numerical methods. These characteristics have changed with the recent digitization of polymer processes and the collection of enormous amounts of data. It is increasingly common to use data-driven modeling techniques to analyze processes, for which analytical and numerical models may not fully describe the process behavior in operational situations. These techniques have significantly extended the set of tools available to the engineer, providing new possibilities of how to develop more accurate process models. As a result, the setup of an appropriate modeling strategy more than ever requires a thorough understanding of the individual modeling techniques. This article was designed to address the potentials and limits of analytical, numerical, and data-based modeling techniques when modeling polymer processes. Moreover, we show how these methods can be combined into one hybrid approach to solve polymer process models not solvable so far. The findings are further illustrated by means of a particular use case, which models the flow of polymer melts in single-screw extruders.



Hybrid Modeling: Implementation of analytical, numerical, and data-based modeling techniques.

POSTER PRESENTATIONS

Digital light processing 3D printing with thiol–acrylate vitrimers

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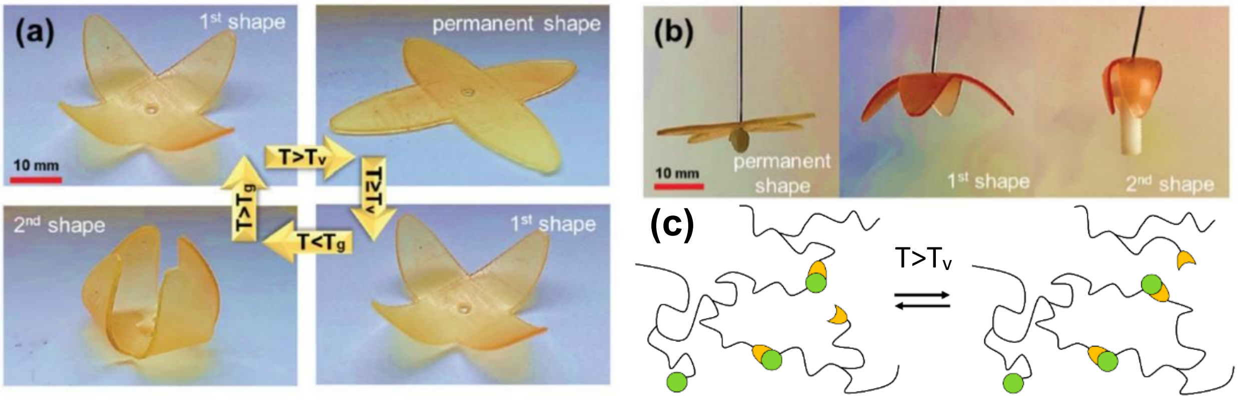
Dynamic covalent bonds result in polymer networks with advanced functions such as self-healability, recyclability, malleability and shape memory. Currently, the most attractive dynamic networks are vitrimers, which rely on thermo-activated exchange reactions of their crosslinks. Owing to these exchange reactions, the viscosity of vitrimers experiences a gradual decrease until they transform into a viscoelastic liquid at the topology freezing transition temperature (T_v). A commonly utilised reaction mechanism to enable this form of bond interchange is the catalyzed transesterification of hydroxyl ester moieties. However, the introduction of dynamic covalent bonds into 3D printable photopolymers is challenging, as typically used transesterification catalysts are poorly soluble, can have an inhibiting influence on cure rate and compromise the pot life of photocurable resins.



(a) Triple-shape memory experiment; (b) DLP-3D-printed gripper; (c) Schematic depiction of the thermo-activated exchange reactions

Herein, a mono-functional methacrylate phosphate is introduced as a new transesterification catalyst, which overcomes these limitations and unlocks a new variety of photocurable vitrimers. Applied in thiol–acrylate vitrimer systems, the fast photopolymerization combined with storage stability enables the successful additive manufacturing of 3D objects with a resolution of up to 500 μm. Once photo-curing through bottom-up digital light processing (DLP) is completed, the dynamic thiol-ene networks have the ability to rapidly undergo rearrangements of their network topology after thermal activation, as shown by stress relaxation experiments. The DLP printing of soft active structures with triple-shape memory and thermal mendability is demonstrated. Due to its versatility this unique class of materials is an ideal candidate for 3D printing of structural and fast acting functional devices in soft robotics, biomedicine and electronics.[1]

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Spatially resolved photoactivation of dynamic exchange reactions in vitrimeric polymers

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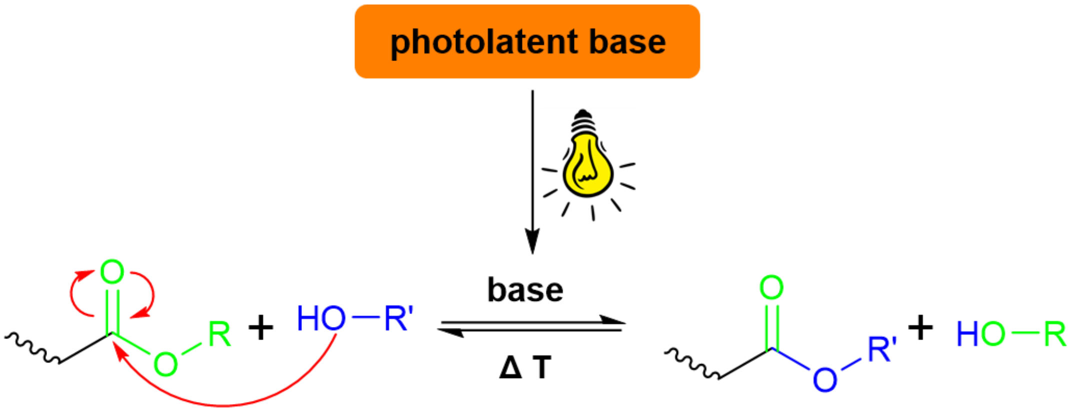
Vitrimers are advanced polymeric materials capable of rearranging their covalently crosslinked network structure by dynamic associative exchange reactions. They generally behave like classic thermosetting polymers. However, when the topology freezing transition temperature (T_v), defined as the onset temperature of the covalent bond exchange reactions, is exceeded, they are able to flow like viscoelastic liquids.[1] Nevertheless, so far, an onset of the exchange reactions could not be prevented or induced in a controlled manner at elevated temperatures when T_v was exceeded.
For overcoming this considerable application boundary, a high temperature stable photolatent base was incorporated into a three-dimensional covalently crosslinked network structure appropriate to undergo base-catalyzed transesterification. The UV-mediated relase of the efficient transesterification catalyst, i.e. a strong guanidine base, enables the controlled onset of the dynamic bond exchange.[2]



Schematic representation of the underlying concept developed for a controlled onset of dynamic transesterification by UV-light.

We demonstrated this behavior by stress relaxation measurements. Even at temperatures considerably above T_v, only a controlled catalyst release, mediated by UV irradiation of the test specimen, enabled the immediate onset of dynamic covalent bond exchange reactions. Moreover, the spatially resolved photoactivation of these vitrimeric properties was examined by means of a reshaping experiment. Exclusively the UV-irradiated parts of a free-standing test specimen are permanently reshapable when T_v is exceed.[2]
In conclusion, our work provides a fundamental building block for the development of thermally stable, spatially resolved photoactivatable vitrimers, which facilitate a locally controlled malleability.[2]

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Digital light processing 3D-printing of photocurable diene-rubber

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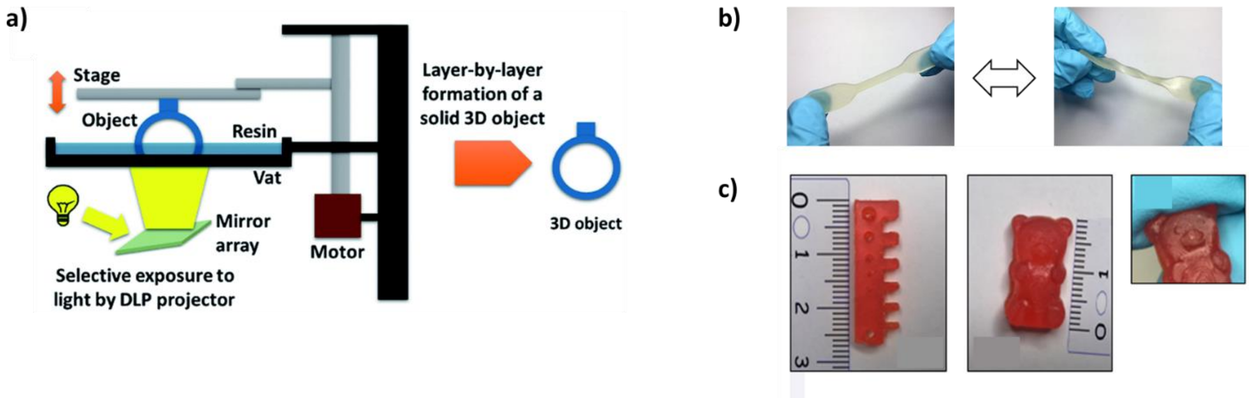
Rubbers are omnipresent in our daily life. Due to their unique material properties such as high elasticity, strength and recovery, diene-rubbers are applied in a vast amount of everyday products like tyres, gaskets or sealants. In general, rubbers are crosslinked in a process called vulcanization, which can be either thermally initiated in the presence of sulfur or peroxides. However, novel routes towards the photo-crosslinking of diene-rubbers have been approached over the last years.[1] This process allows the crosslinking of liquid diene-rubbers, such as liquid isoprene rubber or nitrile butadiene rubber, in the presence of light which makes them interesting candidates for the digital light processing (DLP) 3D-printing. DLP offers distinctive advantages including high resolution and surface quality at low cost and comparably high throughput rates.



Schematic presentation of (a) the DLP 3D-printing process, (b) reversible twisting of the photo-cured rubber specimen and (c) DLP 3D-printed objects with precise structures.

For the DLP 3D-printing of diene-rubbers several challenges have to be faced. In general, the poor photo-reactivity of diene-rubbers makes them not feasible for DLP printing. However, this can be overcome by either introducing photo-sensitive moieties such as acrylates in the sidechain of the rubber or by using thiol-click chemistry.[2] A further critical point is the high viscosity of the liquid rubbers which limits their processability for DLP 3D-printing. With the help of reactive diluents such as acrylates, divinylethers, epoxides or thiols, the liquid rubbers can be tailored towards a suitable viscosity range for the desired applications. Upon the addition of reactive diluents not only the viscosity was adjusted to a processable level but also the photo-reactivity was increased significantly. This led to a successful DLP 3D-printing of liquid rubber specimen with a high precision.

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Influence of volumetric flow on the mechanical properties of short carbon fiber-reinforced polyamide parts printed by Fused Filament Fabrication

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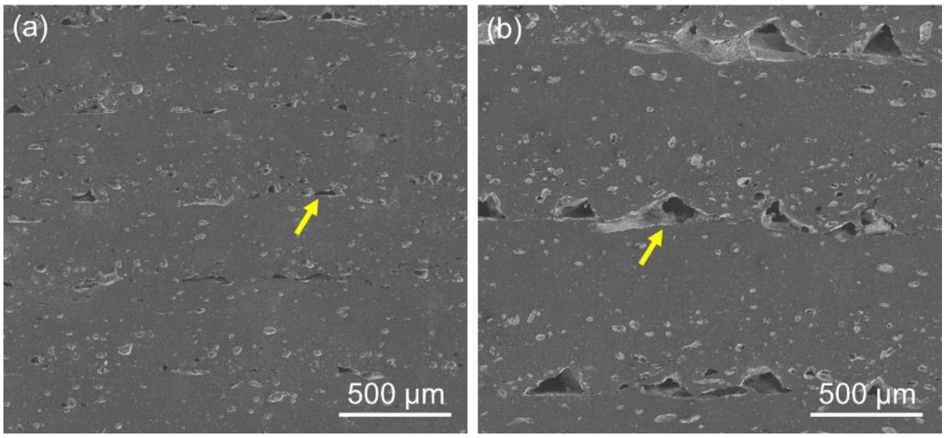
The fused-filament fabrication (FFF) of short fiber-reinforced thermoplastics represents a relatively low-cost alternative to produce near net shape composite parts and structures. However, since the incorporation of short (chopped) fibers into the thermoplastic matrix is difficult, pores turn out to be present in the filament as-produced and therefore are carried over to the 3D-printed composite component. This additional porosity (intra-road) is added to the intrinsic defects present due to the nature of the FFF process (inter-road porosity), which together, depending on the fiber concentration, may even weaken the reinforced part in comparison to an unreinforced one of same matrix. A proposed way to counterbalance the filament-dependent intra-road porosity would be mitigating the formation of the inter-road one by manipulating the volumetric flow during the deposition of each individual road. In the present study, the volumetric flow of individual roads (with a cross-sectional diameter of 0.4 mm, area of 0.126 mm^2) is varied by -10%, +10% and +20% during the printing of tensile and bending specimens, using a polyamide filament reinforced with 6.5 vol.% of chopped carbon fibers. The available space for the road deposition remains constant (square-shaped cross-sectional area of 0.126 mm^2) regardless of the volumetric flow. As a result of the flow increase, a higher amount of molten filament is extruded to fill up the same space, which causes a road-flattening effect and consequently spreads the extruded material to the sides. This eventually reduces the adjacent (inter-road) porosity, see Figure.



Road-flattening effect on 3D-printed PA-CF parts. Inter-road porosity is indicated by yellow arrows. (a) High flattening effect; (b) low flattening effect.

The resulting porosity is to be correlated with the mechanical performance of printed parts under tensile and bending. Moreover, theoretical and actual extruded volumes are to be compared, in order to detect and quantify phenomena such as partial nozzle clogging due to the intentional over-extrusion.

Vulcanization of XNBR- and NR-latex by UV-techniques for the production of non-allergenic surgical and examination gloves

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To reduce allergenic reactions related to accelerator chemicals used in conventional sulfur crosslinking in dipped carboxylated nitrile butadiene rubber (XNBR) and natural rubber (NR) latex articles such as medical gloves, an innovative vulcanization process based on an UV-initiated thiol crosslinking reaction has been developed. In order to achieve better mechanical properties of the final products, a dual curing process is used by the addition of divalent metal oxides (ZnO). Thereby, the photochemical thiol-ene reaction is used to generate covalent crosslinks between the remaining C=C double bonds of the butadiene units whereas the carboxylic moieties are conventionally cured with ZnO at elevated temperature by forming ionic crosslinks. The photochemical curing step can be carried out both as a prevulcanization using a falling film photoreactor and as a postvulcanization by UV irradiation of dried latex films. The new process enables the production of UV crosslinked surgical and examination gloves, which are characterized by excellent physical properties, high aging stabilities and good skin compatibility. Further advantages of the new technology compared to conventional sulfur vulcanization are low energy consumption and short vulcanization times.

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UV-Induced frontal polymerizations for the preparation of gradient magnetic composites

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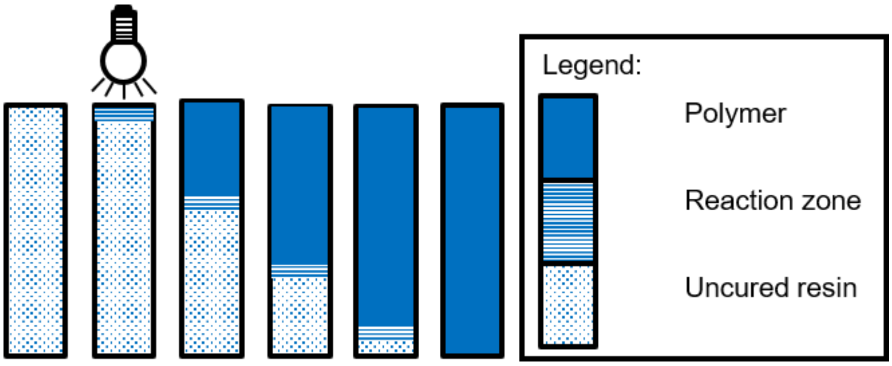
Frontal polymerizations (FPs) are a fast and energy-efficient alternative to conventional manufacturing techniques for thermosetting polymers and composites. FPs and crosslinking reactions are intentionally triggered by stimuli such as UV irradiation.[1] In the course of exothermic reactions, heat is released, which in turn serves as the stimulus for the polymerization or crosslinking of reactants in adjacent areas. The preparation of gradient polymers and composites can be accomplished by modifying the curing formulation near the reaction zone.



Schematic representation of the UV-induced frontal polymerization.

The curing of composites is challenging due to their increased thermal conductivity and the associated energy losses.[2] Hence, the motivation for this study has been the preparation and physicochemical characterization of magnetic composites in combination with the modeling and simulation of the polymerization process according to the finite element method.[3] A transient heat analysis has been performed in order to compare the propagating front for filled and unfilled monomer resins. Special attention has been paid to the functionalization of the particles' surfaces in order to avoid aggregation.[4]

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Dual-cure resins based on aromatic propargylether derivatives for additive manufacturing

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The field of additive manufacturing (AM) has been constantly evolving since the early 1980s. With the continuous spread of UV based printing technologies, the demand for photopolymers with improved thermo-mechanical properties has been steadily increased.[1] In recent years, dual-cure chemistry has been exploited to develop interpenetrating networks (IPNs) that enhance these properties. In this concept, photoreactions were utilized to build up the desired 3D structure within the AM process, while a thermally triggered reaction allows the enhancement of the network properties in a subsequent annealing step. This strategy combines advantages of traditional UV curable monomers with high-performance thermosets.[2]

Here, propargyl-terminated derivatives of bisphenol A were investigated as thermo-curable building blocks in a photosensitive formulation with the aim to increase the heat resistivity of the formed photopolymers. It is well reported that aromatic bispropargyl-ethers undergo a thermal polymerisation reaction due to the formation of cross-linked bischromenes. These networks provide excellent thermal and heat resistance, low moisture uptake, and high strength.[3] After the successful synthesis of the aromatic propargylether derivatives, these compounds were introduced in both acrylate and thiol-methacrylate based resins. The obtained IPNs provide enhanced thermal stability making these resins suitable for the printing of functional 3D parts for high performance applications.

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Biocide coatings for thiol based photopolymers

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Metal ions have been used for centuries to sanitize fluids, solids and tissues. For instance, the ancient Greeks of the pre-Christian era of Hypocrates (400 BC) were the first to discover the disinfecting power of copper.[1] In general, the redox cycling between Cu^{2+} and Cu^{1+}can catalyze the production of hydroxyl radicals, which are able to damage lipids, proteins, DNA and other biomolecules of pathogens. In contrast, Cu is an essential trace element for human beings and it is involved in numerous physiological and metabolic processes. Therefore, the risk of adverse reactions due to dermal contact is extremely low.[2]

In recent years there has been a growing interest in the use of organic-inorganic hybrid materials in medicine, for example protective antibacterial coatings for healthcare devices or dental implants.[3]

In this contribution, biocide coatings for thiol-based photopolymers were investigated. Over the last decade such polymers have been explored for the additive manufacturing of medical devices.[4] First, copper nanoparticles (Cu-NPs) were synthesized according to the protocol of Xiong, *et al*.[5] Due to the non-quantitative conversion of the functional groups in the thiol-ene photopolymerization reaction, free mercapto groups are present on the surface of the cured resin. These moieties have been exploited for the immobilization of the synthesized Cu-NPs exploiting the strong affinity of metallic copper to sulfur.

The formed coating provides a remarkable biocide effect and thus the potential to inactivate pathogens such as SARS-CoV-2, Ebola, Influenza and MRSA at the surface of those photopolymers.

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Formyl thioesters as low-toxic photoinitators for biocompatible resins

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For the production of medical devices, which are in direct contact with human tissue, especially in the case of mucosa or blood, non-network bound components like photoinitiators or their cleavage products, but also residual monomers, stabilizers, degradation products or monomer impurities are of major concern.[1,2] Many of these components state health risks when released to the human body by migration processes.

In this contribution, S-formyl derivatives of aromatic mercaptans have been synthesized and tested successfully as low toxic photo initiators in thiol-(meth)acrylate-based resins. UV irradiation of these molecules leads to a decarbonylation reaction and the formation of highly reactive thiyl radicals. Compared to aromatic thiols, which are also able to form thiyl radicals upon illumination,[3] formyl esters are protected against spontaneous radical/anion formation induced by (hydro)peroxide or basic impurities. These, PIs hardly show any negative effect on the shelf-life of thiol-(meth)acrylate-based resins. Most importantly, the formed cleavage products do not contain reactive aldehyde groups, which are held responsible for skin sensitization reactions, making these PIs interesting for an application in biocompatible resin systems.

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Lignin depolymerisation and use of the products as a sustainable substitute for phenol in resin production

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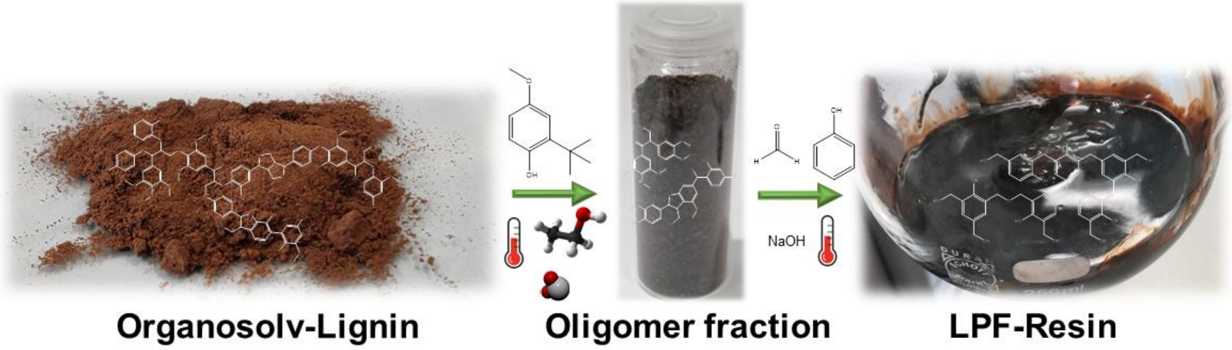
The conversion of lignocellulosic biomass into value-added chemicals and biofuels has been attracting the attention of researchers in recent years. Lignin is an abundant, natural polymer and a major component of lignocellulose characterised by ether linkages, methoxy- and hydroxyl groups. Therefore, it has great potential as a sustainable source to produce basic chemical products.[1] Due to the aromatic structure and the large amount of phenolic hydroxyl groups of lignin and its degradation products, interest as a bio-based substitute for phenol in resins has increased in recent years.[2] In our study, depolymerization and activation of lignin by butylhydroxyanisole (BHA) was investigated with respect to minimising coke formation and maximising the value-added oligomeric fraction. The resulting oligomer fraction was used to produce lignin-modified phenol-formaldehyde resins (LPF) containing 80 wt% lignin. The purchased organosolv lignin, oligomer fractions as well as the resins were characterized using size exclusion chromatography (SEC) to compare the molecular mass distribution. The oligomeric fractions and resins were further characterised by differential scanning calorimetry (DSC), rheometry an thermogravimetric analysis (TGA).



Schematic pathway from organosolv lignin via oligomer fraction to LPF resin

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Multicomponent alginate-based microcapsule post-modified with various polyelectrolytes: Impact on characteristics and in vivo response

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Transplantation of islets of Langerhans encapsulated in alginate-based microcapsules is considered an approach capable of restoring normoglycemia in diabetes type 1 patients.[1] Microcapsules protect encapsulated islets from rejection by the host immune system. The polycation-containing alginate-based microcapsules have shown promising outcomes in clinical trials.[2] However, several studies have indicated that the positive charges of polycations used in the microcapsule design may induce a foreign body reaction and, consequently, graft failure.[3]

This work was aimed at studying the effect of post-modification of the alginate-based polycation-containing microcapsule, involving polyanions sodium alginate (SA) and sodium cellulose sulfate (SCS), and a polycation poly(methylene-co-cyanoguanidine) (PMCG),[4] by various polyelectrolytes, including polycations, on microcapsule characteristics and *in vivo* response. The polyelectrolytes used for post-modification included chitosan, dextran, cellulose, and poly(2-alkyl-2-oxazoline) derivatives. Microcapsules were characterized by various physico-chemical methods and were also implanted intraperitoneally in C57BL/6 mice to assess the effect of post-modification on pericapsular fibrotic overgrowth and stability. This study shows that the post-modification of polyelectrolyte complex-based microcapsules by various types of polyelectrolytes can be used to modulate the microcapsules characteristics and *in vivo* performance.

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Model-guided cellulose nanomaterial acetylation design to tune biopolymer composites

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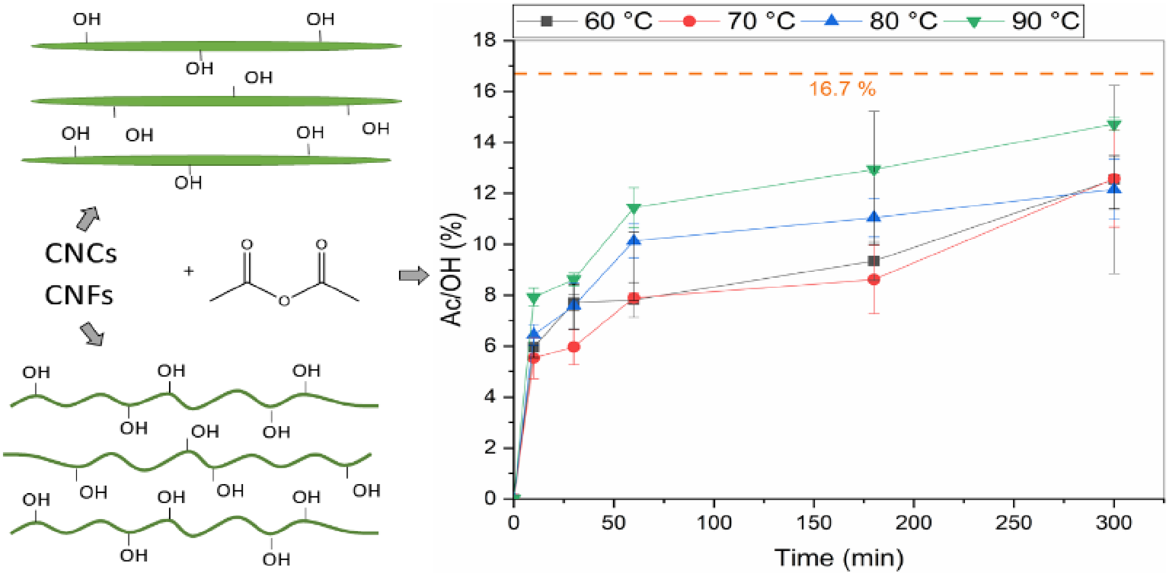
The need for greener materials is emerging and biopolymers have become of focus. Cellulose is particularly interesting because of its wide avaliability, biodegradability and abundancy of surface hydroxyl groups that are susceptible to functionalization. Furthermore, nanoparticles that exhibit high specific surface can be extracted from cellulose. Cellulose nanocrystals (CNCs) are rod-shaped particles, while cellulose nanofibrils (CNFs) are long, fibrilous networks[1]. However, the hydrophilic nature of cellulose and inter- and intramolecular hydrogen bonds cause limitation in practical applications due to aggregation in the non-polar polymer matrices[2]. The solution is to functionalize the surface hydroxyl groups, decrease the free surface energy and provide better dispersion[3].

The aim of this research was to propose the most probable reaction mechanism of cellulose nanomaterials esterification with acetic anhydride through employment of *ab-initio* calculations and to develop a kinetic model. The necessary data was obtained through experimentally carried out reaction. Beforehand, the cellulose nanomaterials were characterized in terms of accessible surface hydroxyl groups, morphology and crystallinity. Lastly, the acetylated nanocrystals were used as a reinforcement in biopolymer films.



Kinetics study of CNCs and CNFs acetylation.

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Is 3-*O*-Methyl-α,β-D-glucose a substrate for alginate producing *Azotobacter vinelandii*?

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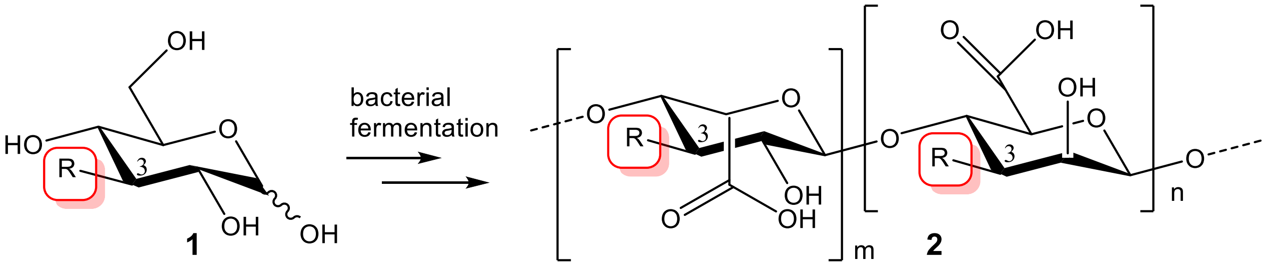
3D Printing in general and 3D bioprinting in particular have become important research fields during recent years showing an exponential increase of contributions in the literature during the last 10 years. 3D bioprinting has paved an avenue for tissue engineering[1] by enabling the fabrication of biobased objects such as blood vessels, skin, cartilage and bone. Carbohydrate based polymers have become valuable materials as basis for bionks.[2] In particular, alginate, a polysaccharide from seaweed, consisting of 1,4-β-D-mannuronic acids and 1,4-α-L-guluronic acid units, which forms long chain anionic oligosaccharide, has been used intensively as bioink. Because of its biocompatibility as well as its solubility, porosity, viscosity, shear-thinning capability properties and hydrogel formation properties this polysaccharide is employed for manifold applications in this respect.[3] Alginate, can be produced by *Azotobacter vinelandii*, a gram-negative bacterium using D-glucose and/or sucrose as main carbon sources.[4]

Herein, we want to investigate if C-3 modified D-glucose units are accepted as substrate by *Azobacter vinelandii* for the biosynthesis of alginate and if the modification is incorporated into the polysaccharide. Experimental details and results of this study will be presented.



R = OCH_3, N_3, C=C, C≡C

Incooperation of C-3 modified D-glucose units during alginate production.

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Initiated chemical vapor deposition of a carbohydrate based polymer

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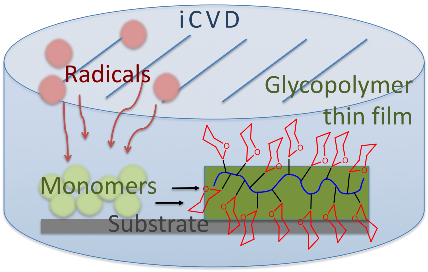
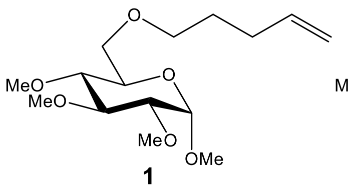
Initiated chemical vapor deposition (iCVD)[1] is gaining more and more industrial significance due to its versatility in polymerizing a large variety of vinyl monomers, the easy thin film processability and scalability. Within iCVD, the monomer and initiator species enter the vacuum chamber as vapors. At a relatively hot filament the initiator decomposes into radicals, which starts with the adsorbed monomer units a free radical chain polymerization on the surface. This technique has demonstrated to produce polymers with conventional structure without loss of functionality or crosslinking,[2] in contrast to most other CVD techniques which fail at retaining the monomer functional groups due to elevated temperature or the presence of plasma.

Synthetic carbohydrate-based polymers are explored as biodegradable, biocompatible, and bio-renewable materials. A thin film of synthetic polymers bearing sugar residues can also offer a good surface for cell attachment and thus, might be applied in biomaterials and tissue engineering. The possibility of having such thin film deposited from the vapor phase would ease the implementation in complex device architectures.

Herein, we investigate if vinyl carbohydrate monomer **1** and acrylate carbohydrate monomer **2** are suitable monomers for thin film polymerization via iCVD. Compounds **1** and **2** were synthesized starting from methyl-α-D-glucopyranoside and polymerized by iCVD leading to thin polymer layers on a Si-substrate. A successful vapor-polymerization of the sugar compound is demonstrated. Experimental details and results will be presented.





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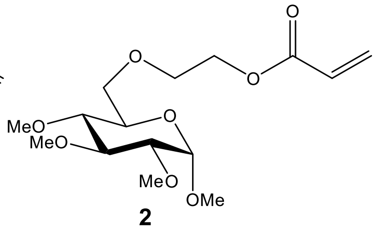

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Schematic of the iCVD process.

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Synthesis of all sugar cellulose conjugates by click chemistry

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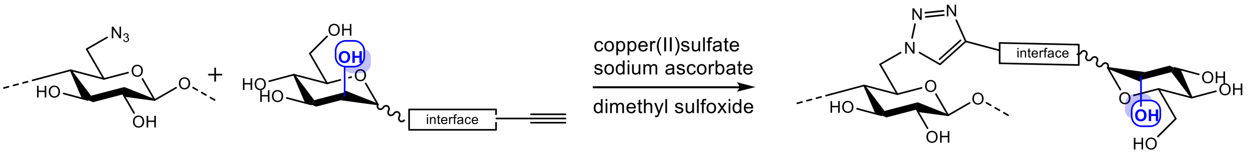
Derivatization of polysaccharides is the most important path to impart further functionalities into the biopolymers and to tailor properties of the biopolymers. In the field of cellulose chemistry, many derivatives have been developed and some are even produced in industrial scale.[1] However, introduction of sophisticated functional substituents require advanced reaction pathways and most of the time the use of rather hazardous reagents. For the modification of the polysaccharide backbone with carbohydrate buildingblocks e. g., glycosylation reactions[2] were studied to generate artificially branched derivatives. In this respect, the copper-catalyzed azide-alkyne cycloaddition was found to be advantageous for the preparation of numerous cellulose derivatives because this reaction proceeds under mild conditions and even in aqueous media.[3] We have demonstrated, that the click chemistry is a versatile tool as conjugation method of small carbohydrate motifs to a cellulose backbone.[4]

Herein, we present the conjugation of alkyne containing D-mannoside components to azide group containing cellulose derivatives. The D-*manno* residues at the cellulose backbone can be considered as recognition units for mannoside specific lectins such as FimH located on the surface of *E. coli* bacteria. As FimH is responsible for host-guest recognition events thereby initiating bacterial urinary tract infection, lectin ligands have potential as therapeutics in adhesion mediated therapy against bacterial infections. Results and experimental details will be presented.



Synthesis of all sugar conjugates from D-mannosides and cellulose via click chemistry

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Solid phase synthesis of various amino acid sequences on chitosan thin films

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Janez Kovač,[b] Martin S. Thonhofer,[a] Patrick Weber,[a] Andreas Wolfsgruber,[a]
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Surface interactions controllable with functionalization of thin films attract much attention and are used as coatings in several industries, from electronics to biomedical applications. Model films offer a direct control of several parameters, such as film thickness and surface morphology and offer many advantages compared to bulk samples.[1] Chitosan model films, to be more specific, could be a potentially great outlet for many surface reactions, because of its amino functional group presence. The surface chemistry of chitosan films could be modified by biofunctionalization involving immobilization of proteins, peptides, as well as glycoconjugates.[2] Herein, we want to develop a concise protocol for on surface immobilization of glycopeptides with a desired amino acid sequence.

A spin coating deposition method for uniform thin films of chitosan onto a solid substrate is applied. Surface changes are analyzed at each step of the experiment with different characterization methods such as profilometry measurements for film thickness, wettability determination by water contact angle, and surface morphology analysis with atomic force microscopy (AFM). Furthermore, elemental composition, as well as chemical state, is determined with x-ray photoelectron spectroscopy (XPS) which aligned, with our assumptions perfectly.

Biofunctionalization is carried out with standard *N*-tert-butyloxycarbonyl (Boc) protected glycine as model substrate and will be observed with an *in-situ* quartz crystal microbalance with dissipation measurement (QCM-D). (Figure 1). Moving forward, biofunctionalization of chitosan surface with synthesized glycoconjugates,[3] composed of a carbohydrate glycon and a lysine residue via an Amadori Rearrangement, is performed. Experimental details and results will be presented.

Figure 1: QCM gold crystal with chitosan film and a biofunctionalized chitosan surface

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Physical properties of thermoplastic starch using dual crosslinking strategy through melt processing

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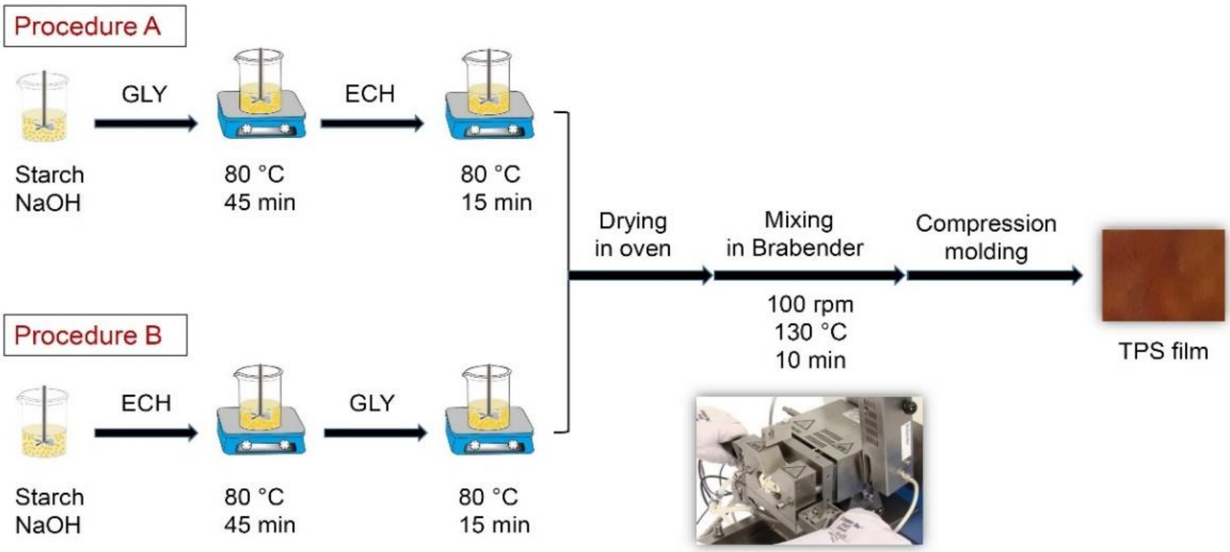
Thermoplastic starch (TPS) is a plasticized nonstructured version of starch. It is usually prepared by incorporation of plasticizers into a starch matrix under heat and shear conditions. TPS materials have attracted the attention of many researchers in the biopolymer industry since they are cost-effective, renewable, abundant in nature, and biodegradable.[1,2] However, TPS suffers from recrystallization phenomena caused by humidity. This evolution is highly detrimental, as it leads to a drastic decrease in its mechanical properties during storage.[3] The mechanical properties of TPS are considered as the important characteristics to achieve success for a broad range of applications.



Process flow diagram for preparation of crosslinked TPS samples

Herein, this contribution is focused on increase the physical stability of TPS toward the improvement of mechanical performance indicated by the increase in the tensile strength. The crosslinked TPS was obtained by dual crosslinking of starch using glycerol and epichlorohydrin in melt processing condition. All results from mechanical properties, DMTA, stability and solubility in water confirmed the formation of both noncovalent and covalent bonds. In particular, a significant increase in the tensile strength and Young's modulus of the crosslinked films was observed. Therefore, the crosslinked TPS produced through this established strategy shows the potential for long-term use in the food preservation and packaging industry.

Acknowledgments This study was supported by projects VEGA 2/0019/18, VEGA 1/0751/21, VEGA 2/0140/20, APVV 19-0487, and APVV 18-0480.

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Influence of crosslinking on the biodegradability of bio-polyester/elastomer - blends

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Polyhydroxyalkanoates represent one of the biomaterials of the future due to their physicochemical properties, biodegradability, and biocompatibility. Poly (3-hydroxybutyrate) and Poly (3-hydroxybutyrate)-co-(3-hydroxyvalerate) (PHBV) with low percentage of valerate units is a promising bio-based and biodegradable thermoplastic but up tp now with restricted industrial applications, due to its brittleness and poor processability, which is caused by a high tendency to recrystallization and a narrow melting intervall.
Rubbery elastomers such as soft low-Tg-PHAs with longer side chains (medium chain length PHAs, mcl-PHAs) and other natural elastomers have been used as impact modifyers.[1,2] To improve rubber dispersion and compatibility between the rubber phase and PHBV and to avoid recrystallization crosslinking/radical grafting was carried out. Besides rheological, crystallization, thermal, mechanical properties especially the biodegradability of these blends was investigated because it is well known, that the length of sidechain, hydrophilicity, crystallinity have strong influence on biodegradability.
In consequence, different extracellular PHB(V)-degrading depolymerases were selected, expressed, and characterized. The purified enzymes were estimated to have an apparent molecular mass between 22.0 and 50.0 kDa. In order to investigate the influence of the elastomaeric blend compound and crossliking on biodegradability a pH dependent assay was established to monitor the degradation. Fluorescein was used to visualize the pH change. Each of the heterologous depolymerases were able to degrade crosslinked PHB/PHBV/elastomer blends. The depolymerase from *P. lemoignei* (P52090) showed the highest activities.[3]

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 860407. BIO-PLASTICS EUROPE project website: www.bioplasticseurope.eu; we thank NaturePlast® for providing us the PHA sanples.

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Impact of long-term polyacrylamide degradation on drag reduction in turbulent pipe flow

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Polymeric drag reduction is lowering the pressure drop associated with turbulence in pipe flow by means of high molecular mass polymer addition. This effect has been widely studied and a vast range of applications has been developed. Polymeric drag reducing agents are applied to reduce pumping costs, to enable higher flow-rates and to increase outlet pressure for example in oil pipelines, fire-fighting or hydraulic fracturing.

These applications are limited by mechanical degradation of the polymers. Shear forces present in turbulent vortices and at the pipe wall can break the polymer backbone. This diminishes the molecular weight and therefore the drag reducing capability.[1] For polydisperse agents the highest weight-fraction provides the main contribution to DR but is also the most prone to breaking.[2, 3]

During the recent years, numerical simulations improved the understanding of the mechanisms which cause polymeric drag reduction. But the majority of current numerical models does not account for chain scission and therefore, they are unable to simulate the long term behaviour of polymeric drag reducing agents in turbulent flow.[4]

Long term drag reduction experiments with polyacrylamide have been performed in a pilot scale flow facility. The facility combines fully developed turbulent pipe flow (in the presented experiments $Re=10^5$) with precise measurement of flow characteristics (flow velocity, pressure drop along the flow path). Utilizing cyclic operation, the polymer solutions were passing up to 70 km. Changes in the molecular weight distribution of the polymer were monitored with triple detection gel permeation chromatography. The experiment verified that not only the mean molecular weight but also the weight distribution determines the level of drag reduction. To our knowledge this is the first time that the importance of weight distribution has been shown in a long-term pilot-scale experiment. The detailed data on polymer degradation provide essential input to incorporate the shear induced polymer degradation into numerical models.

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Reaction control of polycondensations via monomer quantification by HPLC-MS and ^{1}H-NMR spectroscopy

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A complete conversion of monomers is a strongly desired factor in polymer reaction engineering. Residual monomers can affect physical properties like accelerated degradation, changes in glass transition temperature or loss of optical or mechanical properties. Furthermore, a full conversion of monomers to polymer is an important factor because in some cases potentially hazardous residuals have to be removed in a separate step.

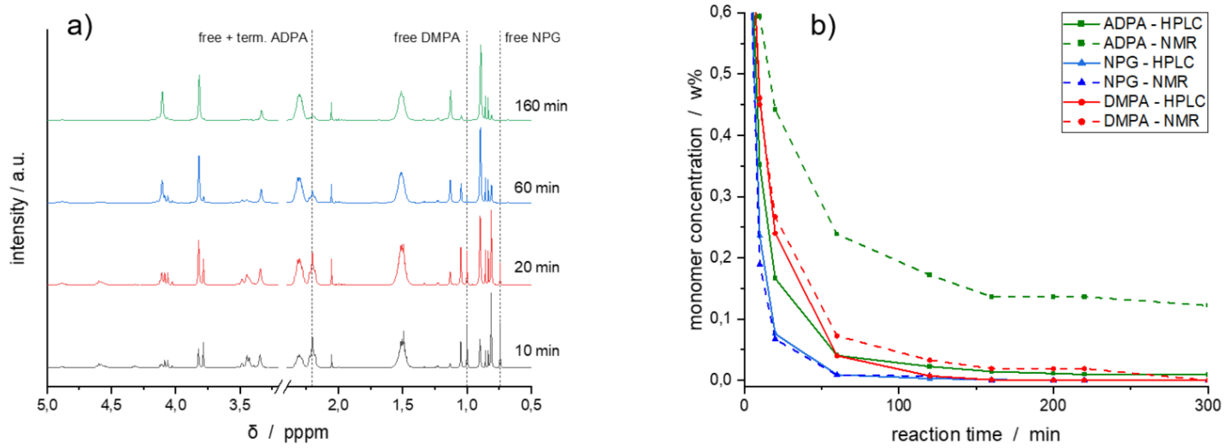

Fig. 1. (a) Time dependent ^{1}H-NMR spectra and (b) decrease of monomer concentration over reaction time in the polycondensation of a three-component polyester system.

Different polyesters containing two to four monomers amongst them isophtalic acid (IPA) and/or adipic acid (ADPA) as diacids, neopentyl glycol (NPG) as diol and dimethylolpropionic acid (DMPA) as bifunctional compound, are produced via melt-polycondensation. As first approach to check the reaction progress, samples were taken during the reaction and analyzed via ^{1}H-NMR spectroscopy, which is already proven as a reliable method.[1] In case of the diols the free monomer is clearly visible as a single peak, but for the acids, polymer peaks and monomer peaks are overlapping and not clearly distinguishable as seen in Fig. 1 (a). Therefore, a HPLC-MS method was developed to monitor monomer concentrations of the acids as well.

In Fig. 1 (b) the reaction progress is visualized by plotting the percentage change of monomer concentration over time. The results for the diol concentrations are very similar for both methods. The big deviation between the adipic acid concentrations obtained by HPLC and by ^{1}H-NMR is due to the fact that the peak of monomer and terminating groups are overlapping in the NMR spectrum which results in a too high value for the monomer concentration. Therefore, a combination of these two methods seems ideal to master the challenges of this complex reaction monitoring task.

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Confocal Raman microscopy: A tool to characterize interdiffusion layers at polymer-polymer interfaces

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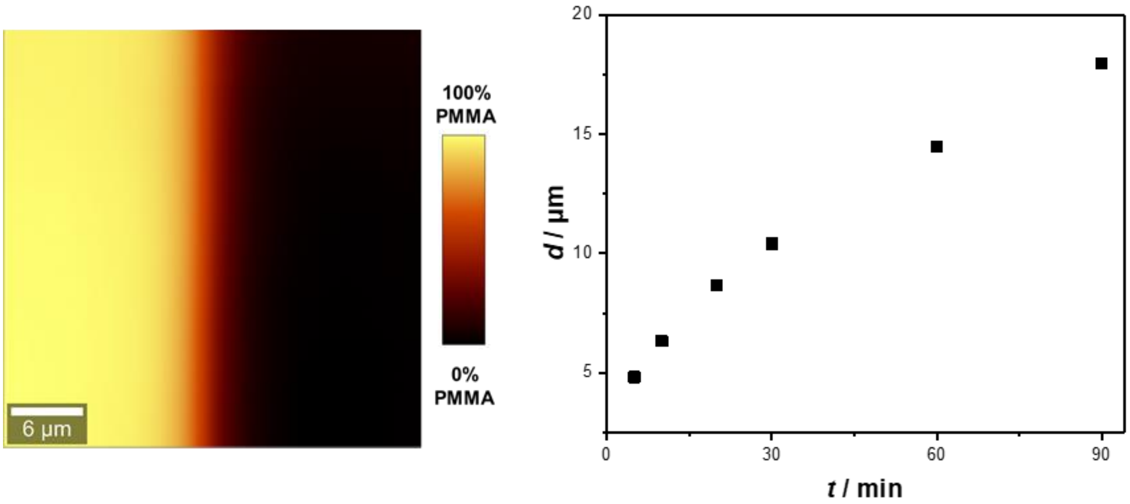
To fulfill the ever-increasing demands for advanced polymer products, the combination of two or more polymeric materials within a multilayer structure is often necessary. The adhesion between the individual layers is of utmost importance to guarantee sufficient product quality. For compatible polymer pairs, the interdiffusion of macromolecules across the interface is the predominant bonding mechanism and the thickness of the interdiffusion layer is a measure for the adhesion strength.[1] Thus, experimental approaches are required to allocate the interdiffusion layer and determine its width. Confocal Raman microscopy has proven to be a well-suited method for this purpose, as it is a label-free technique that enables imaging with a resolution below 500 nm.



Concentration gradient across a polymer-polymer interphase determined via Raman imaging and time-dependency of the interdiffusion layer thickness.

In this work, the dependence of interdiffusion layer thickness on contact time and temperature is investigated for the compatible system poly(methyl methacrylate) and poly(styrene-*co*-acrylonitrile). A set-up for the diffusion under static conditions is developed that allows preparation of highly reproducible samples. The resulting concentration profiles across the interface are determined using confocal Raman microscopy. An evaluation method is developed in order to extract diffusion profiles with statistical significance. With the help of these findings, a correlation between interdiffusion layer thickness, the interlayer adhesion, and the processing parameters can be established. This provides significant insight into occurrences at polymer-polymer interfaces and can aid in the development of multi-layered materials.

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Sorption techniques as a tool for studying the effect of water in pigmented organic coatings

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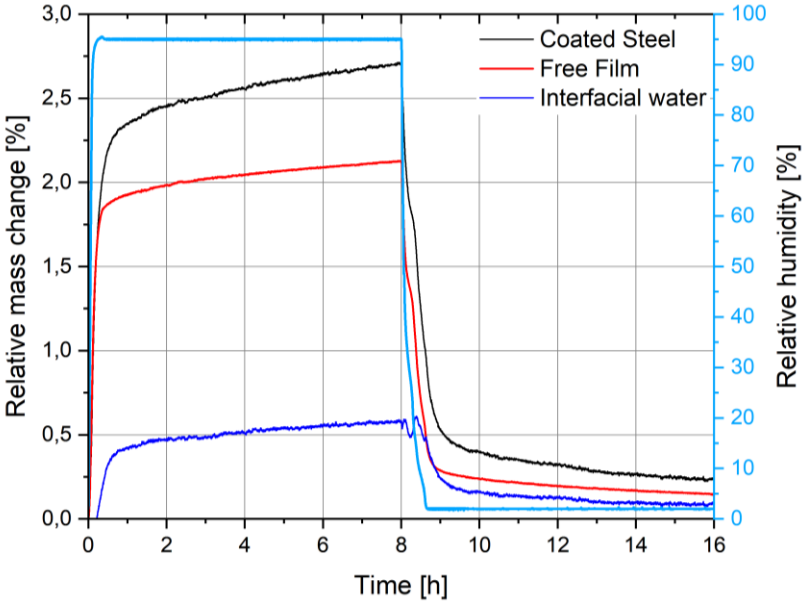
Organic coatings under outdoor exposure are subjected to changing weathering conditions, in particular wet and dry periods. The uptake of water in organic coatings is therefore an important aspect in terms of barrier performance. Water in the coating layer can weaken the adhesion of bonding agents and corrosion can occur. As the equilbrium water contents of organic coatings are typically small (2%-4%), a precise measurement setup is required. A 2-stage sorption process[1] was observed for the measured free films and coated substrates, starting with a fickian diffusion step and subsequent slower mass increase due to swelling. Higher water sorption of coated substrates compared to free films indicated water at the interface.[2] Bosch[3] reported on the plastification of organic coatings by water. Due to the sorption of water in the coating, T_g decreases and hydrogen bridges between binder and water molecules are formed.



2-stage sorption behavior of organic coatings.

Pigmented organic coatings featured higher water uptake than unpigmented coatings. This was explained by water accumulation within the pigment particles and at the polymer-pigment interface. The desorption process revealed a dicontinuous mass loss, which was attributed to the anti corrosive pigment used (zeolithe). The results of the gravimetric method correlated to a manometric technique, for the latter a BET Type II sorption behaviour was determined.

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Superimposed mechanical-environmental ageing testing of electrical steel laminates under hot-dry and -humid conditions

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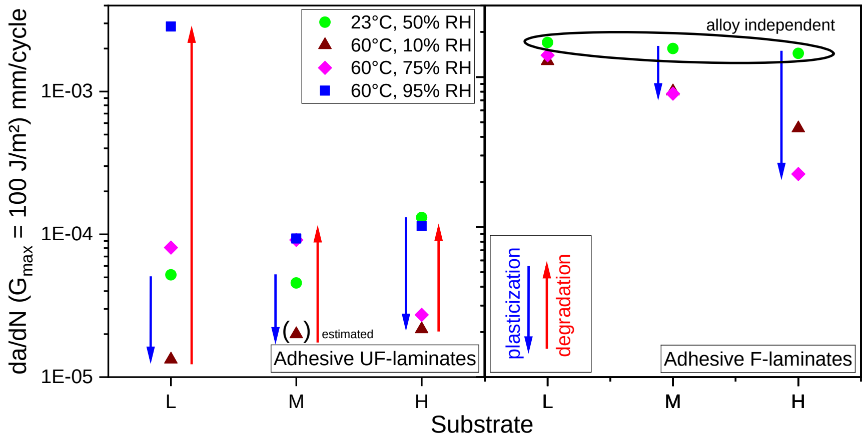
The fatigue crack growth behaviour in adhesively bonded electrical steel laminates under ambient, hot-dry, hot-humid and hot-moist conditions was investigated. A fracture mechanics approach and double cantilever beam specimen were used. Six laminate types based on three different electrical steel alloys (low-, medium- and high-alloyed) and two different epoxy adhesive formulations (unfilled and filled) were examined. Laminates made from the unfilled adhesive exhibited better fatigue performance at ambient conditions (see Fig.). These laminates revealed a crack growth behaviour and a failure mode, which was dependent on the electrical steel alloy. In contrast, a substrate independent fatigue crack growth behaviour and cohesive failure mode was observed for laminates bonded with the filled adhesive.



Crack propagation rate at a defined strain energy release rate (100 J/m²) in ambient, hot-dry, hot-humid and hot-moist (adhesive UF only) environment for all investigated substrates with unfilled adhesive UF (left) and the filled adhesive F (right)

In hot-dry environment (60°C, 10% RH), the fatigue crack resistance was higher for all laminate types. The improved behaviour was explained by increased ductility of the adhesive at 60°C. For laminates based on the unfilled adhesive and low- or medium-alloyed substrates, humidity had an adverse impact on the fatigue crack performance. The failure mode was changing from cohesive in hot-dry to cohesive/interfacial mixed mode in hot-humid environment, in particular for low- or medium-alloyed substrates and the unfilled adhesive. Fatigue tests in hot-moist environment (60°C, 95% RH) exhibited an accelerated crack propagation and mainly interfacial failure for laminates bonded with the unfilled adhesive. In contrast, laminates based on the filled adhesive and low- or medium-alloyed substrates were almost unaffected by increased humidity. Laminates made from the high-alloyed substrate and the filled adhesive revealed an even better performance in hot-humid environment. This phenomenon was attributed to better corrosion resistance of the high-alloyed steel and water vapor induced plasticization of the adhesive. Tensile tests on single adhesive films exposed to hot-humid environment confirmed the plasticization effect. The filler reduces presumably the ingress of water vapor into the adhesive layer and to the steel/epoxy interface.

Development of polyolefinic liner materials with enhanced high temperature resistance

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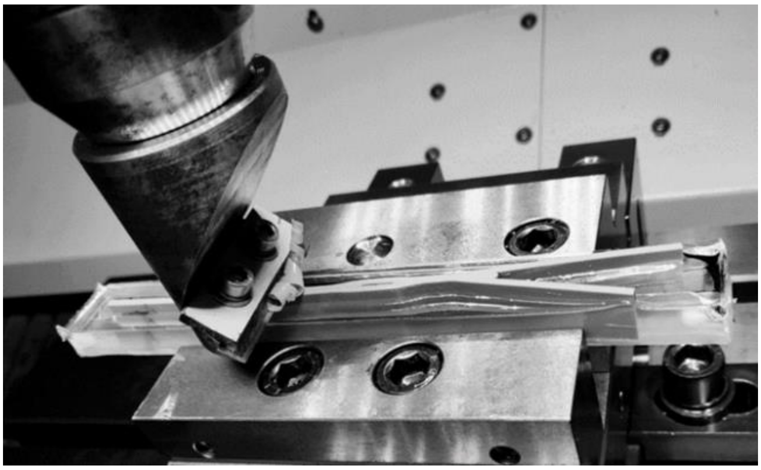
To compensate fluctuating renewable energy sources and heat demand, large thermal energy storages are of utmost importance in district heating networks. Pit thermal energy storages are based on polyolefinic liner materials preventing water losses to the underground. Due to increasing operating temperature levels up to 95 °C and desired lifetime values of more than 30 years, novel polyolefinic liner materials with enhanced durability are under development. For efficient screening of material formulations and welding seams, an lifetime testing method based on micro-sized specimen was used.

While elevated temperature is a common acceleration factor in lifetime testing, miniturization of specimen is a further option due to diffusion limited degradation phenomena.[1] As shown in the Figure below, polyolefin based slices with a well-defined thickness in the range from 50 to 500 µm were manufactured and aged in hot water, damp heat and dry heat at temperatures ranging from 95 to 135 °C. Aged samples were characterized using analytical tools such as HPLC, GPC, DSC or FT-IR and tensile testing. The investigations clearly revealed that the ageing behaviour of commonly used liner materials based on polyethylene raised temperature grades (PE-RT) is more critical in hot water than in dry air. Degradation of PE-RT was significantly diffusion-limited and much more pronounced for microsized specimen. In contrast, ageing of polypropylene random copolymer grades (PP-R) was less diffusion-limited which was attributed to the lower degree of crystallinity and a fine-spherulithic sheaf-like microstructure. A better long-term stability was ascertained for novel PP-R grades with an optimized triple stabilizer package. Hot wedge welding had a negligible impact on stabilization and ageing behaviour.



Micro-sized specimens taken from welded liners by CNC-milling

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Passivation layer thickness of various metal substrates and their interaction with epoxy varnishes

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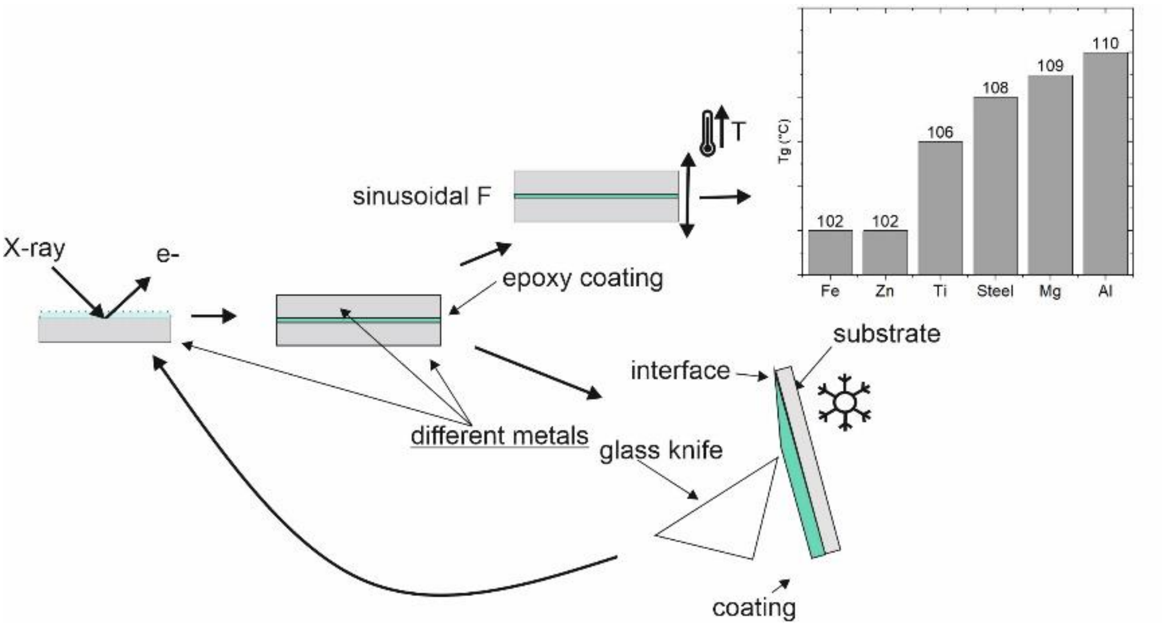
Bonding of metal surfaces with adhesives is heavily influenced by the base-acid interaction between the coating and the metal surface. The isoelectric point of metal oxides, which describes if the surface acts more acidic or basic, varies vastly for different metal oxides.



Schematic representation of the experimental testing and characterization steps

For that reason, sheets of different pure metals were commercially purchased, characterized and coated with epoxy-based varnishes. With dynamic mechanical analysis we could show that the glass transition temperature of the epoxy-based coating is dependent on the metal substrates. Furthermore, the metal surfaces were characterized by X-ray photoelectron spectroscopy (XPS). Beside the detection of impurities on the surfaces, the individual thicknesses of the different metal oxides were determined by evaluating the ratio between the metal and metal oxide photoelectron peaks. To access the interface of the metal oxide reacted with the epoxy-based coating cryo ultra-low angle microtomy (cryo-ULAM) is introduced in order to investigate the uncovered layer with XPS.[1]

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On the importance of sample preparation in polymer mass spectrometry

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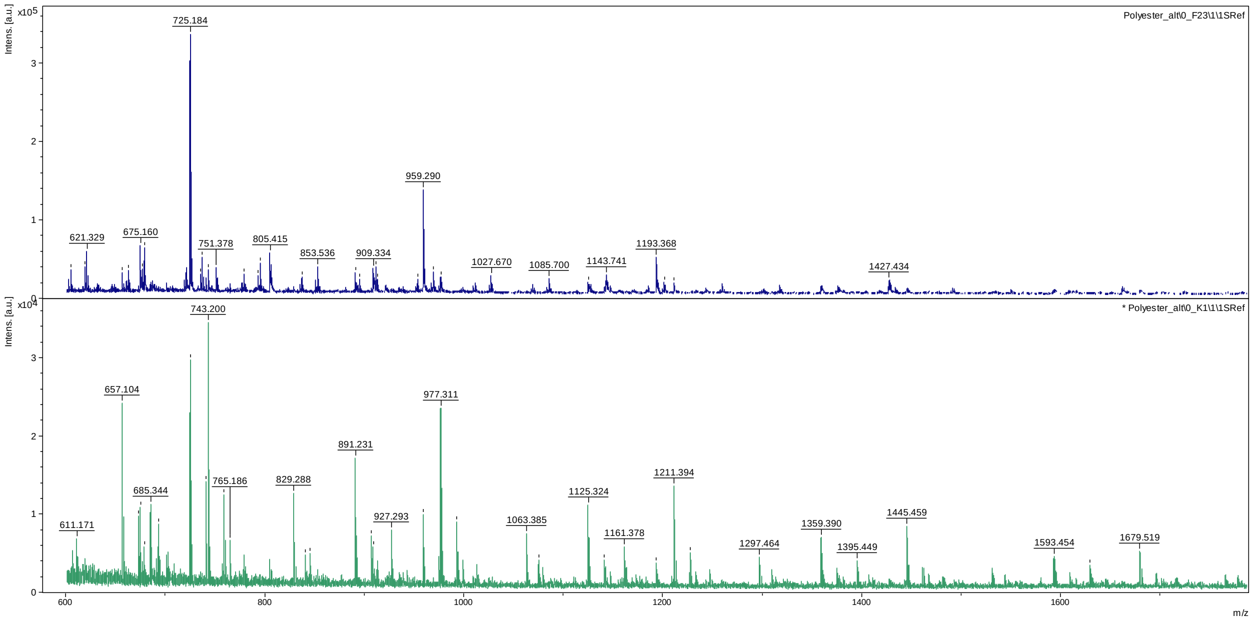
Polymer analysis with MALDI mass spectrometry is a straight forward technique as it offers a wealth of information such as starting and end groups, comonomer distribution, and molar mass / molar mass distribution.[1] Unfortunately, getting those data is very much dependend on how the sample is prepared. The first and most important choice is the matrix, which is necessary to transfer the laser energy onto the polymer molecules. But also the salt and even the solvent can have a great impact on the obtained results.[2-4]



MALDI mass spectra of the same polyester using different matrices showing improved sensitivity for cyclic moieties using DCTB (top) vs. DHB (bottom).

Polyesters are rather complex polymer systems as even a simple linear 2 component polyester can be comprised of molecules with 3 different combinations of end groups as well as cyclic molecules. In this work we investigate multicomponent polyester systems and how sample preparation influences the information obtained from the MALDI mass spectra.

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Experimental study of small hydrocarbons diffusion in semi-crystalline polyolefins interpreted by Free Volume Theory

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Transport of monomer(s) is an essential topic in polymer reaction engineering. Studying the diffusion of monomers in complex semicrystalline polymer structures is improving our knowledge about diffusion and relaxation processes. The aim of this work is the high-quality experimental and systematic investigation of diffusion in semicrystalline polyolefins by differential pressure decay method.

Investigation of small molecules gases is performed on our assembled differential pressure decay. Chamber with polymer sample is systematically pressurized/depressurized to observe pressure evolution due to sorption/desorption into/out the polymer sample. Repeating of high number of experiments across wide concentration range is time effective due to automated experimental procedure. Each diffusion pressure evolution is then processed to obtain single diffusion coefficient.

The objective of our research is to investigate the transport of light-hydrocarbon molecules in semi-crystalline polymers. Polyolefin morphology with stacked crystalline lamellae and the presence of two different amorphous regions represented in Figure 1 is creating the situation with different permeability regions for monomers.

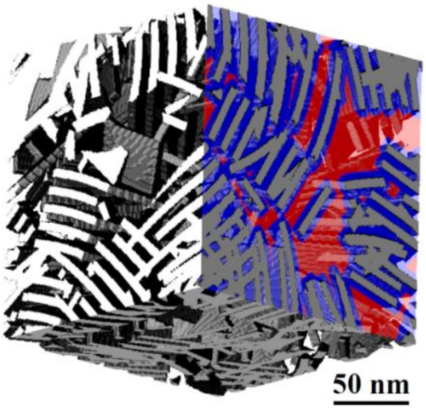

Figure 1: 3D image of semi-crystalline polyethylene. Grey parts represent crystalline phase, red is free amorphous phase and blue is constrained amorphous phase.[1]

Recently modified apparatus is providing equal sorption and desorption ethylene diffusion coefficients and thus thermodynamically correct result. In this contribution we are comparing ethylene diffusion in amorphous phase of various density grades PE to demonstrate effect of impenetrable crystalline phase presence at various temperatures.

Next goal is the extension of diffusion measurements to larger molecules (e.g., propylene, butene or 1-hexene). Sorption isotherms will be measured to calculate volume fraction of penetrant in amorphous phase to compare diffusion coefficients across monomer types. Penetrant volume fraction will be also used for mathematical modelling of diffusion.

Currently we are employing Fickian approach with advanced evaluation program to obtain diffusion coefficients. Disadvantage of this approach is no information about concentration dependency of diffusion coefficient. Free Volume Theory model [2] will be used to interpret concentration dependency of diffusion coefficient and to determine polymer sample fundamental constants.

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Polymeric Donor Materials in Organic Photovoltaics

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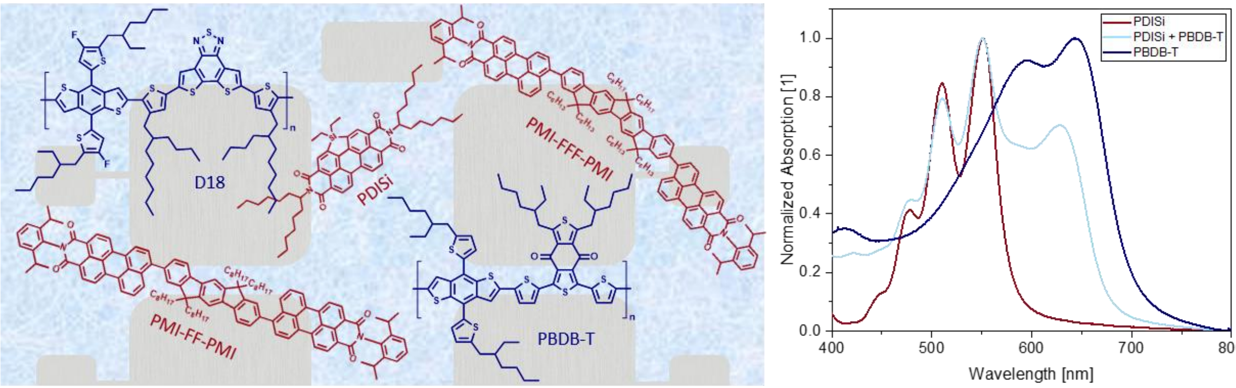
Organic photovoltaics are an emerging technology undergoing a lot of research in the last decade. The absorbing layer of these devices contains an acceptor and a donor molecule, responsible for efficient charge generation and transport. Hereby, non-fullerene acceptors blended with polymeric donors are the most promising composition of the photoactive layer by now and they can reach efficiencies up to 18%.[1]



Polymeric donors and small molecule acceptors used in solar cell devices and an example of absorption spectra of a donor (PBDB-T), an acceptor (PDISi) and the blend used in solar cells.

Herein, we present non-fullerene acceptor materials based on a perylene structure (PDI-Si, PMI-FF-PMI, PMI-FFF-PMI) in combination with some of the most common and most efficient polymeric donors currently used in research, namely PBDB-T and D18. The latter contain fused-ring parts and side chains consisting of aromatic rings combined with branched alkyl chains making them soluble and easily processible. These donor molecules possess a high absorption in the visible range that is complementary to the absorption spectrum of our acceptor molecules, which makes this combination of materials highly suitable for organic photovoltaic devices.

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π-Conjugated polyHIPE beads prepared by Knoevenagel condensation reaction

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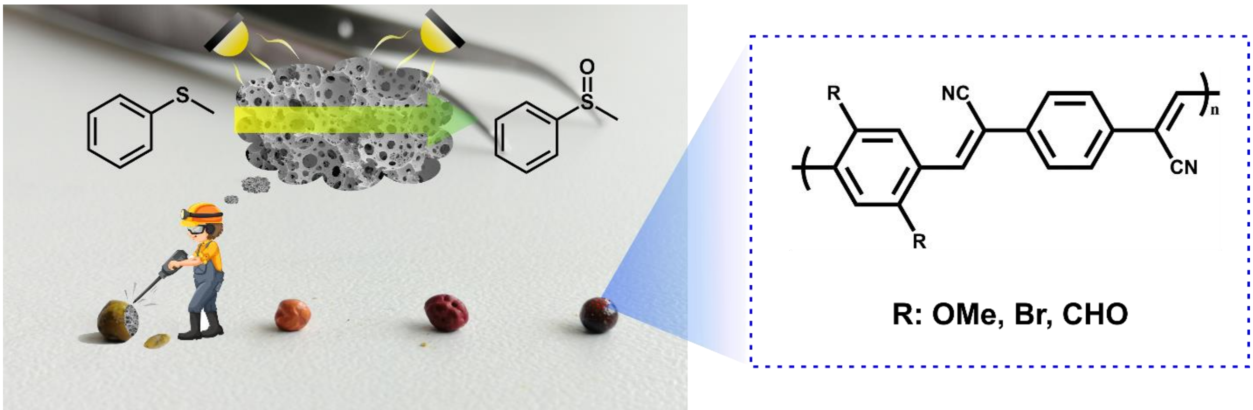
Conjugated porous polymers (CPPs)[1] and especially emulsion-templated ones are an emerging class of porous materials that play an important role in advanced energy and catalysis applications. Conjugated polymerized high internal phase emulsions (HIPEs), referred to as "*π-conjugated polyHIPEs*," are a unique subclass distinguished from other CPPs by additional porosity on a larger length scale (pore sizes between 1–100 µm). The HIPE-templated conjugated polymers are currently synthesized exclusively via transition-metal catalyzed step-growth[2] or chain-growth polymerization[3] and the synthesis process can only produce porous monoliths. While the residual transition metals in the macromolecular structures affect the catalytic performance, the use of a metal-free polymerization chemistry for the preparation of crosslinked polyHIPEs warrants further exploration.



π-Conjugated polyHIPE beads prepared by Knoevenagel condensation reaction for the photocatalytic oxidation of thioanisole

In this work, we therefore demonstrate a remarkably simple and rapid synthetic route that combines an amino-catalyzed Knoevenagel condensation reaction and a non-aqueous oil-in-oil-in-oil (O/O/O) HIPE-based double emulsion system to produce previously unreported highly porous π-conjugated polymer beads. The synthesized millimeter-sized poly(arylene cyanovinylene)-based polyHIPE beads were tested for their photocatalytic activity in visible light-driven aerobic oxidation of thioanisole to methyl phenyl sulfoxide. The reaction was found to be nearly quantitative with excellent chemoselectivity (>99 %).

References:

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Shape memory behavior of porous cross-linked poly(ε-caprolactone) prepared by organocatalyzed ring-opening polymerization within high internal phase emulsion

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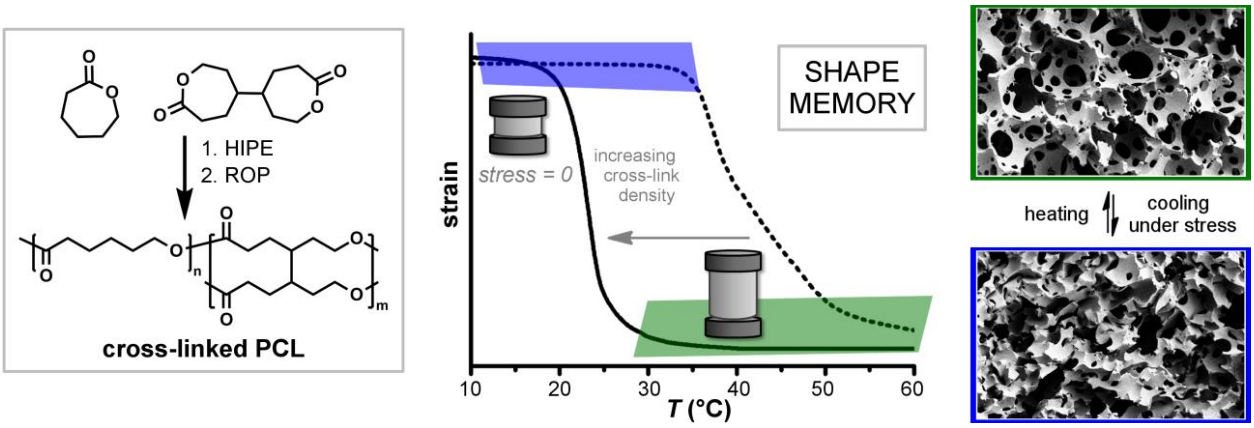
High internal phase emulsion (HIPE) templating offers a route to produce highly interconnected porous polymer foams. Polymerized HIPEs (polyHIPEs) based on poly(ε-caprolactone) (PCL) are attractive due to the good biocompatibility, degradability and control over mechanical properties of PCL. Furthermore, PCL is a semi-crystalline polymer and as such can exhibit shape memory behavior when cross-linked. Porous shape memory polymers can achieve high deformations and have recently become of particular interest in biomedical applications.

In this work, polyHIPEs based on cross-linked PCL were prepared by organocatalyzed ring-opening polymerization (ROP) of ε-caprolactone and 4,4'-bioxepanyl-7,7'-dione within an oil-in-oil HIPE at 50 °C. The thermomechanical properties of the prepared polyHIPEs were studied and found to be strongly dependent on the degree of PCL cross-linking. The melting and crystallization temperatures as well as the degree of crystallinity of PCL-polyHIPE foams decrease with increasing degree of cross-linking. Semi-crystalline polyHIPEs exhibit shape memory behavior with excellent shape fixity and shape recovery as evaluated by cyclic thermomechanical tests. At appropriate degree of PCL cross-linking, the polyHIPE temporary shape can be fixed at room temperature, while a transition to permanent shape occurs when heated to 40 °C. Moreover, a two-way shape memory behavior of the PCL polyHIPEs was observed under the constant stress.[1]



Porous cross-linked PCL prepared by organocatalyzed ROP within HIPE demonstrates shape memory behavior where the transition temperature depends on the cross-link density.

References:

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Shape-memory EPDM/thermoplastic-blends

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Shape-memory polymers (SMPs) are smart materials that can recover from a temporary shape deformation into a predetermined configuration upon external stimuli. Typical triggers are temperature changes, electricity, light or magnetism. Research on SMPs has been fueled by their potential applications in numerous fields, such as biomedical devices, soft robotics, construction or aerospace industry.[1,2] Within a variety of possible routes, polymer blending is a convenient approach to fabricate material systems exhibiting shape memory behavior.[3]

Within this work we present the investigation of dual- and multi-SMPs based on immiscible blends of ethylene-propylene-diene monomer rubber (EPDM) with different thermoplastics (PE, PP or PP-c-PE).

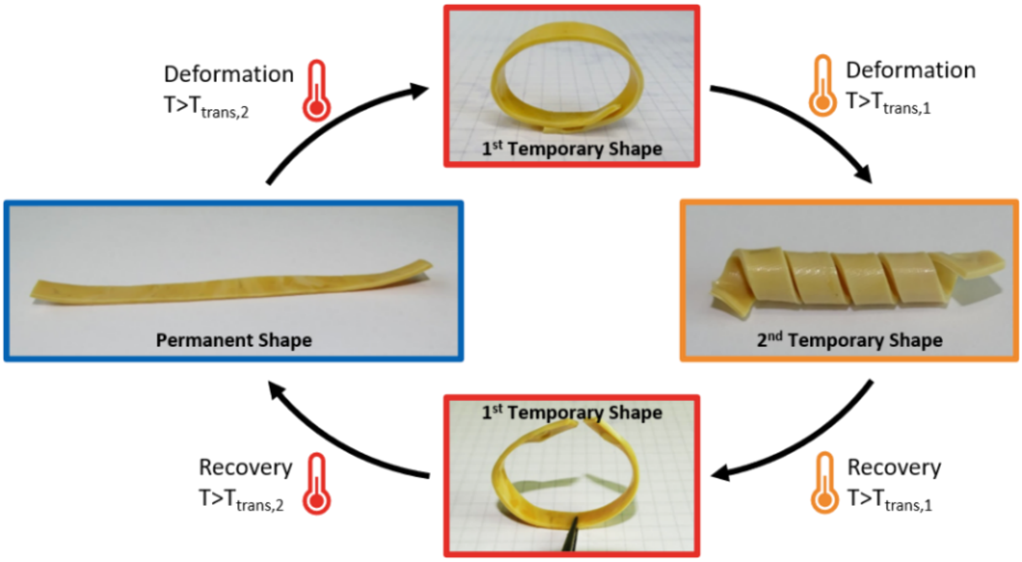

Fig. 1: Triple-shape-memory cycle

Vulcanization characteristics and mechanical properties were investigated by rheological measurements and tensile testing respectively. Dynamic mechanical thermal analysis (DMTA), used to characterize the shape memory behavior, shows maximum fixity rates of up to 98% combined with shape recovery rates of 97% in dual-shape cyclization. Results indicate the tunability of thermo-responsiveness and blend morphology by variation of the elastomer/thermoplastic ratio as well as the choice of polymers. Further, triple- and multi-shape features of selected systems were studied.

References:

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Detection of biomolecules via molecularly imprinted photonic crystal sensors inspired by chameleon skin structures

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The progress of wound healing can be monitored by sensing the increasing concentration of collagen produced in wounds. For the detection of this biomolecule, we developed a hydrogel based on an easily readable color-changing sensing material. Inspired by the nanostructures found in chameleon skin [1], which contains highly organized photonic patterns able to shift the reflection wavelength, and by this means, appearing in different colors, we synthesised molecularly imprinted polymers (MIPs) with ordered crystalline arrays to reflect a visual signal. For this purpose, highly ordered opalescent silica nanoparticles (SiNPs) acted as structure giving matrix which was infiltrated with a solution of methacrylic acid (MAA) as functional monomer, ethylene glycol dimethacrylate (EGDMA) as crosslinker, and an epitope of collagen as the template molecule. After photo-polymerization of these monomers, the SiNPs and the peptide-template were fully removed by etching with hydrofluoric acid resulting in an inverse opal photonic structure [2] in the collagen imprinted polymers. This photonic structure is intended to change its reflected wavelength upon the specific rebinding of collagen, and thus to detect the presence of this biomolecule. This novel approach is being optimized under different preparative conditions and shall allow obtaining a promising sensing material convenient for the detection of biomolecules and their concentration by an easily naked-eye readable color-changing signal upon binding [Fig. 1].

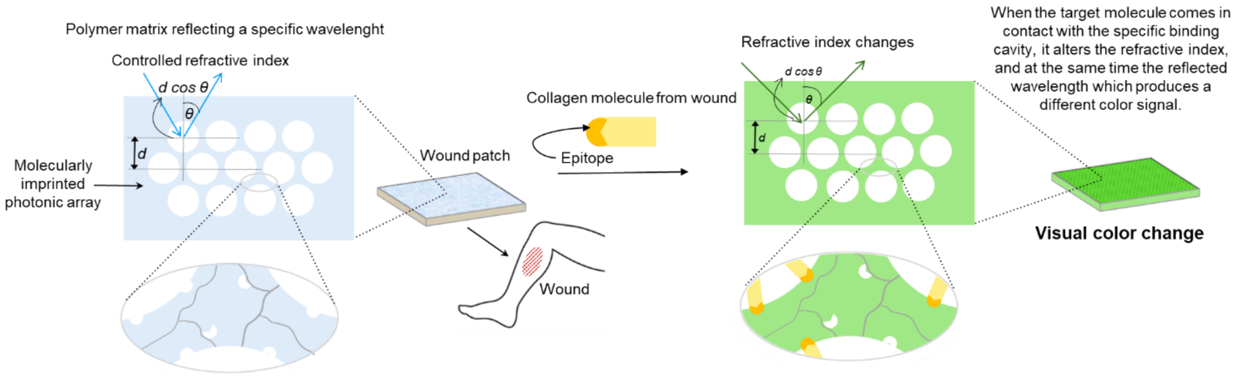

Figure 1. Proposed approach of the visual color-change produced by a shift in reflected wavelength upon selective binding of the target biomolecule.

References:

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Two-dimensional CVD-graphene/polyaniline heterostructures

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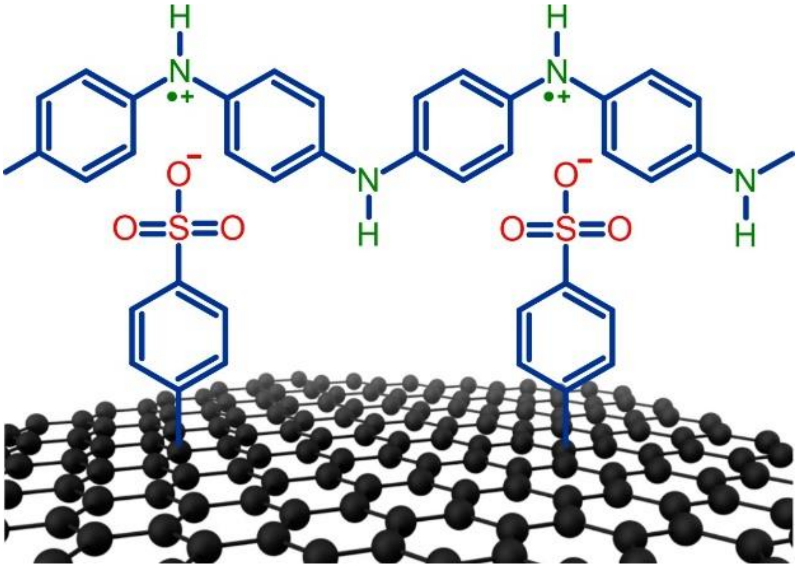
Supercapacitors complement lithium batteries in applications needing high power density. Nanocomposites of graphene materials and polyaniline have been extensively studied as promising materials for electrodes of supercapacitors. While most researchers have combined various graphene and polyaniline nanostructures, there remained a lack of knowledge of the electrochemical transitions in both components. The lack of knowledge was probably caused by the fact that the reported graphene/polyaniline nanocomposites may not be fully uniform in terms of their composition, distribution, and structure.



Schematics of the two-dimensional graphene/polyaniline heterostructure

Here, we present a graphene/polyaniline heterostructure consisting of a CVD-graphene and polyaniline monolayer and its electrochemical operation in a supercapacitor. The synthesis employs functionalization of graphene by *p*-phenylene sulfonic groups and oxidative polymerization of anilinium by ammonium persulfate under reaction conditions, providing no bulk polyaniline. Scanning electron microscopy, atomic force microscopy, and Raman spectroscopy showed the selective formation of polyaniline on the graphene. In situ Raman spectroelectrochemistry and cyclic voltammetry (both in a microdroplet setup) confirm the reversibility of polyaniline redox transitions and graphene electrochemical doping. After an increase within the initial 200 cycles due to the formation of benzoquinone−hydroquinone defects in polyaniline, the specific areal capacitance remained for 2400 cycles with ±1% retention at 21.2 μF cm^{-2}, one order of magnitude higher than the capacitance of pristine graphene.[1]

References:

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Polystyrene microspheres as template for the formation of honeycomb-structured metal sulfide thin films

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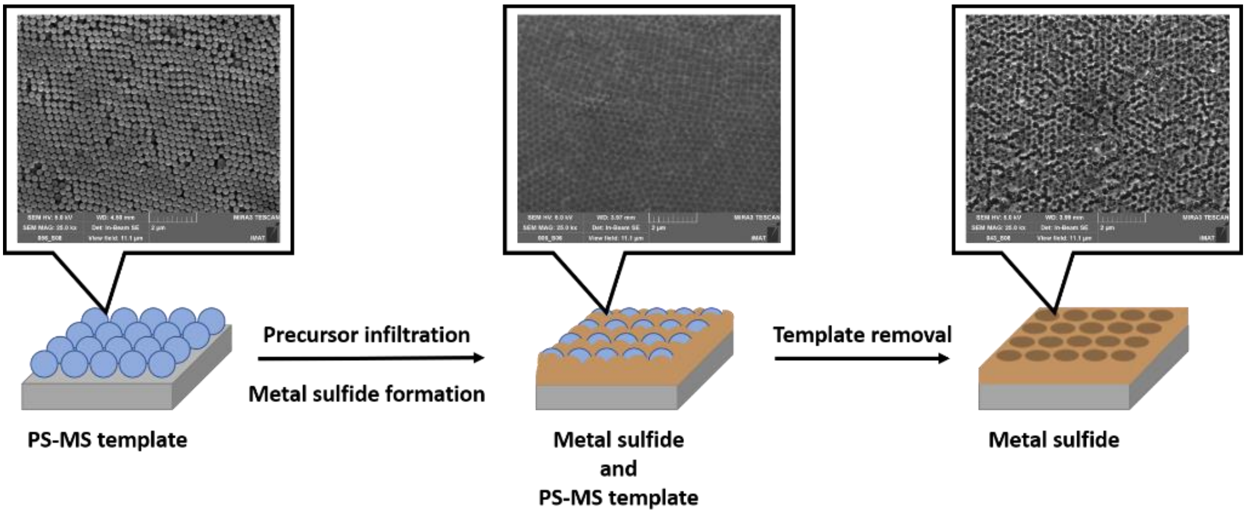
Metal sulfides show an increased interest as they can be employed in a broad area of applications, including solar cells, light-emitting diodes, lithium-ion batteries and others.[1] In literature, there are many reports for the synthesis, characterization and application of metal sulfide films, but only a few deal with structured metal sulfide films. Most of the routes towards structured metal sulfides employ templates, such as lyotropic liquid crystalline templates,[2] and mesoporous silica.[3] Microsphere colloidal lithography is also a templating technique that utilizes monodispersed colloidal particles, such as polystyrene microspheres (PS-MS), as template for the formation of periodically ordered arrays.[4]



Preparation process including SEM images for the formation of highly structured $CuInS_2$ films with the use of a PS-MS template.

Our research is focused on the novel synthesis of honeycombed-structured metal sulfide films via the microsphere colloidal lithography technique. The process consists of three steps, the PS-MS template formation, the metal sulfide precursor infiltration followed by the conversion to the metal sulfide and finally, the template removal. The properties and features of the films are studied via several techniques such as profilometry, FT-IR spectroscopy, X-ray diffraction (XRD) and scanning electron microscopy (SEM).

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A natural rubber waste derived surfactant for high internal phase emulsion templating of poly(dicyclopentadiene)

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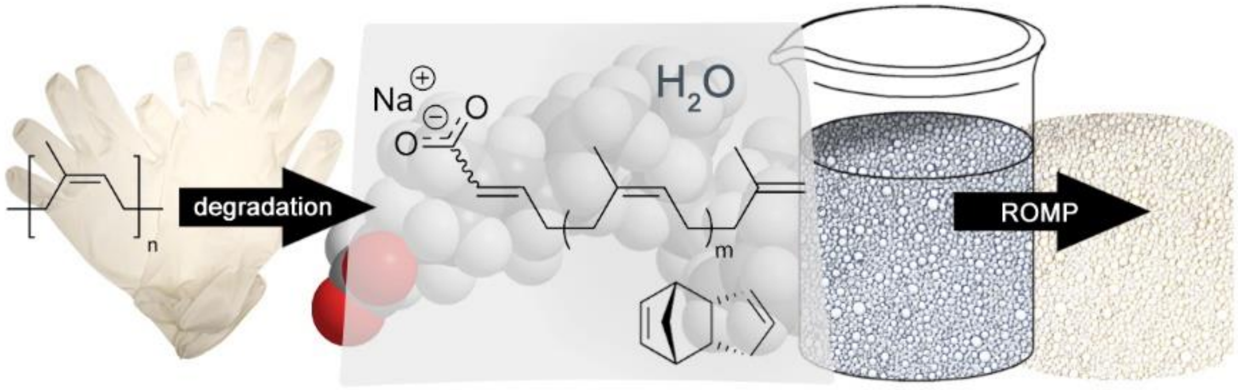
[b] *Christian Doppler Laboratory for Organocatalysis in Polymerization, Stremayrgasse 9, 8010 Graz, Austria; e-mail: viktor.schallert@tugraz.at*

The upcycling of natural rubber (*cis*-1,4-polyisoprene, NR) waste to an ionic stabilizer with a low hydrophilic lipophilic balance is presented.[1] In a first step, the NR glove waste (from laboratory grade rubber gloves) is thermally pre-degraded to yield a solution of short NR chains in toluene (M_n = 1300 g/mol, according to SEC in THF relative to poly(styrene)). Subsequent further degradation is then achieved by cross metathesis with methylacrylate. This approach allowed for reducing the catalyst loading compared to a previously reported degradation protocol using NR snippets.[2] The resulting semi-telechelic oligomer mixture (exhibiting an average number of m of 6.5) is then saponified, yielding a mixture of amphiphilic carboxylic acid sodium salts soluble in cyclohexane.



Preparation and use of the natural rubber waste derived surfactant

The product mixture was then used for the stabilization of water in dicyclopentadiene high internal phase emulsions (HIPE). The versatility of the resulting HIPE was demonstrated by polymerizing the continuous dicyclopentadiene phase via Ring-opening Metathesis Polymerization yielding macroporous poly(dicyclopentadiene) foams[3] with a porosity of 82 %. The use of the ionic surfactant allows for the preparation of foams, which are resistant to absorb water. This property was hitherto not accessible with protocols involving the use of non-ionic surfactants commonly employed in emulsion templating of polymers.

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Sustainable plastics recycling in a global context – General framing and a case study on recyclate quality

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While there is growing awareness for the challenges in terms of recyclate quality and poor physical properties of post-consumer recyclates,[1] the global dimensions and societal implications of plastics recycling are often overlooked, in particular in polymer science and engineering debates. We have recently suggested[2] to use the United Nations Sustainable Development Goals (SDGs) as a comprehensive benchmarking framework for truly sustainable plastics recycling. Introducing three thematic SDG-Nexus-Clusters[2], we found that the issue of waste picking and informal plastic recycling in developing countries[3,4] is at the very core of the *Recycling-Development-Nexus* illustrated in Fig. 1 (a). There is a need to combine the strive for quality recyclates with ambitions to improve on the social and developmental aspects of the circular plastics economy in a global context. We hence investigated the performance profiles of polyolefin recyclates sourced from waste picking activities in Nairobi, Kenya[4] using a methodological toolkit comprising techniques for both physico-chemical analysis (DSC, TGA, and FTIR microscopic imaging) and engineering property characterization (melt flow rate, tensile, and impact strength testing). While inclusions of foreign polymers and other phases (Fig. 1 (b)) are typical for poorly treated recyclates, we demonstrated that significant improvements in recyclate quality, including a 3-fold increase in notched impact strength (NIS) of rPE-HD, can be achieved through a sophisticated state-of-the art reprocessing workflow (Fig. 1 (c)).

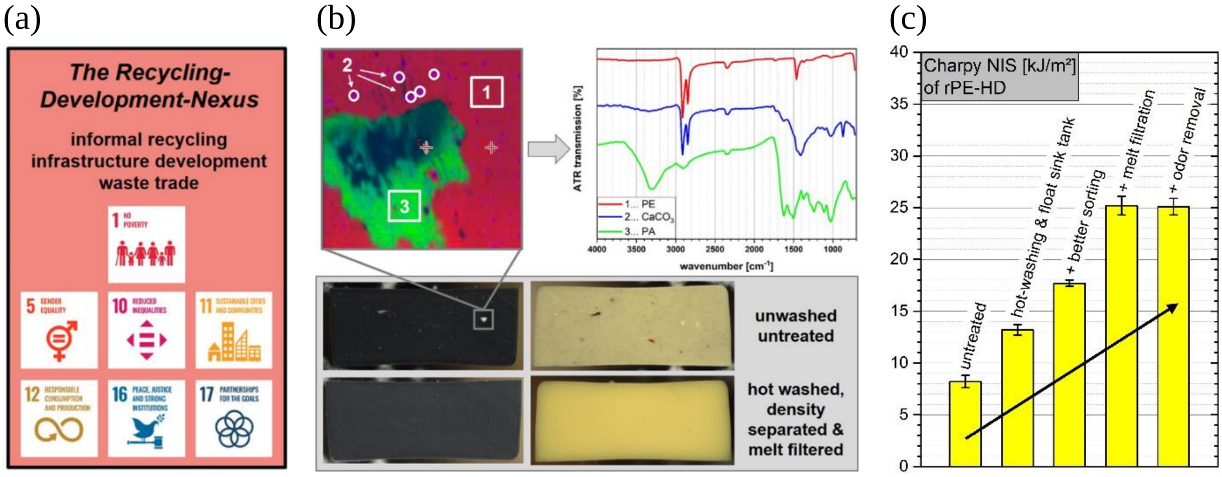

Fig. 1: (a) The Recycling-Development-Nexus in the SDG framework; (b) Cross-sections of rPE-HD specimens (black & yellow) of different qualities including FTIR image and spectra of inclusions; (c) evolution of Charpy NIS of rPE-HD with increasingly better treatment.

References:

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Solubility of solar encapsulants – improvement of recycling processes

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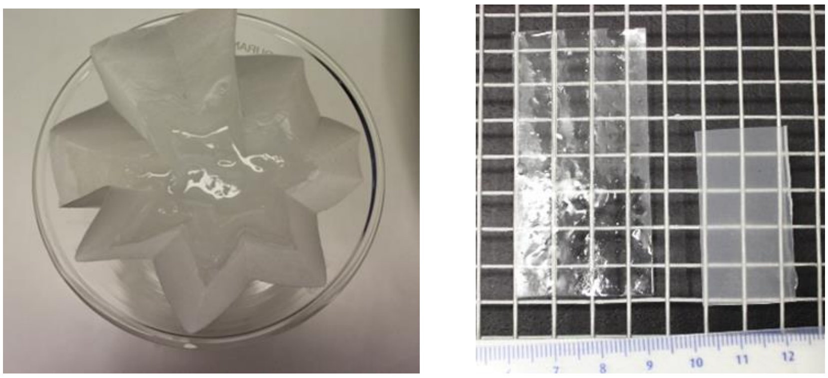
Sufficient protection of solar cells is essential during the lifetime of a photovoltaic (PV) module. Therefore, a polymer encapsulant is used in addition to the front glass and backsheets. Crosslinked ethylene-vinyl acetate (EVA) is currently the dominant encapsulant material[1] in PV modules. Recently, an interest in new encapsulant materials based on thermoplastic polyolefines (PO) has increased to overcome the issues of EVA[2,3] and also meet the challenges of newly designed sustainable photovoltaic modules. The enhanced solubility of PO compared to EVA is beneficial considering economic and ecological End-of-life management. From a recycling point of view, preferably all individual layers of the PV module undergo a separation process. Chemical separation through solvents as a first step in the recycling of PV modules with EVA encapsulants has been previously investigated.[4] For new PO-based encapsulant materials, no information in regard to solubility is available.



Swollen and the untreated PO material (left) and precipitated PO material at room temperature after dissolution at elevated temperature (right)

The aim of this work is to investigate the solubility behaviour of a newly developed polyolefinic encapsulant compared to the most widely used ethylene vinyl acetate (EVA) in the context of separation for recycling purposes. The focus was on environment compatible assessed solvents in comparison with conventional solvents under different thermal conditions.

Important material characteristic for solubility behaviour like surface energy, wettability and thermal behaviour were investigated by infrared spectroscopy, differential scanning calorimetry, zeta potential and contact angle measurements. The degree of solubility and swelling was gravimetrically determined.

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Thermodynamics for ethylene polymerization process in liquid phase

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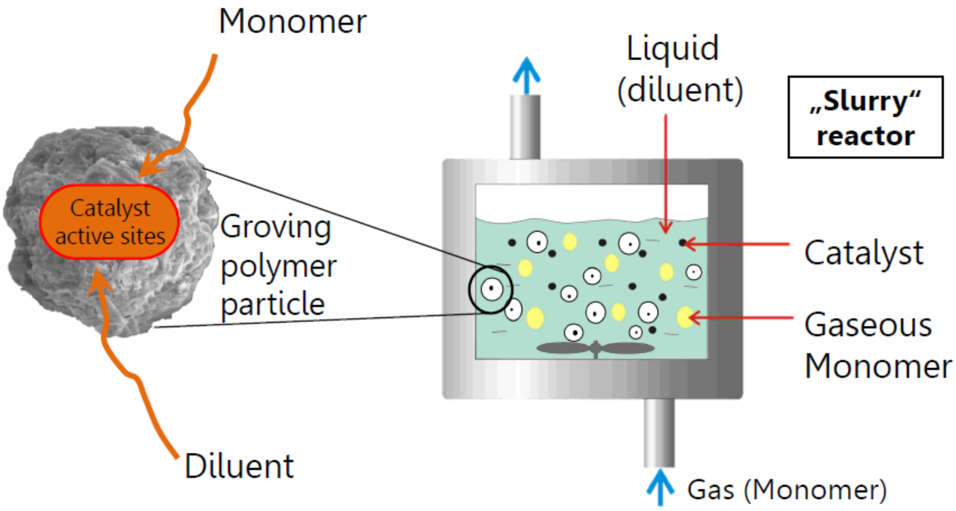
The knowledge of thermodynamic data relevant to the reaction mixture are crucial to operate any polymerization process. Our research is focusing on catalytic ethylene polymerization process and thermodynamic behaviour of its components. Such process can be performed in gas phase or liquid phase (see Figure below) and the related thermoynamic data may vary significantly for these two different processes.



Liquid phase reactor (so called "slurry" reactor)

Several researches were focusing on sorption and swelling equilibria related to gas-phase ethylene polymerizaton[1] but only a few on liquid-phase equilibria[4,5]. In this contribution we present data relevant for slurry polymerization, i.e., sorption equilibria in polymer/diluent(l) systems, which were measured using new methodology developed in our laboratory. We present results for various PE grades (from LLDPE to HDPE) and liquid hydrocarbons (C6 or C8). Solubilities of hydrocarbons in PE are measured at different temperatures. Next, we present swelling equilibria of PE particles in various liquid diluents measured by video-microscopy in pressure cell and complement thus the solubility measurements.

The highly demanded thermodynamic data for slurry polymerization are sorption data for ternary system: PE/liquid diluent/gaseous monomer. We present a new experimental method and mathematical model based on PC-SAFT equation of state, which are able to determine three-phase equilibria for PE-liquid-gas system.

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Organic phosphate and phosphonates as efficient catalysts for thiol-click vitrimers

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Transesterifications-based thermo-activated dynamic networks, in which bond breakage and reformation co-occur and affect viscoelastic properties, have associative nature and maintain connectivity at high temperatures.[1] Below the topology freezing transition temperature (Tv), properties are similar to thermosets. Above Tv, rearrangements cause a viscoelastic reflow of the network.[2] These networks are called vitrimers and are self-healabale, malleable, and reprocessable. While mineral phosphates have been reported as catalysts for transesterification, the catalytic activity of organic ones has not been studied similarly. They could be promising catalysts for preparing vitrimers as they do not affect shelf-life or cure kinetics.[3] In this study, organic phosphates and phosphonates (DMEP, EGMP, VPA, and DEV) were utilized as catalysts for reversible transesterifications in photocurable thiol-click vitrimers.

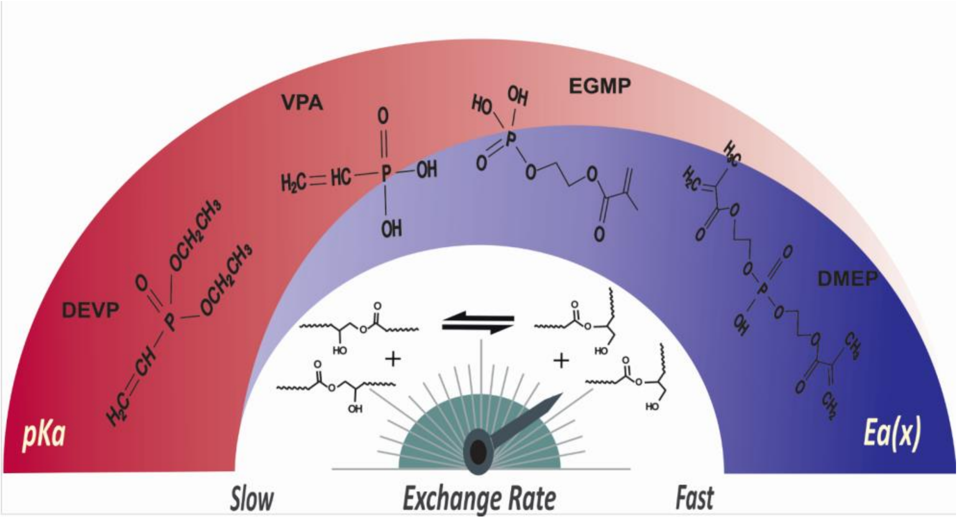

Figure 1. Effect of pK_a on the exchange rate of reactions

FTIR spectrometry was used to study cure kinetics. Stress relaxation analysis and DMA were performed to study the thermo-mechanical properties. The results demonstrated that low-Tg networks were highly mobile at high temperatures and the exchange rate was governed by the acidity of the catalysts (Figure 1). The relaxation rate and Tv were highly affected by pK_a value of the catalysts. It could be concluded that studied organic phosphates and phosphonates are superior in catalyzing exchange reactions in vitrimeric photopolymers. Besides, they facilitate convenient tailoring of kinetics and Tv.[4]

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Microwave-assisted chemical recycling of polyamides for efficient monomer recovery

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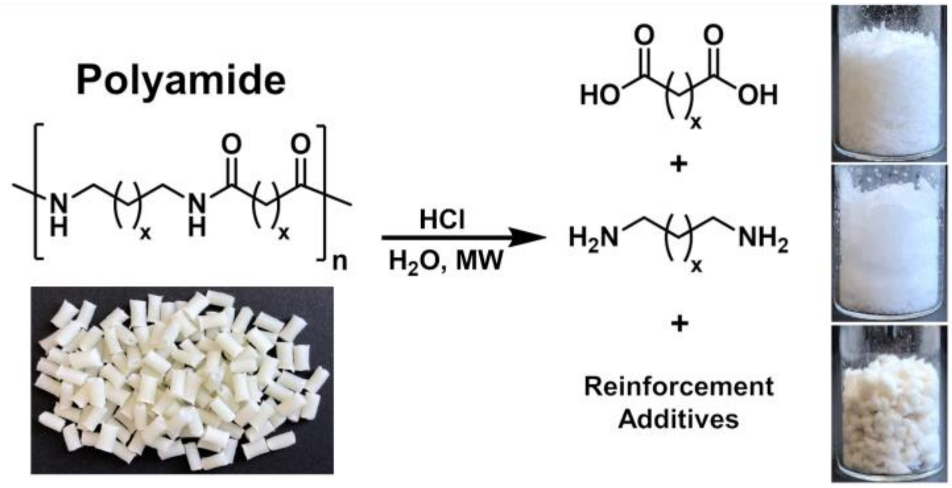
Polyamides (PAs) are used in various application fields ranging from fibers to engineering plastics. The increasing production of PA-based plastic waste is a growing environmental issue, as much of it ends up in landfills or is incinerated to recover at least some of its value in the form of energy. Mechanical recycling is already well established, however, the quality of the recycled products decreases after each processing cycle. An alternative to mechanical recycling is chemical recycling, in which polymer waste is converted to feedstock for monomers, fuel production, or other value-added products and intermediates.



Degradation of aliphatic polyamides by microwaves to recover the monomers and reinforcement fillers.

We report a simple and efficient chemical recycling process for aliphatic polyamides (PA 66, PA 1010, PA 11, PA 12).[1,2] The depolymerization was performed under microwave irradiation in the presence of HCl as an acid catalyst. The rate of PA hydrolysis reaction depends on the PA type, HCl / amide molar ratio, and the type and amount of reinforcing additives in PA. PA 66 is completely converted to the constituent monomers in 10 min at 200 °C and HCl / amide molar ratio of 1.25. Long-chain PAs (PA 11, PA 12, and PA 1010) and PAs with glass or carbon fiber reinforcing additives require longer reaction times at otherwise the same reaction conditions or higher HCl / amide molar ratio. Monomers and reinforcing additives were recovered in high yields and quality comparable to commercially available chemicals.

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Melt-polymerization of acrylamide initiated by nucleophiles: A route towards highly branched and amorphous polyamide 3

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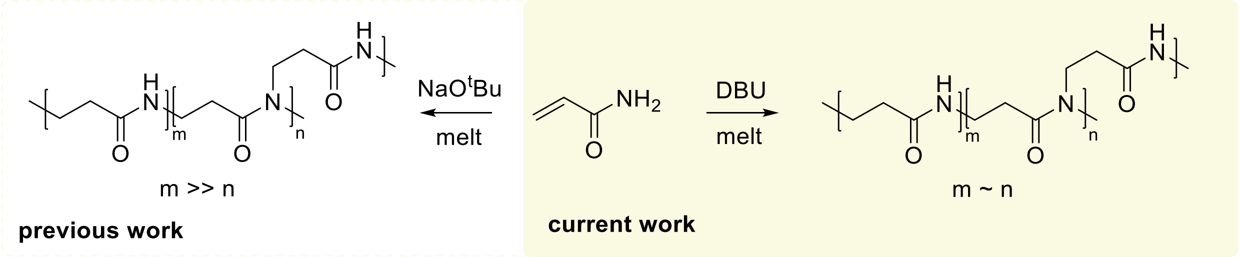
Herein a resource saving method for the preparation of unprecedented highly branched polyamide 3 (PA 3) is presented. Based on work of Roos et al. who disclosed the melt-polymerization of acrylamide with strong bases yielding almost linear PA 3,[1] we show that highly branched PA 3 is obtained when conducting the melt-polymerization with nucleophiles.[2] The high branching renders the polymer water soluble and fully amorphous. Furthermore, the preparation gets along without the use of any solvent and is perfectly atom-economic.



Synthesis of almost linear PA 3 from acrylamide (previous work; Ref. 1) and highly branched PA 3 (current work; Ref. 2)

The polymer and in particular its architecture was thoroughly characterized by manifold techniques (several NMR-techniques, including the investigation of a ^{15}N-marked derivative, MALDI-TOF mass spectrometry, size-exclusion chromatography, thermal analyses and powder-X-ray diffractometry). Further, the reasons for the pronounced branching will be discussed. A combination of the slow initiation and propagation as well as the presence of zwitter-ionic species is held responsible for the formation of the branched polymer architecture.

In a greater context, we believe that our findings contribute towards achieving the overarching aim of creating greener, more sustainable and intensified polymerization processes.

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Electron rich triarylphosphines as nucleophilic catalysts for *oxa*-Michael addition

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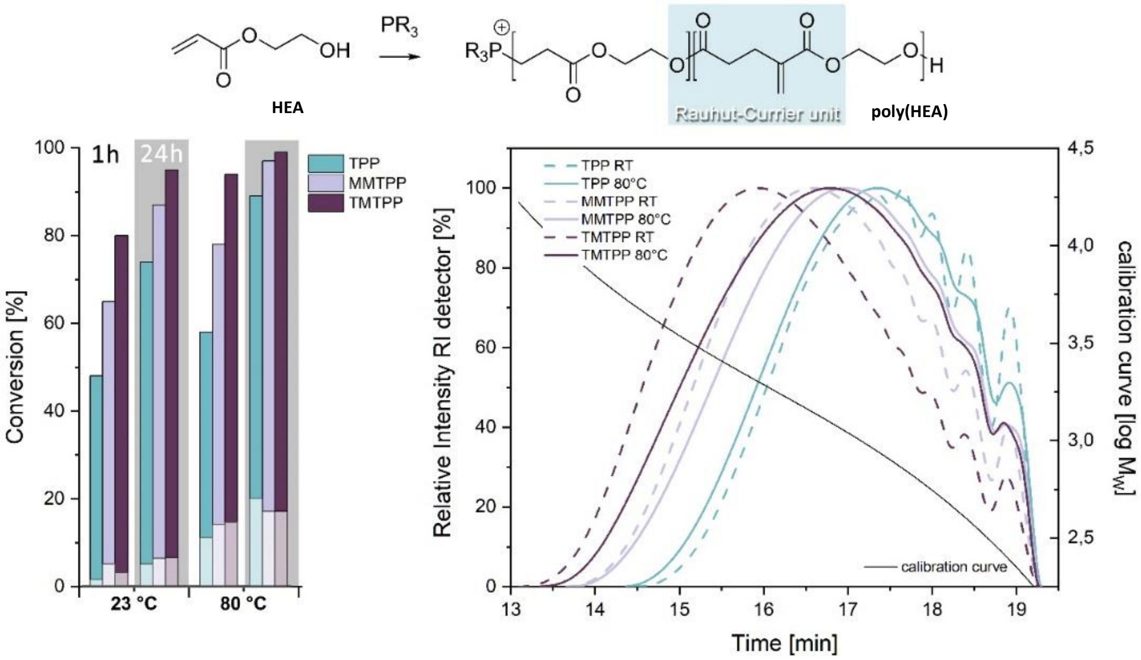
Organocatalytic *aza*- or *thiol*-Michael addition polymerizations using amines or thiols and electrophilic double bond monomers are widely applied in polymer and materials chemistry.[1] Nevertheless, using alcohol-based alternatives would be more attractive because they are generally less expensive, less toxic, and more readily available compared to thiol and amine monomers. However, the lower acidity of alcohols and the lower nucleophilicity of alkoxides require the use of highly active organocatalysts, ideally being stable at ambient atmosphere.[2]



left: double bond conversion of the polymerization of HEA, light sections of the bars represent Rauhut-Currier repeat units; right: size exclusion chomatograms of poly(HEA)

We have found that electron rich arylphosphines (4-methoxyphenyl)diphenylphosphine and tris(4-trimethoxyphenyl)phosphine outperform commonly used triphenylphosphine in catalyzing *oxa*-Michael additions.[3] All reactions are performed without solvent and at ambient atmosphere employing low catalyst loadings of only 1-5 mol%. Generally, tris(4-trimethoxyphenyl)phosphine is the most active catalyst in all cases while being only slightly more sensitive to oxidation than triphenylphosphine.

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Ionic liquids and magnesium-aluminum-alkyls as activator for Ziegler-Natta catalysts

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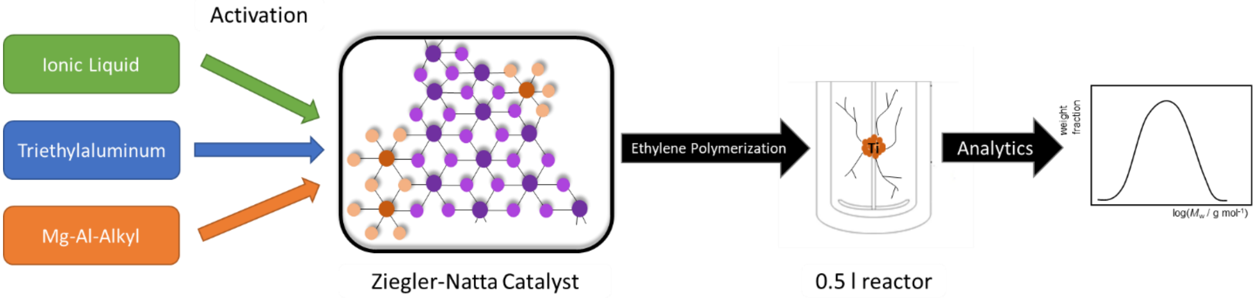
Ionic liquids are widely utilized as catalysts for different applications, like Friedel crafts or isobutane alkylation.[1,2] They are prepared by mixing halide salts with triethylaluminum (TEA).[1] In recent studies, ionic liquids are used as co-catalysts for the coordinative polymerization of ethylene using a Ziegler-Natta catalyst system.[3] Other investigations show, that magnesium-aluminum-alkyls are also applied for the activation of the Ziegler-Natta-catalyst, instead of TEA.[4]



Experimental setup for testing different co-catalysts

The aim of this work is to evaluate the effects of the ionic liquids and the magnesium-aluminum-alkyls in comparison with TEA on the coordinative polymerization of ethylene. This is done by varying the Al/Ti ratio of the catalyst/co-catalyst system. The ionic liquid has to be synthesized using alkylic and aromatic substituted ammoniumchlorids with TEA. The most suitable ionic liquid for our reactor system consists of methyltrioctylammoniumchloride and TEA. For the application with the magnesium-aluminum-alkyls, a solution of butyl-octyl-magnesium (BOMAG) with TEA is prepared. The received polymer is analyzed to determine the effects of the co-catalysts on the molecular weight distribution and the catalyst activity.

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Industrial production of metallocenes – Re-design of an established process

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The discovery of the extraordinary pair of metallocenes and MAO (Methylaluminiumoxan) which act as a highly active catalytic systems allowed the access to a tunable pathway for the production of new grades of polyolefines.[1] Besides the challenges to industrialize the production of the activator MAO in multi ton quantities, efficient routes and pathways for the full scale production of the complemental metallocenes were and still are challenging to meet quality and costing targets.

Many impressive and elegant routes for the synthesis of metallocenes are published in hundreds of scientific papers and patents. The mission of the industrial chemist is extract the information from this sources and develop a process efficient in terms of time, yield and sustainability.

rac-Dimethysilyl(indenyl)zirconium dichloride is one of the most widely used metallocenes on industrial level. Regulatory implications and a changing market situation triggered the need to re-design the established process.[2] After exploring multiple different approaches on lab scale, a few were selected for up-scaling and only one route proved to meet the requirements of the industrial production of metallocenes.[3]

As a result of applying this new approach it was possible to reduce the complexity of the synthesis, to increase the yield and to decrease the cycle time for the plant. The new synthetic route will be transfered into a full commercial production shortly in the following project phase.

An industrial chemist not only has to find a creative approach to fulfil new chemical requirements and react to a changing market conditions but also needs to consider technical and economic factors at the beginning and during the development process.

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Synthesis and characterization of acrylamide-based polyelectrolytes bearing long alkyl spacers

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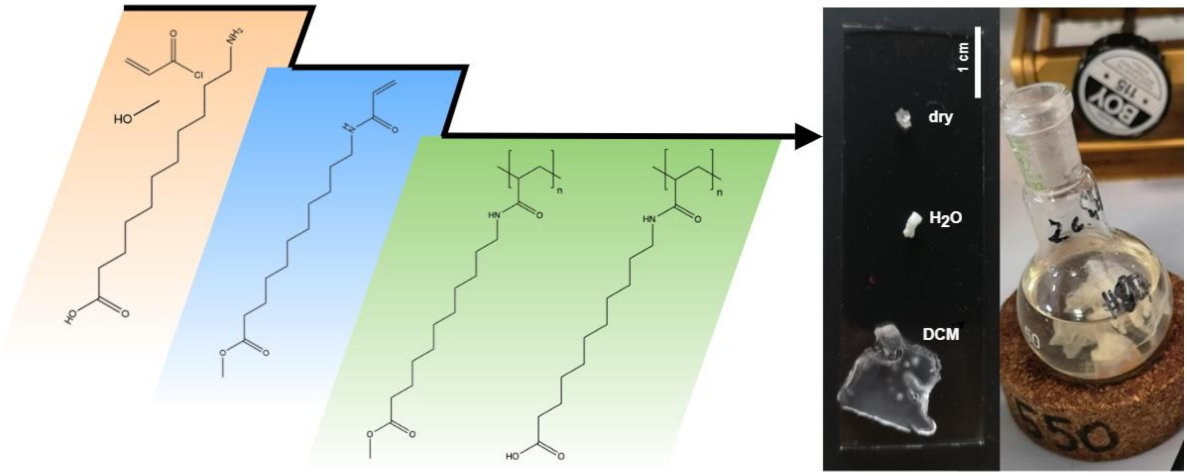
The uses and potential applications of polyelectrolytes are very broad. They are used in the field of enhanced oil recovery[1] and water treatment.[1] Further potential applications in battery technology,[2] sensor design[2] and drug delivery[3] are currently under investigation and in development.



Scheme of monomer and polymer synthesis; ***orange:*** *starting materials and reactants;* ***blue:*** *synthesized monomer;* ***green:*** *polymers synthesized with variable degree of deprotection; left picture: Swelling of bulk polymerized material in water and dichloromethane (DCM); right picture: precipitation of the deprotected polymer through decreasing pH.*

Focussing on the synthesis of poly(methyl 11-acrylamido undecanoate) and the corresponding free acid, a convenient pathway to synthesize a polyacid with long aliphatic spacers was developed. The material synthesized in bulk shows interesting strong swelling behaviour in dichloromethane. Although the novelty of the presented synthesis route lies within the concept of methyl protection and controlled deprotection. This improves solubility and opens the possibility of solution polymerization in common organic solvents. Deprotection after polymerization enables a controllable amount of free acid groups, which is not yet reported for similar polymers in literature.[4] The polymer presented in this work shows different solubilities depending on pH, which makes it attractive in drug delivery applications.[3] The long alkyl spacer may present a potentially beneficial trait in terms of ion conductivity - a property that is currently investigated.

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Propagation rate coefficient for 2-dimethylaminoethyl methacrylate (dmaema) obtained by PLP-SEC method

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The accurate values of propagation rate coefficient, k_p, are essential to understand radical polymerization processes and mechanisms. k_p values together with the rate coefficients for termination and transfer are required to model the rates of polymerization and molar mass distributions of resulting polymer product. The situation regarding the availability of k_p values has been improved by employing the pulsed-laser polymerization in conjunction with size-exclusion chromatography (PLP–SEC).[1] In the last two decades, a significant progress has also been achieved in polymerization of water-soluble monomers in aqueous solutions. Recent examples include understanding of the solvent effects for non-ionized monomers[2] and the impact of counterions on k_p for cationic monomers.[3]

This work aims at determining k_p values for 2-dimethylaminoethyl methacrylate (DMAEMA) in an aqueous solution. The k_p values exist for DMAEMA polymerized in bulk,[4] however, no parallel information is available for polymerization in aqueous solutions. The motivation for this work is that DMAEMA is a non-ionized analogue to cationically ionized [2-(methacryloyloxyethyl)] trimethylammonium chloride (TMAEMC), for which the k_p values exist in a broad range of polymerization conditions.[3] DMAEMA is ionized at acidic pH and non-ionized at pH > 10 that creates the opportunity (1) to compare the k_p values for non-ionized, partially ionized and fully ionized DMAEMA forms by investigating the effect of monomer concentration, temperature and added salt, and (2) to compare obtained k_p values with those for TMAEMC. In this contribution, k_p values obtained for DMAEMA in both non-ionized and ionized forms polymerized over wide ranges of monomer concentration, temperature, salt content, and pH will be reported.

Acknowledgment: This work was supported by the Slovak Scientific Grant Agency VEGA 2/0121/20 and the Slovak Research and Development Agency under the contract number APVV-18-0480.

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Post polymerization modification of aromatic polyimides via irreversible Diels-Alder reactions

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The Diels-Alder reaction of alkynes with cyclopentadienones undergoes a chelotropic evolution of CO gas at high temperatures forming phenylene segments.[1] This type of chemistry can be used to prepare aromatic polyimides, a group of high-performance polymers whose use is indispensable in a wide variety of high demand applications, for example, in the electronics, aircraft and space industry.[2] Recently, we demonstrated the use of this class of chemistry for the preparation of segmented multiblock aromatic polyimides,[3] an endeavor that is known to be rather challenging when using conventional PI step-growth polymerization.

Herein, we demonstrate the post-polymerization functionalization of polyimides bearing triple bonds in their backbone.[4] These “poly-dienophiles” react with cyclopentadienone moieties with the loss of carbon monoxide, as shown in Figure 1. Thereby, functional groups can be introduced into the ready-made polyimide chain. A beneficial aspect of this approach is the introduction of four pending aromatic rings that hinder chain packing and promote solubility. The most appealing aspect, however, is that there are many different tetraphenylcyclopentadienone derivates to choose from, opening up a “toolbox” of post-polymerization functionalization possibilities for triple bond containing polyimides, including polymers with intrinsic microporosity (PIMS) or as proton exchange membranes (PEMS).

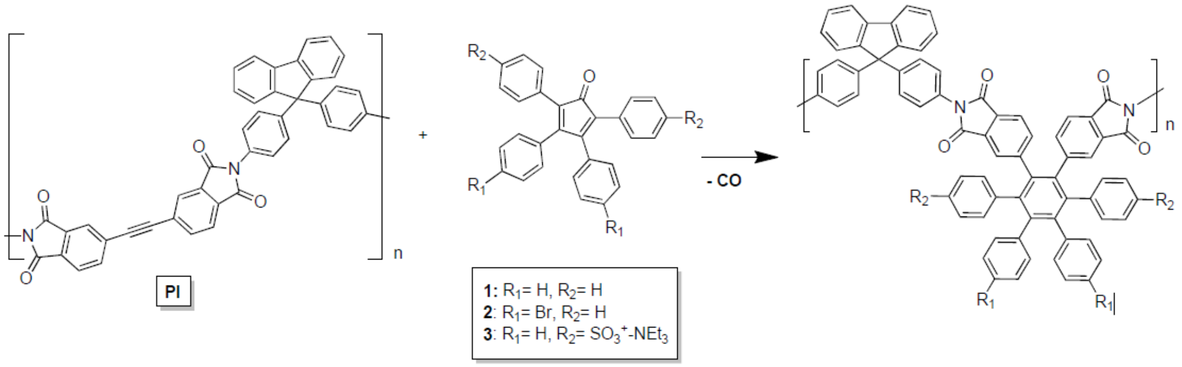

Figure 1: Schematic of post-polymerization functionalization of polyimide via a Diels-Alder reaction [4]

References:

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Reversible adhesives for sustainable photovoltaics: Development of novel elastomeric vitrimers

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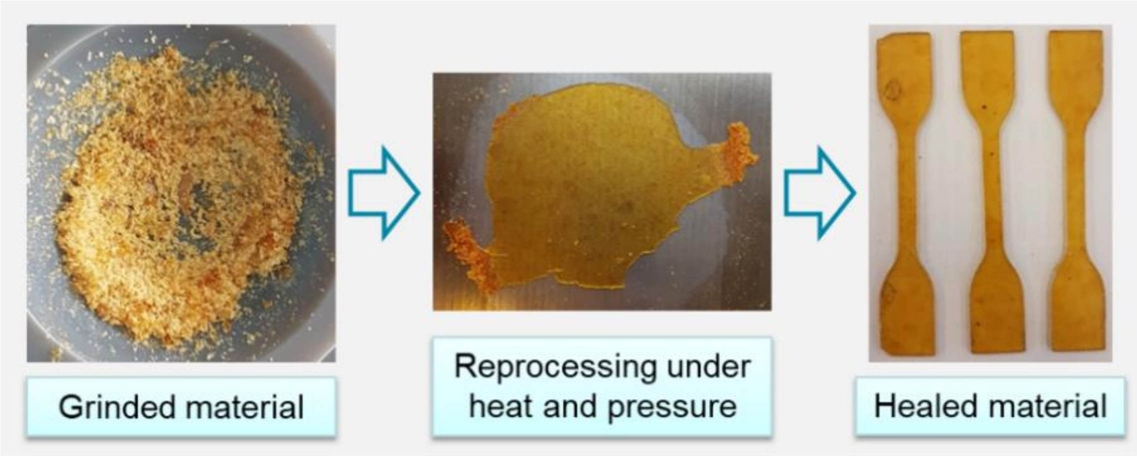
The demand for energy obtained from renewable and sustainable resources, is currently gaining further importance, considering the EU target of at least 32 % share of renewable energy of the final energy consumption by 2030 in order to reduce greenhouse gas emissions, and to conserve resources.[1] In the present work, the development of concepts for reversible adhesive bonds is targeted, with the overall aim to improve the recyclability of photovoltaic (PV) modules, and consequently to increase the sustainability of electricity generation from photovoltaics. Since glued joints are often hard to disassemble without destroying the components, the repair of defective parts and the possibility for recycling of PV modules is significantly improved when bonded joints can be broken without damaging the components.

In order to achieve reversible and reworkable adhesive connections, elastomeric vitrimers based on functionalized poly(dimethylsiloxane) (PDMS) were developed. By exploiting the reaction of epoxide functional groups with anhydrides and carboxylic acids, covalent adaptive networks (CANs) are formed in the presence of suitable catalysts. A reprocessable elastomeric CAN was successfully established by curing epoxidized PDMS with a multifunctional fatty acid and n-butylamine (BA) as a covalently bonded catalyst. In tensile tests, the system showed a remaining strength of more than 85% after reprocessing the grinded material in a hot press for 5 h at 160°C. Lap shear tests were done to evaluate bond strength, rejoining, aging stability, and the ability to weaken the adhesive bond. The elastomeric CAN achieved approximately 20% of the reference silicone adhesive's strength. Tests at 160°C decreased the bond strength by 60%, compared to a reduction of 40% for the reference sample. Temperature cycle tests did not influence the material strength, storage at 120°C for 930 h decreased the bond strength by approximately 20% and in damp heat tests the material exhibited hydrolytic bond cleavage. Rejoining the lap shear samples resulted in a remaining bond strength of more than 70%.



Schematic overview for reprocessing of the elastomeric CAN

References:

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Development and implementation of a simultaneous fatigue crack growth testing system for polymeric hybrid laminates

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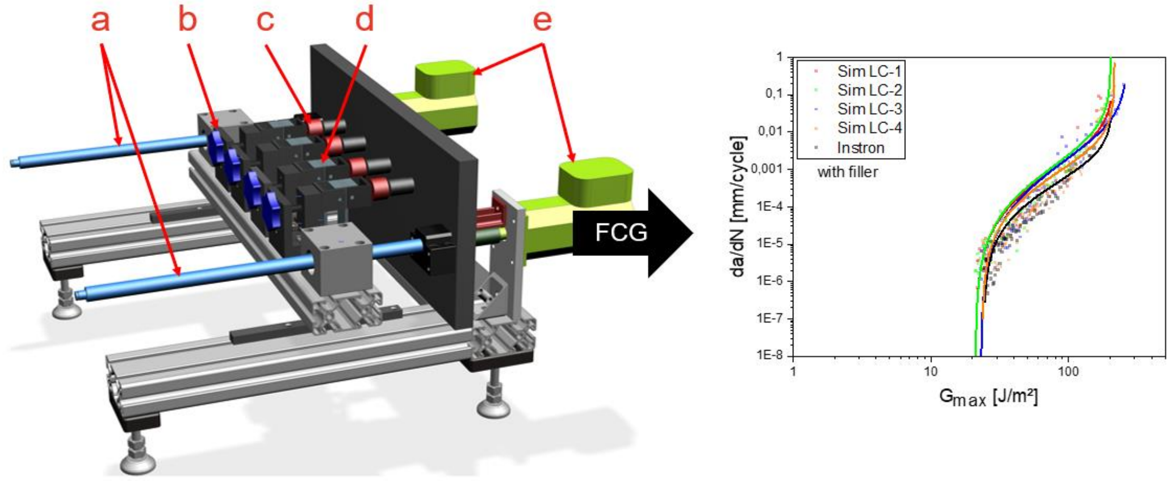
Delamination is a common and highly relevant in-service failure mode of composites or photovoltaic modules. Cyclic mechanical loads superimposed with environmental factors are most critical.[1] To evaluate the cyclic debonding resistance of polymeric hybrid laminates fracture mechanics approaches based on double cantilever beam (DCB) specimens are established. However, conventional fatigue test setups allow for measurement of a single specimen which is often quite time consuming and expensive.

Hence, a novel fatigue test setup for simultaneous characterization of multiple DCB specimens was developed and implemented. The simultaneous fatigue testing system consists of two ball screws (a), an initial crack tip opening positioning system (b), load cells (c), vertically positioned DCB specimens (d) and servomotors (e). These components are mounted on aluminum profiles and rail guides (s. Figure below). To validate the novel test system, electrical steel/epoxy laminates with and without filler in the epoxy adhesive layers were characterized using the novel fatigue test setup and a commercial electrodynamic test machine (ElectroPuls E3000, Instron). Fatigue crack growth data were fitted by a form of the Hartman-Schijve crack growth equation to account for scattering effects especially at low values of the strain energy release rate G.[2] A good agreement of the crack growth kinetics data at ambient conditions was obtained confirming the high quality and reliability of the simultaneous fatigue test setup. Torque and specimen oscillation were reduced significantly by vertical positioning of DCB specimen. Moreover, more reliable data were obtained at the beginning of the displacement-controlled experiments in the instable crack propagation regime.



Left: CAD assembly of the simultaneous test bench; a-ball screw, b-initial crack tip opening positioning system, c-load cell, d-DCB specimen, e-servomotors. Right: Fatigue Crack Growth curves of electrical steel/epoxy laminates with filled epoxy varnish

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Compressive shear behaviour of polymer-glass laminates - Comparison of peroxide-crosslinked EVA and POE encapsulants

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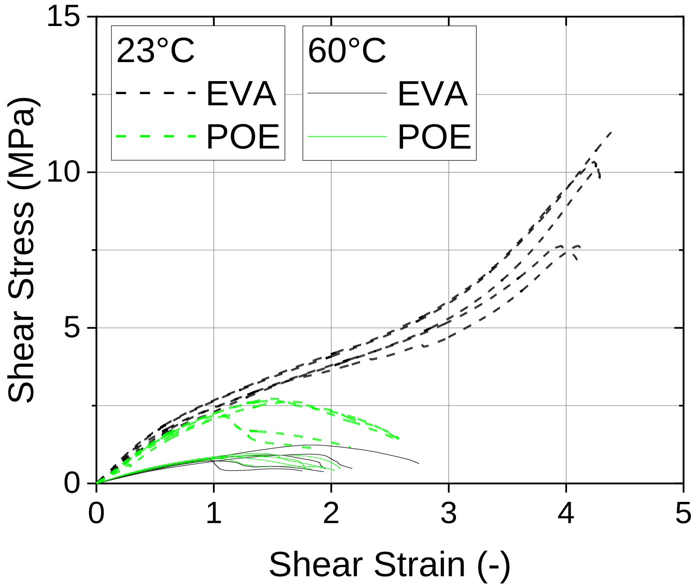
Compressive shear testing (CST) is an established method to assess the adhesion performance of soft adhesive laminates.[1] In this paper, CST was adopted to study the effect of testing temperature on the adhesive strength of glass encapsulant laminates. Glass laminates were manufactured using two UV-transparent, peroxide cross-linked encapsulants (based on ethylene vinylacetate copolymer (EVA) and polyolefin elastomer (POE)) at 155 °C (curing time: 15 min; pressure: 800 mbar). CST specimens with dimensions of 25x25 mm^2 were prepared by water jet cutting. CST experiments were performed in tension mode at 23 and 60 °C on a Zwick-Roell Z020. The displacement rate was 1 mm/min. To detect local failure mechanisms, a digital image correlation system (DIC, Aramis GOM) was implemented. Deformation pictures were evaluated using the open source image processing program GOM Correlate.

A quite different compressive shear behaviour was obtained at 23°C. EVA laminates exhibited up to four times higher shear stresses and two times higher shear strains. Prior to ultimate failure of EVA and POE laminates, interfacial damage and glass fracture was discernible. Interfacial failure was much more pronounced for POE laminates. This was attributed to weaker interfacial bonding to SiO_2 of non-polar POE. Interestingly, both laminate types revealed a comparable CS performance at 60 °C, which is in and slightly below the melting temperature range of cross-linked EVA and POE, respectively. At 60 °C, interfacial delamination, but no glass fracture was observed.



Shear stress strain curves of CST experiments performed at 23 °C and 60 °C.

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Natural Zeolite in polypropylene: Mechanical behaviour and influence of processing on the filler particle size

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Zeolites of natural or synthetic origin have a complex crystalline structure on which substances can accumulate or chemical reactions can take place. They are used in industry for the drying and adsorption of gases (e.g. reduction of bad odour), for ion exchange or as catalysts.[1] In the plastics industry, zeolite is used as a filler, to improve the compatibility of polymers, which are difficult to mix and for the modification of blowing agent systems.[2]
The aim of this work was to evaluate the influence of the filler size and content of natural zeolite in polypropylene on the mechanical properties and to evaluate the interface and the distribution of the particles within the matrix material. Further the particle size was measured before and after processing, to determine the distribution within the matrix material.

Therefore, a homopolymer PP was mixed with different amounts and grades of natural zeolite. Test specimens were produced and mechanically characterised as well as SEM pictures were taken from cryo fractured cross sections. Parts of the produced specimens were heated in a Macro TGA to burn the matrix material and regain the zeolite particles. Micrograpic pictures were taken of the pure zeolite powder before and after processing and compared for their particle size.

It showed, that mixtures up to 50 weight percent are possible, the bonding of zeolite in the polypropylen matrix is excellent and the mechanical properties like E-modulus and tensile strength enhance. The compounding and injection molding process has no influence on the particle size and the distribution within the specimen cross section is consistent.

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Influence of processing conditions on crack growth kinetics of electrical steel/epoxy laminates

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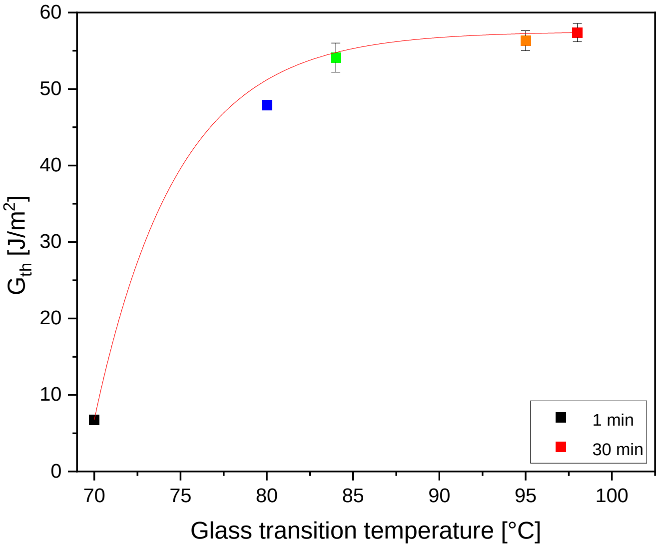
Electrical steel sheets are widely used in stator and magnetic cores of many electrical machines, owing to reduction of core losses provided. Frequently these sheets are isolated and stacked by adhesive bonding to increase energy efficiency. Present work evaluated the effect of processing conditions (curing time, pressure) on crack growth kinetics of electrical steel/epoxy laminates at ambient and elevated temperatures on specimen level. Hence, a linear elastic fracture mechanical method suitable for mode I and cyclic fatigue was employed. Further fractographic investigations were performed on fractured surfaces. Thermo-mechanical properties of electrical steel laminates were characterized employing dynamic mechanical analysis.

Electrical steel sheets supplied by Voestalpine Stahl GmbH were double side coated and pre-cured at specific temperature and time in a convection oven. Double cantilever beam specimens were manufactured by stacking and laminating 6 cut layers. Electrical steel laminates went through final curing step within a heating hydraulic press for 1 up to 30 minutes and different pressures (2.4 or 4.8 MPa).

Laminates exhibited improved crack growth resistance with increasing curing time and pressure at ambient and elevated test temperatures. Laminate's glass transition temperature rose in an asymptotic manner with increasing curing time, ranging from 70 to 95˚C, yet no significant effect was observed by increase of cure cycle pressure. Hence, it was speculated laminate's fatigue behavior and thermo-mechanical properties are dependent on crosslinking degree (curing state) of the epoxy-based adhesive. Fractographic investigations revealed cohesive and interfacial failure of tested specimens at ambient and elevated temperatures, respectively. Thus, changes in temperature affect the adhesive mechanical behavior further altering the crack path in the adhesive or on its interface.



Correlation between glass transition and threshold strain energy release rate at room temperature

Side chain engineering of PTQ10 polymer for green solvent processable organic solar cells (OSC)

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Conversion of sunlight into electrical power is one of the most promising energy scources. Investigation on different photovoltaic systems increased over the last decades, leading to several approaches on new innovative solar cell materials. One approach is the investigation of organic solar cells (OSC). Advantages like the low cost, easy processing, light weight, and flexibility favor the investigation of organic photovoltaics (OPV). However for implenentation in industrial scale the power conversion efficiency (PCE) needs to be improved. Moreover, several starting materials are expensive and multiple synthetic and purification steps are required. With the introduction of the PTQ10 donor polymer new opportunities were born. Synthesis require not expensive starting material, 5 synthetic steps and one column separation.[1,2]

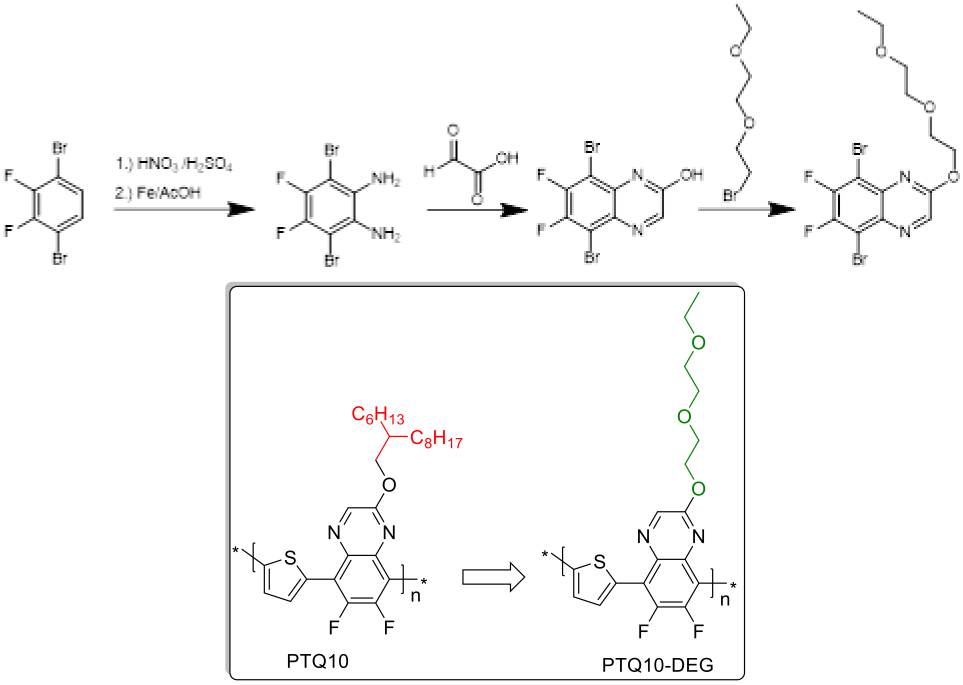

Figure 1: Synthetic scheme and structure of PTQ10 and PTQ10-DEG

Herein, we introduced the synthesis of diethylene glycol side (DEG) chain instead of alkyl chain. Due to the more polar DEG side chain the solubility of the donor polymer changes and green solvents like THF or xylene, instead of chlorbenzol or chloroform, can be used for the fabrication of the solar cells.

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Presenting Participants